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INFLUENCE OF PYROPHORIC SULPHIDES OVER THE FLAMMABILITY PARAMETERS OF LIQUIDS

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Abstract

Fire and explosion prevention requires the knowledge of the explosive or flammability parameters of combustible gases and vapours that can be found in industrial and civil environments, as well as the influence of certain substances in the process on these parameters. In some cases, pyrophoric sulphides can be formed and it is supposed that they may influence the known flammability parameters of the substances used in various industrial processes.

In order to track the influence of iron sulphides on the flammability parameters of liquids, determinations of these parameters (flash point and auto-ignition temperature) were made for a series of flammable liquids that have been contaminated with various quantities of commercial iron sulphide.

Key words: explosions, fires, flammability, pyrophoric sulphides

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1. Introduction

In many countries with advanced chemical technology, specialized laboratories for research of explosive combustion processes have been set up. The research follows both the basic theoretical aspects regarding thermodynamics and kinetics of combustion reactions under various conditions as well as applicative aspects regarding the design of technological installations and explosion protection devices and measures (Krentowski, 2015; Prodan et al., 2014, Sohn et al., 2015; Volchyn et al., 2018).

Units from different industrial branches are often confronted with the occurrence of accidental releases (emissions) into the atmosphere of quantities of fuel which form flammable clouds, in mixture with air. Quite often such clouds can be ignited and the explosion that is generated causes significant material and human losses, both by its thermal effects (flame and thermal radiation) and by the blowing effects (pressure wave) produced (Cioclea et al., 2014; Esclapez et al., 2017; Zanoni et al., 2017).

At one point or another, most refineries experience the spontaneous ignition of iron sulphide either on the ground, or inside the equipment. When this happens inside the equipment such as columns, vessels, tanks and exchangers containing residual hydrocarbons and air, the results can be devastating (Csaszar et al., 2012; Dura et al., 2017; Felegeanu et al., 2016; Ghicioi et al., 2017).

Most often, pyrophoric fires occur during shutdowns, when equipment and pipelines are opened for inspection or maintenance purposes (Schieber, 2011; Steel, 1987; Szollosi et al., 2016; Zalosh et al., 2005). The occurrence of fires in raw columns during revisions, explosions in sulphur storage tanks, or in asphalt tanks, overpressures in vessels etc., due to the ignition of pyrophoric sulphides are common. Often, the cause of such accidents is the lack of understanding of the ignition phenomenon of

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pyrophoric sulphides (Bertani et al., 2006; Cai et al., 2014; James, 2006; Payant et al., 2012).

The idea of the study came after some accidents took place in the gas industry after the residue collected in the gas filters catch fire after being deposited, and after the proximate analysis of the residue which showed that it contained iron sulphides. Also, in case of a lot of accidents which took place in the process industry, it was found the presence of the pyrophoric sulphides. If within a process are used flammable substances with known flammable properties, usually they are processed in places that can facilitate the formation of the pyrophoric sulphides. In this particular case it was found relevant to investigate the influence of this kind of impurities, especially over the flammability properties, which are critically to be known in order to avoid unwanted accidents.

This study aims to investigate the influence of the iron sulphides on the flammability parameters of flammable liquids, i.e. the flash point and the auto-ignition temperature. The evaluation of the explosion and fire hazard generated by the flammable substances requires the knowledge of their explosion and flammable parameters, but also the influence of certain substances that can contaminate, such as the case of iron sulphide.

2. Material and methods

2.1. Flash point determination

The flash point measurements were performed in compliance with standard SR EN ISO 2719:2016 The determination of flash point. Pensky Martens closed cup method. A closed cup automated Pensky–Martens device was used, as presented in Fig. 1, with aliquots of 65 mL, and the experiments were performed at 20°C and 695 mmHg, while the resulted temperature was corrected to standard atmospheric pressure using the equation provided by the equipment software.

2.2. Auto-ignition temperature determination

The auto-ignition temperature measurements were done according to standard SR EN 14522:2006 Determination of auto-ignition temperature for gases and vapours. This test method is used to determine the auto-ignition temperature of flammable gases and vapours in mixture with air or inert air / gas, at atmospheric pressure and temperature up to 650ºC. Therefore, it was used a special oven as indicated in the standard, as can be seen in Fig. 2. The flash point and minimum ignition temperature were determined for three liquid flammable substances, respectively an oil residue probably contaminated with gasoline, the composition being unknown, sampled from a fire accident (Sample 1), an industrial degreaser also with unknown composition (Sample 2), a sample of diesel fuel (Sample 3) from a local gas shop and aniline. The minimum ignition temperature was determined for commercial iron sulphide, crushed and sieved at 0.063 mm.

3. Results and discussion

A series of tests have been performed in order to determine the flammability properties of flammable liquids. In Table 1 and Table 2 are given the results obtained for the flash point and for the auto-ignition temperature. The flash point and the auto-ignition temperature for the diesel fuel are similar with those indicated in the material safety data sheet for the sample analysed and from the literature data (Arpa et al., 2010).

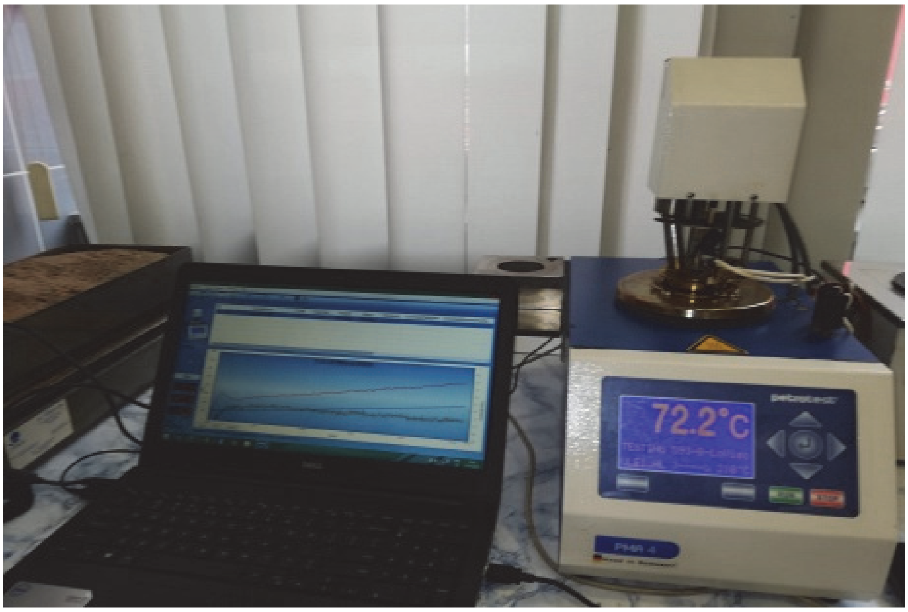

Fig. 1. Pensky Martens closed cup apparatus, automated, Petrotest PMA 4

Fig. 2. Stand for the determination for auto-ignition temperature for gases and vapours

Table 1. Flash points resulted during experiments with samples 1-3

No.	***Sample***	***Flash point [°C]***
1.	Sample 1	<-5°C
2.	Sample 2	21°C
3.	Sample 3	55°C

Table 2. Auto-ignition temperature resulted during experiments with samples 1-3

No.	***Sample***	***Auto-ignition temperature [°C]***
1.	Sample 1	370
2.	Sample 2	450
3.	Sample 3	420

For the other two substances, a correlation could not be provided given the fact that the composition was unknown. In order to monitor the influence of iron sulphides on the flammability parameters of flammable liquids, determinations of these parameters (flash point and auto-ignition temperature) have been carried out for the above-mentioned flammable liquids which were impregnated with various quantities of commercial iron sulphide.

In order to evaluate the variation of these parameters, the ignition temperature of the iron sulphide used for the tests was determined at 63 µm, the sample being ground and sieved, this temperature being 520°C (Fig. 3). The experimental results obtained, i.e. the auto-ignition temperature of 520°C, are in very good compliance with the data presented in the scientific literature for similar experiments. Amyotte et al. (2003) reported auto-ignition temperatures for iron sulphides and pyrite and pyrite samples between 490-620°C. To investigate the influence of pyrophoric sulphides on the flammability of flammable liquids, a number of determinations were made by impregnating the flammable liquids for which the flash point was determined. The powdered and sieved iron sulphide powder was mixed with the flammable liquids to monitor if flashpoint drops occurred. For all the flammable liquids analysed, no decrease in the flash point was achieved, concluding that iron sulphide or pyrophoric sulphide does not influence the flash point of flammable liquids, probably due to the fact that iron sulphide is not a volatile substance, the flash point being given by the temperature at which the vapours above the liquid ignite. A series of attempts have been made to track the influence of pyrophoric iron sulphides on the auto-ignition temperature of flammable liquids. For the three cases of flammable liquids for which the auto-ignition temperature was determined, namely diesel oil, petroleum residue degreaser and industrial degreaser, the liquids were contaminated with iron sulphide powder.

Even in this case, a decrease in the temperature of auto-ignition has not been achieved due to the influence of pyrophoric sulphides. In this situation, it was considered that iron sulphide does not influence the temperature of auto-ignition of the liquid since the auto-ignition temperature of the liquid is lower than that of ignition of the iron sulphide powder.

Fig. 3. Image captured during the determination of commercial iron sulphide ignition temperature

Consequently, attempts were made with a flammable liquid with a higher auto-ignition temperature than the one of the iron sulphide. The test liquid was aniline. In the case of aniline, an auto-ignition temperature of 620°C was determined, and with iron sulphide (pyro-sulphide) impurity, the temperature was lowered by approximately 60°C.

4. Conclusions

Fire and explosion prevention requires knowledge of explosion characteristics (flammability limits, ignition source characteristics, combustion speeds and explosion pressures) of combustion gases and vapours found in industrial and civil environments.

Auto-ignition of pyrophoric sulphides, outside the chemical process (contact of reactive elements, so that the oxidation reaction is possible) is also subject to the influence of some physical factors: the thickness of the layer, the size of the pyrophoric sulphide deposit formed, the presence of impurities with catalytic role, the magnitude of pyrophoric sulphide particles, the specific surface of pyrophoric sulphur contact with oxygen.

Iron sulphide is a pyrophoric material. This means that it can spontaneously ignite in contact with the air. It can be formed when the iron oxide (rust) is converted to iron sulphide in an oxygen-free environment where hydrogen sulphide is present, or where the hydrogen sulphide concentration (H_2S) is higher than the oxygen concentration. When iron sulphide is exposed to air, it oxidizes to iron oxide to form either sulphur or sulphur dioxide. This chemical reaction between iron sulphide and oxygen generates a considerable amount of heat. In fact, so much heat is released that the individual iron sulphide particles become incandescent and burn. This amount of heat can become a source of initiation for both explosions and fires.

Following the tests, it was concluded that pyrophoric iron sulphides influence the temperature of auto-ignition of flammable liquids in the sense of decreasing only for flammable liquids having an auto-ignition temperature higher than the auto-ignition temperature of the iron sulphide powder. The experimental results obtained for the tested substances can support this hypothesis, therefore in prospective research other substances with higher auto-ignition temperatures than the one of iron sulphide will be used in order to validate it.

Considering these observations, namely that the pyrophoric sulphides cause the lowering of the temperature of auto-ignition of the flammable liquids leads to a necessity of re-evaluation of protection to explosion measures in the operation of these types of liquids, so that the explosion hazard is reduced to a minimum.

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