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An Analysis of Flammability and Explosion Parameters of Coke Dust and Use of Preliminary Hazard Analysis for Qualitative Risk Assessment

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Abstract: Appropriate investments are required to achieve sustainable industrial development and safety conditions at the same time. A sufficient safety level is achieved when research outcomes are deployed in practice. This paper comprises a review of ignitability and explosive parameters and thermogravimetric tests of coke dust selected for the needs of the testing The K_{St} value of the tested dust was 64.2 bar m/s, which means that it belongs to explosion hazard class 1 and that it has relatively low explosive abilities. The maximum explosion pressure for the tested dust was found to be 6.84 bar, and the minimum ignition temperature of a coke dust layer with a thickness of 50 mm was 400 °C. The use of the Preliminary Hazard Analysis in plants in which coke dust is present allows for limiting the scope of the risk analysis by eliminating elements that are either insignificant or of low significance from the viewpoint of explosion hazard. The adopted method allows qualitative assessment of the risk associated with threats, dangerous situations, and hazardous events that may take place during the use of devices, machines and their systems, and subsystems, including a qualitative evaluation of potential consequences of an accident or possible health loss. Risk assessment for life safety under building fires and explosions plays an important role in performance-based fire and explosion protection design and fire insurance ratemaking. The motivation for this work was the integrated protection of people, process equipment, building resilient infrastructure, promotion of inclusive and sustainable industrialization, business operation, and the natural environment.

Keywords: risk assessment; fire and explosion safety of coke dust; Preliminary Hazard Analysis sustainable development in process safety

1. Introduction

1.1. Sustainable Development

The rapid development of the economies in many countries around the world that has been observed in recent decades has brought a set of new risks to which society must become resilient. As resources of various kinds available are limited, one of the most fundamental issues to be resolved is how to ensure that the coexistence of mankind and their natural environment will not be harmful to any of the interested parties. The response of the international community is the concept of sustainable development.

The term may be considered generic and may have various shades when used in different contexts. In social sciences, in the context of risk reduction linked to rapid development, it is crucial to focus on implementation of certain safety measures, both to increase societal resilience to potential crisis situations and to ensure efficient engineering tools to conduct cost-effect analyses.

Industry is considered to be a significant source of multidimensional and widely understood threat to the community and the environment. Usually, the role of governments is to prepare large-scale



solutions and restrictions. On a local scale, a crucial role is played by owners and managements of particular industrial plants. National legislation determines the lowest acceptable safety level, which will not necessarily be universal for all industries. In case of an incident, despite personal responsibility, many sustainable development goals (SDGs) devised by the United Nations might be affected. The incident may cause water pollution (goal No. 6), resulting in a decrease in the level of sanitation and, in parallel, harming the life below water (goal No. 14). The consequences of the incident may affect life on land in the vicinity of the plant (goal No. 15). On the other hand, affordable and clean sources of energy require constant research on the process safety (goal No. 7). It is clear that most of the industrial incidents affect local communities in the context of possible growth of unemployment, resulting in a decrease in the living standard (goals 1, 2, 3). Therefore, there are always anticipated long-term consequences, which cannot be neglected [1].

Enhancing the efficiency of processes, along with the deployment of clean technologies and environment-friendly industrial processes, are necessary to achieve sustainable infrastructure and industry by 2030.

Investment in sustainable infrastructure and technology research impacts economic growth, job creation, and in fact promotes prosperity. As an effect, sustainable development goal No. 9 aims to build resilient infrastructure, promotes industrialization, and fosters widely understood innovation. Understanding the flammability and explosion parameters of combustible dusts allows for building safe workspaces.

In general, the described research relates to many aspects of widely understood sustainable development. As an effect, a multidimensional analysis is needed to ensure that a particular economic activity would conform with the sustainable development goals devised by the international community.

1.2. Sustainable Coal Coking Process

Coal coking is a process of thermal coal degasification at a high temperature (450–1000 °C) without the access of air. The main products of this process are remains of solids (coke, biochar) of high mechanical resistance and high chemical reactivity [2]. Moreover, this process leads to the generation of liquid products (coal tar) and gas. Coke is used in the first place in iron smelting in large furnaces in mills, where it fulfils three elementary roles: fuel, reducer, and a kind of scaffolding that allows permeation of gases generated during the process. It is also used as high-quality fuel for the firing of heating boilers (in boiler rooms as well as in workshops and individual households) and in metal foundries. Despite the ability of coal to become crushed when in lumps, it is a specific property for coal with a relatively low content of carbon-for example lignite-but also coke undergoes this phenomenon and causes the generation of dust with explosive properties. The following explosion pentagon best describes the essential conditions for a dust explosion: (I) fuel, (II) oxidant, (III) ignition source, (IV) mixing of the fuel and oxidant, and finally (V) confinement of the obtained mixture [3–7]. Accordingly, it might be possible to prevent or mitigate a dust explosion if one of the sides of the pentagon is removed. Nevertheless, several diverse measures need to be adopted so that the hazard of a dust explosion can be minimized to an acceptable level. A significant role in the devising of performance-based fire and explosion protection designs and in the process of fire insurance fixing of rates is played by risk assessment related to life safety pertaining to building fires and explosions. The definition of risk provided by Wilson and McCutcheon [8] suggests that risk entails a possibility of injury, loss, or harm to the environment arising from a hazard, in the case of which the meaning of risk is a function of the probability (or likelihood) of an undesirable incident and the magnitude of its consequences. A definition should be made of those terms taking into consideration the scale, both spatial and temporal [9,10]. To minimize the potential risk of sustaining occupational injury in a fire department, use was made of a risk management procedure [11]. The outlined research was undertaken to study the deployment of the risk management process for possible use in future. Its further aim was to document changes in fire personnel's knowledge, attitudes, and conduct in the scope of selected control strategies, which have been deployed as part of the risk management procedure. Various

3 of 17

procedures were derived with the aim of evaluating the fire risk, and to design fire protection and allow fire risk mitigation [12]. Papers [13–15] suggested the application of a mathematical model and numerical approach based on experimental data, which indicated how flame propagation speed and minimum ignition energy of a given dust depend on dust concentration, for example for magnesium, iron particles having dissimilar diameters. It has been ascertained that the minimum ignition energy was characterized by lower values with the decrease in particle size.

A report by the International Association of Oil & Gas Producers [16] indicates that it is possible to assess the fire risk with the use of two approaches, namely, the simple mathematical formulae and the Computational Fluid Dynamics (CFD) method. Evaluation of the risk to life safety during a building fire requires the adoption of rational methods. There are three basic categories of methods for assessing the risk to life safety during a building fire, namely, the qualitative, semi-quantitative, and quantitative methods [17]. Given the rapid development of performance-based fire protection, widely ranging research has been performed in the field of quantitative fire risk assessment related to life safety during building fires. The most commonly used approach to handle any uncertainties comprises probabilistic methods, the application of which requires a significant amount of historical data, yet such data are seldom available given the unique nature of building fires. As the data were limited, the fuzzy method and probabilistic method were only able to make subjective assumptions of the membership function and probabilistic density function [18]. This implies that risk ensues from a hazard, namely, the capacity of a mechanism, plant, process, either a material or a physical factor present in the working environment to give rise to harm to people, the environment, assets, or production. Risk management constitutes a complete process that covers comprehending potential risk, risk assessment, and decision-making, which is necessary to guarantee that effectual risk controls are in place and deployed. Paper [19] is oriented at devising a method to allow implementing of a Quantitative Risk Analysis (QRA) for Liquefied Petroleum Gas (LPG)-fueled cars in enclosed car parking lots for a risk-based design of the ventilation and gas-detection system.

An interesting approach to integrating dust explosion probability and consequence severity considerations with a quantitative risk assessment tool is illustrated by a recent initiative undertaken by The Netherlands Organisation (TNO) [19]. In addition, authors [20] have also dedicated their attention to QRA of dust and explosions of hybrid mixture, as well as development of a methodological basis for the management of the abovementioned risks. The proposed methodology is based on computational fluid dynamics for the needs of analyses of the severity of the consequences of a dust or hybrid-mixture explosion with regard to the development of overpressure. Although CFD modelling of gas explosions commenced several years ago, CFD remains a comparatively novel methodology as regards dust explosions. It may be assumed that, at the moment, the most comprehensive package available is the Dust Explosion Simulation Code (DESC), which was developed in Norway by GexCon. As stated by Skjold [21], DESC may prove to be useful as a plant design tool for optimizing mitigation measures, such as, for example, explosion barriers, vents, and suppression systems. In order to facilitate the management of risks caused by materials that cause a dust explosion hazard, the authors have suggested a conceptual framework and an implementation flowchart. The main traits arising from the risk management plan outline comprise a quantitative analysis of the likelihood and consequences of explosions and an unequivocal reflection of the hierarchy of adopted safety controls [22–26]. The validation results of DESC have been verified by Amyotte et al. [27]. Data concerning the essential physical and thermodynamic properties of dust, which may for example be obtained in the Siwek 20-1 chamber, were applied as input to the DESC combustion model.

An explosion of coke dust may spread due to the fact that, under the impact of thermal radiation, dust particles release volatile parts, which allow the formation of a cloud of easily flammable and explosive gas mixture in new areas formed by those volatile parts with air. The front part of the flame in this mixture creates an explosion reaction zone, which is followed by the ignition zone of coked coal particles. Both spheres move from the cloud at very high velocities. As an effect in the reaction zone, not only does static pressure appear (increase in the volume of reaction products, which is a

function of temperature), but also dynamic pressure (movement of masses). As a result, the density of flammable mixture in the explosion reaction zone tends to increase considerably. The increase in gas density in the explosion reaction zone becomes an additional factor for the self-acceleration of the combustion process and explosion development. Solid remains left from dust explosion form a mixture of unreacted coal dust, burnt dust, which is created out of coal particles of a various degree of reaction and ash. The fact that each coal dust explosion is accompanied by the ejection of solid products proves that the combustion reaction in the explosion flame is incomplete.

The ejection of solid explosion products is dangerous for at least three reasons:

- the presence of a high temperature of combustion products and blast force that could affect persons present on the plant premises;
- it may cause the outbreak of a fire;
- it may become an initiator of dust explosion in a confined space under the impact of a preliminary blast when dust becomes "blown off" from the places where it had become settled and formed a large cloud [3].

As regards coal dusts and dusts of coal-derivative materials, in many cases the ignition is initiated by incandescent sources generated as a result of known propensity of those dusts to self-ignition. This propensity grows with the volume of dust and its temperature. In the case of coal dusts stored in a volume comprising a few cubic meters, incandescent sources may already be generated once the temperature of 55–60 °C has been exceeded [5].

Familiarity with ignition and explosion parameters allows:

- making an assessment of explosion hazard and carrying out a correct classification of areas and premises;
- applying adequate prevention from accidental explosions and from consequences of an explosion;
- selecting appropriate devices in the investment process (especially electrical appliances), including installations with explosion-proofing.

Classification of areas need to be consistent with the ATEX Directive 94/9/EC [28] and should comprise the following:

- Zone 20—space in which the explosive atmosphere in the form of an airborne cloud of flammable dust occurs permanently, frequently, or over long periods;
- Zone 21—space in which the explosive atmosphere in the form of an airborne cloud of flammable dust may occur at times during normal operation;
- Zone 22—space in which the explosive atmosphere in the form of an airborne cloud of flammable dust does not occur during normal operation, and even if it does, it does not continue for a long time.

In the present paper, research was undertaken to help shift the field of dust explosion prevention and mitigation from its current emphasis on hazards (with the accompanying reliance on primarily engineered safety features) to a focus on risk (with an accompanying reliance on hierarchical, risk-based, decision-making tools). Employing the principles of Preliminary Hazard Analysis for needs of a qualitative risk assessment of dust coke, a methodological framework for the management of these risks was developed. Hence, the paper presents an outline of the risk assessment method in selected process units of the illustrative generation technology of coke dust.

2. Materials

For experimental research, use was made of one coke dust from a selected coke oven plant. The tested coke dust was obtained from a Polish Coking Plant (the secret of the company). This dust was formed by crushing the coke nuggets formed in the coking plant and was collected from various places of coke storage; therefore, it can be assumed that the tested sample constitutes a representative

group for coke dust present in the selected plant. For individual tests, dust was sieved with the use of a sieve shaker. To determine the minimum ignition temperature of the dust layer (MITDL), coke dust was sieved through a 200 μ m sieve. However, to determine the minimum ignition temperature of the dust cloud (MITDC), dust was sieved through a 71 μ m sieve, while for the determination of explosion parameters it was sieved to a size $\leq 63 \mu$ m. The dust humidity was 5.1% by weight, and the bulk density of the test dust with a basis weight $\leq 200 \mu$ m was 0.379 g/cm³. The elementary composition of tested coke dust was: %C 91.03; %H 4.09; %O 2.78; %N 1.37; %S 0.71. The determined parameters serve as a basis for developing an explosion risk analysis document, but it can also be a source of information about coke dust properties.

3. Methods

3.1. Minimum Ignition Temperatures of Dust

In accordance with standard EN 50281-2-1 [29] and [30], two methods of measuring the MITDL may be applied: Method A—this method is based on the determination of the minimum temperature of a dust layer with a specified thickness on a heating plate; Method B—this method comprises the determination of the MITDC. The testing (Method A) is to be continued until ignition is observed up to maximum on a heated plate heated to 400 °C. In accordance with the abovementioned standard, it shall be considered that ignition of a dust layer has taken place when: glowing or flaming burning is observed, or the measured temperature has achieved the value of 450 °C, or the measured temperature has exceeded by 250 °C the temperature of the heating plate. Glowing is an undeniable process which is the most frequent symptom of ignition of a dust layer. The ignition temperature of a dust layer is perceived according to standard EN 50281-2-1, and it is the lowest furnace temperature, rounded up to a multiple of 10 $^{\circ}$ C, at which ignition takes place. The determination of layer ignition temperature comprised placing a dust sample on a metal ring of planned thickness placed on a heating plate, i.e., 5; 12.5; 25; and 50 mm. It is considered that ignition of a dust cloud has taken place if a flame is visible beyond the bottom end of the oven pipe. Nevertheless, a slight delay is admissible for ignition of a duct cloud. Sparks without a flame are not taken to indicate ignition of a dust cloud. Generally, it is assumed that the minimum dust ignition temperature is [30] the lowest temperature of the furnace at which ignition of a cloud takes place, reduced by 20 °C at the temperature of the furnace over 300 °C or decreased by 10 °C at a lower furnace temperature.

3.2. Explosion Parameters of the Tested Dust Consistent with Standard EN 14034

Experimental testing was conducted in conformity with standard EN 14034 to determine the explosiveness characteristics of dust clouds, which comprise the following two parts:

- EN 14034-1 Determination of maximum explosion pressure p_{max} of a dust cloud [31];
- EN 14034-2 Determination of the maximum rate of explosion pressure rise (dp/dt)max of dust clouds [32].

Testing was performed with the use of a testing stand set up in conformity with standard EN 14034. The main component of this stand was the research chamber, sphere-shaped, with a capacity of 20 dm³. The tested dust was dispersed by a dispersion nozzle, in which overpressure was generated at the level of 0.2 MPa. The time ignition delay of the mixture dust and air was ca. 60 ms.

Ignition was initiated by a chemical explosive, which consisted of ignition heads installed inside, in the central part the sphere. In order to determine the p_{max} and $(dp/dt)_{max}$, two heads were used, each with a capacity of 5 kJ. The producer of the used heads was Nitroerg S.A. The execution of tests of the maximum explosion pressure p_{max} for dust clouds was based on provisions set out by standard PN-EN 14034-1. The test result may be considered to be positive if the pressure increase measured inside the sphere was found to be greater than 0.5 bar or equal to it. Determination of the maximum explosion pressure p_{max} for the tested dust requires a series of tests to be performed at a concentration

of 250 g/m³. In the following tests, this concentration was either increased by 250 g/m³ or reduced by 50% as compared to the previous one. This was continued until the maximum explosion pressure could be identified. It was possible to identify the value of the maximum explosion pressure p_{max} of dust clouds for a minimum of two successive increasing and decreasing concentrations for which the maximum explosion pressure p_{max} for those concentrations was lower. The maximum explosion pressure determined in this way constitutes the p_{max} value of the first series. The standard requires that two more series of measurements should be performed, and p_{max} value for a given type of dust is the arithmetic average of three series of measurements. Taking into consideration the cooling effect in tests, for the execution of which a 20 dm³ sphere was used, the measured maximum explosion pressure p_{max} needs to be adjusted.

In addition, the maximum rate of explosion pressure rise $(dp/dt)_{max}$ of dust clouds was tested pursuant to the provisions of the standard [32] in a spherical testing chamber having a volume of 20 dm³. Determination of the maximum explosion pressure p_{max} for particular dusts required implementation of a series of tests commencing with the concentration of 250 g/m³. During the next tests, an increase by 250 g/m³ or a reduction by 50% in concentration was adopted as compared to the preceding one. It was necessary to continue the tests until it was possible to identify the maximum rate of explosion pressure rise. It was possible to identify the maximum rate of explosion pressure rise (dp/dt)_{max} of dust clouds if, for at least two growing and decreasing concentrations, the maximum rate of explosion pressure rise identified in such a way was the (dp/dt)_{max} of the first series. Pursuant to the abovementioned standard, it was necessary to perform two further series of measurements, and (dp/dt)_{max} for the given dust was the mean arithmetic value of three measurements.

Given that increasing the explosion pressure tends to decrease as the volume grows, and to calculate K_{max} , K_{St} , the so-called cubic law, should be adopted to enable the correct interpolating of test results [32]:

$$K_{St} = K_{max} = \sqrt[3]{0.02} \cdot \left(\frac{dp}{dt}\right)_{max,20l} = 0.2714 \cdot \left(\frac{dp}{dt}\right)_{max,20l} \tag{1}$$

3.3. Thermal Gravimetric Analysis (TGA)

In order to determine the characteristics of the thermal decomposition process and the process of changes that take place in the selected coke dusts within a preset temperature range, samples were tested using a TA INSTRUMENTS Q500 thermogravimeter (New Castle, United States of America). Coke dust samples weighing ca. 30 mg were subjected to a thermogravimetric analysis in the dynamic method in conformity with standard EN ISO 11358 [33]. The measurement was performed within a temperature range of 20 °C to 800 °C at a constant heating rate of 10 °C/min. Platinum pans were used for needs of testing. An oxidizing atmosphere (air) was obtained by maintaining a constant air flow of 90 mL/min and a flow of inert gas—nitrogen—of 10 mL/min. On the basis of our own studies, we estimated the following measurement precision: temperature, 1 °C; sample mass, 0.01 mg; and heating rate, 1 °C/min.

3.4. Heat of Combustion

The heat of combustion of the tested dusts was determined with the use of a bomb calorimeter according to standard EN ISO 1716 [34]. A sample of selected dust of a weight of up to 1 g was burnt in the oxygen atmosphere at a pressure of 2 MPa, at an initial temperature of ca. 20 °C, with maintained constant volume in the calorimetric setup. The sample would undergo complete combustion, and after that, the total heat released from the sample was determined in relation to its mass.

4. Results

Table 1 present the results of ignition and explosion of the tested coke dust.

| Parameter Type | Value | |
|--|------------------------------|---------|
| | Thickness of dust layer [mm] | |
| _ | 5 | >400 °C |
| Minimal ignition temperature of a dust | 12.5 | >400 °C |
| | 25 | >400 °C |
| | 50 | 400 °C |
| Minimal ignition temperature of a cloud dust (MITDC) (°C) | 610 | |
| $\begin{array}{l} \mbox{Maximum explosion pressure } p_{max} \mbox{ (bar)} \\ \mbox{of a dust cloud, at dust concentration for} \\ p_{max} \mbox{ 250 } (g/m^3) \end{array}$ | 6.84 | |
| The maximum rate of explosion pressure rise (dp/dt) _{max} of dust clouds (bar/s) at dust concentration for (dp/dt) _{max} 250 (g/m ³) | 236.89 | |
| Parameter K _{St} max. (bar m)/s | 64.2 | |
| Heat of combustion (kJ/g) | 27.03 | |

Table 1. Listing of results of determined parameters of coke dust.

The relationship between the maximum explosion pressure values in the function of the dust concentration is shown in Figure 1.



Figure 1. The maximum explosion pressure values in the function of the dust concentration.

The relationship between the maximum rate of explosion pressure rise $(dp/dt)_{max}$ in the function of the dust concentration is shown in Figure 2.



Figure 2. The maximum rate of explosion pressure rise $(dp/dt)_{max}$ in the function of the dust concentration.

The value of p_{max} of three consecutive measurements did not differ more than 10%. Typically, the K_{St} value is determined with uncertainty lower than 20%, for K_{St} values between 51 and 100 bar·m/s. Results of thermogravimetric analyses have been presented in Table 2.

| Tested Parameters | Coke Dust |
|---|-----------|
| Temperature of thermal-decomposition beginning (°C) | 401 |
| Temperature of 50% mass loss (°C) | 542 |
| Final temperature of thermal decomposition (°C) | 750 |
| Mass residue after combustion (%) | 12.18 |
| Maximum mass-loss rate (%/min) | 6.4 |
| Temperature of maximum mass-loss rate (°C) | 520 |

Table 2. Results of thermogravimetric analyses.

A collective listing of thermogravimetric curves is presented in Figure 3.



Figure 3. Thermogravimetric curves (TGA) of tested coke dust.

The course of the thermal decomposition and combustion during heating up of a sample of coal dust are presented in Figure 1, and it shows two transformations. The first one starts at the temperature of 401 °C (the beginning of thermal decomposition), with the maximum sample mass loss at 520 °C, after which the second transformation takes place starting at a temperature of 600 °C, with maximum sample mass loss at a temperature of 682 °C. The second transformation of mass loss ends at the temperature of 750 °C. Over that temperature, no further mass losses of the sample were recorded. Remnants from thermal decomposition amounted to 12.18% of the initial mass of the sample. The loss of half of the mass occurred at a temperature of 542 °C. This shows that the analyzed coke sample has undergone thermal decomposition at a temperature higher than 400 °C, which confirms the earlier performed testing of the determination of a dust layer ignition temperature. The first stage of thermal decomposition of coke is probably due to the decomposition of hydrocarbon chemical compounds containing not much oxygen, sulphur, while the second transformation is associated with the decomposition of condensed aromatic rings and carbon molecules.

5. Risk Analysis in a Typical Coking Plant

In a typical coking plant, coke and coal-derivative products are produced and then delivered to the clients, which draws attention to reducing the onerousness of production for the environment and caring for occupational hygiene and safety of the staff and persons present on the site. The subject of operation of such an enterprise is, among others:

- generation of coal coking products;
- processing coal coking products;
- production of briquettes and solid fuels from coal;
- wholesale of liquid, solid, gaseous fuels and derivative products,
- generation of gaseous fuels;
- distribution of gas fuels in a network system.

Production processes are carried out in a few sections:

- bunker, charge coal used to produce a mixture of a specific composition;
- furnace plant, in chambers of coking batteries the process of high-temperature degassing of the coal mixture takes place;
- coal derivatives—the purification process of raw coking gas is performed and recovery of coal-derivative products.

The coke production process starts from the unloading of wagons containing charge coal, through the process of preparing the coal mixture and the coking process in chambers of coking batteries of the furnace and sorting unit, until the point of coke loading and its release for dispatch. The coke production process comprises the following stages:

- acceptance and unloading of charge coal;
- storage of coal;
- production of the coal mixture and its transport to coal towers;
- intake of mixture and loading of chambers;
- operation of batteries of coking furnaces;
- receipt and quenching of coke;
- sorting and loading of coke.

To move coal from the storage yard to the production process area, it is loaded onto wagons and directed to the division to be unloaded. Basically, coal coming from each supplier should be stored in a separate tank. Coal mixture is prepared according to the recipe of the given technology on the plant premises, as the percentage of coal depends on the type of coke and its qualitative parameters.

Specific types of coal are taken from storage and charging tanks with the use of conveyor batchers or plate batchers onto conveyors. The coal mixture is loaded to mills, such as hammer mills and then to assigned tanks of coal towers by hauling them with the use of belt conveyors. During transport of the mixture to the coal towers, in most cases samples are collected for quality testing. The production and loading of coke proceeds to chambers of coking batteries and is strictly connected with the schedule of battery operation fixed on the basis of the production plan (amount and type of coke). The coal mixture loaded to chambers of the coking batteries undergoes the process of high-temperature degassing in strictly defined conditions. Next, coke quenching and grinding take place. Product controllers release coke for dispatch if such coke is found to have qualitative parameters consistent with the client's requirements. In each of such plants, data connected with explosion properties of coke dust present in the plant needs to be analyzed to ascertain in an unambiguous way whether the dust has explosive dust that could cause explosive atmospheres to be created, which gives rise to several consequences with respect to fire and explosion safety. A Preliminary Hazard Analysis (PHA) is an inductive method, which enables qualitative assessment of risk.

As a rule, the Preliminary Hazard Analysis (PHA) is the first endeavor in the system safety process aimed at identifying and categorizing hazards or potential hazards that are associated with the operation of a suggested system, process, or procedure. Before the PHA, a Preliminary Hazard List (PHL) may be developed, which serves as a basis for hazard control and which also points to the need of devising further in-depth analyses, such as, for example, the Subsystem Hazard Analysis (SSHA) and the System Hazard Analysis (SHA). Typically, the PHA is developed with the use of system safety techniques, which are known as Failure Modes and Effects Analysis (FMEA) and/or the Energy Trace and Barrier Analysis (ETBA). The devising of PHA may be simplified to a certain extent by the application of a Preliminary Hazard Matrix that identifies a Generic Hazard Group. The development of the PHA Report is possible on the basis of the evaluation and analysis of system hazard risk [35].

It is designated to evaluate risk connected with hazards, dangerous situations, and hazardous events taking place in connection with the use of devices, machines, and their systems and subsystems. It may be applied in all stages of research, building, and construction, i.e., in all phases of development works, preliminary and technical design, and for modifications of machines and plant. It may also be applied in the operation process and to assess risk, provided that the proposed protective means have been adopted. Hazard analyses with the use of PHA should be corrected and updated according to actual needs in subsequent steps of the risk analysis procedure, in each stage of testing related to structure, construction, and operation. The adoption of PHA allows limiting the scope of risk analysis by eliminating insignificant elements or those of low significance from the viewpoint of explosion hazard. The objective of PHA is as follows:

- (1) identification of hazards connected with the release of hazardous substances at the level of installations or an installation node;
- (2) identification of potential emergency scenarios;
- (3) identification and assessment of security and protection means in the context of their impact on the possibility of occurrence of emission, fire, explosion (frequency and magnitude of anticipated consequences of emission, fire, explosion and the risk level);
- (4) initial proposal for additional safety means and an assessment of their impact on the risk level.

The PHA method takes the following two elements into consideration:

- (1) frequency of occurrence of the hazard connected with the release of a hazardous substance;
- (2) magnitude of consequences arising from such a hazard (in each case, the worst possible consequences that a given hazard may cause are adopted) [4].

The Preliminary Hazard Analysis (PHA) is a matrix, inductive method that allows a qualitative assessment of risk. Risk estimation (R) is the determination of possible losses, by the degree of damage E and the probability P with which the damage may occur.

$$\mathbf{R} = \mathbf{E} \times \mathbf{P} \tag{2}$$

Following the determination of frequency and magnitude of consequences of a hazard causing an emergency event, an assessment was performed of the risk level with the use of the expert risk matrix method (Table 3). Using the risk matrix, the risk of occurrence of emergency scenarios was determined (Table 4). For emergency scenarios, for which the risk has been defined on a non-acceptable level (NA) or tolerable non-acceptable risk (TNA), it is necessary to adopt additional protection means (Table 5).

Table 3. Risk matrix.

| The Probability of | Category Effects (E) from 1 to 5 | | | | | |
|---------------------|----------------------------------|-------|----------|--------|---------------|--|
| Explosion (P)/Level | Negligible/1 | Low/2 | Medium/3 | High/4 | Catastrophe/5 | |
| Certain event/5 | TA | TNA | TNA | NA | NA | |
| Possible/4 | TA | TA | TNA | TNA | NA | |
| Exceptional/3 | А | TA | TA | TNA | TNA | |
| Small/2 | А | А | TA | TA | TNA | |
| Very small/1 | А | А | А | TA | TA | |

A—acceptable risk, no additional safety and protection means are required. TA—tolerated acceptable risk—it is necessary to consider the adoption of additional safety and protection means if they are practically justified. TNA—unacceptable tolerated risk—additional safety and protection means are to be adopted. NA—unacceptable risk—stop the installation and immediately adopt additional safety and protection means.

| The Probability of Explosion | Description/Frequency | | | | |
|------------------------------|-----------------------|--|--|--|--|
| Certain event | 100–101 | | | | |
| | [1/year] | | | | |
| Possible | 10-1-10-2 | | | | |
| 10000010 | [1/year] | | | | |
| Exceptional | 10-2-10-3 | | | | |
| 2. cop uotai | [1/year] | | | | |
| Small | 10-3-10-4 | | | | |
| ontan | [1/year] | | | | |
| Verv small | Below 10-4 | | | | |
| i ci y cintan | [1/year] | | | | |

Table 4. The probability of an explosion.

| Table 5. 7 | Րhe imj | portance | of im | pact ca | tegories |
|------------|---------|----------|-------|---------|----------|
|------------|---------|----------|-------|---------|----------|

| | Short Description | Description | Destruction [%] |
|---|-------------------|---|------------------------|
| 1 | Negligible | No damage | 0–1 |
| 2 | Low | Small damage requiring minor repair | >1-10 |
| 3 | Medium | Medium damage requiring repair of parts | >10-25 |
| 4 | High | Significant damage requiring greater expenditure and renovation | >25-60 |
| 5 | Catastrophe | Major damage, including building structure | >60-100 |

A determinant parameter for the designation of zones that are endangered by the explosion of coke dust is the identification of ignition, explosion, and thermal parameters of dust generated during processes of sorting, transport of coke, as well as dust generated during grinding of coke.

5.1. Classification of Coke Dust Explosion Hazard Zones

On the coking plant premises, there are a lot of substances that may cause an explosion hazard, and hence, in the present paper, we only present the hazard generated by coke dust alone (Table 5). On the other hand, recommendations and the risk of occurrence of emergency scenarios are presented in Table 6. P and E values determined in Table 7 were taken (estimated) from the case studies analysis in the considered example Plant from the statistic of hazard events in this Plant.

| Process/Location | Type of Danger | Frequency of Occurrence | Zone | Range of Zone |
|---------------------------|----------------|-------------------------------------|------|---|
| Belt conveyors | Coke dust | If it occurs, it lasts a short time | 22 | Within 0.5 m around the conveyor belt vertically and horizontally |
| Coke discharge area | Coke dust | If it occurs, it lasts a short time | 22 | coke discharge area Inside the coke semitrailer |
| Coke sorting equipment | Coke dust | If it occurs, it lasts a short time | 22 | Inside the fine coke sorter |

Table 6. Classification of coke dust explosion hazard zones.

Table 7. The some (as sample) explosion risk (R) matrix in sorting line contained tested coke dust.

| Dangerous/ Initiating Event | Effects | Preventive Measures | Safety Systems (Proposal) | Р | E | R | Recommendations/ Remark |
|--|---|--|---|---|---|-----|--|
| Explosion of a combustible mixture (coke dust-air) due to the air being blown up by the air in the dust room | The outbreak. Possible propagation of explosion inside the room. Possible human sacrifices. Damage to the installation, material losses. Stop the installation. | Constant monitoring of technological installations. - Filter unit in the sorting plant. - Installation of central vacuuming in a sorting plant | Within 0.4 m around the conveyor belt vertically and horizontally | 2 | 5 | TNA | Additional security measures should be introduced (cleaning, wetting) |

5.2. Characterisation of Ignition Sources for Coke Dust

Ignition sources present on the premises of the coking plants, including the likelihood of explosion of coke dust, are presented in Table 8. The probabilities of ignition sources (contained in Table 8) were determined from the case studies analysis and expert knowledge in the considered hypothetical Plant.

6. Discussion

In an analysis of results obtained from studies conducted pursuant to standard EN IEC 60079 [36], it is possible to determine the admissible temperatures of devices and machines, which are working in the presence of tested dusts. Hot surfaces, resulting from friction, revolving of parts, damage of equipping functioning at high temperatures, damage to clutches, brakes, galling of mechanisms, etc., constitute effective ignition sources. Generally, the temperature increase caused by the abovementioned phenomena seldom leads to direct commencement of an explosion of a dust cloud. It can cause, however, smoldering of material settled within internal areas inside machines. When it becomes raised, such material may become an effective source of ignition and not only in the place where smoldering has taken place. Given the values of ignition temperatures of the coke dust cloud and the layer of coke dust, the fact of hot surfaces on electrical appliances may cause a potential source of ignition. Pursuant to principles specified in standard PN-EN 50281-1-2, the maximum permissible temperature of the surfaces of devices may not exceed 2/3 of the value of ignition temperature of a dust cloud, or it should not exceed a value lower by 75 K from the minimum ignition temperature of a 5 mm dust layer. To

be assumed is the lower value from among criteria specified above. If, on the other hand, the dust layer on devices has a thickness ranging from 5 to 50 mm, it is necessary to ensure further reduction of the maximum admissible temperature of surfaces on devices used in the presence of flammable dusts, in accordance with the principles specified in item 6.2.2 of standard PN-EN 50281-1-2. Moreover, attention should be drawn to ensuring that the temperature of hot surfaces does not exceed 80% of self-ignition temperatures of flammable gas substances. Consequently, the admissible temperature of the device used in a situation of occurrence of layers of tested coke dust is higher than 325 °C for a 5 mm layer, and for a thickness of 50 mm, this value amounts to 125 °C. On the other hand, the admissible temperature of the surface of the given device in the occurrence zone of clouds of the tested coke dust amounts to 406 °C.

| Ignition Source | Description | Probability of an Effective Ignition Source (Frequency in the Range of 1 to 3) | | | |
|---|--|--|--|--|--|
| | Hot surfaces | | | | |
| Electrical devices and equipment | If normal equipment is used within the designated explosion hazard zones—not intended for use in these spaces | 2 (possible) | | | |
| Electrical devices and equipment | If there are devices working in explosive spaces, together with documentation confirming the correct selection of these devices, e.g., light sources for lamps in explosion-proof setup | 3 (very small) | | | |
| Coke sorting equipment | Coke dust | If it occurs, it lasts a short time | | | |
| | Flame and hot gases (including hot particles) | | | | |
| Human error, e.g., flame of a match (temp. 600 to 700 °C) | Smoking ban in inadmissible places | 3 (very low) | | | |
| Human error, e.g., burning cigarette butt, (temp. 400 to 670 °C) | Smoking ban in inadmissible places | 3 (very low) | | | |
| Human error, e.g., flame of a gas burner (temp. of ca. 3000 °C)—overhaul and repair works | Preparing the working area and execution of fire hazardous works after obtaining a written usage permit | 3 (very low) | | | |
| WOIKS | Sparks generated mechanically | | | | |
| Work tools capable of generating a mechanical spark | On the area of designated explosion hazard zones, the employees use non-sparking tools. | 3 (very low) | | | |
| Generated during modernization works | Preparing the working area and execution of fire hazardous works after obtaining a written usage permit | 3 (very low) | | | |
| | Electrical appliances | | | | |
| Overload, overheating, flashover (electrical fittings) | If on the area of delimited explosion hazard zones the used devices are in common finishing, they are | 2 (possible) | | | |
| Overload, overheating, flashover (electrical | If on the area of delimited explosion hazard zones the | 3 (very low) | | | |
| nungs) | Straw waltage, eathede anticorregion protection | | | | |
| Stray voltage in the event of damage to the electrical system or lightning strike | Electrical wiring ground of installation, technical inspections, and constant supervision over the technical efficiency of electrical wiring ground and lightning protection systems | 3 (very low) | | | |
| | Static electricity | | | | |
| Sparkover between man and device or installation | Required documentation to confirm the adoption of installation electrical wiring ground Lightning strike | Sparkover between man and device or installation | | | |
| Lightning | Lightning protection, periodical technical inspections | 3 (very low) | | | |
| Not identified | Lack of sources in literature tromagnetic universes from 2×1011 Hz to 2×1015 Hz | 3 (very low) | | | |
| Not identified | Lack of sources in literature | 3 (very low) | | | |
| Not identified | Lack of sources in literature | 3 (very low) | | | |
| Not identified | Lack of sources in literature | 3 (very low) | | | |
| Not identified | Lack of sources in literature | 3 (very low) | | | |
| Fro | thermal reactions, including self-ignition of dusts | | | | |
| EXU | Cleaning procedures including removal of settled | | | | |
| Not identified | dust at least once every 6–7 h, installation of a wetting system for dust or coal input | 2 (possible) | | | |

Table 8. Identification of ignition sources on the area of coke-producing technological lines.

The obtained results of explosion parameters enable the presumption that the tested coke dust manifests explosion properties and has been categorized to explosion hazard class 1, determined on the basis of the constant K_{St} . This implies that this dust offers weak explosion properties. The obtained results allow the presumption that it is necessary to adopt adequate explosion protection means in those plants where production, processing, storage, and transport of coke dust take place. What is more, it is necessary to avoid generation of a dust and air mixture which may undergo explosion. The maximum explosion pressure is 6.84 bar and, as compared to coal dust (5.7–7.7 bar), soot (6.0–7.0 bar), or wood dust (6.4–7.3 bar), the values tend to be similar [37]. It may be seen that diverse types of coal and wood products have similar values of p_{max} close to 6.5 bar. Instead of making a comparison of values directly arising from dp/dt_{max}, i.e., K_{St} , which for the tested coke dust amounted to 64.2 (bar m)/s. If we compare this value to coal (85 bar·m)/s, soot (14–22 bar m/s), wood dust (104 bar·m/s), aluminum (155–550 bar m/s), zinc (125 bar m/s), we may find that the K_{St} value of coke dust is closest to the literature value K_{St} for coal, and it is lower than the K_{St} value of metallic and wood dusts, but higher than the K_{St} value for soot [38].

Thermal decomposition of coke dust carried out in the thermogravimetric testing commences at a temperature of 401 °C, and ends at a temperature of 750 °C, and above that temperature, no further sample mass loss has been recorded. Remnants from thermal decomposition amounted to 12.18% of the initial mass of the sample. An additional assumption is possible of the most likely contents of ca. 87%, as remnants of coal.

The combustion heat of tested coke dust amounts to 27.03 KJ·kg⁻¹; as compared to values from literature [39] for coal (22.6 and 26.5 KJ·kg⁻¹) and wooden biomass (17.7 KJ·kg⁻¹), it may be presumed that the coke dust has the highest value of combustion heat from the abovementioned three materials, which arises from the carbon content—the higher its contents, the higher the value of combustion heat. Apart from cleanliness (which causes a lower amount of generated ash), this fact is one of the most important causes for the production of coke—higher value of combustion heat than for coal, from which it is made. In addition, the delimited value of combustion heat allows for setting out the amount of heat generated from a mass of coke dust present in the given installation. The PHA proves to be helpful in proposing additional safety means and the assessment of their impact on the risk level. It consists of the delimitation of places that are potentially hazardous from the explosion viewpoint and an analysis of introducing possible new explosion protection devices. The qualitative risk analysis proposed in the article makes it possible to find technological points which, in the case of increased risk, should be additionally strengthened with appropriate explosion protection.

Based on a conducted PHA analysis on areas where TNA obtained was a tolerated unacceptable risk, additional protection and safety means should be adopted, such as for example:

- Perform an inventory of devices installed in the delimited explosion hazard zones. Next, verification should be done on whether those devices fulfil the necessary requirements with respect to explosion safety, among others, with a view to category, explosion group, and temperature class.
- Change the categorization, amend the range, or, to eliminate the explosion hazard zones, as well as to minimize potential explosion effects, a dusting reduction system should be installed on belt conveyors and coke boosters with the use of water fog.
- Assure that the coke booster in sections of furnace and sorting facilities is made airtight, as well
 as the dump to the coking plant in the sorting unit, because each lack of tightness increases the
 likelihood of creating an explosive atmosphere.
- There is a need for devising, deploying, and following procedures for maintaining the cleanliness of the entire installation (among others, technological belt conveyors, parts of building structures including devices contained inside) in the whole plant to prevent the occurrence of coke dust layers. With this in mind, employees should regularly control cleanliness of the facilities in which dust may occur.

• Within the designated gas explosion hazard zones, appropriate protection means are to be adopted to ensure protection from static electricity, or adopt another technical solution aimed at the discharge of electrostatic charges.

7. Conclusions

Given the results and an analysis of all the conducted coke dust tests, the following conclusions may be drawn:

- The maximum admissible temperature on the surface of a device used in conditions in which layers of coke dust exist depends to a large extent on the thickness of the compiled dust. For a coke dust layer of a thickness of 50 mm, this temperature is threefold lower.
- Consequently, in plants where the analyzed dust occurs, attention should be paid to the type of devices installed in delimited explosion hazard zones, and, in particular, it is necessary to verify whether the abovementioned devices fulfil the relevant requirements related to explosion safety.
- Before locating equipment in a zone where dust may be present, it is necessary to delimit the category, explosion class, and maximum admissible temperature on surface of a devices.
- The rate of coke oxidation is significantly affected by such factors as: coke fragmentation, contents of mineral substances in the coal, hygroscopic moisture, and carbon content; the greater the coal fragmentation, the higher the risk of ignition in the environment. Another parameter that has a great impact on ignition of coke dust is its content of hygroscopic moisture. Moisture is the cause of oxidation of pyrite and other exothermic reactions. Hygroscopic moisture in the process of self-heating is a negative factor, because the greater its content in coal, the higher the risk of ignition.
- The maximum explosion pressure of tested coke dust amounted to 6.84 bar, and the K_{St} value was 64.2 bar m/s, which corresponds with explosion hazard class 1, and the obtained K_{St} value is close to the value found in literature for coal.
- The PHA method is helpful to determine the legitimacy of using additional means aimed at ensuring explosion safety and it allows a qualitative evaluation of their impact on the risk level to bring down the risk in delimited zones to an acceptable level.
- Minimizing the explosion risk may consequently result in minimizing the risk of releasing contaminants and products of thermal decomposition into the environment. If crucial explosion parameters are known, it is possible to prevent coking technology from having a negative influence on sustainable development in process safety.

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