

# Generation of flammable mists from high flashpoint fluids: Literature review

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# Generation of flammable mists from high flashpoint fluids: Literature review

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Hazardous Area Classification (HAC) for explosive gas atmospheres is well established, with guidance published in various standards and industry codes of practice. However, the same situation is not currently the case for high flashpoint liquid releases that could give rise to an explosive mist atmosphere. There is a pressing need for clear guidance on mist hazards to allow operators to determine the extent of areas where flammable mists may be present and to select appropriate equipment for use in those areas.

This report provides a survey of the recent literature on flammable mists and pulls together information that will be useful in developing a HAC methodology for explosive mist atmospheres. It focuses on the three fundamental issues: mist flammability, mist generation and mitigation measures.

The first of these is discussed with reference to five measurable parameters: the Lower Explosive Limit (LEL), Minimum Ignition Energy (MIE), Maximum Experimental Safe Gap (MESG), Minimum Igniting Current (MIC), and Minimum Hot Surface Ignition Temperature (MHSIT). Measurements of these quantities in mists are analysed and models for their prediction are discussed.

The second issue of mist generation is examined under four categories: mists produced by pressurised sprays, condensation aerosols, agitation/splashing/sloshing and air stripping. Of these, the primary focus is on spray releases and condensation aerosols, which are considered to be the most likely sources of mists. Measurements undertaken in sprays are described and models are discussed. Mitigation measures are surveyed briefly, which include mist detection, use of fire-resistant fluids or anti-misting additives, inerting and control of static charge.

Finally, tentative proposals are suggested for developing area classification guidance based on the prediction of the flammable mist cloud size.

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## EXECUTIVE SUMMARY

Hazardous Area Classification (HAC) for explosive gas atmospheres is well established, with guidance published in various standards and industry codes of practice. However, the same situation is not currently the case for high flashpoint liquid releases that could give rise to an explosive mist atmosphere. There is a pressing need for clear guidance on mist hazards to allow operators to determine the extent of areas where flammable mists may be present and to select appropriate equipment for use in those areas.

The objective of this report is to survey the recent literature on flammable mists and pull together information that would be useful to develop a HAC methodology for explosive mist atmospheres. The work provides an update to the substantial literature survey conducted previously by Eckhoff (1995).

Rather than provide a wide-ranging review of the whole field of mist formation, ignition and flammability of liquid fuels, the report concentrates on addressing two fundamental questions. Firstly, when is a mist flammable? And secondly, how can a flammable mist be produced? In answering these questions, efforts are concentrated on the need to develop a relatively simple quantitative method for predicting the likelihood of the formation of a flammable mist in an industrial context. The review also considers briefly some measures that can be used to mitigate mist hazards. The severity and consequences of mist explosions are not examined in detail.

The first central issue of mist flammability is discussed with reference to five measurable parameters: the Lower Explosive Limit (LEL), Minimum Ignition Energy (MIE), Maximum Experimental Safe Gap (MESG), Minimum Igniting Current (MIC), and Minimum Hot Surface Ignition Temperature (MHSIT). Measurements of these quantities in mists are analysed and models for their prediction are discussed.

It is shown that the LEL of a mist can fall to as low as 10% of the LEL of the vapour of the same substance. This reduction in the LEL is related to the size of the droplets in the mist, with the lowest LEL being produced by the largest droplets. For mists composed of small droplets ( $< 20 \mu\text{m}$ ), the LEL is approximately equal to that of the equivalent vapour mixture. An area classification methodology for mists could potentially be based on assuming that the LEL of the mist was equal to the equivalent vapour LEL, or some fraction thereof. Rather than apply a single value of the LEL in all cases, the methodology could take into account the fact that mists produced by sprays tend to be composed of much larger droplets than those produced by condensation aerosols. If the only mechanism that could give rise to a mist was a condensation aerosol, then it may be appropriate to use a higher value of the LEL than for cases where mists are generated by sprays. Similarly, the nature of the potential ignition sources could have an impact on the criteria used to define the flammable mist cloud extent.

In general, measurements reported in the literature indicate that mists are more difficult to ignite than their equivalent vapours. The MIE, MESG and MHSIT are all slightly higher for a mist than they are for the vapour. This may provide a potentially simple route for the selection of equipment for use in mist atmospheres: i.e. equipment for use in a mist atmosphere could be selected based on its rating for the equivalent vapour atmosphere, in terms of gas group and temperature class. Further analysis and measurements are required to confirm that this is a safe approach, as the data is relatively limited.

The second main issue of mist generation is examined under four categories: mists produced by pressurised sprays, condensation aerosols, agitation/splashing/sloshing and air stripping. Of these, the primary focus is on spray releases and condensation aerosols, which are considered to be the most likely sources of mists. Measurements undertaken in sprays are

described and models are discussed. Tentative proposals are suggested for developing area classification guidance based on the prediction of the flammable cloud size in unconfined releases and those in ventilated enclosures.

The principal aim of the present work has been to review the existing literature. Although tentative proposals for the development of an area classification methodology for mists have been put forward, these proposals have not yet been scrutinised rigorously. On closer examination, some of the concepts may be found to be impractical or provide results that are unsustainably under- or over-conservative. In future work, it would be useful to reflect on the proposals and assess whether they would provide a suitable framework for future guidance on mists. A number of specific tasks that should be addressed have been identified. There remain a number of areas of active research related to mist generation and flammability, and it is recommended to revisit this literature survey at intervals in the future to ensure that any guidance on area classification for mist hazards accounts properly for new developments in scientific understanding.



# 1 INTRODUCTION

## 1.1 MOTIVATION

The European ATEX ‘Workplace’ Directive (1999/92/EC)<sup>1</sup>, which is implemented in the UK under the DSEAR regulations<sup>2</sup>, requires employers to identify and classify areas of the workplace where explosive atmospheres may occur. They must then ensure that appropriately certified equipment is used in the hazardous zones.

Hazardous Area Classification (HAC) for explosive gas atmospheres is well established, with guidance published in various standards and industry codes of practice (BSI, 2010a; IGEM, 2010; EI, 2005). Research continues to refine the techniques used, for example recent work (Gant and Ivings, 2005; Ivings *et al.*, 2008) has examined the validity of some of the approaches previously adopted for dispersion of pressurised releases of flammable gases.

The same situation is not currently the case for high flashpoint liquid releases that could give rise to an explosive mist atmosphere. The most recent edition of the relevant standard, BS EN 60079-10-1 (BSI, 2009c) contains a new annex which offers some qualitative guidance on mist explosion hazards, but there is little in the way of quantitative methods. The Energy Institute code of practice, IP15 (EI, 2005), also notes that “there is little knowledge on the formation of flammable mists and the appropriate extents of associated hazardous areas ... Further research is needed”.

A recent literature survey of reported accidents (Santon, 2009), found that the consequences of mist explosions can be potentially very severe. The study identified 37 incidents including 20 explosions, of which nine were collectively responsible for a total of 29 fatalities.

## 1.2 OBJECTIVES

The aim of the present report is to survey the recent literature on flammable mists and pull together information that would be useful in developing a HAC methodology for explosive mist atmospheres. The work provides an update to the substantial literature survey conducted for the Health and Safety Executive (HSE) by Eckhoff (1995).

There has been a significant amount of research over the last six decades on the flammability of mists due to its importance in the design of gas turbines and internal combustion engines, on the safety of marine diesel engines and aircraft fuel tanks, and various other applications. The subject is complex and there remain many uncertainties and areas of active research.

Rather than provide a wide-ranging review across the whole field of mist formation, ignition and flammability of liquid fuels, the present review concentrates on addressing two fundamental questions. Firstly, when is a mist flammable? And secondly, how can a flammable mist be produced?

In answering these questions, the review concentrates on the need to develop a relatively simple quantitative method for predicting the likelihood of the formation of a flammable mist in an industrial context. However, it is important that any models developed for HAC are scientifically robust and any limits on their application are known. It is anticipated that such models would be similar to those used at present for flammable gas releases, i.e. predominantly based on operating conditions (pressures, flowrates, ventilation rates etc.)

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<sup>1</sup> <http://ec.europa.eu/enterprise/sectors/mechanical/documents/legislation/atex/>, accessed March 2011.

<sup>2</sup> <http://www.hse.gov.uk/fireandexplosion/dsear.htm>, accessed March 2011.

rather than requiring complex Computational Fluid Dynamics (CFD) analysis; though as is the case for HAC for flammable gas releases, this remains an option for the user to employ if they so wish. Ideally, the new guidance should also be sufficiently generic to take into account a range of conditions including unobstructed releases in the open air, and those in more congested or enclosed spaces. Given the significant amount of past research, a partial model may be possible. However this has eluded many previous workers.

Where possible, practical guidance is presented for the use of equipment in zoned areas, according to the ignition energy and temperature of hot surfaces. In addition to providing a review of the current state-of-the-art, the present work provides suggestions for where future efforts should be directed in order to develop new guidance.

The review only considers mists, sprays and aerosols of liquids that are below their flashpoint at the ambient temperature. A list of such fluids is given below, indicating the range of materials (and industries) where area classification may be needed:

- Lubricating oil
- Vegetable oil
- Hydraulic oil (both mineral and synthetic types)
- Light fuel oil
- Heavy fuel oil (at operating temperature)
- Heat transfer fluid (at operating temperature)
- Jet fuel/kerosene
- Transformer oils
- Process fluids (e.g. Solvesso)
- Diesel
- Bio-diesel
- White spirit

The review does not consider flashing liquid releases, where the liquid vigorously boils as it exits the pressurised reservoir in which it is contained. The review also does not consider low flashpoint liquids such as gasoline. Guidance on HAC for gasoline and similar substances can be found, for example, in IP15 (EI, 2005). The review also only considers ignition of mists in atmospheric air close to typical ambient temperatures (in the range from 0 °C to 40 °C). This therefore excludes data relating to high-pressure and/or high-temperature ambient conditions that may occur, for example, inside internal combustion engines or gas turbines.

### **1.3 METHODOLOGY**

The remainder of this introductory chapter provides some background to the concept of HAC, and a summary of some terminology used in flammable mist research. The following two chapters then address the central issues of mist flammability and formation of mists. This is followed by a brief chapter which examines mitigation measures, such as use of inert gas. Finally, the conclusion section summarises the findings of the review and provides some tentative proposals for an area classification methodology for mists. Areas to be explored in future work are also described.

The review process has involved detailed literature searches through academic and industrial journals, conference proceedings, reports, theses and text books. In total, nearly 300 separate sources of information have been identified, catalogued and reviewed. The assistance of HSL's Information Centre, and HSE's Knowledge Centre and Information Consultancy Team is gratefully acknowledged.

It should be noted that this review has been conducted over a period of only four months. Each of the various topics encompassed by the review contain such a vast amount of research that the present work can only be considered to scratch the surface. However, it will hopefully provide sufficient insight into each of the fields to focus future work and assist in the development of new guidance.

#### 1.4 AREA CLASSIFICATION CONTEXT

For flammable gases and liquids, the classification of hazardous areas into zones is based on an assessment of the frequency of the occurrence and duration of the explosive atmosphere, as follows:

- **Zone 0:** An area in which an explosive gas atmosphere is present continuously or for long periods;
- **Zone 1:** An area in which an explosive gas atmosphere is likely to occur in normal operation;
- **Zone 2:** An area in which an explosive gas atmosphere is not likely to occur in normal operation and, if it occurs, will only exist for a short time.

A similar approach is used for HAC where combustible dusts may form an explosive atmosphere.

Guidance on the classification of areas for flammable gases, vapours and liquids that are handled above their flashpoint, that could potentially give rise to an explosive atmosphere is provided in BS EN 60079-10-1 (BSI, 2009c).

Within each zone, the type of equipment and protective systems to be used must be selected on the basis of the requirements set out in the ATEX 'Equipment' Directive (94/9/EC)<sup>1</sup> and transposed into UK legislation by the Equipment and Protective Systems Intended for Use in Potentially Explosive Atmospheres Regulations 1996. The regulations and directive require equipment and protective systems to be 'ATEX-certified'. The requirements specify three categories for equipment and protective systems: Category 1 provides a very high level of protection and must be used in Zone 0; Category 2 provides a high level of protection and must be used in Zone 1; and Category 3 provides a normal level of protection and must be used in Zone 2 (n.b. different categories are applied to mining equipment). Broadly speaking, equipment and protective systems to be used in a zone where an explosive atmosphere is more likely is designed to have greater levels of protection to ensure that ignition of the flammable atmosphere is avoided, even under fault conditions. Category 1, for example, has two independent means of protection or is safe when two malfunctions occur independently of each other.

ATEX-certification requires compliance with relevant equipment standards in the 60079 series (BSI, 2010a). This considers not only ignition sources arising from electrical equipment, including connections such as junction boxes, but also ignition sources that might arise from mechanical equipment, such as gearboxes, and those that may arise from accumulation of electrostatic charge.

The ATEX-certification of the equipment categories, is supported by the following:

- **Electrical Protection Concepts:** electrical equipment that is designed such that it is flameproof, enclosed, pressurized, powder, sand, quartz or oil filled, encapsulated, intrinsically safe, non-incendive, or has increased safety or special protection.

Specifications for equipment that fall into these categories are provided in BS EN 60079 standard, parts: 1, 2, 5, 6, 7, 11 and 25 (for details, see BS EN 60079 Part 0: Equipment – General Requirements, BSI, 2009a). The decision to select one or other protection type is based on the Zone it is being used in and the nature of the equipment. For example, heavy current equipment for use in Zone 1 or 2 may be oil filled. A brief description of the various types of electrical protection is also provided in Annex F of IP15 (EI, 2005).

- **Mechanical Protection Concept:** non-electrical equipment is similarly classified into number of categories, including: flow restriction, flameproof, constructional safety, control of ignition sources or liquid immersion. Further information is provided in standard BS EN 13463-1 (BSI, 2001b). The safe design and construction of mechanical equipment to be used in zoned areas is also discussed by Krämer (1995).
- **Temperature Class:** equipment is rated according to one of six temperature classes (T1, T2, T3, T4, T5 or T6) on the basis of the maximum temperature any of its surfaces will reach in a 40 °C ambient temperature environment. Class T1 is the highest (450 °C), and T6 the lowest (85°C). Details are given in BS EN 60079-0 (BSI, 2009b). Equipment of an appropriate temperature class is selected based on its operating environment to ensure that any hot surfaces will not ignite the explosive atmosphere. For gas or vapour explosion hazards, areas are classified using the temperature class system on the basis of the auto-ignition temperature. For example, an atmosphere in which propane may be present, which has an auto-ignition temperature of 450 °C has a temperature class of T2 (BSI, 2010b), and hence requires equipment rated to classes T2 or higher.
- **Equipment Grouping:** electrical equipment is rated into three groups: one that is suitable for mines (Group I), one that is suitable elsewhere with an explosive gas atmosphere (Group II) and one that is suitable for places with an explosive dust atmosphere other than mines (Group III). The Group I equipment is designed to avoid ignition of firedamp or coal dust and is sufficiently robust to be used underground. Group II equipment is subdivided into three subgroups: IIA, IIB and IIC on the basis of the Minimum Ignition Energy (MIE) and the Maximum Experimental Safe Gap (MESG) of the flammable vapour or gas (BSI, 2010b). Gases or vapours with the highest MIE and MESG are classified Gas Group IIA, for which propane is a representative example, whilst those with the lowest MIE and MESG are classified Gas Group IIC, for which hydrogen is a representative example. A representative example for Gas Group IIB is ethylene. In a hazardous area in which a potentially explosive atmosphere might arise from a variety of flammable gases or vapours, the equipment sub-group for the flammable gas or vapour with the lowest MIE or MESG should be used. Group III is similarly subdivided into three sub-groups IIIA, IIIB and IIIC according to the presence of combustible flyings, non-conductive dust and conductive dust. Experiments have recently been performed to investigate the justification for the gas group classification by Langer *et al.* (2011).
- **Ingress Protection (IP):** equipment is given a two-digit IP code according to the ability of the enclosure to provide protection against persons coming into contact with electrically live or moving parts, and against the ingress of dust or liquids. The first digit signifies the protection against ingress of dusts (where, for example, 5 is protected and 6 is tight), and the second digit signifies protection against water (where 4 is splashing, 5 is jets, 6 is powered jets, 7 is temporary immersion and 8 is continuous immersion). Most equipment used in hazardous areas is rated to at least IP54. Further information is given in BS EN 60529 (BSI, 1992).

Standard BS EN 60079-0 (BSI, 2009b) provides the specification for equipment in order to address other potential ignition hazards. This includes maximum power or energy thresholds for emission of electromagnetic or ultrasonic energy radiation, requirements to avoid the build up of electrostatic charge, and precautions to be taken to avoid circulating currents caused by stray magnetic fields.

Further information on the specification and design of equipment for use in hazardous areas may be found in various handbooks (McMillan, 1998; Bottrill *et al.*, 2005; EEMUA, 2010), or from one of the ATEX Notified Bodies, a full list of which is provided by the Department of Business Innovation and Skills (BIS) (formerly Department of Business Enterprise and Regulatory Reform)<sup>3</sup>. Further background information on area classification is provided on the HSE website<sup>4</sup>.

Within the standards mentioned above, there is relatively little information on area classification for flammable mists and the choice of suitable equipment to operate within explosive mist atmospheres. There are some useful recommendations in British Standard BS EN 1127-1 (BSI, 2011a), which deals with explosion prevention and protection in explosive atmospheres. This notes that mists can form an explosive atmosphere at temperatures that are far below the Lower Explosion Point (LEP) (a similar value to the flash point, see Section 1.6). The standard provides recommendations for maximum temperature of equipment, protective systems and component systems to prevent hot surface ignition, based on treating mists in the same way as flammable gases or vapours. For Category 1 equipment, the standard states that surface temperatures should not exceed 80% of the AIT of the combustible gas or liquid in °C, whilst for Category 3 equipment, surface temperatures should not exceed the 100% of the AIT. Requirements are also provided to prevent the potential ignition of explosive mist atmospheres from mechanically-driven sparks, using the same criteria for mists as that of flammable gases and vapours.

The most recent edition of BS EN 60079-10-1 (BSI, 2009c) now has an annex devoted to the issue of flammable mists. Information that is provided there can be summarised briefly as follows:

- The selection of equipment according to BS EN 60079-14 (BSI, 2008b) is not required for mist hazards.
- The assessment criteria in terms of hazardous zones for flammable gases and vapours specified in BS EN 60079-10-1 (BSI, 2009c) may not apply to mists.
- Ignition of mists by contact with hot surfaces generally requires temperatures higher than for vapour ignition.
- The conditions needed to form a flammable mist are so complex that only a qualitative risk assessment approach may be appropriate. To evaluate the degree of the hazard, it is useful to identify the factors involved in the handling of the liquid that may contribute to the formation of the mist, to try evaluate the probability of events occurring that could give rise to the mist, and to assess the mist flammability.
- In some cases where a spray is formed intentionally, which are likely to be considered as continuous or primary grades of release (e.g. spray painting), the area classification will usually be the subject of specific industrial codes and standards, such as BS EN 50176 (BSI, 1997).

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<sup>3</sup> <http://www.bis.gov.uk/files/file44775.pdf>, accessed March 2011.

<sup>4</sup> <http://www.hse.gov.uk/comah/sragtech/techmeasareaclas.htm>, accessed March 2011.

- In most other cases, the grade of release will be classed as secondary grade (which under the guidance for gas explosive atmospheres would usually then be classed as Zone 2, although it may be Zone 1 or even 0 if the degree of ventilation was poor).
- Mists that are flammable are likely to involve such a high concentration of droplets that the mist will be visible, and this may lead to early detection.
- In situations where flammable mists occur internally within equipment, the area should be considered as hazardous, and venting of such areas through breathers or vents should preferably use mist extractors.
- Flammable limits may be of a similar order, or lower, than the equivalent vapour hazard.

The physics of mist formation are described in general terms in BS EN 60079-10-1 (BSI, 2009c) and it mentions, for example, that the flammable aerosol component of a spray release may involve as little as 1% of the total mass released. However, there is little in the way of quantitative methods to help determine when a liquid release will produce a flammable mist hazard, or how to determine the flammable limits, or select appropriate equipment.

In the petroleum industry, guidance on area classification is provided by the Energy Institute in the model code of safe practice, IP15 (EI, 2005). This document acknowledges that there is currently a lack of knowledge to provide suitable guidance on the HAC for flammable mist hazards. Pending further research, it suggests that a material that is not heated to within 5 °C of its flashpoint, and which is stored at atmospheric pressure in a storage tank with only a few metres head, be regarded as non-hazardous (Section A1.1 in EI, 2005). Where such liquids are pumped under pressure, IP15 suggests that they be treated as Category C fluids (i.e. liquids below their boiling point but above their flashpoint) for which hazardous areas are defined in IP15, based on the type of equipment in use.

In IP15, substances with a flashpoint of between 21 °C and 55 °C are classified as Class II(1), and those with a flashpoint between 55 °C to 100 °C as Class III(1). The number 1 in parentheses denotes that these liquids are handled below their flashpoint. Guidance based on the potential formation of flammable mists of Class II(1) and III(1) substances is provided for specific applications. For example, IP15 specifies that in fixed-roof storage tanks, the ullage space should be treated as Zone 0 due to the possibility for a flammable mist or spray to be present. Similarly, for tanker loading operations where the liquid is handled under pressure, it is assumed that Class II(1) and III(1) substances should be treated in the same way as liquids that are handled above their flashpoint, due to the potential for a flammable mist to form. A road tanker transporting kerosene (with a minimum flashpoint of 38 °C) would therefore be treated in a similar manner to a petroleum road tanker, where IP15 specifies an area 1 m in radius around the hose connection point as Zone 1, and another area 1 m in radius around each relief valve as Zone 2. For underground storage tanks (e.g. at commercial filling stations) the standard specifies that for diesel fuels, the formation of flammable mists is unlikely due to the low pressure conditions used for tanker unloading. Therefore the fill-points, manholes and delivery point area may be treated as non-hazardous in this case. For above ground tanks however, due to delivery of liquid at higher pressures, a Zone 2 area is specified.

In the context of the present work, IP15 provides useful data on the equivalent hole sizes for leaks from various sources, including pumps, compressors, flanges, valves. The data is relevant for secondary grades of release, i.e. releases that are unlikely to occur in normal operation and if so will only occur infrequently and for a short duration. The information is taken from Cox, Lees and Ang (1993), and is categorized according to the release frequency. IP15 also provides a methodology for calculating this release frequency.

The general paucity of information on the area classification of mists reflects the difficulty in characterising their behaviour. For a particular flammable gas, suitable test apparatus can be used to determine its MIE, which is well characterised by just its concentration (at standard temperature and pressure). For dusts, the matter is slightly more complex, since the ignition energy is affected by the particle size, the concentration of particles suspended in the air, and the levels of turbulence present in the test apparatus (induced by the air flows needed to keep the dust airborne). For mists, however, the matter is even more complex, since in addition to droplet size, concentration and turbulence, the following factors need to be considered:

- The droplet size produced by a spray is usually non-uniform, and may change due to agglomeration, evaporation or droplet breakup
- Droplets may also deposit on walls and form liquid films
- Vapour may be present, in addition to droplets, due to evaporation
- For multi-component fuels (e.g. diesel), evaporation of volatile fractions may change the composition of the droplets and vapour over time
- Larger droplets tend to fall under gravity and may distort in shape, and this can change the flame-propagating characteristics of the mist.

These factors are all investigated in Section 2, but it should be clear from this brief overview that even relatively simple tasks, such as the measurement of the MIE or MESH of mists, are not trivial.

## 1.5 PREVIOUS EFFORTS TOWARDS AREA CLASSIFICATION OF MISTS

A few approaches have been proposed in the literature that help point towards a potential area classification methodology for flammable mists.

McMillan (1998) stated that the primary factors that were important in determining the extent of hazardous areas from pressurized liquid spray releases were the release pressure and leak orifice geometry. For high pressure releases from small orifices, McMillan (1998) noted that all of the liquid released may form a mist, whilst for lower pressure releases with larger orifices, a smaller proportion of the liquid released would contribute, due to rain-out. In order to provide a conservative estimate of the hazardous area extent, it was suggested that the release velocity and the ambient “wind” speed should be assumed to be low (for the latter, a figure of 2 m/s was suggested). A table of recommended values for the extent of hazardous areas was provided (see Table 1), although it is unclear exactly how these values were determined. McMillan (1998) suggested that the maximum distance that a liquid jet may travel could be determined from a ballistic model, ignoring the effects of air resistance. This was used to help determine the location of the resulting liquid pool. For mists, however, McMillan (1998) recommended calculating the extent of the hazardous area by assuming that it was vapour, using equations suitable for gas releases.

Jagger *et al.* (2003) tentatively proposed guidance on the risk assessment of industrial environments where there was the potential for flammable mists to be present. The approach comprised the assessment of three aspects:

1. The probability that a release may occur, and the release characteristics
2. The likelihood of the release igniting

- The consequences of ignition, in terms of the resulting temperatures, production of smoke and toxic dose.

A flow chart was provided to guide the risk assessment process through each of these elements.

**Table 1** Hazardous areas due to mist formation, from McMillan (1998)

| Release pressure<br>N/m <sup>2</sup> | Extent of hazardous area<br>around leak in m <sup>2</sup> |                           |                          |               |
|--------------------------------------|---|---------------------------|--------------------------|---------------|
|                                      | CAF gasket  | Spirally supported gasket | 'o' ring and olive joint | Screwed joint |
| 1 × 10 <sup>4</sup>                  | 2.0   | 1.0                       | 1.0                      | 1.0           |
| 3 × 10 <sup>4</sup>                  | 2.0   | 1.5                       | 1.5                      | 1.0           |
| 1 × 10 <sup>5</sup>                  | 3.0   | 2.0                       | 2.0                      | 1.0           |
| 3 × 10 <sup>5</sup>                  | 5.5   | 3.0                       | 3.0                      | 2.0           |
| 1 × 10 <sup>6</sup>                  | 8.0   | 4.5                       | 3.5                      | 2.5           |
| 3 × 10 <sup>6</sup>                  | 15.5  | 6.0                       | 5.0                      | 3.5           |
| 1 × 10 <sup>7</sup>                  | 21.5  | 8.0                       | 7.0                      | 5.0           |

Note: The formation of mists was based on the following assumptions for the purposes of this table:

- CAF Gaskets:
  - 5% below 10<sup>5</sup> N/m<sup>2</sup>
  - 10% between 10<sup>5</sup> N/m<sup>2</sup> and 10<sup>6</sup> N/m<sup>2</sup>
  - 20% above 10<sup>6</sup> N/m<sup>2</sup>
- Spirally supported gaskets
  - 40% up to 10<sup>5</sup> N/m<sup>2</sup>
  - 100% above 10<sup>5</sup> N/m<sup>2</sup>
- 'o' Rings, olives and screwed joints:
  - 100% in all cases

Information on the probability of a release (Item 1) was not considered in detail, but it was noted that this could be obtained from historical data. To address Item 2, i.e. to determine the likelihood of ignition, was considered a serious challenge. For a full risk assessment, it was suggested that this should entail examination of the full inventory of potential ignition sources, including the location and temperature of any hot surfaces, the presence of lagged pipes or unsealed electrical equipment. Temporary activities, such as hot working would also need to be considered. They suggested that in some circumstances, various ignition sources could be discounted. For example, if surfaces were below the hot manifold ignition temperature it may be necessary to consider only fault conditions. Similarly, if the presence of naked flames in the environment was controlled, the possibility of open flame ignition might be discounted or at least reduced to a low level which allows for the occurrence of faults or unauthorised introduction.

Although the study of Jagger *et al.* (2003) considered specifically the ignitability of liquid releases of 'fire-resistant' hydraulic oils, it was noted that quantitative data from these experiments should be interpreted with care, since measures such as the spark energy or hot manifold ignition temperature are known to be influenced by many variables, such as the spray droplet size, concentration, and degree of confinement. A potential release of liquid could have quite different characteristics to those measured in their experiments. To address this uncertainty, they recommended that risk assessments for liquid releases should incorporate an element of expert judgement, to consider both the nature of the industrial environment and the relevant test data. The risk assessment would involve probability weighting factors for the likelihood of various scenarios occurring. Jagger *et al.* (2003) provided various examples and suggested a tentative methodology for how these might be determined. They also proposed that the classification of the hazard posed by fire resistant



hydraulic fluid releases be categorised into three classes: low, medium and high (see Table 2). This classification was undertaken on the basis of three potential liquid release scenarios (sprays, bulk fluid releases and fluids absorbed on a substrate) and, for each of these scenarios, three potential ignition mechanisms were considered (from sparks, hot surfaces or small open flames). Jagger *et al.* (2003) stressed that this was only a tentative proposal and that further analysis, in particular to assess the effects of the scale of releases, would be necessary before it could be adopted for widespread use.

Their risk assessment procedure proposed by Jagger *et al.* (2003) also considered the severity of the consequences of particular release events (Item 3). This is of less relevance to the present work, since current HAC methodologies do not usually account for the consequences of a release, although this may be taken into account by upgrading the specification of equipment within zones where there may be severe consequences from an ignition.

**Table 2** Tentative classification of liquid release hazards for use in a risk-assessment scheme, from Jagger *et al.* (2003).

| <i>Release</i>       | <i>Hazard</i>                      | <i>Low</i>         | <i>Medium</i>      | <i>High</i>      |
|----------------------|------------------------------------|--------------------|--------------------|------------------|
| Sprays               | Spark ignition energy limits, J    | $E > 50$           | $1 < E < 50$       | $E < 1$          |
|                      | Hot surface temperature limits, °C | $T > 600$          | $400 < T < 600$    | $T < 400$        |
|                      | Response to small open flame       | Immediate ignition | Transient flame    | Continuous flame |
| Bulk fluid           | Spark ignition energy limits, J    | Non-credible event |                    |                  |
|                      | Hot surface temperature limits, °C | $T > 600$          | $400 < T < 600$    | $T < 400$        |
|                      | Response to small open flame       | ?                  | ?                  | ?                |
| Fluid on a substrate | Spark ignition energy limits, J    | Non-credible event |                    |                  |
|                      | Hot surface temperature limits, °C | $T > 200$          | $100 < T < 200$    | $T < 100$        |
|                      | Response to small open flame       | No ignition        | Continuous burning |                  |

? indicates limits have yet to be developed

It was suggested by Puttick (2008) that primary assessment of the explosion hazard posed by mists should follow a similar approach to that taken currently for dusts. The primary assessment for combustibility or ambient temperature flammability (using a large ignition source) could be used to classify mists into combustibility groups, similar to the A/B classification adopted for dusts. A secondary assessment could then be made for sensitivity to ignition, i.e. the MIE. Puttick (2008) noted that this secondary assessment would be complicated by the sensitivity of the MIE to the temperature (due to the presence of fuel vapour), but proposed using flashpoint to provide a cut-off below which temperature effects would be unimportant. To account for the size range of droplets produced by a typical leak, it was noted that large droplets may rain-out leaving smaller ( $< 30 \mu\text{m}$ ) droplets suspended in the air. It was suggested that tests could be conducted using relatively monodisperse mists that were representative of the smaller size droplets produced from a spray release.

As noted in Section 1.4, the Energy Institute model code of safe practice, IP15 (EI, 2005) provides some limited guidance on the area classification of mists for application to the petroleum industry. For instance, it suggests that a material that is not heated to within 5 °C of its flashpoint, and which is stored at atmospheric pressure in a storage tank with only a few metres head, be regarded as non-hazardous (Section A1.1 in EI, 2005). Where such liquids are pumped under pressure, IP15 suggests that they be treated as Category C fluids (i.e. liquids below their boiling point but above their flashpoint) for which hazardous areas are defined in IP15, based on the type of equipment in use.

## 1.6 DEFINITION OF TERMS

**Aerosol:** The term “aerosol” is used generically here to describe a mist of fine droplets. It is defined more formally in BS EN 60079-10 (BSI, 2009c) as small (sub 50 µm) particles suspended in the atmosphere.

**Auto-Ignition Temperature (AIT):** The lowest temperature at which a flammable mixture will spontaneously ignite, without the presence of an energetic ignition source such as a pilot flame or spark. A description of a test method for measuring the AIT is given in BS EN 60079-20 (BSI, 2010b).

**Capillarity number:** The capillarity number,  $Ca$ , is the ratio of the Weber number,  $We$ , to the droplet Reynolds number,  $Re$ :

$$Ca = \frac{We}{Re} = \frac{\mu_L U}{\sigma} \quad (1.1)$$

where  $\mu_L$  is the liquid dynamic viscosity,  $U$  the relative droplet velocity and  $\sigma$  the surface tension. This dimensionless quantity was used by Bowen and Shirvill (1994) to express the ratio of the viscous to surface tension forces.

**Equivalence ratio ( $\phi$ ):** The ratio of the actual fuel-to-air ratio to the stoichiometric fuel-to-air ratio. Rich mixtures have an equivalence ratio greater than one, and lean mixtures an equivalence ratio less than one.

**Firepoint:** The firepoint of a liquid is defined as the lowest temperature at which ignition of the vapours on the surface of the liquid in an open cup is followed by sustained burning. The firepoint is higher than the flashpoint for hydrocarbons. For n-decane, for example, the firepoint is 62 °C whilst the flashpoint is 52 °C (Drysdale, 1998). A standard means of determining the firepoint (and related flashpoint) is the Cleveland Open Cup test method (BSI, 2001a). Data on firepoints is given by Kuchta and Cato (1968), Khan (1992) and Drysdale (1998).

**Flashing:** The process of flashing involves the near-instantaneous boiling of a liquid, due to a sudden change in pressure or temperature. For example, when Liquefied Petroleum Gas (LPG) is released into the air at atmospheric pressure, the liquid rapidly flashes to produce gas.

**Flashpoint:** The flashpoint is the temperature at which the saturated vapour and air mixture above the surface of the liquid is capable of propagating a flame, momentarily, when ignited with a rapid sweep of a small gas pilot flame over the liquid surface. The flashpoint coincides with the temperature at which the ratio of the saturation vapour pressure to the atmospheric pressure is equal to the lower explosive limit (expressed in terms of a volume fraction). The flashpoint is determined using standardised equipment, typically the Abel Closed Cup apparatus (BSI, 2008a). The flashpoint of a substance is primarily controlled by its volatility

and, to a lesser extent, its chemical reactivity. This contrasts to the AIT, for example, which is solely a function of the reactivity (see, for example, Babrauskas, 2003).

**Flow number:** The flow number for a nozzle is calculated from ratio of the liquid flow rate through the nozzle to the square-root of the pressure difference across the nozzle, see Lefebvre (1989).

**Fog:** A cloud of droplets usually produced by condensation of saturated vapour. Normally, most of the droplets have diameters less than 10  $\mu\text{m}$  (Lees, 2005), whilst meteorological fog (or cloud) droplets have typically a diameter of between 10  $\mu\text{m}$  and 15  $\mu\text{m}$  (Lefebvre, 1989).

**Gas Group:** A classification system for flammable gases defined by BS EN 60079-20 (BSI, 2010b) consisting of four groups (I, IIA, IIB, IIC) – see Section 1.4 (Equipment Grouping).

**Hazardous area (on account of explosive gas atmospheres):** A hazardous area with respect to explosive gas atmospheres is defined by BS EN 60079-10-1 as “an area in which an explosive gas atmosphere is or may be expected to be present, in quantities such as to require special precautions for the construction, installation and use of equipment”.

**Heterogeneous:** Something that is non-uniform in composition. In the context of mists, this refers to a mixture where the concentration is non-uniform due to the presence of droplets, see for example Ballal and Lefebvre (1981b).

**Homogeneous:** Something that is uniform in composition with zero spatial gradients in all directions. The term ‘homogeneous mixtures’ is used in some mist flammability studies to refer to pure gas mixtures, where there are no droplets present.

**Intrinsically safe:** Electrical equipment that is classified as being intrinsically safe is designed such that any sparking that may occur is incapable of causing ignition of the flammable atmosphere. Further information can be found in the standard BS EN 60079-11 (BSI, 2007).

**Laplace number,  $La$ :** The Laplace number, sometimes referred to as the Ohnesorge number, is a dimensionless parameter which expresses the ratio of the surface tension to the viscous forces acting on a droplet, see Equation ( 3.41 ).

**Lean limit:** The lowest concentration of fuel vapour in air (or oxygen) that can sustain the propagation of a flame away from a pilot ignition source. Usually this is expressed in terms of percentage by volume of the mixture.

**Lower Explosive Limit (LEL):** The lowest concentration of a mixture that will just support the propagation of a flame away from a pilot ignition source. Also known as the Lower Flammability Limit (LFL).

**Lower Explosion Point (LEP):** The temperature at which the saturated vapour above the surface of a liquid is at a concentration equal to the LEL. This measure is similar to the flashpoint, but it can be defined more exactly based on known values of the LEL and saturation vapour pressure of the substance. According to Brandes *et al.* (2004), the LEP should be expected to be around 5 °C below the flash point. A methodology for determining the LEP is given in BS EN 15794 (BSI, 2009a).

**Mass Median Diameter (MMD):** A measure used to characterise the size of droplets in a spray. According to its definition, half of the total spray mass lies above the MMD and half is less than the MMD.

**Maximum Experimental Safe Gap (MESG):** The MESG is measured for gases according to the BS EN 60079-20 standard (BSI, 2010b) using apparatus consisting of two chambers, one inside the other, that are both filled with a mixture of flammable gas and air. The inner spherical chamber is linked to the outer chamber by a slot-shaped gap around its circumference, and the wall thickness around this gap is such that the path length between inner and outer chambers is 25 mm. The mixture is ignited in the inner chamber and the flame propagation into the outer chamber is assessed. When the gap width is sufficiently small, the flame is quenched as it passes from inner to outer chambers, and the flammable mixture in the outer chamber is not ignited. The MESG is defined as the maximum gap between the two parts of an explosion chamber that prevents ignition of the external gas mixture, for all concentrations of the tested substance in air. According to the BS EN 60079-20 standard, either the MESG or the Minimum Igniting Current (MIC) can be used to classify a flammable gas into one of four “gas groups” (I, IIA, IIB and IIC). Suitable flameproof equipment is then selected for use in potentially flammable atmospheres on the basis of this gas group classification.

**Minimum Hot Surface Ignition Temperature (MHSIT):** The minimum temperature of a hot surface that is sufficient to ignite fluid with which it is in contact.

**Minimum Igniting Current (MIC) Ratio:** The minimum current required from an inductive spark discharge to ignite the most easily ignitable mixture of gas, mist or dust in air, relative to that required to ignite a methane-air mixture. For details, see Babrauskas (2003) and BS EN 60079-11 (BSI, 2007).

**Minimum Ignition Energy (MIE or  $E_{min}$ ):** The smallest amount of energy needed to create a spark that can ignite the most easily ignitable flammable mixture of gas, mist or dust in air. To measure the MIE, the electrode shape, circuit capacitance, spark gap and the spark duration must be “optimum” values, where either a smaller or larger spark gap, or a shorter or longer duration spark, would produce a higher ignition energy. The MIE for flammable dusts is measured experimentally using a Hartmann tube apparatus, according to BS EN 13821 (BSI, 2002) or, for flammable gases, using an explosion sphere, according to ASTM E582-07 (ASTM, 2007). Various methods have been devised for measuring the MIE of mists, see for example Burgoyne (1963) or Rao and Lefebvre (1976). Models for the prediction of the MIE of mists have been developed by Ballal and Lefebvre (1978; 1979; 1981b) and Peters and Mellor (1980). In many texts (e.g. Britton, 1992), the MIE is considered to be the minimum spark energy needed to ignite a mixture of concentrations other than just the most easily ignitable mixture. Using this definition, a graph of the MIE against concentration is roughly parabolic in shape, decreasing from a maximum value at the LEL to a minimum, and then rising to a maximum at the UEL .

**Mist:** The term “mist” is used generically here to describe a collection of droplets of liquid suspended in a gas medium. It is usually distinguished from sprays in having lower momentum and behaving more as a quiescent cloud. In the context of fire suppression, water mists are generally assumed to be composed of smaller droplets than water sprays.

**Monodisperse:** A mist in which the droplets have a uniform size.

**Ohnesorge number,  $On$ :** The dimensionless Ohnesorge number,  $On$ , which is also sometimes referred to as the Laplace number or ‘Z’ number, characterises the viscous effects on the droplet breakup, see Equation ( 3.41 ).

**Polydisperse:** A mist composed of droplets of different sizes.

**Quenching distance:** Flames cannot propagate through very small spaces due to the heat losses to the surrounding solid surfaces. The quenching distance is the limiting size of opening through which a flame can only just pass. This is larger than the MESG, as the

MESG allows for re-ignition of the gas by hot combustion products or chemical radicals even if the flame is temporarily quenched.

**Rosin-Rammler distribution:** The Rosin-Rammler distribution is often used to characterise the size of droplets in sprays, and is given by:

$$1 - \nu = \exp\left[-(D/\delta)^\gamma\right] \quad (1.2)$$

where  $\nu$  is the fraction of the total liquid volume contained in droplets smaller than diameter  $D$ ,  $\delta$  is the Rosin-Rammler diameter and  $\gamma$  is a constant indicating the range of droplet sizes. A higher value of  $\gamma$  indicates that the spray is composed of more uniformly-sized droplets. A typical range of values for  $\gamma$  for pressure-driven atomizers is between 2.0 and 2.8 (Lefebvre, 1989).

**Self-similar:** A term used to describe the behaviour of velocity and concentration in jets, where the radial profiles of velocity or concentration at different axial positions have the same shape and, when suitably normalized, are coincident when plotted on the same graph axes.

**Shear-thinning:** A non-Newtonian liquid in which the viscosity reduces at high shear rates. This property is used in paints to enable easy application and for the viscosity to increase once the applied shear stress has been removed.

**Spalding mass transfer number,  $B$ :** A dimensionless number used to describe fuel volatility, which can be calculated from:

$$B = \frac{Y_s - Y_\infty}{1 - Y_s} \quad (1.3)$$

where  $Y_s$  and  $Y_\infty$  are the vapour mass fractions at the droplet surface and far from the droplet surface, respectively, (Turns, 2000).

An alternative expression for the transfer number was given by Lefebvre (1989):

$$B = \frac{c_{p,g}(T_f - T_b)}{L + c_{p,f}(T_b - T_{F0})} \quad (1.4)$$

Equation (1.4) applies to cases where the droplets that are just starting to ignite, and hence they have an initial internal temperature  $T_{F0}$ , below the boiling point,  $T_b$ . Other terms in this expression are the flame temperature,  $T_f$ , the latent heat of vaporization,  $L$ , the specific heat capacity of the gas,  $c_{p,g}$ , and the specific heat of the fuel,  $c_{p,f}$ . Further definitions are provided by, for example, Sirignano (2005).

Values for  $B$  for six common hydrocarbons were given by Ballal and Lefebvre (1978) as follows: heavy fuel oil = 1.5, light fuel oil = 2.5, diesel oil = 2.8, gas oil = 3.1, kerosene = 3.7, iso-octane = 6.1.

**Spray:** A momentum driven collection of droplets usually produced by atomisation of liquid though mechanical forces, e.g. a pressurized release through a nozzle. Typically, most of the droplets in spray have diameter greater than 100  $\mu\text{m}$  (Lees, 2005).

**Spray Flammability Parameter (SFP):** A measure developed by Khan (1992) to characterise the flammability of sprays based on the potential chemical release rate from the spray igniting, and the critical heat flux for ignition.

**Stoichiometric:** The concentration of fuel which in an ideal combustion process is burned completely, resulting in no excess of fuel or oxygen.

**Stokes number,  $St$ :** The ratio of the droplet momentum response time to a characteristic time relating to the surrounding flow field. For a mist in air for which  $St \ll 1$ , the droplets respond very quickly relative to changes in the flow field and therefore have a velocity similar to the surrounding air. For  $St \gg 1$ , the droplets have little time to respond to changes in the surrounding air velocity, and their trajectory will not be significantly influenced by the motion of the air, see Crowe *et al.* (1998).

**Sauter mean droplet diameter (SMD or  $D_{32}$ ):** The droplet diameter for an equivalent set of uniform spherical droplets with the same total volume to surface area ratio as the mist or spray. It is calculated from:

$$SMD = D_{32} = \frac{\sum N_i D_i^3}{\sum N_i D_i^2} \quad (1.5)$$

where  $N_i$  is the number of droplets and  $D_i$  is the middle of the size range  $i$ , where summation is applied across the full range of droplet sizes. The SMD is often used to characterise the size of droplets in sprays and mists, although it was argued by Aggarwal and Sirignano (1986) than an alternative measure,  $D_{20}$ , is more appropriate for assessing spray flammability, since it provides a more accurate representation of the average surface area, which is the dominant factor in ignition of polydisperse sprays.

**Temperature Class:** According to BS EN 60079-14 (BSI, 2008b) a gas or vapour is given one of six temperature classes (T1, T2, T3, T4, T5 or T6) on the basis of its auto-ignition temperature, where T1 has the highest AIT (greater than 450 °C), and T6 has the lowest AIT (between 85°C and 100°C). The temperature class is used to select appropriate equipment for use in atmospheres that are potentially flammable. Temperature classes are provided for a range of common pure substances in Annex B of BS EN 60079-20 (BSI, 2010b).

**Upper Explosive limit (UEL):** The highest concentration of a mixture that will ignite and burn with a flame. Also known as the Upper Flammability Limit (UFL).

**Varicose:** A term used to describe the appearance of a liquid jet as it breaks up under the influence of radially symmetric waves resulting from the interaction of primary disturbances in the liquid and surface tension forces. For further information, see Lefebvre (1989).

**Volatility:** A measure of the ease of producing vapour upon heating a liquid. Liquids are highly volatile if they have a high vapour pressure (i.e. low boiling point) and the enthalpy of vaporization is low.

**Weber number:** The dimensionless Weber number,  $We$ , is the ratio of the disruptive hydrodynamic force to the stabilizing surface tension force:

$$We = \frac{\rho V^2 D}{\sigma} \quad (1.6)$$

where  $\rho$  is the density of the fluid continuum surrounding the droplet,  $V$  is the relative velocity between droplet and fluid continuum,  $D$  is the droplet diameter and  $\sigma$  the surface tension of the droplet.

## 2 FLAMMABILITY OF MISTS

There are a number of potential physical mechanisms that could cause a mist to ignite. Sources of ignition include: heat energy; electrical energy; mechanical energy; and chemical energy (HSE, 2003). It is outside the scope of the present work to consider all the possible ignition sources. A number will be peculiar to the nature of the industrial activity and require the Dutyholders through their workplace risk assessments to determine that adequate control measures are in place to prevent ignition. This review particularly concentrates on those ignition mechanisms that are relevant to the design of equipment to be used in zoned areas, namely: electrical sparks, hot surfaces, and hot gases or flames. The discussion therefore focuses on the Minimum Ignition Energy (MIE), Lower Explosive Limit (LEL), Maximum Experimental Spark Gap (MESG), Minimum Igniting Current (MIC) and Minimum Hot Surface Ignition Temperature (MHSIT).

The aim here is to summarise information that will help to identify when a mist will be flammable, and determine the specification of equipment to be used in flammable mist atmospheres. Following the standard approach taken in HAC, the consequences of mist ignition will not be examined in detail.

### 2.1 MINIMUM IGNITION ENERGY (MIE) AND LOWER EXPLOSIVE LIMIT (LEL)

#### 2.1.1 Physics of spark ignition and flame propagation

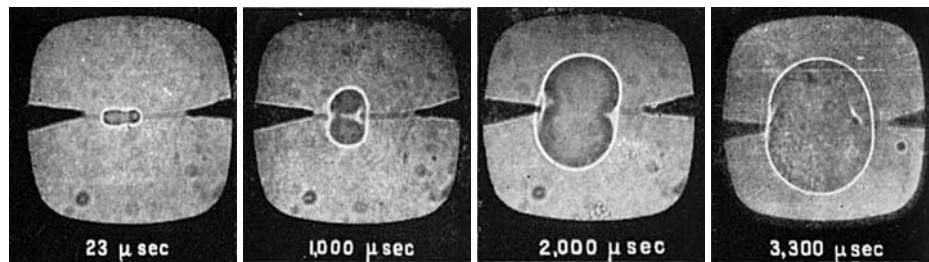
When a spark is generated between two electrodes submerged in a mist of fine droplets, the temperature rapidly increases within a small, roughly spherical, volume of gas and droplets, known as the spark kernel. Within this volume, any fuel droplets rapidly vaporise and the fuel vapour rapidly mixes with the surrounding air. Since the temperature is high, reaction rates tend to be extremely fast and the fuel vapour is almost instantly transformed into combustion products, releasing heat in the process.

If the rate of heat release due to reaction of the evaporated fuel droplets is higher than the rate of heat loss from the spark kernel to the surrounding unburnt gas, high temperatures will be sustained, the spark kernel will grow and a self-sustaining flame will start to propagate through the mist. If, on the other hand, the rate of heat release within the ignition kernel is less than the heat loss to the surroundings, the temperature within the kernel will fall, the rate of fuel evaporation will decrease and the spark kernel will be extinguished. These two processes are illustrated in Figure 1 for the case of gas ignition, which exhibits similar behaviour to ignition of a mist of fine droplets.

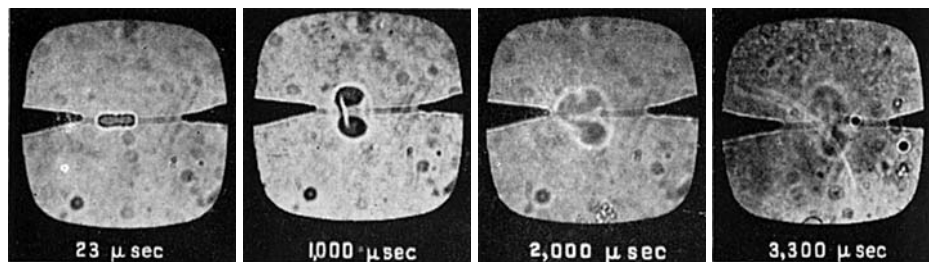
When the mist droplets are very small (with diameter less than 10  $\mu\text{m}$ ), as the flame propagates through the mist, the droplets vaporise ahead of the flame front and the flame travels through essentially a vapour-air mixture. The flammability limits for the mist in this case are therefore similar to that of the corresponding vapour-air mixture (Zabetakis, 1965; Burgoyne and Cohen, 1954; Faeth and Olson, 1968).

For larger droplets, there is insufficient time for the droplets to vaporise completely before becoming engulfed in the advancing flame front. Each droplet then burns with its own diffusion flame, rather than as a homogeneous gas mixture. For droplets larger than around 40  $\mu\text{m}$ , heat transfer from one burning droplet to its neighbours becomes the dominant mode of flame propagation through the mist (Burgoyne and Cohen, 1954). Flame propagation will then not occur if the distance between neighbouring droplets is large. At the Lower Explosive Limit (LEL), Burgoyne and Cohen (1954) found that the mean distance between droplet

centres was around 22 times the droplet diameter for droplets smaller than 10  $\mu\text{m}$ , and around 31 times the droplet diameter for droplets with diameter larger than 40  $\mu\text{m}$  (see Figure 2).



Case A: Kernel expands and leads to ignition



Case B: Kernel dies away and does not lead to ignition

Figure 1 Ignition kernel propagation and non-propagation, from HMSO (1957)

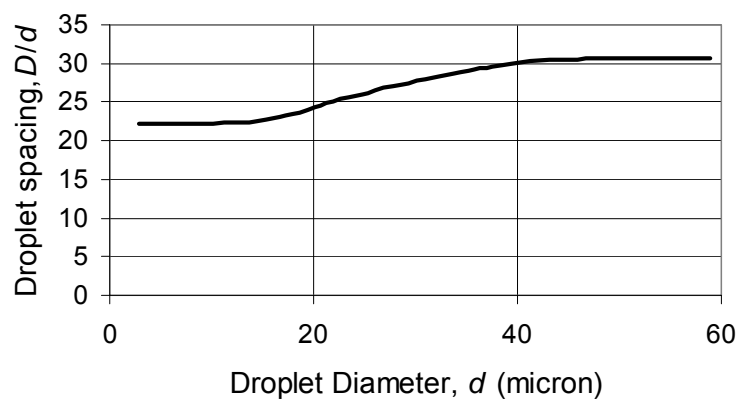


Figure 2 Droplet spacing in monodisperse tetralin mists at the LEL, from Burgoyne and Cohen (1954).

The LEL of mists with droplets larger than around 20  $\mu\text{m}$  has been found to depend strongly on the experimental apparatus used to measure the LEL. Many studies have used flame tubes in which the mist is quiescent or moving very slowly when it is ignited. Usually in these experiments, the mist is ignited at the bottom of the tube, and the resulting flame propagates vertically upwards. Examples include the experiments of Burgoyne and Richardson (1949), who studied quiescent mists in a closed-end flame tube, Burgoyne and Cohen (1954) and Taylor (1957), who studied mists flowing downwards in flame tube at speeds of around 0.03 m/s, and Danis *et al.* (1988) who studied slightly higher mist speeds of between 0.25 to 1.5



m/s. In these studies, the mists were monodisperse and the various sets of measured LEL were fairly consistent. A few other measurements have been reported using different experimental arrangements, where the flow has been momentum-dominated and the mist has been produced by a spray, with a range of droplet sizes (Anson, 1953; Rao and Lefebvre, 1976). The measured LEL and MIE in these cases has been quite different from those recorded with nearly-quiescent mists.

In nearly quiescent mists with droplets larger than around 20  $\mu\text{m}$ , the LEL is lower than in mists composed of smaller droplets or just vapour. The measurements of tetralin mists by Burgoyne (1963) showed that the LEL decreased from around 48  $\text{g/m}^3$  to around 5  $\text{g/m}^3$  as the droplet diameter was increased from around 10  $\mu\text{m}$  to 150  $\mu\text{m}$ . To put these concentrations into context, in atmospheric clouds or fog, the water droplet concentration varies between around 0.05  $\text{g/m}^3$  and 1.5  $\text{g/m}^3$ , with droplet diameters of between 1  $\mu\text{m}$  and 30  $\mu\text{m}$  (Middleton, 1952). Flammable mists are therefore likely to be optically dense, i.e. visibility will be limited.

Several explanations have been proposed to explain the reduction in LEL with increasing droplet size. The most physically consistent appears to be that of Burgoyne (1957; 1963) who related the behaviour to the mist droplets falling downwards under gravity, i.e. the sedimentation effect. For an upward propagating flame, the presence of droplets falling vertically downwards leads to an increase in the relative speed between the flame front and the droplets. This has the effect of increasing the flow rate of fuel into the advancing flame front. Hence the concentration of fuel can be reduced below the LEL of a static mixture, whilst maintaining the local LEL concentration at the rising flame front. This model explains the reverse behaviour that is observed for downward propagating flames, where the presence of falling droplets reduces the flow rate of fuel into the advancing flame front and the LEL is increased, or in some cases downward flame propagation is not possible at all. This theory has also been used to explain the behaviour of flammable dusts by, for example, Rasbash (1986).

An additional factor relates to the presence of the diffusion flame around individual droplets. As droplets increase in size, the sedimentation speed increases and the elongated “tails” of the surrounding diffusion flame grow longer. This enhances radiative heat transfer between neighbouring droplets, which enhances flame propagation (Burgoyne, 1963).

Lewis and von Elbe (1987) noted similarly that larger droplets become distorted due to their greater inertia and slower response to acceleration of the surrounding air (i.e. higher Stokes number). This distortion could arise from either them falling under gravity relative to the air or from an acceleration of the surrounding flow. They proposed that the non-symmetric expanding flame around the distorted droplets would produce an unbalanced thrust force, causing the large droplets to accelerate. Larger droplets would therefore communicate flame more readily than small droplets, which would be more spherical in shape and therefore not exhibit significant flame-driven accelerations. Since the flame could be propagated with a greater separation distance between droplets for mists composed of large droplets, the LEL would therefore be reduced.

The heterogeneous nature of the vapour concentrations, due to the presence of droplets has also been thought to contribute to the reduction in the LEL of mists (Danis *et al.*, 1988). Droplet evaporation creates localised regions where the vapour concentration is within the flammable range, despite the overall (average) concentration of the mixture being below the LEL.

Sprays produced by a release of pressurized liquid through an orifice are usually composed of larger droplets (with diameters typically 20  $\mu\text{m}$  to 200  $\mu\text{m}$ ) than those formed by condensation of a saturated vapour (diameters usually less than 20  $\mu\text{m}$ ). Due to the greater sedimentation speed of larger droplets, the LEL could be lower in a spray than in a

condensation aerosol. However, in sprays the flame propagation direction may not necessarily be downwards, the sedimentation speed may be small in comparison to the droplet velocity and there may be other effects related to droplet breakup, the entrainment of fresh air and turbulence. In some experiments, this appears to have led to the LEL increasing rather than decreasing as the droplet size has increased (Anson, 1953; Rao and Lefebvre, 1976).

The above considerations apply equally well irrespective of the volatility of the flammable liquid. It is not necessary to have vapour concentrations in the flammable range at ambient temperatures in order for a flame to propagate through the spray. Fine sprays of heavy fuels or cleaning oils with a flashpoint above 300 °C can still ignite and produce severe explosions at room temperatures (von Pidoll, 2001). In the previous review of spray and mist explosions, Eckhoff (1995) concluded that a spray of any combustible liquid in air will be explosive at atmospheric pressure and normal temperature provided droplets are less than 100 µm in diameter and the droplet mass concentration in air is between 100 g/m<sup>3</sup> and 500 g/m<sup>3</sup>, regardless of the fuel volatility.

The minimum ignition energy (MIE) necessary to produce a self-propagating flame in a mist is affected by a number of factors. The most significant of these is the droplet size, but the fuel concentration, volatility, air velocity and the presence of any fuel vapour (in addition to the droplets) are also important. These factors were studied in detail by Ballal and Lefebvre (1978; 1979; 1981b) and Peters and Mellor (1980), who developed models for the ignition energy and quenching distance that were shown to be in good agreement with experimental data for a range of mists and sprays of various substances.

For a given mist concentration (in terms of mass of liquid within a given volume of air), as the droplet size decreases, the effective surface area available for evaporation increases and therefore the MIE decreases. For monodisperse mists, the optimum droplet diameter which requires the minimum MIE appears to be between 10 µm and 30 µm (Singh and Polymeropoulos, 1985; Danis *et al.*, 1988). Within this size range, the droplets seem to be sufficiently large to still create some wrinkling of the flame front (and enhance combustion), whilst being sufficiently small to evaporate quickly. It has been thought that flame speeds in mists with the optimum droplet size may exceed those of the equivalent vapour mixture, for the same overall fuel concentration (Polymeropoulos and Das, 1975; Hayashi *et al.*, 1976; Ballal and Lefebvre, 1981a; Danis *et al.*, 1988; Bowen and Cameron, 1999). However, recent laboratory-scale experiments did not find any significant increase in flame speeds due to the presence of droplets within this optimum size range (Lawes *et al.*, 2006), although laminar flames in mists were found to become more unstable than those in gaseous mixtures. This matter has recently been investigated further by Sulaiman and Lawes (2010) and Lawes and Saat (2011).

For fuel concentrations close to stoichiometric, the ignition energy for a mist is usually greater than that of the equivalent vapour-air mixture, due to the need for the spark to first provide sufficient energy to vaporise the liquid droplets and then raise the vapour temperature sufficiently for ignition to occur. However, at much lower concentrations, approaching the vapour LEL, the ignition energy necessary to ignite a fuel mist can be lower than that required to ignite the equivalent vapour mixture (Danis *et al.*, 1988). This follows from the fact that mists composed of droplets larger than around 20 µm can be ignited at concentrations below the vapour LEL, whereas (by definition) vapour cannot be ignited at this concentration (see discussion below in Section 2.1.2 and, in particular, Figure 12).

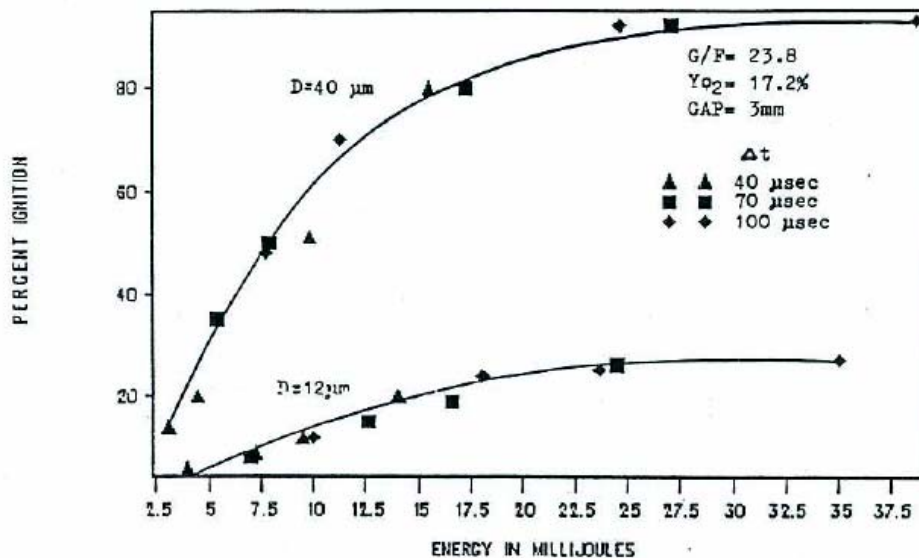
The presence of any vapour reduces the MIE of a mist (Ballal and Lefebvre, 1981b). As the fuel volatility is increased, the amount of energy required to vaporise the droplets is reduced and therefore the ignition requires less energy (Peters and Mellor, 1980).

Further details of the underlying physics involved in spark ignition of mists is given by Ballal and Lefebvre (1978; 1979; 1981b), Kuo (1986) and von Pidoll (2001). A summary of recent efforts to understand spray ignition and combustion behaviour, using sophisticated Direct Numerical Simulation (DNS) models, is provided by Mastorakos (2009).

### 2.1.2 Effect of droplet size and concentration

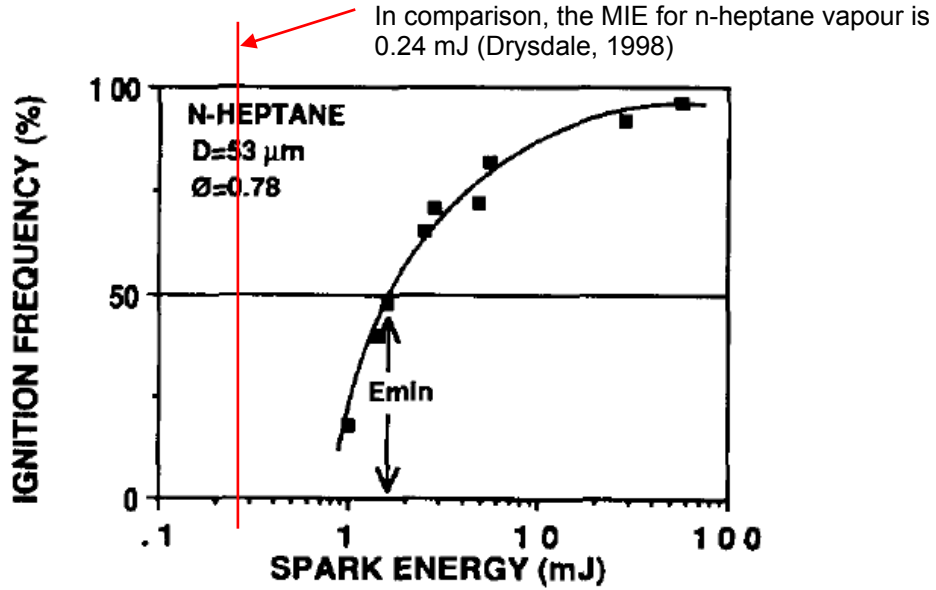
A number of studies have used spark ignition systems and flame tubes to measure the LEL and MIE of mists, and examine their variation as a function of the droplet size and concentration. The ignition behaviour reported in these studies is usually probabilistic. There is often no well-defined cut-off in spark energy below which ignition does not occur. Instead, the likelihood of ignition occurring each time a spark is generated decreases as the ignition energy is decreased. For example, in the study by Singh and Polymeropoulos (1985), the measured ignition frequency<sup>5</sup> decreased smoothly with spark energy below around 30 mJ (see Figure 3). For ignition energies higher than this, the ignition frequency was essentially constant. Their study was aimed at identifying the optimum droplet size to minimise the MIE. For the results shown in Figure 3 (a gas to fuel droplet ratio of 23.8, oxygen concentration of 17.2% vol/vol, spark gap of 3 mm and spark durations of between 40  $\mu$ s and 100  $\mu$ s), the larger 40  $\mu$ m droplets were found to produce higher ignition probabilities of nearly 90%, as compared to less than 30% for the 12  $\mu$ m droplets, provided that the spark energy was above 30 mJ. The optimum droplet size required to minimise the MIE was found to be between 22  $\mu$ m and 26  $\mu$ m (this is discussed further below). Singh and Polymeropoulos (1985) also provided measurements of MIE based on 20% and 60% ignition frequency.

In the study by Danis *et al.* (1988), the MIE was defined as the spark energy required to produce a flame which extended at least 5 cm into the mixture for an ignition frequency of 50% (i.e. the mist was ignited in half of the ignition attempts). Slightly smaller spark energies could ignite the mist less frequently (Figure 4).



**Figure 3** Variation of ignition frequency with ignition energy for monodisperse tetralin mists, from Singh and Polymeropoulos (1985)

<sup>5</sup> i.e. the percentage of ignition attempts that successfully result in a flame kernel being produced.



**Figure 4** Measured ignition frequency as a function of spark energy in a spray of n-heptane with droplet diameter  $D = 53 \mu\text{m}$  and equivalence ratio  $\phi = 0.78$ , from Danis *et al.* (1988).

In comparison, for flammable gases, the standard approach to measure the MIE described in ASTM E582-07 (ASTM, 2007) is to attempt ignition in around six tests, for a given spark energy and electrode spacing, and then if ignition is not successful, to incrementally adjust the energy or spacing until one of the six repeat spark tests produces ignition. Similarly, for flammable dusts, BS EN 13821 specifies that the MIE should be determined by reducing the spark energy in repeat tests until no flame propagation is observed in ten consecutive tests.

As mentioned above, for small droplets of tetralin with diameter of  $14 \mu\text{m}$  or less, Burgoyne and Cohen (1954) showed that the droplets vaporize completely before they are engulfed in an approaching flame front. Under these circumstances, the flame propagates into a vapour-air mixture, and the flammable limits were found to be the same as the corresponding vapour-air system (at the slightly elevated temperature necessary to vaporise the droplets).

In quiescent mists or low-momentum sprays, larger droplets fall under gravity faster than smaller droplets. The sedimentation speed of the droplets can be determined from Stokes Law (see Section 3). For flames propagating upwards, the mass flow rate of fuel into the advancing flame front is enhanced by the falling droplets, which lowers the LEL.

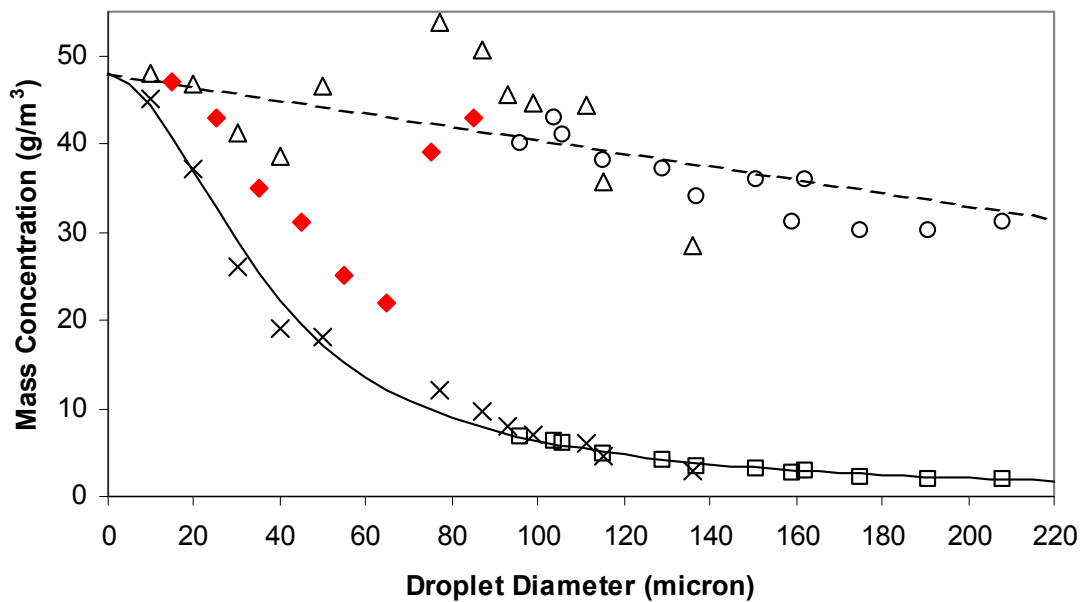
The effect of the particle sedimentation speed on the flammability limits for flames propagating either upwards or downwards was investigated by Burgoyne (1957; 1963). The analysis considered the “flame front” or “kinetic” concentration,  $C_k$ , given by:

$$C_k = C_s \left( \frac{V_s + V_f}{V_f} \right) \quad (2.1)$$

where  $C_s$  is the concentration of the suspended liquid,  $V_s$  is the downward sedimentation speed and  $V_f$  is the upward flame speed. The kinetic concentration can be considered to be the concentration of fuel into the flame front, using a reference frame that is moving upwards through the mist at the flame speed. As the droplet size is increased, the sedimentation speed increases and hence, for a given flame speed and static concentration, the kinetic concentration increases.

Results compiled for the static and kinetic concentrations in tetralin mists and methylene bistearamide are shown in Figure 5, using experimental data from Burgoyne and Cohen (1954), Burgoyne (1957) and Taylor (1957) and Browning *et al.* (1957). A similar figure to this was presented by Burgoyne (1963), without the methylene bistearamide data. For tetralin, the fine droplet mists were generated by condensing a saturated vapour, whilst those composed of larger droplets were produced from a battery of hypodermic needles. In all of the experiments, the mists were practically monodisperse. For very small droplets, less than 10  $\mu\text{m}$  in diameter, the results show that the LEL tends towards a value of around 48  $\text{g}/\text{m}^3$ , a common value for the LEL for many hydrocarbons (Drysdale, 1998).

In the early experiments by Burgoyne and Cohen (1954) and Burgoyne and Taylor (1957), they measured the static fuel concentration, from which the kinetic concentration has been calculated using Equation (2.1). These results are referred to in Figure 5 as “ $C_s$  measured” and “ $C_k$  calculated”, respectively. Subsequently, Burgoyne (1957) and Taylor (1957) devised an experimental method to measure directly the kinetic concentration, from which the static concentration has been determined by rearranging Equation (2.1). These results are referred to as “ $C_k$  measured” and “ $C_s$  calculated” in Figure 5. The flame speed,  $V_f$ , for tetralin has been assumed constant in these calculations, based on the value of 4.6 cm/s determined by Burgoyne (1963).



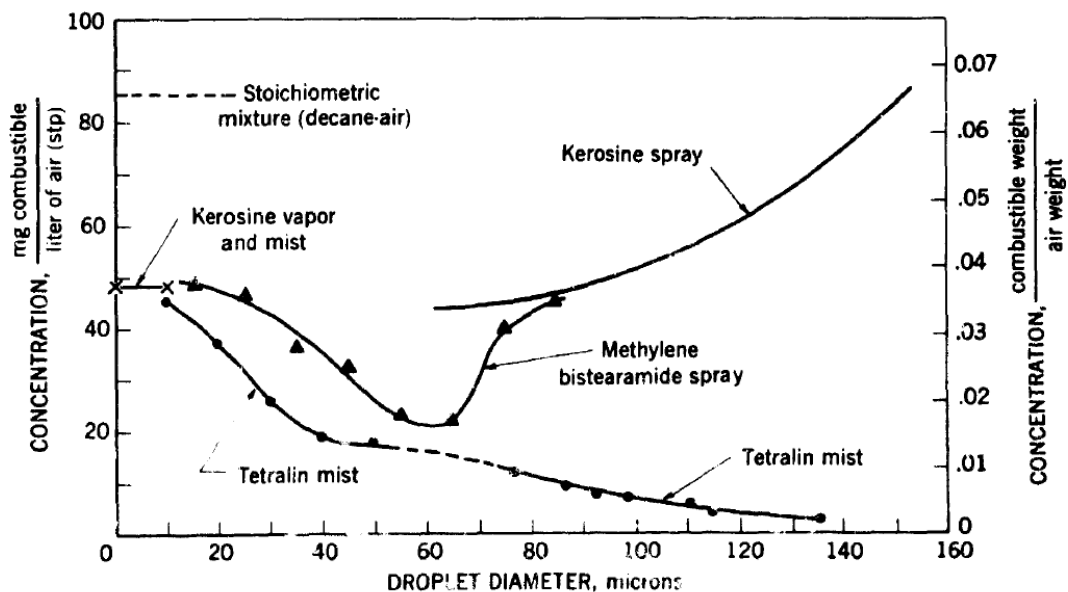
**Figure 5** Lower explosive limit for monodisperse mists expressed in terms of the static concentration ( $C_s$ ) and the kinetic concentration ( $C_k$ ), for tetralin:  $\times$   $C_s$  measured,  $\square$   $C_s$  calculated,  $\circ$   $C_k$  measured,  $\triangle$   $C_k$  calculated; and for methylene bistearamide:  $\blacklozenge$   $C_s$  measured. Lines show empirical fit: - -  $C_k$ ; —  $C_s$ .

Figure 5 shows that the kinetic concentration does not vary significantly with droplet size, decreasing approximately linearly from 48  $\text{g}/\text{m}^3$  for a droplet size of a few microns, to around 31  $\text{g}/\text{m}^3$  for a droplet diameter of 200  $\mu\text{m}$ . Assuming a linear fit between these two values, Burgoyne (1963) calculated the static concentration from Equation (2.1) (shown as the solid line in Figure 5) which matches the tetralin data well. However, these trends do not match the methylene bistearamide measurements from Browning *et al.* (1957). The substance, methylene bistearamide, is a solid wax, and in their experiments the particle suspension was circulated in a closed loop and ignited with an electric arc. The difference in behaviour of the

methylene bistearamide and tetralin may be related to evaporation effects or the non-quiet nature of the flow.

This matter was investigated further by Zabetakis (1965), who collated data from various ignition studies including the kerosene vapour and mist measurements from Zabetakis and Rosen (1957), the kerosene spray measurements from Anson (1953), the tetralin mist measurements from Burgoyne and Cohen (1954) and Burgoyne (1957), and the methylene bistearamide measurements from Browning *et al.* (1957). The results, presented in Figure 6, show that the increase in the static LEL for methylene bistearamide above a droplet size of 65  $\mu\text{m}$  is in agreement with the kerosene spray measurements of Anson (1953). The kerosene spray here shows the opposite trend to that observed for the quiet tetralin mists. Whilst the tetralin measurements showed a continuing decline in the LEL with increasing droplet size, the kerosene results showed an increase in LEL. Zabetakis (1965) attributed the result to the different flame propagation directions and experimental arrangements of Burgoyne and Cohen (1954), Browning *et al.* (1957) and Anson (1953). Whereas Burgoyne and Cohen (1954) and Burgoyne (1957) examined nearly-quiet mists, the studies of Browning *et al.* (1957) and Anson (1953) involved sprays or rapidly-flowing mixtures. This issue is discussed further in Section 2.1.4.

Due to the potential for quiet mists to produce a very low LEL, Zabetakis (1965) concluded that in situations where an explosive mist could form, all ignition sources should be removed or the oxygen concentration should be reduced to render the mixture inert.

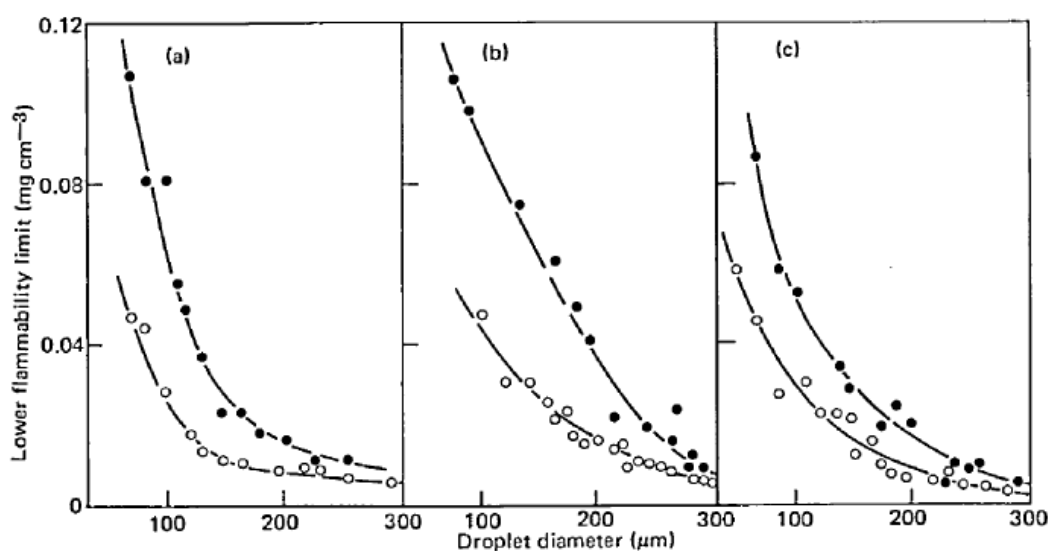


**Figure 6** Lower explosive limit of mists as a function of droplet diameter and fuel concentration, from Zabetakis (1965)

Measurements were undertaken by Cook *et al.* (1977) to determine the LEL of mists composed of relatively large droplets. In their experiments, a nearly monodisperse mist was created in a 1.5 m long vertical glass tube, 5 cm in diameter, using an array of hypodermic needles with an air co-flow. The mist was ignited at the open bottom of the tube using a hand-held turbulent diffusion flame. It was found that the mists could not be readily ignited using an electrical spark. Early test results showed that for small-diameter droplets the LEL was higher than previously reported by Taylor (1957) and Mizutani and Ogasawara (1965), who

found that the LEL for tetralin mists was around  $10 \text{ g/m}^3$  for droplets with diameter of  $100 \mu\text{m}$ . Cook *et al.* (1977) attributed this to the effect of the air co-flow down the tube impeding the upward propagation of the flame. The equipment was then modified using a cross-piece from which air was removed by suction, to reduce the co-flow effects. Results were reported for the flammability limits both with and without the suction present (Figure 7). Three liquids were tested: a general-purpose lubricating oil (OM 13), a hydraulic fluid (OM 33) and tetralin<sup>6</sup>. The results, shown in Figure 7, exhibited a clear trend for the LEL to decrease as the droplet size was increased up to the maximum droplet size tested of  $300 \mu\text{m}$ , for which the LEL was found to be less than  $10 \text{ g/m}^3$  for all three liquids.

Cook *et al.* (1977) also investigated the effect of the ignition source on the flammability limits by either changing the flow rate or the type of gas used in the hand-held diffusion flame that was used to ignite the mist. Significant differences were obtained with the various ignition sources (Figure 8). It was found that the height of the flame appeared to have a stronger influence on the mist ignition behaviour than the combustion intensity (i.e. the amount of energy released per unit flame volume).

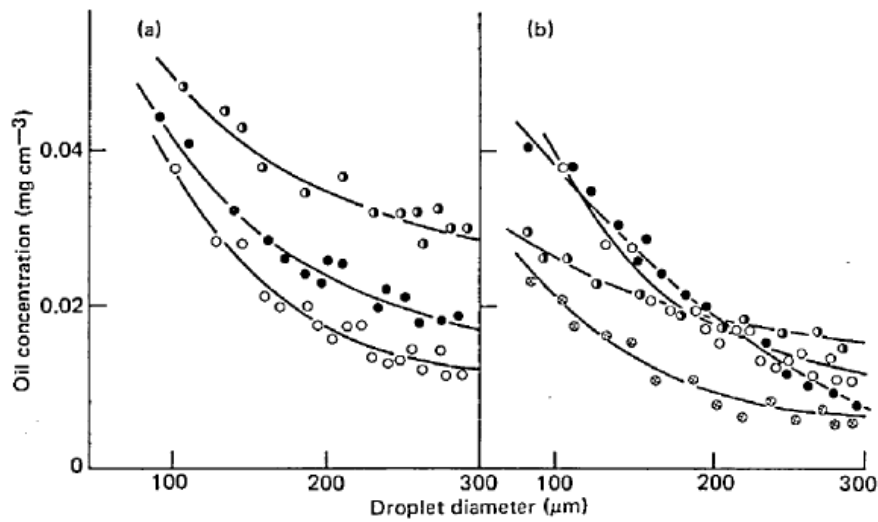


**Figure 7** Lower explosive limits for mists composed of different droplet sizes of a.) OM 13 oil; b.) OM 33 oil and c.) tetralin; ● without suction; ○ with suction. From Cook *et al.* (1977)

A comprehensive study of the quenching distance and MIE in quiescent mists was undertaken by Ballal and Lefebvre (1978). Their experiments were conducted with varying fuel equivalence ratio, air density, mean droplet size and fuel volatility. The effect of oxygen enrichment on the MIE was also investigated. A rotary cup atomizer was used which produced droplets that were practically monodisperse. The conditions tested included droplet SMDs of between  $30 \mu\text{m}$  and  $180 \mu\text{m}$ , and air pressures of between 0.2 bar and 1.0 bar. The ratio of oxygen to (oxygen + nitrogen) in the test atmosphere was varied between 15% and 50% and the fuels tested included: iso-octane, kerosene, gas oil, diesel oil, light fuel oil and heavy fuel oil. All of the tests were performed at room temperature at or below stoichiometric

<sup>6</sup> The number following OM in the Joint Service designation indicates the approximate kinematic viscosity in centistokes. The flashpoints of these liquids are approximately  $144 \text{ }^\circ\text{C}$  for OM 13, a minimum of  $160 \text{ }^\circ\text{C}$  for OM 33 and  $77 \text{ }^\circ\text{C}$  for tetralin (MOD, 1978; 2001).

concentrations. In the vicinity of the spark igniter, fuel vapour concentrations were practically zero, so that the tests could examine the ignition of the droplets, rather than any vapour.



**Figure 8** Influence of the ignition source on the lower explosive limits of OM 33 oil mists, from Cook *et al.* (1977): a.) coal gas with different symbols indicating flow rates of 93.5 cm<sup>3</sup>/s, 55 cm<sup>3</sup>/s and 37 cm<sup>3</sup>/s, b.) different ignition gases with different symbols indicating coal gas, hydrogen, propane and carbon monoxide.

In addition to presenting the results from experimental tests, Ballal and Lefebvre (1978) developed the following simple equation to predict the quenching distance,  $d_q$ , as a function of the droplet diameter ( $D$ ), the liquid fuel and air densities ( $\rho_f$  and  $\rho_a$ ), equivalence ratio ( $\phi$ ) and fuel volatility:

$$d_q = D \left[ \frac{\rho_f}{\rho_a \phi \ln(1 + B_{st})} \right]^{1/2} \quad (2.2)$$

where  $B_{st}$  is the Spalding transfer number for a stoichiometric mixture (see definition of terms, Section 1.6).

The model was derived by balancing the rate of heat loss through conduction on the spark kernel surface to the amount of heat released by combustion of the fuel within the spark kernel. It was assumed that the flow was quiescent, and that thermal heat transfer from the spark kernel was primarily through conduction with the surrounding air (thermal radiation and convection effects were assumed to be negligible in comparison). To produce a spark of sufficient energy to ignite the mixture it was assumed that the spark should release sufficient energy to raise the temperature of the spark kernel to the flame temperature.

The model predicted that the quenching distance was directly proportional to the droplet diameter and inversely proportional to the square root of the air density. If the concentration of droplets in the air increased (an increase in  $\phi$ ) the model predicted the quenching distance to decrease. Decreasing the liquid fuel density had the effect of increasing the surface area available for evaporation (for a given fuel concentration), which decreased  $d_q$ . Similarly,  $d_q$  was decreased by an increase in the fuel volatility (accounted for by  $B$ ).



The experiments undertaken by Ballal and Lefebvre (1978) showed that the quenching distance,  $d_q$ , predicted by Equation ( 2.2 ) was related to the optimum spacing between the electrodes needed to minimise the ignition energy,  $d_g$ , as follows:

$$d_q = 0.8d_g \quad (2.3)$$

Equations ( 2.2 ) and ( 2.3 ) can be used to predict the spacing between spark electrodes that is likely to give rise to the minimum ignition energy in quiescent mists with low vapour concentrations.

A limitation of Equation ( 2.2 ) is that the model predicts the quenching distance to approach zero as the mist droplet diameter,  $D$ , approaches zero, which is clearly unphysical. To address this matter, Ballal and Lefebvre (1978) presented a simple formula for the critical droplet size below which the mist behaved similarly to a flammable vapour, when Equation ( 2.2 ) was no longer considered valid. This was derived from the earlier work of Ballal and Lefebvre (1977), who derived the following expression for the quenching distance in gas mixtures:

$$d_q = \frac{10k}{c_p \rho S_L} \quad (2.4)$$

where  $S_L$  is the laminar flame speed in the vapour-air mixture,  $k$  is the thermal conductivity and  $\rho$  the density. The critical droplet size below which the mist behaved as a vapour, in terms of its ignition characteristics, was then given as follows:

$$D_{crit} = \left( \frac{10k_a}{c_{p,a} S_L} \right) \left[ \frac{\phi \ln(1 + B_{st})}{\rho_a \rho_f} \right]^{1/2} \quad (2.5)$$

Using this formula, Ballal and Lefebvre (1978) showed that in air at normal atmospheric temperature and pressure, the critical droplet sizes for iso-octane and heavy fuel oil were 26  $\mu\text{m}$  and 16  $\mu\text{m}$  respectively.

Ballal and Lefebvre (1978) also presented a model for the MIE, which was determined from the amount of energy required to raise a spherical volume of air of diameter  $d_q$  to the stoichiometric flame temperature:

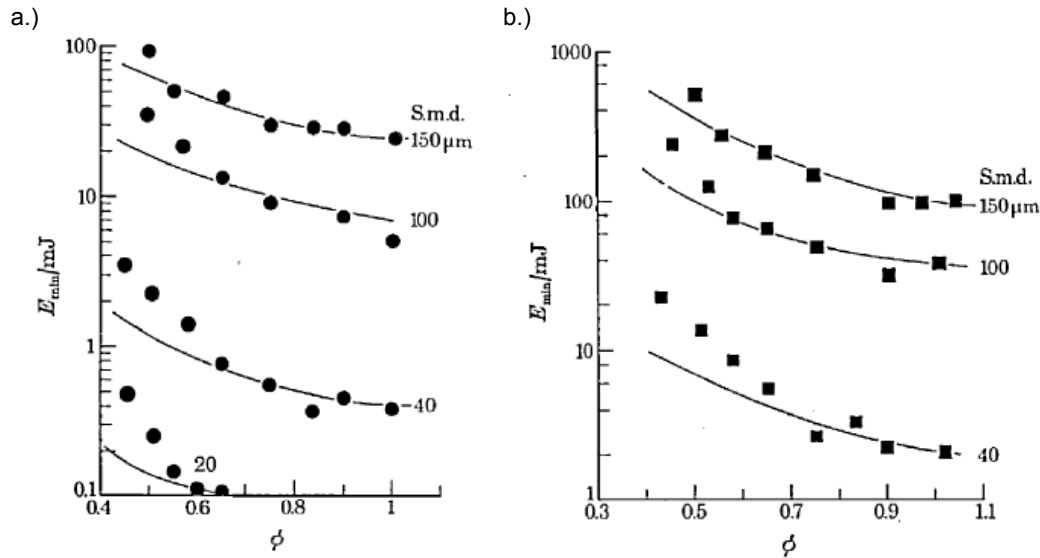
$$E_{min} = \frac{1}{6} \left( \frac{\pi c_{p,a} \Delta T_{st} D^3}{\rho_a^{1/2}} \right) \left[ \frac{\rho_f}{\phi \ln(1 + B_{st})} \right]^{3/2} \quad (2.6)$$

where  $\Delta T_{st}$  is the temperature increase from ambient to the adiabatic flame temperature at the stoichiometric condition ( $\phi = 1$ ) and  $c_{p,a}$  is the specific heat capacity of air. Tabulated values for the stoichiometric adiabatic flame temperature are provided in combustion textbooks and computer programs such as Gaseq<sup>7</sup>. According to Equation ( 2.6 ), in quiescent monodisperse mists, the ignition energy is proportional to the cube of the droplet diameter.

Predictions of the MIE using Equation ( 2.6 ), were found to be in good agreement with measurements taken in quiescent fuel mists, as shown in Figure 9. The results demonstrated that the MIE increases very rapidly as the droplet size increases (note the logarithmic vertical scale in Figure 9). The MIE was also shown to decrease if the fuel concentration was increased up to the stoichiometric concentration. As expected, the more volatile iso-octane fuel also required lower ignition energies.

<sup>7</sup> <http://www.gaseq.co.uk>, accessed February 2011.

Further analysis was undertaken subsequently by Ballal and Lefebvre (1979) for ignition of non-quietest, flowing mists. A unified set of models for spark ignition of flammable vapours and mists were later presented by Ballal and Lefebvre (1981b) that also took into account potential presence of vapour. The underlying physics in these models extended the ‘rate’-based approach described above. Since there are two rate-controlling processes when both vapour and droplets are present, the more sophisticated approach proposed by Ballal and Lefebvre (1981b) assumed that for a spark kernel to propagate, the time required for the fuel to evaporate and burn must be equal to or less than the time required for the cold mixture to quench the spark kernel by conduction and turbulent diffusion.



**Figure 9** Measured and predicted MIE at different equivalence ratios ( $\phi$ ) for quiescent mists of a.) iso-octane and b.) heavy fuel oil, in air at a pressure of 1 atm from Ballal and Lefebvre (1978): Solid line: predictions; symbols: measurements.

The unified set of models presented by Ballal and Lefebvre (1981b) (Table 3) account for fuel evaporation, reaction kinetics, fluid dynamics effects (including turbulence), different ambient pressures, fuel-air ratio, droplet size, the presence of polydisperse droplets, and fuel volatility. In the formulae given in Table 3, the symbol  $\Omega$  is the ratio of the mass of fuel vapour to the total fuel mass. From these equations, the MIE can be calculated by assuming that it is equal to the energy required to raise the temperature of a spherical volume of mixture of diameter  $d_q$  to the flame temperature:

$$E_{\min} = \frac{\pi}{6} c_p \rho \Delta T d_q^3 \quad (2.7)$$

If droplets are present, the specific heat capacity ( $c_p$ ) and density ( $\rho$ ) are those of the ambient air, and  $\Delta T$  is the increase in temperature from the ambient to the adiabatic flame temperature under stoichiometric conditions. For gaseous or fully-vaporised mixtures (i.e. when droplet sizes are small), the values of  $c_p$  and  $\rho$  are for the gas mixture.

The models of Ballal and Lefebvre (1981b) were found to produce results in very good agreement with measurement data (see Figures 10 and 11). Their validation only considered concentrations at or below stoichiometric, but Danis *et al.* (1988) subsequently showed that their models gave good predictions at concentrations up to an equivalence ratio of 1.8 (see discussion below).

**Table 3** Equations for the quenching distance in mists, from Ballal and Lefebvre (1981b)

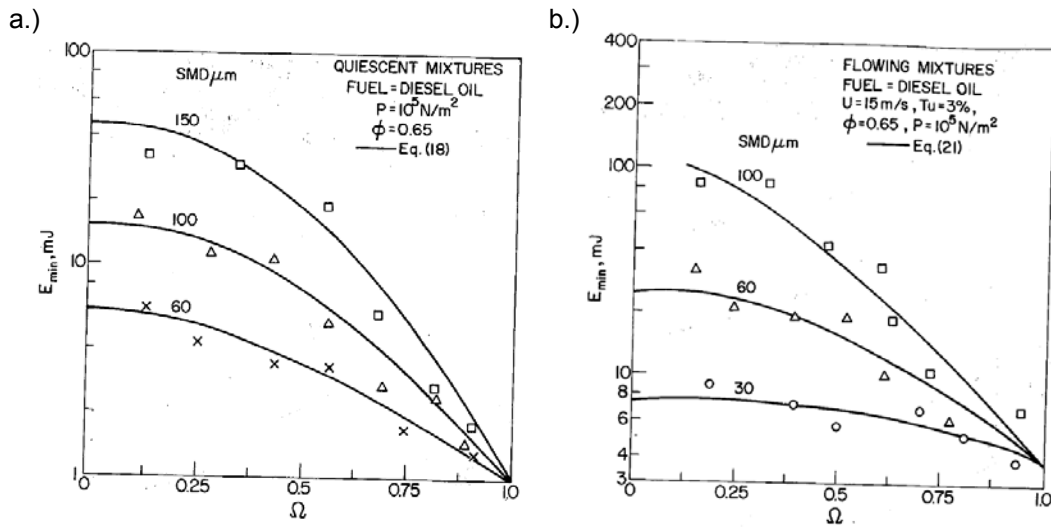
| TYPE of MIXTURE   | RELEVANT EQUATIONS         | EQUATIONS  | EXAMPLES of APPLICATIONS |
|---|----------------------------|--|--------------------------|
| Homogeneous, quiescent  | (3),(12)<br>(15),(16)      | $d_q = \frac{10\alpha}{S_L}$   | Ref. 2, Fig.3            |
| Homogeneous, low turbulence   | (2),(13),(15)              | $d_q = \frac{10\alpha^{0.5} (\alpha + 0.08u'd_q)^{0.5}}{(S_L - 0.16u')}$   | Ref. 2, Figs. 4 to 7     |
| Homogeneous, high turbulence  | (4),(14)<br>(15),(17)      | $d_q = \frac{10\alpha}{(S_L - 0.63u')}$  | Ref. 2, Fig. 8           |
| Heterogeneous, monodisperse, quiescent, $t = 0, \Omega = 0$         | (3),(10)<br>(15),(20)      | $d_q = D \left[ \frac{\rho_f}{\rho_g \phi \log(1 + B_{g1})} \right]^{0.5}$   | Ref. 3, Figs. 7 to 10    |
| Heterogeneous, monodisperse, quiescent, $t_c = \text{finite}$       | (3),(10)<br>(12),(18)      | $d_q = \left[ \frac{(1-\Omega) \rho_f D_{32}^2}{\rho_g \phi \log(1 + B_{g1})} + \left( \frac{10\alpha}{S_L} \right)^2 \right]^{-0.5}$  | Fig. 2                   |
| Heterogeneous, polydisperse, quiescent, $t_c = \text{finite}$       | (3),(10)<br>(12),(15),(18) | $d_q = \left[ \frac{C_3^2 (1-\Omega) \rho_f D_{32}^2}{C_1 \rho_g \phi \log(1 + B_{g1})} + \left( \frac{10\alpha}{S_L} \right)^2 \right]^{-0.5}$  | Figs. 4 to 6             |
| Heterogeneous, polydisperse, low turbulence, $t_c = \text{finite}$  | (2),(9)<br>(13),(15),(21)  | $d_q = [1 + 0.08u'd_q/\alpha]^{0.5} \left[ \frac{C_3^2 (1-\Omega) \rho_f D_{32}^2}{C_1 \rho_g \phi \log(1 + B_{g1}) (1 + 0.25 C_2^{0.5} Re_{D_{32}}^{0.5})} + \left( \frac{10\alpha}{S_L - 0.16u'} \right)^2 \right]^{-0.5}$ | Figs. 7, 8               |
| Heterogeneous, polydisperse, low turbulence, $t_c = 0$              | (2),(9)<br>(15),(21)       | $d_q = [1 + 0.08u'd_q/\alpha]^{0.5} \left[ \frac{C_3^2 (1-\Omega) \rho_f D_{32}^2}{C_1 \rho_g \phi \log(1 + B_{g1}) (1 + 0.25 C_2^{0.5} Re_{D_{32}}^{0.5})} \right]^{-0.5}$  | Fig. 3                   |
| Heterogeneous, polydisperse, high turbulence, $t_c = \text{finite}$ | (4),(11)<br>(14),(15),(22) | $d_q = \frac{0.32 Pr (1-\Omega) \rho_f D_{32}^{1.5} u'^{0.5}}{Z \rho_g^{0.5} \mu_g^{0.5} \phi \log(1 + B_{g1})} + \frac{10\alpha}{(S_L - 0.63u')}$   |                          |
| Heterogeneous, polydisperse, high turbulence, $t_c = 0$             | (4),(11)<br>(15),(23)      | $d_q = \frac{0.32 Pr (1-\Omega) \rho_f D_{32}^{1.5} u'^{0.5}}{Z \rho_g^{0.5} \mu_g^{0.5} \phi \log(1 + B_{g1})}$   | Ref. 1, Fig. 12          |

The Ballal and Lefebvre (1981b) models predict that the ignition energy increases as either the size of the droplets increases or the proportion of the fuel composed of droplets, instead of vapour, increases. The same trends are produced in both quiescent and flowing mixtures.

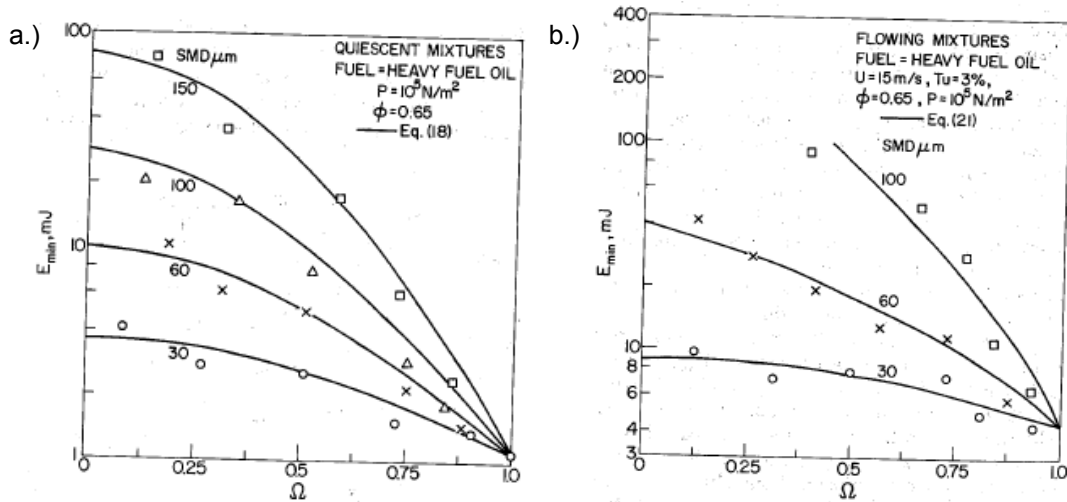
Danis *et al.* (1988) measured the MIE in monodisperse n-heptane and methanol sprays and compared the data against the relevant Ballal and Lefebvre model (1981b) and the similar Characteristic Time Model (CTR) model of Peters and Mellor (1980). In their experiments, Danis *et al.* (1988) used a vibrating orifice monodisperse aerosol generator which produced a range of droplet diameters ( $d$ ) from 30  $\mu\text{m}$  to 57  $\mu\text{m}$ . The droplets were discharged downwards into a 1.6 cm diameter test section into which spark electrodes protruded. Tests were conducted for equivalence ratios ( $\phi$ ) of between 0.44 and 1.8. In comparison, the lower and upper flammability limits for n-heptane vapour, in terms of equivalence ratio, are 0.56 and 3.6, whilst for methanol vapour they are 0.55 and 2.9 (Zabetakis, 1965).

The measurements showed that the MIE was reduced by decreasing  $d$  or by increasing the fuel volatility. For n-heptane, the MIE also decreased as  $\phi$  was increased up to around 1.5, but Danis *et al.* (1988) could not generate richer mist mixtures to establish the Upper Explosive Limit (UEL) or optimum fuel concentration for minimizing the MIE. In comparison, the minimum MIE for a pure vapour mixture (i.e. without any droplets) of n-heptane was obtained with an equivalence ratio of between 1.5 and 2.0. Measurements of mist

MIE were found to be in good agreement with predictions obtained using the models of Peters and Mellor (1980) and Ballal and Lefebvre (1981b) (see Figure 13).



**Figure 10** Influence of vapour concentration and mean droplet size on MIE for polydisperse diesel sprays: a.) quiescent mixtures; b.) flowing mixtures, Ballal and Lefebvre (1981b).

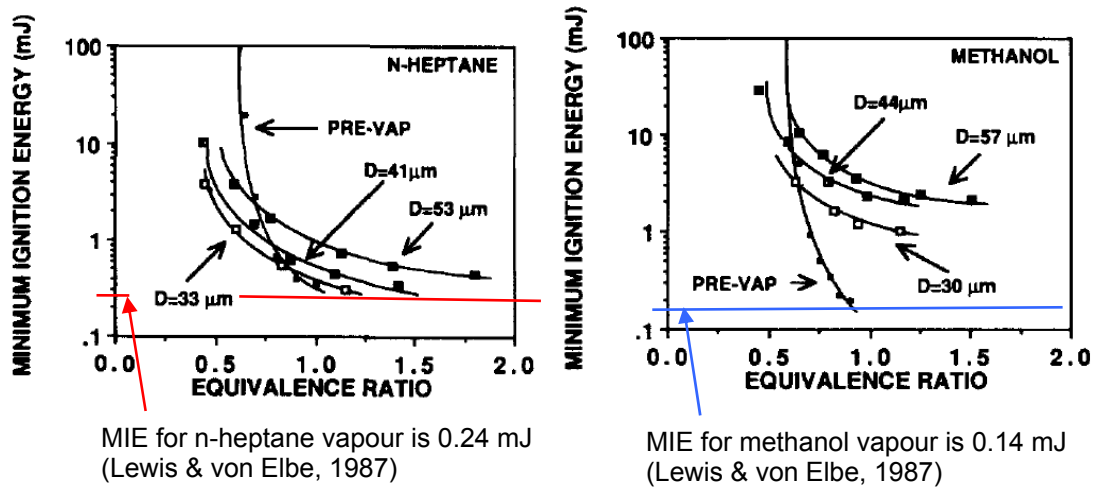


**Figure 11** Influence of vapour concentration and mean droplet size on MIE for polydisperse heavy fuel oil sprays: a.) quiescent mixtures; b.) flowing mixtures, Ballal and Lefebvre (1981b).

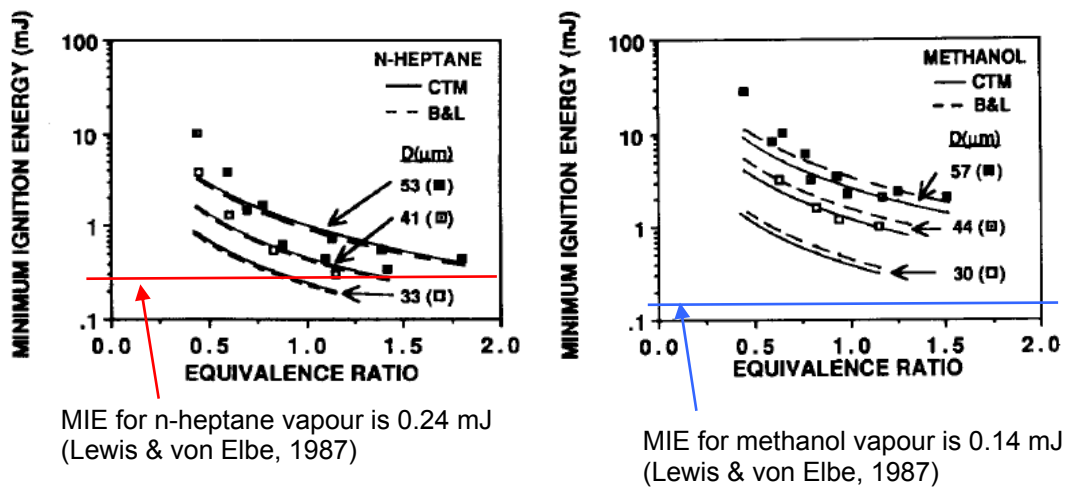
The effect of the equivalence ratio on the MIE was also studied by Dietrich *et al.* (1990), using mists of n-decane. In their experiments, the MIE was found to decrease monotonically as the equivalence ratio was increased from 0.7 to 2.2.

Tests undertaken by Hansen and Wilkins (2004) suggested that the UEL of mists may be higher than that of an equivalent vapour mixture. Using a  $6.0 \times 1.25 \times 1.25$  m explosion chamber, they found that explosion overpressures increased as the fuel equivalence ratio was

increased from one to five, for crude oil. They noted that mists may exhibit similar behaviour to dusts, in which the UEL is considerably higher than for flammable gases.



**Figure 12** Measurements of the MIE for monodisperse sprays of n-heptane and methanol with different droplet diameters ( $D$ ) compared to pre-vaporized gaseous mixtures, from Danis *et al.* (1988). Values of the MIE of n-heptane and methanol vapour from Dysdale (1988) are shown for comparison.



**Figure 13** Measured and predicted MIE for monodisperse sprays of n-heptane and methanol, from Danis *et al.* (1988). Lines: model predictions; symbols: measurements. Values of the MIE of n-heptane and methanol vapour from Dysdale (1988) are shown for comparison.

The LEL of the mists examined by Danis *et al.* (1988) were found to be less than the equivalent pre-vaporized mixtures, in agreement with the earlier findings of Burgoyne (1963) and Cook *et al.* (1977). Danis *et al.* (1988) also found evidence that the optimum droplet diameter for minimising the MIE was probably between 10  $\mu\text{m}$  and 30  $\mu\text{m}$ . However, this could not be confirmed experimentally due to the droplet size limitations of the nozzle used in their tests.

It was shown previously by Singh and Polymeropoulos (1985; 1986) for tetralin condensation aerosols, that the minimum MIE was obtained with droplet sizes between 22  $\mu\text{m}$  and 26  $\mu\text{m}$  (Figure 14). Similar results were also reported by Chan (1982) (see Babrauskas, 2003).

The results presented by Ballal and Lefebvre (1978; 1979; 1981b) and Danis *et al.* (1988) suggest that the MIE required to ignite a mist is probably higher than the MIE required to ignite a vapour-air mixture of the same substance at its optimum concentration for ignition. The trends shown in Figure 12, from Danis *et al.* (1988), particularly that for methanol, show that the pre-vaporised mixtures give lower MIE than mists.

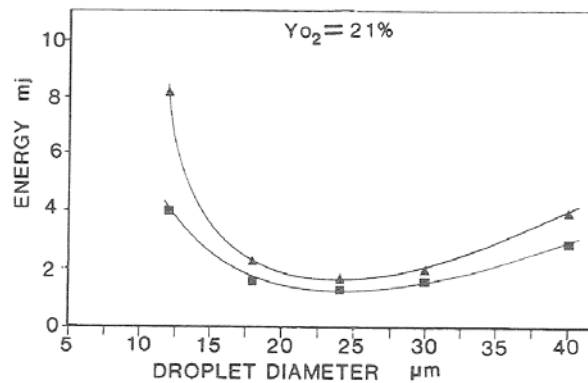
However these data are limited and the results are not conclusive. The experiments of Danis *et al.* (1988) were not conducted at sufficiently high fuel concentrations to establish clearly the value of the MIE across all possible fuel concentrations and the smallest droplet size was limited to 30  $\mu\text{m}$ .

Measurements of the ignition energy for n-heptane and methanol vapour were reported by Lewis and von Elbe (1987) across the full range of fuel concentrations. The resulting MIE, obtained for the most readily ignitable fuel concentration, are shown overlaid in Figure 12 against the Danis *et al.* (1988) data. This shows that the Lewis and von Elbe (1987) values are higher than would be obtained by extrapolating the pre-vaporised ignition energies measured by Danis *et al.* (1988). This is likely to be due to the considerable difficulty in obtaining consistent measurements of MIE, as discussed by Rose and Priede (1959a; 1959b).

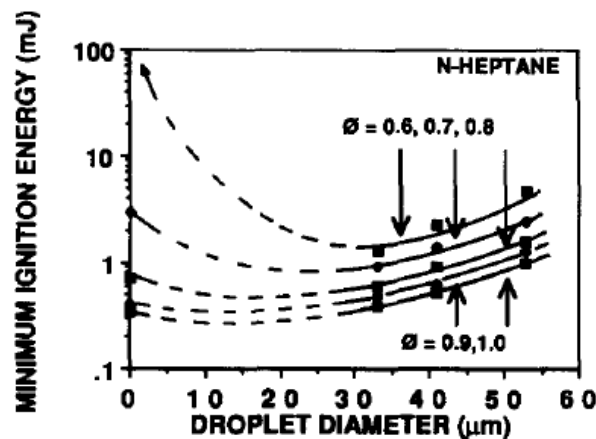
Danis *et al.* (1988) extrapolated the curves of ignition energy for n-heptane to show that a monodisperse mist composed of droplets within the optimum size range of 10  $\mu\text{m}$  to 30  $\mu\text{m}$  could have a lower ignition energy than the vapour, for equivalence ratios less than one (Figure 15). The vapour MIE is shown in this graph as a droplet diameter of 0  $\mu\text{m}$ . At the lowest equivalence ratio of 0.6, the comparison is striking, with a 33  $\mu\text{m}$  diameter droplet mist requiring nearly two orders of magnitude lower ignition energy than the equivalent vapour. These results are not surprising, however, since this fuel concentration is close to the vapour LEL.

The same figure from Danis *et al.* (1988) is reproduced in the well-known book on ignition by Babrauskas (2003), who asserted that the results show that a mist composed of droplets of the optimum size will be more readily ignitable than a pure vapour. However, this statement has only been validated for lean fuel concentrations by Danis *et al.* (1988). For rich mixtures, the ignition energy decreases for both pure vapours and mists. In fact, extrapolating the results of Danis *et al.* (1988) shown in Figure 12, to higher fuel concentrations, suggests that the true minimum MIE, based on the most readily ignitable fuel concentration, is probably lower for a pure vapour than it is for a mist.

Many of the measurements of MIE in mists, e.g. Singh and Polymeropoulos (1985; 1986), Burgoyne and Cohen (1954) and Cook *et al.* (1977), have used tetralin. Unfortunately, there appears to be no vapour MIE data in the literature for tetralin to establish whether the mist MIE is greater than the equivalent vapour. In any case, comparing the MIE of tetralin vapour to tetralin mists is not straightforward, since the boiling point is high (approx. 207  $^{\circ}\text{C}$ ) and comparisons would need to take into account the change in MIE with temperature, or pressure.



**Figure 14** Variation of MIE as a function of droplet size for monodisperse tetralin mists, from Singh and Polymeropoulos (1986)



**Figure 15** MIE in monodisperse n-heptane mists, from Danis et al. (1988). Dashed lines show extrapolations from measured values, shown as symbols. Results are shown for various values of the equivalence ratio ( $\phi$ ).

### 2.1.3 Effect of fuel volatility

The previous work reviewed above has shown that for hydrocarbon liquids, increasing the fuel volatility has two effects: firstly, increasing the amount of vapour present in the atmosphere surrounding the droplets, and secondly, decreasing the energy required to vaporise the remaining droplets. Mists produced by higher volatility hydrocarbon fuels therefore tend to have a lower MIE.

In quiescent or slow-moving mists, studies of the ignition behaviour of different hydrocarbon fuels include:

- Haber and Wolff (1923): measurements of LEL of fine mists of a petroleum fraction, tetralin and quinoline. For a review of this study, see Burgoyne (1957).

- Burgoyne and Richardson (1949) and Burgoyne *et al.* (1954): measurements of LEL with various mineral cutting oils, lubricating oil, sperm quenching oil and pool diesel oil using a vertical tube with pilot flame ignition.
- Burgoyne and Cohen (1954), Burgoyne (1957) and Taylor (1957): measurements of LEL of tetralin mists composed of small and large droplets, respectively, using a vertical tube with pilot flame ignition.
- Cook *et al.* (1977): measurements of the LEL of OM 13, OM 33 and tetralin mists composed of relatively large droplets, with and without a coflow.
- Ballal and Lefebvre (1978; 1979): measurements of the MIE in quiescent and flowing fuel mists of iso-octane, kerosene, gas oil, diesel oil, light fuel oil, heavy fuel oil
- Singh and Polymeropoulos (1985; 1986): measurements of the MIE of tetralin mists in a laminar air flow.
- Danis *et al.* (1988): measurements of the MIE and LEL of quiescent mists of n-heptane and methanol.
- Lee *et al.* (1996): measurements of the MIE of monodisperse two-component mixtures of n-heptane and n-decane sprays.

The models developed by Ballal and Lefebvre (1978; 1979; 1981b) and Peters and Mellor (1980) showed that the influence of the fuel volatility in the above cases appeared to be well-approximated using the Spalding mass transfer number.

Tests involving higher-momentum hydrocarbon sprays, or those in a fast-moving air stream include:

- Anson (1953): measurements of LEL in kerosene sprays
- Rao and Lefebvre (1976): measurements of LEL and MIE of horizontally-directed kerosene sprays in a fast co-flowing air stream.

The latter study was aimed at providing information to study flame-out and re-ignition of aero-engines.

Both the quiescent mist and higher-momentum spray studies mentioned above have been undertaken in carefully controlled laboratory conditions with the aim of isolating and measuring the influence of the various factors affecting LEL and/or MIE, such as fuel volatility, droplet size and concentration.

Further work on the flammability of mists and sprays has been undertaken using less well-controlled conditions that are closer to the scenarios likely to occur in industrial releases or incidents. This includes the work on JP-8 jet fuel by Kuchta *et al.* (1971), maize oil sprays by Tolson and Bennett (1996), fire-resistant hydraulic oils by Jagger *et al.* (2003) and Yuan (2006), and a range of substances (diesel, turpentine substitute, ethylene glycol, brake fluid, hydraulic oil and methanol) by Hawkworth *et al.* (2001). These works provide qualitative and some quantitative data on LEL and MIE, although the conditions present at the ignition source, in terms of droplet size and concentration, were in many cases less well quantified, and it is unclear whether the spark gap and duration were optimised in order to record the lowest value of the MIE.

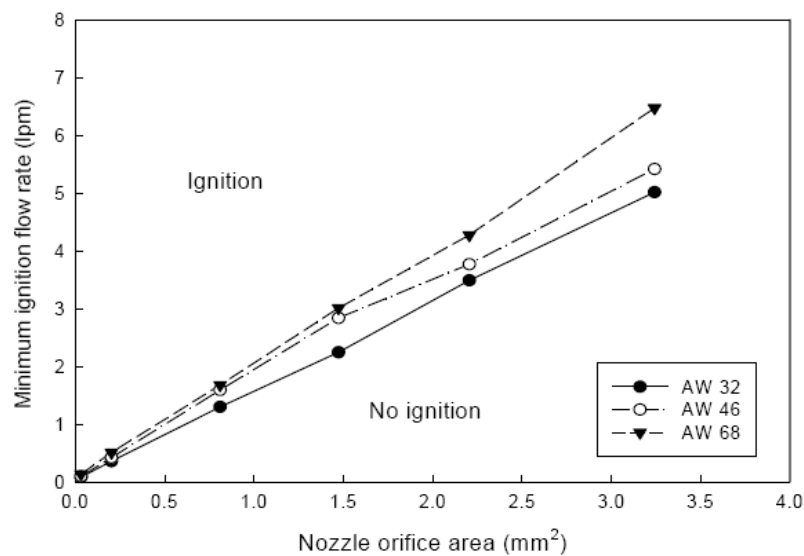
In the Hawkworth *et al.* (2001) study, a spray was generated using an air blast atomising system with an air pressure of between 0.25 barg and 1.5 barg. This produced a full-cone



spray with a cone angle of 15° to 22°, fuel concentrations of between 20 g/m<sup>3</sup> and 170 g/m<sup>3</sup>, and a droplet size range (Sauter mean diameter) of between 12 µm and 120 µm. The spark ignition system produced spark energy of up to 4.5 J, although details of the spark gap or duration were not provided.

For diesel, Hawkworth *et al.* (2001) found there to be a general trend for the ignition energy to decrease as the concentration increased from 50 g/m<sup>3</sup> to 150 g/m<sup>3</sup> on the jet axis. Sprays of a turpentine substitute exhibited similar trends in terms of the ignition energy decreasing as the fuel concentration increased. Ethylene glycol sprays could not be ignited for concentrations up to 170 g/m<sup>3</sup> with spark energies up to 4.5 J. Even a very powerful ignition source produced by oxyacetylene flame was unable to produce any sustained burning of the spray for this case. This was attributed to the high flashpoint (115 °C), low heat of combustion and the relatively poor atomisation that resulted from the high viscosity of the liquid (0.0091 kg m/s for ethylene glycol, as compared to 0.047 kg m/s for diesel and 0.0018 kg m/s for the turpentine substitute). Hawkworth *et al.* (2001) noted that their results showed good agreement with the findings from the literature. A spark energy of 33 mJ was required to ignite the diesel spray, which compared favourably to the spark ignition energy of 30 mJ measured by Ballal and Lefebvre (1978) for a droplet SMD of 50 µm.

In the study by Yuan (2006), sprays of various hydraulic fluids and diesel were generated by impingement-type nozzles and ignited using a methane diffusion flame. The average droplet sizes were in the range 30 µm to 150 µm, which were considered to be within the typical size range for sprays resulting from a leak in a hydraulic system. Tests were performed for different values of nozzle to ignition source spacing, the nozzle orifice area, and the fluid temperature. Typical results are shown in Figure 16, where the open flame was located 20 cm from the nozzle and the fluid temperature was 20 °C. For an orifice area greater than 1 mm<sup>2</sup>, the fluid pressure necessary to produce a flammable spray became almost constant, which produced the linear increase in flow rate with orifice area. The study provided useful information on the flammability trends, although the fuel concentration and the droplet size were not measured, and a specific type of nozzle was used, making it difficult to extract information that could be used to construct general-purpose HAC models.



**Figure 16** Minimum oil flow rate for given nozzle orifice areas found necessary to produce a flammable spray, from Yuan (2006).

Recently, Lian *et al.* (2010) conducted pilot ignition experiments on heat transfer fluids generated by electrospray. Measurements were reported for the droplet size spectrum, flame length and flame speed, but not the LEL.

The studies by Jagger *et al.* (2003) and Hawkworth *et al.*(2001) provided useful practical information in the context of the choice of fire-resistant hydraulic fluids and minimum hot surface ignition temperatures, and are discussed further in Section 3.

Von Pidoll (2001) studied the ignition behaviour of various mixtures containing water, and showed that these could respond quite differently from hydrocarbons, due to the high specific heat capacity and inerting effect of water. At normal ambient temperatures, von Pidoll (2001) noted that some mixtures of alcohol and water exhibited particularly unusual behaviour, where it was not possible to ignite a spray, even when the liquid was at a temperature above its flashpoint.

The main purpose of the study by Von Pidoll and Krämer (1997), and the subsequent study by Von Pidoll (2001), was to develop criteria that could be used to determine whether a given water-based paint was likely to be flammable when sprayed. They showed that the LEL of aqueous solutions containing more than one flammable component could be calculated from the LEL of binary mixtures of each flammable component with water, in an additive manner. For solutions composed of  $N$  flammable components, the mass fraction of water necessary to render it non-flammable when sprayed, was found to be well-approximated by:

$$y_{water} > \sum_{i=1}^N (A_i^{LEL} \times y_i) \quad (2.8)$$

where  $y_{water}$  is the mass fraction of water in the mixture,  $y_i$  is the mass fraction of the flammable component  $i$  in the mixture and  $A_i^{LEL}$  is the ratio of the water mass fraction to the flammable component mass fraction in a binary system at the LEL. Equation (2.8) is only applicable when the ignition source is an open flame. Ignition with electric sparks was found to be more difficult in their experience, even with spark energies of up to 10 J. Values of  $A_i^{LEL}$  for various substances were given by Von Pidoll and Krämer (1997) and von Pidoll (2001). For butyl diglycol and isopropanol, the minimum water mass fraction needed to suppress ignition was found to be 55% and 76%, respectively.

Von Pidoll and Krämer (1997) gave a simpler empirical criteria for the mass fraction of water necessary render the paint mixture non-flammable:

$$y_{water} > \frac{63}{37} y_{solvent} + \frac{49}{51} y_{solid} \quad (2.9)$$

where  $y_{solvent}$  and  $y_{solid}$  are the mass fractions of organic solvents and organic solids present in the mixture, respectively. The presence of organic solids in the paint was found to have a small inerting effect at concentrations greater than 25% by mass.

Förster *et al.* (1995) found that two-component mixtures of higher aliphatic hydrocarbons and water could be ignited with a water content of up to 77% by mass. The experiments were undertaken with millimetre sized droplets, and it was found that the droplet size had only a small effect on the flammability limits. Similar work by Hirsch *et al.* (1998) found that water-hydrocarbon mixtures with a water content in excess of 76% by volume could not be ignited by electrical sparks with energies up to around 10 J. Details of the particular hydrocarbon fuels used in these ignition tests were not provided. It was concluded that mist explosion protection measures were unnecessary if the water content exceeded 80% by volume.

Useful data on volatility and other material properties for application to spray ignition was summarised by Kanury (2002). Kuchta and Cato (1968) also provided a compilation and review of ignition temperature and flammability data for over 90 lubricants and hydraulic fluids. Britton (1992) provided MIE, LEL and UEL data for a wide range of chemicals, many of which are liquids at standard temperature and pressure. Measurements of the vapour LEL of various high flash-point paraffin hydrocarbons were also presented by Zabetakis *et al.* (1951).

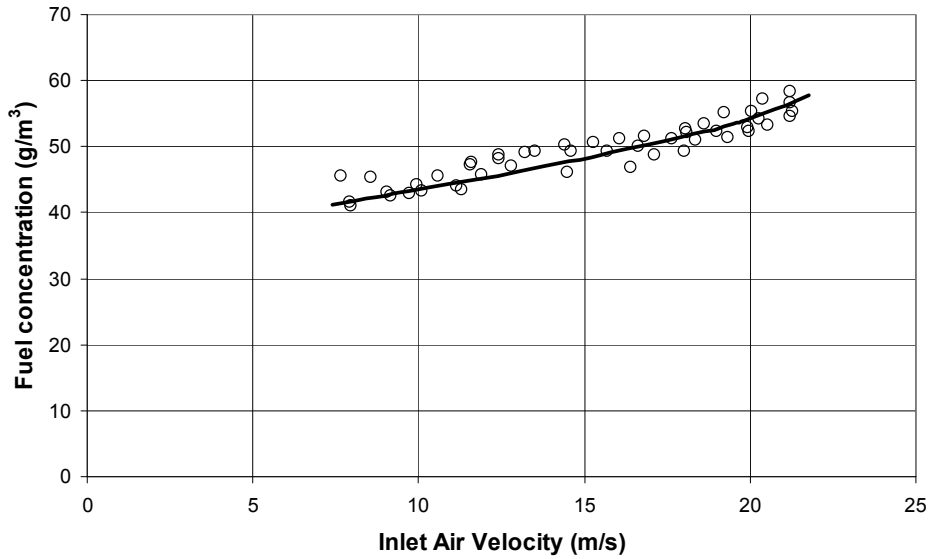
#### **2.1.4 Effect of flow speed**

As previously noted, the ignition behaviour of high-momentum sprays, particularly those injected into a fast-moving stream of air, can be different from that of nearly-quiescent mists (see Figure 6). The physical mechanisms responsible for the change in MIE and LEL under these circumstances does not appear to have been examined in detail in the literature. The primary mechanism responsible for the reduction in LEL in quiescent mists appears to be the settling of the droplets under gravity. For high speed sprays, this is not likely to have a significant effect and instead, the evaporation rate, flame speed and turbulence levels appear to play a more significant role.

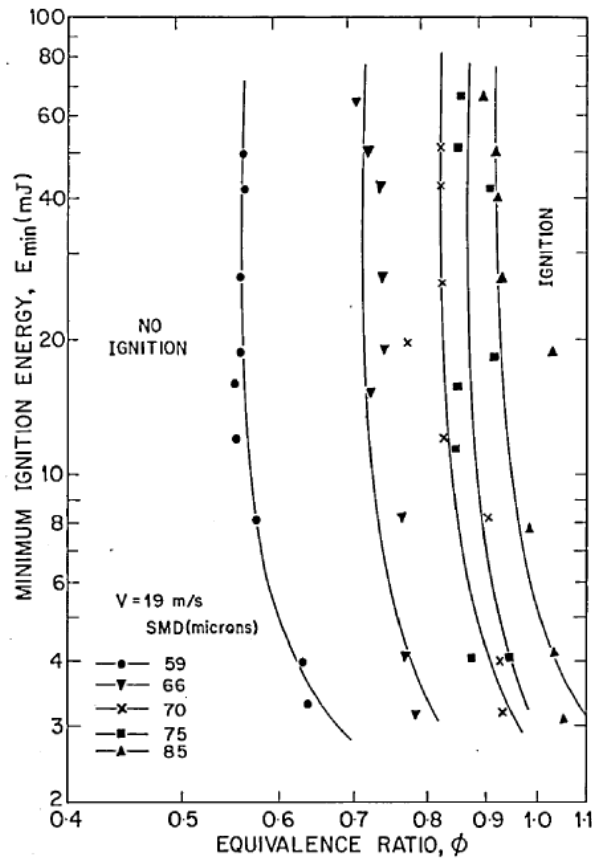
Analysis of the effect of droplet size and fuel concentration in high speed sprays was presented by Rao and Lefebvre (1976), who conducted experiments using a horizontally-directed kerosene spray produced using a simplex atomizing nozzle in a co-flowing air stream that was moving at speeds of between 19 m/s and 50 m/s. The results showed that the LEL increased as the droplet size was increased. This trend is in agreement with the kerosene spray data presented in Figure 6, from Anson (1953), who measured the Sauter mean diameter of droplets that gave rise to unstable combustion in a flame tube, where the flow speed was around 15 m/s and the flame was stabilized in the wake of a flat annular baffle. The reverse trend was observed by Burgoyne and Richardson (1949), Burgoyne *et al.* (1954) and Cook *et al.* (1977), in experiments in which the mist was slow moving or quiescent, where the LEL decreased as the droplet size increased. Further results from Anson (1953), showing the increase in fuel concentration necessary to achieve stable combustion for air inlet velocities of between 7 m/s and 22 m/s are presented in Figure 17.

For a given fuel concentration, Rao and Lefebvre (1976) found that a relatively small increase in the droplet size required a very significant increase in spark energy to produce ignition. In one case, an increase in SMD from 52  $\mu\text{m}$  to 66  $\mu\text{m}$  led to nearly a three-fold increase in the MIE, from 4 mJ to 11 mJ. They noted that this had practical consequences for the design of aero-engines with respect to flame-out and re-ignition. The results suggested that even a slight improvement in atomization quality, from increasing the fuel injection pressure or redesigning the nozzle, would be very beneficial to ignition.

Rao and Lefebvre (1976) also found that an increase in the air velocity reduced the LEL, if the fuel concentration was maintained constant. However, this effect was shown to be caused by a reduction in the droplet size, since for a given nozzle the pressure in the liquid supply needed to be increased at the same time as the air velocity, in order to maintain the same fuel to air ratio. If the droplet size was instead held constant, an increase in the air velocity caused an increase in the LEL, due to the increased heat losses from the spark kernel and because the spark heated a larger volume of mixture at higher flow speeds (in effect lowering the initial ignition kernel temperature).



**Figure 17** Kerosene fuel concentrations at the weak limit for flame stability, from Anson (1953). Symbols show measured values and the line indicates the best fit to the data. The results have been digitally scanned from the results given in the paper, and fuel concentrations shown have been calculated from air/fuel mass ratios given by Anson (1953) assuming atmospheric pressure and a temperature of 20 °C.



**Figure 18** Ignition energy for kerosene sprays in a co-flowing air stream moving at 19 m/s, from Rao and Lefebvre (1976)

### 2.1.5 Other effects

A summary of the effects of temperature and pressure on the MIE of mists and sprays was given by Babrauskas (2003). Kuchta (1973) and Liebman *et al.* (1965) found that reducing the temperature of a mist of jet fuel or gasoline from around 20 °C to -40 °C led to a linear increase in the MIE. Ballal and Lefebvre (1978) also showed that decreasing the ambient pressure leads to an increase in the MIE.

Some limited data exists on the effect of turbulence on the flammability of mists. In turbulent flows, the concentration fluctuates above and below the mean level. This can lead to fuel concentrations momentarily being within the flammable range even if the mean concentration is below the LEL. Babrauskas (2003) reviewed the study by Förster *et al.* (1995), which showed that the LEL decreased as the turbulence intensity increased. Further work on the effect of turbulence on the combustion of mists was undertaken by Kuznetsov (1988), and more recently, Lawes and Saat (2011). The latter study examined the flame speed in mists and found that the presence of mist droplets increased the flame speed in low turbulence, but had negligible effect in highly turbulent flows. The effect of turbulence on the quenching distance and on the flame speed in mists was also taken into account in the models developed by Ballal and Lefebvre (1981b) and Gauthier *et al.* (1996), respectively.

## 2.2 MAXIMUM EXPERIMENTAL SAFE GAP (MESG)

Flameproof electrical equipment is designed such that the enclosure is sufficiently strong to withstand the maximum overpressure from an internal explosion. Any holes, slits or joints in the enclosure walls are also sufficiently narrow that they will prevent transmission of a flame from inside the enclosure to the outside.

The key parameter which indicates whether or not a flame will be transmitted through the narrow gaps in the enclosure walls is the MESG. This is measured for gases according to the BS EN 60079-20 standard (BSI, 2010b) using apparatus consisting of two chambers, one inside the other, that are both filled with a mixture of flammable gas and air. The inner spherical chamber is linked to the outer chamber by a slot-shaped gap around its circumference, and the wall thickness around this gap is such that the path length between inner and outer chambers is 25 mm. The mixture is ignited in the inner chamber and the flame propagation into the outer chamber is assessed. When the gap width is sufficiently small, the flame is quenched as it passes from inner to outer chambers, and the flammable mixture in the outer chamber is not ignited. The MESG is defined as the maximum gap between the two parts of an explosion chamber that prevents ignition of the external gas mixture, for all concentrations of the tested substance in air.

For gases, the MESG and/or the Minimum Igniting Current (MIC) is used to classify the gas into one of four “gas groups” (I, IIA, IIB and IIC). Suitable flameproof equipment is then selected for use in potentially flammable atmospheres on the basis of this gas group classification.

The only study which has aimed to measure the MESG of mists appears to be the work of Capp (1988), who used an 8 litre internal explosion sphere filled with a flammable mixture of propane and air, and a 90 litre outer cylindrical volume filled with mist. The mist was generated by an air-driven spray gun which was mounted such that the spray was directed tangentially to the circumferential gap in the inner sphere. This position was found to be more likely to produce ignition than when the spray was directed towards the gap. Four different liquids were tested: butanol, kerosene, hexanol and ethylene glycol.

Capp (1988) found that relatively low release pressures of only 0.7 barg generated the most ignitable mists. The mean droplet sizes were measured using a Malvern laser system and are given in Table 4. The injected mixture of fuel and air through the nozzle was fuel rich and a separate air supply was provided to the external cylindrical volume. Values of the air and fuel supply rates were all varied to find the optimum conditions for transmission of ignition. If the spray was switched off before ignition of the propane-air mixture, there was no transmission of ignition.

For butanol, kerosene and hexanol, the MESG was found to be between 15% and 23% higher than the MESG for the equivalent vapour, which was measured at a higher temperature necessary to vaporise the liquid by Lunn and Phillips (1973) and Lunn (1982), see Figure 19. The ethylene glycol could not be ignited at the highest available gap width of 2.6 mm, even when the outer volume was also filled with a 4.4% by volume mixture of propane and air. This was attributed to its high boiling point, density and latent heat of vaporisation.

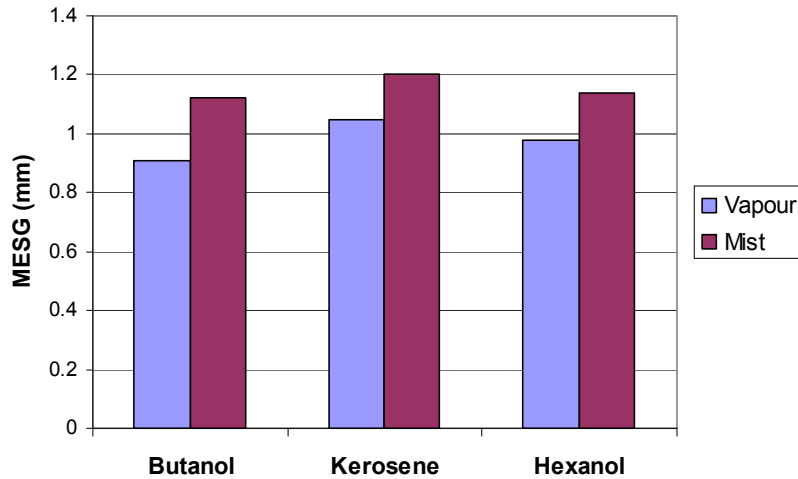
The MESG results were analysed by Capp (1988) using a simple model to predict the proportion of fuel droplets evaporated as a function of the heating time. This showed that an increase in fuel volatility or reduction in droplet size led to an increase in the fuel vaporization rate, and hence increased likelihood of ignition transmission.

Capp (1988) concluded that the three substances, butanol, kerosene and hexanol, could be classified in Group IIA of the BS EN 60079-20 standard (BSI, 2010b) system, for which MESG is greater than 0.9 mm, irrespective of whether they were in vapour or mist form. Capp (1988) also noted that some substances which may be classified in Group IIB (for which, the MESG is between 0.5 mm and 0.9 mm) on the basis of their vapour properties, could perhaps be classified in Group IIA if they were only present in mist form. However, their classification into Group IIB would provide a degree of conservatism, which might be prudent if there were any hot surfaces present that could vaporise the mist.

**Table 4** Experimental conditions for the MESG tests conducted by Capp (1988)

|                                     | <i>Butanol</i> | <i>Kerosene</i> | <i>Hexanol</i> | <i>Ethylene glycol</i> |
|-------------------------------------|----------------|-----------------|----------------|------------------------|
| Flashpoint (°C)                     | 29             | 38              | 63             | 111                    |
| Boiling point (°C)                  | 118            | 150-300         | 157            | 197                    |
| Latent heat of vaporisation (kJ/kg) | 589            | 251             | 451            | 798                    |
| Density (kg/m <sup>3</sup> )        | 810            | 800             | 820            | 1100                   |
| Fuel equivalence ratio at nozzle    | 10             | 13              | –              | 4                      |
| Droplet mean diameter in spray (µm) | 31             | 25              | –              | 29                     |
| MESG for vapour (mm)                | 0.91           | 1.05            | 0.98           | –                      |
| MESG for mist (mm)                  | 1.12           | 1.2             | 1.14           | (a)                    |

(a) Transmission of ignition not possible



**Figure 19** Comparison of vapour and mist MESGs, from Capp (1988)

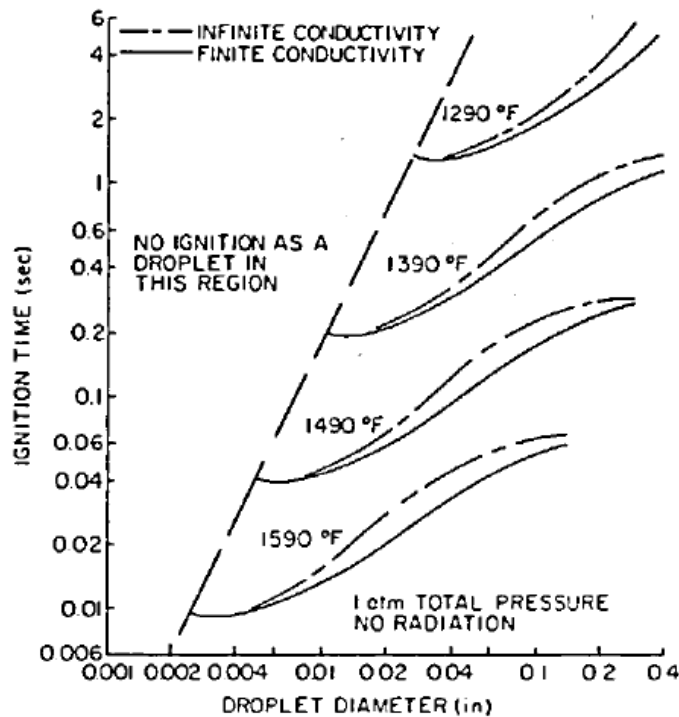
One of the significant limitations of the study by Capp (1988) is that the mist occupied only the outer chamber of the measurement apparatus, whilst the initiating flammable substance inside the inner chamber was propane gas, not mist. The measurements therefore provided an indication of whether the propane-air flame was quenched as it passed through the narrow slot, or whether it had sufficient remaining energy to initiate combustion of the mist in the outer chamber. In other words, it was not a true indication of the mist MESG. The main practical interest in the MESG of mists is to determine whether ignition of a flammable mist inside an item of electrical equipment, for example, could transmit a flame to the outside of the enclosure.

As previously noted, the study by Capp (1988) appears to be the only direct measurement of the MESG of mists. In the study by Hansen and Wilkins (2004), mists were ignited in a similar manner to the approach taken by Capp (1988), using an ignited propane-air mixture, but the gap width was considerably larger ( $0.212 \text{ m}^2$ ) and the focus of the study was on the overpressures generated by different mists, rather than the transmission of ignition.

In principle, it may be possible to gain further useful insight into the MESG of mists from measurements and mathematical models for the ignition behaviour of droplets in a high-temperature gas environment. There is a significant body of literature which examines this scenario, due to its importance in internal combustion engines and gas turbines. Reviews are provided by, for example, Law (1982), Babrauskas (2003), and Sirignano (2005).

A number of studies have examined the ignition behaviour of individual droplets, in which the droplet is suspended on a fine wire, which is then inserted into a furnace. Measurements of the time delay before ignition show that smaller droplets usually ignite faster than larger ones. Below a certain critical size, however, an individual droplet in an ambient environment of hot air does not ignite. This behaviour was explained by Faeth and Olson (1968) in terms of the time required for chemical reactions associated with ignition to take place. For droplets smaller than the critical size, the droplet vaporizes and the vapour diffuses away into the ambient environment before the chemical reactions have time to produce ignition. Their analysis was undertaken on the basis that the fresh air surrounding the droplet was quiescent and buoyancy effects were negligible (their experiments were conducted in zero gravity, using a drop tower). The critical droplet size was a function of the temperature of the ambient environment, with a hotter environment tending to reduce the critical droplet size. Typical

results are shown in Figure 20 for iso-octane, using a model developed by Faeth and Olson (1968), which was validated against measurements of delay time.



**Figure 20** Predicted ignition time for an isolated iso-octane droplet in air, from Faeth and Olson (1968)

Later studies include the work of Saitoh *et al.* (1982), who studied the ignition delay time of droplets of n-heptane, n-hexadecane and acetone, and Wong *et al.* (1993), who examined the auto-ignition of non-dilute monodisperse clouds of n-heptane. Further detailed analyses of droplet combustion, including a thorough examination of the effects of convection, radiation and multi-component droplet composition were presented by Sirignano (2005).

Given the lack of experimental data for the MESG of mists, it may be possible to use the computational models described by Sirignano (2005) to predict the MESG values. However, a survey of the literature has failed to identify any studies that have explored this approach. To predict the occurrence of flame quenching in the presence of fuel droplets would not be trivial.

It would clearly be beneficial to conduct true measurements of the MESG of mists. These should ideally examine mists generated by both condensation and spray atomization. In these tests, both the inner and outer spheres of the measuring equipment should be filled with mist, rather than using propane as the initiating gas within the inner sphere.

### 2.3 MINIMUM IGNITING CURRENT (MIC)

Low voltage equipment for use in flammable atmospheres is selected on the basis of “intrinsic safety” according to the Minimum Igniting Current (MIC) ratio, rather than the Minimum Ignition Energy (MIE). The MIE is measured by applying a sufficiently large voltage between two electrodes held a fixed distance apart, whereas the MIC is measured using a break-spark apparatus in which ignition is effected by mechanically breaking current-carrying wires (Babrauskas, 2003). If the same classification system for the selection of intrinsically safe



equipment was to be used for mists as it is currently for gases, this means that the MIE measurements for mists discussed in Section 2.1 are not directly applicable to the choice of equipment.

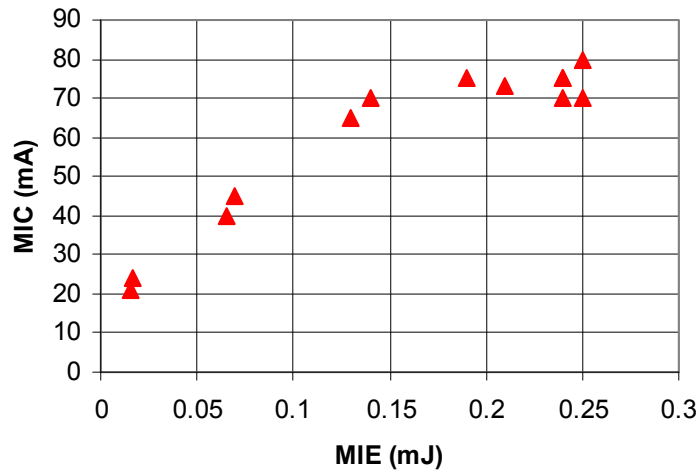
There appear to be no measurements of the MIC of flammable mists reported in the literature. However, the MIE, MIC and MESG for flammable vapours are correlated with one another, as shown in Table 5 and Figures 21 and 22. It is unclear whether the MIE, MIC and MESG would be similarly correlated for flammable mists.

Some factors affecting the MIE are known to be different from those affecting the MIC. For example, Zborovszky (1976) showed that the fuel concentration had relatively little effect on the MIC provided that fuel concentration was in the flammable range, whereas the MIE is known to be strongly affected by the fuel concentration (see Section 2.1).

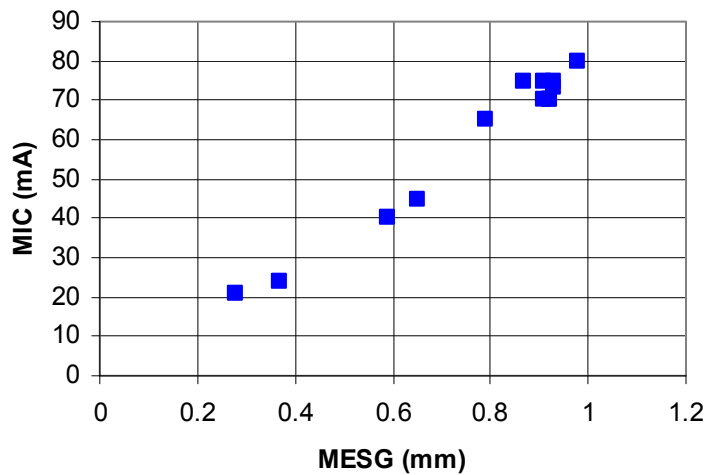
In terms of selecting electrical equipment for use in explosive mist atmospheres, it would be useful in further work to establish whether, for instance, the MIC of a mist is greater than the MIC of its equivalent vapour. Intrinsically safe equipment that is rated for a flammable gas atmosphere of a particular substance might then be used safely in a flammable mist of the same substance.

**Table 5** MIE, MESG and MIC for flammable vapours, from Britton (1992) and BS EN 60079-20 (BSI, 2010b)

| <i>Material</i> | <i>MIE(mJ)</i> | <i>MESG (mm)</i> | <i>MIC (mA)</i> | <i>Gas Group</i> |
|-----------------|----------------|------------------|-----------------|------------------|
| butane          | 0.25           | 0.98             | 80              | IIA              |
| ethane          | 0.24           | 0.91             | 70              | IIA              |
| heptane         | 0.24           | 0.91             | 75              | IIA              |
| hexane          | 0.24           | 0.93             | 75              | IIA              |
| pentane         | 0.21           | 0.93             | 73              | IIA              |
| methanol        | 0.14           | 0.92             | 70              | IIA              |
| propane         | 0.25           | 0.92             | 70              | IIA              |
| 1,3-butadiene   | 0.13           | 0.79             | 65              | IIB              |
| Diethyl ether   | 0.19           | 0.87             | 75              | IIB              |
| ethylene        | 0.07           | 0.65             | 45              | IIB              |
| ethylene oxide  | 0.065          | 0.59             | 40              | IIB              |
| acetylene       | 0.017          | 0.37             | 24              | IIC              |
| hydrogen        | 0.016          | 0.28             | 21              | IIC              |



**Figure 21** MIE versus MIC for the flammable vapours given in Table 5



**Figure 22** MESG versus MIC for the flammable vapours given in Table 5

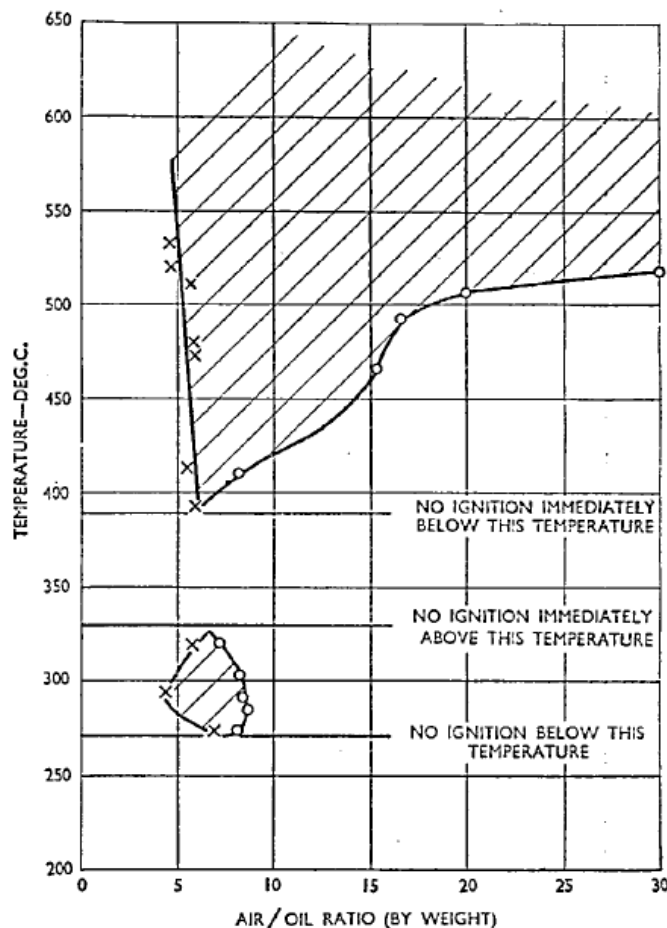
## 2.4 MINIMUM HOT SURFACE IGNITION TEMPERATURE (MHSIT)

To ignite a spray or mist using a hot surface, it is necessary for the hot surface to first vaporise a sufficient quantity of fuel to produce flammable concentrations of vapour and, secondly, for the temperature of the flammable vapour to be sustained at a high level for sufficiently long to overcome the chemical ignition delay period. The effectiveness of hot surface ignition therefore depends on many factors, including the physical properties of the liquid, the concentration of fuel in the air, the droplet size and the shape and extent of the heated surface. Ignition becomes more likely as the temperature or the extent of the hot surface is increased. The contact time and the concentration and temperature gradients near the surface, which are affected by the local ventilation flow, are also important parameters. The type of material used to make the surface, and any surface treatments, can have an effect, due to the formation of either film or nucleate boiling and its effect on heat transfer rates. Some materials may also

produce catalytic reactions or form an insulating oxidation layer, which also affect heat transfer rates. Reviews of the physical mechanisms involved in hot surface ignition are provided by Bennett (2001) and Babrauskas (2003).

One of the earliest comprehensive studies of lubricating oil mist ignition by hot surfaces was conducted by Freeston *et al.* (1956), for application to crankcase explosions. Small-scale tests were conducted using a heated ignition tube measuring 305 mm long and 38 mm in diameter, through which known concentrations of oil mist were passed. The mists were generated by condensation of a saturated oil vapour, and progressively leaner or richer mixtures were tested to establish the flammability limits. Various different metals were used for the ignition tube, to match those materials commonly found in marine diesel engines.

Using this apparatus, Freeston *et al.* (1956) showed that there were two separate temperature regions in which hot surface ignition of oil mists was possible: a low-temperature region from 270 °C to 350 °C, and a high temperature region which extended upwards from 400 °C. In between these two temperature regions, ignition was not possible (see Figure 23). The occurrence of this isolated “low-temperature ignition peninsula” is likely to have been related to the occurrence of cool flames (see, for example, Lewis and von Elbe, 1987).



**Figure 23** Hot surface ignition tube measurements for lubricating oil mists, from Freeston *et al.* (1956), using a mild steel tube. Hatched areas show regions where ignition took place; × rich limit; ○ lean limit.

The oil tested was a typical engine oil of SAE 30 viscosity and it was considered that similar results would be obtained with any other engine oil. No measurements were made of the mist droplet size, although it is likely to have been relatively small, since it was formed by condensation. Measurements of the flashpoint or AIT of the oil were also not provided.

In the low-temperature ignition region, it was found that there was a significant ignition delay time (of the order of a few seconds), compared to the high-temperature ignition region. It was postulated that this could explain some of the known incidents involving delayed ignition, where a diesel engine had shown some signs of over-heating and been stopped, and then, several minutes later, an explosion had occurred. It was thought that the engine may have passed through the lower-temperature ignition region as it overheated, but ignition of the oil mist did not occur, due to the ignition delay period. The engine then reached temperatures of between 350 °C and 400 °C, at which point the oil was vaporizing but ignition could not take place. Once the engine was stopped, the mist cooled into the low-temperature flammable region and an explosion occurred.

Further tests were reported by Freeston *et al.* (1956) using a 21 cubic foot explosion vessel, to test the efficacy of explosion relief valves and flame traps. A full-scale test involving a 1,100 h.p. Sulzer diesel engine was also performed in which a flammable mist in the crankcase was ignited. The force of the resulting explosion was sufficient to damage the building in which the engine was housed. The tests showed that explosion venting of marine diesels was in itself insufficient to limit the maximum overpressures, and that some measures to prevent a flame from spreading throughout the crankcase were necessary.

A wide-ranging review of the ignition of droplets, sprays and spills by hot surfaces was undertaken by Babrauskas (2003). This showed that in tests involving spray impingement on a hot surface, the Minimum Hot Surface Ignition Temperature (MHSIT) exceeded the AIT by some margin. The review considered a variety of fuels (lubricating oils, gasoline, kerosene, hydraulic oils etc.) and both open and semi-confined geometries. There was considerable scatter in the MHSIT for the same fuel, depending upon the particular experimental arrangement. For unconfined flat plate surfaces, ignition was found to require surface temperatures more than 200 °C higher than the AIT. As the geometry became progressively more confined, it was found that the minimum ignition temperature was reduced until it was equal to the AIT, in the full-confined case.

Babrauskas (2003) offered practical guidance on the MHSIT, whereby if the space was approximated as a cube and the hot surfaces occupied more than one face of the cube, the substance should be assumed to ignite at the AIT. For unconfined release scenarios with just one heated surface, provided that the substance was not prone to cool-flame ignition, Babrauskas (2003) suggested following the American Petroleum Institute guidance (API, 1991) which states that hot surfaces are liable to ignite fuel vapour if the surface temperature exceeds the AIT by 200 °C.

Other work on hot surface ignition of sprays includes the study undertaken by Bennett (1997) to support the investigation into a gas turbine generator explosion, which was suspected to have been caused by a high-pressure release of naphtha. Experiments were performed using a spray gun inside a modified 220 litre steel drum with the hot plate arranged vertically. Estimated ignition temperatures for naphtha and diesel were 780 °C and 745°C, respectively, i.e. nearly 500°C higher than the AIT (which for naphtha is between 232°C and 288°C, and for diesel between 225°C and 256°C).

Further examination of the MHSIT of sprays was undertaken by Hawksworth *et al.* (2001) and Jagger *et al.* (2003). In the former study, tests on common high flashpoint liquids were performed using a 65 cm × 40 cm flat stainless steel plate at temperatures in the region 700 – 800 °C. In the latter study by Jagger *et al.* (2003), hot surface ignition tests were performed on

fire resistant hydraulic fluids using three types of nozzles and liquid flow rates of up to 500 ml/min. Droplet sizes in terms of SMD were estimated to be in the range 50 µm to 60 µm.. The sprays were directed along a 2 metre long ventilated chamber with the small heated plate located vertically on the axis of the spray jet. The occurrence of any flame, even momentarily, was taken as indication of ignition. No ignitions were obtained for the mineral oil or polyol ester at temperatures up to 500 °C.

Tests were also carried out using a larger stainless steel heated plate positioned vertically either perpendicular or at an angle to the spray axis. Mineral oil with an AIT of 341 °C was found to ignite in 5 out of 7 tests with a plate temperature of only 400 °C. For a polyol ester with an AIT of 400 °C, the measured MHSIT was 490 °C. No ignition was obtained for water-based fluids or a phosphate ester, and it was considered likely that the same behaviour would be seen for a rapeseed oil derivative and a poly glycol ether that were subjected to other tests. There was no observed dependence on the angle of the spray impact. The main factor affecting ignition behaviour appeared to be the time period during which vapour was present in the vicinity of the hot plate. It was noted that if the shape of the hot surface was such that vapour could be trapped for a period of time, ignition was more likely.

Further hot surface ignition tests were performed on streams of liquid rather than sprays, using the hot manifold test procedure described in ISO 20823 (ISO, 2003). Measurements were also made of each of the fluids auto-ignition temperature using the method described in DIN 51794 (DIN, 2004). The results from these tests are summarised in Table 6. The MHSIT was found to be less than 100 °C higher than the AIT in some cases, demonstrating clearly that the API guidance (API, 1991; 2003) is not conservative. Instead, the AIT provides a more suitable, conservative estimate of the MHSIT for sprays or liquid streams.

Although not related directly to MHSIT, it was demonstrated by Jagger *et al.* (2003) that the temperature at which a substance can ignite may be considerably lower if the liquid is soaked into porous insulating material, such as pipe lagging, due to oxidative self-heating. This phenomenon was examined using a measurement procedure similar to that described in UN Test N.4 (UN, 2009). A small cube of mineral silicate insulation soaked in the test fluid was placed inside a supporting stainless steel gauze container, which was then placed into an oven. The oven temperature was increased in stages from 110 °C to 210 °C and self-heating was judged to occur if the sample temperature exceeded that of the oven by 60 °C. At each of the selected oven temperatures, a constant oven temperature was maintained for 24 hours whilst the sample temperature was monitored. The onset temperatures for runaway self-heating are given in Table 6. For most of the hydraulic fluids tested, the runaway temperature was several hundred degrees Celsius lower than the AIT.

Whilst the AIT appears to provide a conservative upper limit for surface temperatures to avoid hot surface ignition of sprays or mists, the work of Jagger *et al.* (2003) indicated that if the liquid released happened to soak into insulation it could ignite at lower temperatures.

Practical guidance on measures to reduce the likelihood of lagging fires, such as use of closed cell insulation near leak points, was provided by Fuhr (1992).

**Table 6** Hot manifold ignition test results, temperatures for runaway oxidative self-heating and auto-ignition temperatures, from Jagger *et al.* (2003)

| <i>Fluid</i>        | <i>Hot manifold ignition temperature<sup>8</sup> (°C)</i> | <i>Runaway temperature (°C)</i> | <i>AIT (°C)</i> |
|---------------------|---|---------------------------------|-----------------|
| Water glycol        | > 704 ± 7   | 132.5 ± 7.5                     | 425             |
| Mineral oil         | 386 ± 5   | 200 ± 10                        | 341             |
| Oil water emulsion  | > 704 ± 7   | 180 ± 10                        | 385             |
| Rapeseed derivative | 466 ± 5   | 180 ± 10                        | 390             |
| Polyol ester        | 436 ± 5   | 155 ± 15                        | 400             |
| Poly glycol ether   | 396 ± 5   | 155 ± 15                        | 380             |
| Phosphate ester     | > 700 ± 5   | > 210                           | 425             |

The ignition of hydraulic oil sprays by hot surfaces was also recently studied by Yuan (2006). Two different nozzles were used with pressures of between 7 barg and 14 barg. The tests considered eight non-fire-resistant hydraulic oils, four fire-resistant hydraulic oils and diesel fuel. Droplet sizes were in the range 30 µm to 150 µm. The spray was impinged onto the heated surface for 10 seconds and if there was no ignition, the spray was then turned off and the hot surface temperature increased by 10 °C. The test procedure was repeated until the spray ignited. As the pressure was increased from 7 barg to 14 barg, it was found that the surface ignition temperature decreased by around 30 °C to 40 °C for two of the oils tested. In some cases, ignition occurred shortly after the spray was stopped, due to the surface no longer being cooled by the spray.

In some of the tests involving sprays impinging vertically downwards onto a hot surface, Yuan (2006) found that it was difficult to obtain ignition due to the rapid dilution of the flammable vapour by the air entrained into the spray. Using the same orientation of release, but with a dripping oil supply rather than a spray, the droplets were found to ignite immediately upon impact. Similar findings were reported previously by Myronuk (1980), who found that increasing the local airflow velocity close to the hot surface increased the MHSIT.

The various works cited above showed that the flashpoint does not provide a useful measure of the MHSIT. In the work of Yuan (2006), the MHSIT increased as the flashpoint of the material was increased, whilst in one of the studies reviewed by Babrauskas (2003), the reverse trend was produced and the MHSIT decreased as the flashpoint was increased. Hawksworth *et al.* (2001) also found that the MHSIT either increased or decreased with the flashpoint, depending upon whether the hot surface was vertical or horizontal. Babrauskas (2003) suggested that the reason for this behaviour was due to the MHSIT being a function of both the volatility and reactivity. For unconfined releases, both of these factors affect the MHSIT in roughly equal amounts. In confined releases, the MHSIT is more dominated by the reactivity of the substance. The flashpoint, on the other hand, is primarily a function of the volatility of the substance, and to a lesser extent the reactivity.

Burgoyne (1957) noted that for spark ignition in the vicinity of hot surfaces, prolonged contact between mists of liquid hydrocarbons and hot surfaces could result in cracking and the

<sup>8</sup> In some cases, hot surface ignition was not obtained. This was the case, for example, for water glycol at surface temperatures up to 704 °C.

formation of vapours which do not share the combustion properties of the original hydrocarbons. The generation of hydrogen or acetylene, for instance, could significantly lower the flammability limits. It was noted that this would need to be taken into account if the mist explosion hazard in a hot environment was to be controlled using either inert gases or suitably rated flameproof or intrinsically-safe equipment.

Guidance on the ignition of mists by hot surfaces is provided in the Code of Practice for Atmospheric Oil Mist Detectors, issued by the International Maritime Organisation (IMO, 2003). This notes that temperatures as low as 150 °C may be sufficient to cause ignition.

In terms of practical guidance, the review of the literature suggests that to prevent ignition, a conservative approach would be to ensure that surface temperatures that could potentially be exposed to the spray or mist do not exceed the AIT. This may be considered over-conservative by a few hundred degrees Celsius in some cases. Additional measures might also be necessary to avoid oxidative self-heating in porous media such as pipe lagging. Care should also be taken if in addition to hot surfaces, there is a possibility of spark ignition of the hot mist, due to the possibility that the fuel may thermally degrade to produce more volatile components.

## **2.5 SUMMARY**

### **Lower Explosive Limit (LEL)**

- The LEL of mists composed of small droplets (< 20 µm) is approximately equal to that of the equivalent vapour mixture.
- Mists produced by condensation of a saturated vapour, which are usually composed of small droplets, are therefore likely to have an LEL similar to that of the equivalent vapour.
- The LEL of mists composed of larger droplets is strongly affected by the method of measurement.
- In quiescent mists or low-momentum sprays with larger droplets (> 20 µm), the sedimentation effect reduces the LEL significantly, for an upward-propagating flame.
- The LEL has been observed to fall to around 10% of its vapour equivalent for mists with droplet diameters greater than around 120 µm.
- In high-momentum sprays or rapidly flowing mixtures, the sedimentation effect appears to be insignificant and the LEL has been found to increase, rather than decrease, as the droplet size is increased.
- A semi-empirical correlation has been presented for the LEL of monodisperse quiescent mists as a function of the droplet size, but only for the substance, tetralin (Burgoyne, 1963). No general-purpose models for the LEL of mists appear to have been developed.

### **Minimum Ignition Energy (MIE)**

- Predictive models for the ignition energy have been produced by Ballal and Lefebvre (1981b) for quiescent and flowing mists, with and without vapour present, for both mono- and polydisperse droplets. These models have not been validated at high concentrations, much greater than stoichiometric, to establish the true MIE of mists (i.e. the ignition energy at the most easily-ignitable concentration). Neither have they been validated for very low concentrations, to provide a means of predicting the mist LEL.
- Mists composed of smaller droplets require less energy to ignite than those composed of larger droplets, since they have a higher surface area available for evaporation.
- In quiescent monodisperse mists, the ignition energy is probably lowest for droplet diameters between 10  $\mu\text{m}$  to 30  $\mu\text{m}$ , and it increases in proportion to the cube of the droplet diameter above this size.
- For lean concentrations, close to the vapour LEL, the ignition energy is lower for a quiescent mist than the vapour of the same substance (this follows logically from the LEL of the mist being lower than that of the vapour).
- The ignition energy reduces as the fuel concentration of the mist increases above the LEL. Experiments have not been conducted for sufficiently rich mixtures to establish the MIE for mists (at the most easily-ignitable concentration).
- At the optimum fuel concentration and droplet size, the MIE required to ignite a mist appears most likely to be equal to or greater than the MIE required to ignite a vapour-air mixture of the same substance at its optimum concentration for ignition. This assertion is based on model predictions and data extrapolation, rather than direct measurement. Direct comparison between mist and vapour MIE is difficult for high boiling-point substances.
- The ignition energy is lower for more volatile substances, since there is often vapour already present and the droplets require less energy to vaporise.

### **Maximum Experimental Safe Gap (MESG)**

- There appears to be no reliable measurement data for the MESG of mists.
- The only relevant study appears to be that of Capp (1988), who found that the MESG of a mist was greater than that of its equivalent vapour. However, the test method used in that study did not measure the propagation of flame within a mist, but instead examined the propagation of flame from a propane-air mixture into a mist. It also only considered spray-generated mists rather than condensation aerosols.
- In principle, it may be possible to use sophisticated computational models to predict the MESG, although there are no reported studies of this in the literature.

### **Minimum Igniting Current (MIC)**

- There is no data on the MIC of mists in the literature. In principle, it may be possible to correlate the MIC to MIE and/or MESG, or to measure it experimentally.



### **Minimum Hot Surface Ignition Temperature (MHSIT)**

- The hot surface ignition temperature depends on many factors, including the physical properties of the liquid, the concentration of fuel in the air, the droplet size and the shape and extent of the heated surface. High mass flux impinging sprays may cool the surface.
- The measured MHSIT of unconfined sprays is typically more than 60 °C above the AIT, but drips or streams can ignite at slightly lower temperatures, and confinement around the hot surface can also decrease the MHSIT.
- In the absence of an appropriate MHSIT, a conservative approach is to assume that the MHSIT is equal to the AIT.
- Some lubricating oils have been found to produce cool-flame ignition, at temperatures below the AIT.
- Liquid soaked into porous insulating material, such as pipe lagging, will ignite at temperatures below the AIT. This could form an energetic flaming ignition source for a mist cloud.

## 3 FORMATION OF FLAMMABLE MISTS

Sprays and mists are used in a wide range of applications, including internal combustion engines, gas turbines, fire and explosion suppression systems, agricultural fertilizer and pesticide applications and spray-dryers. Over the last century, a considerable amount of research has therefore been undertaken within the science and engineering community to understand the physical processes involved in producing sprays and mists. Detailed reviews of this large body of work are provided by Lefebvre (1989), Crowe *et al.* (1998) and Sirignano (2005).

In the context of industrial hazard scenarios, there are four principal ways in which mists are usually formed:

1. **Spray discharge from a pressurized liquid reservoir:** This includes both intentional releases (e.g. spray painting) and accidental releases (e.g. from a hole in a pressure vessel or damaged pipework). The primary mechanism for mist formation is from spray breakup in the jet, although subsequently liquid droplets may hit nearby solid surfaces and further fragment.
2. **Condensation of a saturated vapour:** The mist here is generated when hot vapour, perhaps produced as a result of liquid coming into contact with a hot surface, cools and produces an aerosol cloud. The physics involved in this process is the same as that which produces the visible mist of water droplets from a boiling kettle.
3. **Agitation and splashing:** This includes a diverse range of flows which all involve some external force that moves the liquid and induces breakup. For example, mists produced by machine tool lubrication systems and those formed by froth, foams or sloshing in moving fuel tanks.
4. **Air stripping:** The mist is produced here by the action of a fast-moving air current over the surface of a liquid pool, which strips droplets from the liquid surface.

For the purposes of area classification, it is important to understand, and if possible predict, the potential production rate and characteristics of the mists generated in each of these types of release. The following sections provide an introduction to droplet dynamics, and then discuss each of the four scenarios in turn. Primary and secondary droplet breakup are described under the section on spray discharges.

### 3.1 FUNDAMENTALS OF DROPLET DYNAMICS

#### 3.1.1 Droplet forces

The interaction between droplets and air involves the exchange of momentum, mass and heat. The evolution of momentum is governed by Newton's second law: net force equals the rate of change of momentum. For droplets or particles, this is expressed in terms of the Basset-Boussinesq-Oseen (BBO) equation (see Crowe *et al.*, 1998):

$$\begin{aligned}
\underbrace{m \frac{d\mathbf{v}}{dt}}_{\text{Rate of change of droplet momentum}} &= \underbrace{\frac{1}{2} \rho_c C_D A |\mathbf{u} - \mathbf{v}| (\mathbf{u} - \mathbf{v})}_{\text{Drag Force}} + \underbrace{V_d (-\nabla p + \nabla \cdot \boldsymbol{\tau})}_{\text{Pressure gradient \& shear stress}} \\
&+ \underbrace{\frac{\rho_c V_d}{2} (\dot{\mathbf{u}} - \dot{\mathbf{v}})}_{\text{Virtual mass force}} + \underbrace{\frac{3}{2} d^2 \sqrt{\pi \rho_c \mu_c} \left[ \int_0^t \frac{\dot{\mathbf{u}} - \dot{\mathbf{v}}}{\sqrt{t-t'}} dt' + \frac{(\mathbf{u} - \mathbf{v})_0}{\sqrt{t}} \right]}_{\text{Basset Force}} + \underbrace{mg}_{\text{Gravitational Force}}
\end{aligned} \tag{5}$$

where  $\mathbf{u}$  and  $\mathbf{v}$  are the gas and droplet velocity vectors respectively,  $m$  is the mass,  $\rho$  density,  $C_D$  the droplet drag coefficient,  $A$  the projected frontal area of the droplet,  $V_d$  the particle or droplet volume,  $p$  pressure,  $\boldsymbol{\tau}$  shear stress,  $d$  the droplet diameter,  $t$  time and  $g$  gravity. Subscript  $c$  refers to properties of the continuous (gas) phase, subscript 0 to an initial condition at time  $t = 0$ , and a dot above a letter to the time-derivative. The variable  $t'$  in the Basset force term represents a time-scale that varies from 0 to time  $t$ . The BBO equation is applicable to a wide range of flows, not only droplets but particles and bubbles. The carrier phase can also be either liquid or gas. Additional source terms may result from electromagnetic force terms.

In the BBO equation, the combined pressure gradient and shear stress term represents the forces on the droplet due to acceleration of the continuous phase. It is only significant when the continuous phase has a density comparable or larger than that of the droplet (e.g. oil droplets in water). The virtual mass force term represents the force required to accelerate the surrounding fluid. This is important in bubbly flows where the displaced fluid mass exceeds the particle mass. The Basset force, sometimes known as the ‘history’ term, accounts for the deviation of the flow behaviour around the particle from the steady state flow conditions, due to the development of the boundary layer around the droplet as the relative velocity changes with time. The Basset force can be important in unsteady flows, however Rudinger (1980) noted that the term is insignificant for a 10  $\mu\text{m}$  particle in a stream oscillating at less than 700 Hz. For the present application of mists, this leaves the dominant terms as the drag force and the gravitational settling term.

CFD models using a Lagrangian or particle-tracking approach solve the BBO equation to determine the trajectory of droplets. Commonly, the pressure/stress gradient, virtual mass, and Basset force terms are neglected.

Droplet trajectories can be influenced by turbulence in the ambient environment, which tends to disperse the droplets over a wider area. A number of different CFD turbulent dispersion models have been proposed to try to introduce disturbances to the particle trajectories to account for turbulence effects, e.g. Gosman and Ioannides (1981), MacInnes and Bracco (1992) and Gouesbet and Berlemont (1999). These are based on trying to reconstruct the instantaneous velocity field ( $\tilde{\mathbf{u}}$ ) by adding some stochastic velocity fluctuation to the mean velocity. The modelled instantaneous velocity field is then used in the BBO equation for the particle motion.

In the context of area classification, one of the key parameters of interest in the BBO equation is the drag coefficient. From this, it is possible to determine the how fast droplets fall in quiescent air under gravity (the sedimentation speed). This is important in order to determine the residence time of the mist in the air. It also has an important effect on the LEL of mists, as discussed in Section 2.1.

### 3.1.2 Sedimentation speed and droplet drag coefficient

Droplets suspended in quiescent air fall under gravity at a rate governed by form and friction drag. When the flow around a spherical droplet is laminar and there is no flow separation in the wake, the drag force is governed by Stokes' Law:

$$F_d = 3\pi d \mu_a U_\infty \quad (3.1)$$

where  $d$  is the droplet diameter,  $\mu_a$  is the dynamic viscosity of the ambient fluid (in this case, air) and  $U_\infty$  is the velocity of the falling droplet. For droplets falling at terminal speed, the drag force is balanced by the gravitational force, which for a spherical droplet is given by:

$$F_g = \frac{4}{3}\pi \left(\frac{d}{2}\right)^3 \rho_l g \quad (3.2)$$

where  $\rho_l$  is the liquid droplet density and  $g$  the acceleration due to gravity.

Stokes Law is only valid for very small droplets in air, when the Reynolds number,  $Re$ , is less than 0.1. The Reynolds number is calculated here from:

$$Re = \frac{U_\infty d}{\nu} \quad (3.3)$$

where  $\nu$  is the kinematic viscosity of air ( $\nu = \mu / \rho$ ). At room temperature, for a water droplet with a density of around  $1000 \text{ kg/m}^3$ , this means that Stokes Law is only applicable up to a droplet diameter of around  $36 \text{ }\mu\text{m}$ <sup>9</sup>, i.e. roughly the size of a water droplet in a atmospheric cloud, but many times smaller than the average droplet size in most spray releases.

To examine the sedimentation speed of larger droplets, rather than express the speed as a function of droplet size it is common practice instead to relate the droplet drag coefficient to the Reynolds number. This dimensionless form of the equations makes it possible to compare droplets or spheres of different materials falling through different fluids, and takes into account the effects of density and viscosity.

The drag coefficient is calculated from the ratio of the drag force to the product of the dynamic pressure and frontal area:

$$C_D = \frac{F_d}{\left(\frac{1}{2}\rho_a U_\infty^2 A\right)} \quad (3.4)$$

where the frontal area of the circular droplet,  $A$ , is  $(\pi d^2/4)$ .

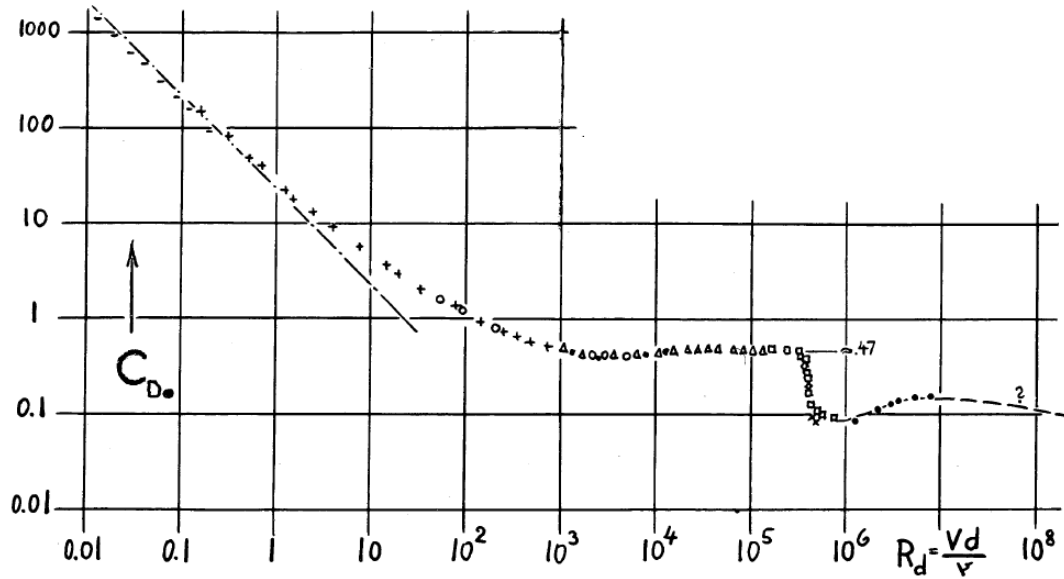
Rearranging Equations ( 3.1 ) and ( 3.4 ), it can be shown that Stokes Law is equivalent to the following:

$$C_D = \frac{24}{Re} \quad (3.5)$$

The change in the drag coefficient of a sphere with Reynolds number is shown in Figure 24. As the Reynolds number is increased above 0.1, a laminar separated flow region is formed in

<sup>9</sup> This value has been calculated based on the empirical correlation for the drag coefficient from Massey (1983), presented below.

the wake of sphere. The rate of change of  $C_D$  with  $Re$  then decreases as  $Re$  increases. For  $Re$  values of between  $10^4$  and  $10^5$ ,  $C_D$  reaches a fairly constant value of 0.47. At the “critical” Reynolds number of around  $4 \times 10^5$ , there is a sudden drop in  $C_D$  to around one-fifth of its previous value. This is associated with the boundary layer around the sphere becoming turbulent, which reduces the extent of the wake and hence the drag. This drag crisis is not usually reached for single liquid droplets falling in quiescent air under gravity. For water droplets in air with a diameter of  $200 \mu\text{m}$ , the Reynolds number is around 10, whilst for 1 mm diameter droplets, the Reynolds number is around 300. However, sprays produced by pressure-atomized nozzles are likely to be turbulent.



**Figure 24** Drag coefficient of spheres as a function of Reynolds number, from Hoerner (1965). Symbols: measurements; straight line: Stokes Law.

Various models have been developed to account for the effects of inertia and flow separation on the drag coefficient of spheres. The Oseen law, which is valid for  $Re < 1$  is given by:

$$C_D = \frac{24}{Re} \left( 1 + \frac{3}{16} Re \right) \quad (3.6)$$

This can be rearranged to express the settling velocity in terms of the droplet diameter by means of a simple quadratic equation.

Massey (1983) presented the following empirical formula, which is valid for higher  $Re$ , up to 100:

$$C_D = \frac{24}{Re} \left( 1 + \frac{3}{16} Re \right)^{1/2} \quad (3.7)$$

Solution of this equation is more complex, and is easiest to achieve using a Newton-Raphson iterative method.

An empirical correlation that gives similar results, but which is easier to use in practice, was developed by Davies (1945). It is composed of two parts, the first of which is valid for  $Re < 4$  or  $(C_D Re)^2 < 140$ :

$$Re = \frac{1}{24} (C_D Re^2) - a_1 (C_D Re^2)^2 + a_2 (C_D Re^2)^3 - a_3 (C_D Re^2)^4 \quad (3.8)$$

and the second part, which is valid for  $3 < Re < 10^4$  or  $100 < (C_D Re)^2 < 4.5 \times 10^7$ :

$$\log_{10}(Re) = b_1 + b_2 \log_{10}(C_D Re^2) + b_3 [\log_{10}(C_D Re^2)]^2 + b_4 [\log_{10}(C_D Re^2)]^3 \quad (3.9)$$

where the constants are:  $a_1 = 0.00023363$ ,  $a_2 = 2.0154 \times 10^{-6}$  and  $a_3 = 6.9105 \times 10^{-9}$ ,  $b_1 = -1.29536$ ,  $b_2 = 0.986$ ,  $b_3 = -0.046677$ , and  $b_4 = 0.0011235$ . The quantity  $(C_D Re^2)$  in these expressions is solely a function of the droplet and air conditions:

$$C_D Re^2 = \frac{4\rho_f g d^3}{3\rho_a \nu^2} \quad (3.10)$$

where  $\rho_f$  and  $\rho_a$  are the droplet and air densities,  $g$  is the gravitational acceleration,  $d$  the droplet diameter and  $\nu$  the kinematic air density. This approach allows direct solution for the velocity in terms of droplet diameter.

For a spherical water droplet in air at 20 °C, the settling velocities predicted using Stokes' Law and Oseen's Law and the empirical formulae from Massey (1983) and Davies (1945) are shown in Figure 25. The Massey (1983) and Davies (1945) formulae give practically identical settling velocities. The results show that a 150  $\mu\text{m}$  diameter water droplet will fall at around 0.5 m/s whereas a 15  $\mu\text{m}$  droplet will fall at only 0.007 m/s.

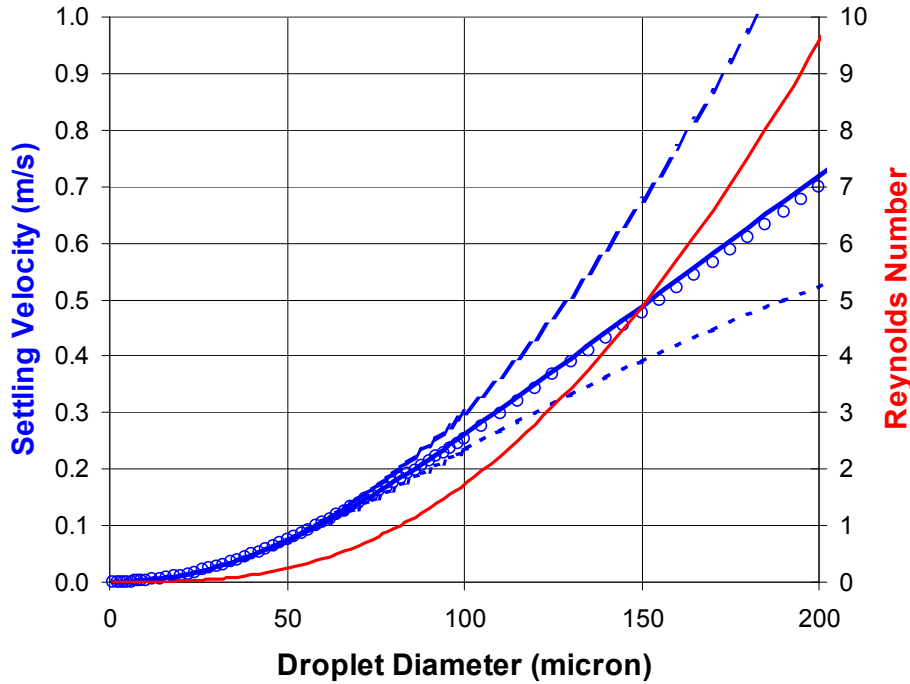
To put these values into context, IP15 specifies that in well-ventilated open areas, where vapours are readily dispersed by wind and natural convection, air velocities should be rarely less than 0.5 m/s and frequently about 2 m/s (EI, 2005). Measurements of natural ventilation velocities on offshore platforms were reported by Saunders and Ivings (2005), who found velocities to be non-uniform and highly dependent upon wind speed and direction, with measured values less than 0.5 m/s in many cases. For indoor workplaces, measurements of air velocities were reported by Baldwin and Maynard (1996), who found an arithmetic mean velocity of around 0.3 m/s, but with a highly skewed distribution, such that 85% of the individual measurements were below this value.

Further drag models for spheres include the Schiller-Naumann (1993) correlation, given by:

$$C_D = \max \left[ \frac{24}{Re} (1 + 0.15 Re^{0.687}), 0.44 \right] \quad (3.11)$$

which is often used in Lagrangian CFD models. Several alternative correlations for the drag coefficient are also summarised by Clift *et al.* (1978) and Lefebvre (1989).

The models described above are all only strictly valid for spherical particles. However, Gosman & Clerides (1998) noted that the inaccuracies due to absence of droplet distortion effects are minor in CFD model predictions.



**Figure 25** Predicted settling velocities for water droplets of different size falling in air calculated from: ---: Stokes Law; ····: Oseen Law; —: Massey (1983) Equation ( 3.7 ); ○: Davies (1945) Equations ( 3.8 ) and ( 3.9 ); —: predicted Reynolds number from Massey (1983) Equation ( 3.7 ).

The evaporation of vapour from a liquid droplet leads to thickening of the laminar boundary layer surrounding the droplet. This so-called “blowing” effect leads to a drop in the drag coefficient. Crowe *et al.* (1998) describe a number of approaches used to take account of blowing effects. A widely-used correlation is that of Eisenklam *et al.* (1967):

$$C_D = \frac{C_{D,0}}{1 + B} \quad (3.12)$$

where  $C_{D,0}$  is the drag coefficient without evaporation effects and  $B$  is the transfer number determined from:

$$B = \frac{c_p \Delta T}{h_L} \quad (3.13)$$

where  $c_p$  is the specific heat at constant pressure and  $h_L$  the latent heat of vaporisation. For methanol droplets with a temperature difference of 20 °C, this gives a modest reduction of 4% in the drag coefficient.

It should be noted that in dense sprays of falling droplets, momentum will be exchanged between the droplets and the surrounding air, inducing air currents which will influence the motion of nearby droplets. Calculating residence times in these cases assuming the air to be quiescent is likely to lead to a conservative result (i.e. a longer residence time). However, if there are strong buoyancy forces, due to heated surfaces for example, or significant ventilation flow rates, this could lead to mist droplets recirculating, and remaining suspended in the air for longer.

### 3.1.3 Droplet-droplet collisions

At the lower explosive limit, Burgoyne and Cohen (1954) showed that the mean distance between droplet centres was around 22 times the droplet diameter for droplets smaller than 10  $\mu\text{m}$ , and around 31 times the droplet diameter for droplets with diameter larger than 40  $\mu\text{m}$  (see Figure 2 in Section 2.1). In the near-field of pressurized spray releases, the spacing between droplets will be less than this, and in dense mists there is clearly the possibility for droplets to collide.

The collision between two droplets in a dense spray or mist can lead to a number of possible outcomes: coalescence, bouncing (recoiling and rebounding), temporary coalescence followed by breakup, or shattering. Fundamental studies have been undertaken to classify these possible outcomes on the basis of the impact direction and droplet Weber number (see Sirignano, 2005). These have shown that there is a low probability of collisions in sprays where the droplets are travelling in parallel directions or along divergent paths. O'Rourke and Bracco (1980) noted that collisions are still important near a spray orifice. Computational models for collision-dominated flows, which involve the tracking of individual droplets, were presented by Crowe *et al.* (1998). These models provide insight into the flow physics but as they require tracking of individual droplets, would seem impracticable to use, per se, for HAC.

In the context of flammable mists generation, Eckhoff (1995) noted that in dense clouds of very small 1  $\mu\text{m}$  diameter droplets with a concentration within the flammable range, the droplets would not be stable for any significant length of time due to the effects of droplet coalescence. This assertion was probably based on empirical correlations similar to those developed by Gillespie and Langstroth (1952) (see Green and Lane, 1964). They measured the rate at which smoke particles coagulated and determined rate constant,  $K$ , for various materials according to the following formula:

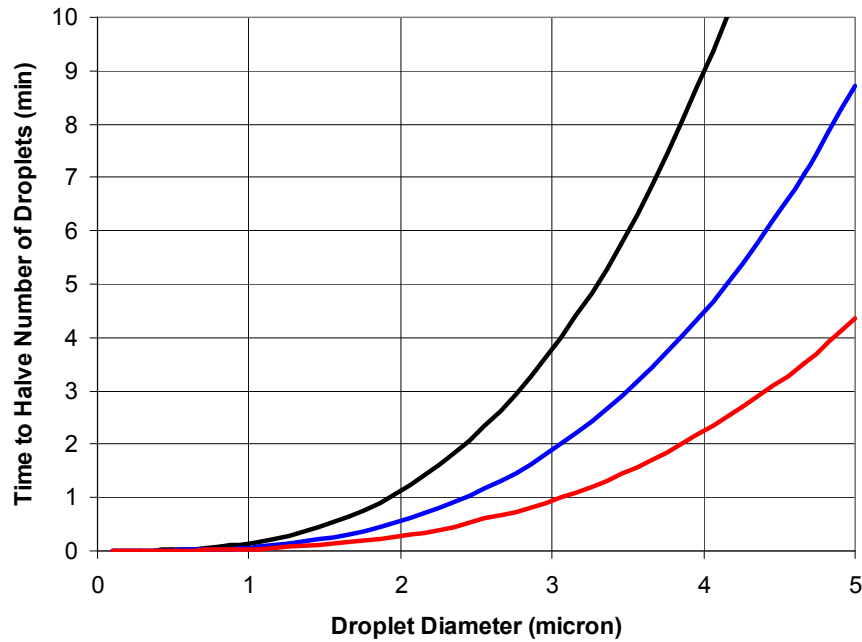
$$-\frac{dn}{dt} = -Kn^2 \quad (3.14)$$

where  $n$  is the number of particles (or droplets) per unit volume. For aerosols of paraffin oil they obtained a value of  $K$  of  $0.5 \times 10^{-9} \text{ cm}^3/\text{s}$ . Figure 26 shows the behaviour implied by Equation (3.14), for paraffin oil with mass concentrations of 50  $\text{g}/\text{m}^3$ , 100  $\text{g}/\text{m}^3$  and 200  $\text{g}/\text{m}^3$ . The lowest concentration of 50  $\text{g}/\text{m}^3$  is similar to the LEL of many hydrocarbons (Drysdale, 1998). The rate of reduction in particles ( $dn/dt$ ) is expressed in Figure 26 in terms of the time for half of the droplets to coagulate. For droplets of a few  $\mu\text{m}$  in diameter, coalescence clearly has an important effect. To halve the number of droplets in a mist composed of 1  $\mu\text{m}$  droplets takes just a few seconds. The increase in coalescence time with droplet diameter is exponential, however, due to the greater separation between droplets as their size is increased, for a given mass concentration. For droplets more than around 5  $\mu\text{m}$  in diameter, at concentrations close to the LEL, coalescence appears to have a very slow effect, over the order of tens of minutes.

The effects of various factors on the rate of aerosol coalescence were reviewed by Green and Lane (1964), who noted that polydisperse mists coagulate at a faster rate than monodisperse mists. This is caused by both the probability of collision being greater between droplets of unequal size (due to the higher statistical collision frequency given the greater number of droplets for a given concentration) and due to the larger droplets falling faster under gravity, increasing the chances of collision with the slower-moving smaller droplets. The latter effect is thought to be important in developing large raindrops in clouds, in the Langmuir chain-reaction process (Langmuir, 1948). Turbulence also increases the collision frequency and speed, which has been found to increase the rate of coalescence in oil smoke aerosols. Further



discussion of the effect of static charge and acoustic forcing on droplet coalescence was given by Green and Lane (1964).



**Figure 26** Predicted time for the halving of the number of droplets due to coagulation, for a monodisperse paraffin oil mist with a mass concentration of:  
— 50 g/m<sup>3</sup>, — 100 g/m<sup>3</sup>, — 200 g/m<sup>3</sup>.

### 3.1.4 Evaporation

The propensity of a substance to evaporate is often expressed in terms of its saturation vapour pressure. The concept of the vapour pressure is described in most fluid mechanics or chemical engineering textbooks (e.g. Massey, 1983), but it is briefly reviewed here, as it is crucial to later discussions.

Normal humid atmospheric air can be treated as an ideal gas mixture whose pressure,  $P$ , is equal to the sum of the partial pressures of water vapour,  $P_A$ , and dry air,  $P_B$ :

$$P = P_A + P_B \quad (3.15)$$

Here, the partial pressure of the water vapour,  $P_A$ , can be thought of as the pressure the water vapour would exert if it existed alone at the temperature and volume of the mixture. Considering the case of water droplets suddenly introduced into a container filled with dry air, the liquid droplets will start to evaporate and the amount of water vapour in the air will gradually rise until the conditions within the container reach an equilibrium. At this equilibrium condition, the water vapour is in balance with the liquid and there is no tendency for the material to evaporate or condense. The value of the partial pressure of the water vapour at this point is the equilibrium, or saturation, vapour pressure,  $P^{sat}$ .

The concentration of water vapour in the mixture under these conditions is given by:

$$X_A^{sat} = \frac{P_A^{sat}}{P_A^{sat} + P_B} \quad (3.16)$$

The denominator in this expression is the total pressure (since  $P = P_A + P_B$ ). For water in equilibrium with air at 15°C, which has a saturation vapour pressure of 1.68 kPa, the molar fraction is therefore (1.68/101.3) or a concentration of 1.7% water vapour by volume. Substances with a saturation vapour pressure greater than 101.325 kPa exist as a vapour under equilibrium conditions at 1 atm. For example, butane has a saturation vapour pressure of 173 kPa at 15°C.

The saturation vapour pressure for a particular substance changes as a function of the temperature. There are two empirical correlations commonly used to express this relationship. The first is the Clausius-Clapeyron equation:

$$P^{sat} = \exp\left[\frac{h_{fg}}{R} \left(\frac{1}{T_b} - \frac{1}{T}\right)\right] \quad (3.17)$$

where  $h_{fg}$  is the latent heat of vaporization,  $R$  the gas constant for the substance,  $T_b$  the boiling point at a pressure of 101.325 kPa and  $T$  the temperature. The second relation is Antoine's equation:

$$P^{sat} = P_{ref} \exp\left(A - \frac{B}{T + C}\right) \quad (3.18)$$

where  $P_{ref}$  is standard atmospheric pressure and  $A$ ,  $B$  and  $C$  are material-specific coefficients.

The above equations can be used to determine the percentage of a pure substance that will exist in air under equilibrium conditions, assuming that the substance evaporating is a pure liquid.

For droplets composed of multiple components, the equilibrium concentration can often be determined using Raoult's Law, which states that the molar fraction of species  $A$  in the air is the ratio of the saturation vapour pressure to the total pressure, scaled by the molar fraction of species  $A$  in the liquid droplet,  $x_A$ :

$$X_A = \frac{P_A^{sat}}{P} x_A \quad (3.19)$$

This means, for example, that if a cloud of droplets were composed of 50% hexane and 50% decane, by volume, the saturation vapour pressure of hexane in the air would be half of the value that it would be if the droplets were composed of pure hexane. The law holds true for 'ideal' solutions where the intermolecular forces between molecules of the pure substances are similar to the forces between molecules of one component and another. This is a good approximation for mixtures of hydrocarbons but it is not appropriate for polar solutions, such as mixtures of water and ethanol.

Equations ( 3.17 ), ( 3.18 ) and ( 3.19 ) may be useful in the context of an area classification, to develop simple models for the occurrence of a condensation aerosol. For instance, it may be possible to derive models that determine the mass of aerosol produced by mixing a known quantity of fresh air (from, say, the ventilation flow rate through an enclosure) with an

estimated quantity of liquid that has been released and subsequently vaporised within the enclosure.

### 3.1.5 Droplet mass and heat transfer

The rate of change of the droplet temperature is governed by four physical processes: conduction, convection, radiation and phase change (evaporation or condensation). For most applications considered in the present work, radiation may be ignored. The mean temperature of a droplet,  $T_d$ , is then governed by the following energy equation:

$$mc_p \frac{dT_d}{dt} = \dot{Q} + h_{fg} \frac{dm}{dt} \quad (3.20)$$

where  $c_p$  is the specific heat capacity at constant pressure for the droplet,  $\dot{Q}$  is the rate of heat transfer to the droplets (accounting for conduction and convection) and  $h_{fg}$  is the latent heat of evaporation of the droplet material. CFD models of sprays often evaluate  $\dot{Q}$  using empirical correlations involving dimensionless heat transfer parameters, such as the Nusselt number.

Evaporation and condensation involve a change of phase between liquid and vapour at the droplet surface and transport of droplet vapour to/from the droplet surface. For the applications considered here, the droplets are not boiling and the driving force for evaporation is the concentration gradient between the droplet surface and the free-stream. This is expressed by Fick's Law:

$$\frac{dm}{dt} = -D_v A \frac{\partial \rho}{\partial n} \quad (3.21)$$

where  $D_v$  is the diffusion coefficient for the particular species,  $A$  is the area across which the mass transfer takes place and  $\partial \rho / \partial n$  is the density gradient of the particular species in the direction normal to the surface. CFD models for droplet mass transfer often approximate  $D_v$  using empirical correlations.

In systems in which there is no external input of heat, the evaporation of droplets is accompanied by a reduction in temperature, due to the heat required to change the phase from liquid to vapour. This is responsible for the familiar evaporative cooling effect produced by perspiration. The converse effect is produced as a saturated vapour condenses to form a mist, when latent heat is released. In the earth's atmosphere, this is responsible for the temperature reducing with altitude at a slower rate when the air is saturated with vapour (i.e. in clouds), than when the air is dry.

In the context of area classification, to calculate the mass of condensation aerosol produced in an enclosure from the mixing of hot vapour and cold air, an iterative approach may be necessary in order to account for latent heat effects. Condensation of the vapour will release latent heat, which will act to raise the local temperature and increase the saturation vapour pressure, meaning that less vapour should condense. In order to reach an equilibrium solution, this calculation process needs to be iterated. For a given system, the feedback loop provides a natural limit on the amount of condensation (or evaporation) that can take place.

## 3.2 PRESSURIZED LIQUID RELEASES

### 3.2.1 Mass release rate

The discharge rate from a leak in a pressurized liquid reservoir can be determined from Bernoulli's equation as follows:

$$\dot{m} = C_D A \sqrt{2\rho P_g} \quad (3.22)$$

where  $A$  is the orifice area,  $P_g$  is the gauge pressure of the liquid,  $\rho$  is the liquid density and  $C_D$  is the discharge coefficient, which is often taken to be around 0.6 for a sharp-edged orifice (Drysdale, 1998; Mather and Lines, 1999).

The discharge coefficient appearing in Equation ( 3.22 ) accounts primarily for two effects: the narrower effective hole area or “vena contracta” due to the flow converging through the orifice, and frictional effects that are ignored in Bernoulli's idealised analysis. The latter is typically small compared to the effect of the vena contracta (Massey, 1983). The discharge coefficient of 0.6 is therefore usually assumed to produce an effective orifice area that is 60% of the actual hole area, whilst the release velocity is assumed to be given by:

$$V = \sqrt{\frac{2P_g}{\rho}} \quad (3.23)$$

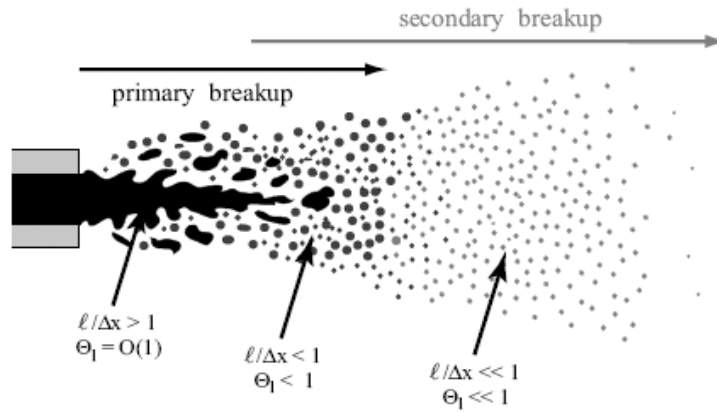
The effect on  $C_D$  due to changes in the orifice shape, Reynolds number and nozzle length-to-diameter ratio were investigated by Ohrn *et al.* (1991a). They found that edge defects produced a substantial variation in  $C_D$  for nominally sharp-edged orifices, and values of  $C_D$  were always higher than for a perfectly sharp-edged orifice. Rounding the inlet to the orifice was found to increase  $C_D$ . For sharp-edged orifices (defined as those with a radius of rounding on the inlet less than 0.2 times the diameter) the value of  $C_D$  was independent of the Reynolds number in the range from 7,000 to 30,000.

Woodward and Mudan (1991) provided simple engineering models for predicting the release rate of liquids from pressurized vessels, accounting for the change in pressure over time as the vessel depressurizes.

### 3.2.2 Primary and secondary breakup

The process of forming droplets from a release of liquid under pressure through an orifice is usually divided into two consecutive steps: primary and secondary breakup (see Figure 27). During primary breakup the liquid stream flowing through the orifice is fragmented to form large droplets (often highly non-uniform in shape) under the action of internal processes and the surrounding gas flow. These large droplets are often above a critical size that is aerodynamically stable, and as they are convected further downstream, they fragment due to the combined action of aerodynamic forces and droplet collisions, in a process known as secondary breakup.

Scientific analysis of primary and secondary droplet breakup was first undertaken by Plateau (1945), Savart (1833) and Rayleigh (1878) (for a summary, see Lefebvre, 1989 ). These early studies examined the stability of liquid jets and the resulting size of individual droplets. At low release velocities, when the liquid jet was laminar, Rayleigh (1878) showed that the average drop size was nearly twice the diameter of the undisturbed jet. Significant developments were made in these early analyses, but they relate only to flow rates well below that typical of accidental releases from pressurized liquid systems on industrial sites, and are therefore not directly relevant here.



**Figure 27** Breakup of a liquid jet, from Herrmann (2003)

Later work of more practical importance to the present study was undertaken by Ohnesorge (1936), who characterised the behaviour of liquid jets using the liquid Reynolds number,  $Re_l$ :

$$Re_l = \frac{\rho_l U_l D}{\mu_l} \quad (3.24)$$

and a dimensionless parameter now known as the Ohnesorge number<sup>10</sup>,  $Oh$ :

$$Oh = \frac{\mu_l}{\sqrt{\rho_l D \sigma}} \quad (3.25)$$

where  $\mu_l$  and  $\rho_l$  are the dynamic viscosity and density of the droplet, respectively,  $U_l$  is the liquid velocity,  $D$  is the orifice diameter and  $\sigma$  is the surface tension. For a given liquid and orifice size the value of  $Oh$  is constant.

### Primary Breakup

In the analysis of Ohnesorge (1936), subsequently developed further by Miesse (1955) and Reitz (1978), primary liquid breakup was classified into a number of regimes. The Reitz (1978) classification, shown in Figures 28 and 29, consists of four regimes: Rayleigh breakup, first wind induced, second wind induced, and atomization. In the first wind induced regime, breakup occurs many jet diameters downstream of the orifice and the diameter of droplets is similar to the orifice diameter. In the second wind induced regime, primary breakup occurs closer to the orifice, and the average droplet size is smaller than the orifice diameter. In the atomization regime, the liquid jet breaks up completely at the orifice and droplets are much smaller than the orifice.

The transition to atomization breakup was determined by Ohnesorge (1936) to take place at Ohnesorge numbers given by<sup>11</sup>:

<sup>10</sup> Also referred to as the Laplace number or 'Z' number.

<sup>11</sup> The coefficients in this equation have been determined by scanning digitally the graph in the original Ohnesorge (1936) paper.

$$Oh = 745Re_i^{-1.22} \quad (3.26)$$

This empirical correlation was based on measurements undertaken with various oils, glycerine, aniline, and water using orifices diameters of between 0.5 mm and 4.0 mm.

Subsequently, Miesse (1955) conducted experiments with water and liquid nitrogen, and found that the transition to atomization breakup occurred at slightly different conditions, given by:

$$Oh = 100Re_i^{-0.92} \quad (3.27)$$

In the experiments of Miesse (1955), the liquid nitrogen results are difficult to interpret, since the liquid will have flashed or boiled as it was released into the air. The only measurements that spanned both atomizing and non-atomizing regimes were obtained for a single 1.0 mm diameter nozzle.

Using both the Ohnesorge (1936) and Miesse (1955) correlations, and Bernoulli's equation for the exit velocity:

$$\Delta P = \frac{1}{2} \rho U_i^2 \quad (3.28)$$

the pressure differential ( $\Delta P$ ) needed to produce atomization breakup can be determined as a function of hole size for a range of substances (Figure 30). A summary of material properties used to generate Figure 30 is given in Table 7.

There are quite significant differences between the Ohnesorge (1936) and Miesse (1955) correlations, shown in Figure 30. For example, to produce atomization breakup of common hydrocarbon liquids (methanol, n-hexane and n-decane) with a 2 mm diameter orifice requires a pressure difference of around 4 bar according to Miesse (1955), but less than 0.5 bar according to Ohnesorge (1936). This may relate to differences in the geometry of the nozzles used in the two sets of experiments, which is known to have a significant impact on the breakup behaviour. Care should be taken in extrapolating the data to pin-hole orifices, with diameters smaller than 0.5 mm, or orifices much larger than 4 mm, due to the limited experimental data that was used to obtain the correlations. It should also be noted that Figure 30 only describes the release conditions that produce atomization of the liquid jet at the orifice. Mists may still be generated at lower pressures than those given by these correlations, due to secondary aerodynamic breakup or impingement of the jet on nearby surfaces. These two issues are discussed further below.

The transition from one breakup regime to another has alternatively been characterised in terms of the Weber number,  $We$ , which is determined from:

$$We = \frac{\rho_l U_d^2 d_d}{\sigma} \quad (3.29)$$

where  $U_d$  is the relative velocity between droplet and the air, and  $d_d$  is the droplet diameter. Criteria for the breakup regimes in terms of  $We$  are given in Table 8. Further analysis of the transition between spray breakup regimes, was given by Faeth (1990).

An alternative classification system for primary breakup, based on the jet stability curve shown in Figure 31, was reviewed by Lefebvre (1989) and Birouk and Lekic (2009). Empirical correlations for the locations of the critical points  $B$  and  $C$  on the curve were described in these reviews, based on the Reynolds, Ohnesorge and Weber numbers, together

with a discussion of the phenomenological differences between laminar and turbulent spray releases.

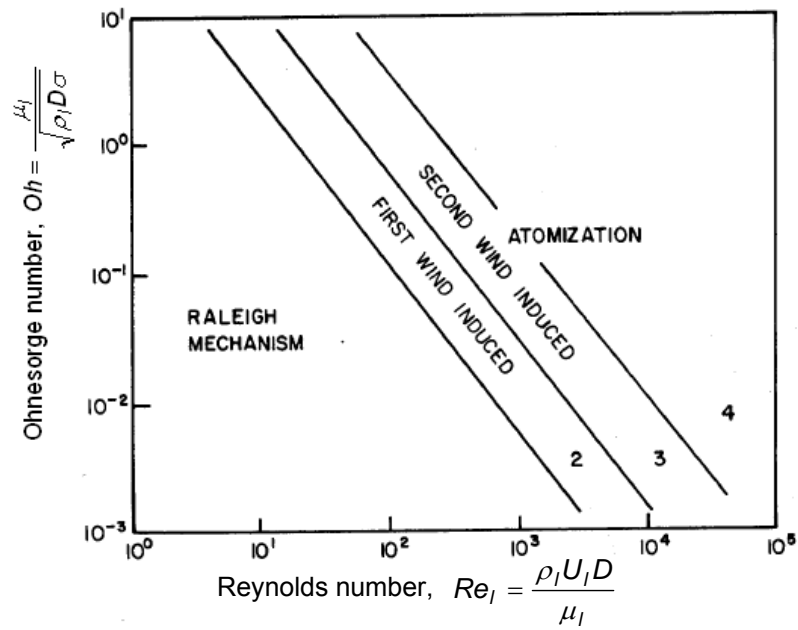


Figure 28 Spray breakup regimes (from Lefebvre, 1989)

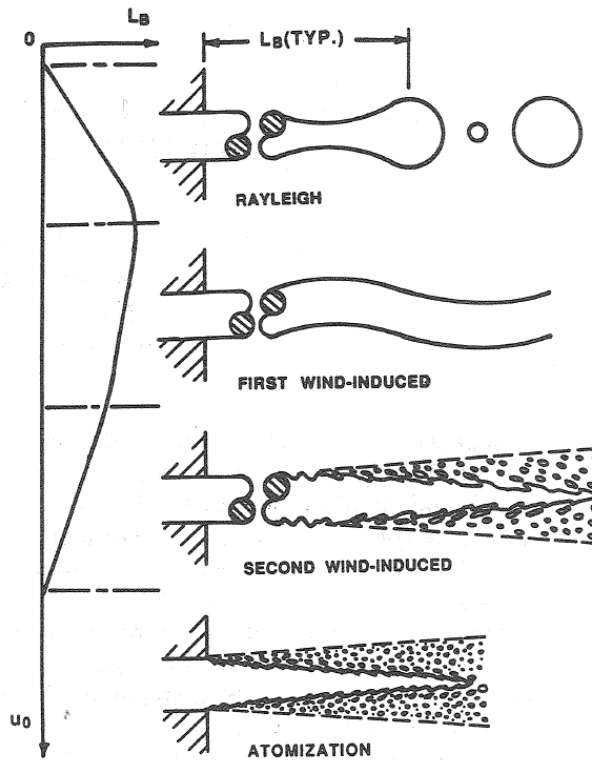
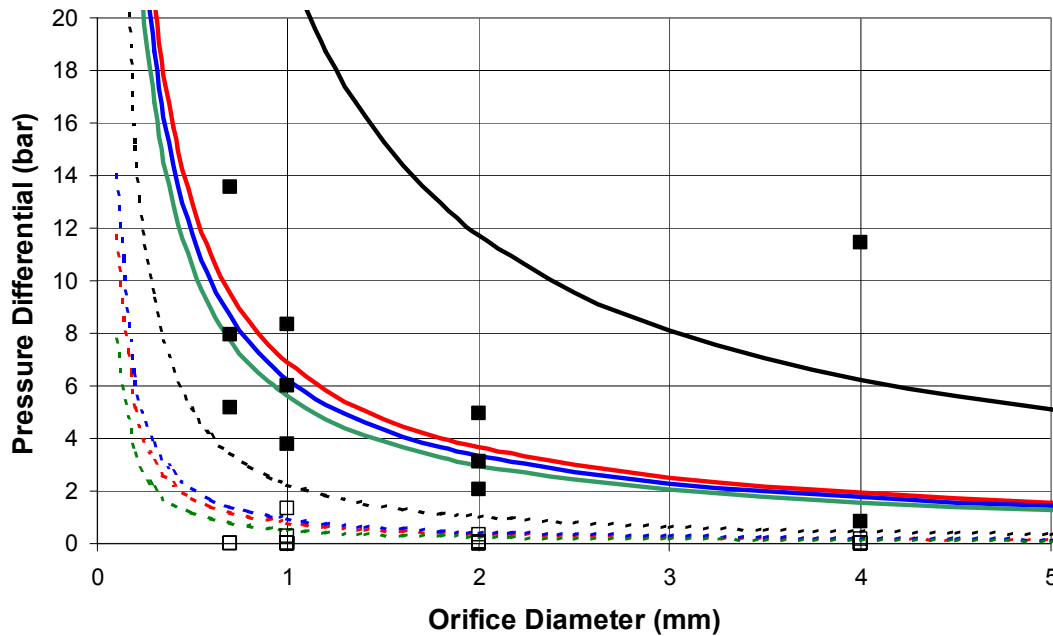


Figure 29 Spray breakup regimes for non-turbulent round liquid jets in quiescent air, from (Faeth, 1990).



**Figure 30** Pressure differential required to produce transition to atomization breakup regime for spray releases of: — water, — methanol, — n-decane and — n-hexane using the empirical correlations of Ohnesorge (1936) (broken lines) and Miesse (1955) (solid lines). Symbols show the water measurements of Ohnesorge (1936) for: ■ atomizing sprays, □ non-atomizing sprays.

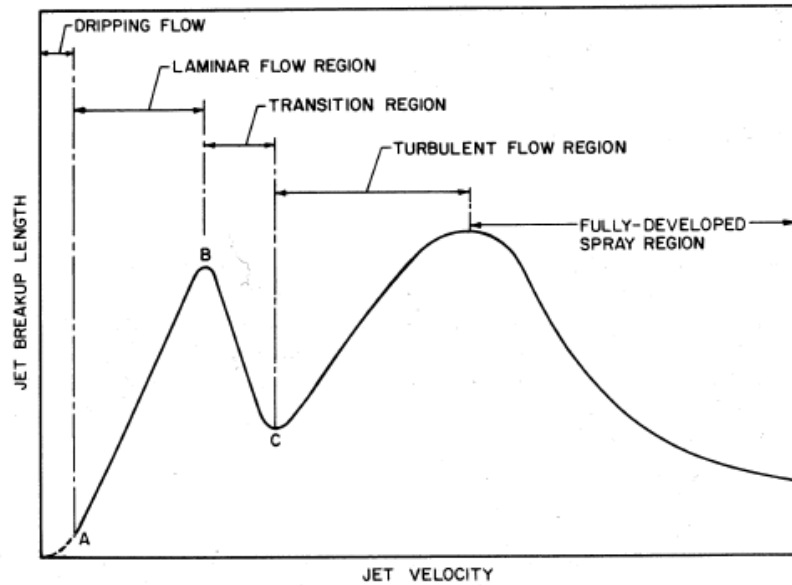
**Table 7** Summary of material properties at 15 °C and atmospheric pressure; sources: Lide and Kehiaian (1994) and Yaws (1999).

| <i>Chemical Name</i> | <i>Composition</i>           | <i>Density, <math>\rho</math><br/>(<math>\text{kg/m}^3</math>)</i> | <i>Viscosity, <math>\mu</math><br/>(<math>\text{N.s/m}^2</math>)</i> | <i>Surface<br/>Tension, <math>\sigma</math><br/>(<math>\text{N/m}</math>)</i> | <i>Saturation<br/>Vapour<br/>Pressure, <math>P^{\text{sat}}</math><br/>(<math>\text{Bar}</math>)</i> |
|----------------------|------------------------------|--|--|---|--|
| n-Hexane             | $\text{C}_6\text{H}_{14}$    | 665  | $3.25 \times 10^{-4}$  | $1.91 \times 10^{-2}$   | 0.128  |
| n-Decane             | $\text{C}_{10}\text{H}_{22}$ | 736  | $10.04 \times 10^{-4}$   | $2.44 \times 10^{-2}$   | 0.0008   |
| Water                | $\text{H}_2\text{O}$         | 1037   | $11.62 \times 10^{-4}$   | $7.56 \times 10^{-2}$   | 0.0168   |
| Methanol             | $\text{CH}_3\text{OH}$       | 796  | $6.19 \times 10^{-4}$  | $2.49 \times 10^{-2}$   | 0.0988   |



**Table 8** Classification of droplet breakup regimes, from Reitz (1978), Lefebvre (1989), Faeth (1990) and Birouk and Lekic (2009).

| <i>Regime</i>       | <i>Predominant Forces</i>  | <i>Resulting Droplet size</i> | <i>Range</i>                           |
|---------------------|--|-------------------------------|--|
| Rayleigh-induced    | Surface tension  | Nearly twice jet diameter     | $We < 0.4$<br>$We < 1.3 + 3.4Oh^{0.9}$ |
| First wind-induced  | Surface tension and aerodynamic, helical instability of liquid jet               | Approx. equal to jet diameter | $0.4 < We < 13$                        |
| Second wind-induced | Surface tension and aerodynamic, helical and surface instabilities of liquid jet | Less than jet diameter        | $13 < We < 40$                         |
| Atomization         | Predominantly aerodynamic, breakup begins right from the orifice                 | Much less than jet diameter   | $We \geq 40$                           |



**Figure 31** Jet stability curve indicating change of breakup length with jet velocity, from Lefebvre (1989)

In most cases of interest to area classification, primary breakup is likely to occur within the atomization region. The length of the unbroken liquid core within the primary breakup region of the jet is typically between 200 to 400 orifice diameters. A model for the length of the liquid core,  $L_c$ , based on the aerodynamic breakup analysis of Taylor (1940) was presented by Ruff *et al.* (1990) as follows:

$$\frac{L_c}{D} = C_c \left( \frac{\rho_f}{\rho_g} \right)^{1/2} \quad (3.30)$$

where  $\rho_f$  and  $\rho_g$  are the densities of the liquid and air, respectively,  $D$  is the orifice diameter and  $C_c$  is a model constant. Chehroudi *et al.* (1985) found that for round liquid jets in

quiescent air within the atomization breakup regime,  $C_c$  has a value of between 7 and 16. For a given release scenario within an enclosure of known dimensions, Equation ( 3.30 ) may be used to determine whether primary spray breakup is completed prior to the liquid impinging on a nearby surface.

For high velocity jets, primary breakup is controlled principally by the action of the surrounding air on the liquid stream. A secondary factor affecting the nature of primary breakup is the presence of turbulence in the liquid stream issuing from the orifice. For flow in long pipes at Reynolds numbers greater than around 2000, the flow is likely to be turbulent (Massey, 1983). The presence of turbulence disturbs the surface of the liquid jet, making it more susceptible to aerodynamic breakup. Primary breakup is therefore enhanced by either an increase in the liquid velocity or by a decrease in the liquid viscosity. The atomization process is always accelerated by an increase in air resistance, hence an increase in air density enhances the breakup process. These factors are examined in more detail in the reviews of Lefebvre (1989) and Birouk and Lekic (2009).

Sprays produced by both non-turbulent and fully-developed turbulent liquid flows were studied by Ruff *et al.* (1990) and Faeth (1990) for application to fuel injectors. They presented the following semi-empirical expression for the Sauter Mean Diameter of droplets produced by primary breakup in the atomization regime from non-turbulent liquid flows:

$$\frac{\rho_a d_{SMD} U_r}{\sigma} = 2\pi C_B \quad (3.31)$$

where  $d_{SMD}$  is the Sauter Mean Diameter,  $U_r$  is the relative speed of the droplets in the air and the value of  $C_B$  was derived from limited tests to have a value of approximately 0.4. It was acknowledged by Faeth (1990) that further work was necessary to establish the universality of this expression.

For sprays produced by fully-turbulent liquid releases in the atomization regime, they provided the following expression for the droplet diameter:

$$\frac{\rho_l \Lambda \overline{v_f'^2}}{\sigma} \left( \frac{d}{\Lambda} \right)^{5/3} \geq 6C_t \quad (3.32)$$

where  $C_t$  is a constant of order unity,  $d$  is the droplet diameter,  $\Lambda$  is the radial turbulent integral scale of the liquid turbulence and  $\overline{v_f'^2}$  is the variance of the fluctuating radial velocity in the liquid. Faeth (1990) and Ruff *et al.* (1990) suggested that  $\Lambda$  could be assumed to be between 10% and 15% of the spray orifice diameter. They determined  $\overline{v_f'^2}$  from the relationship between velocity fluctuations and the turbulence length scale in pipe flows, for which data is available from Laufer (1950).

On the periphery of the liquid core, Faeth (1990) and Ruff *et al.* (1990) found that the droplets produced by turbulent primary breakup were a factor of eight times larger than those produced by non-turbulent breakup. The differences in mean droplet size diminished further downstream due to secondary breakup. It was noted that for most spray injection nozzles, their small length in comparison to the orifice diameter meant that turbulence would not become fully-developed at the orifice, and hence turbulent primary breakup was probably not a major feature of most practical dense sprays. This may also apply for leaks through small path lengths, e.g. a leak through a small pipe flange.

Further theoretical analysis of primary breakup has been undertaken by Zimmels and Sadik (2001) and Sadik and Zimmels (2003), who examined the effect of superimposed disturbances on jet stability and the non-axial evolution of droplets.

### Nozzle Geometry

It should be noted that the above correlations were developed for circular orifices. In accidental release scenarios, where a vessel has ruptured due to corrosion or accidental damage, for example, the orifice is more likely to be irregular in shape. The effect of this on the resulting breakup length and droplet size has not been studied extensively in the literature. Long cracks in pressurized vessels are likely to give rise to sprays that show greater similarity to slot releases or flat fan nozzles. Intuitively, it seems likely that a thin irregular crack would lead to a shorter core length and more rapid atomization.

The performance of agricultural flat-fan nozzles was studied by Miller *et al.* (1996) who measured droplet sizes and velocities, and developed a model to predict the entrained air velocities. Further relevant works on different nozzle shapes include the studies of water sprays by Vahedi Tafreshi and Pourdeyhimi (2003) and Spangelo *et al.* (2009), diesel injectors by Payri *et al.* (2004; 2005; 2009), Desantes (2005) and Qin (1999), plain orifice atomizers by Ohrn *et al.* (1991a; 1991b) and a novel stepped orifice by Hoverman *et al.* (2003).

The study by Vahedi Tafreshi and Pourdeyhimi (2003) showed that a constricted nozzle in which the water flow stayed detached all the way through the nozzle produced first wind-induced breakup behaviour at higher Reynolds numbers than was expected from the Ohnesorge classification (Figure 28).

Spangelo *et al.* (2009) studied the effect of changing the aspect ratio and contraction angle within the nozzle. The velocity profile in the spray was observed to become flatter as the aspect ratio of the nozzle was increased from 4 to 10, due to an increase in turbulence intensity. Larger contraction angles produced a more parabolic velocity profile at high delivery pressures, which was attributed to detached flow within the nozzle.

Ohrn *et al.* (1991a; 1991b) measured the effect of orifice shape, Reynolds number and nozzle length-to-diameter ratio ( $l/d$ ) on the discharge coefficient and spray cone angle. They found that the spray cone angle increased with flow velocity for sharp-edged orifices. The effects were particularly significant when surface defects were present or the orifice inlet radius was small. For orifices with a smooth, curved inlet section, the effect of the flow velocity on the cone angle was small. For sharp-edge orifices, a nozzle  $l/d$  of 4 produced the largest cone angle. Values of  $l/d$  smaller or larger than this produced smaller cone angles. Overall, their work showed that the orifice shape could have an overriding effect on the resulting breakup behaviour and that this largely explained some of the conflicting trends reported in the literature. For example, they noted that some previous studies showed that the cone angle increased with  $l/d$ , whilst others reported it decreasing. Ohrn *et al.* (1991b) demonstrated that this was because this parameter was strongly affected by the shape of the inlet to the nozzle.

The experiments conducted by Hoverman *et al.* (2003) showed that a small step-like change in diameter near the orifice inlet could have a significant effect on the droplet size distribution in the resulting spray. This behaviour was explained by the reduction in cavitation at the inlet, due to the presence of the step.

Further, detailed analysis of the effect of nozzle geometry, including consideration of the contraction ratio, aspect ratio, surface roughness and curvature of surfaces was provided by Birouk and Lekic (2009).

## Secondary Breakup

Pilch and Erdman (1987) identified six different mechanisms involved in secondary breakup of spray droplets (Figure 32). Each mechanism was found to be characteristic of a particular Weber number range. Below a critical Weber number,  $We_c$ , secondary droplet breakup does not occur and the droplet size remains stable. An empirical correlation describing how this critical Weber number varies as a function of the Ohnesorge number was developed by Brodkey (1969):

$$We_c = 12(1 + 1.077On^{1.6}) \quad (3.33)$$

This equation can be rearranged to express the relative speed of the droplets through the surrounding air as a function of the maximum stable droplet diameter and other material and flow properties, as follows:

$$V = \left\{ \frac{12\sigma}{\rho d} \left[ 1 + 1.077 \left( \frac{\mu_d}{\sqrt{\rho_d d \sigma}} \right) \right] \right\}^{0.5} \quad (3.34)$$

The relationship between slip velocity,  $V$ , and the maximum stable droplet diameter,  $d$ , for various substances are shown in Figure 33. For a droplet-to-air slip velocity of 15 m/s, the maximum stable droplet diameter for water is approximately 3.3 mm, compared to 0.8 mm for n-hexane and 1.1 mm for n-decane and methanol. For comparison purposes, the size of droplets produced in many common aerosols, mists and sprays are shown in Figure 34.

In a mist deflagration, once a mist has ignited, the pressure wave that travels ahead of the flame front will accelerate droplets and may produce secondary atomization, which in turn may increase evaporation rates and enhance overpressures. This was considered to be a potential factor in the tests reported by Hansen and Wilkins (2004). Whilst explosion-driven droplet fragmentation can have a significant effect on the consequences of a mist explosion, such post-ignition phenomena are not considered as part of area classification.

Because of the difficulty in examining secondary breakup mechanisms experimentally, recent work has investigated alternative high-quality direct numerical simulations to understand the underlying physical processes, see for example Tauber and Tryggvason (2000) and Cristini and Renardy (2006).

There are numerous, mainly empirically-derived correlations for secondary droplet breakup, which are often used in Lagrangian CFD models to predict the droplet size as a function of the local flow conditions, see for example Reitz and Diwakar (1986), O'Rourke and Amsden (1987), Pilch and Erdman (1987), Hsiang and Faeth (1992) and Habchi *et al.* (1997).

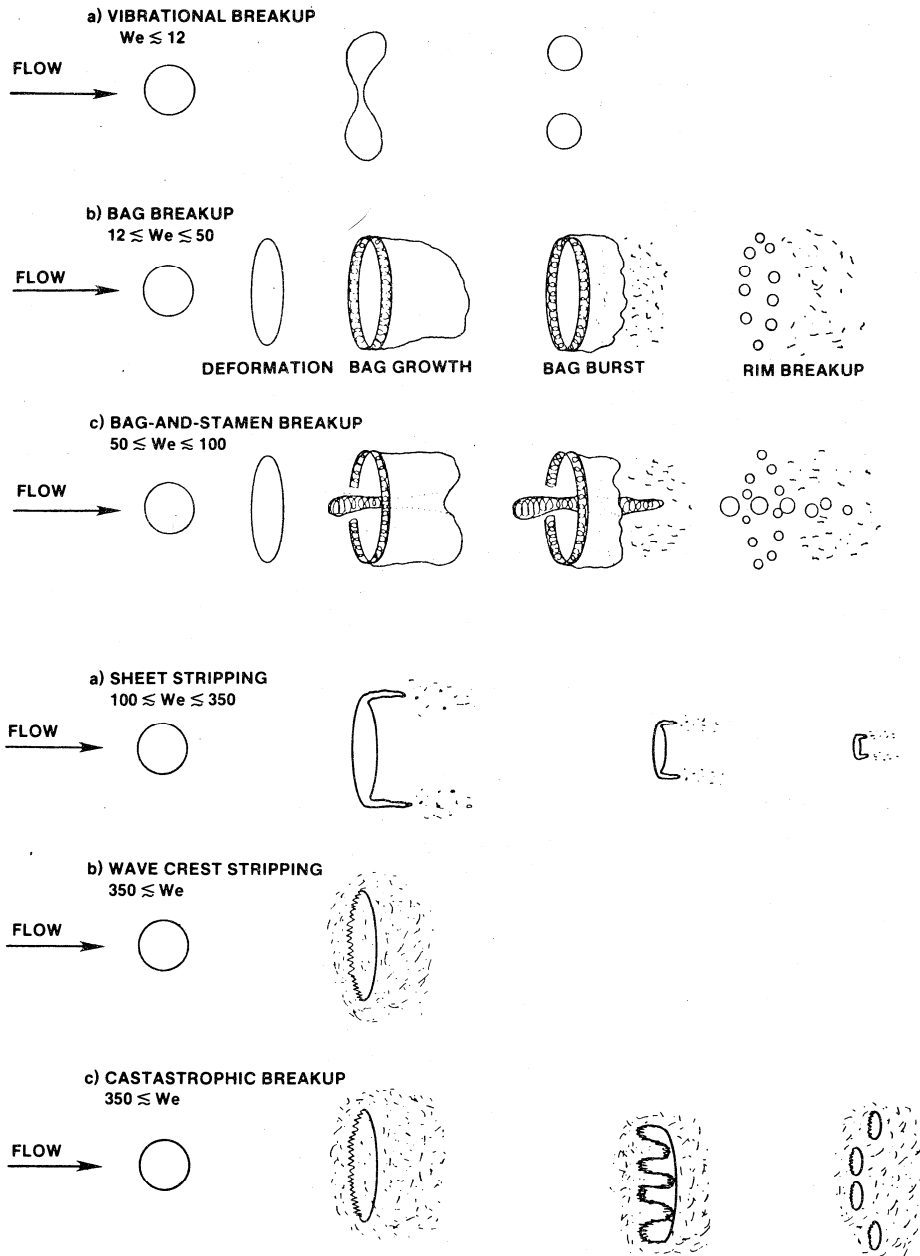
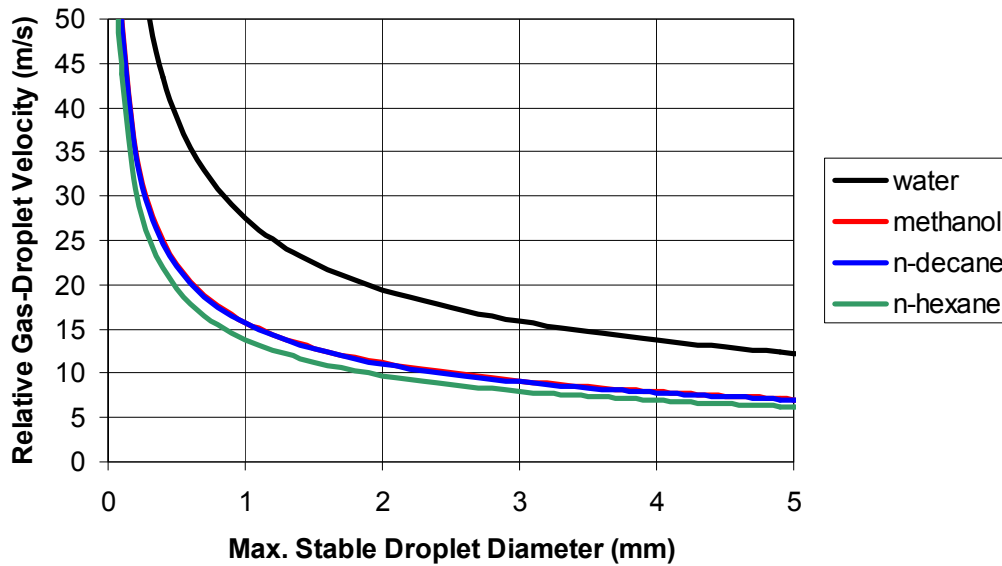
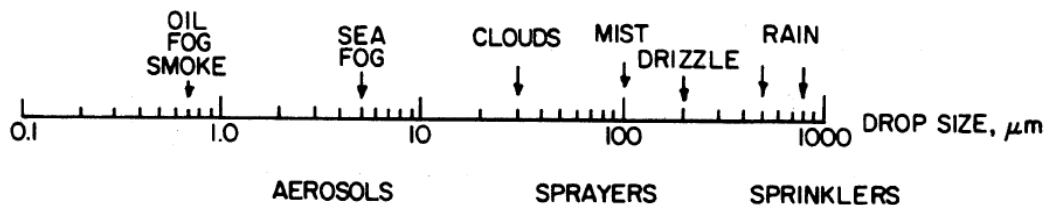


Figure 32 Secondary droplet breakup mechanisms, from Pilch & Erdman (1987).



**Figure 33** Maximum stable droplet sizes as a function of the relative velocity between the droplets and surrounding air using the empirical formula of Brodkey (1969).



**Figure 34** Droplet sizes for common aerosols, sprays and mists, from Lefebvre (1989).

### 3.2.3 Spray models

The above discussion has introduced primary and secondary breakup and described some useful empirical correlations from Ruff *et al.* (1990), Faeth (1990) and Brodkey (1969) for the resulting droplet sizes. In addition to these studies, there exists a large body of literature devoted to analysing the behaviour of different types of sprays. This includes consideration of various types of nozzle: plain orifice, pressure-swirl, rotary, air-assist, air-blast, effervescent, electrostatic, ultrasonic and whistle atomizers. For a summary of these works, see Lefebvre (1989).

There are currently two types of approach that could be used to predict the behaviour of a given spray release, in terms of the resulting droplet size and velocities in the far field. Firstly, there are CFD-based models, which compute the flow in both the air and the liquid phases and predict primary and secondary breakup (e.g. Trinh *et al.*, 2007). These are complex and costly, and therefore are not currently used routinely for hazard analysis. Secondly, there are engineering models, which are based more heavily on empiricism or on simplifications such as the assumption of Locally Homogenous Flow (LHF). In principle, it may be possible to use

these engineering models for the purposes of HAC, and therefore they are reviewed briefly below.

Accidental liquid releases from damaged vessels or pipework are most likely to exhibit behaviour similar to plain orifice nozzles, rather than those of swirl, rotary or air-assist type. Therefore, only models developed for plain nozzles are examined here. A particular aim in HAC is to identify the extent of the flammable region. Key parameters of interest are therefore the droplet size, cone angle, penetration depth and dispersion characteristics, i.e. the mass distribution across the width of the spray.

## Droplet Size

Sprays produced by pressurized liquid releases are rarely monodisperse. The spread in droplet sizes is usually reported using certain mathematically-defined functions. These include the normal, log-normal, Rosin-Rammler, modified Rosin-Rammler, Nukiyama-Tanasawa, and upper-limit distributions. A chapter in the book by Lefebvre (1989) is devoted to their specification and analysis, and other useful information is given by Mugele and Evans (1951) and Babinsky and Sojka (2002).

Often, rather than specify the complete size spectrum, a single mean size is used to characterise the spray. Commonly, the Sauter Mean Diameter (SMD) or the Mass Median Diameter (MMD) are used (see Definition of Terms, Section 1.6). Aggarwal and Sirignano (1986) argued that an alternative measure, the average surface area of the spray droplets ( $D_{20}$ ), was more appropriate for studying the ignition behaviour of polydisperse sprays, although its value is rarely reported in experimental studies.

There is a significant body of research in the literature on the measurement and prediction of spray droplet sizes, in addition to those discussed briefly in Section 3.1. Predictive methods for spray breakup have been classified into three different approaches: empirical methods, the Maximum Entropy (ME) method and the Discrete Probability Function (DPF) method. Each of these was reviewed by Babinsky and Sojka (2002) and recommendations provided on their use. For the purposes of developing area classification models, both ME and DPF methods appear overly complex, and empirical models are likely to be best suited, due to their simplicity and ease of use.

In most cases, empirical correlations presented in the literature have been developed with reference to a particular nozzle and set of operating conditions. The accuracy of predictions made by extrapolating outside of this experimental range is uncertain.

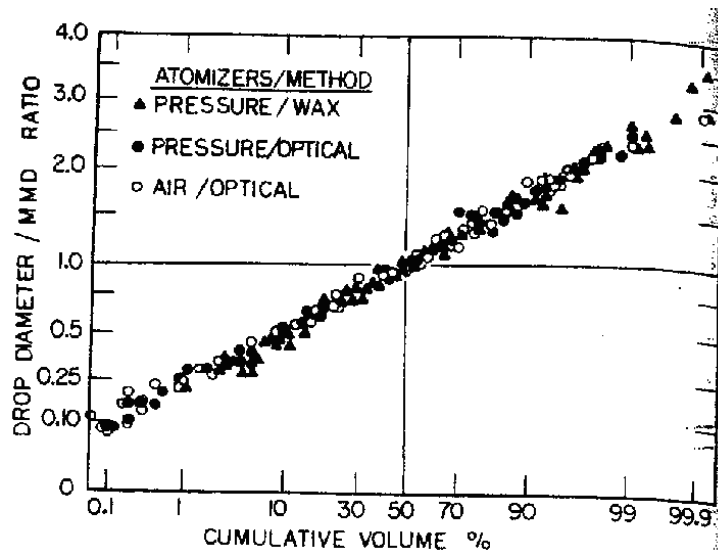
Simmons (1977) provided a particularly useful correlation for the droplet size spectrum produced by many different pressure and air-assist fuel nozzles used in aircraft or industrial gas turbines. The test data examined included results for a range of different fuels, with viscosities varying by an order of magnitude, fuel pressures ranging from 0.07 bar to 21 bar and release rates from 1.3 g/s to 38 g/s. The results were presented using a particular arrangement of graph axes whereby the measured droplet size spectrum plotted against the cumulative volume<sup>12</sup> produced a single straight line (Figure 35). The vertical axis in this graph shows the droplet size,  $d$ , made dimensionless using the Mass Median Diameter (MMD) and it is plotted using a square-root scale (equivalent to plotting  $\sqrt{d/MMD}$  on a linear scale). The horizontal axis shows the cumulative volume plotted using a normal probability scale. Such graphs are known as “root/normal” plots.

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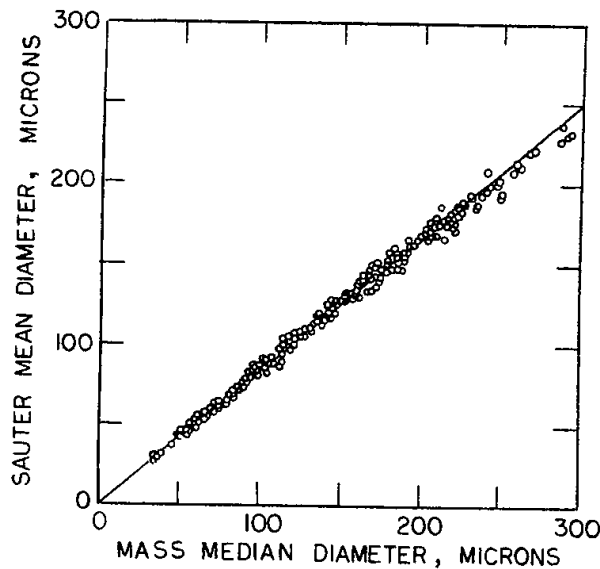
<sup>12</sup> i.e. the volume of liquid in the spray below the specified droplet size.

Simmons (1977) showed that the MMD in the sprays was well approximated as 1.2 times the SMD (Figure 36). Using this finding, a graph was produced which expressed the cumulative volume as a function of the SMD (Figure 37). The utility of Figure 37 is that it enables the volume of liquid enclosed in droplets below a certain size range to be determined, simply by knowing the SMD. An empirical correlation was also developed for the of the spray droplet size in terms of the number distribution, rather than the cumulative volume.

Simmons (1977) acknowledged that the types of sprays examined in this study were designed especially to provide optimum combustion in gas turbines, and therefore more general purpose nozzle sprays (or those produced from accidental releases) may contain a greater proportion of larger droplets.

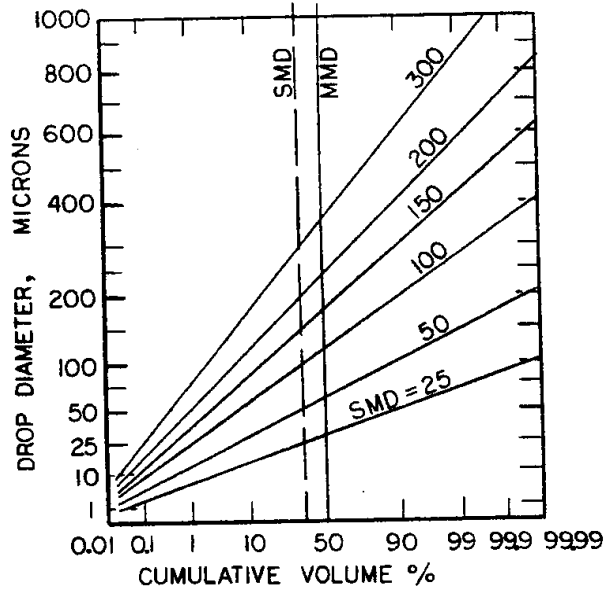


**Figure 35** Normalised droplet size distribution obtained by optical and wax-droplet methods using both pressure and air-atomizing nozzles, from Simmons (1977)



**Figure 36** Correlation of MMD to SMD for 200 tets on fuel nozzles of various designs, from Simmons (1977)





**Figure 37** Chart for estimating droplet-size/volume fraction relationship for a spray, given either the SMD or MMD, from Simmons (1977)

Measurements were presented by Ruff *et al.* (1990) for the droplet size distribution produced by pressurized water sprays, directed vertically downwards in still room air, which agreed well with the correlations of Simmons (1977).

Lefebvre (1989) provided a summary of the likely range of droplet sizes for nozzles of various different types. A number of empirical correlations for plain orifice nozzles (closest to the type of spray produced in an accidental release) are given in Table 9.

**Table 9** Droplet size correlations for plain orifice nozzles, from Lefebvre (1989)

| Investigators                 | Equation  |
|-------------------------------|---|
| Merrington and Richardson [2] | $\text{SMD} = \frac{500d_o^{1.2}v_L^{0.2}}{U_L}$  |
| Panasenkov [3]                | $\text{MMD} = 6d_o\text{Re}_L^{-0.15}$  |
| Harmon [4]                    | $\text{SMD} = 3330d_o^{0.3}\mu_L^{0.07}\rho_L^{-0.648}\sigma^{-0.15}U_L^{-0.15}\mu_G^{0.78}\rho_G^{-0.052}$                     |
| Miesse [6]                    | $D_{0.999} = d_o\text{We}_L^{-0.333}(23.5 + 0.000395\text{Re}_L)$   |
| Tanasawa and Toyoda [7]       | $\text{SMD} = 47d_oU_L^{-1}\left(\frac{\sigma}{\rho G}\right)^{0.25}\left[1 + 331\frac{\mu_L}{(\rho_L\sigma d_o)^{0.5}}\right]$ |
| Hiroyasu and Katoda [8]       | $\text{SMD} = 2330\rho_A^{0.121}Q^{0.131}\Delta P^{-0.135}$   |
| Elkobt [9]                    | $\text{SMD} = 3.08v_L^{0.385}(\sigma\rho L)^{0.737}\rho_A^{0.06}\Delta P_L^{-0.54}$   |

A summary of measured droplet size spectrums from various experiments was provided by Pimentel (2006), which included the following:

- Sprays of JP-10 jet fuel using a common-rail diesel fuel injection nozzle and an air-assist nozzle by Pimentel (2003).
- Water sprays from a 60° solid-cone swirl pressure jet nozzle, by Bhatia *et al.* (1994)
- Heavy fuel oil sprays from a swirl pressure jet nozzle, by Paloposki (1994)
- Water sprays into air and saturated steam with a various nozzles, by Lee and Tankin (1982)
- Water sprays using 20° to 80° hollow cone nozzles, by Tishkoff (1979)
- Sprays of nigrosine-in-water solutions using hollow cone and solid cone nozzles by Tate and Olson (1962)
- Sprays of high-temperature beta-naphthol (a solid at room temperature) from swirl pressure jet nozzles by Turner and Moulton (1994)

Pimentel (2006) fitted three different types of size distributions to each of these data sets, using the beta, Nukiyama-Tanaswawa and “Pearson Type III” functions. Additional measurement data were also presented using a solid-cone air-assist atomizer for JP-10 jet fuel. CFD simulations of the sprays were performed, using a customised initial size distribution for the droplets based on a prescribed beta function that was tailored to the type of nozzle used in these experiments.

Measurements of droplet size, in terms of SMD, produced by sprays of heat transfer fluids from two different sub-millimetre diameter holes were presented by Sukmarg *et al.* (2002). Three different pressures were examined, ranging from 11 barg to 36 barg, at five different operating temperatures. The data was subsequently analysed by Krishna *et al.* (2003a), who developed empirical correlations for the droplet diameter in terms of the Weber number, Reynolds number, liquid-air viscosity ratio, liquid-air density ratio and distance from the jet orifice. The correlations showed that increasing the density, reducing the viscosity or reducing the surface tension of the liquid produced smaller droplets. Increasing the reservoir pressure also produced smaller droplets closer to the orifice and smaller droplet diameters overall. It was later proposed by Krishna *et al.* (2003b), based on the assumption that mists composed of smaller droplets pose a greater hazard, that heat transfer fluids should be selected to minimise the risk of forming small spray droplets. This methodology is consistent with the fact that burning rates are thought to be enhanced in mists composed of droplets within the transitional size range of 8 – 15  $\mu\text{m}$  (Polymeropoulos, 1984)<sup>13</sup> and it is also consistent with the lower ignition energy of mists composed of smaller droplets. However, it does not account for the fact that mists composed of larger droplets can be flammable at significantly lower concentrations (see Section 2.1). Krishna *et al.* (2003b) did not perform any ignition tests to confirm their assumed hazard potential.

Droplet size distributions and ignition frequencies were reported by Puttick (2008) for tetralin and kerosene, using reservoir pressures of 1 bar to 5 bar and either a single-fluid or an air-atomizing nozzle. Tests with the first of these nozzles (the type was not specified) showed that increasing the pressure decreased the mean droplet size, and increased the ignition frequency. For the air-atomizing nozzle, there were insufficient repeat tests to derive trends.

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<sup>13</sup> Although, this matter is still being investigated experimentally and does not appear to always be a significant factor (Lawes *et al.*, 2006; Sulaiman and Lawes, 2010; Lawes and Saat, 2011).

Sidahmed (1996; 1997; 1998) developed a model for the droplet size and velocity in sprays, based on the assumption that the energy or the force in the spray was balanced. The technique was subsequently applied by Sidahmed *et al.* (1999) to predict the behaviour of flat fan nozzles. In their study, the model constants were determined using a velocity to droplet size correlation that was tuned to selected measurement data. Predictions were found to be generally in good agreement with measurements of droplet sizes and velocities.

Details of the method used to determine droplet sizes in the DNV software, PHAST, are documented in the software theory manual (DNV, 2006). The original discharge model for pressurized releases used a breakup correlation developed by Johnson and Woodward (1999) for the Sauter mean diameter:

$$d = \frac{\sigma We_{crit}}{u_f \rho_a} \quad (3.35)$$

where  $u_f$  is the velocity of the fluid leaving the orifice once it has reached atmospheric pressure (calculated in PHAST for non-flashing releases from Bernoulli's equation),  $\rho_a$  is the ambient air density and  $We_{crit}$  is the critical Weber number, which is assumed to be 12.5 following the recommendations of the TNO Yellow Book (TNO, 1997), based on the work of Brown and York (1962) and Heinze (1955). In recent releases of the software, additional criteria on the droplet size have been specified, based on Weber and Reynolds number correlations taken from the TNO Yellow Book (TNO, 1997), which itself is based on the work on flashing jet releases by Appleton (1984) and Wheatley (1987a).

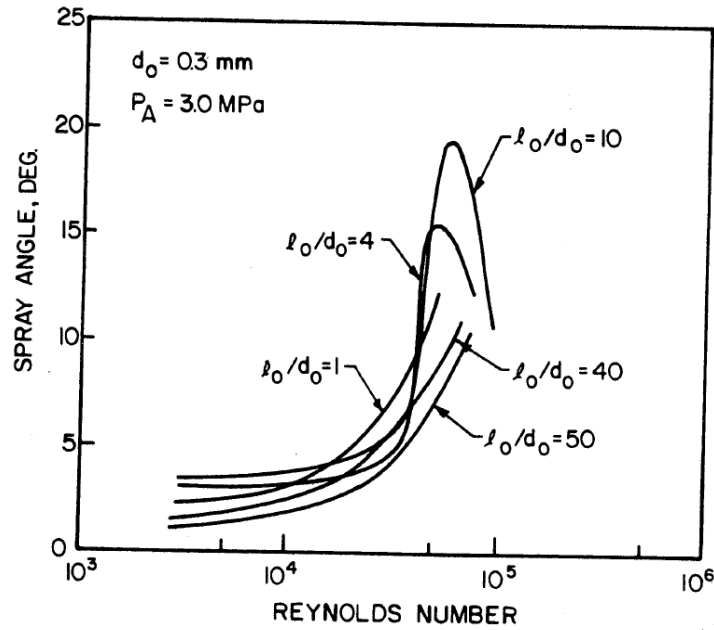
### Cone Angle

Plain-orifice nozzles tend to produce a narrow cone angle with a fairly even distribution of droplets across the spray volume, sometimes described as a “solid” cone (Lefebvre, 1989). The cone angle is defined here by the angle,  $\theta$ , between the jet axis and a line stretching from the orifice to the periphery of the spray at a distance of typically 60 orifice diameters. Abramovich (1963) provided the following simple model for  $\theta$  based on the ratio of the densities of air and the liquid (c.f. Lefebvre, 1989):

$$\tan(\theta) = 0.13 \left( 1 + \frac{\rho_a}{\rho_l} \right) \quad (3.36)$$

which was derived on the basis that the spray exhibited similar behaviour to a homogeneous free-jet of variable density material. The model was shown to produce good predictions of the specific flow rate (measured in  $\text{g}/\text{cm}^2$ ) and spray half-width in kerosene spray experiments, in which the reservoir pressure was 100 bar and orifice diameter was 0.75 mm.

Lefebvre (1989) presented further empirical correlations for the cone angle, which were expressed as a function of the Reynolds and Weber numbers. The change in spray angle with Reynolds number for nozzles with various length-to-orifice-diameter ratio ( $l_o/d_o$ ) is shown in Figure 38, based on the measurements of Hiroyasu and Arai (1980).



**Figure 38** Variation of spray angle with Reynolds number and nozzle length to diameter ratio, from Lefebvre (1989) based on the results of Hiroyasu and Arai (1980)

### Penetration

The penetration distance is defined as the maximum distance that the spray droplets reach in quiescent air, and is controlled by the balance of the initial momentum of the spray and the opposing aerodynamic resistance of the air. Narrow sprays usually penetrate further than wide sprays, due to their smaller overall drag.

A simple ballistic model gives the maximum vertical extent of a liquid jet release as follows:

$$h_t = \frac{(u \cos \alpha)^2}{2g} \quad (3.37)$$

and its horizontal extent:

$$x_t = \frac{u^2 \sin(2\alpha)}{g} \quad (3.38)$$

where  $u$  is the jet exit velocity,  $\alpha$  is the angle of the release to the vertical and  $g$  the acceleration due to gravity (c.f. Mather and Lines, 1999<sup>14</sup>). The horizontal extent,  $x_t$ , is greatest for a jet angle of  $45^\circ$ . Equations (3.37) and (3.38) were derived assuming that complex effects such as liquid breakup and aerodynamic drag are negligible. Cox *et al.* (1993) mentioned a rule-of-thumb, which was attributed to O'Shea (1982), that for actual jet releases featuring breakup and drag effects, the horizontal range of a jet is half the value given by Equation (3.38). The original paper by O'Shea (1982) provided no justification for the 50% reduction in horizontal range apart from a statement that it is based on observation of liquid jets. Furthermore, O'Shea (1982) noted that: "this fairly arbitrary modification is potentially a

<sup>14</sup> N.B. The formula given by Mather and Lines (1999) contains a typographical error where  $h_t$  is stated to be a function of  $\sin(\alpha)$  instead of  $\cos(\alpha)$ . Mather and Lines (1999) also noted that there was an error in the formula for the horizontal extent,  $x_t$ , given by Cox *et al.* (1993).

significant source of error, the actual fraction of the theoretical distance being dependent on a number of factors including wind speed and release rate”. It would be useful to examine this matter in future work, with comparison of model predictions to measurement data.

Further formulae were provided by Mather and Lines (1999) for the horizontal extent of non-flashing liquid jets that takes into account the effects of air resistance:

$$x = \frac{u \cos \alpha}{k} [1 - \exp(-kt)] \quad (3.39)$$

$$t = \left( \frac{u \sin \alpha}{g} + \frac{1}{k} \right) [1 - \exp(-kt)] \quad (3.40)$$

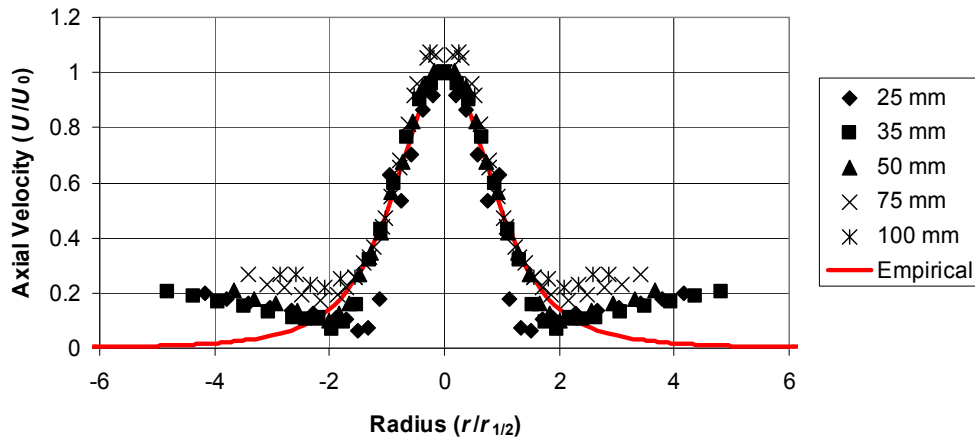
where  $x$  is the horizontal extent and  $t$  is time. Equation (3.40) must be solved iteratively. Mather and Lines (1999) suggested a value of 0.3 for the constant  $k$ , although they noted that this was a significant assumption and its value strongly affected the resulting horizontal extent. They also noted that Equations (3.39) and (3.40) assumed that air resistance was linearly related to the droplet velocity and did not account for droplet breakup or atmospheric effects, and, furthermore, that such simple models needed to be treated with extreme caution. CFD simulations by Gant (2010) of gasoline spray releases from pipelines angled at 45° to the horizontal found that the horizontal distance predicted by Equations (3.39) and (3.40) with  $k = 0.3$  was more than a factor of two larger than that predicted by the CFD model. A simplified analysis of liquid jet trajectories, ignoring the effects of air resistance was also given by McMillan (1998).

Jet penetration has been studied in depth for application to diesel engines, due to the fact that over-penetration and impingement of the spray on the walls of the cylinder can lead to fuel wastage. Measurements and various mathematical models are provided in the works of Hiroyasu *et al.* (1978; 1980; 1985; 2003) and Lefebvre (1989). Care should be exercised in applying empirical correlations developed for the high-pressure environment of internal combustion engines to atmospheric releases that are relevant for area classification. Spray atomization is accelerated by an increase in air density, due to the increased air resistance, which can lead to quite different flow behaviour (Manaka *et al.*, 2009).

## Dispersion

In the near-field of a pressurized spray release, the flow is momentum-dominated and it exhibits some characteristics similar to that of high-pressure gas jets. Moving further downstream, as air becomes entrained into the spray and the aerodynamic drag reduces droplet momentum, the effects of gravity become more dominant. For horizontally-directed sprays, large droplets may then diverge from the jet axis and fall to the ground, a process known as “rain-out”. Very fine droplets are likely to remain suspended in the air for longer periods and their dispersion becomes influenced by local air currents.

Sprays produced by atomization using circular plain-orifice nozzles feature flow velocities in the near-field that are approximately “self-similar” in that the velocity profiles at different axial positions have the same shape and, when suitably normalized, the results are coincident when plotted on the same graph axes. This is illustrated in Figure 39 for the methanol spray data from McDonnell and Samuelsen (1995). The experimental points are compared here to a simple single-phase turbulent free-jet model given by Pope (2000).



**Figure 39** Predicted axial velocity profiles from Gant *et al.* (2007) for the McDonell and Samuelsen (1995) liquid methanol spray, made dimensionless using the spray half-width and centreline velocity. The red line is an empirical free-jet profile taken from Pope (2000).

Simple models for spray dispersion in the jet-dominated region of the flow commonly assume self-similar behaviour, and furthermore assume that the droplets and surrounding air have the same speed at any point and are in thermodynamic equilibrium. A model for axisymmetric sprays using this “Locally Homogeneous Flow” (LHF) assumption was presented by Abramovich (1963) which provided axial and radial profiles of mean velocity and concentration. The simplifying assumptions inherent to the model were justified by Abramovich (1963) on the basis that for air-atomized sprays, the ratio of the volume of air to the volume of liquid in the jet source is of the order of a thousand, and that even for pure liquid sprays, the entrainment of air produces behaviour similar to that of a gas jet in which there was a homogeneous suspension of dense material. The model was shown to produce good predictions of the specific flow rate and spray half-width in high-pressure kerosene sprays.

A more sophisticated one-dimensional model for the average air velocity in a downward-directed vertical spray was developed by Ghosh *et al.* (1991). The model split the spray into three axial zones: a near-field zone where droplets drive the air motion, a second intermediate zone where there is no forcing of the air velocity and the droplets and air travel at approximately the same speed, and a third far-field zone where droplets travel at the terminal velocity and the momentum flux is constant with downstream distance. The location of the transition between the first and second zones was determined from experimental observations. Model predictions of the induced air velocity in axisymmetric and flat fan nozzles were shown by Ghosh and Hunt (1994) to be in good agreement with experimental measurements.

The one-dimensional model of Ghosh *et al.* (1991) was extended to provide predictions of the radial velocity profile and droplet distribution, assuming that the flow was self-similar. This required the solution of a second-order non-linear momentum equation using an iterative solution method. Ghosh and Hunt (1994) showed that the predicted values of the centreline velocity and mass of entrained air were in good agreement with the water spray measurements of Binark and Ranz (1958). The model was also used to show that in the first spray-driven zone and the final far-field zone, the air velocity decayed with axial distance,  $z$ , at a rate proportional to  $z^{-1/2}$ , whilst in the intermediate zone it decayed with  $z^{-1}$ . In comparison, in turbulent single-phase free-jets, the velocity decays throughout at a rate proportional to  $z^{-1}$ .

Ghosh *et al.* (1993) also extended the model to account for cross-winds. For cross-wind speeds less than the entrainment velocity, a simple approach was proposed using elliptic integrals. For higher cross-wind speeds, however, a more complex approach was used in which streamlines were computed numerically and droplet trajectories were then calculated by integrating the Euler equations.

Further related work on the air entrainment into sprays includes that of McQuaid (1975), who developed a correlation for the air entrainment into bounded axisymmetric sprays, which was validated subsequently by Buchlin (1979). Heskestad (1976) also presented a model for an isolated spray discharging vertically downwards in quiescent air, and an array of nozzles discharging in close proximity to produce a curtain spray. Predictions of the air entrainment rates were found to be in reasonably good agreement with measured values for both single and multiple water sprays.

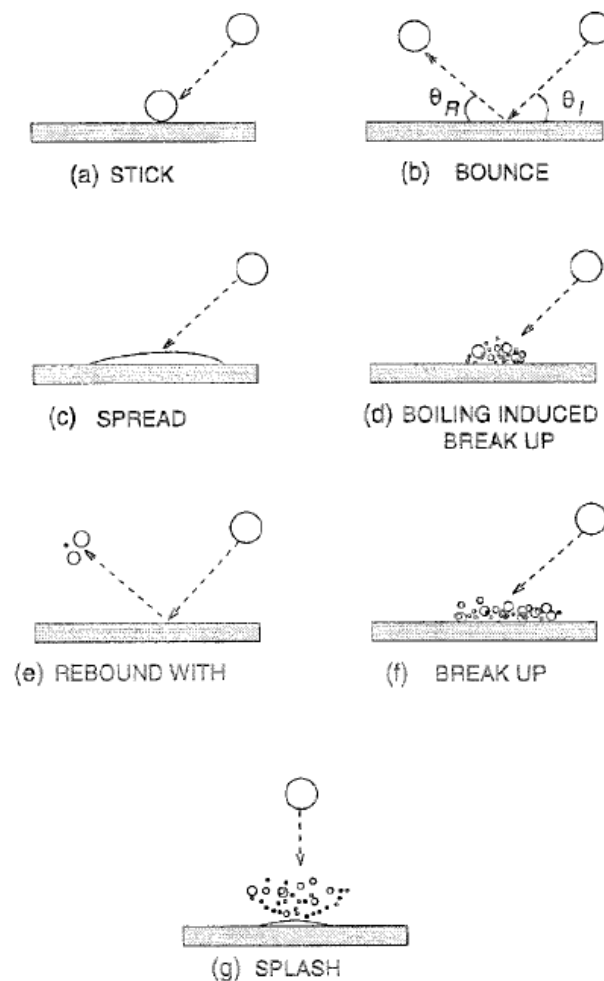
The spray dispersion model used in PHAST was described by Woodward *et al.* (1995). It involves the solution of a set of ordinary differential equations for the vapour-phase mass, momentum heat-transfer, water-vapour transfer and cross-wind spreading. For the dispersed droplet phase, another set of ordinary differential equations is solved for the conservation of mass, momentum and energy. Droplet trajectories are calculated using drag correlations, and incorporate terms to account for the settling velocity. Droplet evaporation or condensation is accounted for in the mass and energy balance equations. The concentration profile in the vapour phase is determined using analytical functions proposed by Webber *et al.* (1992) which allow the modelling of a sharp-edged jet in the near-field, whilst in the far field the profile tends to a more Gaussian shape. In the near-field, the jet is assumed to be circular whilst in the far field it is allowed to become elliptical. The spray cone angle is not prescribed but is determined instead from the jet entrainment model.

The droplet evaporation and trajectory models in PHAST were tuned sequentially using decoupled experiments. For this, Woodward *et al.* (1995) used the single droplet evaporation data from Ranz and Marshall (1952), and compared results to the data from Fuchs (1959) and Eisenklam *et al.* (1967). For the droplet trajectories, “standard” correlations for the drag coefficient of deformable droplets based on the Reynolds number were used (details were not provided). The model assumes non-equilibrium conditions, in that the droplet temperatures are determined through an unsteady-state energy balance and typically the temperatures of evaporating droplets are predicted to fall below that of the surrounding vapour phase. The initial version of the model only allowed for a single droplet size (expressed in terms of SMD), which usually reduced with distance from the release point. Once the modelled droplets hit the ground, it was assumed that all of the liquid rained out. This model was later extended to allow for a droplet size distribution, where a proportion of droplets were assumed to remain suspended in the cloud after rainout (DNV, 2006). Further details of the PHAST two-phase dispersion model and its application to flashing releases and multi-component substances are given by Papadourakis (1995), Muralidhar *et al.* (1995a; 1995b) and Witlox *et al.* (2002; 2007; 2009). Recent research to improve the prediction of rain-out in PHAST, coordinated by DNV, is to be published shortly.

Other models that have been developed for two-phase releases include TRAUMA (Wheatley, 1987a; 1987b; 1987c) and EJECT (Tickle *et al.*, 1998), although these were focussed primarily on flashing jet releases rather than liquid sprays. The underlying equations solved in these models are for the conservation of mass, momentum and enthalpy. For entrainment, either the Morton, Taylor and Turner (1956) or Ricou and Spalding (1961) models are used. The EJECT model accounts for the effect of gravity and cross-flow on the trajectory and dilution of the jet, which were ignored in the simpler TRAUMA model.

### 3.2.4 Impinging sprays

Spray droplets impinging onto solid surfaces can splash, bounce or spread rapidly to produce a liquid film. The droplets ejected from the surface by splashing or bouncing may be smaller or, in some cases, larger than the incident droplets, depending upon whether the surface is wetted or not. If the surface is hot, droplets hitting the surface may also fragment due to boiling. A summary of different impact regimes is given in Figure 40. The type of behaviour produced on impingement is affected by the incident droplet velocity, size, temperature and angle relative to the wall, the liquid properties (viscosity and surface tension) and the characteristics of the solid surface, in terms of the surface roughness, wall temperature, liquid film thickness (if present), and boundary layer behaviour.



**Figure 40** Droplet impingement regimes, from Bai *et al.* (2002).

Research in this area has been largely driven by applications to gasoline and diesel direct-injection internal combustion engines. Semi-empirical CFD models aimed at predicting spray impingement have been developed by, amongst others, Naber and Reitz (1988) and Bai and Gosman (1995). The latter model characterised the type of behaviour (stick, rebound, spread or splash) according to the droplet Weber number and Laplace number,  $La$ , which is given by:



$$La = \frac{\rho\sigma d}{\mu^2} \quad (3.41)$$

where  $\rho$  is the liquid density,  $\sigma$  the surface tension,  $d$  the droplet diameter and  $\mu$  the liquid viscosity. The value of  $La$  indicates the relative importance of surface tension and viscous forces acting on the droplet. In the model of Bai and Gosman (1995), transition from the rebound to the spreading regime was assumed to occur at a Weber number of 5, for a wetted wall. In the later study by Bai *et al.* (2002), this was revised to a Weber number of 20. The transition from spreading to splashing was assumed to occur at a Weber number given by:

$$We = 1320 La^{-0.18} \quad (3.42)$$

The secondary (post-impingement) droplet sizes were given a chi-squared droplet size spectrum by Bai *et al.* (2002), which was determined using an empirical correlation based on the incident droplet diameter, the Weber number and the splashing-to-incident droplet mass ratio,  $r_m$ . They noted that  $r_m$  was difficult to quantify but provided indicative values based on experimental observations. A methodology for predicting the secondary droplet velocity was also proposed, based on randomly sampling the likely range of droplet impingement angles. The model was validated using the gasoline spray experiments of Arcoumanis *et al.* (1997). The strengths and weaknesses of this, and other spray impingement models, were reviewed by Cossali *et al.* (2005).

A model for the formation of crown-like ejections from the impact of a droplet onto a liquid film at relatively high velocity was developed by Roisman and Tropea (2002). Three different cases of impact were considered: normal axisymmetric impact of a single droplet, oblique impact, and interaction between two droplets.

Detailed measurements of spray impingement were undertaken by Mathews *et al.* (2003) using iso-octane fuel for a range of impingement angles. The aim of the study was to provide data to evaluate droplet impingement models and measurements included pre- and post-impingement droplet sizes and velocity, flow visualization and liquid film thickness.

Moreira *et al.* (2007) examined experimentally the effect of surface heat transfer on droplet impingement using single droplets of water and iso-octane. A range of heating conditions were tested from film-vaporization up to the Leidenfrost regime.

The effect of the solid surface moving either tangentially or in a direction normal to the incident droplet was recently examined by Bird *et al.* (2009) and Kyriopoulos *et al.* (2009), respectively.

Releases in which the orifice is located very close to a nearby solid surface may exhibit spray characteristics similar to fire sprinkler sprays. Recent work in this area includes the study by Zhou and Yu (2011), who presented an integral model for the thickness and speed of the water sheet on the deflector plate, and also developed an empirical correlation for the spray flux. Other related work on sprinkler sprays includes that of McCreery and Stoots (1996), Walmsley (2000) and Lueptow *et al.* (2001).

Research into spray impingement of more direct relevance to area classification of high flashpoint fluids was undertaken by Maragkos and Bowen (2002), who conducted an experimental study involving both spray measurements and ignition tests. The characteristics of impinging sprays were first examined using water with pressures of up to 12 bar and orifices between 0.5 mm and 2 mm in diameter. The impingement plate was positioned at distances of between 100 mm and 500 mm from the orifice, and tests were conducted to assess the effect of the impingement angle and plate surface roughness. The mass of

secondary spray droplets produced by droplet impingement and their size, in terms of Sauter mean diameter (SMD), were measured. A second series of tests was conducted using diesel and gas oil (with flashpoints of 38°C and 68°C respectively), which were ignited using either electrical sparks or a small propane pilot flame.

The experiments showed that between 20% and 80% of the mass flow rate of liquid rebounded from the impingement plate in the secondary spray. The amount of spray droplets produced by the impingement was found to be a strong function of the distance to the plate, the release pressure and orifice size, and a weaker function of the surface roughness and impingement angle. The flow behaviour appeared to be controlled by the jet breakup length, i.e. the length of the unbroken liquid core within the primary liquid spray, as compared to the distance to the impingement plate. Measurements for a pressure of 6 bar and orifice diameter of 1 mm showed that the post-impingement droplet SMD were reduced by around 50% as compared to the non-impinging droplet size.

In the ignition tests, Maragkos and Bowen (2002) found that the primary spray was difficult to ignite, whereas the secondary (post-impingement) spray was easily ignited, producing a luminous flame. A low-energy 100 mJ spark was sufficient to ignite the secondary spray for a 10 bar release of gas oil.

They concluded that spray impingement increased the ease of ignition of sprays of high flashpoint fluids, and that this was important to consider in risk or hazard analyses, in particular since most practical release scenarios are likely to involve some spray impingement.

### 3.2.5 Towards practical models for area classification

In view of the wealth of data on spray droplet sizes documented in the studies mentioned above, it does not seem necessary to pursue a comprehensive programme of experiments to measure droplet sizes in sprays as part of efforts to develop an area classification methodology for mists. There is already a very significant volume of literature on this topic. These studies show that the shape of the orifice has a significant effect on the resulting spray. In accidental spray releases relevant to area classification, the shape of the orifice is unknown and it may exhibit significant variability. In view of this, it would seem prudent to make some simplifying assumptions and attempt to provide reasonably conservative predictions.

Simple models for area classification of spray releases must account for a number of factors:

1. **Mist flammability:** to quantify the following:
  - a. **Ease of ignition:** in terms of the MIE, MIC, MESG, etc. that would be used to select appropriate equipment.
  - b. **LEL:** the value of which would determine the volume of flammable material (similar to approaches used for flammable gas releases, where the potentially flammable volume is often defined as that above a concentration of half-LEL)
2. **Dispersion distances:** to determine where rain-out occurs and define the maximum distance that the mist will reach from the source. This can be split into two cases:
  - a. **Unconfined spray releases:** i.e. outdoor releases or those in large, open, well ventilated environments

## b. **Confined spray releases:** in ventilated enclosures

To address item 1a, a potential route forward would be to base the selection of equipment for use in explosive mist atmospheres on the ignition properties of the equivalent vapour, which are easier to quantify. In general, measurements reported in the literature indicate that mists are more difficult to ignite than their equivalent vapours. The MIE, MESG and MHSIT are all slightly higher for a mist than they are for the vapour. Equipment for use in a mist atmosphere could therefore be selected based on its rating for the equivalent vapour atmosphere, in terms gas group and temperature class. Further analysis and measurements are required to confirm that this is a safe approach, as the data is relatively limited. For multi-component substances (e.g. diesel), the matter is complex since lighter fractions evaporate preferentially in a spray, producing airborne droplets with a different composition to that of the liquid in the pressurized reservoir. A conservative approach may be to base the selection of equipment on the most reactive component in the liquid (i.e. the component with the lowest MIE, MIC and MESG). Consideration also needs to be given to environments where hot surfaces are present, which could result in cracking of liquid hydrocarbons, as noted by Burgoyne (1957).

With respect to item 1b, the review in Section 2 showed that the LEL could be lowered significantly in mists composed of large droplets, due to the sedimentation effect. A plausible “worst-case” scenario would involve a spray directed onto the ceiling of an enclosure, producing a continuous widespread mist of falling droplets in the size range of 100  $\mu\text{m}$  to 150  $\mu\text{m}$ . The LEL in this case has been found to be around 10% of the value of the equivalent vapour (see Figure 6). Taking half-LEL to define the extent of the hazardous area would then be equivalent to 5% of the vapour LEL. This is important in setting appropriate alarm levels for mist detectors, and is discussed further in Section 4.1.

Such a low value of the mist LEL may be considered overly conservative in some cases. For example, if the source of ignition was located on the ceiling of an enclosure, the effect of droplet sedimentation may be limited. The mist droplets would not be falling downwards from any height in these circumstances, and it might be considered that the extent of the hazardous area should therefore be defined at a considerably higher concentration than 5% of the vapour LEL.

It is also uncertain whether the sole reason for the low values of the LEL measured in flame tube experiments is the speed at which the droplets are falling relative to the air. If this were the case, then a spray could potentially also drive droplets into a flame at a similar rate to the falling droplets in a flame tube, and lead to a similar reduction in the LEL. Similar considerations may also apply if the ignition source was situated in a location where the ventilation flow projected a high mass flux of droplets against the ignition source, such as in the ventilation outlet of a gas turbine enclosure. One of the arguments against this hypothesis is that is that the measured LEL in high-momentum sprays has been found to be higher than the vapour LEL (see Figures 6 and 17). However, these findings are based mainly on data from one study by Anson (1953). Another consideration in the flame tube experiments is that the buoyancy-driven flame travels vertically up the tube in these tests, which increases the relative speed between the droplets and the flame. It is unclear whether this motion of the flame is necessary to enhance the fuel concentrations at the flame front and lower the LEL. This subject merits further investigation to identify the dominant physical mechanisms responsible for the reduction in the LEL, and deduce whether it is appropriate to use a slightly higher mist LEL under certain circumstances, depending upon the nature of the spray or mist, and location and nature of potential ignition sources.

To ignite mists composed of large droplets requires a high-energy ignition source. In the spray measurements undertaken by Cook *et al.* (1977), for example, it was found that mists could not be readily ignited using electrical sparks and instead a hand-held diffusion flame was used. In environments where only relatively low-energy ignition sources are present (i.e.

those produced by small electrical sparks), it may therefore be appropriate to use a higher LEL to define the extent of the flammable region in the HAC methodology. Further work is necessary to determine appropriate levels. This may involve analysis of the variation of LEL and MIE with droplet size, assessment of the MIC ratio and MESH, and examination of the typical range of MIE, MIC ratio and MESH for electrical equipment. In environments where naked flames are present (such as furnaces or boilers) or where hot surfaces could produce a strong ignition source, it might be appropriate to assume 5% of the equivalent vapour LEL for the HAC methodology, but this needs to be confirmed by further analysis.

To address Item 2a, for unconfined releases a maximum distance for the spray jet could be obtained from a simple modified ballistic trajectory model, i.e. Equations ( 3.37 ) and ( 3.38 ). This type of model provides only an indication of the distance travelled by the droplets from the source, not their concentration. Assuming a release angle of 45° would give the largest range. The ballistic model neglects aerodynamic effects, droplet breakup and droplet evaporation, and is therefore likely to be highly conservative. It may nevertheless be useful for initial scoping studies. Future work should examine the accuracy of the model as compared to experimental data, such as the recent work by Witlox *et al.* (2011) and Bettis and Jagger (2011). If the distances predicted by these simple equations are not supported by the experimental studies, it may be necessary to use a more sophisticated model, such as that provided by PHAST, CFD or similar. Equations ( 3.37 ) and ( 3.38 ) provide the maximum distance that a spray jet would reach, but do not account for mist formation as the droplets then impinge on the ground and disperse as a more passive cloud of small droplets. Theoretical studies, using the sedimentation speed and wind advection speeds, based on a post-impingement droplet size spectrum and initial cloud height, could be used to investigate this further. This would need to be combined with analysis of the fraction of liquid that is deposited on impingement. The results could also be confirmed with some experiments. It may be that the inherent over-conservatism of the ballistic model would compensate for it neglecting the advection of the post-impingement mist cloud.

The flammable cloud volume for unimpeded spray releases in the open air could be determined using the LEL, defined above, by making various assumptions about the orifice characteristics, breakup behaviour and spray entrainment. This would be particularly useful in order to provide a limiting release size, below which the flammable cloud would be so small that its ignition would not pose a significant hazard. For secondary releases (i.e. those not anticipated to occur during the course of normal plant operation), it could result in an area being classified as non-hazardous. This approach is consistent with the concept of “negligible extent”, described in existing area classification standards for flammable gas releases (BSI, 2009c). To develop this model, rather than simply assume a particular type of spray breakup behaviour based on a single set of experiments, a sensitivity study could be undertaken, considering a range of different empirical correlations previously developed for different types of nozzles, to account for the possible range in release conditions. This could include, for instance, correlations for both circular orifices and flat-fan types of nozzle. Rather than require plant operators to conduct detailed simulations using PHAST, CFD or similar models to define the volume of the flammable cloud, a range of operating conditions could be examined using these models and the results presented in terms of look-up tables or graphs, to make the results more readily usable.

For spray releases in ventilated enclosures (Item 2b), the approach described above could be used to determine the rate at which mist is produced. A similar approach could then be taken to that recommended by Webber *et al.* (2011) for flammable gas leaks in enclosures, in which the volume of the flammable cloud is assessed in relation to the ventilation rate of the enclosure. As noted by Webber *et al.* (2011), it may also be necessary to develop rules of thumb to cope with confined spaces around potential leak sources, where sprays impinging on nearby surfaces combined with poor local-ventilation could result in the build up of significant mist volumes.

The suggestions presented above, which have been derived from the review of existing literature, provide some tentative ideas for future work in order to develop an area classification methodology for mists produced by pressurized spray releases. They are not proposed, nor intended to be implemented at this juncture. On closer examination, some concepts may be found to be impractical or provide results that are unsustainably under- or over-conservative; and indeed other concepts may emerge as a consequence of the future work proposed.

### 3.3 CONDENSATION AEROSOLS

Condensation aerosols are produced when the concentration in a vapour-air mixture rises above the saturation vapour pressure. This can happen when vapour at high temperature is mixed with cold air, for example, in the plume of the visible “steam” produced from a boiling kettle. Alternatively, condensation aerosols can be produced by reducing the temperature and/or pressure of a saturated vapour. This is the mechanism responsible for atmospheric cloud formation, where air that is forced over hills or rising in thermals is cooled adiabatically below the dew point as it ascends into a region of lower pressure. The phase change associated with condensation is accompanied by a release of latent heat that acts to raise the temperature and limit the degree of super-saturation. Models that predict the saturation vapour pressure from the pressure and temperature were described in Section 3.1.

In the context of industrial hazards, condensation aerosols are known to be partly responsible for production of flammable mists in crankcases of marine diesel engines (Freeston *et al.*, 1956). Here, an overheated surface of a malfunctioning bearing, for example, vaporizes lubrication oil that subsequently condenses as it passes into cooler regions of the crankcase. The source of ignition is often the same heated surface that produced the vapour. In principle, similar behaviour could be produced if a combustible liquid was spilled onto a hot surface, such as an engine exhaust manifold.

It is not necessary to raise the temperature of liquid above its boiling point in order to produce sufficiently rich vapour concentrations that may give rise to a condensation aerosol. For example, if one breathes out on a cold winter day, a visible aerosol cloud can be produced even though the expelled water vapour mixture is at a temperature of only around 37 °C (well below the boiling point of 100 °C).

The process of forming condensation aerosols is described in most textbooks on meteorology and particulate physics, e.g. Green and Lane, (1964), Mason (1971) and Barry and Chorley (2009). Aerosol droplets are usually formed first by liquid condensing on minute particles suspended in the air, known as nuclei. These sub-micron particles are present in the air naturally in the form of soil particles, clay, dust and salt crystals. In a sealed, clean environment without the presence of nuclei, condensation does not readily occur and super-saturated vapour can be sustained in a meta-stable state. This behaviour is exploited in Wilson cloud chambers that are used in particle physics experiments.

Droplets produced from condensation aerosols are usually small in size and the mist is relatively monodisperse. For this reason, this method of mist formation is frequently used in fundamental studies of mist flammability, see Section 2. In the apparatus used by Burgoyne and Cohen (1954), a saturated vapour was cooled in a nitrogen atmosphere with a controlled concentration of nuclei. Oxygen was then added to the mist to produce the same ratio of nitrogen to oxygen as that present in air. Monodisperse mists were produced with droplets ranging in diameter from 7 µm to 55 µm. Subsequent tests by Taylor (1957) and Burgoyne (1957), in which scrupulous attention was paid to the cleanliness of the apparatus, were able to extend the range of droplet sizes to diameters above 0.1 mm. In situations relevant to

area classification, it is very unlikely that condensation aerosols will be produced with such large droplets.

In the apparatus used by Hayashi *et al.* (1974; 1976), a mechanical piston-cylinder arrangement was used to expand the saturated vapour mixture and generate aerosols. Hayashi and Kumagai (1974) produced droplet SMDs of up to 7  $\mu\text{m}$ , and between 16  $\mu\text{m}$  and 25  $\mu\text{m}$ , whilst Hayashi *et al.* (1976) produced droplet SMDs of between 20  $\mu\text{m}$  and 40  $\mu\text{m}$ . Droplet sizes were found to be controlled principally by the expansion ratio and expansion rate. Similar apparatus was developed by Cameron and Bowen (2001) specifically with the aim of producing mists with droplet sizes within the “transitional” size range for optimum combustion of between 5  $\mu\text{m}$  to 15  $\mu\text{m}$ .

In normal atmospheric conditions, the degree of super-saturation in atmospheric clouds is usually less than 1% (Green and Lane, 1964). For the purposes of developing condensation aerosol models for area classification, it may therefore be sufficient to assume that condensation starts once the vapour concentration reaches saturation levels.

For a single-component substance, it should be relatively straightforward to develop a simple model for the production rate of aerosol, based on mixing a given amount of hot vapour with a known quantity of cold fresh air. The former quantity could be determined from the temperature and surface area of the vaporizing liquid pool or spray (given an empirically-derived mass transfer rate and the liquid properties), while the latter could be determined from the ventilation rate in an enclosure, assuming as a first approximation, adiabatic full-mixing. Aerosol droplets could be assumed to be sufficiently small that the LEL of the mixture is comparable to the LEL of the equivalent vapour (see Section 2).

As a first attempt at developing an area classification methodology for condensation aerosols, it may be sufficient to take the source of hot vapour (from the evaporating pool or spray) and apply existing methodologies used currently for gas releases, or vapour produced from low flashpoint evaporating liquid pools.

For multi-component liquids (e.g. diesel), a simple aerosol model would be more complex to develop, although useful guidance may be found in previous work on multi-component spray modelling, for example, that of Muralidhar *et al.* (1995a; 1995b). A more sophisticated model for aerosol formation, for application to sulphuric acid absorption in a gas cleaning process was developed by Wix *et al.* (2010).

### **3.4 AGITATION AND SPLASHING**

There are a number of studies reported in the literature that examine the formation of mists from agitation and splashing, i.e. movement-induced breakup of liquid. This includes consideration of machine tool systems (Michalek *et al.*, 2003; Nguyen and Zhang, 2005), sloshing in fuel tanks (Nestor, 1967; Ott, 1970; Shepherd *et al.*, 1997) and vibration-induced atomization (Boukra *et al.*, 2009). Relevant incidents include:

- Possible explosion of flammable mist and vapours in a fuel tank on Boeing 747 Flight TWA800 in 1996 (Shepherd *et al.*, 1997).
- Ladbroke Grove train incident in 1999, in which several thousand litres of diesel were dispersed in the air by the impact of two trains colliding, which ignited, resulting in a large fireball (Hawksworth *et al.*, 2000; Jagger and Atkinson, 2000).
- Locomotive fire during the construction of the Channel Tunnel rail link in 2005, which followed a gearbox explosion (Stewart *et al.*, 2008).

The flammability of foam produced by bubbling gas through gas oil and kerosene was investigated by Thomas (1956). It was found that foams could be produced that were flammable well below the flashpoint. Flame propagation appeared to be associated with the foam collapsing to form a mist of suspended droplets. Subsequent work by Zabetakis and Rosen (1957) found that an anti-foaming agent was not effective in reducing the flammability of agitated kerosene mixtures. Nestor (1967) and Ott (1970) also showed using spark-ignition tests that mists formed in aviation fuel tanks above the liquid surface were within the flammable range.

The research on oil mists generated by machining equipment appears to be focussed primarily on occupational exposure rather than assessing risks of fire and explosion. In the study by Michalek *et al.* (2003), the mist generation rate and characteristics were measured in an enclosed machining centre. Mass concentrations of up to 400 mg/m<sup>3</sup> were obtained for wet machining, whilst dry machining gave concentrations of around 5 mg/m<sup>3</sup>. These values are several orders of magnitude below the typical LEL of hydrocarbon vapours and fine mists, of around 48 g/m<sup>3</sup> (Drysdale, 1998). Tests without cutting were undertaken to investigate the relative roles of atomization and condensation of vapour in the generation of the mist. The concentration of mist with cutting were between 14 and 400 times greater than those without cutting. It was inferred from this that condensation aerosols were primarily responsible for mist formation in cutting operations. A higher release rate or tool speed was found to lead to an increase in mist concentration, irrespective of the rate of metal cutting.

Sullivan *et al.* (1947) investigated the flammability of mists produced by firing an incendiary bullet through one gallon cans filled with a variety of different hydrocarbon liquids. Measurements were reported in terms of the height of the resulting flame.

### **3.5 AIR STRIPPING**

The generation of a flammable mist by the action of a fast-moving air current over the surface of a liquid is thought to be responsible in part for at least two incidents. In the first incident, studied by Tolson and Bennett (1996), maize oil that had collected on a filter cloth was atomized when a jet of compressed air was used to remove the oil. The oil then passed into an electrostatic precipitator and subsequently there was an explosion.

In another incident described by Eckhoff (1995), the cause of the mist explosion was attributed to oil leaking from a seal into the gas stream of a compressor test loop, which was moving sufficiently fast to atomize the oil. The oil remained suspended in the air and was not drained from the system so that over time the mist concentration increased. The resulting explosion killed 6 people and injured 30.

In both of these incidents, there was a means of increasing the initial concentration of the mist produced by the stripping of the droplets from the liquid surface. It is unclear whether, for example, a leak in a compressed air line adjacent to the surface of a liquid pool would be sufficient on its own to produce a significant flammable mist.

The process of atomizing liquid using air utilizes the same principles that are applied in air-assist or air-blast spray nozzles, described by Lefebvre (1989). The underlying physics involved in creating disturbances on the surface of a liquid due to air currents were described by Taylor (1940).

In industrial plant, for a flammable mist to be produced by air stripping would appear to require deliberate action, or a number of events to occur contemporaneously. Consideration of such particular circumstances is outside the scope of the present work, which focuses on flammable mist generation mechanisms that can readily occur accidentally.

### 3.6 SUMMARY

There are four potential mechanisms for mist formation: pressurized liquid sprays, condensation aerosols, agitation/sloshing and air stripping. Of these, the primary focus here has been on spray releases and condensation aerosols.

#### Pressurized spray releases

- For releases from plain, circular orifices in quiescent air, empirical correlations can be used to determine whether atomization will take place, based on the reservoir pressure, orifice diameter and liquid properties.
- Typically, the average droplet size in sprays produced by atomization is larger than 100  $\mu\text{m}$  and the sprays are usually polydisperse (i.e. there is a range of droplet sizes).
- Smaller droplets tend to be produced by increasing the liquid density, reducing the viscosity or reducing the surface tension. Increasing the reservoir pressure also usually produces smaller droplets closer to the orifice and smaller droplet diameters overall.
- The nozzle shape strongly affects the droplet size and spray cone angle.
- There have been many measurements of the droplet size spectrums produced by sprays. Empirical correlations for the size spectrum are mostly only valid for a particular nozzle and set of operating conditions.
- The droplet size that is aerodynamically stable, and will not be subject to further breakup, can be determined from empirical correlations, although this requires knowledge of the slip velocity between the droplet and the surrounding air which can only be predicted using quite sophisticated models.
- The droplet size is usually decreased when droplets impact on solid surfaces, and empirical models have been developed to predict this. For spray releases relevant to area classification, a size reduction of 50% has been observed in spray impingement experiments.
- The distance travelled by sprays can be predicted by simple ballistic models, although these do not take into account aerodynamic drag, spray breakup or evaporation, and therefore tend to be highly over-conservative. These models also do not take into account the subsequent dispersion of mists of fine droplets produced by the spray impinging on solid surfaces.
- More sophisticated models are available in commercial software for simulating spray dispersion that take into account aerodynamic effects, spray breakup, evaporation and impingement.

#### Condensation Aerosols

- Condensation aerosols are produced when the vapour given off by a heated liquid mixes with cooler air, which lowers the saturation vapour pressure and causes the vapour to condense. A common example is the visible plume of “steam” from a boiling kettle.
- Mists produced by condensation aerosols tend to be relatively monodisperse and are composed of small droplets, usually with a diameter less than 50  $\mu\text{m}$ .



- Condensation aerosols are thought to be partly responsible for the severe explosions which have been produced in marine diesel crankcases.
- Models do not appear to have been developed to predict the production rate of condensation aerosols, from a given liquid vaporization rate and ventilation rate, although in principle it should be reasonably straightforward to do so.

## 4 MITIGATION MEASURES

### 4.1 MIST DETECTION

The International Association of Classification Societies (IACS, 2006) provides a testing procedure for oil mist detection systems used in marine diesel crankcases. This sets out acceptance criteria for the accuracy of detection levels, whereby mist detectors are required to have an accuracy of  $\pm 10\%$  for concentrations of oil mist in air at levels either up to 10% of the LEL, or up to twice the alarm set point concentration. The procedure suggests that for oil mists the LEL can be taken as approximately  $50 \text{ g/m}^3$ . This value appears to have been selected on the basis that the droplet size is small<sup>15</sup>, and in this case it is consistent with the measurements of Burgoyne (1957) and Cook *et al.* (1977), reviewed in Section 2. Alarm set points were recommended to be set at a maximum of 5% of the LEL or approximately  $2.5 \text{ g/m}^3$ .

The procedure provided by IACS (2006) is aimed at marine diesel crankcases where the primary concern is the formation of flammable mists composed of fine droplets, produced by condensation aerosols. However, as was discussed in Section 2, in mists composed of larger droplets, the LEL can be significantly lower than  $50 \text{ g/m}^3$ . Burgoyne (1957) and Cook *et al.* (1977) showed that the LEL could fall to as low as  $5 \text{ g/m}^3$  in mists with droplet sizes greater than around  $130 \text{ }\mu\text{m}$  and  $250 \text{ }\mu\text{m}$ , respectively (see Figures 6 and 7). If the IACS (2006) methodology was adopted for pressurized spray releases, where large droplets could potentially be produced within this size range, an alarm set point of  $2.5 \text{ g/m}^3$  may not therefore afford the same degree of safety as anticipated by the IACS testing procedure.

The International Maritime Organisation (IMO, 2003) provides a Code Of Practice (COP) for oil mist detectors. This notes that flammable mist hazards occur when either pressurized spray releases or condensation aerosols produce droplet sizes of between  $3 \text{ }\mu\text{m}$  and  $10 \text{ }\mu\text{m}$ , at concentrations within the flammable range. The COP notes that potential sources of spray releases may include pump seals, leaking injectors, loose or incorrectly fitted pipe fittings, weld fractures or poorly maintained equipment, or condensation aerosols. Potential sources of ignition are taken to be the hot surfaces of heat exchangers, exhaust pipes, turbochargers, electrical contacts, static discharges, faulty wiring and high- or low-pressure turbines. It recommends that the location of mist detectors (either single systems or multiple sampling systems) be selected following smoke tests, to assess the local air flow in the plant room. It notes that air will be drawn towards ventilation extract ducts and turbochargers, and therefore detectors should be located close to machinery and away from ventilation inlets, where fresh air is brought into the space which will rapidly dilute any mist. Alarm set points are not prescribed, although it is recommended that two set points be used, one for early warning and one for full alarm. The precise concentration level of alarm is recommended to be set by considering the specific application, and it notes that in some environments such as oil purifier rooms, small amounts of mists may always be present. For the early warning alarm, the COP states that the maximum level should not exceed 2 ppm. Assuming this expresses the concentration in terms of a mass fraction (kg of oil per kg of air/mist mixture) and the air density at room temperature is around  $1.2 \text{ kg/m}^3$ , this relates to a concentration of oil in air of  $0.0024 \text{ g/m}^3$ , or around 1000 times lower than the maximum alarm set point recommended by IACS (2006). If instead the 2 ppm is a concentration by volume, and the density of the oil is around  $750 \text{ kg/m}^3$ , it equates to a concentration of approximately  $1.5 \text{ g/m}^3$ , or 40% lower than that recommended by IACS (2006). It is unclear from the COP whether the concentration is by mass or volume.

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<sup>15</sup> They recommend certification tests be performed with maximum mist droplet sizes of  $5 \text{ }\mu\text{m}$

Holness and Smith (2002) discussed a number of issues related to mist detection in both marine diesel crankcases and the external machinery space. They recommended using a combination of oil mist detectors and thermosensors in the crankcase to detect the thermally generated mist generated by an overheated surface. In external machinery spaces, where the atmosphere is expected to be substantially cleaner, and mists may be generated by spray releases rather than condensation aerosols, they noted that a different approach may be appropriate. For instance, a mist detector may need to take into account the faster sedimentation speed of the larger droplets, and the different optical properties. The alarm level may also need to differ, due to the lower LEL in mists composed of larger droplets, although in an atmosphere which is expected to be clean, a low alarm threshold may be set in any case.

Holness and Smith (2002) also discussed the main characteristics of optical oil mist detectors based on light scattering or on obscuration. They noted that some detectors consisted of both systems working in parallel so that dirt on the lenses, for instance, was not falsely interpreted as an oil mist alarm. In crankcases, where large amounts of oil are usually present, a lengthy pipe run to the detector is sometimes used to trap large droplets whilst allowing the fine droplets to be detected. Holness and Smith (2002) noted that this could lead to unacceptable delay times in detecting flammable mists and recommended instead using a labyrinth that allows the detector to be placed close to the atmosphere being monitored, to reduce response times. These labyrinths are unnecessary in external machinery room environments, where the air should be considerable cleaner.

Bettis (2006a) produced a comprehensive review of oil mist detection, which included analysis of the types of mists to be detected (their likely source and characteristics), and the instruments currently available commercially to detect them. The types of oil mists detectors examined included electrochemical, optical attenuation, optical scattering and various other techniques used for monitoring prolonged exposure to low concentrations, for application to occupational health. It was noted that most detectors are influenced by the size of droplets present in mists, and few can discriminate between hazardous mists and other aerosols, such as dusts or water sprays. The strengths and weaknesses of point and line detectors were discussed and the factors involved in selecting the ideal location of detectors was analysed. Bettis (2006a) recommended that the type of oil mist detectors be selected based upon the particular operating environment, and a number of conditions that should be assessed in selecting suitable detectors were identified. A potential test protocol for oil mist detectors was proposed and methodologies suggested for assessing detector performance in a range of environments, including those featuring high-speed flows or where water vapour condensation aerosols may be present. Experiments to investigate the test methodology for mist detectors were also reported by Bettis (2006b).

Guidance on the use of oil mist detection on offshore platforms is given on the HSE website<sup>16</sup>. This recommends that oil mist detection be installed in the exhaust ducts of turbine enclosures. The need for dedicated oil mist detection in engine rooms was also highlighted in HSE Offshore Information Sheet 8/2009<sup>17</sup>, which describes an incident on a Floating Production, Storage and Offloading (FPSO) vessel that resulted in the generation of a large oil mist from a diesel engine in an engine room.

## **4.2 CHOICE OF FLUID**

A number of studies have been reported in the literature that provide advice on the choice of heat-transfer or hydraulic fluids from the point of view of minimizing the mist explosion

<sup>16</sup> <http://www.hse.gov.uk/offshore/infosheets/is10-2008.pdf>, accessed May 2011.

<sup>17</sup> <http://www.hse.gov.uk/offshore/infosheets/is8-2009.htm>, accessed May 2011.

hazard. Frequently, these have also examined the material cost, heat transfer properties, operating conditions and toxicity. In addition, a significant amount of research has been conducted on the use of long-chain polymer additives to fluids to reduce the likelihood of them forming mists. These studies are reviewed briefly below. The effect of fluid composition on the flammability of mists was also discussed in Section 2.1.3.

#### 4.2.1 Fire-resistant hydraulic fluids

In the context of potential leaks from high-pressure hydraulic oil systems, the Energy Institute Code of Practice, IP15, states that use of fire-resistant hydraulic fluids should be considered when it is not possible to remove all ignition sources (Section 8.2.6.4, EI, 2005).

A number of test methods have been developed to determine the fire resistance of hydraulic fluids (Roberts and Brookes, 1981; Holmstedt and Persson, 1985; Little *et al.*, 1991; Yule and Moodie, 1992; Khan, 1992; 1996; Jagger *et al.*, 2003; BSI, 2000; 2011b). The FM Global test (Khan, 1992; 1996) involves a high-pressure spray through a hollow cone nozzle surrounded by a propane ring burner. A Spray Flammability Parameter (SFP) is derived from the test results, which accounts for the combined effect of the chemical heat release rate and critical heat flux for ignition or firepoint. Fire-resistant hydraulic fluids are grouped into three categories based on their SFP values.

The New Buxton Spray Test (Yule and Moodie, 1992), described in British Standard BS EN 15029-2 (BSI, 2011b), was used to assess the flammability of a number of fire resistant hydraulic fluids by Jagger *et al.* (2003). The fluids tested included: mineral oil, water glycol, oil in water emulsion, a rapeseed derivative, poly glycol ether, polyol ester, and phosphate ester. In addition to spray releases, the study involved bulk liquid releases and ignition tests using sparks, open flames and hot surfaces. Measurements were made of the ignition behaviour, heat release rate, flame length, smoke evolution and generation of toxic products. The test results were used to classify each of the generic fluids in terms of an aggregated hazard score and a simplified risk assessment procedure was tentatively suggested in order to assist in the selection of hydraulic fluids.

A summary of the spray ignition test results of Jagger *et al.* (2003) is provided in Table 10. For the mineral oil, all of the sparks tested in the experiments produced ignition. For the water glycol, however, sparks with energies even up to 120 J were unable to ignite the spray. The measured ignition energy is dependent upon many variables, and therefore it should not be assumed that mists of these substances could not be ignited from sparks with smaller energies under slightly different conditions. Ignition test results are also shown in Table 10 using an oxyacetylene torch with a heat output in excess of 100 kW/m<sup>2</sup>, and a standard match flame conforming to BS 5852 (BSI, 2000) with a heat output of between 30 kW/m<sup>2</sup> and 40 kW/m<sup>2</sup>. No measurements were reported for the droplet size spectrum or concentration in the vicinity of the ignition source. Once the ignition source was removed from the spray, the duration of the spray flame was recorded. The results show that a flame was produced that persisted indefinitely for the mineral oil, rapeseed derivative and polyol ester. The flames produced by the oil water emulsion, polyglycol ether and phosphate ester persisted for only a few seconds before self-extinguishing. Water glycol spray releases were even more resistant to ignition. Mists were found to ignite similarly from either the match or the much larger oxyacetylene torch, which demonstrated that even the smallest flaming sources could give rise to ignition. Notwithstanding the water glycol case, it was considered that it might be necessary to assume that all fire resistant hydraulic fluid sprays, should they encounter any flaming source, would ignite.

The fire hazards associated with spray releases of various fluids was also studied at HSL in the earlier work of Hawksworth *et al.* (2001). Two series of tests were performed involving

spray releases of six hydraulic fluids (mineral oil, organic ester, phosphate ester, water in oil emulsion and two polyglycols in water solution). In the first series of tests, the liquids were sprayed at rates between 1 kg/min and 4 kg/min through different nozzles into a diffusion flame. In the second series, higher mass flow rates of between 7 kg/min and 30 kg/min were used, and the liquids were sprayed onto either a diffusion flame or a hot metal plate. Four different nozzles and four different hydraulic pressures (from 50 bar to 250 bar) were used to span a range of possible leak scenarios. Measurements were made of the flame length, temperature, thermal radiation, auto-ignition temperature, combustion efficiency, radiative fraction and rate of production of smoke and toxic gases.

**Table 10** Spark ignition energies and observations of flaming response produced by introduction of open flames into an ISO15029-1 spray source, from Jagger *et al.* (2003)

| <i>Fluid</i>        | <i>Spark Ignition Energy (J)</i> | <i>Oxy-acetylene torch</i> | <i>BS 5852 match</i>     |
|---------------------|----------------------------------|----------------------------|--------------------------|
| Water glycol        | > 120                            | Immediately extinguished   | Immediately extinguished |
| Mineral oil         | < 0.90                           | Continuous                 | Continuous               |
| Oil water emulsion  | 56.7 ± 2.06                      | Transient, 2 s             | Transient, 4 s           |
| Rapeseed derivative | 0.98 ± 0.08                      | Continuous                 | Continuous               |
| Polyol ester        | N/A <sup>18</sup>                | Continuous                 | Continuous               |
| Poly glycol ether   | 28.5 ± 1.46                      | Transient, 4 s             | Transient, 24 s          |
| Phosphate ester     | 3.00 ± 0.20                      | Transient, 4 s             | Transient, 3 s           |

The tests showed that the combustion efficiency, i.e. the ratio of the heat generation to the theoretical heat of combustion of the fluid released, varied from around 30% for the polyglycols in water solutions, to around 90% for mineral oil. Combustion efficiencies were relatively independent of the hydraulic pressure, nozzle type and ignition source. Similar results were obtained using four different diffusion flame ignition sources, varying from a cigarette lighter to a 200 kW propane burner.

In the tests in which the liquid was ignited by a hot metal plate, Hawksworth *et al.* (2001) found that the mineral oil and organic ester started high-intensity pool fires whereas the phosphate ester and water-in-oil emulsions only gave rise to small pool fires. The two polyglycol in water solutions produced a small local fire at the ignition source. Auto-ignition temperatures were also determined by spraying the fluids against hot surfaces of varying temperatures and results were found to be broadly in agreement with manufacturer's data. The study showed that sprays of hydraulic fluids can ignite and burn, even though they may have been characterised as fire resistant.

In the study by Holmstedt and Persson (1985), spray ignition tests were performed on six hydraulic fluids using different nozzles at a range of pressures with release rate of between 1 kg/m<sup>3</sup> and 4 kg/m<sup>3</sup>. Sprays were ignited using either a diffusion flame or hot metal plate. A

<sup>18</sup> Measurement not available.

test method to determine the flammability hazard of fire-resistant hydraulic fluids was proposed, based on the combustion efficiency, heat of combustion, radiant fraction and rate of production of smoke and toxic products.

Earlier work on fire-resistant hydraulic fluids includes the studies by Romans and Little (1983) and Little *et al.* (1991). Ignition of non-fire-resistant hydraulic fluids by open flames and hot surfaces was also recently studied by Yuan (2006).

#### **4.2.2 Anti-misting additives**

Additives have been included in fuels, hydraulic oils and other fluids to reduce their tendency to form fine mists in the event of a spray release. Commonly, the long-chain polymer, polyisobutylene (PIB), has been used. A number of studies have examined the addition of anti-misting additives to jet fuel to investigate its effect in mitigating against spray fires or fireballs in the event of a loss of integrity of the aircraft fuel tanks (Fleeter *et al.*, 1982; Yaffee, 1986; Little *et al.*, 1983; 1990). To operate aircraft engines on so-called Anti-Misting Kerosene (AMK) requires “degraders” on each engine to condition the fuel, as otherwise it causes operational problems, such as blocking of filters and poor atomisation in the engine combustors. The combustion performance of degraded AMK has been shown to be less than the fuel without anti-misting additives. The research in this area includes the full-scale “Controlled Impact Demonstration” experiment in 1984, when a Boeing 720 running on AMK fuel was piloted remotely and crashed into a desert test site. A large fireball was produced following the ignition of a significant quantity of fuel by one of the damaged engines. It was concluded that the anti-misting additive was not sufficiently beneficial, although it probably reduced the severity of the fire (Yaffee, 1986).

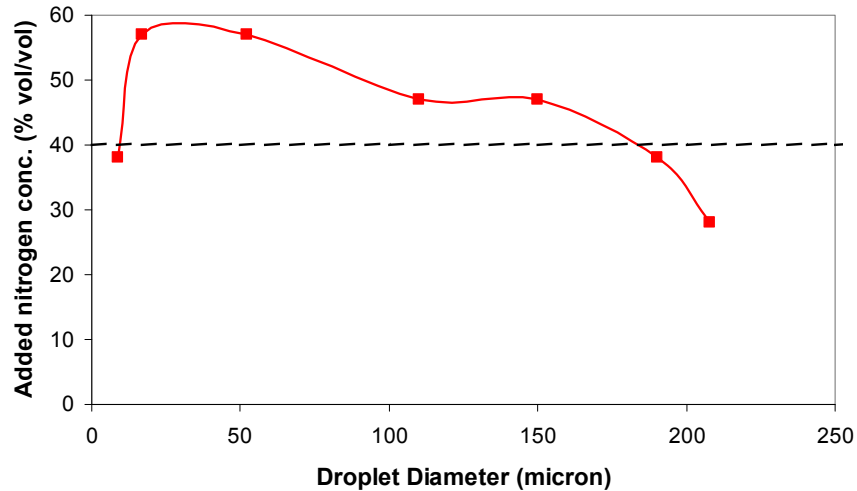
The use of PIB and other additives in hydraulic oils was discussed by Romans and Little (1983). One of the limitations of using long-chain polymers to reduce mist formation from leaks in hydraulic systems is that the polymers tend to degrade quickly, due to the high shear forces and wear in moving parts, such as pumps. Research on anti-misting additives in machining fluids has also been conducted with the aim of reducing occupational exposure to mists (Smolinski *et al.*, 1996; Marano *et al.*, 1997). This has demonstrated that in some cases mist concentrations can be reduced by as much as 50% using suitable additives.

Anti-misting additives have also been used in agricultural crop spraying to reduce the formation of very fine droplets, which are swept away by the wind (i.e. spray drift). Spray studies involving surfactants, polymers and other additives have been reported by Zhu *et al.* (1997) and Butler Ellis and Tuck (1999), using a variety of different nozzles.

### **4.3 INERTING**

Early research on inerting fuel mists was summarised by Burgoyne (1963). In the work of Burgoyne *et al.* (1954), it was found that carbon dioxide concentrations of 28.3% vol/vol were required to inert condensation aerosols of lubricating oil mists in which droplet diameters were predominantly less than 10  $\mu\text{m}$ . This concentration is similar to that typically required to inert hydrocarbon vapours. In subsequent work on tetralin mists, Burgoyne (1963) and Taylor (1957) confirmed that the concentration of nitrogen needed to inert mists with very small droplets was close to that required to inert flammable hydrocarbon vapour (an addition of around 40% vol/vol nitrogen). However, with larger droplets, up to around 150  $\mu\text{m}$  in diameter, a higher nitrogen concentration was required to inert the mist (see Figure 41). The maximum inerting nitrogen concentration was 57 % vol/vol, for mists composed of droplets with diameters of 17  $\mu\text{m}$  and 52  $\mu\text{m}$ . For large droplets, in excess of 150  $\mu\text{m}$  in

diameter, the concentration necessary to inert the mist fell below 40% vol/vol. It was postulated by Burgoyne (1963) that higher concentrations of inert gas were required for larger droplets to compensate for the enhanced radiative heat transfer between droplets. Radiative heat transfer was thought to increase with droplet size due to the elongated “tail” of flame around each droplet growing longer as the sedimentation speed increased.



**Figure 41** Concentration of nitrogen added to tetralin mists in air to suppress ignition of the mixture. Symbols show data from Burgoyne (1963) with line of best fit. Broken line shows typical inerting nitrogen concentration for hydrocarbon vapours.

Ballal and Lefebvre (1978) investigated the ignition behaviour of quiescent fuel mists in different atmospheres with the ratio of oxygen to (oxygen + nitrogen) varying between 15% and 50% vol/vol. The purpose of these tests was primarily to validate their model for the MIE of mists (see Section 2). Enhancing the nitrogen levels increased the MIE and this agreed well with their model predictions.

Kuchta and Cato (1968) summarised the measurements of Sullivan *et al.* (1947) on the minimum oxygen concentration required to inert spray releases of jet fuel and lubricating fluids in oxygen-nitrogen mixtures. Data on the auto-ignition temperature of two lubricants in nitrogen-enriched atmospheres were also provided. The AIT was found to increase by approximately 100 °C as the oxygen concentration in the atmosphere was reduced from 21% to around 8%. Although these tests were performed on liquids in heated vessels, rather than mists, the data may be useful for application to hot surface ignition of mists in inerted atmospheres.

Zabetakis and Rosen (1957) presented the flammability limits for kerosene vapour in air at 150 °C with three different inert gases: carbon dioxide, nitrogen and flue gas. They suggested that these limits could equally be used for fine kerosene mists in inerted atmospheres, with a small correction to take account of the lower temperature of the mist.

The mist formed when filling fuel tanks generally occupies a fairly narrow layer above the liquid surface. Zabetakis and Rosen (1957) suggested that an inert blanket of dense gas could therefore be used to prevent the propagation of a flame in the event of ignition in the tank. They cited one example of a fuel tanker where inerting had been achieved by introducing crushed solid carbon dioxide “dry ice” into several tanks prior to loading. Measurements indicated that the oxygen concentration was maintained at a sufficiently low level to inert the vapour-mist-foam layer above the surface of the liquid kerosene in the initial phase of tanker

filling. However, the effectiveness of a blanket of inert gas was disputed by D. T. Rogers from the Esso Research and Engineering Company, in a response provided in an addendum to the paper by Zabetakis and Rosen (1957). Rogers noted that in their company's experience a CO<sub>2</sub> blanket is rapidly dispersed by the hydrocarbon mist in the loading operation, and that the best means of preventing mist formation was to use low loading rates, particularly at the beginning of a loading operation, to avoid splashing. It was also pointed out that the low sublimation rate of CO<sub>2</sub> can lead to insufficient inert gas being produced by the crushed dry ice, unless there is a significant delay between the introduction of the dry ice and the start of the loading operation. Instead, it was recommended to introduce gaseous inert gases. An alternative successful method was suggested in the addendum to the paper of Zabetakis and Rosen (1957) by C. L. Boyle, of the Sun Oil Company, which involved inerting fuel tanks using flue gases from the ships boilers.

#### **4.4 CONTROL OF STATIC CHARGE**

Due to charge separation, organic liquids become electrically charged when they move past the surface of a liquid or solid. This can lead to the build up of charge in liquid flowing through pipes. In addition, the atomization process in which a liquid stream is fragmented into droplets is also responsible for producing charged droplets. In practice this means that a spray produced from a fracture in a pipeline or vessel is likely to produce charged droplets.

The likelihood of a cloud of droplets igniting spontaneously due to the build up of static charge was investigated by Napier and Rossell (1978). They identified the following four key factors as controlling the ignition likelihood:

- flammability of the liquid
- proximity of the discharge to a flammable fuel-air mixture
- quantity of the charge and its energy
- incendiivity of the discharge.

To investigate these factors, they performed spray release experiments and measured the droplet charges. Tests were performed using paraffins, aromatic hydrocarbons and aliphatic alcohols. It was found that the build up of charge in a mist was unlikely to lead to ignition of the cloud itself. However, if the charge from the mist was transferred to electrically-isolated items or equipment in the vicinity of the spray, these may accumulate sufficient energy to produce an incendive spark. Their study showed that the charge produced on spray droplets did not appear to be sensitive to the electrical conductivity of the liquids. They also noted that the use of anti-static additives, commonly used in the handling of liquid hydrocarbons, was unlikely to prevent the potential build-up of static charge.

A discussion of electrostatic spark formation during the filling of large tankers with liquid hydrocarbons was given in the appendix to the paper by Zabetakis and Rosen (1957) based on the experience from various incidents and a programme of research sponsored by the Esso Standard Oil company in the 1950's. A model for the static charge generated during cleaning operations of storage tanks using high-velocity jets of water or solvents was developed by Williams and Jones (2001).

Pratt (2000) described the mechanisms responsible for formation of charged mists from various sources, including liquid flows in pipes, washing operations, splash loading tanks and steaming. Details were also provided for the charge decay in mists and the use of antistatic additives to hydrocarbon liquids.



Several incidents involving ignition of fuel mists by static discharge in tank filling operations were described by Britton (1999).

Guidance on static electricity and the control of ignition hazards is given in British Standard Codes of Practice, BS 5958 and PD CLC/TR 50404 (BSI, 1991; 2003).

#### **4.5 OTHER**

Holmstedt and Persson (1985) and Oetinger (2002) mention a number of simple measures that can be used to help reduce the likelihood of a mist explosion due to a leak of pressurized fluid, or minimize the severity of the hazard. These include:

- Provision of adequate ventilation to prevent build-up of vapour or mist.
- Location of fired equipment, such as boilers, in another area.
- Use of bunds to contain spills.
- Use of warning systems, hose break valves and fluid stop systems.
- Provision of isolation and bleed valves to enable regular maintenance without needing to shutdown the whole system.
- Use of double-walled pipe systems, accompanied by suitable leak collection and alarm systems. This is mandatory for high-pressure fuel delivery lines in ships, under Chapter II-2 (Paragraph 2.2.5.2) of the International Convention for the Safety of Life at Sea (SOLAS) (IMO, 2009).
- Use of flange guards to contain any sprays produced from leaking flanges by absorbing the liquid within a porous medium, allowing it to coalesce and drip away (Bowen and Shirvill, 1994). A standard for the approval of flange guards has been produced by FM Global (2007).
- Use of explosion suppression, water sprinklers and fog systems. For application of these systems to mist explosions, see for example Vincent *et al.* (1976; 1976).
- Use of explosion relief valves. This is mandatory for marine engine crankcases with a volume greater than 0.6 m<sup>3</sup>, or a cylinder diameter larger than 200 mm under Part C, Regulation 27 (Paragraph 4) of SOLAS (IMO, 2009).
- Installation of valves with their stems sideways so that any leaks run down the stem and away from the (potentially hot) pipework.
- Use of bypass systems to avoid overheating of fluid during cold start-ups, when the viscosity of the cold fluid is high and it has poor heat transfer properties.
- Use of properly-sized expansion tanks, rather than oversized vessels, since in the event of a leak, tanks can provide a continuous source of fuel to a fire.
- Installation of an emergency shut-off valve in line with the expansion tank.
- Use of closed-cell insulation on valves, filters and other potential sources of leaks, and on pipe runs for around 0.5 m either side of possible leak sources, with weep holes drilled in the bottom of the insulation to drain any leaking fluid.

- Avoidance of the use of insulation around flanges, pump seals and shaft areas.
- Avoidance of the use of plastic ties to attach weather shields, as these can melt and cause the insulation to fall off in the event of a fire.
- Use of pressure sensors in the fluid system connected to a safety interlock system to shutdown any burners in the event of a low-flow situation.

## 5 CONCLUSIONS

### 5.1 MAIN FINDINGS

The aim of this wide-ranging literature review has been to survey information that could be used to develop a HAC methodology for explosive mist atmospheres. The important findings are as follows:

#### Lower Explosive Limit (LEL)

- The LEL of mists composed of small droplets ( $< 20 \mu\text{m}$ ) is approximately equal to that of the equivalent vapour mixture.
- The measured LEL of mists composed of larger droplets is strongly affected by the test method.
- The LEL has been observed to fall to around 10% of its vapour equivalent in nearly-quiet mists with droplet diameters greater than around  $120 \mu\text{m}$ .
- In high-momentum sprays or rapidly flowing mixtures, the LEL has been found to increase, rather than decrease, as the droplet size is increased.

#### Minimum Ignition Energy (MIE)

- Mists composed of smaller droplets require less energy to ignite than those composed of larger droplets, since they have a higher surface area available for evaporation.
- In quiescent monodisperse mists, the ignition energy is probably lowest for droplet diameters between  $10 \mu\text{m}$  to  $30 \mu\text{m}$ , and it increases in proportion to the cube of the droplet diameter above this size.
- For lean concentrations, close to the vapour LEL, the ignition energy is lower for a quiescent mist than for the vapour of the same substance (this follows logically from the LEL of the mist being lower than that of the vapour).
- At the optimum fuel concentration and droplet size, the MIE required to ignite a mist appears most likely to be equal to or greater than the MIE required to ignite a vapour-air mixture of the same substance at its optimum concentration for ignition. This assertion is based on model predictions and data extrapolation, rather than direct measurement. Direct comparison between mist and vapour MIE is difficult for high boiling-point substances.
- The ignition energy is lower for more volatile substances, since there is often vapour already present and the droplets require less energy to vaporise.
- If the water content of the liquid exceeds 80% by volume, the mist may effectively be inert.

#### Maximum Experimental Safe Gap (MESG)

- There appears to be no reliable measurement data for the MESG of mists.
- The only relevant study appears to be that of Capp (1988), who found that the MESG of a mist was greater than that of its equivalent vapour. However, the test method did not measure the propagation of flame within a mist, but instead examined the

propagation of flame from a propane-air mixture into a mist. It also only considered spray-generated mists rather than condensation aerosols.

- In principle, it may be possible to use sophisticated computational models to predict the MESH, although there are no reported studies of this in the literature.

#### **Minimum Igniting Current (MIC)**

- There is no data on the MIC of mists in the literature. In principle, it may be possible to correlate the MIC to MIE and/or MESH, or to measure it experimentally.

#### **Minimum Hot Surface Ignition Temperature (MHSIT)**

- The hot surface ignition temperature depends on many factors, including the physical properties of the liquid, the concentration of fuel in the air, the droplet size and the shape and extent of the heated surface. High mass flux impinging sprays may cool the surface.
- The measured MHSIT of unconfined sprays is typically more than 60 °C above the AIT, but drips or streams can ignite at slightly lower temperatures, and confinement around the hot surface can also decrease the MHSIT.
- In the absence of an appropriate MHSIT, a conservative approach is to assume that the MHSIT is equal to the AIT.
- Some lubricating oils have been found to produce cool-flame ignition, at temperatures below the AIT.
- Liquid soaked into porous insulating material, such as pipe lagging, will ignite at temperatures below the AIT. This could form an energetic flaming ignition source for a mist cloud.

#### **Generation of mists**

- There are four potential mechanisms for mist formation: pressurized liquid sprays, condensation aerosols, agitation/sloshing and air stripping. Of these, the primary focus here has been on spray releases and condensation aerosols.

#### **Pressurized spray releases**

- For releases from plain, circular orifices in quiescent air, empirical correlations can be used to determine whether atomization will take place, based on the reservoir pressure, orifice diameter and liquid properties.
- Typically, the average droplet size in sprays produced by atomization is larger than 100 µm and the sprays are usually polydisperse (i.e. there is a range of droplet sizes).
- Smaller droplets tend to be produced by increasing the liquid density, reducing the viscosity or reducing the surface tension. Increasing the reservoir pressure also usually produces smaller droplets closer to the orifice and smaller droplet diameters overall.
- The nozzle shape strongly affects the droplet size and spray cone angle.

- There have been many measurements of the droplet size spectrums produced by sprays. Empirical correlations for the size spectrum are mostly only valid for a particular nozzle and set of operating conditions.
- The droplet size that is aerodynamically stable, and will not be subject to further breakup, can be determined from empirical correlations, although this requires knowledge of the slip velocity between the droplet and the surrounding air which can only be predicted using quite sophisticated models.
- The droplet size is usually decreased when droplets impact on solid surfaces, and empirical models have been developed to predict this. For spray releases relevant to area classification, a size reduction of 50% has been observed in spray impingement experiments.
- The distance travelled by sprays can be predicted by simple ballistic models, although these do not take into account aerodynamic drag, spray breakup or evaporation, and therefore tend to be highly over-conservative. These models also do not take into account the subsequent dispersion of mists of fine droplets produced by the spray impinging on solid surfaces.
- More sophisticated models are available in commercial software for simulating spray dispersion that take into account aerodynamic effects, spray breakup, evaporation and impingement.

### **Condensation Aerosols**

- Condensation aerosols are produced when the vapour given off by a heated liquid mixes with cooler air, which lowers the saturation vapour pressure and causes the vapour to condense. A common example is the visible plume of “steam” from a boiling kettle.
- Mists produced by condensation aerosols tend to be relatively monodisperse and are composed of small droplets, usually with a diameter less than 50 µm.
- Condensation aerosols are thought to be partly responsible for the severe explosions which have been produced in marine diesel crankcases.
- Models do not appear to have been developed to predict the production rate of condensation aerosols, from a given liquid vaporization rate and ventilation rate, although in principle it should be reasonably straightforward to do so.

## **5.2 POSSIBLE FUTURE DIRECTIONS FOR AREA CLASSIFICATION OF MISTS**

On the basis of these findings, future work towards developing an area classification methodology has been tentatively proposed as follows:

### **Selection of equipment**

To select the appropriate equipment for use in zoned areas, consideration needs to be given to the MIE, MESG, MIC, MHSIT of the mist. In general, measurements reported in the literature indicate that mists are more difficult to ignite than their equivalent vapours. The MIE, MESG and MHSIT all appear to be slightly higher for a mist than they are for the vapour. Equipment for use in a mist atmosphere could therefore be selected based on its rating

for the equivalent vapour atmosphere, in terms of gas group and temperature class. Further analysis and measurements are required to confirm that this is a safe approach, as the data is relatively limited. For multi-component substances (e.g. diesel), the matter is complex since lighter fractions evaporate preferentially in a spray, producing airborne droplets with a different composition to that of the liquid in the pressurized reservoir. A conservative approach may be to base the selection of equipment on the most reactive component in the liquid (i.e. the component with the lowest MIE, MIC and MESG). Consideration also needs to be given to environments where there is the potential for prolonged contact between mists and hot surfaces, which could result in cracking of liquid hydrocarbons and the formation of hydrogen or acetylene vapours.

### **Definition of the flammable cloud extent**

The value of the mist LEL is important since the area classification would use this to determine the extent of the flammable cloud. In nearly-quiescent mists, the LEL decreases as the droplet size is increased, due to the sedimentation effect. A plausible “worst-case” scenario would involve a spray directed onto the ceiling of an enclosure, producing a continuous widespread mist of falling droplets in the size range of 100  $\mu\text{m}$  to 150  $\mu\text{m}$ . The LEL in this case has been found experimentally to be around 10% of the equivalent vapour LEL. Taking half-LEL to define the extent of the hazardous area would then be equivalent to 5% of the vapour LEL.

Such a low value of the mist LEL may be considered to be overly conservative in some cases. For example, if the source of ignition was located on the ceiling of an enclosure, the effect of droplet sedimentation may be limited. The mist droplets would not be falling downwards from any height in these circumstances, and it might be considered that the mist LEL should therefore be considerably higher than 5% of the vapour LEL.

It is also uncertain whether or not the sole reason for the low values of the LEL measured in flame tube experiments is the speed at which the droplets are falling relative to the air. If this were the case, then a spray could potentially also drive droplets into a flame at a similar rate to the droplets falling in a flame tube, and lead to a similar reduction in the LEL. Similar considerations may also apply if the ignition source was situated in a location where the ventilation flow projected a high mass flux of droplets against the ignition source, such as in the ventilation outlet of a gas turbine enclosure. One of the arguments against this hypothesis is that the measured LEL in high-momentum sprays has been found to be higher than the vapour LEL. However, these findings are based mainly on data from one study by Anson (1953). Another consideration in the flame tube experiments is that the buoyancy-driven flame travels vertically up the tube in these tests, which increases the relative speed between the droplets and the flame. It is unclear whether this motion of the flame is necessary to enhance the fuel concentrations at the flame front and lower the LEL. This subject merits further investigation, in order to identify the dominant physical mechanisms responsible for the reduction in the LEL.

Mists produced by condensation aerosols tend to have droplet sizes smaller than 50  $\mu\text{m}$ . If the only means of generating a mist is from a condensation aerosol, rather than a spray, it may be appropriate to use a higher level to define the flammable cloud extent than 5% of the equivalent vapour LEL.

To ignite mists composed of large droplets requires an energetic ignition source, such as a naked flame. In environments where only relatively low-energy ignition sources are present (i.e. those produced by small electrical sparks), it may therefore be appropriate to use a higher LEL for the cloud extent. Further work is necessary to determine an appropriate safe level. This would involve analysis of the variation of LEL and MIE with droplet size, assessment of the MIC ratio and MESG, and examination of the typical range of MIE, MIC ratio and MESG

for electrical equipment. In environments where flames are present (such as rooms containing furnaces or boilers) or where hot surfaces could produce a strong ignition source, it might be appropriate to assume 5% of the equivalent vapour LEL for the HAC methodology, but this needs to be confirmed by further analysis.

### **Unconfined spray releases**

Where there is the possibility to generate a mist from a pressurized spray release, an initial calculation could be performed to assess whether the operating pressure is sufficient to cause liquid atomization. At pressures below a certain level, for a given hole size, it may be appropriate to assume that no significant mists will be produced. This is conditional upon the liquid being released in an unconfined space where it is unlikely to impinge on nearby surfaces and break up.

For pressures above this threshold, the maximum extent of the hazardous zone could potentially be obtained from a simple ballistic trajectory model. This model neglects aerodynamic effects, droplet breakup and droplet evaporation, and is therefore likely to be highly conservative but it may nevertheless be useful for an initial scoping study. In future work, the accuracy of this approach should be assessed by comparing predictions to experimental data, such as the recent measurements of Witlox *et al.* (2011) and Bettis and Jagger (2011). If the distances predicted by these simple equations are not supported by the experimental studies, it may be necessary to use a more sophisticated model. Ballistic models do not account for mist formation when spray droplets impinge on nearby solid surfaces, and the subsequent dispersion of the mist as a more passive cloud. Theoretical studies of the sedimentation speed and wind advection speeds, based on a post-impingement droplet size spectrum and initial cloud height, could be used to investigate this further. The results could also be confirmed with some experiments. The inherent over-conservatism of the ballistic model could potentially compensate for it neglecting the advection of the post-impingement mist cloud.

The flammable cloud volume for unimpeded spray releases in the open air could be determined using the LEL, as defined above, by making various assumptions about the orifice characteristics, breakup behaviour and spray entrainment. This would be particularly useful in order to determine a limiting release size, below which the flammable cloud would be so small that its ignition would not pose a significant hazard. For secondary releases (i.e. those not anticipated to occur during the course of normal plant operation), it could result in an area being classified as non-hazardous. This approach is consistent with the concept of “negligible extent”, described in existing area classification standards for flammable gas releases (BSI, 2009c). To develop this model, rather than simply assume a particular type of spray breakup behaviour based on a single set of experiments, a sensitivity study could be undertaken, considering a range of different empirical correlations previously developed for different types of nozzles to account for the possible range in release conditions. This could include, for instance, correlations for both circular orifices and flat-fan types of nozzle. Rather than require plant operators to conduct detailed simulations to define the volume of the flammable cloud, a range of operating conditions could be examined using these sophisticated models and the results presented in terms of look-up tables or graphs.

### **Confined spray releases in ventilated enclosures**

For spray releases in ventilated enclosures, the approach described above could be used to determine the rate at which a mist is produced. A similar approach could then be taken to that recommended by Webber *et al.* (2011) for flammable gas leaks in enclosures, in which the volume of the flammable cloud is assessed in relation to the ventilation rate and size of the enclosure. As noted by Webber *et al.* (2011), it may also be necessary to develop rules of thumb to cope with confined spaces around potential leak sources, where sprays impinging on

nearby surfaces combined with poor local-ventilation could result in the build up of significant mist volumes.

### **Condensation aerosol mists**

Models for mist formation by condensation aerosols do not currently exist, but should be reasonably straightforward to develop, based on certain input conditions of liquid release rate, ventilation rate, area of spill and so on, and assuming a certain (monodisperse) droplet size. To determine the mixing rates it may be possible to use empirical correlations developed for buoyant plumes. Similar approaches could be used to those described above for unconfined releases and those in ventilated enclosures. The model would need to be validated through comparison to experimental measurements. The aim of this would be to provide a simple means of predicting the mist cloud volume and extent for a given set of release conditions.

## **5.3 KNOWLEDGE GAPS AND POTENTIAL FUTURE WORK**

The suggestions given above provide some tentative ideas for the development of an area classification methodology for mists. On closer examination, some of the concepts may be found to be impractical or provide results that are unsustainably under- or over-conservative. The principal aim of the present work has been to review the existing literature and there has been little time to scrutinise these proposals rigorously. In future work, it would be useful to reflect on these proposals and assess whether they would provide a suitable framework for area classification guidance on mists. Other, more specific tasks that would be useful to address in future work are as follows:

### **1. Selection of equipment**

- a) Confirm that the MIE required to ignite a mist is always equal to or greater than the MIE required to ignite a vapour-air mixture of the same substance at its optimum concentration for ignition. This should be done under idealised conditions, to prove or disprove the hypothesis, and also under more realistic conditions (involving both unobstructed and impinging sprays, preferably) to determine whether a mist with such a low MIE is often achieved in practice.
- b) Explore whether mists can be ignited at temperature below the AIT. In particular, the conditions necessary for cool flames should be examined, which featured in the work of Freeston *et al.* (1956).
- c) Undertake experiments to measure the MESG of mists using condensation aerosols with droplets in the size range of between around 15  $\mu\text{m}$  to 30  $\mu\text{m}$ , to verify that the MESG of a mist at the optimum concentration for ignition is greater than that of its vapour equivalent. It would also be useful to measure the MESG of spray-generated mists, if possible.
- d) Explore whether experiments could be conducted to measure the MIC of mists.
- e) Undertake additional measurements of the vapour properties of the substances listed in Section 1.2, where necessary.
- f) Undertake measurements of the ignition properties (MIE, MESG, MIC) of mists at elevated pressures and ambient temperatures, to help develop area-classification guidance for hyperbaric environments, such as compressed-air caissons. Whilst some data exists on fuel mist ignition at high pressures from



research on internal combustion engines and gas turbines, this is mainly restricted to temperatures considerably higher than 25 °C.

- g) Undertake an impact analysis to assess whether it is feasible to require equipment for use in zoned areas (for mists) to be selected on the basis of the ease of ignition of the equivalent vapour
- h) Examine whether ingress protection provides a suitable means of protection against ignition of flammable mists.

## **2. Definition of the flammable cloud extent**

- a) Assess whether it is justified to define the flammable cloud extent for a spray-generated mist to be 5% of the equivalent vapour LEL.
- b) Assess whether a higher concentration than 5% of the equivalent vapour LEL is appropriate for environments where the only ignition sources are relatively low-energy sparks (and not hot surfaces or flames). This would involve a careful review of existing data on the flammability of mists with different droplet sizes and their ignition energy. Most of the existing data is based on monodisperse sprays, whereas spray-generated mists are composed of a spectrum of droplet sizes, and it would be important to take this into account. Some useful data may be obtained from models for the ignition energy of mists, which have been developed by, for example, Ballal and Lefebvre (1981b). However, these have not been validated for very fuel-rich mists where ignition energies are lowest. Some further experiments may be required.
- c) Assess whether a higher concentration than 5% of the equivalent vapour LEL is appropriate for condensation-aerosol generated mists. This should examine mists generated in an industrial context, with a droplet diameter typically less than 50 µm, rather than the carefully-controlled laboratory experiments, such as those undertaken by Burgoyne and Cohen (1954) and Burgoyne (1957) who examined larger droplets. It may be possible to undertake this work by analysing existing data, although it would be useful to investigate a wider range of substances.
- d) Examine the primary physical mechanisms responsible for the reduction of LEL with increasing droplet size. The effect is known to be related to droplet sedimentation, but it is unclear whether a spray could potentially also drive droplets into a flame at a similar rate to the droplets falling in a flame tube, and lead to a similar reduction in the LEL. This work should also seek to quantify the effect of flame propagation direction on the LEL.

## **3. Mist generation**

- a) Determine the threshold reservoir pressure which leads to primary spray breakup that is in the atomization and second-wind breakup regimes, for the range of substances of interest. The aim of this would be to determine the maximum safe working pressure below which an unobstructed spray would not generate a significant flammable mist hazard. Various simple empirical correlations reviewed in the present work may help with this work. It would also be useful to examine the effect of orifice geometry.
- b) Examine the significance of mist production from liquid releases and sprays impinging on nearby solid surfaces. This should examine, for instance,

whether spray releases at pressures below the threshold for second wind induced breakup could still generate a significant mist hazard. It is likely to require some additional experiments and detailed examination of existing data in the literature. There are a large number of variables (distance from release orifice to impingement plate, plate angle, surface shape, characteristics of impinging spray etc.). Ideally, an empirical model would be derived from these experiments to determine the post-impingement mist cloud characteristics for a range of releases of practical interest. The required analysis could be based on correlating the effect of spray breakup length on the post-impingement secondary spray characteristics, following the approach taken by Maragkos and Bowen (2002).

- c) Compare the maximum range of sprays predicted by ballistic models to existing experimental data and the results of more sophisticated models.
- d) Perform a sensitivity study on mist formation from different types of nozzle, using a range of existing empirical correlations taken from the literature. On the basis of these tests, develop simple look-up tables or graphs to enable the volume of a flammable mist cloud produced by an unconfined spray release to be determined for a given range of hole sizes, pressures and liquid properties. A number of assumptions would be necessary to undertake this analysis, such as the orientation of the release and the occurrence (or not) of rainout. The matter may be complicated by the large breakup lengths produced by some types of spray nozzle.
- e) Develop a model to predict the flammable mist cloud size produced by spray-generated mists in ventilated enclosures. This could be based on the approach taken by Webber *et al.* (2011) for flammable gas leaks in enclosures. The model will need to consider the consequences of spray impingement.
- f) Develop a simple model for the formation of mists by condensation aerosols in unconfined releases and ventilated enclosures. This is likely to involve a number of assumptions, such as the droplet size. Such assumptions should be based on cautious best-estimates.
- g) The principle outcome of the work described above is to produce practical guidance which describes the maximum safe working pressures for common high flashpoint fluids, based on a predefined 'low-energy' spark ignition and certain input parameters, such as whether the release is unobstructed or obstructed, the ventilation rate, etc. Any guidance should be provided in a suitably simple and easy-to-use format, such as look-up tables.

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# Generation of flammable mists from high flashpoint fluids: Literature review

Hazardous Area Classification (HAC) for explosive gas atmospheres is well established, with guidance published in various standards and industry codes of practice. However, the same situation is not currently the case for high flashpoint liquid releases that could give rise to an explosive mist atmosphere. There is a pressing need for clear guidance on mist hazards to allow operators to determine the extent of areas where flammable mists may be present and to select appropriate equipment for use in those areas.

This report provides a survey of the recent literature on flammable mists and pulls together information that will be useful in developing a HAC methodology for explosive mist atmospheres. It focuses on the three fundamental issues: mist flammability, mist generation and mitigation measures.

The first of these is discussed with reference to five measurable parameters: the Lower Explosive Limit (LEL), Minimum Ignition Energy (MIE), Maximum Experimental Safe Gap (MESG), Minimum Igniting Current (MIC), and Minimum Hot Surface Ignition Temperature (MHSIT). Measurements of these quantities in mists are analysed and models for their prediction are discussed.

The second issue of mist generation is examined under four categories: mists produced by pressurised sprays, condensation aerosols, agitation/splashing/sloshing and air stripping. Of these, the primary focus is on spray releases and condensation aerosols, which are considered to be the most likely sources of mists. Measurements undertaken in sprays are described and models are discussed. Mitigation measures are surveyed briefly, which include mist detection, use of fire-resistant fluids or anti-misting additives, inerting and control of static charge.

Finally, tentative proposals are suggested for developing area classification guidance based on the prediction of the flammable mist cloud size.

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