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Mist Can Explode, but Still No Standard! Proposal of a Combustible Sprays Test Method

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Hydrocarbon mists can explode even at temperatures well below their flashpoints. Nevertheless, fuel mist hazards are often disregarded and improperly classified due to the lack of tools and standards to assess and investigate their occurrence. The aim of this study is to propose a new test method to determine the ignition sensitivity and the explosion severity of fuel mists using a single existing standard equipment already available in laboratories or industries. The standardized 20L explosion sphere was selected and modified: a Venturi mist generation set-up and an automated system controlling the inlet concentrations and allowing an optimum evaluation of explosion results were implemented. Once the technical feasibility was established, seven fluids (ethanol, isooctane, kerosene, diesel, lube oil, light fuel oil, and biodiesel) of both industrial interest and different physicochemical properties were chosen to be tested under a wide range of conditions. Extensive studies were performed on their droplet size distribution (DSD), turbulence level, flammability, and explosion severity. To study the behaviour of the mist before ignition, particle image velocimetry and in-situ DSD measurements were performed. Then, sensitivity studies were carried out to examine the influence of parameters, such as the ignition source (spark or chemical igniters), the ignition energy, the DSD, the initial turbulence, the chemical nature of the fuel, the liquid temperature, and the sphere temperature, on the thermo-kinetic explosion parameters P_{max} and dP/dt_{max}. Results showed that this new procedure permits to measure sensitivity parameters such as minimum ignition energy and lower explosive limit, in addition to the above-mentioned severity parameters. This study establishes that it is indeed possible to assess fuel mist flammability and explosibility using a standardized apparatus based on the 20L explosion sphere, and thus allows a comparative ranking of hydrocarbon mists.

1. Introduction

Explosive atmospheres can be found in a variety of sectors, including chemical, petrochemical, pharmaceutical, food processing, and power industries, where hazardous areas should be identified and classified as implemented by the European ATEX Workplace Directive 1999/92/EC. All equipment and products used in such environments should fulfil stringent criteria to prevent them from becoming a source of ignition in the case of any flammable release. These releases can comprise gases or dusts, but mist releases should not be disregarded. Indeed, even high flashpoint liquid releases can be considered as flammable, as such fluids, when aerosolized, can ignite and engender an explosion (Bowen and Shirvill, 1994). While standards are well established and clear for gases and dusts, it is still not the case for high flashpoint liquid aerosols. Qualitative guidance can be found in some standards including the Energy Institute code of practice EI15 and NF 60079-10-1, but there exists a lack of quantitative methods permitting to correctly assess mist explosions and classify linked hazardous areas. As pointed out by Gant (2013), the matter is more complex for mists than for gases and dusts. In addition to the droplet size distribution, turbulence level, and concentration in the case of dusts, mist releases are not usually uniform and stable, mostly due to eventual evaporation, droplet breakup, coalescence, or sedimentation. Moreover, with high flashpoint liquids being multicomponent fuels, the presence of volatile fractions renders studying their flammability and explosivity rather challenging. A significant research effort was made in the past to achieve a better understanding of these aspects. For instance Burgoyne and Cohen (1954) notably studied the effects of droplet sizes on the flammability of the mist cloud. Ballal and Lefebvre (1978)

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conducted several studies to measure and predict the ignition energy and quenching distance of quiescent and turbulent fuel mist clouds. Over the years, a considerable number of mist-related incidents have been reported in parallel. Eckhoff (2005) dedicated a chapter of his book to shed light on the explosions of liquid droplets and past related incidents. Other incident reviews were published by Santon (2009) and Lees et al. (2019). The list of dedicated studies is far from being exhaustive, but there is still no standard test method for mist ignition and explosion assessment. A first approach could be to use an existing standard. Indeed, Puttick (2008) proposed that the primary assessment for ambient temperature ignition of mists be performed following a similar approach to that employed for dusts. Consequently, based on the 14034 European standard series for the determination of explosion characteristics of dust clouds, this study proposes a test method for the experimental determination the lower explosive limit (LEL), the maximum explosion pressure P_{max}, and the maximum rate of pressure rise dP/dt_{max} in a single already-standardized test vessel. An experimental approach was also proposed to determine the minimum ignition energy (MIE) in the 20L explosion sphere.
The determination of the mentioned parameters provides a framework for hazard identification and explosion prevention. The selected test vessel was a closed 20 L explosion sphere in which mists were injected using a Venturi-based spray nozzle. An area classification system established by Gant et al. (2016) served as a basis through which seven fluids were chosen, characterised, and tested. Experiments were performed to prove the feasibility of this proposed test procedure and to highlight the necessity of high-flashpoint fuel mist classification.

2. Test method

The outline of this article is directly inspired by the structure of international standards such as 14034 series.

2.1 Test apparatus

The standard 20 L explosion sphere was employed for this study. As it is mainly used to characterize dust clouds (EN 14034 1-4), some modifications were carried out and will be discussed in the following sections.

Explosion vessel

The 20 L explosion sphere comprises an inlet for purge air, two outlets for exhaust gases and vacuuming, a manometer for the determination of the initial pressure, two piezoelectric pressure sensors for the recording of the pressure-time evolution, two stainless steel electrodes and two electronic valves for the mist injection system described later in the text. It is equipped with a temperature controlling water jacket. The existing outlet valve, rebound nozzle and dust container were removed for the purposes of this study.

Mist injection system

The liquid to be aerosolized was placed in a temperature-controlled metallic reservoir under ambient pressure. Compressed air was injected through a three-way ball valve leading to a Venturi effect forcing the liquid up the tube and through the nozzle where it could be atomized (Figure 1). Two electronic valves were placed on the liquid and the compressed air inlets to control the injected concentration and the liquid/air ratio and to prevent backflow due to the explosion. The body of the nozzle spray was designed to fit into the support ring already used for dust explosion. The height of the vertical sphere support was also modified from 16 to 27 cm to allow for the mist injection system to fit underneath the sphere (Figure 1b). This system was hence placed at the base of the sphere with the nozzle set mounted inside the vessel allowing upward mist injection. The nozzle set was a twin fluid external mixing nozzle comprising an air cap and a fluid cap of different orifice diameters ranging between 0.5 and 4.5 mm (Figure 1a). The DSD, concentration and turbulence level of the mist cloud were varied by controlling the air injection pressure, the injection time, and/or the orifice diameter. This mist generation system was chosen to mimic industrial pressurized liquid releases and generate sufficient mist concentrations while being well adjusted and convenient to a confined, relatively small, vessel.

Ignition sources

The ignition source proposed by the EN 14034 standard comprises two chemical ignitors, each of 5 kJ. Such ignitor contains zirconium metal, barium nitrate, and barium peroxide. In order to widen the range of ignition energies available, two types of ignition sources were tested: chemical ignitors of energies ranging from 100 J to 10 kJ (Sobbe GmbH) and spark ignition. The high-voltage spark ignition system was developed by the LRGP to test lower ignition energies starting from about 100 mJ. This system consisted of a Brandenburg 3590-1320 DC/DC converter 12 V to 10 kV voltage with a total power of 5 W and a maximum input current of 0.5 mA. The output of this converter is adjustable, allowing the variation of the delivered energy to the mist cloud.
Throughout this paper, it will be seen that the choice of the ignition source would depend on the type of liquid tested and the intention of the test. The ignition source, whether chemical or spark ignitors, would be placed in the centre of the sphere and be actuated by a new control system bypassing the standard KSEP control box.

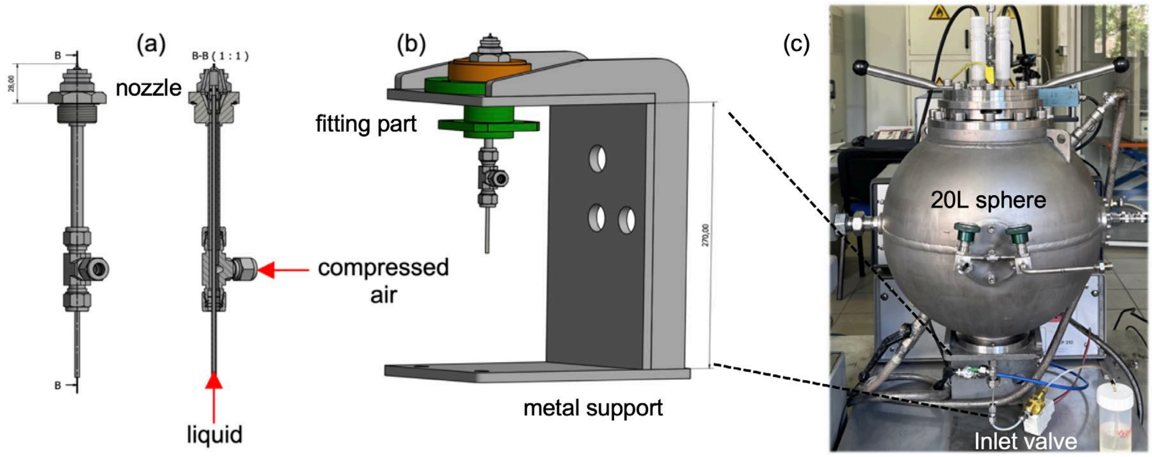

Figure 1: (a) Scheme of the mist injection system, (b) Mist injection system adapted to the 20L sphere, (c) 20L sphere modified for mist testing

Control and data acquisition unit

A control and data acquisition system was developed by the LRGP allowing to operate under different chosen conditions and to ensure safe manoeuvre. This system was based on a Mbed NXP LPC1768 type microcontroller as well as on a National Instruments NI-USB 6002 acquisition card. A software, specifically developed on LabVIEW, was used allowing the control of the electronic valves, hence the mist injection duration, the ignition delay t_v, the actuation of the ignition sources, and the start of the recording system. An electromechanical relay ensures authorization of system operation, only if the sphere's safety switch is closed. As for the data recording, the USB acquisition card allows visualization of pressure data and real-time monitoring of the output signal of the low-energy spark ignition source described previously (current, voltage, and ignition duration values). When performing a sequence, the microcontroller sends a synchronization signal to the acquisition card. For this application, the acquisition frequency was limited to 5000 Hz per channel.

2.2 Fuel selection and characterization

Fuels were chosen to cover a wide range of physicochemical properties and of industrial use, as explosive mist atmospheres can occur in a variety of industrial sectors. Following an existing classification (Gant et al., 2016), five fluids were selected: aviation kerosene jet fuel - Jet A1, diesel, light fuel oil (LFO, Total Energies - CPE), biodiesel (Valtris Champlor) and Mobil DTE VG 68 Heavy Medium. They are all complex high-flashpoint liquids with increasing dynamic viscosity. Ethanol and isooctane, two liquids largely used in numerous chemical processes, were added to this study both for their industrial interest and also their single-components liquids of well-known properties and combustion behaviours.
Characterization tests were carried out on all seven fluids under ambient conditions. Viscosity measurements were performed using the Hoeppler Falling-Ball Viscometer (Brookfield KF30 model) according to DIN 53015. In addition, surface tension measurements were performed following the Pendant Drop method. As for the flashpoint, tests were performed using the Setaflash Series 3 flashpoint tester according to ASTM D3278-96 standard. The measured physicochemical properties were determined at ambient temperatures and are shown in Table 1; they may differ from one supplier to another and lead to discrepancies in the release classes (R.C.).

Table 1: Physicochemical properties of the seven chosen fluids

Fluid	Ethanol	Isooctane	Jet A1	Diesel	LFO	Biodiesel	Mobil DTE
Density ($kg.m^{-3}$)	870	690	850	880	880	920	930
Dynamic viscosity (mPa.s)	1.31	0.45	1.23	2.95	2.88	6.3	154.28
Surface tension ($kg.s^{-2}$)	0.022	0.018	0.026	0.027	0.025	0.031	0.03
Flashpoint (°C)	13	-12	> 38	65	58	250	220
HSE Release Class	-	-	R.C. I	R.C. I	R.C. I	R.C. IV	R.C. III
R.C. (Gant et al., 2016)	-	-		More volatile / more atomising		Less volatile / more atomising	Less volatile / less atomising

2.3 Mist cloud characterization

The mist concentration, the DSD, and the level of turbulence being the most influencing factors on a mist cloud, they have been characterized under different conditions in an identical replica of the 20 L sphere equipped with borosilicate glass windows to allow visual access. The fuel mass injected was weighted systematically, which allows the determination of the mist concentration. Wide ranges of mist concentrations are available, depending on the fluid and nozzle type as well as on the injection pressure. For instance at 3 bar, concentrations up to 600 g/m^3 are attainable with a flowrate that varies between 0.2 and 1.1 g/s. Beyond such concentrations, the rain-out of the fuel at the sphere wall becomes non negligible. Measurements were repeated at least 3 times for each specified injection condition and a precision of ± 0.06 g/s. In addition to the aerosolised liquid, compressed air contributes by increasing the pressure inside the closed vessel. For instance, pressure contribution of 0.04 bar/s (0.55 bar/s) was found with 3 bar (5 bar) injections through a 0.5 mm (3 mm) nozzle.

The seven fluids were all tested using different air injection pressures and orifice diameters. Measurements were performed at the height of the ignition sources using an in-situ laser diffraction sensor (Helos KR/Vario) with an acquisition frequency of 2000 Hz. Droplets diameters as low as 5 µm and as high as 100 µm can be reached with an injection pressure maintained between 2 and 5 bar. Higher droplet diameters are reachable when using the twin fluid external mixing nozzles with a larger orifice diameter, but this study was limited to 3 nozzle sets N1, N' and N2 (El – Zahlanieh et al., 2022). A correlation linking the Sauter mean diameter (SMD) to the fluid properties, the release velocity, and the orifice diameter was established using a full factorial design. The level of turbulence of the mist was also determined by performing particle image velocimetry (PIV) and by calculating the root-mean-square velocity v_{rms}. Results showed that vertical velocity vectors reach 15 m/s during injection with a v_{rms} of 2 m/s with an air injection pressure of 3 bar. Finally, a CFD model based on a Euler-Lagrange approach was developed to study the biphasic flow development inside the test apparatus and assess conditions prevailing to the fragmentation and the coalescence of the dispersed phase.

2.4 Test procedure

For every ignition sensitivity or explosion severity test, the following steps were taken. The liquid was prepared and placed in its metallic reservoir. An air injection pressure was then chosen as well as the required injection duration (or mist average concentration). The temperature-controlled sphere was vacuumed to a calculated initial pressure allowing the attainment of an atmospheric pressure after injection. The mist injection was launched and then the chosen ignition source was actuated after a specific delay time. According to the EN 14034 standard, when the observed overpressure P_{ex} (effect of chemical igniters taken into consideration) is greater than or equal to 0.5 bar, an explosion is regarded to have occurred (same criterion for LEL tests).

Exhaust gases were then evacuated, and the sphere was thoroughly cleaned and prepared for the following experiment. dP/dt_{ex} is determined by calculating a five-point derivative of the pressure rise. P_{max}, dP/dt_{max} are the highest values of the maximum pressure and rate of pressure rise over a range of mist concentrations.

2.5 Calibration and verification: determination of mists ignition sensitivity and explosion severity

Tests were performed thrice with a good repeatability. Figure 2 shows some examples of explosion curves obtained for ethanol mists at various concentrations and for 100 J ignition energy. P_{max} reaches 9 barg and a dP/dt_{max} of 795 bar/s. Verification tests were performed by igniting ethanol vapours and comparing the explosion thermo-kinetic parameters with the literature as well as the CEA NASA program (El – Zahlanieh et al., 2022).

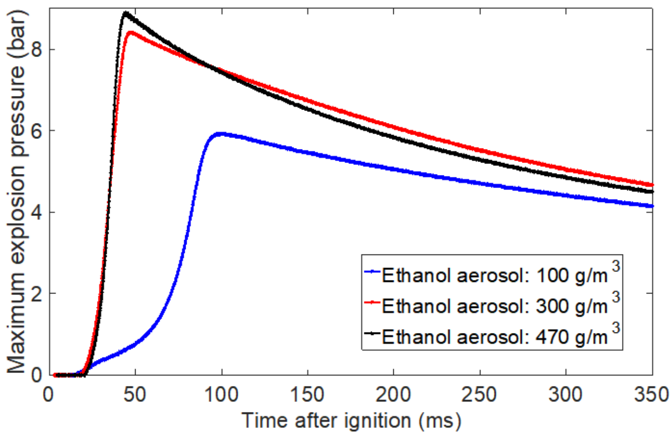

Figure 1: Pressure-time evolution of ethanol mists explosion (N2 nozzle, injection pressure: 8 bar, T: 27 °C)

The results presented here are non-exhaustive and only serve as examples of the possible outcomes of such a test method. It should be highlighted that an extensive parametric sensitivity analysis has been performed, which represents more than 350 explosion tests. The influences of the following parameters were studied: a) the ignition delay time; b) the liquid temperature; c) the sphere temperature; d) the ignition energy; e) the nature of the ignition source; f) the droplet size distribution; g) the mist concentration and h) the nature of the fuel. In summary, the following trends were observed, respectively: a) maximum safety parameters were found at t_v = 3 ms after injection. In a conservative approach (worst-case scenario), this delay was usually chosen; b) the thermal equilibrium time of the fine droplets is very small, which highlights the influence of the sphere temperature; c) when increasing the temperature, even below the flashpoint, a significant increase in the explosion severity is observed; d) strong chemical igniters can lead to DSD modification and overdriving; e) the ignition energy and source nature affect the local temperature of the mist and therefore the vapour/liquid ratio; f) the explosion severity globally decreases with increasing droplet diameters; g) maximum of the explosion severity is reached at rather low concentration for volatile fuels, but is harder to identify for fuels with high flashpoint; h) parameters such as the vapor pressure and flashpoint are key elements driving the mist ignitability.

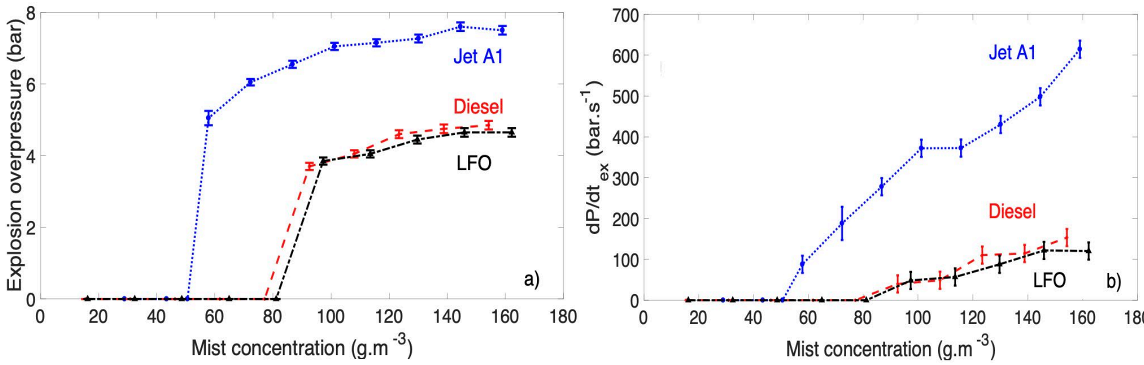

Figure 2: (a) Variation of the explosion overpressure (b) Variation of the maximum rate of pressure rise of three fuels: LFO, diesel and Jet A1 mists of 8 - 10 µm at T = 40 °C (sphere temperature) and P_{inj} = 3 bar

For illustrative purposes, Figures 3a and b compare the evolution of the explosion severity of Jet A1, diesel, and LFO mists generated under the same conditions at 40 °C. These tests show that kerosene mist explosions are much more severe than for LFO or diesel mists. In general, maximum pressures are reached on the tested concentration range, while dP/dt_{ex} reaches a plateau for diesel and LFO but continues to increase for Jet A1. Similarly, tests were performed on isooctane mists using two injection pressures. As seen in Figures 4a and 4b, the increase of the turbulence level tends to slightly elevate the explosion severity of isooctane mists and decreases their LEL. This shift can notably be explained by the slight decrease in the DSD of the mist cloud, which promotes its ignition sensitivity. For isooctane aerosols, P_{max} and dP/dt_{max} reach 7.8 bar and about 700 bar/s for a fuel equivalence ratio of 1.7. These values are conservative, especially with regard to the results obtained by Yuan et al. (2019) for n-octane for a fuel equivalence ratio of 1: 6.2 bar and 75 bar/s, respectively.

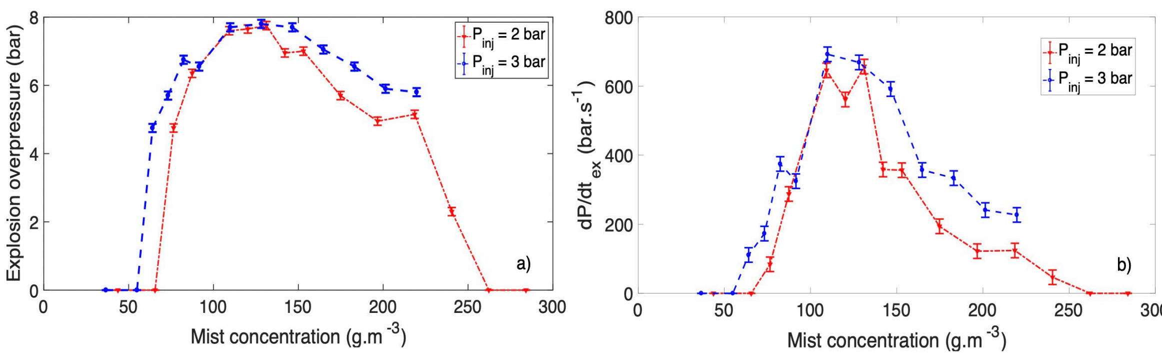

Figure 3: a) Variation of the explosion overpressure and b) variation of the maximum rate of pressure rise of iso-octane mists of 8 - 10 µm at T = 27 °C and P_{inj} = 2 and 3 bar (ignition energy: 100 J)

Lower explosive limit

Figure 3a shows the evolution of LEL of some mists at 40°C. Table 2 presents the LEL determined for the fuels at 20°C with 100 J chemical ignitors (5 kJ for biodiesel). It notably appears that the LEL of hydrocarbon mists is slightly greater than the LEL of the corresponding vapours (39 g/m^3 for isooctane and 66 g/m^3 for ethanol).

Table 2: Lower explosive limit of the seven fluids under ambient conditions

Fluid	Ethanol	Isooctane	Jet A1	Diesel	LFO	Biodiesel*	Mobil DTE
LEL (g.m^{-3})	77	64	94	123	113	103 (5 kJ)	No ignition

Minimum ignition energy

Table 3 clearly shows the flammability difference, in particular for the MIE, between the seven fluids tested. Some ignite at energies below 100 mJ, others above 1 kJ. Therefore, the ignition energy should be adapted to avoid overdriving the flame propagation.

Table 3: Minimum ignition energy of fuels under ambient conditions and a droplet size of about 8 - 10 µm

Fluid	Ethanol	Isooctane	Jet A1	Diesel	LFO	Biodiesel	Mobil DTE
MIE (J)	< 0.1	< 0.1	0.2	0.3	0.3	5000	> 10000

3. Conclusion and perspectives

This study is a step forward towards establishing a standardized procedure to test mist clouds explosions. It proposes a procedure using a single apparatus available in most laboratories, accepted by researchers, standardized, and proven to be versatile. The reproducibility and repeatability of this test method were verified with hundreds of tests. Ignition sensitivity (LEL, MIE) and explosion severity tests were conducted on seven different industrial fluids under varying conditions allowing to compare their behaviour. Tests conditions were adapted to the fluid properties (ease of atomization, flashpoint…). This benchmark will be exploited to classify industrial liquids and help industries to meet requirements for ATEX and DSEAR regulations. Nevertheless, this test method is appropriate for mist explosion testing and adaptable to industrial or conservative conditions. As warned by Eichhorn more than 60 years ago: ‘mist can explode’, but new assessment tools are now ready!

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