Experimental Determination of Flash Points of Flammable Liquid Aqueous Solutions

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The flash point is considered as a determinant parameter to classify the flammable liquids, regarding the European CLP regulation, as well as the transport of dangerous goods regulation.
In the case of some low concentrated flammable liquid aqueous solutions, the existence of a flash point is not very well defined, and their flammability is not precisely known.
The experimental measurements of flash points are described in numerous national or international standards, which differ by their range of validity and by the specified experimental conditions.
The flash point of ethanol, acetone, acetic acid and formic acid aqueous solutions was measured using Abel and Pensky-Martens in close cup methods, chosen regarding predicted values of flash point.
Results obtained show that, for the most flammable products, such as acetone or ethanol, weakly concentrated aqueous solutions still remains flammable. In the case of acetic or formic acid aqueous solutions, a threshold concentration can be determined under which the solutions are considered as non flammable, regarding the European CLP regulation and the transport of dangerous goods regulation.

1. Principle of flash point determination

The flash point is defined as the lowest temperature at which a liquid generates flammable vapours which can be ignited in air by a flame above its surface. The flash point is determined experimentally by heating a vessel containing the tested liquid. A flame is presented at regular intervals to the liquid surface. If a flash occurs in the vessel, it indicates that the temperature of the tested liquid has reached (or exceeded) the flash point. The test vessel can be open or close. The flash point is then measured respectively in "open-cup" or in "closed-cup".
The experimental determination of flash point is described in many national and international standards, which differ in their scope and in the specified experimental conditions.
The value of the flash point is a key parameter for the flammable liquids classification, as defined in European CLP Regulation (EC, 2008).
However, it should be noted that the flash point is not sufficient to assess the risk associated to the use or the storage of a flammable liquid in conditions of liquid-vapour equilibrium.
Indeed, in a closed container, liquid-vapour equilibrium can be established. In this case, the atmosphere in the container consists of a homogeneous mixture of vapour and air and, if the vapour concentration is included in the flammability range, comprised between the lower flammability limit (LFL) and the upper flammability limit (UFL), an explosive atmosphere is present in the closed container.
The lower point of explosion (LPE) of a liquid is defined as the temperature at which the concentration of vapours emitted by this liquid, in thermodynamic liquid-vapour equilibrium conditions and when mixing with air at atmospheric pressure, is equal to the lower flammability limit (LFL).
As showed on Figure 1, the lower point of explosion (LPE) is only a few K below the flash point in the case of pure liquids. This difference may be one to three tens of K in the case of different volatilities liquid mixtures.

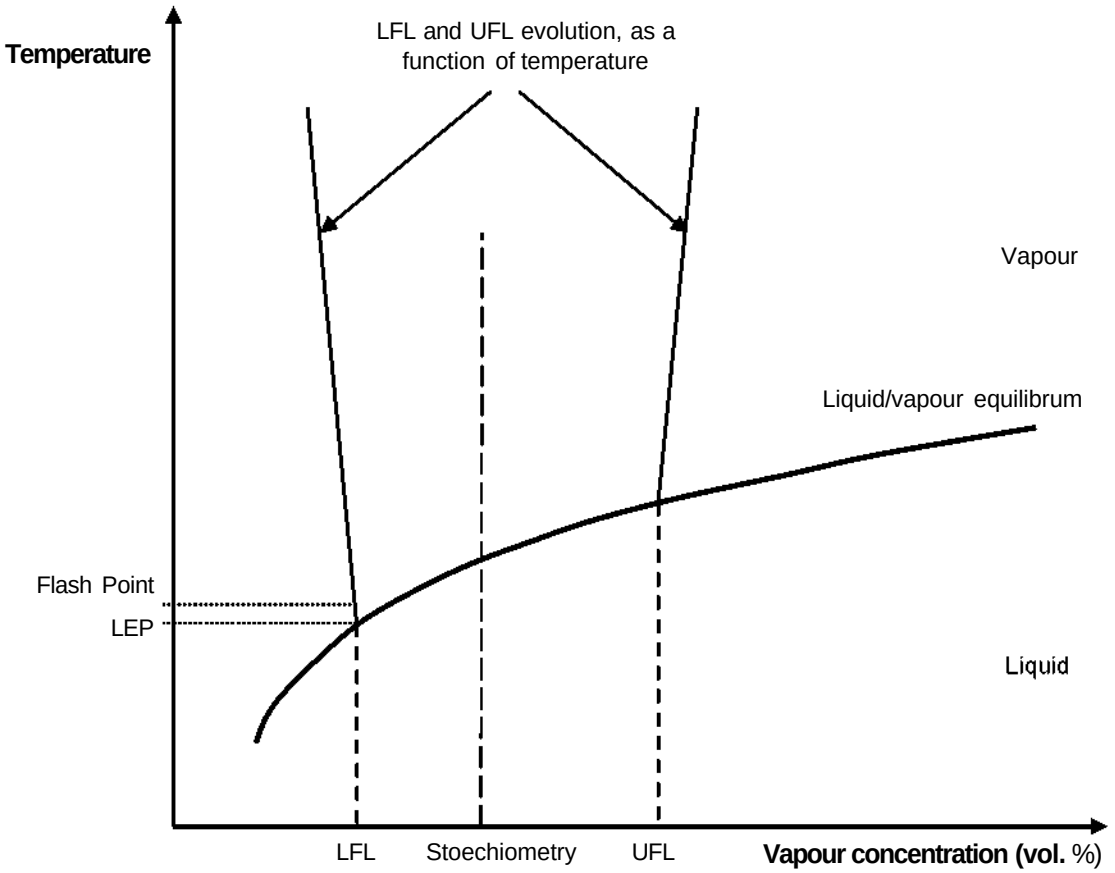


Figure 1: Graphical representation of the influence of temperature on the flammability of the vapour/air homogeneous mixture in a closed vessel containing a flammable liquid, under atmospheric pressure (Chaineaux et al., 2009)

This difference is related to the operating conditions for measuring the flash point, whatever the standard applied. Even in the case of determinations in closed-cup, the conditions of the liquid-vapour equilibrium cannot be satisfied at the time of presentation of the flame to the liquid surface.
Therefore, beyond the issue of regulatory classification of flammable liquids, to assess the risk of formation of an explosive atmosphere in a flammable liquid closed container, it is wise to consider the lower point of explosion (LPE). If this information is not known, it is possible to rely on the flash point, retaining a safety margin of a few K for a pure liquid, and up to 30 K for a mixture of different volatilities liquids.

2. Experimental

Materials tested and methods used are described below.

2.1 Methods used for experimental measurement of flash points

The experimental determination of flash points of flammable liquid solutions was performed using two methods, depending on their scope:

- Abel closed-cup method: EN ISO 13736 (ECS, 2008) standard, and
- Pensky-Martens closed-cup method: EN ISO 2719 (ECS, 2003) standard.

Abel closed-cup method is applicable to combustible liquids having flash points between - 30.0 °C and 70.0 °C, inclusive.
INERIS manual Abel apparatus is presented on Figure 2.



Figure 2: View of INERIS manual Abel closed-cup flash point apparatus

The experimental parameters prescribed are the following:

- Heating rate of the test portion in the cup: 1°C/min,
- Stirring speed: 30 r/min, in a clockwise rotation. Stirring must be continuing for the duration of the test, but not during the application of the test flame,
- The test flame must be applied every 0.5 °C rise in temperature,
- The temperature read at the time the test flame application caused a distinct flash in the interior of the test cup must be recorded as the observed flash point.

Presumed flash point between - 30 and 18.5 °C:

- When the temperature of the test portion reaches ~35 °C or at least 9.0 °C below the expected flash point, the test flame must be applied for the first time,
- The first flame presentation for the following tests must be performed when the temperature of the test portion reaches ~35 °C or 17.0 °C below the observed flash point.

Presumed flash point between 19 and 70 °C:

- When the temperature of the test portion reaches 10 °C or at least 9.0 °C below the expected flash point, the test flame must be applied for the first time,
- The first flame presentation for the following tests must be performed when the temperature of the test portion reaches 10 °C or 17.0 °C below the observed flash point.

Pensky-Martens closed-cup method is applicable to combustible liquids, liquids with suspended solids, liquids that tend to form a surface film under the test conditions and other liquids. It is applicable for liquids with a flash point above 30 °C.

- Procedure A is used for the determination of the flash point of paints and varnishes that do not form a surface film, unused lubricating oils and other petroleum products not covered by Procedure B.
- Procedure B is used for the determination of the flash point of residual fuel oils, cutback bitumens, used lubricating oils, liquids that tend to form a surface film, liquids with suspensions of solids and highly viscous materials such as polymeric solutions and adhesives.

INERIS manual Pensky-Martens apparatus is presented on Figure 3 below.



Figure 3: View of INERIS manual Pensky-Martens closed-cup flash point apparatus

The experimental parameters prescribed are the following:

- Heating rate of the test portion in the cup: up 5 to 6°C/min,
- Stirring speed: up 90 to 120 r/min, in a clockwise rotation,
- The temperature read at the time the test flame application caused a distinct flash in the interior of the test cup must be recorded as the observed flash point.
- When the temperature of the test portion reaches 23 °C below the expected flash point, the test flame must be applied for the first time,
- The test flame must be applied every 1 °C rise in temperature if the flash point is less than or equal to 110 °C and every multiples of 2 temperatures if the flash point is greater than 110 °C.

2.2 Materials tested

The flammable liquids selected for these tests are listed in Table 1. It also indicates the method used for the flash point measurement. These liquids come from chemicals suppliers. Aqueous solutions were prepared at INERIS.

Table 1: List of liquids selected for the tests and method used

Flammable liquid	Purity	Flash point measurement method used
Acetone	99.5 %	EN ISO 13736 - Abel in closed cup
Ethanol	96°/	EN ISO 13736 - Abel in closed cup
	99.5 %	EN ISO 13736 - Abel in closed cup
Acetic acid	99- 100%	EN ISO 2719 Method A - Pensky-Martens in closed cup
Formic acid	99°/	EN ISO 2719 Method A - Pensky-Martens in closed cup

3. Results

Table 2 below summarizes the results of experimentally determined flash points.

Table 2: Results of flash point measurement on different aqueous solutions

Concentration (vol. %)	Flash points measured (°C)				
	Commercial acetone solutions	96 % commercial ethanol solutions	99.5 % commercial ethanol solutions	Commercial acetic acid solutions	Commercial formic acid solutions
100	-23.5	13.5	10.0	39.5	52.0
95	*	*	*	44.5	*
90	-21.0	17.5	15.5	51.0	62.0
85	*	*	*	54.0	*
80	-19.5	19.5	17.5	59.0	72.0
75	*	*	*		*
70	*	21.5	20.0		
60	-15.0	22.5	21.5		
50	-12.5	24.5	23.5		
40	-9.5	27.0	26.0	No flash point	No flash point
30	-5.0	31.5	30.0		
20	3.0	39.0	36.5		
10	16.0	50.5	48.0		
5	29.5	68.0	*		

*: Not measured

4. Impact on classification as flammable liquids of solutions tested

The classification as "flammable liquids" of aqueous solutions studied depends on the value of flash point. Table 3 indicates classification criteria, according to current regulations.

Table 3: Classification criteria for flammable liquids used in current regulations, based on ebullition temperature and flash point value

Flash point	≤ 0 °C	≤ 21 °C	≤ 23 °C	≤ 55 °C	≤ 60 °C	≤ 100 °C
CLP Regulation (EC,2008)	 If Teb<35°C: - Flammable liquid Cat. 1 - Danger - H224 If Teb > 35°C: no pictogram - Flammable liquid Cat. 2 - Danger - H225			 Flammable liquid Cat. 3- Warning - H226		Not considered as a « Flamable liquid »
European Dangerous substances (EC, 1967)and preparation (EC, 1999) Directives	If Teb<35°C:  -  Extremely flammable - R12 If Teb>35°C: Flammable - R11	Easily flammable - R11	No pictogram - Flammable - R10		Not considered as a « Flamable liquid »	

- Teb: ebullition temperature
- Hazard statements:
  - R12: Extremely flammable
  - R11: Easily flammable
  - R10: Flammable
  - H224: Very highly flammable liquid and vapour
  - H225: Highly flammable liquid and vapour
  - H226: Flammable liquid and vapour

The results obtained show that, for the most flammable products such as acetone and ethanol, flash points of aqueous solutions containing only a few % flammable liquid remain below the classification as flammable liquid threshold. Nevertheless, it is specified in the CLP regulation (EC, 2008) that liquids with a flash point of more than 35°C need not be classified in Category 3 if negative results have been obtained in the sustained combustibility test L.2, Part III, section 32 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria (UNO, 2009). This may allow the exclusion of these solutions of the flammable liquids class.

In the case of solutions of acetic and formic acids, the concentration below which the aqueous solution is no longer classified as flammable is much higher, i.e. between 75 and 80 % for acetic acid and between 90 and 100 % for formic acid.

5. Conclusion

This work has been devoted to the study of the flammability of aqueous solutions of some common flammable liquids, by characterizing their flash points at various concentrations.

These values are necessary for the classification of flammable liquids, which is based on flash point and ebullition temperatures.

However, these values should be used with caution if they are used to assess the safety of a process in which equilibrium conditions can be reached. In this particular case, it is safer to use lower explosion point (LEP) instead of flash point.

References

Chaineaux J., Janès A., Sallé B., Petit J.M., 2009, Conditions de formation d'une atmosphère explosive lors de la mise en œuvre d'un liquide inflammable - ND 2313-216-09, Hygiène et Sécurité du Travail, 16,23-31, INRS, Paris, France.

European Commission (EC), 1967, Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances, Official Journal of European Community 196, 1-98, EC, Brussels, Belgium.

European Commission (EC), 1999, Directive 1999/45/EC of the European Parliament and of the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations, Official Journal of European Community L200, 1-68, EC, Brussels, Belgium.

European Commission (EC), 2008, Regulation 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) 1907/2006, Official Journal of European Community L 353, 1-1355, EC, Brussels, Belgium.

European Committee for Standardization (ECS), 2003, EN ISO 2719, Determination of flash point - Pensky-Martens closed-cup method, ECS, Brussels, Belgium.

European Committee for Standardization (ECS), 2008, EN ISO 13763, Determination of flash point-Abel closed-cup method, ECS, Brussels, Belgium.

United Nations Organization (UNO), 2009, Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, ST/SG/AC.10/11/Rev.5, UNO, Geneva.