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SELECTED ALIPHATIC ALCOHOLS AS FLAMMABLE LIQUIDS AND THE DETERMINATION OF THEIR LOWER EXPLOSIVE LIMITS

There are specified the volumes of flammable liquids (methanol, ethanol, 1-butanol) by calculation and their experimental determination of lower explosion limits was investigated in this paper. We compared them then with the technical characteristics of fire safety data sheets. The reliability of technical equipment VK 100 was confirmed by methodology.

Key words: explosive chamber, lower explosiveness limit, flammable liquids vapours, aliphatic alcohols, alcohol fuels

1. Introduction

Although fossil fuels have become the dominant energy resource for the modern world, alcohol has been used as a fuel throughout history. The aliphatic alcohols, methanol, ethanol, and 1-butanol 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. One advantage shared by all three alcohols is their high octane rating.

Determination of the lower explosiveness limit (LEL) has an extraordinary importance for the assessment of explosion danger inside technological systems, where an explosive atmosphere is present formed by flammable liquid vapours as are methanol, ethanol and 1-butanol, 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.

2. Knowledge about an explosion

An explosion can occur under a condition if in a closed area 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’s vapour or mist, stirred flammable dust or a combination of these materials called hybrid blend [1].

The measurement method for determining the lower explosiveness 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 initiating by a sufficiently powerful initiation is able to develop a temperature high enough to ignite next, not yet reacting layers of the mix [1].

3. The amount of the explosive mixture

The density of flammable liquid vapours with air is given by the pressure of liquid’s vapours, which depend on temperature. Vapours of a liquid methanol, ethanol and 1-butanol with lower density than the air rise faster the lower is their density. During this process they gradually mix with air. The coefficient of diffusion determines the amount of an explosive mixture in closed space only if in this space there is no air flow. In the case of air flow the amount is influenced especially by convection.

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

In the case of liquids as are methanol, ethanol and 1-butanol, the surface area of vaporization and the working temperature have also influence on the formation of an explosive atmosphere.

4. Liquids vapourization into a stagnant environment

Vaporization of flammable liquid as are methanol, ethanol and 1-butanol into a stagnant environment is called molecular diffusion. It is a relatively slow process, which unables the liquid's vapours to spread to large distances. On the contrary, it enables the vapour to concentrate at its source and hence it leads to creation of local explosive concentrations.

The concentration change above the surface can be described by the formula:

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

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 [-].

5. Laboratory Part

5.1. Experimental equipment VK 100

Explosive Chamber VK 100 is a cubic. Its length l is less or equal to two diameters d : 1 ≤ 2.d. With the increasing capacity of the vessel decreases the rapidity of explosive pressure's growing. This characteristic is in the case of cubic vessels described by the so-called cubic relation:

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

where:

$\left(\frac{dp}{dt}\right)_{\max}$ – the maximum speed of the explosive pressure's growth $[\mathrm{MPa} \cdot \mathrm{s}^{-1}]$ or $[\mathrm{bar{\cdot}s}^{-1}]$,

V – capacity of the vessel $[\mathrm{m}^3]$,

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

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's turbulence, the same kind and energy of the initiating source as realised in the VK 100. Validity of the cubic relation according to [3] in the case of flammable liquids vapour mixtures begins from vessel's capacity 5 l and in the case of dust-air mixtures from capacity 40 l.

5.2. Description of the technical apparatus for measuring the lower explosiveness limit and in the explosiveness extent

The technical apparatus for the lower explosiveness 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 electrical.

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 (Fig. 1, 2).

Two high voltage electrode leads aimed at initiation are inserted to the chamber's s inner space. The chamber has further a gas input, an electrovalve for flammable liquid gases stirring, an electrovalve for chamber cleaning and an electrovalve 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 safe operation and forecloses an accidental hanging.

Fig. 1. *Operator control unit with HT60B*

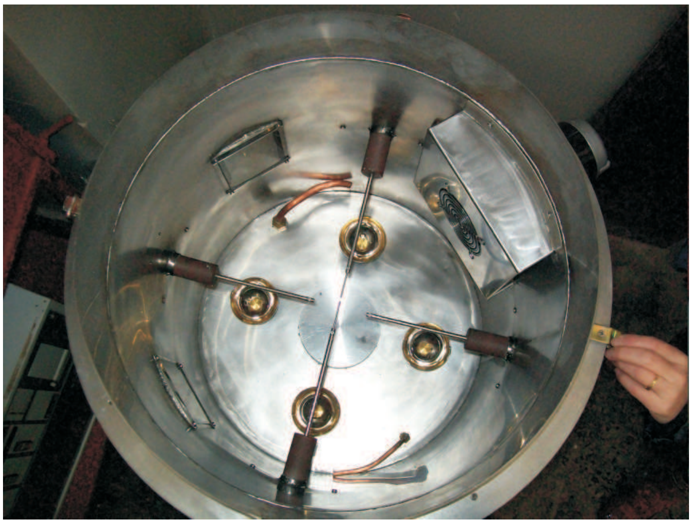

Fig. 2. *Inner space VK 100*

6. Experimental substance Methanol, Ethanol and 1-butanol – a flammable liquid belonging to alcohol group

Most methanol is 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 both be derived from fossil fuels, biomass, or perhaps most simply, from carbon dioxide and water and ethanol has most commonly been produced through fermentation of sugars, and methanol has most commonly been produced from synthesis gas, but there are more modern ways to obtain these fuels. Methanol is the simpler molecule, and ethanol can be made from methanol, can be produced industrially from nearly any biomass, including animal waste, or from carbon dioxide and water or steam by first converting the biomass to 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 to asked purity is another method. Ethanol is the basic component of alcoholic drinks. It is also used as solvent (medicines, cosmetics, cleaning and disinfecting agents, etc.) and as base material for further processing (acetaldehyde, butadiene, diethyl ether, ethylene, vinegar, etc.) [4]

Butanol is considerably less toxic and less volatile than methanol. In particular, butanol has a high flash point of 35°C, which is a benefit for fire safety, but may be a difficulty for starting engines in cold weather. Energy Environment International developed a method for producing butanol from biomass, which involves the use of two separate micro-organisms in sequence to minimize production of acetone and ethanol byproducts [4].

Table 1. Basic characteristics of methanol [5]

Molecular formula	**CH_3OH**	**Structural formula**	**$H_3C\text{-}OH$**
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 volume, %	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·mol^{-1}
melting temperature	–114,15°C	boiling temperature	78,39°C
density at 20°C	789,42 kg·m^{-3}	vaporization heat	836,99 kJ·kg^{-1}
heat of formation	–277,6 kJ·mol^{-1}	combustion heat	29,67 MJ·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:

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

Table 3. Basic characteristics of 1-butanol [5]

Molecular formula	**C_4H_9OH**	**Structural formula**	**$CH_3(CH_2)_2CH_2$-OH**
CAS number	71-36-3	molecular weight	74,12 g·mol^{-1}
melting temperature	–89,3°C	boiling temperature	117,73°C
density at 20°C	809,8 kg·m^{-3}	vaporization heat	584,05 kJ·kg^{-1}
heat of formation	–327,3 kJ·mol^{-1}	combustion heat	36,1 MJ·kg-1
LEL	1,4 volume, %	UEL	11,2 volume, %
flash temperature	29°C	self-ignition temperature	343°C

Aerosols of liquids and mists create drops with a size less than 1 mm. Practically there are often aerosol and mist drops with proportions of 0,001 mm and 0,1 mm. In the 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:

$$k_{B1} \cdot LEL < c_{skut} < k_{B2} \cdot UEL \quad (4)$$

$k_{B1} = 0,5$,
$k_{B2} = 1,04$ 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).

7. Methods of results assesment calculation method for the assesment of volume concentration for methanol, ethanol and 1-butanol

The mode of evaluation is based on physical, chemical and dynamic principles of a liquid's behaviour. Vapours concentration above the liquid's surface is directly proportional to the saturated vapours pressure

$$c_{skut} = \frac{p_n}{p_o} \cdot 100\% \tag{5}$$

where:
c_{skut} – vapour concentration [volume %],
p_n – liquid's saturated vapours pressure [Pa],
p_o – pressure of the surrounding [Pa].

The molar volume V_t at the temperature t_{PRAC} is to calculate:

$$V_t = V_o \cdot \frac{T_{PRAC}}{T_o} \frac{p_o}{p_{PRAC}} \tag{6}$$

where:
V_o = 22,4135 $m^3 \cdot kmol^{-1}$ (at T_o and p_o),
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's capacity results from the state equation of a perfect gas which has the form:

$$p \cdot V = n \cdot R \cdot T \tag{7}$$

whereas for the amount of substance n stands:

$$n = \frac{m}{M} \tag{8}$$

Because the liquid's weight is a non-measurable quantity it is necessary to express it via capacity and via density using the formula:

$$m_{kvap} = V_{kvap} \cdot \rho \tag{9}$$

Through the combination of formulas (11) and (12) we get the final form of the formula for liquid’s volume calculation:

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

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]
P – liquid density [$kg \cdot m^{-3}$]
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 liquid’s vapours concentration [6].

8. 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):

$M = 30{,}04\ g \cdot mol^{-1}$
P $= 791{,}8\ kg \cdot m^{-3}$
$T = 20°C$
$V_{výbuchového\ priestoru} = 100\ l$ (volume of the outburst space)

On the basis of calculations we get the results listed in Table 4.

Table 4. Needed amount V_{kvap} for assessment of methanol LEL

Measuring number	V_{kvap} [ml]	Vapour capacity in the *VK* [m³]	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 5. 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 basis of the experiments the low explosiveness limit (LEL) for methanol was confirmed as 6,0 volume %. It corresponds with the literature 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):
$M = 46{,}07\ \mathrm{g \cdot mol^{-1}}$
$\mathrm{P} = 789{,}42\ \mathrm{kg \cdot m^{-3}}$
$T = 20°\mathrm{C}$
$V_{\text{výbuchového priestoru}} = 100\ \mathrm{l}$ (volume of the outburst space)

On the basis of calculations we get the results listed in Table 6.

Table 6. Needed amount V_{kvap} for assessment of ethanol LEL

Measuring number	V_{kvap} [ml]	Vapour capacity in the *VK* [m³]	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 7. 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.	8,98	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 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.

Calculation Results of the needed volume V_{kvap} of the flammable liquid 1-butanol for its LEL assessment are presented. The presented calculation is realised under the given conditions (Table 3):

$M = 74{,}12\ \mathrm{g \cdot mol^{-1}}$

$\mathrm{P} = 809{,}8\ \mathrm{kg \cdot m^{-3}}$

$T = 20\ °\mathrm{C}$

$V_{\text{výbuchového priestoru}} = 100\ \mathrm{l}$ (volume of the outburst space)

On the basis of calculations we get the results listed in Table 8.

Table 8. Needed amount V_{kvap} for assessment of 1-butanol LEL

Measuring number	V_{kvap} [ml]	Vapour capacity in the VK [m^3]	Liquid mass [g]	LEL [volume, %]
1.	5,71	0,0015	4,622	1,5
2.	5,33	0,0014	4,314	1,4
3.	4,95	0,0013	4,006	1,3
4.	4,57	0,0012	3,698	1,2
5.	4,19	0,0011	3,390	1,1

Table 9. 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.	5,71	1,5	P	P	P	P	P
2.	5,33	1,4	P	N	P	P	N
3.	4,95	1,3	N	N	N	N	N
4.	4,57	1,2	N	N	N	N	N
5.	4,19	1,1	N	N	N	N	N

On basis of the experiments the low explosiveness limit (LEL) for ethanol was confirmed as 1,4 volume %. It corresponds with the literature Wiley, VCH [5] stated in Table 3.

9. Conclusion

The measurements principle was 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 whereat in the mixture at the given initiatory energy an explosion spread occurs. Experiments were carried out by atmospheric pressure and the VK 100 chamber's structural temperature.

Acknowledgement

The author wishes to thank for the financial support of the grant project GD 1/0436/09.

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SUMMARY

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SELECTED ALIPHATIC ALCOHOLS AS FLAMMABLE LIQUIDS AND THE DETERMINATION OF THEIR LOWER EXPLOSIVE LIMITS

The explosion Chamber VK 100 is introduced in the paper, in which we determined the lower explosive limits (LEL) of selected aliphatic alcohols as flammable liquids methanol, ethanol, 1-butanol. First, the calculations of the volume of flammable liquid necessary for setting of LEL were carried out. Next, the lower explosive limit of methanol, ethanol, 1-butanol was carried out experimentally. All three aliphatic alcohols (methanol, ethanol and 1-butanol) are considered as fuels.