Journal of Loss Prevention in the Process Industries 43 (2016) 203–211

Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

journal homepage: www.elsevier.com/locate/jlp

The composition of gaseous products of low-temperature oxidation of coal mass and biomass depending on temperature

Katerina Derychova*, Michaela Perdochova, Hana Veznikova, Ales Bernatik

VSB – Technical University of Ostrava, Faculty of Safety Engineering, Lumírova 13, 700 30, Ostrava – Výškovice, Czech Republic

A R T I C L E I N F O

Article history:
Received 10 November 2015
Received in revised form
29 March 2016
Accepted 18 May 2016
Available online 20 May 2016

Keywords:
Coal
Biomass
Low-temperature oxidation
Gaseous products

A B S T R A C T

Coal and biomass emit gases during storage. The composition and quantity of these gases is dependent on many factors. This study deals with gaseous products that are released during coal and sawdust heating to find how the composition of gaseous products varies in dependence on temperature changes and how these changes can be used to indicate the condition of the stored materials. Samples were examined in a furnace, being placed in a cube-shaped basket whose side measured 5 cm. The samples were heated in the temperature range of 50–200 °C with increments of 50 °C for 180 min. Qualitative and quantitative analysis of the generated gases was performed using a FTIR spectrometer and a gas analyzer. The analysis indicated that these gaseous products primarily contain water vapour, carbon oxides and aliphatic hydrocarbons. At 200 °C, methanol appeared in the gaseous products released by the wood material. The measured results show that the amount of CO_2, CO and CH_4 increases with heating temperature. It has also been found that the CO/CO_2 ratio is temperature - dependent in coal while this dependence is not so clear for sawdust. The results are useful for assessing the impact of temperature on the amount of gaseous products polluting the working and living environment and can help in selecting appropriate security measures.

1. Introduction

In the EU countries, the dependence on fossil energy sources such as oil or coal is high. Replacing fossil fuels with other sources is one of a decisive factor for reducing emissions of greenhouse gases and increasing the safety based on energy supply through diversification and reduced dependence on imported fossil fuels.

Solid biofuels for energy purposes are prepared from suitable types of biomass including wood in various forms such as logs, briquettes, pellets, wood chips or sawdust. (Klass, 1998) With regard to their properties, they are replacement for solid fossil fuels, i.e. mainly for coal. Although the use of solid biofuels has a range of benefits against the use of coal, it also brings certain dangers that arise from their flammability, propensity to spontaneous combustion (self-ignition) and properties of the products of their heating.

Spontaneous combustion is a complex process in which the material is spontaneously heated due to processes occurring in the material itself, usually upon exposure to atmospheric oxygen. Spontaneous combustion begins at normal ambient temperatures and is accompanied by the release of gaseous products of the running reactions. The composition and amount of gaseous products vary with changing temperature. If the generated heat is not sufficiently dissipated to the surroundings of the material, its temperature increases as well as the speed of running reactions, usually oxidizing. Under appropriate conditions, a sharp rise in the temperature (thermal runaway) may even lead to ignition. The temperature rise and gaseous products of running processes are used to detect self-heating (spontaneous heating) and design the respective safety measures.

Spontaneous combustion of coal mass is a long-term problem which is present in mining, transportation as well as storage; therefore, coal is a material which is most studied in relation to spontaneous combustion. Based on the large amount of research work and practical experience of the past years, the use of coal is subject to regulations designed to reduce the likelihood of spontaneous combustion, its early detection and suppression while maintaining work safety.

Wood-based solid biofuels are prone to spontaneous combustion as well as coal. The use of biomass as a fuel means that it is transported and stored in much larger quantities than ever before;

* Corresponding author. Tel.: +420 597 322 835.
E-mail address: katerina.derychova@vsb.cz (K. Derychova).

http://dx.doi.org/10.1016/j.jlp.2016.05.022
0950-4230/

therefore, its self-heating is more likely. Unlike coal mass, however, there are no sufficient experiences regarding the behaviour of biomass in large volumes and operating instructions for detecting spontaneous combustion as well as measures against its occurrence are often not prepared.

The purpose of this paper is to highlight the potential hazards associated with storage and use of wood-based solid biofuels in large volumes, i.e. their self-heating and emergence of gaseous products which are released during oxidative self-heating. Hazardous properties of these gaseous products, such as toxicity and explosiveness, represent a major threat to safety. Since they are formed from materials with elevated temperature due to spontaneous heating, the danger of ignition of fire or explosion also increases.

We assessed many gaseous products released upon heating and their composition in dependence on the temperature at which they arise. These gases are released not only during combustion of wood mass but also in the phase of self-heating. The composition of these gaseous products is influenced by many factors, such as chemical composition of the burned material, thermodegradation temperature, particle size, moisture content, etc. The analysis was performed in the solid biofuel in the form of sawdust as well as coal in order to compare both of these materials.

This paper deals with gaseous products that are released during coal and sawdust heating in the temperature range of 50–200 °C. In addition to qualitative analyses, we also conducted quantitative analyses of the generated carbon dioxide, carbon monoxide and methane. The aim was to determine how the composition of gaseous products varies in dependence on temperature changes and how these changes can be used to indicate the condition of the stored materials and design safety measures.

2. Gaseous products of low-temperature oxidation

In the areas where coal is mined, a common phenomenon is the release of mine gases (particularly methane and carbon oxides) in the mine atmosphere. In the mines, an explosive mixture or non-breathable environment can then be created.

If the coal is exposed to atmospheric oxygen at normal ambient temperature, it leads to a slow oxidation producing heat and releasing reaction products, particularly gases and moisture. The speed of coal oxidation increases with coal temperature.

Many studies deal with the release of gases. The composition of the gaseous products is dependent on the properties of coal, humidity and conditions of storage. Oxidation processes are mainly influenced by temperature. Gases such as carbon monoxide and carbon dioxide, methane, hydrogen, ethane, ethylene and propane, iso-butane, n-butane and propylene were identified at higher temperatures up to 200 °C (Adamus et al., 2011).

Compositions and amounts of gases produced by low-temperature coal oxidation at various temperatures were studied by (Lu et al., 2004). They divided the coal oxidation at low-temperatures into four phases. These phases were identified based on changes in concentrations of carbon monoxide and ethylene. Carbon monoxide and ethylene are never present in gaseous products at temperatures up to 50 °C. The presence of carbon monoxide in gaseous products is characteristic for the temperature range of 50–60 °C while ethylene is still missing. However, concentrations of these gases slowly increase with the temperature. The concentrations of carbon monoxide and ethylene rapidly grow at temperatures between 130 and 140 °C. If this phase continues to develop, the concentration of components further sharply increases until the ignition temperature is reached. According to (Lu et al., 2004), carbon monoxide and ethylene can be considered as the main gases indicating spontaneous combustion.

A detailed review of the literature dealing with the low-temperature oxidation (Wang et al., 2003) shows that lower hydrocarbons, carbon monoxide, carbon dioxide and water are generally considered the most important gaseous products of coal oxidation in mines with respect to the indication of running self-heating. However, opinions on their usefulness for this purpose are not entirely uniform as well as the view of the kinetics of low-temperature oxidation; most recently, carbon dioxide is prevailingly designated as the primary product of the low-temperature oxidation, rather than the previously mentioned carbon monoxide.

According to (Davidi et al., 1995), the main product of coal oxidation is carbon dioxide which is accompanied by carbon monoxide, low molecular hydrocarbons and molecular hydrogen. Davidi also states that the interpretation of the composition of coal mass oxidation products can be used to determine the relative resistance of fuel to oxidation and its suitability for long-term storage.

Coal storage in open space may have a negative impact on the environment because the gases released during spontaneous heating contribute to the greenhouse effect. According to (Carras et al., 2009), the main components of greenhouse gases from coal oxidation at ambient temperature are carbon dioxide and methane which may potentially represent a major contribution to the greenhouse effect.

As describe above, the main gaseous products of the low-temperature coal oxidation are carbon oxides, water and lower hydrocarbons, especially methane and ethane. At a certain concentration, these gases released during coal self-heating may cause oxygen depletion in a closed storage space. Their toxicity can endanger people working in these areas or in their neighbourhood.

The release of gases from coal mass during its mining, processing or storage is addressed by many studies. Fewer papers deal with gases that are released from biomass in similar technological operations. Nevertheless, their number is increasing with the growing importance of biomass as a replacement fuel and raw material for alternative fuels which are used as a renewable energy source.

Main components released during storage of the biomass, specifically wood pellets, are considered carbon oxides, methane, aldehydes and terpenes (Kuang et al., 2009). At the temperature of 10–55 °C, the main identified gaseous products of biomass oxidation were carbon oxides and methane whereas the highest concentration was that of carbon dioxide while the lowest concentration was detected for methane. Hydrocarbons (such as ethylene and propylene) and aldehydes were detected in very small quantities (Kuang et al., 2008).

Higher emission values are associated with a higher temperature; the storage temperature is therefore a key factor that affects the release of gases from stored mass. Increased concentrations of these gases in an enclosed storage area (space) causes a decrease in oxygen concentration and the toxicity of these gases may pose risk to persons working in storage areas or around bins; in addition, some of these gases may have a negative impact on the environment (Kuang et al., 2008).

Wood materials contained in dumping places also represent a source of greenhouse gases. Greenhouse gas emissions are very closely assessed by (Wihersaari, 2005; Jäppinen, 2014), for example. Both of these studies indicate that greenhouse gases, such as methane, are released into the atmosphere during the storage of wood residues; according to some data, these gases also include dinitrogen oxide. As one of the recommendations for reducing the emissions, they propose the shortest possible storage time because a long-term storage is associated with an increase in temperature inside the heaps, resulting in the release of large quantities of methane (Wihersaari, 2005). At pulped wood, the maximum