LIQUID MISTS AND SPRAYS FLAMMABLE BELOW THE FLASH POINT – THE PROBLEM OF PREVENTATIVE BASES OF SAFETY

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Preventative bases of safety (BoS) (i.e. absence of flammable atmospheres or avoidance of ignition sources) are the most economic to establish, so there are clear drivers for using them where possible. However, where they are used they must be robust and maintainable. For example solvents can be used below flash point (with a safety margin) to avoid flammable atmospheres or dusts can handled where possible electrostatic discharges are below the MIE. To establish such a BoS the material must be well characterised relative to the possible ignition sources present.

Sprays and mists can be created deliberately in processing (e.g. cleaning vessels; and spraying materials onto substrates) as well as from leaks. A number of workers (e.g. Burgogne & Richardson, 1949) have identified that mists can be flammable below the flash point. A figure often quoted is that mists can be flammable as much as 60K below flash point. However, results from Syngenta's legacy organisation shows sprays to be flammable as much as 125K (Maddison, 1983) below the flash point; with no upper limit having been determined. There may be an upper limit but it will not help us for many materials. To use the BoS absence of viable ignition sources the sensitivity of the mist to ignition must be established in an analogy to dust MIE. Little work has been done in this field particularly for hazard assessment.

A rig has been built to spray materials at ambient temperature and perform ignition tests with pyrotechnic and electrostatic ignition sources. Electrostatic ignition presents some challenges in making reliable measurements: electrodes are wetted by the spray; the presence of droplets between the electrodes can lead to early breakdown and discharge below the desired voltage. Full scale nozzles use large quantities of fluid and ignitions can contaminate this. Characterisation of the spray will be necessary so that measurements are made at a relevant droplet size possibly with a much smaller nozzle. Several fluids have been tested.

FORMATION IN CHEMICAL MANUFACTURE

Mists can be formed accidentally, incidentally or deliberately during manufacturing processes. Mechanical formation can be from release through orifices, impingement, bubble collapse or disengagement from liquid surfaces. Condensation can results from change in temperature or pressure. Operations and activities leading to mist formation can include leaks and loss of containment; material transfer (tail end of blow transfers, splash filling, addition by tail pipes); cleaning (spraying) operations through jets, nozzles or spray-balls; and deliberate processes such as formulation where material may be sprayed on to substrates. This last case is of primary interest in this paper.

HAZARDS OF MISTS

The twofold hazards of mists are documented and fairly well known, and have been associated with a number of incidents (Bright *et al.* 1975; Kletz, 1988 & 1995; Kohlbrand, 1991;Owens & Hazeldean, 1995), some fatal. However, to re-iterate: mists of combustible liquids can be flammable even below flash-point; and the formation of mists is associated with charge separation processes that can lead to an electrostatically charged mist, and ultimately to incendive discharges. This paper will only look at the flammability hazards.

BASIS OF SAFE OPERATION

Chemical plants are (or at least should be operated) with a clearly stated basis for safe operation. By having a principle for safe operation it is possible to define the limits to that principle and consequently necessary precautions to maintain safe operation.

Bases of safe operation come under two categories

- **Preventative** where the basis of safety is designed to prevent the hazardous event
- **Protective** where the hazardous event may initiate, but the basis of safety is designed to protect people and plant from the consequences

When considering fire and explosion hazards, *Preventative Bases of Safety* are implemented by eliminating one element of the fire triangle, either by controlling flammable atmospheres or ignition sources. Controlling flammable atmospheres can be either by the fuel or oxidant concentrations, with appropriate safety factors. Obviously this requires detailed knowledge of the flammable boundaries of the system concerned. To control ignition sources it is vital to understand the sensitivity of the atmosphere to ignition.

As an example for liquids, control of fuel concentration is normally achieved by operating lower than the flash point less a safety margin (usually 5–10 K below the flash-point).

For *Protective Bases of Safety* it is necessary to understand the behaviour of the atmosphere once it has already ignited, particularly concerning flame speed and over-pressure.

MIST FLAMMABILITY

HISTORY OF FIELD

Sprays of liquid fuels have been in use for over 100 years (Williams, 1973) and as such there is a body of knowledge within the combustion literature. The formation of aerosols is an acknowledged way of making fuels of limited volatility easier to ignite for burners and the principle is also used in the auto-motive industry, particularly in diesel engines. Some work is associated with jet fuels and re-ignition (e.g. Ballal & Lefebvre, 1978).

Researchers as early as the 1920s are credited with measurement of mist flammability limits (Burgoyne, 1963), but the bulk of work started to be published after the second World War where some of these papers were directly concerned with safety (Burgoyne & Richardson, 1949; Sullivan *et al.*, 1947).

A certain amount of work has been associated with flame speeds and the possibility that for certain droplet size ranges flame speed may even be enhanced over vapour flame speeds (Polymeropoulos & Das, 1975). Although this is intrinsically interesting, and important for setting Protective Bases of safety, as well as other applications, it is of little relevance to setting Preventative Bases of Safety.

RELATIONSHIP TO MATERIAL FLASH POINT

As a measure of mist flammability the often quoted statistic is that mists can be flammable as much as 60 K below the flash point (Bowen & Cameron, 1999; Kletz, 1995) based on a 1982 report by the HSE. However, work conducted within this group (Maddison, 1983) has shown sprays to be flammable at ambient temperatures as much as 125 K below the material flash-point for solvent systems (see Table 1). Note that this work does not show limits of how far below the flash point a material may be flammable; rather the lower temperatures have been imposed by ambient temperature. Earlier work (Sullivan, 1947), which defined the flammability limits of sprays based on the limiting oxygen requirement, had an example where a fluid was shown to be flammable at ambient temperatures and oxygen concentration more than 200 K below the flash-point.

The interesting question raised here is "*is there a temperature (below the material flash point) at which the mist is no longer flammable?*" This question is difficult to definitively answer since most studies have been conducted at ambient conditions, and often only positive results have been reported. Another difficulty is the literature concerned with spray testing of hydraulic fluids, since this area uses quite high strength ignition sources compared with those that could be present on a chemical plant (e.g. BSI, 1979; Yule and Moodie, 1992). Yule and Moodie discuss how the strength of the propane burner ignition source needs to be high in order to create a stable flame. Ultimately many materials can be made to burn if provided with enough energy. Although for certain types of hazard assessment such ignition sources are important, they are largely irrelevant for much of the chemical industry, and would only lead to excessively conservative evaluations.

Data from Beattie (1988), shown in Table 2, on aqueous solvent mixtures shows that some are flammable a few degrees below the flash point, but at high water fractions they

Table 1. Ignition data from Maddison (1983)

Liquid	Droplet diameter (μm)	Flash point (°C)	Measured LEL (mg/l)	Temperature of mist at ignition (°C)
kerosene	42	47	30	20
tetralin	65	77	45	23
diphenyl ether	38	116	30	23
dimethyl phthalate	70	146	40	20
benzyl bezoate	86	148	60	23

Table 2. Ignition data for aqueous solvent mixes from Beattie (1988)

Solvent	Solvent concentration (% v/v)	Droplet diameter (μm)	Flash point (°C)	Ignition energy (mJ)	Combustion tube entry temperature (°C)
methanol	55	131	22.8	500	20
	50	119	28.3	5000	26
	50	119	28.3	no ignition	20
	25		41	no ignition	34–37
ethanol	50	134	25.6	110	20
	45	127	26.7	500	20
	40	137	27.8	no ignition	20
	25		35	5000	27–28
isopropanol	50		20	5000	17
	30	115	24.4	no ignition	20
	25		27.5	5000	26–27
	10		41	no ignition	33–36
THF	10	111	6	no ignition	20
acetone	7.5	108	22	no ignition	20

cease to be ignitable under the experimental conditions used. It is difficult to tell whether the water is having an inerting effect entirely due to its heat capacity, or whether the droplet sizes are also contributing to the limit, as there may be some mass transfer limitations within the droplets limiting the fuel concentration in the air surrounding the droplets.

The work from Sullivan and co-workers (1947) is one of the most comprehensive in terms of numbers of fluids studied. It was conducted at different oxygen concentrations some of them much above ambient showing that some fluids could only be made flammable at ambient temperature in oxygen enriched atmospheres, despite having measurable flash points.

The amount a mist may be flammable below its flash point will depend on physical properties as well as combustion parameters. Relevant parameters include: heat of combustion; combustion stoichiometry; vapour pressure; latent heat; heat capacity; and droplet size.

FLAMMABLE LIMITS

Since mists can settle out there is (in most cases) no useful upper flammability limit, since at some point it will cross back through the flammable range if left to itself. Although it is worth pointing out that droplets sized below about 20–30 μm will not settle out at any appreciable rate (Bowen & Shirvill, 1994).

For droplets less than approximately 10 µm in size then the mist will burn homogeneously much as vapour with the same flammability limits. Below this size range droplets will evaporate completely in advance of the flame. However, for droplet sizes above about 20 µm then LFL starts dropping and the burning is by individual droplets without complete evaporation. The flames will propagate from droplet to droplet (Burgoyne & Cohen, 1954). Local vapour concentrations may be high surrounding the droplets. Burgoyne (1963) suggested that heat transfer may be dominated by radiation rather than convection (as would be the case in homogeneous vapour combustion). Thermal radiation is absorbed better by the droplets than intervening air. This may explain some aspects of the apparent lower flammable limit, since there is no requirement for all the air, or even all the fuel to reach the same temperature. The other aspect is that the fuel concentration only needs to be high around the droplet. Burgoyne (1963) defined a dynamic concentration based on flame speed. LFL still drops with increasing droplet size, but much less dramatically.

IGNITION SENSITIVITY

The general trend of MIE is towards increasing MIE with increasing droplet size. (E.g. Chan, 1982; Law & Chung, 1980.) Ignition frequency is seen as the most appropriate approach since flammable region is not as clear cut as for vapour systems. However it has been developed for systems where ignition is wanted (such as jet re-ignition). Typically MIE is taken as 50% ignition (Danis *et al*., 1980). Singh (1986) mapped out for 50% and 20% ignition frequencies for tetralin (unfortunately do not have pure vapour data for comparison).

In hazard assessment for dusts the MIE is mapped out across a range of parameters to be a minimum. However, the location of the minimum is rarely recorded; it is just important that there is one, and it has been determined. Ignition frequency will also be at a very low level, unlike automotive and jet systems which have often been studied. Many of these studies also make little reference to the ignition circuit which may be tuned to give minimum energy sparks, whereas we tend to use pure capacitative sparks as the model for discharges on plant.

TENDENCY TOWARDS AEROSOL FORMATION

Bowen and co-workers (Bowen & Shirvill, 1994; Bowen & Cameron, 1999; Maragkos & Bowen, 2002), and Krishna and others (Krishna *et al.*, 2003; 2003a; 2004) have both looked at the mechanical formation of aerosols through releases. Bowen & Shirvill (1994) reviewed the existing literature and looked at possible break-up mechanisms concluding that aerosol formation and consequent hazards were a real possibility. Krishna (2003) looked at 6 heat transfer fluids from an intrinsic safety point of view where fluid choice might be made on the basis of the fluid's likelihood to atomise. This was related as a dimensionless correlation for each fluid, and can be used to give a relative idea of better or worse. Unfortunately there are no ignition data to give an absolute measure of flammability.

LEAKS AND LOSS OF CONTAINMENT

The primary preventative basis of safety for mists external to process equipment is always containment, supported by normal plant controls over ignition sources (zoning etc.) to reduce the residual risk to acceptable levels. In some cases, such as for possible leaks from heat transfer fluid system flanges, it is possible to mitigate using gauze coalescers, which can trap spray and allow it to drip away in comparative safety (Bowen & Shirvill, 1994).

HOW TO TREAT COMBUSTIBLE MISTS FROM A HAZARD ASSESSMENT AND BASIS OF SAFETY POINT OF VIEW

Mists are most logically treated in a similar manner to combustible dusts i.e. there should be a primary assessment for combustibility or ambient temperature flammability with a relatively large ignition source, rather akin to the group A/B classifications for dusts. Then a secondary assessment for sensitivity to ignition, which would allow appropriate precautions to be defined. A potentially complicating aspect is that a mist is most analogous to a hybrid atmosphere: the droplets can be assumed to be analogous to dust particles; but there will also be some flammable vapour present too. The amount of flammable vapour present will depend on temperature, and the MIE of a mist should be expected to be much more sensitive to changes in temperature than a dust would. The work of Puttick & Gibbon (2004) on solvents in powders developed a criterion where 40 K or more below the flash point and the vapour contribution, hence hybrid behaviour, could be ignored.

Another issue will be droplet size, and droplet size distribution. In a polydisperse mist how will the MIE be affected by the fraction of 'small' droplets? Even so in a confined and un-drafted vessel it is possible that larger droplets will rain out anyway, leaving us with a possible worst case in the 20–30 μm and less range.

It would be interesting to develop a test methodology for mists with similar concepts to those used in the MIKE3 apparatus for dusts. This would require being able to vary spark energies and other discharge characteristics, and concentration ranges. Gibson and Harper (1988) developed an approach to MIE using ignition frequencies for dusts systems, where the flammable boundaries are not hard edged. The frequency approach limits the requirement for large numbers of repeat measurements; it does assume a form to the frequency distribution to allow extrapolation. In dust testing it is usual to sieve samples to less than 63 μm to obtain a reasonable worst case measurement, for a mist it may be necessary to determine droplet size distribution from a nozzle and perform experiments on a relatively mono-disperse mist at the lower end of the distribution.

EXPERIMENTAL WORK

A rig has been built to investigate the issues involved in testing sprays of solvents for MIE. The rig was used with nozzles similar to those used in formulation processes within the company (supplied by Spraying Systems Co). One was a single fluid nozzle (Figure 1), and the other a two fluid system (Figure 2). Both were tested at a range of solvent (and for the

Figure 1. Single fluid nozzle

two fluid nozzle air) pressures. The rig sprayed fluids at ambient temperature, but this could be easily adapted to spray heated fluids into an ambient atmosphere. The nozzles were also tested on a laser particle size analyser using water as the test fluid. The test bed used is normally used for testing agricultural spray nozzles and is not set up to deal with potential flammable hazards. Typical droplet size distributions are shown in Figures 3 and 4.

Two different solvents were used (kerosene and tetralin) with others planned for the future. Ignition tests were with 2 sizes of pyrotechnic igniters (84 and 250 J) and an electrostatic spark circuit.

ISSUES

Tests with the real nozzles use large quantities of solvent which is difficult to re-use since it becomes contaminated with burnt material. This is another driver towards doing tests on a relatively mono-disperse mist possibly generated by a much smaller ultrasonic or piezo-electric nozzle, to give a worst case.

Figure 2. Twin fluid nozzle

The hemi-spherical electrodes in the first spark system tended to bridge with solvent, and so stopped sparking. Another problem was that the mist seemed to encourage breakdown between the electrodes at much lower voltages than in air. This meant that the capacitor discharged at a lower voltage (that could not be accurately determined) than the intended 10,000 V. Hence some discharges (including some incendive discharges) were at lower energy than the nominal circuit energy. These problems meant that a moving electrode system was developed, using spare components from a MIKE 3 dust tester.

RESULTS

Single Fluid Nozzle

Testing the single fluid nozzle on kerosene ignitions were not obtained for 1 or 2 bar solvent pressure with the 84 J igniter, but there were positive results for the higher pressures. 1 bar corresponds to a Sauter Mean diameter (SMD) on water of 338 µm, 2 bar an SMD of 179 µm and 3 bar to 129 µm (or fractions below 100 µm of 3%, 10% and 25% respectively). Using a 250 J igniter and the 1 and 2 bar generated sprays both ignited,

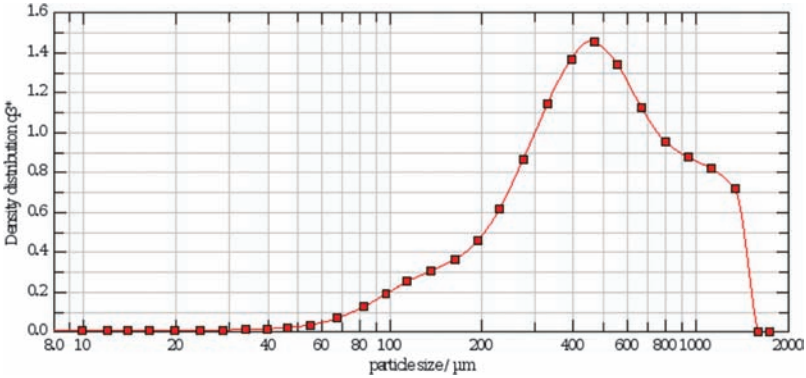

Figure 3. Droplet size distribution for single fluid nozzle at 1 bar using water as a model fluid

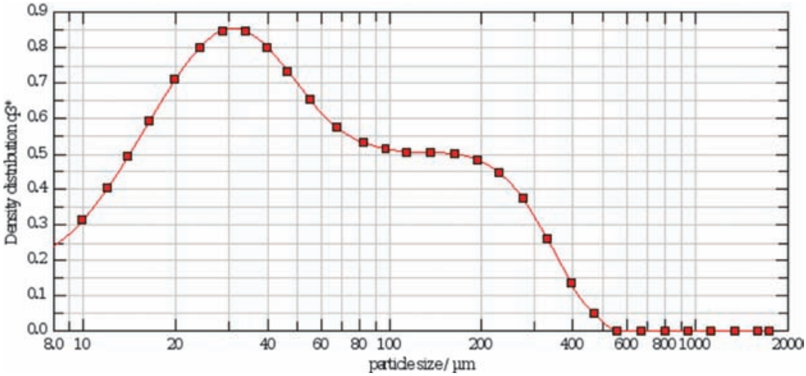

Figure 4. Droplet size distribution for twin fluid nozzle at 3 bar air and 4 bar water pressure using water as a model fluid

although the 1 bar spray was only at 50% frequency. The single fluid nozzle was also tested with the 84 J igniter in a variety of positions across the spray and towards the nozzle. There was some variation in ignition frequencies.

This bears out the observations that ignition energy trends down with droplet size, but that high strength sources can force ignition. The variation in ignition frequency across the spray indicates that there may be some variation in droplet size in different locations in the spray, and that concentration, which can affect ignition energy, probably varies across the spray.

Table 3. Ignition frequencies for kerosene using various settings for twin fluid nozzle with size distribution (water) for comparison (572 mJ spark)

Gas pressure (bar)	3		4			5	
Solvent pressure (bar)	3	4	3	4	5	4	5
Ignition frequency (%)	19	10	20	16	11	7	6
SMD (µm)	27.6	22.5	31.5	25.1	21.9	28.0	24.0
VMD (µm)	53.1	40.5	72.1	49.4	44.2	62.3	53.9

Table 4. Ignition frequencies for tetralin using various settings for twin fluid nozzle with size distribution (water) for comparison (281 mJ spark)

Gas pressure (bar)	3		4	5
Solvent pressure (bar)	4	5	4	3
Ignition frequency (%)	5	8	8	4
SMD(µm)	22.5	19.6	25.1	33.9
VMD(µm)	40.5	36.1	49.4	90.3

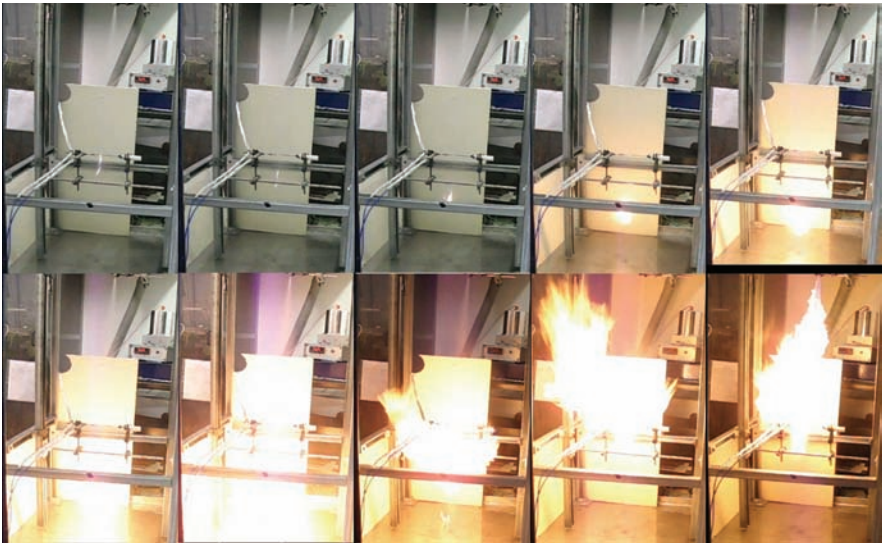

Figure 5. Kerosene ignition sequence by spark using twin fluid nozzle

Twin Fluid Nozzle

The twin fluid nozzle was tested with both kerosene and tetralin and a variety of conditions varying solvent and air pressure both between 1 and 5 bar. Some results are presented in Tables 3 and 4. There is no convincing trend for increasing ignition frequency with decreasing drop size. It is possible that there are simply too few tests to derive a trend, or more likely that issues of mist concentration and mist velocity are affecting the results. Hence a wider number of parameters might need to be measured.

An ignition can be seen in a series of video stills in Figure 5. It shows a small ignition near the spark, which drops and enlarges near the floor. This then spreads back up against the flow of the spray. Some ignitions near the spark did not enlarge and propagate; others enlarged a little, but did not propagate back against the flow.

CONCLUSIONS

There has been some development of a possible test method for the ignitability of sprays of high flash point solvents. Long-term the methodology requires smaller spray volumes to be practical. Some analysis of spray size distribution is also required to decide whether flammability can be dominated by a certain fraction of small droplets.

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