



Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.journals.elsevier.com/process-safety-and-environmental-protection

Assessing genuine flammability hazard of halogenated species for their safe processing and use: Case studies

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ARTICLE INFO

Keywords:

Halogenated substances
Flammability
Experimental methods
Regulation

ABSTRACT

It is recognized that the combustion of halogenated substances (gas and liquids) may present specific features compared to traditional hydrocarbons. As a matter of facts, the standardized flammability characterization methods referenced by the various regulations (transport, labeling, etc.) do not necessarily take the specific features of these substances into account. Subsequently, this may lead to an underestimation of the risk associated with their use (physical hazard such as explosion). Through two case studies of interest, one concerning a fluorinated liquid, the other focusing on a fluorinated gas, this work reveals technical difficulties that may arise in appraising actual flammability hazards of halogenated hydrocarbons, due to their combustion specific behavior, when applying existing flammability methods without appropriate expert judgement. In the case of the liquid ethoxy-nonafluorobutane (Novec 7200™) this work highlights that this substance can be erroneously considered non-flammable due a clear pitfall of flash point methods, whilst its genuine flammability can be revealed otherwise. Regarding gaseous halogenated species, we show that operating conditions shall be carefully selected to reveal the genuine flammability behavior of such substances. Indeed, this is not necessarily correctly identified in all possible flammability hazard rating standard methods. In this study, the application of European standards allows to confirm that R1234ze(E) is flammable at temperatures below 30 °C, at atmospheric pressure and at a humidity of 50%RH.

1. Introduction

Halogenated organic compounds (molecules containing mainly fluorine, chlorine, and bromine atoms) are either reputed 'non-flammable' (due to their strong flame retardancy properties) or hardly flammable depending on their molecular structure and more precisely their degree of halogenation. For several years now, new gases (refrigerants, propellants) and liquids (degreasing and cleaning solvents) have been made available on the market, replacing brominated or chlorinated compounds progressively banned due to their toxicity and environmental impact (more specifically, the impact on the ozone layer and the so-called global warming potential (GWP) (Yang et al., 2012). It appears that the flammability properties of these new substances are often ignored or carelessly characterized by standardized experimental methods originally calibrated for substances composed of molecules containing mainly carbon, hydrogen, and oxygen atoms and do not consider the specificities of halogenated organic compounds in terms of combustion (e.g., impact of air moisture, effect of the test volume,

influence of hydrogen /halogen (H/X) molar ratio, resilience to flame propagation, etc.). Flammability hazard rating methods are for example cited in the regulations applicable for the transport of dangerous goods and for the classification and labeling of chemicals in principle transposed from the GHS (Globally Harmonized System of Classification and Labelling of Chemicals, 2021) developed by United Nations technical committees such as the Regulation (EC)No 1272, 2008 (Classification for labeling and packaging of Substances and mixtures so called CLP Regulation). Therefore, these artefacts may lead to an underestimation of the genuine flammability hazard profile of halogenated substances and mixtures and the associated fire and explosion risks. In addition to a review of the available literature on the matter, the present study provides a practical insight on these problems through testing the flammability of one fluorinated gas, namely cis-1,3,3,3-tetrafluoropropene used as refrigerant, and one fluorinated liquid, the ethoxy-nonafluorobutane used as a cleaning or degreasing solvent, by applying standardized and regulatory methods. In particular, the study reveals that for gases, the choice of the method for determining the

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<https://doi.org/10.1016/j.psep.2023.04.046>

Received 16 December 2022; Received in revised form 7 April 2023; Accepted 25 April 2023

Available online 27 April 2023

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flammability limits (FLs) is essential; and that in the case of liquids, none of the flash point methods conventionally used are suitable for assessing the actual flammability of halogenated liquids: in this latter case, other alternative but still standardized methods must be used (explosion or flammability limits (Molnarne et al., 2017) and/or Lower Explosion Point (LEP) EN 15794 (2017), also known as Lower Temperature Flammability Limit (LTFL) ASTM E1232-07 (2019).

GHS and parent CLP classification schemes define a gas and gas mixture as flammable if it has a flammability range at 20 °C and 101.3 kPa in air. In the absence of available data on the flammability of a gas, these two legislations refer to standard ISO 10156 (2017) proposing an experimental method to define the flammability potential (flammable or non-flammable) of a gas or gas mixture. However, this document indicates that "the compressed air must be analyzed and have a moisture content of less than or equal to 0.01%", i.e., the test shall be performed with use of dry air. This moisture-free air requirement for assessing gas flammability property originally aims at determining the most severe flammability constraints in a general manner. However, it does not reflect current scientific evidence of the actual impact of humidity on the flammability of halogenated organic compounds, although well-established since a decade (Kondo et al., 2012, Kondo et al., 2017). In GHS text, it is specified that the competent authorities may use an equivalence method in the absence of sufficient data. The European Chemicals Agency (ECHA) guidance on the application of CLP regulation (Guidance on the Application of the CLP Criteria Guidance to Regulation, 2017) also cites European standard EN 1839 (2017) as relevant to determine the FLs of a gas for its classification among one of the "flammable gas" hazard categories. Worth to notice, in the appendix, this standard proposes an experimental method specifically adapted to hardly flammable substances (including halogenated organic compounds). It states: ". it is necessary to establish a relative humidity of the air of 50% (measured at room temperature) for halogenated hydrocarbons having a degree of halogenation greater than 0.8". Regarding regulatory texts, a gas can be classified as non-flammable by reference to ISO 10156 (2017) and still have a flammable range according to EN 1839 (2017), due to discrepant requirements about the relative humidity of the air (dry or humidified) in the underpinning testing protocols of the mentioned standards. When dealing with emerging refrigerants, of which many are halogenated, flammability assessment is often carried out according to other standards, i.e., ANSI/ASHRAE-34 (2019) or ISO 817 (2014). In these latter standard, the flammability assessment is based solely on the lower flammability limit (LFL) determined in the test apparatus described in the American standard ASTM E681-09 (2015). This latter test protocol also requires the air to have a relative humidity (%RH) of 50%.

More problematic than halogenated gases are halogenated liquids whose formal classification in the category "flammable liquid" in the context of hazmat regulations are based on both the flash point and the boiling point. New cleaning and degreasing solvents have been developed in recent years to timely replace those that no longer meet newly worldwide established targets regarding safe (reduced flammability and toxicity) and environment-friendly chemicals (not promoting greenhouse gases emissions or ozone depletion contributors), such as trichloroethylene and n-propyl bromide banned for their toxicity. Among the physical hazards to be assessed, the flammability of liquids is mainly defined in official hazard classification schemes by the flash point. However, the existing standard methods for measuring flash points are not suitable for many halogenated liquids, which sometimes results in an underestimation of the fire and explosion risks associated with these chemicals. Subsequently this may result to a misleading understanding of the apparent 'non-flammable' character because of conventional hazard classification. In fact, the absence of the hazard statement "flammable" on the SDS or on the bottle (pictogram) does not mean that the contained liquid is unable to generate vapors that can be ignited, in mixture with air, by a sufficient source of ignition. Some liquids or mixtures of liquids do not have a flash point but can

nevertheless generate explosive atmospheres (ATEX) due to the existence of a flammability range determined with the appropriate method EN 1839 (2017); ASTM E681-09 (2015). For halogenated liquids, flammability may not be correctly assessed by using flash point measurement methods because the volume of the test vessel is too small compared to the flame extinction distance of these vapors and is not suitable. For this type of liquid, ASTM E502-21a (2021) advises to determine the lower flammable temperature limit (LFTL), ASTM E1232-07 (2019) equivalent to the lower explosion point (LEP), EN 15794 (2017). Clearly, the flammability range of vapours generated by a liquid would also be a parameter to consider.

As a further step to what was recently published by Tribouilloy et al., 2022, as well as by some rare pioneering teams, we address this issue in a practical way by further testing one fluorinated liquid with various methods targeting the evaluation of the flammability hazard, as case studies. These case studies were selected for both the emerging interest for their use and existence of previously published works that allow for some useful comparisons.

2. Flammability of gases according to EU, US, and international standards

Table 1 shows the specifications of the European (proposed by the European Committee for Standardization – (CEN/TC 305/WG 1, 2007)), American (proposed by American Society for Testing and Materials) and the International Organization for Standardization (ISO) methods used by the various regulations to classify gases in terms of flammability. The flammability of a substance depends not only on its intrinsic properties but also on the procedures applied. For gases, the US (ASTM) and EU (EN) standards are quite different in terms of test equipment, protocols, and ignition criteria (Molnarne et al., 2017; Brandes et al., 2008).

Only EN 1839 (2017) and ASTM E681-09 (2015) standards consider the specificities of difficult-to-ignite substances with large quenching distances, including ammonia, amines, and partially halogenated compounds, as well as mixtures containing high proportions of these substances.

3. Case studies

3.1. 1,3,3,3-Tetrafluoropropene and its arguable flammability

1,3,3,3-tetrafluoroprop-1-ene (Fig. 1) is a hydrofluoroolefin (HFO) also identified as trans-1,3,3,3-tetrafluoroprop-1-ene or R1234ze(E) and cis-1,3,3,3-tetrafluoroprop-1-ene or R1234ze(Z).

Among other emerging applications (as a gas propellant or a refrigerant component), R1234ze(Z) can also be used in specific applications like high temperature heat pumps, whereas R1234ze(E) will show operating conditions and applied costs in line with R-134a (1,1,1,2-tetrafluoroethane) according to system and compressor sizes.

A specific safety classification for refrigerant use also exists, where R1234ze(E) is classified as A2L (slightly flammable) as derived from the international standard ISO 817 (2014), which is referenced by and ASTM E681-09 (2015). This classification means the absence of a flammability range at 23 °C and 101,3 kPa using the method described in Annex B of ISO 817 (2014), more precisely described in ASTM E681-09 (2015) (one of the four conditions to be met in addition to the criterion of propagation of flame at 60 °C with LEL >0.10 kg/m³, heat of combustion, and the optional burning velocity measurement). Significant controversy has however paved the market development of this gas, which was proposed as a replacement of R-134a, subsequently raising concerns to define safe handling and processing practices for its use (Bellair et al., 2019). The debate was raised by the application of different operating conditions and due to the strong impact of relative humidity characteristics of the air used as the oxidant for performing the tests.

In their review paper, Bellair et al., 2019 reported that according

Table 1
Different experimental methods for the classification of flammable gases.

Standards	ASTM E681-09	EN 1839-T	EN 1839-B	ISO 10156	EU Test A.11
Date	2015	2017	2017	2017	2008
Test vessel	Flask, spherical V= 5 dm ³ cf Annex A1 for substances which may be difficult to ignite V = 12 dm ³	Clear tube (glass or polycarbonate) Ø = 80 mm, H ≥ 300 mm cf Annex A for substances which may be difficult to ignite H = 500 mm	Closed sphere or cylinder H/Ø = 1–1.5, V > 5 dm ³ The bomb method has been found to be unsuitable substances which may be difficult to ignite	Glass tube Ø ≥ 50 mm H ≥ 300 mm	Glass tube Ø ≥ 50 mm H ≥ 300 mm
Used in this work ?	No	Yes	Yes	Yes	Yes
Ignition source	Induction spark (duration 0,2 s and 0,5 s) or fuse wire	Induction spark (duration 0,2 s)	Induction spark (duration 0,2 s) or fuse wire (E between 10 J and 20 J)	Induction spark (duration 0,2 s and 0,5 s / E = 10 J)	Induction spark (duration 0,5 s)
Criterion for ignition	Flame visually propagates upward and outward from the ignition point, with arc > 90°	Visual, flame detachment > 100 mm or aureole H > 240 mm from the spark gap	Pressure increase ≥ 5% + ignition pressure in air	Visual, 100 mm flame detachment from the spark gap	Visual, Flame detachment
Increment	Freely selectable, to be specified in report if x > 10% (rel.) of the test substance fraction	10% (rel.) to 0.2 mol% (abs.), depending on the test substance fraction	10% (rel.) to 0.2 mol% (abs.), depending on the test substance fraction	0.1% by volume for FL < 10% and 0.2% by volume for FL ≥ 10%	Not specified
Number of repetition test	1	4	4	4	Not specified
Oxidizer	Room air or air cylinder with O ₂ = 20,94% vol ± 0,1%vol RH of air: 50% for substances which may be difficult to ignite	Air, which must be water-free or synthetic air RH of air: 50% for substances which may be difficult to ignite		Compressed air must be analysed and have a moisture content of 0.01% or less	Air



Fig. 1. The HFO-1234ze isomers: (E) left and (Z) right [PubChem](#)

R1234ze(E) was not rated as flammable at 20 °C because of a study making use of [ISO 10156 \(2017\)](#) and A.11 European test protocol [Council Regulation \(EC\) 440, 2008](#) with dry and moist air. In this same study, the determination of the flammability limits of R1234ze(E) was carried out at 25 °C according to the [ANSI/ASHRAE-34 \(2019\)](#) method (i.e., with a spherical volume of 12 liters and not 5 liters, for reasons of quenching distance [Richard, 1994](#)). The FLs obtained were respectively 5.7%(vol) and 13.3%(vol) under ambient conditions. It was shown ([Kondo et al., 2012](#)) by applying the same method that from 10%RH of the air corrected to 23 °C, R1234ze(E) become flammable at 35 °C. At this temperature, with 50%RH, flammability of R1234ze(E) ranges from 5.95%vol to 12.7%vol and from 6,2%vol to 12.4%vol at 20 °C. The application of US standards has highlighted that R1234ze(E) reveals to have a flammability range even under ambient conditions (i.e., atmospheric pressure, between 20 °C et 25 °C). Considering these different results, it was decided to complement these results by carrying out tests according to the method described in Annex A of [EN 1839 \(2017\)](#). Others were carried out in the tubes described in [ISO 10156 \(2017\)](#) and the method proposed by the European test A.11 with air having a relative humidity of 50%RH. Additional tests were carried out in a 20 dm³ sphere to compare the results with those obtained with conventional methods.

The objectives of these tests were not only to ensure that we were able to retrieve the published data ([Bellair et al, 2019](#)) from the tests derived from the European regulation, but also to highlight a possible influence of volume of the test on the flammability of R1234ze(E) by applying the standards mentioned regulation and proposed by the

working group of the European Committee for Standardization (CEN TC 305 WG1).

3.1.1. Experimental study

3.1.1.1. Test devices and procedures. The experimental set-up for the tube tests is shown in [Fig. 2](#).

A cylinder of compressed air (1) (Supplier: Air Liquide, product ALPHAGAZ 2) and a cylinder of R1234ze(E) (Supplier: INVENTEC) (2) are connected to a 1 dm³ pressure-resistant stainless-steel cylinder vessel (3). It is equipped with a magnetic stirrer (4), a 50 bar piezoresistive pressure sensor (manufacturer KISTLER, Type 4045A50) and a thermocouple (type K). In this 1 dm³ cylinder the test mixture air/R1234ze(E) is prepared at approximately 30 bar by the partial pressure method ([Wu et al., 2014](#)) at room temperature. This method makes it possible to define the composition of the mixture provided those gaseous components are assumed to follow the law of perfect gases, whatever the test temperature, the relationship below is obtained which links the molar fraction of component *i* (*x_i*) in the mixture, the partial pressure of component *i* (*p_i*) in the mixture and the total pressure of the mixture (*P_T*) ([Eqn 1](#)).

$$x_i = (p_i / P_T) \text{ with } \sum p_i = P_T \quad (1)$$

The mixture thus prepared is then totally discharged into the test apparatus. It is passed through a first wash bottle (5) filled with glass beads and water to saturate it with moisture, then into a second (6), filled with glass beads but free of water, immersed in a thermostatic bath (7). The latter is set at the dew point temperature of the water corresponding 50%RH at atmospheric pressure. This temperature is between 12 °C and 14 °C. The gas flow then passes through a glass cylinder (8) equipped with a thermohydrimetric probe to monitor %RH of the mixture. It sweeps from bottom to top through a vertically positioned glass tube (9) placed in an oven (10). The tube is equipped at its base with two electrodes 5 mm apart, between which inductive sparks are generated. This is obtained by means of a high-voltage transformer (11), with an effective voltage of 15 kV and a short-circuit current of 30 mA.

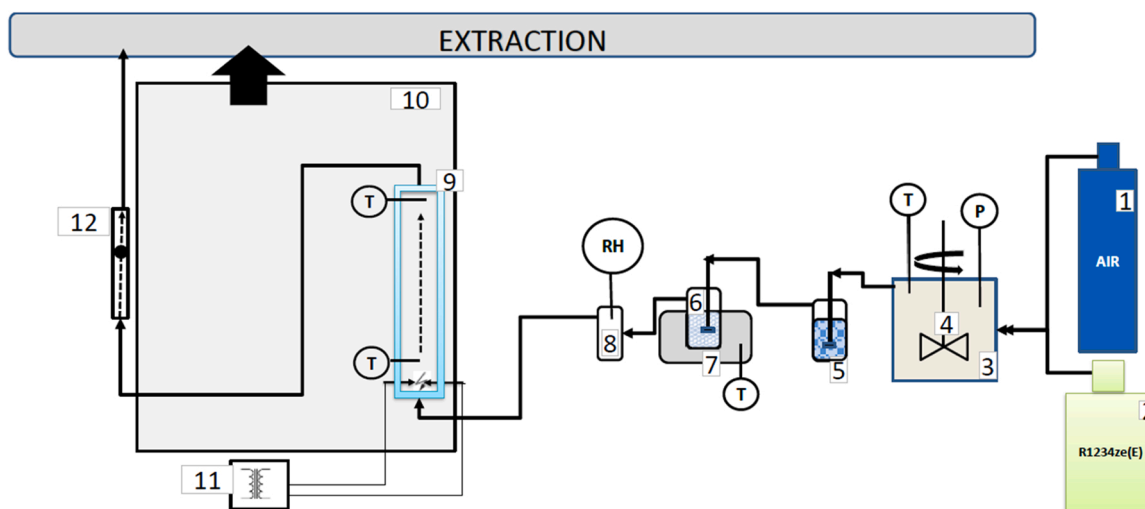


Fig. 2. Schematic diagram of the test set-up for the application of the glass tube method (Annex A EN 1839 (2017)).

The spark discharge time is set at 0.5 s. The outlet of the tube is connected to a flowmeter (12) to ensure the proper flow of the mixture through the whole experimental device. After discharging the full content of the 1 dm³ cylinder into the tube, the mixture is allowed to stand for approximately one minute before attempting to ignite it. The mixture is deemed to be ignitable when self-sustaining combustion is observed in the tube. The tests consist of gradually varying the content of R1234ze (E) in air to define the low (LFL) and high (UFL) limit between the flammable and non-flammable range of R1234ze(E) in air.

The experimental set-up for the tests in 20 dm³ sphere is shown in Fig. 3.

The sphere is equipped with a K-type thermocouple, a piezoresistive pressure transducer (4045A5) for the preparation of the mixtures and a piezoelectric transducer for measuring the explosion overpressure generated by the ignition of the test mixture. Two electrodes, 5 mm

apart, are positioned in the center of the sphere and connected to the same transformer described above. After evacuating the sphere, R1234ze(E) is introduced until the desired partial pressure is reached. Then ambient air is added at the bottom to about 1 bar. The moisture of the incoming air is measured. The mixture is left to rest before the ignition attempt. Ignition of the mixture is considered to have occurred when the ratio of [Maximum Absolute Explosion Pressure (P_{ex})]/[Initial Pressure (P_i)] is greater than or equal to 1.05 (criterion defined by the EN 1839 (2017) bomb method).

3.1.1.2. Flammability limits measurement: experimental results and discussion. The experimental data obtained for the determination of the FLs according to the volume used in this study (see Table 1) are listed in Table 2, Table 3, and Table 4. These tables contain all the operating conditions used in the tests, which indicate either: the composition of

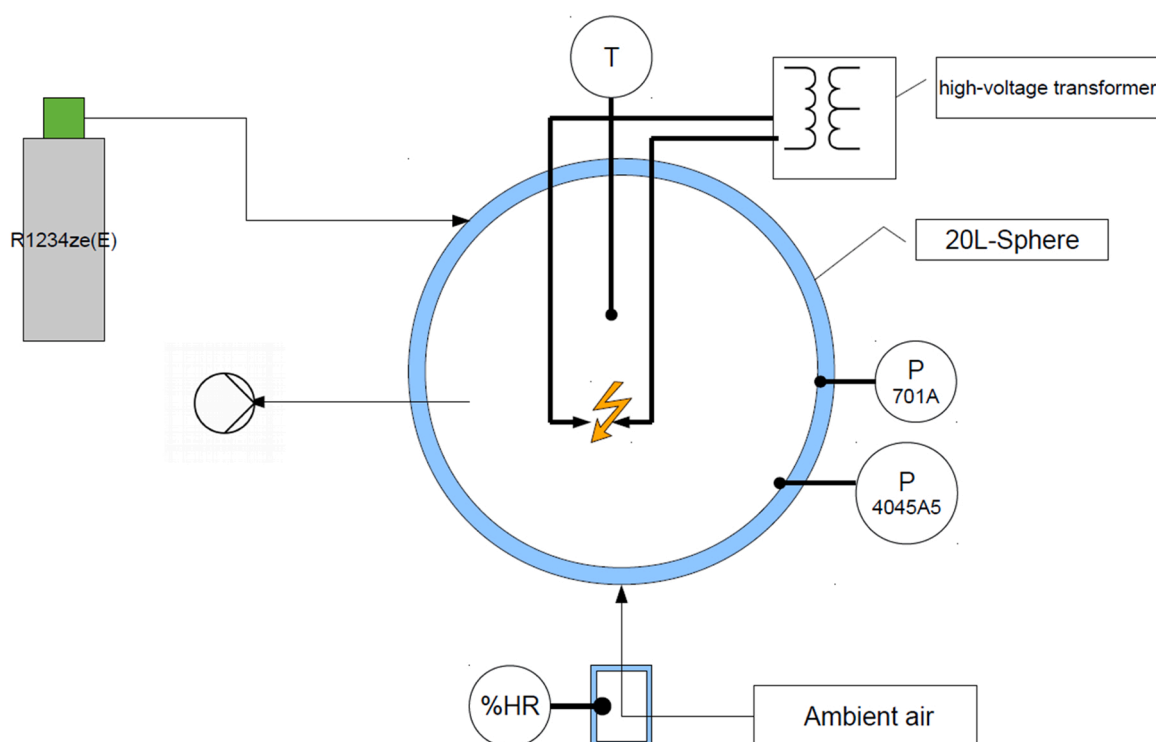


Fig. 3. Schematic diagram of the test set-up for the 20 L-Sphere tests (EN 1839-B, 2017).

Table 2

Flammability limit of R1234ze(E) in moist air in the tube described in ISO 10156/E.U Test A.11.

R1234ze (E) content in air (% vol)	%HR of mixture	Test temperature (°C)	Ignition?
5,0	57	23	No
6,0	50	24	Yes
5,0	51	25	No
5,8	52	25	Yes
5,6	54	25	No
5,6	53	25	No
5,6	53	24	No
5,6	52	24	No
5,6	49	25	No
12,8	52	23	No
12,4	49	24	No
12,0	51	24	No
11,0	52	25	Yes
11,3	53	25	Yes
11,8	49	24	No
11,6	49	25	Yes
11,8	52	25	Yes
12,0	53	25	No
12,0	52	25	No
12,0	53	24	No
12,0	51	25	No

Table 3

Flammability limit of R1234ze(E) by application of the method described in Annex A of EN 1839 (difficult to ignite gases and vapours).

R1234ze (E) content in air (%vol)	%HR of mixture	Test temperature (°C)	Ignition ?
5,6	48	25	Yes
5,4	47	25	No
5,4	50	25	No
5,4	48	25	No
5,4	51	25	No
5,4	52	25	No
5,8	54	24	Yes
13,3	53	23	No
12,5	52	23	Yes
12,6	52	24	Yes
12,8	50	25	Yes
13,0	51	24	No
13,0	51	24	No
13,0	51	24	No
13,0	52	24	No
13,0	53	24	No
12,8	51	24	No

the mixture, the relative humidity (of the test mixture for the tube method and of the ambient air introduced for the 20-liter sphere), the temperature measured in the test volume, the flammability or non-flammability of the test mixture. The investigation of the lower (LEL) and upper (UEL) flammability limits of the respective concentration levels was carried out in a stepwise process using increments of increasing or decreasing concentration of 0.2 vol% R1234ze(E). The flammability limits are confirmed by four additional tests and are shown in bold. As a result of this procedure, the flammability in air of R1234ze (E), determined in the tubes described by the regulatory standards ISO 10156 (2017)/EU Test A11, was found to be between 5.6%vol and 12.0%vol (Table 2).

From the results obtained by applying ISO 10156 (2017)/EU Test A.11 with a humidified mixture, we therefore observed that R1234ze(E) is flammable under ambient conditions.

From the test results, we can conclude that adopting ISO 10156 (2017)/EU Test A.11 testing protocols where the test mixture is humidified highlights that R1234ze(E) is flammable in air under ambient conditions.

Applying the same procedure to screen the flammability limits of

Table 4

Flammability limit of R1234ze(E) measured in 20 dm³ sphere by application of the method described in EN 1839 (Bomb method).

R1234ze (E) content in air (%vol)	%RH of ambient air introduced	Test temperature (°C)	Ignition?
6,0	55	21	Yes
4,9	55	22	No
5,4	55	23	No
5,8	55	22	No
5,8	50	22	No
5,8	49	23	No
5,8	50	22	No
5,8	51	23	No
10,0	57	22	Yes
12,0	60	23	No
11,1	61	22	Yes
11,6	60	22	Yes
11,8	59	23	Yes
12,0	61	23	Yes
12,2	61	23	Yes
12,6	61	23	Yes
13,0	59	23	No
12,8	59	22	No
12,8	57	23	No
12,8	55	23	No
12,8	54	23	No
12,8	51	23	No

R1234ze(E) but referring to testing method defined in EN 1839 / Annex A, the flammability range lies between 5.4%vol and 13.0%vol. (Table 3).

These two series of tests in tubes of different volumes (in terms of internal diameter and height) confirm that R1234ze(E) is flammable under ambient conditions of pressure, temperature, and moisture. However, there is some impact of the tube size essentially on the UFL.

The flammability range determined in 20 L-Sphere by application of EN 1839 (2017) (Bomb method) is between 5.8%vol and 12.8%vol. (Table 4).

Table 5

Flammability limits of R1234ze(E) measured by various US and European standard methods.

Referential	Moisture (%RH)	Temperature (°C)	LFL – UFL (%vol)	Range of flammability (%vol)
ISO 10156/EU test A.11	49–57	23–25	5,6 – 12,0	6,4
EN1839-Tube / Annex A	47–54	21–25	5,4 – 13,0	7,6
EN 1839-Bomb / 20 dm ³ sphere	49–61	21–23	5,8 – 12,8	7,0
ASTM E681/ASHRAE (Kondo et al., 2012)	50	20	6,2 – 12,4	6,2
ASTM E681/ASHRAE (Bellair Robert, Hood, 2019)	50	25	5,7 – 13,3	7,6
ASTM E681 / ASHRAE (Yang et al., 2015)	67–70	25–27	7,2 – 14,6	7,4
ASTM E681 (adapted) (Zhai et al., 2019)	50	25	8,7 – 13,0	4,3
ASTM E681 (adapted) (Zhai et al., 2019)	20	25	No FLs	0
ASTM E681 / ASHRAE (Yang et al., 2015)	0	25–27	No FLs	0

For comparison, all experimentally determined FLs values in this study are reported in Table 5 with those published by other authors such as Kondo et al., 2012, Bellair et al, 2019, Yang et al., 2015 and Zhai et al., 2019.

Table 6 shows the estimated absolute measurement uncertainties for each parameter presented in Table 5.

With dry air, Yang et al., 2015 and Kondo et al., 2012, found no evidence of a flammability range (Fig. 4). The ignition devices used in their testing protocols develop low energy levels ranging between 5 J and 20 J. By contrast, Askar et al., 2018 showed that R1234ze(E) could ignite in dry air but with high ignition energies over 500 J. The flammability range observed spreads between 6.5 vol% and 12.0 vol%.

It is counter-intuitive to think that the addition of moisture to the air promotes the combustion of R1234ze(E) and other halogenated substances resulting in the widening of the flammability range. The two oxidation equations, Eqn 2, and Eqn 3, associated with their enthalpy of reaction, presented in Fig. 5, help to understand this phenomenon (Zhai et al., 2019).

Dry air: $C_3H_2F_4 + 5/2 O_2 \rightarrow 2 HF + COF_2 + 2 CO_2$, $\Delta H_r = -1157 \text{ kJ/mol}$ (2)

Humidified air: $C_3H_2F_4 + 5/2 O_2 + H_2O \rightarrow 4 HF + 3 CO_2$, $\Delta H_r = -1458 \text{ kJ/mol}$ (3)

The oxidation reaction in the presence of water, Eqn 2, is favored by a higher enthalpy of reaction than with dry air, Eqn 1. The water molecule allows the fluoride radicals to be trapped to form HF and avoid the formation of COF_2 and other non-flammable fluorinated molecules.

R1234ze(E) is therefore flammable under ambient conditions (pressure, temperature, humidity) as shown by the results obtained by American or European standards, where the use of humid air is recommended for difficult-to-ignite substances. Moreover, the measured FLs are essentially the same, while the procedures, devices and flammability criteria are very different. However, this flammability can be superficially eliminated by applying the ISO 10156 (2017) standard, cited by the GHS regulation, and using dry air (Kondo et al., 2012). On the other hand, according to the European CLP regulation, based on flammability limits, R1234ze(E) should be classified as a category 1 flammable gas (i.e., extremely flammable).

3.2. Ethoxy-nonafluorobutane: a 'non-flammable' liquid unexpectedly revealing some explosive atmosphere hazard at low temperature

The application of the various flash point determination methods for testing the flammability hazard rating of halogenated liquids may result in negative errors, since the ignition criterion, defined as being a flame propagation phenomenon on the liquid surface (so-called "flash") cannot be observed due to test configuration limitations (size effect). However, two other flammability related safety parameters can be used to assess the flammability potential of these liquids: the LEP (Brandes et al., 2007) or/and the LFL. We have illustrated this with experimental work on ethoxy-nonafluorobutane (a fluorinated degreasing solvent whose flash point is reputed non defined according to published material safety data sheets 3M™ Novec™ 7200 Engineered Fluid) and therefore classified as 'non-flammable' according to CLP).

The ethoxy-nonafluorobutane is a hydrofluoroether (Tsai, 2005) of formula $C_4F_9OC_2H_5$, delivered as mixture of two inseparable isomers (Fig. 5) with essentially identical properties.

Ethyl nonafluoroisobutyl ether has no flash point and ethyl

Table 6

Estimated uncertainty of measured parameters.

Measured parameter	Absolute uncertainty on the parameter
Moisture	± 1%RH
Temperature	± 2 °C
Flammability Limit	± 0,5%vol

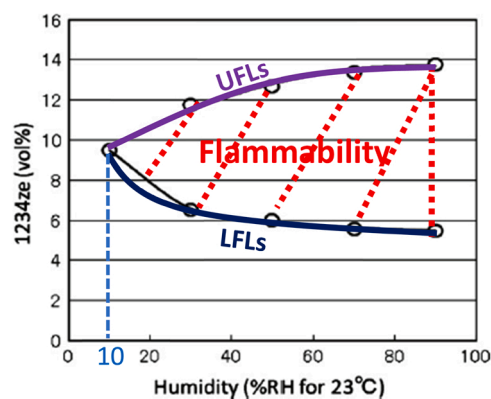


Fig. 4. Influence of relative humidity on the flammability range of R1234ze(E) at 23 °C

(adapted from Kondo et al., 2012).

nonafluorobutyl ether has a flash point of 39 °C (PubChem).

Published flammability data from a major supplier are reported in Table 7.

3.2.1. Experimental study

3.2.1.1. Flash point. It is important to observe carefully the ignition process and potential flame propagation phenomenon on the surface of the sample when the flame used as an ignition source is brought close to the surface of the liquid being tested during determination of the flash point. For this purpose, the Cleveland open-cup apparatus described in ISO 2592 (2000) was selected for testing ethoxy-nonafluorobutane. Since only open-cup type of flash point apparatus may allow this observation. As the flame passes over the surface of the liquid, it grows with the temperature of the liquid (so called "halo"), without spreading a flame over the surface of the liquid (Fig. 6).

Gorbett et al., 2004 refer to this phenomenon as "outgassing" which also occurs with closed cup flash point methods (see Fig. 3 and Fig. 7 in Gorbett et al., 2004), however, the non-propagation of the flame onto the surface of the test liquid in this work was hardly visible due to the type of test vessel used.

"Outgassing" can mask the true flammable nature of a substance when it occurs during the flash point test. Gorbett et al., 2004 confirm that products containing certain hydrocarbons, such as dichloromethane, are capable of producing dangerously flammable atmospheres, without exhibiting formally a flash point, and are therefore not classified as flammable. Moreover, in the American guidance document, for the selection of closed cup flash point methods ASTM E502-21a (2021), it is stated that some liquids, such as trichloroethylene, cannot propagate the flame due to the small volume of the test vessels (about 10 cm³). It should be noted that similar issues have been addressed previously for mixtures of flammable liquids containing a chlorinated liquid fraction (trichloroethylene and methyl chloride) (Rybicky et al., 1981; Fayet et al., 2020).

3.2.1.2. Alternative methods for characterizing the flammability of a liquid

3.2.1.2.1. Tests devices and procedures. LEP is the term used in the European standard EN 15794 (2017), whilst the American standard ASTM E1232-07, 2019 uses the term LFTL. These two terms are synonymous since they are consistently defined as the minimum temperature at which a liquid gives off enough vapor to form a flammable mixture with air under equilibrium conditions.

In this work, the LEP of ethoxy-nonafluorobutane was determined according to the method described in EN 15794 (2017), that is making use of a glass tube of 100 mm inner diameter and of 290 mm height. The temperatures of the liquid and gas phases are measured by type K thermocouples of 1 mm diameter (marked 1 and 2 on Fig. 7a). A third

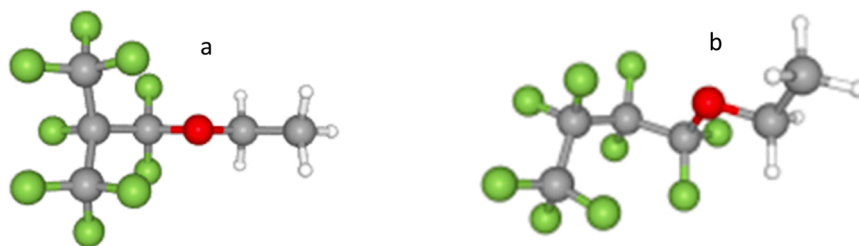


Fig. 5. The two isomers of ethoxy-nonafluorobutane: a) ethyl nonafluoroisobutyl ether (cas n°163702–06–5), b) ethyl nonafluorobutyl ether (cas n°163702–05–4) [PubChem](#)

Table 7

Reported flammability volatility and flammability parameters of ethoxy-nonafluorobutane (NOVEC 7200 trademark, 3 M product information 2023).

Name	Boiling (°C)	Flash Point	Flammability Range in Air (% vol)
ethoxy-nonafluorobutane	76 °C	None	2,4 – 12,5



Fig. 6. : Pilot flame above the liquid ethoxy-nonafluorobutane at a temperature of 32 °C.

0.5 mm diameter K-type thermocouple (3) placed just below the lid allows early detection of any temperature rise. About 10 mm above the surface of the liquid, two stainless steel electrodes (4) are placed opposite to each other at 5 mm. These electrodes are connected to a high

voltage transformer (5) (effective voltage between 13 kV and 16 kV and short circuit current between 20 mA and 30 mA). A magnetic bar is added to stir the liquid (6). This tube is placed in a climate chamber capable of varying from -20 – 200 °C. The duration of the arc generated between the two electrodes is set at 0.2 s and 0.5 s if the first attempt is negative (no ignition).

The LEL of ethoxy-nonafluorobutane was determined by applying the method described in Annex A of [EN 1839 \(2017\)](#), for substances that are difficult to ignite due to large quenching distances but also their ability to generate flame inhibitors during combustion. For halogenated hydrocarbons with a degree of halogenation greater than 0.8, the explosion limits and limiting oxygen concentration shall be determined with moist air (50%RH at ambient temperature) to avoid the formation of flame inhibitors (such as COF_2 , CF_3H , $\text{C}_2\text{F}_5\text{H}$, etc.) through the formation of hydrogen fluoride, which testing condition was indeed applied for testing ethoxy-nonafluorobutane, since this chemical has a degree of halogenation equal to 1.8.

The tests are performed in a vertical glass tube (marked 1 on [Fig. 8](#)) of 80 mm inner diameter and 500 mm height (for standard gases, the tube can be 300 mm high). At its base, 60 mm from the bottom, the same electrodes (2) described in paragraph 2.3 are connected to the same high voltage transformer (3). At the top and bottom of the tube are two 1 mm diameter type K thermocouples (4) (5). The base of the tube is connected to an evaporator (6) for the evaporation of the liquid to be tested. Between the two pieces of equipment, a pneumatic valve (7) is installed to direct the air/vapor flow towards the test tube or the evacuation (to avoid stopping the flowmeter between two tests, thus ensuring the stability of the air/vapor mixture). The assembly is placed in an oven (8).

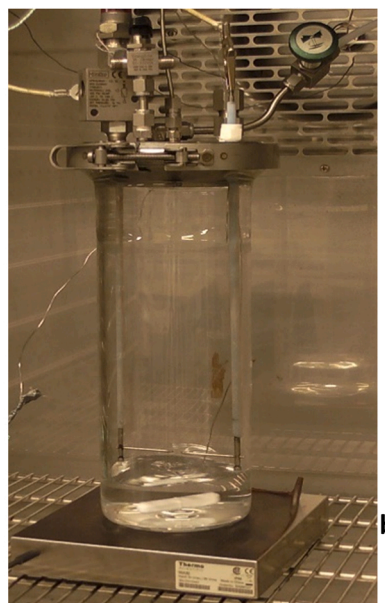
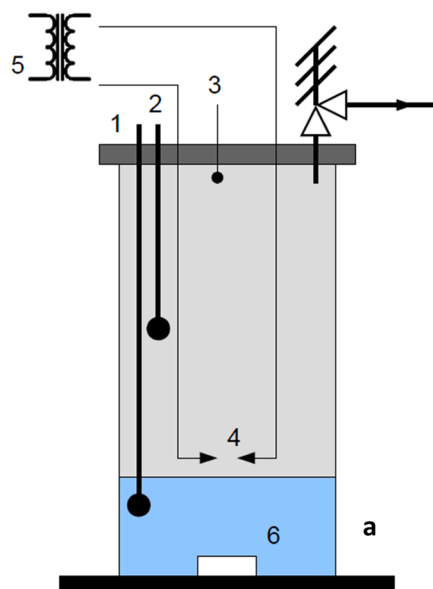


Fig. 7. : a) Schematic diagram of the setup described in [EN 15794](#), b) a view of the tube.

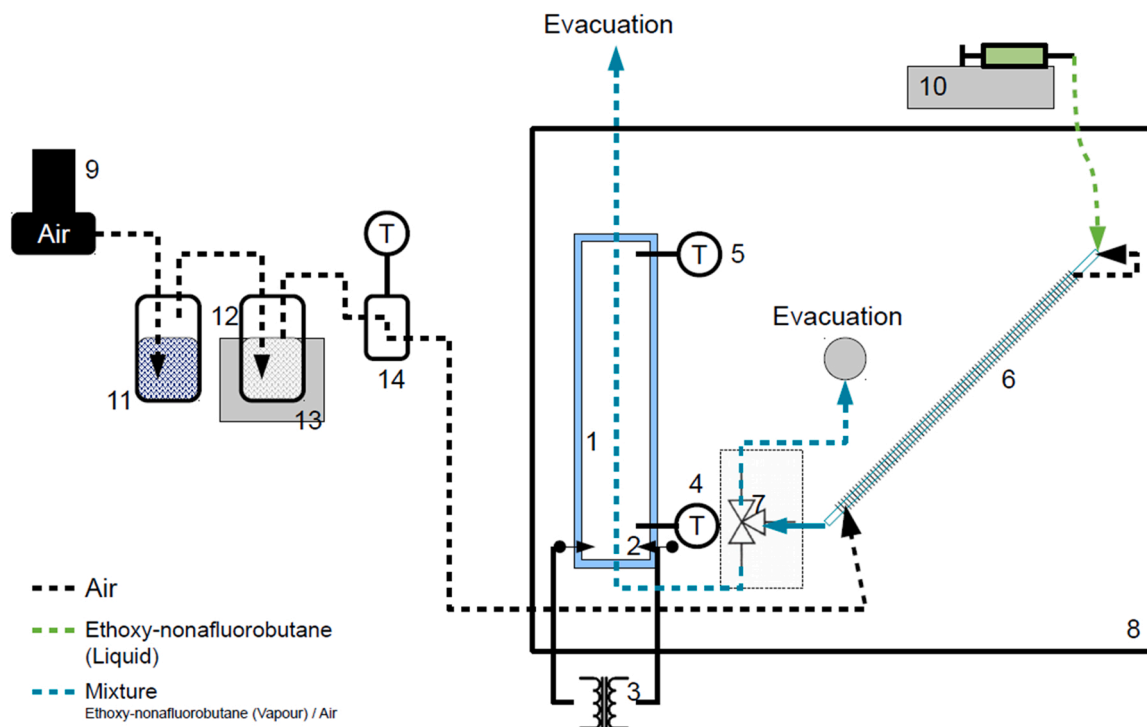


Fig. 8. Schematic diagram of the setup described in annex A of EN 1839 - Tube method.

The composition of the air/steam gas mixture is prepared by flow measurement. The air flow rate is adjusted with a mass flow controller (9) and the liquid with a syringe pump (10). The air flow is saturated with water by bubbling through a flask (11) containing glass beads and filled with water. At its exit, the air stream is sent to an identical flask (12), without water, placed in a cooling bath (13) whose temperature is adjusted to achieve a relative humidity of 50% (as determined at room temperature) at its exit (marked (14) on Fig. 8).

3.2.1.2.2. Experimental results and discussion

3.2.1.2.2.1. LEP measurement

The tests were carried out with a filling rate of 20% by volume. The results obtained of ethoxy-nonafluorobutane sample are reported in Table 8. This first test is primarily used to determine whether liquid ethoxy-nonafluorobutane can generate vapors which, when mixed with air, can be ignited by an ignition source. Ignition is occurring at a liquid phase temperature of 7.5 °C Fig. 9. A second test with a second sample was performed to confirm the first value obtained. Ignition was observed at 3.3 °C (no ignition at 3.0 °C). Fig. 10 shows the development of the flame in the test vessel (video captures).

The development of the flame in the test vessel is clearly visible (video captures – Fig. 9) when the test is performed at 3.3 °C.

This is a self-sustaining combustion phenomenon (flame detachment, ignition criterion) and not a halo phenomenon as in the case of the

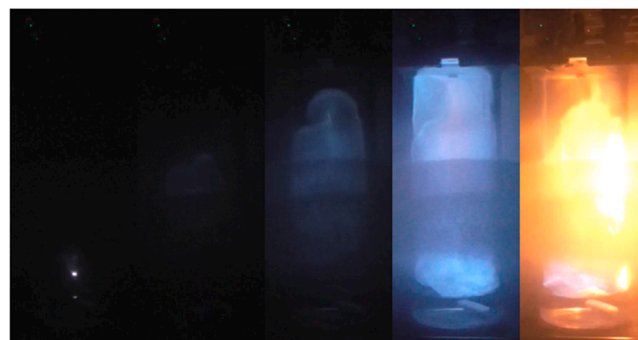


Fig. 9. LEP: Flame development (left to right) in the gas phase (liquid temperature: 3.3 °C) after spark generation.

flash point ignition test. It should be noted that prior to these tests targeting the assessment of LEP of the studied chemical, other tests were carried out at higher temperatures, always with the aim of observing potential ignition. From the corresponding results presented in Table 9, this temperature range appears to correspond to the upper explosion point (UEP) zone, i.e., between 12.5 °C and 17.3 °C.

The flame development in the test vessel (video captures – Fig. 10) is

Table 8

LEP determination of ethoxy-nonafluorobutane.

First sample for estimation											
Liquid phase temperature T_{liq} (°C)	-8,9	-7,7	-5,9	-4,8	-2,3	0,1	1,7	3,4	5,6	6,7	7,5
Gaseous phase temperature T_{gas} (°C)	-10,5	-8,5	-6,6	-4,5	-2,6	-0,7	1,2	3,2	5,2	4,2	5,5
ΔT (°C) ^a	1,6	0,8	0,7	0,3	0,3	0,8	0,5	0,2	0,4	2,5	2,0
Ignition?	No	No	No	No	No	No	No	No	No	No	Yes
Second sample for confirmation											
Liquid phase temperature T_{liq} (°C)	3,3	2,7	3,0								
Gaseous phase temperature T_{gas} (°C)	1,7	1,7	2,1								
ΔT (°C)	1,6	1,0	0,9								
Ignition?	Yes	No	No								

^a ΔT (°C) is the absolute value of the difference between T_{liq} and T_{gas}

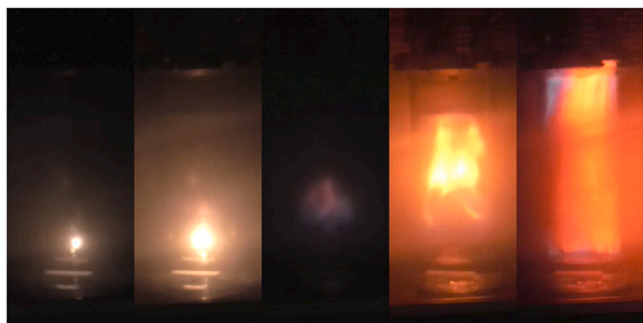


Fig. 10. UEP: Flame development (left to right) in the gas phase (liquid temperature: 12.5 °C) after spark generation.

Table 9

UEP estimation of ethoxy-nonafluorobutane.

Liquid phase temperature (°C)	17,3	22,7	28,5	12,5
Ignition?	No	No	No	Yes

observed for test performed at 12.5 °C.

3.2.1.2.2.2. LEL measurement

To ensure evaporation of the liquid at the evaporator outlet, we had to work at 38 °C. The different concentrations of the vapors of the solvent in air tested, with a relative humidity close to 50% at ambient temperature, are presented in Table 10. The LEL is equal to 3.4%vol by applying annex A of the EN 1839 standard, with an ignition observed at 3.6%vol. (Fig. 11).

LEP test results for ethoxy-nonafluorobutane have shown that this chemical can generate flammable vapors in air, including at low temperatures., well below the flash point of ethanol, which is classified as "highly flammable liquid". This ability to generate explosive risks (ATEX) was confirmed by measuring its LEL according to the method described in Annex A of EN 1839 (2017) at 38 °C and atmospheric pressure.

4. Conclusions / recommendations

Given the particularity of halogenated substances and in particular fluorinated substances currently flooding the international market to reduce their impact on the environment (ozone layer depletion, global warming, ...), they are sometimes sold as 'non-flammable' chemicals by reference to standard methods that are not necessarily adapted to the specificities of these substances in terms of their potential implication in a combustion process, such as the influence of the relative humidity of the combustion air when dealing with a gaseous substance. For example, R1234ze(E) gas can indeed be declared as 'non-flammable' by application of ISO 10156 (2017) (GHS regulation), slightly flammable (according to ASHRAE standard), and even rated as "extremely flammable" by application of EN 1839 (2017)/Annex A (2017) in the context of the European Chemicals Directive.

Even more critical is the fact that in the case of halogenated liquids, some of them although potentially falling outside of the class of flammable liquids according to international classification schemes for dangerous substances (CLP in the EU, other legal texts transposing the GHS in other parts of the world). Such substances are often subsequently abusively rated as nonflammable but however may develop an explosive atmosphere risk from mixture of their vapors in air at ambient conditions: this was clearly illustrated in this work with ethoxy-nonafluoroethane.

For halogenated liquids, the small volume of the test vessels proposed by the experimental flash point methods associated with the outgassing phenomenon can lead to some of these liquids being claimed as non-flammable ("false negatives") and thus underestimate the risk of

Table 10

LEL determination of ethoxy-nonafluorobutane in according to annex A EN 1839 / 50% RH.

Concentration (%vol)	3,0	3,4	3,6	3,8
Tube temperature (°C)	38	38	38	38
Moisture (%RH)	49,7	50,2	50,9	50,9
Ignition?	No	No	Yes	Yes

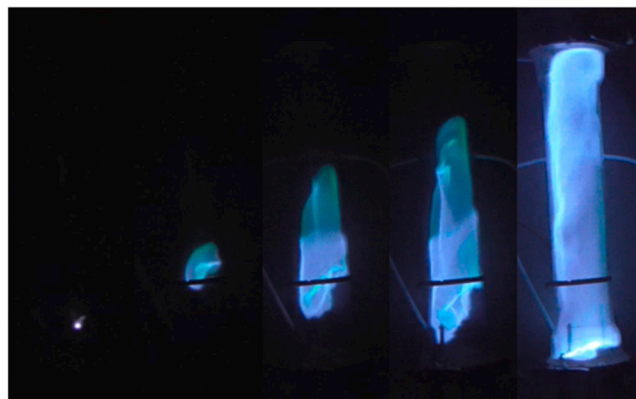


Fig. 11. LEL- Flame development (left to right) in the tube of mixture air/ ethoxy-nonafluorobutane (vapor 3,6%vol in air) after spark generation.

explosion and fire that these liquids may present. For example, in the context of storage, we have been able to demonstrate that a sufficiently energetic ignition source can ignite the gas overhead of a liquid classified as non-flammable at much lower temperatures than hydrocarbons classified as highly flammable. It is therefore essential not to rely solely on the flash point to characterize the flammability of these liquids, but also, and more importantly, to assess the lower explosion point and/or the explosive limits.

These substances are considered difficult to ignite because they have a high minimum ignition energy (several joules compared to a few millijoules for hydrocarbons) and a large flame extinction distance characterized by a high maximum experimental safety gap (MESG) (Takizawa, 2015; Askar et al., 2018; Kim et al., 2018), to which must be added the influence of ambient air humidity on their combustion. As revealed by this work, complexity of combustion behavior of halogenated substances often requires expert judgement to select appropriate flammability assessment methods of such chemicals among all available testing protocols referenced by applicable regulations and other guiding documents in the field. In addition to the risks associated with their flammability, there is also the problem of toxic risk from the products resulting from their combustion, such as hydrogen fluoride (HF), which is also very corrosive in an aqueous medium) and carbonyl fluoride (COF₂).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was supported by the French Ministry of Energy Transition.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the

online version at [doi:10.1016/j.psep.2023.04.046](https://doi.org/10.1016/j.psep.2023.04.046).

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