“DANGERS DURING STORAGE AND FIRES OF FLAMMABLE SUBSTANCES”

Professional paper

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“Abstract”

Flammable substances are all substances that can be ignited by an external ignition source or by themselves. It is necessary to distinguish flammable substances in order to minimize the danger to people and the environment. Combustible substances are divided according to the aggregate state in which they are found. This is how we learn about flammable gases, flammable solids and flammable liquids. Improper storage may cause self-ignition. In the event of spontaneous combustion, there is a great danger of a large-scale fire precisely because of the late reaction or late notification to the emergency services. In such situations, devices for early detection and fire alarm come to the fore. Precisely because of the danger to people and property, it is mandatory to observe all safety measures in the field of fire protection.

Keywords: Self-immolation, Flammable gases, Flammable liquids, Flammable solids.

1 Introduction

Flammable substances are substances that, when ignited by an external source or by themselves, can cause a burning process, and thus cause a fire that endangers people, animals and material goods. We divide substances according to their aggregate state, gases, liquids and solids. In the case of fire and ignition of each of the individual categories, different actions on the same fire are required.

Combustible gases, in combination with air, form a flammable mixture which, if it is in the flammability area, can burn independently or with an external source. By burning gases, there is a possibility of a rapid combustion or explosion.

When flammable liquids burn, the liquids evaporate and their flammable vapors burn. Vapors evaporate from the liquids, which in concentration in the air, if in sufficient concentration, can cause ignition or self-ignition. The burning of a liquid depends on the type of flammable liquid and its boiling point. The lower the boiling point temperature, the more flammable the liquid is more dangerous and has the ability at a lower temperature, in sufficient concentration with oxygen, to cause a violent reaction of ignition and even explosion.

Solid substances are substances of constant shape and volume. When burning solids, we distinguish burning by pyrolysis, burning with a change in aggregate state and direct burning. As with flammable liquids, solid substances evaporate when ignited flammable vapors that ignite on the surface of solids and thereby promote burning. This paper describes in more detail the process of burning solids that we encounter every day (wood, paper and coal). Information on the characteristics and state of the substances that burn is interesting, and therefore changes during the burning process.

Self-ignition of materials of plant origin is possible because, during improper storage, biological microorganisms act that accelerate the rise in temperature, smoldering and therefore in the presence of oxygen and fire. By the process of self-ignition of hay which is not stored dry enough, the self-ignition process of any fuel of plant origin is also described.

2 Flammable Gases

Flammable gases are compressed, liquid or pressurized dissolved gases that have a critical temperature lower than 323.15 K (50°C) or at 323.15 K (50°C) a vapor pressure of more than 300 kPa (3 bar) and which mixed with air, they can ignite and/or explode (National Newspaper, 2022).

Gaseous substances are substances that do not have a constant volume or shape and are shaped according to the container or space in which they are located. The main characteristic of all gases, a moreover, even those that are flammable is that their molecules can move freely within the available space. Some of the most common flammable gases are: butane, hydrogen, propane, methane and the like. During gas burning, gas molecules combine with oxygen molecules from the atmospheric air, and heat is released in this process. It is this released heat that supports the fuel mixture above the ignition temperature and heats it up at even higher temperatures.

For the process of igniting flammable gas, a certain amount of oxygen mixture and sufficient heat are required. Gases are flammable liquids that are above the boiling point and are therefore in a gaseous aggregate state, and when flammable gases are ignited, a visible flame is created. Ignition and further combustion, in a mixture with air, forms a flame front that travels through the gas mixture. There are two types of flame fronts: stationary and traveling.

A stationary flame front is formed when the ignited gas mixture travels towards the flame front at the same speed as the flame front moves towards the gas mixture. A traveling flame front is a front that occurs when the gas mixture is at rest and the flame is burning the front travels through the gas mixture (Ivančić, 2010)

Ignition of flammable gases in a mixture with air or oxygen can be forced and thermal. With forced ignition, a mixture of flammable gases and air is ignited in the explosive area at room temperature, by an external ignition source. Possible external sources of ignition are open flames, sparks and the like. When the mixture of flammable gases and air or oxygen in the area of explosiveness is heated by the entire volume until it ignites without an external source of ignition, we call it thermal ignition. Thermal ignition can occur by heating the entire mass of gas, an increase in pressure in the tank and similarly (Pačelat and Zorić, 2003).

2.1 Flammable area

Flammable gases can ignite and/or explode only when they are in the so-called flammability/explosive area. The area of flammability or the area of explosion is a limited area with the maximum and minimum volume fraction of flammable gas in it mixed with air that can be ignited and continue further burning. Figure 1 shows the flammability area (Pavelić and Pavelić, 2011).

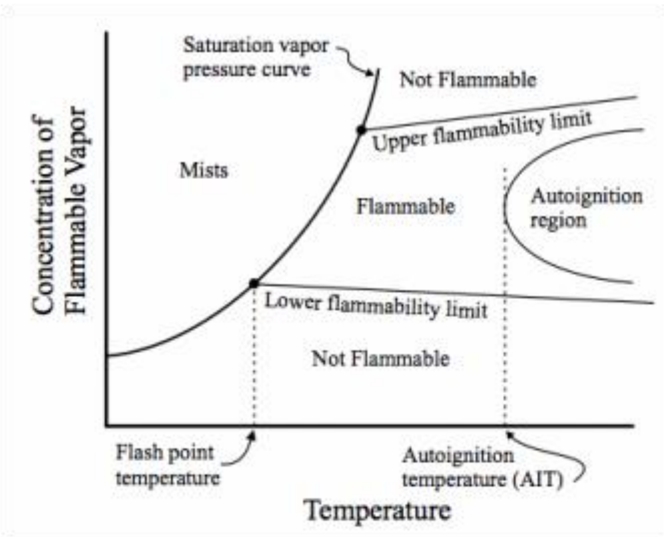

Figure 1. Flammability area (Source: Crowl, 2003, p14)

The flammability/explosive range lies between the lower flammability/explosive limit (LFL/LEL) and upper flammability/explosive limits (UFL/UEL). In the area below lower flammability/explosive limits (LFL/LEL), the gas concentration in the air is very small. We call such a mixture too lean fuel component (small quantities of flammable gas, and large quantities of substances that support burning, i.e. oxygen in air), that the mixture of flammable gas and air could ignite at all, let alone explode. Such a mixture can only be ignited coronally, i.e. glow in so-called cold flame in direct or indirect contact with the energy source ignition, but such a flame will not spread to the rest of the mixture and cause it to ignite and then no explosion. Further in the area above the upper limit flammability/explosiveness (UFL/UEL), concentration of a mixture of flammable gases and air is too large, i.e. the mixture is too rich in the fuel component (excessive quantities combustible, and too little oxygen in the air), so that it could catch fire or explode. Areas of flammability, explosiveness and detonation area of flammable gases are expressed in volume percentages (vol.%) (Pavelić and Pavelić, 2011).

A stoichiometric mixture of gases is the concentration of a combustible substance in the mixture at which complete oxidation occurs, that is, in simpler terms, it is the mixture which is most suitable in order to achieve ignition or explosion. The stoichiometric mixture is between the lower and upper explosive limits (Čurin, 2015).

Figure 2 shows in detail the extent and limits of explosiveness, i.e. the lower limit of explosiveness, the area of explosiveness and the upper limit of explosiveness.

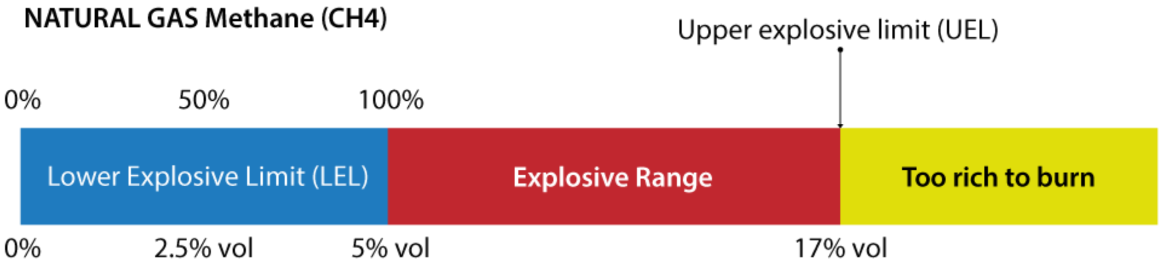

Figure 2. Extent and limits of explosiveness (Source: Mike, 2022)

Table 1 shows the 8 most common flammable gases. We can encounter each of these gases on a daily basis. When encountering flammable gases, it is necessary to know their basic characteristics such as LEL and UEL and the stoichiometric mixture. Limits or mixtures are expressed in volume percentages (vol%) (Pocrnić, 2019).

Table 1. Flammability limits and stoichiometric mixtures of flammable gases (Source: Pocrnić, 2019, p7)

Flammable gas	Explosive Range (vol%)		Stoichiometric mixture (vol %)
	Lower explosive limit	Upper explosive limit	
Methane (CH4)	5,3	14,9	9,5
Ethane (C2H6)	3,1	12,5	5,64
Propane (C3H8)	2,1	9,5	4,02
Butane (C4H10)	1,86	8,41	3,12
Ethyne (acetylene) (C2H2)	2,5	80,5	7,72
Hydrogen (H2)	4,0	75,2	29,50
Ammonia (HN3)	15,5	26,6	21,82
Carbon monoxide (CO)	12,5	74,2	29,50

3 Flammable Liquids

According to the ordinance on flammable liquids (OG 54/99), flammable liquids are substances that have a penetration greater than 300 penetration units (1/10 mm) and whose vapor pressure at 323.115 K (50°C) is less than 300kPa (3 bar) , and are divided according to the flash point temperature into flammable (highly flammable) liquids, whose flash point temperature is equal to or lower than 311.15 K (38°C) and combustible liquids whose flash point temperature is above 311.15 K (38°C) (National Newspaper, 1999).

3.1 Properties and burning of flammable liquids

The main characteristic of flammable liquids is that they evaporate quickly and easily, and their vapors mixed with air are easily ignited and often a process of rapid combustion or explosion occurs, if the cause of ignition is present (e.g. open flame, electric spark, friction, cigarette and the like). Burning flammable liquids, killing is the same as burning flammable vapors and gases because liquids do not burn, but vapors that are above the liquid and evaporate from it.

The rate of combustion of flammable liquids depends on the rate of evaporation of the liquid into the vapor phase. The speed of the evaporation process is higher, the larger the liquid evaporation surface and the higher the temperature of the atmosphere above the liquid surface.

Combustion of flammable liquids is possible if enough is created above the liquid the concentration of flammable vapors which, in a mixture with air, will be a sufficient concentration to create a flammable mixture. The concentration of liquid vapor must be in the area between the upper and lower flammability limits, which we also stated in the chapter on flammable gases (Pačelat and Zorić, 2003)

3.2 Hydrocarbons and their characteristics

Hydrocarbons are chemical compounds consisting only of carbon and hydrogen atoms. Saturated hydrocarbons or alkaline are those in which the carbon atoms are connected by a single bond covalent bond, and the typical representative is methane, while pure propane is the most common working substance. Unsaturated are those hydrocarbons that have a double or triple covalent bond between carbon atoms. A typical representative of unsaturated hydrocarbons is ethene, while propene, better known by its old name propylene, is used for cooling (Kušter, 2016).

Figure 3 shows the structural formulas of methane, ethane, propane and propylene.

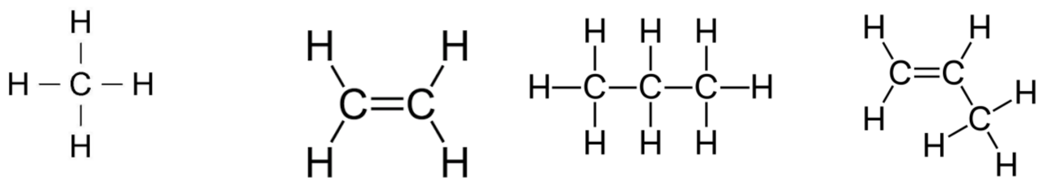

Figure 3. Structural formulas of methane, ethene, propane and propylene (Source: Kušter, 2016, p1)

3.3 Temperature characteristics of flammable gases

Table 2 shows the properties and boiling range of some of the most common liquid fuels.

Table 2. Boiling point of some liquid fuels (Source: Pocrnić, 2019, p9)

Type of liquid fuels	**Boiling point (°C)**
Crude gasoline	50 to 200
Lighting oil (kerosene)	150 to 300
Gas oil (diesel)	200 to 350
Lubricants and paraffin oils	More than 350

The lowest temperature at which enough steam is formed above the liquid to form a flammable mixture with air that will ignite in contact with an ignition source is called the flash point of the liquid. Liquids with a lower boiling point have a greater risk of formation fire. Self-ignition temperature is the lowest temperature required to cause self-sustaining combustion of a substance in the absence of an external or additional source of ignition (spark, flame). The auto-ignition temperature is in most cases higher than the boiling point of a liquid. In the case of liquids, this temperature, of course, refers to flammable vapors that are created by the evaporation of the liquid (Pocrnić, 2019).

4 Flammable solids

Substances that are in a dry state and can be more or less flammable in contact with an external source of ignition. According to the origin, solid fuels can be divided into natural

and artificial. The burning of solids largely depends on the chemical composition, so we can distinguish between:

- Burning with pyrolysis,
- Burning with a change in aggregate state and
- Direct burning.

During the burning of solid combustible material, the mass is first dried, and then the process of thermal decomposition and extraction of volatile components begins. The amount of volatile components, i.e. vapors formed above the solid, depends on the type of solid mixed with air, and together they create a specific flammable mixture around the solid.

Immediately upon ignition, the ignition temperature of the mixture is reached. The burning process is accompanied by the emission of smoke containing solid, gaseous and liquid particles. After burning solids, ash remains, which is a mixture of inorganic substances (Pačelat and Zorić, 2003).

4.1 Burning wood

Wood is a solid substance that belongs to the group of combustible solid substances. In everyday life, a large number of various wooden materials are used, which are processed in various designs, depending on the need and purpose of the same. The degree of flammability of wood depends on the type, density, type of fire resistance, protective coatings, treatment, degree of humidity and the like.

Wood burns faster, if its specific weight is lower and the wood layer is thinner, and the area accessible to combustion is large. The flammability of wood also depends on the type of wood, for example, oak is more resistant than softwood, smooth planed wood is more flammable than rough planed wood, etc.

Wood is a weak conductor of heat, and the flame that affects the outer surface of the wood progresses slowly, i.e. it spreads slowly towards the interior. If the solid wood material is found in large pieces, the burning can stop by itself without special intervention in the form of extinguishing. The cause of such cessation of wood burning is the formation of a layer of coal that is located in the outer zone of the wooden structure and protects the interior from further spreading of the flame front (Pocrnić, 2019).

Table 3 shows the values of the burning temperature for certain types of wood, and thus it is clear to us the possibility of spreading and igniting other substances that they are around the burning wood.

Table 3. The value of the burning temperature of the type of wood (Source: Pocrnić, 2019, p13-14)

Type of woof	Burning temperature (°C)
Elm, Ash, Spruce	270
Beech, Hornbeam, Walnut	275
Mahogany, Plywood	285
Oak	290

4.2 Burning paper

Paper is one of the most ubiquitous, common and cheapest materials used in everyday life. The demand for paper is increasing day by day. The main raw material for the production of paper is perennial plants, i.e. trees and annual plants. In the production of paper, various other substances are used, such as fillers, minerals, bleaches, paints, recycled old paper, etc.

Paper, as a flammable solid, belongs to the group of highly flammable solids that intensely burning. The speed of burning and combustion of paper largely depends on the type of paper, the method of production and the method of packaging. If the paper is stacked in the form of sheets placed on top of each other, due to the lack of oxygen in the interior between the sheets, the combustion of the paper will take place only on the outer edges or outer edge parts. Substances such as books, folded papers, etc. are especially exposed to such combustion (Pocrnić, 2019).

Paper, like other flammable materials, is subject to ignition when a certain temperature is reached. The paper, as such, can be ignited by an external ignition source such as e.g. holding an open flame against the paper. The temperature of the open flame, in this case, is between 800°C and 1300°C. However, paper can also catch fire without any external influence. We call such a process self-ignition. Self-ignition occurs when the ambient temperature reaches a certain critical level. The critical level, or in this case the self-ignition temperature of paper, depends on density, moisture and similar indicators, but it is set at 450°C. Therefore, we can to say that, if there is no external source of ignition, and by heating the space to 450°C, the paper will ignite by itself (ANTIAIM, 2010).

4.3 Coal burning

Coal is a natural solid fossil fuel that is extracted from various depths of the Earth's crust, where it is covered by sedimentary layers, often forming huge deposits. Coal belongs to the group of caustobiolites, rocks of organic origin that can burn. It is precisely coal that is a very important energy source in today's time.

Coal itself has three basic parts:

- Pure fuel substance,
- ash and
- water.

Pure fuel is an organic component of coal, primarily consisting of carbon and hydrogen, as well as oxygen, nitrogen and sulphur. Sulfur is an element of coal that is in elemental form and in the form of sulfides and sulfates. It is elemental and sulphide sulfur that increases the heat value of coal, but it is undesirable, because the product of their combustion has a devastating effect on devices and pollutes the air. As a result, elemental parts and sulfides increase the self-ignition of coal, after which coal as such is difficult to store.

Ash is a substance that remains after burning coal, and it originates from inorganic, mineral impurities. Ash and water in coal reduce its heating value.

The calorific value of coal ranges in a very wide range from 6000kJ/kg to 30,000kJ/kg (for anthracite and more than 35,000kJ/kg). Volatiles or vapors from coal are released when coal is heated to 875°C. (Croatian encyclopedia, 2021).

4.3.1 Self-ignition of coal

The tendency of coal to self-ignite depends on the type of coal, but also on the amount of moisture in the chemical composition, the degree of fragmentation, and the place and method of storage. When the temperature in the interior of the mass rises to a value of 400°C to 500°C, the oxidation process is most intense and then the burning process begins. An important factor affecting the self-ignition of coal is the amount of moisture. A smaller amount of moisture allows coal particles to absorb oxygen more intensively, and with a higher percentage of moisture, this process is difficult. The higher the coal temperature and the smaller the pieces of coal, the greater the degree of oxidation and the possibility of self-ignition (Pačelat and Zorić, 2003).

5 Spontaneous Combustion of Plant Origin

Materials of plant origin that are prone to self-ignition are: hay, straw, kindling, clover, grains, flour, wood shavings, etc. Self-ignition of materials is caused by various irresponsible and inappropriate storage. Self-ignition of plant material occurs due to various biological processes. During self-ignition, thermal energy is released, which is divided into smaller parts. It drains into the environment, and most of it accumulates in the mass of matter. Such accumulated energy increases the temperature of the mass and therefore accelerates the further process of release and further accumulation of thermal energy. The amount of accumulated substance depends on the type of substance and the ignition point. When a certain amount of accumulated substance reaches a value, the process of smoldering begins, which creates glowing cores. The material does not burn, that is, smolders equally. In places where the material is less compacted, the concentration of oxygen is increased and thus promotes faster combustion that spreads towards the outer surface. The speed of fire spread depends on the air flow, and the path is usually not straight. The path of the flame moves in such a way that it burns first where the material is less dense, i.e. there is more oxygen, and then towards places where there is less oxygen.

Self-ignition of material of plant origin depends on the basic condition, which is a larger amount of stored material, poor ventilation and the presence of a certain amount of moisture in

the material.

External signs that may indicate the self-heating process exists the possibility of self-ignition is subsidence and the occurrence of subsidence, the development of heat, smoke and the smell of burning. The time required for self-ignition to occur is ten days from the moment of storage and up to three or four months (Pocrnić, 2019).

5.1 Self-ignition of hay

Hay is food for domestic animals. It is prepared by mowing and drying grasses, buttercups and other plants that grow in natural or artificial meadows. The quality of hay depends on its plant composition, the time of mowing and the method of drying and storage. (Croatian Encyclopedia, 2021).

When the mass decays due to the action of microorganisms, for example, when the hay is not dry enough after mowing, the plant mass becomes wet, and in inadequate conditions of storage of large amounts of hay due to the presence of moisture contained in inside, microorganisms develop. From the mentioned case, the process of rotting and decomposition of plant material results and with hay temperatures of around 70°C. This the process takes approximately three to four days. After this process, there are physical and chemical changes in the substance, along with the intense generation and accumulation of heat and the process of self-heating of the mass in the interior (temperatures from 220°C to 240°C). At the specified temperature, red-hot cores form and the fire spreads further through fire channels that are enriched with oxygen, towards the bottom or the sides.

The time required for hay to self-ignite is ten days from the moment of storage and up to three or four months. If the hay contains about 45% moisture, self-ignition processes begin on the first or second day after storage, and a maximum of fifteen days (Pocrnić, 2019).

6 Conclusion

In conclusion, through the research for this paper, we come to some interesting facts. Free we can say that flammable substances in all three aggregate states have similarities, but also some differences.

When igniting all three types of combustible substances, their flammable vapors burn are released by the action of heat. The amount of combustion, i.e. the calorific power of combustion of certain materials depends on the type of material, the speed of action, the amount of exposure, but also the speed of evaporation of certain materials. In order for the burning process to occur, a mixture of flammable gases/steam in concentration with air (oxygen) is required, in the area of flammability/explosiveness. Between the upper and upper flammability limits there is a flammability area in which all burning can take place freely. The area of flammability is different for each individual substance, and it depends on the temperature of evaporation, i.e. the boiling point of the liquid, the evaporation of the solid, etc. During self-ignition of material of plant origin, a specific oxidation process occurs in which heat is generated.

The development of heat, in addition to the fuel material and the presence of oxygen, creates the third necessary condition for combustion, and thus combustion. The speed of the oxidation process, i.e. the speed of self-ignition of a substance largely depends on the type of substance, condition, amount of moisture and storage method. If the material is stored poorly, without the necessary ventilation and with a large amount of moisture in the air, the so-called self-ignition or spontaneous comustion.

In conclusion, there is a need for further training and informing and training of the civilian population as well as workers at workplaces, in order to familiarize them with the types of combustible substances, their characteristics of ignition, self-ignition, and the like.

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