Lower Flammability Limits – Experimental and Theoretical Determination Methods for Gaseous and Liquid Fuels. State of the Art

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Abstract: This work is an in-depth discussion of the experimental methods of lower flammability limit (LFL) determination and estimation in gases and the vapours of liquids. The focus here includes the dependences and drawbacks of each method. The work also outlines past research and discoveries that relate to the determination of explosion limits.
Keywords: flammability limits, single-component fuels

1. INTRODUCTION

Environmental protection continues to be a valid problem throughout the world, and especially in the petrochemical and refinery sectors. According to numerous assessments, these two sectors remain the most environmentally harmful of all of mankind's industrial activities, next to power engineering. There have been nearly 500 incidents of industrial fire over the last 50 years alone, and the number seems to grow over time (and depending on the reference source) [1]. The most tragic, known and referred to such events in Poland include the fire at the Czechowice-Dziedzice refinery plant in 1971, the fire of a tank at the Gdańsk refinery in 2003, and the fire during the transfer of a petrochemical product to a tanker vehicle at a Płock plant operated by PKN Orlen in 2003. Given these events it is only justified to claim that there has been a very high risk of fire at refinery and petrochemical plants, and each such event can easily be qualified as a local cataclysm. The root causes of the observed scale of this hazard are based on the main raw material being processed by the refinery and petrochemical sectors. Crude oil is a mixture of a wide variety of hydrocarbons, for the most part aromatic ones [2]. Hydrocarbons give a highly fumigating flame, while the combustion products contain high volumes of particulates and compounds that are carcinogenic, toxic and harmful to humans, animals and plants [3, 4].

It would seem to be obvious that the prevention of industrial fires and the maximum containment of their effects should be an essential and highly desirable measure of environmental protection and human safety. The assessment of the hazards related to the hazardous chemicals used in industrial plants (including refineries and petrochemical installations) is the speciality of industrial safety engineers [5]. An important factor in industrial hazard reduction is an understanding of the explosion parameters of the substances used in such industrial processes. Here the flammability limits are critical safety parameters, forming a key tool in the evaluation of explosion viability, the predictability of industrial fire and containment risks, and protection engineering.

Hence an attempt is required to review the state of knowledge concerning the experimental and theoretical methods of LFL determination in gaseous and liquid fuels.

2. EXPERIMENTAL METHODS OF FLAMMABILITY LIMIT DETERMINATION

The concept of flammability limits has been known for over 200 years, and there have been several noteworthy breakthroughs in the discipline.

Humboldt and Gay-Lussac provided the first documented observations on flammability limits in 1805 [6] during their work on altering the composition and pressure of atmospheric air. They discovered that the air ratio in a closed volume of space affects the ability of flammable substances to be ignited. However, they did not pursue any investigation into the phenomenon.

The second milestone in the research into flammability limits was the first experimental determination of LFL (lower flammability limit). This was done on methane gas by Sir Humphry Davy in 1816 [7]. Sir Davy, as a professor of physics and chemistry at the Royal Institution in England, was investigating the explosion processes when the British guild of head miners turned to him with a specific problem. The cause of many explosions in underground mines at that time was excess airborne levels of mine gas in galleries being exploited. The direct source of ignition often involved the kerosene lamps that were used as light sources. Another direct source, albeit a less frequent one due to its inherently low ignition energy, was sparking from mining picks. Davy spent many years researching mine gases, which is chiefly methane. His scientific efforts were focused on methane combustion under various conditions, including combustion in pure oxygen and normal air. Davy's experimental instrument was a vessel which resembled a bottle with a very thin neck. This test vessel was positioned with the mouth upright, while the ignition source was a candle. The lower and upper flammability limits established by Sir Davy were 6.2% and 14.3%, respectively, and the values are extremely accurate given the rather imperfect scientific method[1]. Sir Davy's research was undeniably pioneering work in industrial safety engineering.

At the end of the 19th century, Ernest-Francois Mallard and Henri Louis Le Chatellier were also researching the flammability limits of substances with the objective of improving mine safety [8]. Their work on combustion and explosiveness allowed them to formulate a theory on the thermal structure of laminar flames and to define the parameter of laminar flame speed. Both research efforts investigated the kinetics of chemical reactions with a special focus on concentration-rich mixtures which are close to the upper flammability limits. Their overall efforts were the third milestone in the history of research into flammability limits.

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[1] Of note: according to an MSDS from Linde Gaz Polska, a leading industrial, flammable and atmospheric gas supplier, the LFL and UFL of methane are 4.9% and 15.5%, respectively.

The theory of flammability limits would recur as a topic of scientific interest for Jouget (1913) [9], Daniell (1930) [10], Lewis and Elbe (1934) [11], and Zeldovich (1985) [12], who researched flame propagation in various reactor geometry configurations. The works of these researchers would only vary by test substance and physical conditions (i.e. temperature and pressure) at the time of initiating combustion. The overall efforts of these researchers before the 1950s were the fourth and an incredibly fertile milestone in the history of research into the explosiveness of fuels.

As was mentioned before, the concept of flammability limit concentrations is two centuries old, and yet the most interesting, reliable and significant scientific work in this field began only 50 years ago. In terms of theory (modelling and description of phenomena) and practice (experiments), the fundamental research in the field was made by USBM (the U.S. Bureau of Mining) by Zabetakis, Coward, Jones and Kuchta [13-15]. USBM functioned from 1910 to 1995 with the statutory mission of scientific research and information distribution in the mining, processing, use and protection of mineral resources. Already by the 1950s, these American researchers were the first ever to propose a unified method of experimental flammability limit determination, and to substantiate it. The team completed a huge number of measurements on a great variety of chemical substances, with a focus on gases. Hence the aggregated efforts of Zabetakis, Coward, Jones and Kuchta were the fifth milestone in the history of research into flammability limits.

The sixth and latest breakthrough in the field of fuel explosiveness happened 1972, when a counter-proposal was formulated for the unified methodology of experimental flammability limit determination. This was the brainchild of Coffee, Vogl and Wheeler [16]. The three scientists were working on commission from Eastman Kodak R&D[2]. Their counter-proposal aside, Coffee, Vogl and Wheeler also demonstrated that the flammability limit values depend on several factors that can be divided into two general groups:

1. Process factors: test vessel (form and capacity), ignition source (point of application, energy volume and execution method), criterion of ignition (the condition to be met to qualify the tested process as ignition of a flammable substance);
2. Physiochemical factors: pressure, temperature, mixture turbulence, forces acting on the test vessel (e.g. overstraining), oxidizing atmosphere humidity (especially in air), inert (non-flammable) substance content.

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[2] R&D – *research and development*: a scientific, engineering and research organisational unit the main objective of which is the development of innovative solutions within a specific field of study. R&D work may include further discoveries, inventions, novel hypotheses, concepts or theories beyond the available state of the art and potentially contributory to the commercial success of the R&D owner's business. In recent years, R&D activities have become the benchmark for business on a global level.

Note that there have also been several Polish researchers who have contributed to the theory of flammability limits. Much work in Poland in this field was undertaken in the 1980s by Jarosiński at the Institute of Aviation in Warsaw [17] and the team of the Warsaw University of Technology, Faculty of Power and Aeronautical Engineering, Institute of Heat Engineering, Department of Aircraft Engines [18-20].

The very definition of flammability limits has been a subject of scientific debate for the last three decades[3]. Some researchers define the flammability limits as *the concentration limits of a flammable substance between which a flame can propagate across the mixture in a direction opposite to the source of ignition* [21-23]. Others claim that a better definition is *the concentration limits of a flammable substance outside of which the mixture is insensitive to the activity of an ignition source* [21-23]. In this work the authors have adopted a definition by which *the flammability limits are a range of flammable substance concentrations outside of which no conditions will cause its ignition*. This complies with the definition of PN-EN 1839 [24] which is a valid Polish standard methodology for the experimental determination of flammability limits.

As mentioned before, experimentally determined limit values largely depend on the test methodology, or the process factors [23-25]. A common characteristic of all currently known and practised methods is their origin: either the original USBM method or the original Kodak method. The three main aspects of the process factors are listed by the specific method of determining the experimental flammability limit. These are discussed below.

The first aspect is the test vessel. The form (shape) and size (capacity) determine the direction of flame propagation and the course and intensity of heat loss from the reaction zone. The effects of the geometry of the test vessels under normal conditions on the determination of LFL were investigated by Takahasi [26], who obtained several interesting results. First, cylindrical vessels of small diameter and large height are conducive to flattening of the reaction zone which extinguishes the initiated flame. Hence the LFL values determined with this type of apparatus are always somewhat inflated. Second, in cylindrical vessels of low height the experimentally determined LFL value depends on the self-heating of the unburned portion of fuel by the initiating flames, as an effect of hot gas accumulation in the top part of the vessel. The reaction zone flattening effect may also take place under these conditions.

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[3] Flammability limits are construed as the concentration limits of explosiveness or flammability limits. Both definitions are interchangeable in the reference literature, although Polish sources include reports that differentiate between the two. This differentiation is a mistake caused by erroneous attempts at the direct translation of English sources. The matter of proper nomenclature for flammability limits is discussed elsewhere [18, 19].

Third, if the capacity of a test vessel is large enough to make the aforementioned effects negligible, the experimentally determined LFL value will be approximate to the value determinable by microgravity testing. Takahasi and Kondo claim that spherical geometry for the test vessel provides the best conditions of EL determination [27-32]. The effects obtained with cylindrical vessels could be referenced to the effects of determination in spherical vessels if the tube minimum internal diameter is 30 cm and the minimum tube internal height is 60 cm. However, larger cylindrical vessels are also permitted, if the same diameter to length (or height) ratio is maintained.

The second aspect to be contemplated here is the ignition source. Depending on the point of application, energy volume and execution of an ignition source, the fuel-air mixture response may vary.

The most popular ignition sources include candle flames or methane burner flames, electrical discharge (sparks), glowing resistance wires, and pyrotechnical charges [33]. The ignition source energy volume should be adjusted by the minimum ignition energy of the test substance [34-36].

The third aspect is the criterion of ignition. The first experimental methods were based on ignition detection with a visual criterion. This criterion is divided into two subcriteria: types I and II visual criteria. The type I visual criterion states that the ignition of a fuel-air mixture is deemed to have occurred when any visual symptom that is not a component of the ignition source appears in the test vessel. The type II visual criterion states that the ignition has occurred when a new flame has reached a specific height or it has propagated for a specific distance (which depends on the specific method of determination and the translation of the applicable reference standard). A temperature criterion was introduced later when researchers observed that the visual criterion cannot be impartial. The visual criterion can be subjective when two researchers disagree on the actual occurrence of ignition during the same test. The temperature criterion was not widely accepted by the scientific community [37], which is due to the simple fact that flammable materials vary in combustion heat and combustion dynamics as a result of the different fuel oxidation reaction rates. Hence, it does not seem possible to find a universal temperature measurement point within a test vessel for all possible substances and test methods. The current generally accepted criterion is pressure. The application of dynamic pressure piezoelectric sensors (or other suitable pressure sensor types) with advanced instrumentation has enabled determination of flammability limits by measurement of pressure time curves. However, this means adding other explosiveness parameters to characterize the explosion dynamics, such as explosion pressure (P_{ex}) and the explosion pressure increase rate (($dp/dt)_{ex}$). Unfortunately, the introduction of the two parameters brought about certain doubts concerning the measurement series procedures for flammability limit determination.

Before the pressure criterion of ignition was introduced, the limits were determined by successive application of an ignition source to mixtures of gradually decreasing (or increasing, depending on the limit being determined) concentrations until the ignition fails to occur. Then it was valid to assume that the lowest (or, respectively, the highest) concentration is equivalent to LFL (or UFL). Hence each measurement would provide a binary output: ignition or no ignition. Since the pressure increase measurements allow plotting curves to illustrate the relationship between P_{ex} and the flammable concentration, a question was soon raised: where exactly are the limits? Industrial safety engineers want outputs from the measurement of combustion and explosion phenomena to be as reliable as possible, but they also must be obtainable in an economically viable manner. Two of the most popular flammability limit estimation methods are based on measurement series which output the data on explosion pressure as a function of concentration.

These are the tangential method and the min-max method. The tangential method definition states that an flammability limit occurs at the concentration where the steepest line between each two successive measurement points intersects the initial pressure lines. The min-max method assumes that the LFL (UFL) occurs at a concentration that is the arithmetic mean of two concentration values: the lowest (highest) concentration at which the explosion pressure increase is measured or ignition occurred and the highest (lowest) concentration at which ignition failed. Fig. 1 provides a visual comparison of these two methods. Vanderstraeten et al. [38] claim that the min-max method should be used to determine the UFL and the tangential method should be applied to determine the LFL; however, some researchers do not seem to agree [39]. They include Razus et al. [40], who presented an alternative method of flammability limit estimation, which used P_{ex} as a function of the concentration of fuel.

In the currently used methods, the ignition criterion is the explosion pressure parameter with the valid standards applied [24, 41-44]. Ignition is deemed to have occurred when the pressure increase determined during the measurement exceeds the pressure increase caused by the presence of the same ignition source by ± 5%. The references report research work into the selection of this pressure increase threshold (and not at 5%, but at 2% and 7%) [23]. This criterion seems to be impartial and raises no doubts, its only potential drawback is a malfunction related to the measurement instruments. This risk is precluded by periodic calibration of the sensors [38].

Legislation-wise, the standard PN-EN 1839, on *Determination of the flammability limits of gases and vapours* [24] applies officially in Poland, which permits two methods of flammability limit determination and assumes them to be equivalent. The first method is known as the tubular or T-method.
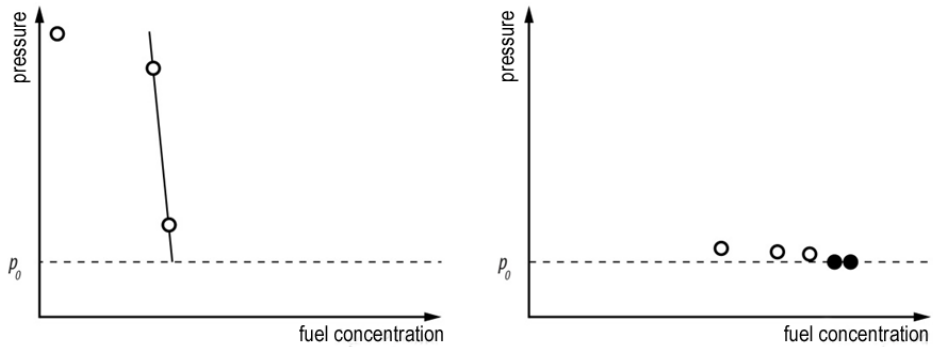
Fig. 1. Comparison of the tangential method (left-hand chart) to the min-max method
(right-hand chart) [proprietary]

It is a derivative of the original method established at USBM. The second method is known as the bomb or B-method, and is derived from the Eastman Kodak research. Moreover, the T-method has been adapted to form the foundation of the German DIN 51649 standard [43], whereas the B-method is the backbone of the U.S. ASTM E681 standard [41]. The following table provides a comparison between the PN-EN 1839 compliant [24] T-method and the B-method.

PN-EN 1839 [24]	
T-Method: tubular method	**B-Method: bomb method**
Test vessel	
An upright cylindrical vessel made of glass or another transparent material (e.g. polycarbonate) with an internal diameter (80±2) mm and a minimum length of 300 mm	A horizontal cylindrical vessel or a spherical vessel with a minimum capacity of 5 litres. If a cylindrical vessel is used, the L/d (length to diameter ratio) should be 3:2
Ignition source	
A series of induction sparks	A series of induction sparks or burning of a flux wire
Ignition criterion	
Visual: separation of flame	Pressure: a suitable pressure increase value

Note that research indicates that there can be up to a 10% difference in the results obtained from the B-method and the T-method, albeit in extreme cases only those that apply to UFL determination; the difference in the LFL determination results oscillate below 1%.

A commentary is due on the sources of the differences in the results between the T-method and the B-method. The most likely causes include the physicochemical preconditions of the self-sustainable and propagating combustion reaction. If a flammable mixture makes contact with an ignition source strong enough, the visual effect of the resulting phenomena is a flame (i.e. ionised gas) that will tend to displace away, or even to "escape", from the ignition source in all possible directions. The testing of the phenomenon made with sufficiently large volumes and in Earth's gravity have allowed the observation that from the ignition source applied to the flammable medium, a reaction zone forms around the point of application (contact), and the reaction zone radius grows asymmetrically in all directions [45, 46]. However, when the same is done a microgravity environment, the reaction zone radius grows nearly symmetrically in all directions [77]. The hot combustion products are thinner (less dense) than the unignited flammable medium; hence the gravitational interaction causes them to lift and form convection currents.

It would seem to be logical that the downward propagation of a flame is not possible in a mixture where the convection current velocity is larger than the flame propagation velocity in a stationary mixture [22, 38]. This is evident especially at concentrations approximate to the LFL and the UFL. These considerations can be reduced to the conclusion that certain concentration values exist within the flammability range at which the flame can propagate upwards and not downwards. Given this the T-method establishes that the ignition source shall only be applied to the lowest point within the test vessel to assure the best propagation conditions for the flame. The convection currents that form along the moving reaction zone will propel the flame when it propagates upwards. One result of this is that applying the ignition source at the lowest part inside a cylindrical test vessel will result in a determination of the parameters under the best possible conditions of combustion and with a satisfactory safety level. Spherical vessels seem to be a compromise between the downward and upward propagation of the flame. Given this, the pressure in spherical tanks should be measured at two points, above and below the ignition source. Spherical vessels as a test standard can only be partially justified. Moreover, an understanding of the explosiveness parameters (and not just the flammability limits) should not end with a single direction of flame propagation, it should cover all possible directions of this propagation for a comprehensive picture of the explosion hazards caused by hazardous substances.

De Smedt et al. [23] compared the two methods of LFL and UFL determination and proposed a conversion method for the results.

	Comparison of flammability limits between the T-method and the B-method					
	B-method			**T-method**		
	LFL$_{2\%}$	**LFL$_{7\%}$**	**UFL$_{2\%}$**	**UFL$_{7\%}$**	**LFL$_T$**	**UFL$_T$**
Methane	4.58 ± 0.11	4.85 ± 0.11	15.9 ± 0.3	15.1 ± 0.3	4.60 ± 0.06	16.2 ± 0.2
Ethane	2.46 ± 0.09	2.53 ± 0.09	14.1 ± 0.2	13.8 ± 0.2	2.39 ± 0.05	14.8 ± 0.2
Propane	1.85 ± 0.07	1.93 ± 0.07	10.2 ± 0.2	9.4 ± 0.2	1.82 ± 0.04	10.5 ± 0.2
Butane	1.38 ± 0.04	1.55 ± 0.04	8.6 ± 0.2	8.1 ± 0.2	1.34 ± 0.03	8.9 ± 0.2

Two pressure criteria thresholds were compared for the B-method: 2% and 7%. With the table above, de Smedt et al. [23] proposed a linear correlation for conversion of the flammability limit values between these two experimental methods.

$$LFL_{2\%} = 0.98 \cdot LFL_T$$
$$UFL_{2\%} = 0.97 \cdot UFL_T$$
$$LFL_{7\%} = 1.03 \cdot LFL_T + 0.11$$
$$UFL_{7\%} = 0.98 \cdot UFL_T - 0.76$$

These correlations have their applicability proven only for the first four representatives of the alkane homologous series (i.e. methane, ethane, propane and butane), as duly noted by the authors [23].

Discrepancies may also occur within the same method. Testing indicates that the diameter of the tube in the T-method has a significant impact on the result. For example: Coward and Jones [13] obtained a LFL of $4.90 \pm 0.03\%$ for a methane-air mixture contained in a dia. 50 mm tube, whereas Zabetakis [14, 33] obtained a methane-air mixture LFL of $5.15 \pm 0.05\%$ in a dia. 24 mm tube.

Industrial safety wise, it is more prudent to understand the LFL rather than the UFL. The flammability limits of gases and liquids are most often expressed by volume fraction, i.e. the volumetric ratio of fuel to the entire volume of the explosive atmosphere, or to the total volume of oxidising gases, inert gases and flammable gases. Fuel-air mixtures are deprived of their destructive potential by making the mixture inert [49]. Adding an inert agent to an explosive atmosphere will thin it out, i.e. reduce the volume fraction of fuel.

If a volume of inert gas is added to the entire given volume of an atmosphere to reduce the fuel concentration in the total mixture below its LFL, the atmosphere will lose its destructive potential.

It is theoretically possible to add a volume of fuel high enough to exceed the UFL; however, in practice and due to cost efficiency, this method is hardly practised. Given these arguments, the determination of flammability limits by experimentation is time consuming and requires special instruments, safety measures, qualified personnel, and high costs.

The assumptions behind the experimental methods do not clear all doubts, nor does the universality of the results obtained with their use. Although the scientific world has managed to determine the flammability limits of most concerned chemicals over the last 50 years, this field of knowledge remains rather unpopular and far from unified [4, 34]. It would seem justified to continue the attempts at applying methods which are equivalent, or substitutive at worst.

Given the difficulty of determining explosive concentration limits, the main objective of this work is to review the existing methods of estimation of the lower flammability limit, especially when there is no access to special databases with the desired reference data, and to present other tools applied in LFL estimation.

3. EMPIRICAL AND SEMI-EMPIRICAL METHODS OF LFL DETERMINATION

The methods of estimating flammability concentration limits presented in the reference literature largely concern LFL values, since this limit is most important in industrial safety engineering [34-36]. As was mentioned before, an explosive atmosphere can be deprived of its destructive potential by reducing the flammable concentration of the mixture below the LFL or increasing it above the UFL [50-51]. The first method is easier to achieve in practice; this is why LFL is a more desired parameter for MSDS data [52-54]. The available methods of flammability concentration limit estimation can be assigned to several groups [55-60]. The first group includes empirical methods that permit calculation of the LFL based on:

- theoretical number of oxygen atoms necessary to burn a defined number of flammable molecules;
- molar heat of combustion;
- stoichiometric concentration;
- known nuclear composition of the flammable compound;
- flash point and boiling point of the liquid;
- saturated vapour pressure at the flash point.

Note that the last two methods apply to liquids only. The first method of the group, based on the theoretical number of oxygen atoms necessary to burn a defined number of flammable molecules, is used to calculate the LFL of individual (isolated) flammables and homogeneous air gas mixtures [55].

The proposed formula related to the first method is:

$$LFL = \frac{100\%}{4.76 \cdot (N-1)+1}$$

with: N is the theoretical number of oxygen atoms required to burn 1 molecule of the flammable in the mixture.

The N value can be calculated from an equation for perfect mixture combustion. One of the best known and simplest empirical methods is the Spakowski method [63]. The method involves applying a proportion reverse to the standard molar heat of combustion, ΔH_c, expressed in kJ/mol.

$$LFL = \frac{-4354}{\Delta H_C}$$

References feature works with the results of validation of the method on a group of 454 different chemicals [62]. The standard deviation of the method for the tested ensemble is 1.35% of the volume fraction, whereas the maximum error is 14.02%. The coefficient of determination, $\boldsymbol{R^2}$ is 0.83.

This value may range from 0 to 1, and the model fit is better the closer the coefficient of determination is to unity. The coefficient of determination values tend to increase with the number of characteristics represented in a model. The Spakowski method permits estimations of the LFL only, since the mechanism of combustion of fuel-poor mixtures are rather thermodynamic than chemical [63]. In this case the flame may still propagate if the difference between the amount of heat generated by fuel combustion and the amount of heat dissipated from the flame front is not high enough to smother the reaction. In the case of fuel-rich mixture combustion, chemical mechanisms (such as the formation and development of fuel-oxygen bonds) dominate over the thermodynamic mechanisms (i.e. the heat balance). Hence it is difficult to find a similar relationship for UFL [64-67]. The method of LFL estimation with the molar heat of combustion is quite similar; the aforementioned statistical analysis helped to demonstrate a low coefficient of correlation between the actual and estimated values.

The third empirical method is the Jones method [70]. This relates to the stoichiometric concentration $\boldsymbol{C_{st}}$ of the combusted substance. The idea is: specific coefficients have been determined for specific groups of chemical compounds. When multiplied by the stoichiometric concentration value $\boldsymbol{C_{st}}$, they provide the flammability limit values [62, 68].

This method permits estimation of both LFL and UFL; however, it has a much better experimental correlation for LFL values.

$$LFL = 0.55 \cdot C_{st}$$
$$UFL = 3.5 \cdot C_{st}$$

For example: methane (the air C_{st} of which is 10.5%) should, according to the relationships described, have the flammability limits of 5.7% and 36.7%, respectively, whereas the experimental limit values for this gas are 5.3% and 15%. However, this method has seen a more thorough validation than the first of the group. The resulting standard deviation was 0.07% of the volume fraction with the maximum error of 5.7% and the coefficient of determination, R^2 of 0.89. Hence, the Jones method provides results more precise than with the Spakowski method. However, Sheldon's calculations have proven that the methods of both Spakowski and Jones provide unsatisfactory results for low molecular mass compounds [63, 68].

The Jones method also has a general form with a constant A:

$$LFL = A \cdot C_{st}$$

The coefficient A most often applied in the Jones method is 0.55 for LFL and 3.5 for UFL. According to what has been assured by their creators, the coefficients help determine the limits by overestimating LFL and underestimating UFL to produce a sufficient safety margin. Hilado proposed a wide set for coefficient A in his paper [70] published in the discontinued Journal of Fire and Flammability.

The coefficient A is 0.692 for amines, 0.609 for chlorides, 0.716 for dichlorides, 0.947 for bromides, 0.577 for compounds with atomic sulphur, and 0.537 for compounds with atomic carbon, hydrogen and oxygen only. Zabetakis and Pintar [33, 70] proposed a coefficient A of 0.512 for esters and 0.5 for alcohols, ethers, aldehydes and ketones. Unfortunately, the coefficient A database for UFL is not as extensive.

The UFL can be estimated with known atomic compositions of chemicals in many ways, and for this purpose the fourth empirical method is actually an entire subgroup. The first formula of this subgroup was proposed by White; given its gross defects, E. Oehley proposed a supplemented formula [71-72]:

$$LFL = \frac{44}{\sqrt{4C + H + 4S - 2O - N - 2Cl - 3F - 5Br}}$$

with: *C, H, S, O, N, Cl, F* and *Br* are the numbers of atoms of corresponding elements in a single molecule of a given flammable compound (according to the structural formula).

Apart from the Oehley formula [71], known formulas include those from Catoire and Naudet, which require the initial temperature of the flammable substance [73]:

$$LFL = 519.957 \cdot \left(1 + 5 \cdot C + \frac{5}{4 \cdot H} - \frac{5}{2} \cdot O\right)^{-0.70936} \cdot C^{-0.197} \cdot T^{-0.51536}$$

with: *C, H* and *O* being the numbers of atoms of the corresponding elements in a single molecule of a given flammable compound (according to the structural formula), with temperature *T* given in Kelvin.

If the elementary composition of a compound, the LFL of which is being determined, and the chemical is a liquid under ambient conditions, a viable relationship enables the LFL determination with ignition point T_{ign} and boiling point T_{boil} of the liquid [55, 74]:

$$LFL = \frac{132\sqrt{2}}{\sqrt{T_{wrz} - T_{zap}}}$$

The sixth empirical method is based on the saturated vapour pressure at flash point. The method formula is:

$$LFL = \frac{p_{FP}}{p_{atm}}$$

with: p_{FP} being the saturated vapour pressure of the liquid at its flash point, and p_{atm} the barometric pressure [75].

4. METHODS OF LOWER FLAMMABILITY LIMIT DETERMINATION FOR ISOLATED CHEMICALS BASED ON MOLECULAR STRUCTURE

The above methods are empirical, their final forms originating from the extent of known (examined) reality. Since their applicability and precision have always left much to be desired, science began to search for other methods of LFL estimation. Upon researching the problem, it was discovered that several macroscopic properties of chemicals are functions of their structure, which is the premise behind the SGC methodology (*structural group contribution*), a group of functional dependencies that include structural elements. The authors of the SGC methodology are Benson and Buss [76-78]. The development of the SGC method allowed the definition of several models to help estimate various parameters of a chemical compound if the ratios and weights of all the structural elements (atoms, atomic groups, bond types, functional groups, etc.) are known. A large group of flammability limit estimation methods has been derived from the SGC theory.

Albahri proposed an implementation of the SGC methodology in industrial safety engineering by proposing in a 2003 edition of Chemical Engineering Science [62, 75] non-linear relations (formulas) for the estimation of various explosiveness parameters (including flammability limits) for a wide variety of chemical compounds.

The general form of the formula is:

$$\Phi = a + b \cdot \left(\sum_i (\Phi)_i \right) + c \cdot \left(\sum_i (\Phi)_i \right)^2 + d \cdot \left(\sum_i (\Phi)_i \right)^3 + e \cdot \left(\sum_i (\Phi)_i \right)^4$$

with: Φ denotes either flash point, auto-ignition point, lower flammability limit or upper flammability limit; *a, b, c, d, e* are the respective constant values from an empirical determination, whereas $\sum_i (\Phi)_i$ denotes the contribution, which is a total of the weights (also empirically determined) for the individual structural elements. The calculations for 1,4-diethylbenzene can be used to illustrate its use. 1,4-diethylbenzene is a benzene molecule with two ethyl groups as the substituents for a para constitutional isomerism.

The chemical features the following structures: two ethyl structures ($-C_2H_5$), four aromatic structures ($=CH-$), one unsaturated aromatic structure ($>C=$), and one unsaturated para positioned aromatic structure ($p->C=$). The weights of the structures for the LFL estimation are as follows (respectively): -1.4407; -0.8736; -0.8891; and -0.2847. Hence the contribution can be calculated:

$$\sum (LFL)_i = 2 \cdot (-1.4407) + 2 \cdot (-0.8736) + 2 \cdot (-0.8891) + 2 \cdot (-0.2847) = -8.754$$

With the total of weight calculated, the LFL can be calculated: The values of the empirical constants *a, b, c, d, e* at this LFL are (respectively): 4.4174; 0.80930; 0.0689; 0.00265; 3.76E-05. Eventually:

$$LFL = 4.174 + 0.093 \cdot (-8.754) + 0.0689 \cdot (-8.754)^2 + 0.00265 \cdot (-8.754)^3$$
$$+ 3.76 \cdot 10^{-5} \cdot (-8.754)^4 = 0.81\%$$

The value is extremely precise when compared to the experimentally established LFL of 1,4-diethylbenzene equal to 0.8%.

The coefficient values in the aforementioned equation were chosen from a group of 464 compounds, and their accuracy remains satisfactory. The exact weight values and the detailed function of Albahri's equations are available in the references [62, 75]. The greatest deficiency of the SGC method is its applicability. The proposed weight values will provide satisfactory results only for the compounds used for their calculation, and these include hydrocarbons. Calculating the weights of other compounds will increase their applicability. The CAS Registry currently includes millions of well-identified chemical compounds, and it is continuously being supplemented with hundreds (and sometimes thousands) of new chemicals, including their indirect products which have not yet been isolated in their pure forms [79].

Given the sheer amount of this data, it seems impossible to derive universal weight values that would ensure satisfactory determination results and a wide applicability for all known chemicals.

The third large group of flammability limit determination methods are based on QSPR models (*quantitative structure-properties relationship*), which are quantitative models of the relationships between the compound structure and properties. This is a derivative method of QSAR (*quantitative structure-activity relationship*), which consists of the identification and analysis of the relationships between the chemical structure (e.g. molecular geometry or electron structure) and reactivity or biological activity. QSAR is usually applied in drug design, for example. The QSPR and the variety of its modifications are currently researched by scientists across the world, as evidenced by the works available from Gharagheizi, Pan or Katrizky [80-83]. QSPR is only recommended in highly complex and difficult cases. It is suggested that easier empirical methods are used for the estimation of flammability limits, such as those mentioned previously.

Bagheri [84] presented an example of QSPR implementation for LFL determination. Bagheri's primary objective was to determine the effect of the molecular structure of pure organic and inorganic flammables on their LFL values. Bagheri used ANFIS (*Adaptive Neuro-Fuzzy Inference System*) to test 1615 substances and then compare them with existing results provided with other methods applied in neural networks. The data about the properties of specific substances used to teach the neural networks were taken from the DIPPR database [79]. The LFL values for the substances in the neural teaching set were between 0.1% and 12% of the volume fraction. The molecular structure parameters were defined by the HYPERCHEM software (from Hypercube Inc.). The software generated up to 3224 parameters (depending on the specific compound), including the geometrical indicators that allow the definition of the atomic structure. From this slew of parameters, Bagheri [84] chose 312 with the largest effect on the macroscopic properties of substances, and applied a non-linear regression method to drill down to those parameters that enable a LFL determination with the lowest error in comparison to the experimental data. In a further stage, Bagheri divided the input number of 1615 substances into two sets. The first set (80% of 1292 pure substances) served to build a model, and the other one (20% of 323 pure substances) served to validate the model. The calculations were done in MATLAB. Bagheri also demonstrated that a three-parameter equation would suffice for a relatively exact LFL description.

Pan et al. [80] also attempted to estimate flammability levels with QSPR in combination with SVM (*Support Vector Machine*) for organic substances. The model allowed the estimation of explosive limits with an absolute error which does not exceed 0.25% of the volume fraction. However, the model's relative error is higher.

The same work provides an error range distribution in reference to the number of chemical compounds, and a comparison of the calculation results to the experimental data. The work identified the parameters with the highest impact on LFL. These include: the molecular topology of atoms, the charge of atoms, and the geometric data of the molecule. The results obtained by Pan et al. [85] demonstrate that the combination of QSPR and SVM permits estimations of LFL with an RMSE (root mean square error) of 0.068 and an AAE (average absolute error) of 0.050. A comparison of the model to other models available in the reference sources demonstrate the clear superiority of the former.

As far as flammable liquids are concerned, their known parameters include, aside from flammability concentration limits, the so-called temperature explosion limits. LTFL (*lower temperature flammability limit*), or LEP (*lower explosion point*) is a temperature value at which liquid vapours reach their explosion pressure (i.e. the maximum partial pressure) and LFL at the same time. Both flammability limits and vapour pressure (according to Antoine's equation) are temperature functions.

Dalton's law and the gas equations of state can be applied to convert pressure into the volume fraction. In other words, given the pressure of a liquid (the relationship between its saturation pressure and temperature) and the LEP, it is possible to calculate LFL. Gharagheizi proposed a model for determination of LFL with QSPR [81-81]. The model was designed from the test results of 1171 measurement samples, mainly hydrocarbons. Each sample represented an isolated substance, the properties of which were taken from DIPPR 801 [79]. The RMSE of the results was 15.61K, whereas the AAE was 3.69%.

Gharagheizi et al. [83] also designed a different model, which served for the determination of LEP by CSM (*Corresponding State Method*). This methodology was based on van der Waals' principle of corresponding states.

1480 chemical substances were tested and divided into 77 chemical groups. The input variables of the model describing each substance were critical temperature, critical pressure, acentric factor, and boiling point under normal conditions. The model was used to find a relationship between all input parameters:

$$LTFL = 1.9876 + 0.4282 \cdot T_C + 0.1833 \cdot \omega \cdot$$
$$\cdot \left[T_B - 0.2116 \cdot \omega \cdot \left(\frac{0.4943 \cdot T_B + 0.2116 \cdot T_C}{p_C} \right) \right]$$

with: T_C is critical temperature in [K], p_C is critical pressure in [Pa], ω is acentric factor[4] and T_b is the boiling point under normal conditions in [K].

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[4] It includes a factor proposed in 1955 by Professor Pitzer. The factor is highly useful when describing the state of matter and expresses the measure of *non-sphericity* of molecules. The factor value depends on the vapour pressure. The example factor values are 0.022, -0.220, 0.253, and 0.187 for oxygen, hydrogen, ammonia, and acetylene, respectively.

According to the definition, LEP is the temperature at which LFL is equal to the pressure of a liquid. Given the vapour pressure of a flammable at LEP, Dalton's law and Avogadro's rule, the LFL of that flammable substance is calculated as a quotient of the partial pressure and barometric pressure. The following compound parameters derived from the model were validated and sequentially arranged, e.g. aromatic alcohols: 36 chemical compounds; standard deviation: 1.3%; the experimental LEP values were between 348 K and 542 K, and the calculated LEP values were between 352 K to 553 K; for 1-alkenes (a double bond between the first and second carbon atom): 20 chemical compounds; standard deviation: 1.0%; the experimental LEP values were between 124K and 510 K, and the calculated LEP values were between 128 K and 516 K; cycloalkanes: 5 chemical compounds; standard deviation: 2.1%; the experimental LEP values were between 179 K and 301 K, and the calculated LEP values were between 181 K and 308 K.

Gharagheizi et al. [83] gave no detailed results (for any individual chemical compound) in their work, instead they gave a website link to that data.

The fourth large family of methods include methods based on calculated adiabatic flame temperature (CAFT). The first attempts at a CAFT method were made by Vidal [85]. The CAFT is a purely theoretical (computational) concept, because its assumption is that the combustion reaction occurs in a reactor with zero loss of heat, which implies that the reactor walls are adiabatic (not admitting heat). The researchers agree that flammability limits are related to certain critical amount of energy released from chemical bond cleavage, to a certain temperature within the reaction zone. Research suggests that CAFT values for many organic substances are approximately at near-LFL concentrations.

The basic assumption for Vidal's algebraic model is that the pressure during the combustion process is constant and that the enthalpies of substrate formation and transformation products are equal. Note that this model is true for single compounds only. An expanded model version applicable to mixtures of flammables was provided by Zhou [86]. This version expands the applicability of Vidal's model [85].

The CAFT-based method for LFL estimation is straightforward, because it involves simple algebraic equations and basic laws of thermodynamics and the stoichiometry of chemical reactions. Given an adiabatic system (a system without any energy exchange with the ambient environment) in which a chemical reaction occurs and which remains at a constant volume (i.e. it does not exchange energy with the ambient environment through any work), the system's internal energy before the transformation (i.e. reaction) is equal to the internal reaction after the transformation.

If the given system is a reactive adiabatic system with a constant pressure (where an energy exchange with the ambient environment may occur), then, by definition of the enthalpy of creation, the total enthalpy of products must be equal to the total enthalpy of the substrates.
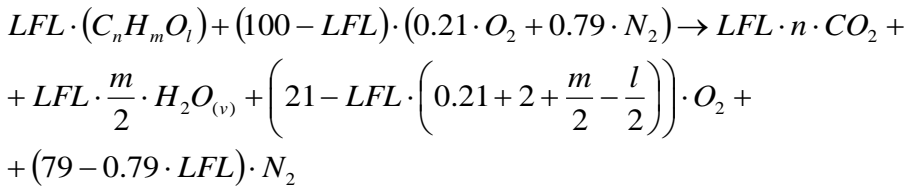
Hence, given the combustion reaction of a compound with the structure $C_nH_mO_l$ and a concentration near LFL (with an excess of oxygen), the thermal balance can be expressed as follows:

$$H_f^i + v_{a_0} \cdot H_a^i = n \cdot H_{CO_2}^{ad} + \frac{m}{2} \cdot H_{H_2O}^{ad} - \beta \cdot H_{O_2}^{ad} + v_{a_0} \cdot H_a^{ad}$$

with: H_f, H_a, H_{CO_2}, H_{H_2O} and H_{O_2} are the total molar enthalpy values of: fuel, air, carbon dioxide, steam, and oxygen, respectively; β is the stoichiometric coefficient for the total and complete combustion reaction of $C_nH_mO_l$ in oxygen; the superscript *ad* and *i* denote the adiabatic conditions and the initial conditions, respectively. This is a development of the general CAFT formula with the first law of thermodynamics:

$$\sum_i \left(H_{sub}(T_i,P)\right)_i = \sum_i \left(H_{prod}(T_{ad},P)\right)_i$$

Hence, when studying the stoichiometry of the combustion reaction of a compound with the structure $C_nH_mO_l$ and a concentration near LFL (with excess of oxygen), the notation is:

$$LFL \cdot \left(C_nH_mO_l\right) + \left(100 - LFL\right) \cdot \left(0.21 \cdot O_2 + 0.79 \cdot N_2\right) \rightarrow LFL \cdot n \cdot CO_2 +$$
$$+ LFL \cdot \frac{m}{2} \cdot H_2O_{(v)} + \left(21 - LFL \cdot \left(0.21 + 2 + \frac{m}{2} - \frac{l}{2}\right)\right) \cdot O_2 +$$
$$+ \left(79 - 0.79 \cdot LFL\right) \cdot N_2$$

with: index *v* denotes a volatile state. The last missing equation is the mathematical expression for LFL:

$$LFL = \frac{100}{1 + v_{a_0}}$$

with: v_{a_0} is the ratio of air mole number to fuel mole number for the LFL. Solving this system of four equations will determine the LFL, if the total molar enthalpy of the substrates in the reaction and the total molar enthalpy of chemical reaction products are known. Vidal [87] expanded his method with the capacity of estimating the effects of inert gas on the resultant LFL value. The results thereof are very satisfactory. For example: ethene diluted with a dioxide at a ratio of (per volume in fuel) 80%: 20%, 50%: 50% and 20%: 80% has LFL values (determined experimentally) equal to 3.8%, 6.0% and 16.5%, respectively.

The same values estimated with Vidal's method are, respectively: 3.39%, 5.49%, and 14.47%. A comparison of these Vidal method results to the experimentally determined values gives a very accurate relationship.

The fifth large method of the group of LFL estimation methods includes those methods formulated with algorithms inspired by biological mechanisms, including artificial neural networks. By definition, a neural network is a mathematical structure, and its software or hardware model, which calculates or processes signals with tiers of elements known as artificial neurons. Generally speaking, artificial neural networks are tools that can provide a machine or an algorithm with a set of behaviours and attitudes. This set permits the adaptation of the controlled device to existing conditions and permits the device to operate in a more "creative" way. Hence, artificial neural networks can be qualified as an ersatz form of AI (*artificial intelligence*). Currently, artificial neural networks are the only viable solution for problems for which one can define an objective, but cannot define the way to achieve it. A good example of this is facial recognition. Flammability limit estimation seems to be a similar problem. By another common definition, ANN (*artificial neural networks*) are an interdisciplinary field of design engineering, teaching and capability testing of various neural network types. Those interested in this field should read more in the references [88-92].

The references given here and the research results they provide are purely academic, since the relationship between accuracy and application facility of the methods is far from satisfactory, as far as industrial applications are concerned.

In 2009, Gharagheizi [93] proposed a method of estimating LFL in volume fractions based on an artificial neural network algorithm. The method estimates flammability limits with the number of functional groups of chemical compounds. This is a certain hybrid of the SGC and ANN methodologies. The set input to the algorithm was 1057 chemical compounds from DIPPR 801 [79]. From the compounds in the set, 105 functional groups were distinguished and reflected in a literature study done by Gharagheizi in coordination with AIChE. The model was developed in MATLAB (Mathworks) and comprised a feed-forward network with three hidden layers. This is yet another attempt by Gharagheizi to apply ANNs in chemical engineering. In his reported works he applied ANN to estimate the flash point [94], lower critical solubility temperature [81] and autoignition point [94]. In the referenced work Gharagheizi provides a website link from which a complete batch m-file can be downloaded for MATLAB. The batch file enables a ready-to-use LFL estimation tool [93]. Gharagheizi's method can be viewed as an approach with a good balance between model accuracy and complexity, provided that the user has basic skills in MATLAB and an elementary knowledge of ANN.

Albahri also attempted to estimate LFL values with ANN and presented his results in a published paper [95].

Albahri used a set of 543 samples, each of which was described with a combination of different functional groups froma defined set of 30 elements. His method has also proven to be very accurate, and actually much more accurate than empirical methods. However, Albahri did not provide a ready batch m-file for use in MATLAB.

Although this proposal gives slightly better results than Gharagheizi's method [93], it is much less useful as there is no software tool available.

Between the achievements of Gharagheizi [93] and Albahri [95], Lazzus also proposed a proprietary model for LFL estimation [97]. The model was designed with ANNs combined with a PSO (*particle swarm organization*). However, Lazzus' model has not been widely recognised.

Di Benedetto [98] presented an interesting method of flammability limit estimation based on simple thermodynamic relationships and calculated mechanisms of chemical reactions. Her model requires solving two coupled equations of heat balance along the flame with consideration for heat losses to the environment and chemical equilibrium equations of the individual components of the investigated substance. Di Benedetto termed her model "adiabatic flammability limits" (AFL). The flammability limit values it provides are much wider for a very large group of chemicals than the values from experimental determination.

For example: the adiabatic LFL and UFL of methane were 2.5% and 33% (experimental: 5.3% and 15%), methane 1% and 55% (experimental: 3.0% and 12.5%), propane 0.8% and 40% (experimental 2.1% and 9.5%). This means that the method provides a very wide safety margin. If applied in industrial safety engineering, di Benedetto's model guarantees a very high safety threshold (which is economically unjustified).

Given all the relationships discussed in this subsection, the effect of chemical compound structure on flammability limits can be analysed. Such work has indeed been attempted [99], and according to its results, both LFL and UFL show similar dependencies on the same structural elements. For example, the flammability limits of paraffin depend heavily on the total number of carbon atoms and the number, type and branch level. The effect of branch locations is negligible in LFL and UFL. The flammability limits seem to be insensitive to the location of the pendant alkyl in aromatic compounds and olefins [62]. No impact was found on the cis-/trans- configuration on olefins. However, the results of the attempts to implement empirical relationships having limited applicability to actual cases to other chemicals must be approached very conservatively. Although the effect of molecular structures on the flammability levels of chemical compounds has been investigated (and experimented with) and the research results well documented, this paper only reviews the knowledge about the subject matter, i.e. the experimental determination methods and theoretical estimation methods of LFL in gases and liquid vapours.

5. METHODS OF RESULTANT LFL DETERMINATION FOR FLAMMABLE MIXTURES

All the methods presented so far in this work have concerned the estimation of flammability limits in homogeneous substances in air mixtures. However, industrial practice dictates that explosive atmospheres rarely include a single type of flammable substance; most often it is an entire gamut of chemicals. Le'Chatelier proposed a method [100] of determining a resultant LFL of mixtures with the following formula:

$$LFL = \frac{100\%}{\sum_i \frac{r_i}{LFL_i}}$$

with: r_i is the volume concentration of the i-th flammable component; LFL_i is the lower flammability limit of the i-th flammable component. The assumption behind the formula is that when mixed, several chemical substances at concentrations equal to their specific LFL values will give a mixture the concentration of which will also be at LFL. Hence the formula is also valid for the calculation of UFL. An interesting aspect of Le'Chatelier's law involves those situations in which one flammable substance is made inert by the presence of other mixture components, because the concentration of the first substance will be so low when compared to the entire explosive atmosphere that the substance will be outside its flammability limits. Pofit-Szczepańska [55] provides calculated examples of those conditions. There are also situations in which the accuracy of Le'Chatelier's law becomes questionable (to say the least): this applies to substances in different states of aggregation (e.g. in mixtures of gases and liquid vapours) or substances with greatly different combustion heat values. Different expansions of the law exist that may help minimise these divergences. The subject has been researched by many authors, and a review of all possible supplements to Le'Chatelier's law warrants a separate publication [101-102].

The noteworthy cases here include explosive mixtures that features non-flammable substances, such as CO_2 or N_2. The resultant LFL for this type of mixtures is calculated with the formula [55, 103-104]:

$$LFL = LFL_{EX} \cdot \frac{\left(1 + \frac{Z}{100 - Z}\right) \cdot 100\%}{100 + LFL_{EX} \cdot \frac{Z}{100 - Z}}$$

with: Z is the content of explosively inert gases of the flammable mixture; LFL_{EX} is the resultant LFL of explosively non-inert substances.

6. SUMMARY

This paper provides an overview of LFL determination methods in experiments, with semi-empirical relationships and theoretical models. When using any of the discussed methods, it is important to remember that even the most accurate model can never replace an experimentally determined LFL value, even if the latter has a certain margin of error [103]. Doubts may concern those conditions at which the LFL determination criteria are met. Safety of handling and use of hazardous substance can only be assured when the conditions of LFL determination reflect the real-life conditions in industrial environments. The latter are often different from standard conditions in terms of oxygen levels, temperature or pressure. It is not always possible to make measurements where the results can represent the actual conditions at an industrial plant; hence it is essential to be able to estimate the effects of various factors on the LFL values, or at least understand what they are.

REFERENCES

[1]   Lasota Wiktor. 2008. „Pożary w przemyśle naftowym – przebieg zdarzeń, przyczyny powstawania". *Bezpieczeństwo i Technika Pożarnicza* 4: 157-168.

[2]   Asinger Friedrich. 1961. *Wstęp do petrochemii*. Warszawa: WNT.

[3]   Pofit-Szczepańska Melania. 2003. „Środowisko w niebezpieczeństwie – pożary paliw ropopochodnych". *Przegląd pożarniczy* 10: 17-20.

[4]   Baubraskas Vytenis. 2003. *Ignition Handbook: Principles and Applications to Fire Safety Engineering, Fire Investigation, Risk Management and Forensic Science*. Issaquah WA. Fire Science Publications.

[5]   Spellman R. Frank. 2009. *The Handbook of Safety Engineering: Principles and Applications.* Government Institutes. Plymouth. USA.

[6]   von Humboldt Alexander, Joseph Louis Gay-Lussac. 1805. "Experiénce sur les moyens oediométriques et sur la proportion des principes constituants de l'atmosphére". *Journal of Physics* 60: 11-45.

[7]   Britton G. Laurence. 2002. "Two hundred years of flammable limits". *Process Safety Progress* 21: 1-11.

[8]   Mallard Ernest-François, Henri Louis Le Chatelier. 1881. "On the propagation velocity of burning in gaseous explosive mixture". *Comptes rendus de l'Académie des science*s 931: 5-48.

[9]   Jouguet Emilie. 1913. "Sur la propagation des deflagration dans les mélanges". *Comptes rendus de l'Académie des sciences* 156.

[10] Daniell P. 1930. The theory of flame motion. In *Proceedings of the Royal Society* A 126: 393-405.

[11] Lewis Bernard, Guenther von Elbe. 1948. Theory of flame propagation. In *Proceedings of the Symposium on Combustion* 1-2: 183-188.

[12] Zeldovich Yakov Borisovich, Grigory Isaakovich Barenblatt, V.B. Librovich, Georgy M. Makhviladze. 1985. *Mathematical theory of combustion and explosion*. New York. USA. Springer-Verlag New York Inc.

[13] Coward H.F., G.W Jones. 1952 "Limits of flammability of gases and vapors". *Bulletin of Bureau of Mines* 503.

[14] Zabetakis Michael George. 1965. "Flammability characteristics of combustible gases and vapors". *Bulletin of Bureau of Mines* 627.

[15] Kuchta J.M. 1985. "Investigation of Fire and Explosion Accidents in the Chemical, Mining and Fuel-Related Industries – a Manual". *Bulletin of Bureau of Mines* 680.

[16] Coffee D. Robert, Philip Jr. C. Vogl, John J. Wheeler. 1972. "Flammability Characteristics of Methylene Chloride (Dichloromethane)". *Journal of Chemical and Engineering Data* 17: 89-93.

[17] Jarosiński Józef. 1986. „Granice palności gazów". *Prace Instytutu Lotnictwa*, 3-4.

[18] Grabarczyk Marcin, Rafał Porowski, Andrzej Teodorczyk. 2013. „Badanie granic wybuchowości par cieczy palnych w podwyższonych temperaturach". *Przemysł Chemiczny* 92 (11): 2097-2099.

[19] Grabarczyk Marcin, Rafał Porowski, Andrzej Teodorczyk. 2014. "Flammability characteristics of butanol fuel blends at various initial temperatures". *Archivum Combustionis* 34 (1): 49-69.

[20] Rarata Grzegorz. 2008. Badania górnej granicy wybuchowości wodoru oraz gazowych homologów metanu w powietrzu i tlenie w warunkach podwyższonego ciśnienia i temperatury. *Phd thesis*. Warsaw University of Technology. Faculty of Power and Aeronautical Engineering. Warsaw. Poland.

[21] PN-EN 1127-1:2011. Polish-European Standard. *Explosive atmospheres. Explosion prevention and protection. Part 1: Basic concepts and methodology*.

[22] Spalding D.B. 1957. A theory of inflammability limit and flame quenching. In *Proceedings of the Royal Society* A240: 83-100.

[23] De Smedt G., F. de Corte, R. Notele, J. Berghmans. 1999. "Comparison of two standard test methods for determining explosion limits of gases at atmospheric conditions". *Journal of Hazardous Materials* 70 (3): 105-113

[24] PN-EN 1839:2012-03. Polish-European Standard. *Determination of explosion limits of gases and vapours*.

[25] Podstawka Tadeusz. 2014. *Ocena ryzyka w miejscach pracy zagrożonych występowaniem atmosfer wybuchowych*. Sandomierz: Wyd. Sannort.

[26] Takahashi Akifumi, Urano Youkichi, Tokuhashi Kazuaki, Kondo Shigeo. 2003. "Effect of vessel size and shape on experimental flammability limits of gases". *Journal of Hazardous Materials* 105 (1-3): 27-37.

[27] Hilado C.J. 1975. "A method for estimating limits of flammability". *Journal of Fire and Flammability* 6: 130-139.

[28] Sheldon M. 1984. "A study of the flammability limits of gases and vapors". *Fire Prevention* 174.

[29] Cashdollar L. Kenneth, Martin Hertzberg. 1985. "20-L explosibility test chamber for dust and gases". *Review of Scientific Instruments* 56 (4): 596-602.

[30] Kondo Shigeo, Takahashi Akifumi, Takizawa Kenji, Tokuhashi Kazuaki. 2011. "On the pressure dependence of flammability limits of CH2=CFCF3, CH2F2 and methane". *Fire Safety Journal* 46: 289-293.

[31] Kondo Shigeo, Takahashi Akifumi, Takizawa Kenji, Tokuhashi Kazuaki. 2011. "On the temperature dependence of flammability limits of gases". *Journal of Hazardous Materials* 187 (1-3): 585-590.

[32] Kondo Shigeo, Takahashi Akifumi, Takizawa Kenji, Tokuhashi Kazuaki., Sekiya Akira. 2008. "A study on flammability limits of fuel mixtures". *Journal of Hazardous Materials* 155 (3): 440-448

[33] Zabetakis M.G., S. Lambiris, G.S. Scott. 1959. Flame temperatures of limit mixtures. In *Proceedings of the 7th Symposium (International) on Combustion*. Butterworths Scientific Publications. London: 484-487.

[34] Sawicki Tomasz. 2005. „Wybuchy przestrzenne". *Bezpieczeństwo pracy: nauka i praktyka* 11: 22-25.

[35] Baranowski W. 1979. „Wybuchy przestrzenne mieszanin powietrzno-gazowych". *Problemy Kryminalistyki* (38).

[36] Ryng Marian. 1985. *Bezpieczeństwo techniczne w przemyśle chemicznym – poradnik*. Warszawa: WNT.

[37] Mayer E. 1957. "Theory of flame propagation limits due to heat loss". *Combustion and Flame* 1 (4): 438-452.

[38] Vanderstraeten B., D. Tuerlinckx, J. Berghmans, S. Vliegen, E. Van't Oost, B. Smit. 1997. „Experimental study of the pressure and temperature dependence on the upper flammability limit of methane/air mixtures". *Journal of Hazardous Materials* 56 (3): 237-246.

[39] Giurcan Venera, Domnina Razus, Maria Mitu, Dumitru Oancea. 2015. "Prediction of flammability limits of fuel-air and fuel-air-inert mixtures from explosivity parameters in closed vessels". *Journal of Loss Prevention in the Process Industries* 34: 65-71.

[40] Razus Domnina, Codina Movileanu, Venera Brinzea, Dumitru Oancea. 2007. "Closed vessel combustion of propylene–air mixtures in the presence of exhaust gas". *Fuel* 86: 1865-1872.

[41] ASTM E681-09(2015). American Standard. *Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases).*

[42] PN-EN 15967:2011. Polish-European Standard. *Determination of maximum explosion pressure and the maximum rate of pressure rise of gases and vapours*.

[43] DIN 51649-1:1986-12. German Standard. *Bestimmung der Explosionsgrenzen von Gasen und Gasgemischen in Luft*.

[44] PN-EN 14756:2008. Polish-European Standard. *Determination of LOC for gases and vapours*.

[45] Gieras Marian, Rudolf Klemens, Piotr Wolański. 1986. "Experimental and theoretical study of ignition of single coal particles at zero gravity". *Acta Astronautica* 13 (5): 231-239.

[46] Jarosinski Józef, Jerzy Podfilipski, Andrzej Gorczakowski. 2002. „Experimental study of flame propagation in propane–air mixture near rich flammability limits in microgravity". *Combustion Science and Technology* 174 (9): 21-48.

[47] Furno A.L., E.B. Cook, J.M. Kuchta. 1971. "Some observations on near-limit flames". *Symposium (International) on Combustion* 13 (1): 593-599.

[48] Bradley Derek, Alan Mitcheson. 1976. "Mathematical Solutions for Explosions in Spherical Vessels". *Combustion and Flame* 26 (2): 201-217.

[49] Maria Molnarne, Peter Mizsey, Volkmar Schroder. 2005. "Flammability limits of gas mixtures, Part 2 – Influence of inert gases". *Journal of Hazardous Materials* 121 (1-3): 45-49.

[50] VDS 3527. German Standard. *Guidelines for inerting and oxygen reduction systems*.

[51] EN/TR 15821. 2005. *Guidance on inerting for the prevention of explosions*. CEN.

[52] Grabarczyk Marcin, Rafał Porowski, Andrzej Teodorczyk. 2013. „Stężeniowe granice wybuchowości par cieczy w podwyższonej temperaturze". Scientific Conference of PhD Students and Young Scientists: Youth for Technology 2013. Płock. Poland.

[53] Porowski Rafał, Wojciech Rudy, Andrzej Teodorczyk. 2012. „Analiza metod badawczych granic wybuchowości cieczy palnych". *Bezpieczeństwo i Technika Pożarnicza* 28 (4): 63-70.

[54] Porowski Rafał, Wojtek Rudy. 2011. „Przegląd badań w zakresie parametrów flash point i explosion point dla cieczy palnych". *Bezpieczeństwo i Technika Po*żarnicza 23 (3): 41-54.

[55] Pofit-Szczepańska Melania. 1971. *Chemia palenia – obliczenia chemiczne w zastosowaniu pożarniczym*. Warszawa: Wyd. Wyższa Oficerska Szkoła Pożarnicza.

[56] Pilc Aleksander. 1955. „Zapobieganie wybuchom mieszanin palnych par i gazów z powietrzem – część I". *Przemysł chemiczny* 38 (1).

[57]   Pilc Aleksander. 1955. „Niebezpieczeństwo wybuchów mieszanin palnych par i gazów z powietrzem – część II". *Przemysł chemiczny* 38 (7).

[58]   Pilc Aleksander. 1955. „Niebezpieczeństwo wybuchów mieszanin palnych par i gazów z powietrzem – część III". *Przemysł chemiczny* 38 (7).

[59]   Pilc Aleksander. 1956. „Niebezpieczeństwo wybuchów mieszanin palnych par i gazów z powietrzem – część IV". *Przemysł chemiczny* 39 (8).

[60]   Pilc Aleksander. 1957. „Niebezpieczeństwo wybuchów mieszanin palnych par i gazów z powietrzem – część V". *Przemysł chemiczny* 40 (10).

[61]   Bodhurtha P. Frank. 1980. *Industrial explosion prevention and protection*. Mc-Graw Hill. New York. USA.

[62]   Albahri A. Tareq. 2003. "Flammability characteristics of pure hydrocarbons". *Chemical Engineering Science* 58 (16): 3629-3641.

[63]   Vidal M., W.J. Rogers, J.C. Holste, M.S. Mannan. 2004. "A review on estimation methods for flash points and flammability limits". *Process Safety Progress* 23 (1): 47-55.

[64]   Baran Tadeusz, Aldona Polich. 2004. *Wybuch i jego skutki – kryminalistyczne badania materiałów i urządzeń wybuchowych*. Warszawa: Wyd. Centralnego Laboratorium Kryminalistycznego KGP.

[65]   Węsierski Tomasz. 2010. „Analiza właściwości palnych podstawowych grup związków organicznych". *Bezpieczeństwo i Technika Pożarnicza* 19 (3): 83-98.

[66]   Gieras Marian, Rudolf Klemens, Allen Kuhl, Paweł Oleszczak, Waldemar Trzciński, Piotr Wolański. 2008. "Influence of the chamber volume on the upper explosion limit for hexane–air mixtures". *Journal of Loss Prevention in the Process Industries* 21 (4): 423-436.

[67]   Cashdollar L. Kenneth, Isaac A. Zlochower, Gregory M. Green, Richard A. Thomas, Martin Hertzber. 2000. "Flammability of methane, propane, and hydrogen gases". *Journal of Loss Prevention in the Process Industries* 13 (3-5): 327-340.

[68]   Jones J. Clifford. 1993. *Combustion Science: Principles and Practice*. Millenium Books. Newtown. Australia.

[69]   Hilado J. Carlos. 1975. "A method for estimating limits of flammability". *Journal of fire and flammability* 6 (10-11): 130-139.

[70]   Pintar A.J. 1999. Predicting lower and upper flammability limits. In *Proceedings on International Conference on Fire Safety* 28.

[71]   Oehley E. 1953. „Ableitung empirischer gleichungen für die untere explosionsgrenze und den flammpunkt". *Chemie Ingenieur Technik* 25 (7): 399-403.

[72] White D., C.L. Beyler, C. Fulper, J. Leonard. 1997. "Flame spread on aviation fuels". *Fire Safety Journal* 28 (1): 1-31.

[73] Catoire Laurent, Valerie Naudet. 2005. "Estimation of temperature -dependent lower flammability limit of pure organic compounds in air at atmospheric pressure". *Process Safety Progress* 24 (2): 130-137.

[74] Jones J.C. 1998. "Reid vapor pressure as a route to calculating the flash points of petroleum fractions". *Journal of Fire Sciences* 16 (3): 222-229.

[75] Albahri A. Tareq. 2003. "Structural group contribution method for predicting the octane number of pure hydrocarbon liquids". *Industrial and Engineering Chemistry Research* 42 (3): 657-662.

[76] Benson W. Sidney, Jerry H. Buss. 1958. "Additivity rules for the estimation of molecular properties - thermodynamic properties". *Journal of Chemical Physics* 29 (3): 546-572.

[77] Cranium – Property Estimation Software. Molecular Knowledge Systems Inc. http://www.molknow.com

[78] Poling E. Bruce, John M. Prausnitz, John P. O'Conell. 2001. *The properties of gases and liquids*. Mc-Graw Hill. New York.

[79] http://www.aiche.org/dippr/events-products/801-database

[80] Yong Pan, Jiang Juncheng, Wang Rui, Cao Hongyin, Cui Yi. 2009. "A novel QSPR model for prediction of lower flammability limits of organic compounds based on support vector machine". *Journal of Hazardous Materials* 168 (2-3): 962-969.

[81] Gharagheizi Farhad. 2009. "A QSPR model for estimation of lower flammability limit temperature of pure compounds based on molecular structure". *Journal of Hazardous Materials* 169 (1-3): 217-220.

[82] Gharagheizi Farhad. 2009. "Prediction of upper flammability limit percent of pure compounds from their molecular structures". *Journal of Hazardous Materials* 167 (1-3): 507-510.

[83] Gharagheizi Farhad, Poorandokht Ilani-Kashkouli, Amir H. Mohammadi. 2013. "Estimation of lower flammability limit temperature of chemical compounds using a corresponding state method". *Fuel* 103: 899-904.

[84] Mehdi Bagheri, Rajabi Mansoure, Mirbagheri Marziyeh, Amin Mohammad. 2012. "BPSO-MLR and ANFIS based modeling of lower flammability limit". *Journal of Loss Prevention in the Process Industries* 25 (2): 373-382.

[85] Vidal M., W. Wong, W.J. Rogers, M.S. Mannan. 2006. "Evaluation of lower flammability limits of fuel–air–diluent mixtures using calculated adiabatic flame temperatures". *Journal of Hazardous Materials* 130 (1-2): 21-27.

[86] Zhou Minyong, Donald J.E. Gauthier. 1999. "A new method for adiabatic flame temperature estimations of hydrocarbon fuels". *Fuel* 78 (4): 471-478.

[87] Vidal M., W.J. Rogers, M.S. Mannan. 2006. "Prediction of Minimum Flash Point Behaviour for Binary Mixtures". *Process Safety and Environmental* 84 (1): 1-9.

[88] Dayhoff E. Judith. 1990. *Neural Networks Principles*. Prentice-Hall International. Upper Saddle River NJ. USA.

[89] Khanna Tarun. 1990. *Foundations of Neural Networks*. Addison-Wesley Publishing Company. Boston. USA.

[90] Kosiński Robert. 2002. *Sztuczne sieci neuronowe – dynamika nieliniowa i chaos*. Warszawa: WNT.

[91] Osowski Stanisław. 2000. *Sieci neuronowe do przetwarzania informacji*. Warszawa: Oficyna Wydawnicza Politechniki Warszawskiej.

[92] Rybarczyk Andrzej. 2008. *Sztuczne sieci neuronowe – laboratorium* (2nd revised edition). Poznań: Wydawnictwo Politechniki Poznańskiej.

[93] Gharagheizi Farhad. 2009. "A new group contribution-based model for estimation of lower flammability limit of pure compounds". *Journal of Hazardous Materials* 170 (2-3): 595-604.

[94] Gharagheizi Farhad. 2011. "An accurate model for prediction of autoignition temperature of pure compounds". *Journal of Hazardous Materials* 189 (1-2): 211-221.

[95] Albahri A. Tareq. 2015. "MNLR and ANN structural group contribution methods for predicting the flash point temperature of pure compounds in the transportation fuels range". *Process Safety and Environmental Protection* 93: 182-191.

[96] Albahri A. Tareq. 2013. "Prediction of the lower flammability limit percent in air of pure compounds from their molecular structures". *Fire Safety Journal* 59: 188-201.

[97] Lazzus A. Juan. 2011. "Neural network/particle swarm method to predict flammability limits in air of organic compounds". *Thermochimica Acta* 512 (1-2): 150-156.

[98] Di Benedetto Almerinda. 2013. "The thermal/thermodynamic theory of flammability – The adiabatic flammability limits". *Chemical Engineering Science* 99: 265-273.

[99] Seaton H. William. 1991. "Group contribution method for predicting the lower and the upper flammable limits of vapors in air". *Journal of Hazardous Materials* 27 (2): 169-185.

[100] Le Chatelier Henri Louis, Octave Boudouard. 1898. "Limits of flammability of gaseous mixtures". *Bulletin de la Société Chimique de France* (19).

[101] Kondo Shigeo, Takizawa Kenji, Takahashi Akifumi, Tokuhashi Kazuaki. 2006. „Extended Le Chatelier's formula for carbon dioxide dilution effect on flammability limits". *Journal of Hazardous Materials* 138 (1-2): 1-8.

[102] Kondo Shigeo, Takizawa Kenji, Takahashi Akifumi, Tokuhashi Kazuaki. 2006. "Extended Le Chatelier's formula and nitrogen dilution effect on the flammability limits". *Fire Safety Journal* 41 (5): 406-417.

[103] Yusuke Koshiba, Takashi Hasegawa, Bongchan Kim, Hideo Ohtani. 2017. "Flammability limits, explosion pressures, and applicability of Le Chatelier's rule to binary alkane–nitrous oxide mixtures". *Journal of Loss Prevention in the Process Industries* 45: 1-8.

[104] Ma Tingguang. 2011. "A thermal theory for estimating the flammability limits of a mixture". *Fire Safety Journal* 46 (8): 558-567.

Eksperymentalne i obliczeniowe metody oznaczania dolnej granicy wybuchowości paliw gazowych i płynnych – przegląd stanu wiedzy

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Streszczenie. W publikacji szczegółowo omówiono eksperymentalne metody oznaczania oraz szacowania dolnej granicy wybuchowości gazów i par cieczy. Przedmiotem dyskusji są także zależności oraz niedostatki poszczególnych metod. Dodatkowo, w pracy przedstawiony został zarys historycznych odkryć i badań dotyczących określania granic wybuchowości.

Słowa kluczowe: granice wybuchowości, granice palności, paliwa jednoskładnikowe