



Safe storage of selected fuels with regard to their tendency to spontaneous combustion



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ABSTRACT

European standard EN 15188 is dedicated to the assessment of the tendency of solid flammable substances to spontaneous combustion. Fossil fuels and biofuels that substitute them are a frequent reason of fires caused by spontaneous combustion. Even though having different properties, both types of fuels can be assessed according to this standard by the method of the determination of the dependency of self-ignition temperature against the ratio of volume to surface area of geometrically exactly defined solid body, or based on the theory of thermal explosion according to Frank-Kamenetskii. The comparison of calculated values confirmed the agreement of both methods results, and the tendency of fuels to spontaneous combustion can be assessed by them.

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1. Introduction

Spontaneous combustion of solid combustible substances is a frequent cause of many fires and explosions during storage, handling and transport of many materials. Therefore, it presents permanent danger to health, property, and environment. The primary cause of spontaneous combustion can differ in accordance with the material type and can be of physical, chemical, or biological character but it is always connected with the generation of heat. Self-heating occurs when the heat generated by exothermic reactions is higher than the heat conducted away into environment.

The result of spontaneous combustion process is the ignition and following burning of a substance in flame or flameless manner. Self-ignition temperature means the lowest temperature at which the exothermic processes start in the substance without external heat source, leading to the ignition of the substance.

Many materials are liable to spontaneous combustion. One of those materials able to react with air oxygen at normal temperature is bituminous coal. Spontaneous combustion of coal represents serious safety problem that occurs in the mining industry during the storage and transport of bituminous coal.

It follows from the statistics of the Fire and Rescue Service of the Czech Republic for the year 2010 (see Fig. 1) that the spontaneous combustion of coal during storage or transport is the most frequent cause of self-ignition fires. Statistical data for other years are similar.

With respect to long-time usage of large quantities of coal, close attention is paid to its assessment from the point of view of the tendency to spontaneous combustion (Bowes, 1984).

Fossil solid fuels are being replaced by alternative ones to a larger degree. The alternative fuels are made of organic materials in the first place. Those fuels also tend to spontaneous combustion but unlike coal substance, this dangerous property is not sufficiently considered during their storage and transport. The number of fires of this class of materials is not statistically monitored at present. Their portion cannot be deduced from the statistics (see Fig. 1), since they can be classified either as farming products or other products. Spontaneous combustion occurs during their storage as proves a history of many accidents that took place for example in Nyrsko, Czech Republic (Jakoubková, 2012), and in Tyne Harbor, UK (Butcher, 2011). That is why a close attention is paid to wood-based fuels like pellets made of sawdust particles and wood waste, with regard to their assessment from the point of view of spontaneous combustion (García, Gómez, Aragón, Olmedo, & Medicpejic, 2012; Ramírez, Torrent, & Tascón, 2010; Věžníková & Hütter, 2008). It follows from measured results that self-ignition temperature

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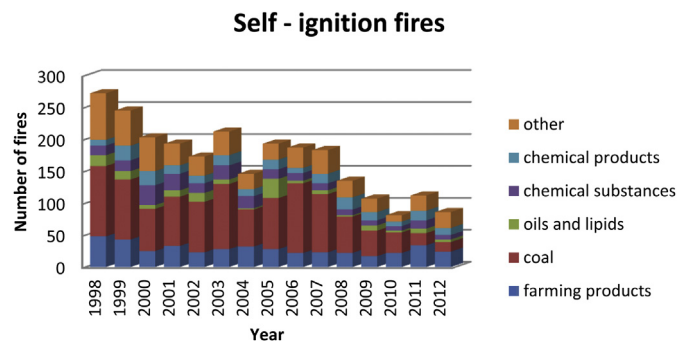


Fig. 1. Number of self-ignition fires according to material (Statistic yearbooks, 2010).

decreases and induction time increase with growing amount of stored material.

Oxidation is the main process leading to spontaneous combustion. Three ways how oxygen affects this process can be distinguished: physical adsorption of oxygen, action of oxygen on highly active coal centres, and chemical action of oxygen on coal. Generally, the oxidation spontaneous combustion proceeds gradually in several phases, during which the fuel temperature increases up to the flash point. During this so called induction time, gases are released from heated material. Some of these gases are explosive or toxic. These products of combustion represent additional danger connected to self-heating, endangering lives and environment as well.

According to Van Krevelen (1961), the process of spontaneous combustion of coal can be divided into the following phases:

1. chemisorption of oxygen with increasing weight – up to 70 °C,
2. initial release of oxidation reactions products and of inner water (70–150 °C),
3. production of larger amounts of oxidation reactions products (150–230 °C),
4. fast burning including production of soot – above 230 °C.

The release of gaseous products of self-heating occurs in larger amounts, according to this scheme, from 70 °C but detectable changes in atmosphere composition have been observed already from 40 °C (Adamus & Věžníková, 1999).

The liability to spontaneous combustion is influenced by various factors, mostly by chemical and physical properties of the substance but also by the conditions under which the self-ignition runs (Krishnaswamy, Gunn, & Agarwal, 1996; Lohrer, Krause, & Steinbach, 2005). The concentration of oxygen belongs to conditions that influence the development of self-heating of porous materials in the first place (Bowes & Thomas, 1966).

The liability of coal to spontaneous combustion depends on the degree of carbonification, represented approximately by the contents of volatile combustible and ash matter (Adamus, 2004). That is why brown coal demonstrates the highest liability to spontaneous combustion, followed by bituminous coal. Anthracite and coke are not susceptible to spontaneous combustion.

The influence of particle size and pore distribution on the process of the low-temperature oxidation of coal is described in (Nugoro, McIntosh, & Gibbs, 2000). This influence was quantified by keeping the samples in baskets in oven at constant temperature. The assessment was done using the crossing-point method and the results were compared with the assessment according to the Frank-Kamenetskii method. The comparison determined that the crossing-point method provides better results. However, this method requires more complex technique of measurement than

the Frank-Kamenetskii method. The influence of particle size and of the size and availability of inner surface area was ascertained experimentally, especially for highly coalified coal types.

The development of low-temperature oxidation of subbituminous brown coals was studied on samples filled into baskets of different sizes by means of two different methods, namely the crossing-point method and assessment according to Frank-Kamenetskii method (Sujanti, Zhang, & Chen, 1999). Kinetic constants acquired by both methods were in agreement; however, the authors considered the crossing-point method faster.

In spite of differences in properties and behaviour of coal and biofuels, one model can be used for their assessment with regard to the liability to self-heating, namely the Frank-Kamenetskii model of thermal explosion (Bowes, 1984). Crushed or powder coal, as well as wood sawdust particles demonstrate the same behaviour during oxidation self-heating. They belong to the group of substances demonstrating thermal instability of TD type (thermal decomposition) (Kotoyori, 2005). During the self-heating of these substances, gradual increase of temperature can be observed with approximately linear dependency of temperature against time. After reaching certain temperature, rapid temperature increase can be observed, leading to ignition, i.e. thermal explosion. Critical temperature is the lowest temperature at which the thermal explosion of TD type gas-permeable substance of certain defined shape and size and placed in air at isothermal conditions, cannot occur (Kotoyori, 2005).

Tests used for the assessment of the liability of porous solid to spontaneous combustion should be conducted in a scale as close to real size as possible. Unfortunately this is not the case in most instances due to time and economic demands. That is why the tests are conducted in laboratory scale at higher temperature and with lesser amount of sample. The results are then extrapolated to real conditions on the basis of theoretical procedures. The results of extrapolation can be shifted, since some circumstances are neglected and/or simplified.

According to the summary of methods (Babrauskas, 2003), two groups of variously modified laboratory methods are used most often. The first one is basket test based on Frank-Kamenetskii's theory, whose variant according to the standard (CSN EN 15188, 2008) is used in this work. The second is the group of tests conducted in Dewar vessels, mostly connected to the theory of spontaneous combustion according to Semenov. Crucial difference between these two groups lies primarily in spatial arrangement of tests. In addition, the Semenov method is used above all for liquids.

Basket tests are conducted in baskets of certain size and shape, e.g. cube or cylindrical shape. The heating regime is isothermal, thus the environment of sample is heated to constant temperature. Since the temperature of environment changes during self-heating of tested material, these tests are called isoperibolic.

The basket test is used for the assessment of liability to spontaneous combustion in the form of EN 15188 standard (CSN EN 15188, 2008) and also as a method of the assessment of the danger of spontaneous combustion at international transport of dangerous goods (UN Recommendation, 2009).

The regulation (UN Recommendation, 2009) contains test methods and procedures for dangerous goods classification. Unlike the standard (CSN EN 15188, 2008), the average between the lowest temperature at which the self-ignition occurs, and the highest temperature at which the self-ignition does not occur, is considered the temperature of self-ignition.

In this article, the liabilities to spontaneous combustion of brown coal, of two types of bituminous coal, and of wood pellets and sawdust were compared using the method according to the standard (CSN EN 15188, 2008). This method determines the temperature and time at which the sample self-ignites, depending on

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