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FIRE SAFETY – DETERMINATION THE LOWER EXPLOSION LIMIT IN EXPLOSION CHAMBER FOR SELECTED FLAMMABLE LIQUIDS

Abstract: *This article describes the experiments in explosion chamber VK 100. The chamber is used to determine the lower explosive limit (LEL) of selected aliphatic alcohols (methanol, ethanol) as flammable liquids. First, the calculations of the volume of flammable liquid necessary for setting LEL were carried out. Secondly, the lower explosive limit of methanol and ethanol was determined experimentally. We compared them with the technical characteristics of fire safety data sheets. All two aliphatic alcohols (methanol, ethanol) are considered as fuels.*

Key words: flammable liquids vapours, lower explosive limit, methanol, ethanol, alcohol fuels, explosive chamber.

INTRODUCTION

Although fossil fuels have become the dominant energy resource in the modern world, alcohol has been used as a fuel throughout the history. The aliphatic alcohols - methanol and ethanol - are of interest as fuels because they can be synthesized chemically or biologically, and they have characteristics which allow them to be used in current engines. Mutual characteristics for all four alcohols is their high octane rating.
Determination of the lower explosivene limit (LEL) has an extraordinary importance for the assessment of explosion danger inside technological systems with explosive atmosphere which is formed by flammable liquid vapours, such as methanol, ethanol and air oxygen. Knowledge of the LEL value is directly used to determine the atmosphere, with respect to fire danger or flammable liquid vapours explosion, according to technical standard STN EN 1127-1 Explosive atmospheres.

EXPLOSION

An explosion can occur in a closed area if a finely dispersed flammable material in sufficient concentration is blended with an oxidizing agent. In addition, a sufficiently strong source of initiation must be present. Flammable material may be flammable gas, flammable liquid vapour or mist, stirred flammable dust or a combination of these materials called hybrid blend [1].

The measurement method for determining the lower explosivene limit is based on the ability of flammable liquid vapours to burn explosively with oxygen after they have been ignited by a source of ignition. The lower explosiveness limit is the minimum concentration of the flammable liquid vapours with an oxidizer, which enables the spread of the explosive burning. It forms the boundary between an explosive and non explosive mixture. It is a number determining the minimum amount of homogeneously dispersed combustible matter in an oxidizing atmosphere (air) that, after being initiated by a sufficiently powerful initiation, is able to develop a temperature high enough to ignite next, not yet reacting layers of the mix [1].

THE AMOUNT OF THE EXPLOSIVE MIXTURE

The density of flammable liquid vapours with air is given by the pressure of liquid vapours, which depend on the temperature. Vapours of a liquid methanol and ethanol, with lower density than of the air, rise faster since their density is lower. During this process, they gradually mix with air. The coefficient of diffusion determines the amount of an explosive mixture in a closed space, only if there is no air flow. In case of the air flow, this amount is influenced especially by convection.

The formation of an explosive atmosphere is influenced by operating conditions - if the material is in closed space, if there is an outflow possibility, aerating or the spatial distribution. For example, we must take into account the presence of flammable materials and mixtures in spaces which are not ventilated enough, such as holes, sewers and shafts. In case of gases and vapours, even small air ventilation (a natural draught, movement of a person) can cause air to mix with combustible substances [2].

In case of liquids such as methanol and ethanol, the surface area of vaporization and the working temperature have influence on the formation of an explosive atmosphere.

LIQUID VAPOURIZATION IN A STAGNANT ENVIRONMENT

Vaporization of flammable liquids, such as methanol and ethanol, into a stagnant environment is called molecular diffusion. It is a relatively slow process, which does not enable the liquid vapours to spread to large distances. On the contrary, it enables the vapour to concentrate at its source, and hence creating local explosive concentrations.

The concentration change above the surface can be described by the formula as in Eqn. (1),

$$c = a \,.\, y^n + b \tag{1}$$

Where:

c - vapour concentration at the considered point over the flammable liquid surface [volume %]

y - distance of the considered point from the origin of the coordinate system [m]

a, b - constants, which can be defined from the boundary conditions [-]

LABORATORY PART

Experimental equipment VK 100

Explosive Chamber VK 100 is a cubic. Its length l is less or equal to two diameters d : $l \leq 2.d$. With the increasing capacity of the vessel decreases the rapidity of explosive pressure growing. In case of cubic vessels, this characteristic is described by the so-called Cubic relation as in Eqn. (2),

$$\left(\frac{dp}{dt}\right)_{\max} .V^{\frac{1}{3}} = konst. = K_G, resp. K_{St} \tag{2}$$

where:

(dp/dt)max - the maximum speed of the explosive pressure growth [$MPa.s^{-1}$] or [$bar.s^{-1}$]

V - capacity of the vessel [m^3]

K(G), K(St) - cubic constant for gases or dusts [$MPa.m.s^{-1}$] or [$bar.s^{-1}$]

This cubic constant can be a technically safety parameter if the following conditions are satisfied – the optimal concentration of explosive mixture, the same shape of the vessel, the same rate of mixture turbulence and the same kind and energy of the initiating source - as it is the case with VK 100. Validity of the cubic relation according to [3] in case of flammable liquids vapour mixtures begins from a vessel capacity 5 l and in the case of dust-air mixtures from a capacity 40 l.

Description of the technical apparatus for measuring the lower explosive limit and the explosiveness volume- area

The technical apparatus for the lower explosive limit measuring - explosion chamber VK 100 - is laboratory equipment for the determination of explosiveness limits of flammable liquid vapours. The equipment has a frame construction, the chamber itself is on the upper part of the frame; on the bottom part, there are the pneumatic valves, the stirring equipment, the explosion source, the fire extinguishing equipment and the additional electronics.

Inside the chamber, there is a heating plate which can be taken out and which serves the evaporation of the tested liquid. This plate is powered by 24 VAC, the temperature is scanned by a thermocouple and regulated by a HT60B regulator (Figure 1, 2).

Two high voltage electrode leads aimed at initiation are inserted into the chamber inner space. The chamber has further a gas input, an electro valve for flammable liquid gases stirring, an electro valve for chamber cleaning and an electro valve of the fire extinguishing equipment. Inside the chamber, an intensive streaming can be carried out by the use of a blender with variable rotation speed. The device control is provided by an external desk, where the operating elements are placed in vertical plane. Their functions are mutually locked-out in the particular modes. This allows a safe operation and forecloses an accidental hanging.

Figure 1. *Operator control unit VK 100*

Figure 2. *Inner space of VK 100*

EXPERIMENTAL SUBSTANCE - METHANOL AND ETHANOL - FLAMMABLE LIQUIDS BELONGING TO ALCOHOL GROUP

Methanol is mainly produced from natural gas, although it can be produced from biomass using very similar chemical processes. Ethanol is commonly produced from biological material though fermentation processes. When obtained from biological materials and/or biological processes, they are known as bioalcohols (e.g. bioethanol). There is no chemical difference between biologically produced and chemically produced alcohols [4].

Methanol and ethanol can be both derived from fossil fuels, biomass, or perhaps most basically, from carbon dioxide and water. Ethanol has most commonly been produced through fermentation of sugars, while methanol has most commonly been produced from synthesis gas, but there are more modern ways to obtain these fuels. Methanol is the simple molecule, whereas ethanol can be made from methanol and produced industrially from nearly any biomass, including animal waste, or from carbon dioxide and water or steam by first converting the biomass into synthesis gas in a gasifier. It can also be produced in a laboratory using electrolysis or enzymes [4].

For industrial use, ethanol is produced by a reaction of ethylene with sulphuric acid, by catalytic hydratation of ethylene and by synthesis from fossil materials or gas. The so-called ethanol fermentation and the following distillation of ethanol is another method. Ethanol is the basic component of alcoholic drinks. Also, it is used as solvent (medicines, cosmetics, cleaning and disinfecting agents, etc.) and as a base material for further processing (acetaldehyde, butadiene, diethyl ether, ethylene, vinegar, etc.) [4].

Table 1. *Basic characteristics of methanol [5]*

molecular formula	CH_3OH	structural formula	H_3C-OH
CAS number	67-56-1	molecular weight	30,04 $g{\cdot}mol^{-1}$
melting temperature	- 97°C	boiling temperature	64,7°C
density at 20°C	791,8 $kg{\cdot}m^{-3}$	vaporization heat	1098,94 $kJ{\cdot}kg^{-1}$
heat of formation	- 239,2 $kJ{\cdot}mol^{-1}$	combustion heat	22,68 $MJ{\cdot}kg^{-1}$
LEL	6,0 volum %	UEL	36,5 volume%
flash temperature	12°C	self-ignition temperature	464°C

Table 2. *Basic characteristics of ethanol [5]*

molecular formula	C_2H_5OH	structural formula	CH_3-CH_2-OH
CAS number	64-17-5	molecular weight	46,07 $g{\cdot}mol^{-1}$
melting temperature	-114,15°C	boiling temperature	78,39°C
density at 20 °C	789,42 $kg{\cdot}m^{-3}$	vaporization heat	836,99 $kJ{\cdot}kg^{-1}$
heat of formation	- 277,6 $kJ{\cdot}mol^{-1}$	combustion heat	29,67 $MJ{\cdot}kg^{-1}$
LEL	3,5 volume %	UEL	15 volume%
flash temperature	13°C	self-ignition temperature	363°C

Formula of 1 mol fuel complete combustion is as in Eqn. (3),

$$C_2H_5OH+3O_2+11{,}28N_2 \xrightarrow{-1366{,}83\ kJ} 2CO_2+3H_2O+11{,}28N_2 \qquad (3)$$

Aerosols of liquids and mists create drops with a size less than 1 mm. Practically, there are often aerosols and mist drops with proportions of 0,001 mm and 0,1 mm. In case of gases and superheated vapours of flammable liquids in mixtures with air, oxygen, chlorine and other oxidizing agents, an explosion hazard threatens if:

Safety factors are usually considered as in Eqn. (4),

$$k_{B1} \cdot LEL < c_{SKUT} < k_{B2} \cdot UEL \qquad (4)$$

k_{B1} = 0,5,
k_{B2} = 1,04 till 1,1 for low UEL rate
k_{B2} = 1,32 till 2,52 for high UEL rate (e.g. H_2, C_2H_2, CH_3OH.)

METHODS OF RESULTS ASSESMENT

Calculation method for the assessment of volume concentration for Methanol and Ethanol

The mode of evaluation is based on physical, chemical and dynamic principles of a liquid behaviour. Vapour concentration above the liquid surface is directly proportional to the saturated vapours pressure, as in Eqn. (5),

$$c_{SKUT} = \frac{p_n}{p_o} \cdot 100\% \qquad (5)$$

Where:
c_{skut} - vapour concentration [volume %]
p_n - liquid saturated vapours pressure [Pa]
p_0 - pressure of the surrounding [Pa]

The molar volume V_t at the temperature t_{PRAC} is used for calculation as in Eqn. (6),

$$V_t = V_o \cdot \frac{T_{PRAC}}{T_o} \frac{p_o}{p_{PRAC}} \qquad (6)$$

Where:
V_o = 22,4135 $m^3 \cdot kmol^{-1}$ (at T_0 and p_0)
p_o = $1{,}01325 \cdot 10^5$ Pa
$T_{PRAC} = t_{PRAC} + 273{,}15$ K
T_o = 273,15 K
t_{PRAC} - working temperature [°C]
p_{PRAC} - working pressure [Pa]

The calculation of the gas capacity results from the state equation of a perfect gas which has the form Eqn. (7),

$$p \cdot V = n \cdot R \cdot T \qquad (7)$$

whereas for the amount of substance n stands as in Eqn. (8),

$$n = \frac{m}{M} \qquad (8)$$

Because the liquid weight is a non-measurable quantity, it is necessary to express it via capacity and via density, using the formula as in Eqn. (9),

$$m_{kvap} = V_{kvap} \cdot \rho \qquad (9)$$

Through the combination of formulas (11) and (12), we get the final form of the formula for liquid volume calculation as in Eqn. (10),

$$V_{kvap} = \frac{V_{plyn} \cdot M \cdot p}{\rho \cdot R \cdot T} \qquad (10)$$

Where:
n - amount of substance [mol]
m - mass of the gas [g]
M - gram molecule of the gas [$g \cdot mol^{-1}$]
R - universal gas constant [8,314 $Pa \cdot m^3 \cdot K^{-1} \cdot mol^{-1}$]
T - gas temperature [K]
ρ - liquid density [$kg.m^{-3}$]
p - gas pressure [Pa]
V - gas volume at the given pressure and temperature [V]

The introduced mathematical procedure was used for the theoretic calculation of flammable liquids vapours concentration [6].

RESULTS AND DISCUSSION

Calculation Results of the needed volume V_{kvap} of the flammable liquid methanol for its LEL assessment are presented. The presented calculation is realised under the given conditions (Table 1.):
M = 30,04 $g \cdot mol^{-1}$
ρ = 791,8 $kg \cdot m^{-3}$
T = 20°C
$V_{\text{výbuchového priestoru}}$ = 100 l (volume of the outburst space)
On the basis of calculations, we get the results listed in Table 3.

Table 3. *Needed amount V_{kvap} for assessment of methanol LEL*

Measuring number	V_{kvap} [ml]	vapour capacity in the VK [m^3]	liquid mass [g]	LEL [volume %]
1.	8,83	0,0056	6,994	5,6
2.	8,99	0,0057	7,119	5,7
3.	9,15	0,0058	7,243	5,8
4.	9,31	0,0059	7,368	5,9
5.	9,46	0,0060	7,493	6,0

Table 4. *Experimental assessment of low explosiveness limit*

Measuring number	Flammable liquid ethanol amount [ml]	LEL [volume %]	Test results P- positive N- negative				
			Number of the experiment				
			1.	2.	3.	4.	5.
1.	8,83	5,6	P	P	P	P	P
2.	8,99	5,7	P	P	P	P	P
3.	9,15	5,8	P	P	P	P	P
4.	9,31	5,9	P	N	P	P	N
5.	9,46	6,0	N	P	P	P	P

On the basis of the experiments, the low explosiveness limit (LEL) for methanol was confirmed as 6,0 % volume. It corresponds to the literature by Wiley, VCH [5], stated in Table 1.
Calculation Results of the needed volume V_{kvap} of the flammable liquid ethanol for its LEL assessment are presented. The presented calculation is realised under the given conditions (Table 2.):
M = 46,07 $g \cdot mol^{-1}$
ρ = 789,42 $kg \cdot m^{-3}$
T = 20°C
$V_{\text{výbuchového priestoru}}$ = 100 l (volume of the outburst space)

On the basis of calculations, we get the results listed in Table 5.

Table 5. *Needed amount V_{kvap} for assessment of ethanol LEL*

Measuring number	V_{kvap} [ml]	Vapour capacity in the VK [m^3]	Liquid mass [g]	LEL [volume %]
1.	8,98	0,0037	7,087	3,7
2.	8,73	0,0036	6,895	3,6
3.	8,49	0,0035	6,704	3,5
4.	8,25	0,0034	6,512	3,4
5.	8,01	0,0033	6,320	3,3

Table 6. *Experimental assessment of low explosiveness limit*

Measuring number	Flammable liquid ethanol amount [ml]	LEL [volum %]	Test results P- positive N- negative				
			Number of the experiment				
			1.	2.	3.	4.	5.
1.	8,98	3,7	P	P	P	P	P
2.	8,73	3,6	P	P	P	P	P
3.	8,49	3,5	P	N	N	P	N
4.	8,25	3,4	N	N	P	N	N
5.	8,01	3,3	N	N	N	N	N

On the basis of the experiments, the low explosiveness limit (LEL) for ethanol was confirmed as 3,5 % volume It corresponds with the literature Wiley, VCH [5] stated in Table 2.

CONCLUSION

The measurement principle was used to create flammable liquid vapours with air oxygen and to produce an explosive system initiated by an energy source - starter. The purpose of the measuring was to find the minimum of a flammable liquid vapour or mist concentration in air, whereas an explosion spread occurs in the mixture at the given initiatory energy. Experiments were carried out by atmospheric pressure and the VK 100 chamber structural temperature. The results serve as the basis for technical protection systems in fire safety.

REFERENCES

[1] Damec, J.: Protivýbuchová prevencia [Explosion prevention]. SPBI Ostrava 2005, 188 p. ISBN 80-86111-21-0

[2] Mynarz, M .: Stanovení odezvy stavební konstrukce od výbuchu plynovzdušné směsi [Assessment of Response of Building Structure from Explosion of Gas-Air Mixture]. Paper proceedings XX. International Conference „Požární ochrana 2011“. SPBI Ostrava 2011, pp. 225-227. ISBN 978-80- 7385-102-6.

[3] Bebčák, A. – Serafín, J. - Damec, J. – Mynarz, M: Vliv inertních plynů na maximální výbuchové parametry hybridní směsi [Influence of Inert Gases on the Maximum Explosion Parameters of Hybrid Mixtures] Paper proceedings XX. International Conference „Požární ochrana 2011“. SPBI Ostrava 2011, pp. 10-13. ISBN 978-80- 7385-102-6.

[4] Alcohol fuel. Date (17.08.2011) The full text to web site http://en.wikipedia.org/wiki/Alcohol_fuel

[5] Wiley, V.CH. Ullman´s Encyclopedia of Industrial Chemistry – CD version. VI. Edition. Weinheim: Wiley-VCH, 2003. 30080 s. ISBN 3527303855.

[6] Groh, H.: Explosion Protection, Elsevier Butterworth-Heinemann Printed and bounded in Great Britain, 2004, 524 s. ISBN 0 7506 4777 9.

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BIOGRAPHY

Eva Mračková was born in Zvolen, Slovak Republic.
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ODREĐIVANJE DONJE GRANICE EKSPLOZIVNOSTI U KOMORI ZA SAGOREVANJE ZA POJEDINE ZAPALJIVE TEČNOSTI SA ASPEKTA ZAŠTITE OD POŽARA

Eva Mračkova

Apstrakt: *U radu je dat opis eksperimenata u komori za sagorevanje (eksplozivnoj komori) VK 100. Komora se koristi za određivanje donje granice eksplozivnosti (DGE) određenih alifatičkih alkohola (metanol, etanol) kao zapaljivih tečnosti. Najpre je izvršena kalkulacija količine zapaljivih tečnosti neophodnih za određivanje donje granice eksplozivnosti. Nakon toga, donja granica eksplozivnosti metanola i etanola je eksperimentalno utvrđena. Sva dva alifatična alkohola (kao što je methanol, etanol) se smatraju gorivima.*

Ključne reči: isparenja zapaljivih tečnosti, donja granica eksplozivnosti, metanol, etanol, alkoholna goriva, komora za sagorevanje (eksplozivna komora).