



Full Length Article

Towards indication gases of spontaneous heating of biomass

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ABSTRACT

Gases evolved during aerial oxidation of biomass in temperature range 40–160 °C were studied in view to consider possible indicators of spontaneous heating. Three samples of lignocellulosic biomass and a sample of subbituminous coal (as “reference” basis) were analysed and the following gaseous compounds were determined: carbon monoxide, carbon dioxide, methane, ethane, propane, ethylene, propylene, acetylene, butanes/butenes (sum), methanol, acetaldehyde, dimethyl ether and hydrogen. Measurements with wet and dried biomass were carried out to differentiate between microbial and chemical origins of the released gases. As a result, carbon dioxide, unsaturated hydrocarbons and methanol were clearly recognized as compounds produced from biomass mostly due to microbial activity at low temperatures. On the other hand, ethane, propane, dimethyl ether as well as carbon monoxide appear to originate primarily of chemical oxidation of biomass. With respect to detection of the spontaneous heating, carbon monoxide confirmed its exclusive role in monitoring the “spon-com” process (also) of biomass. Unsaturated hydrocarbons that hold principal role in the indication of self-heating of coals were found unsuitable for the purpose for lignocellulosic biomass. Due to their exclusive microbial origin, traces of the propylene/ethylene can be detected already at temperature of 40 °C, making thus their relation to early heating process unreliable. Ethane is presented as a promising indication gas.

1. Introduction

Increasing demand on biomass as an alternative energy source to replace traditional fossil fuels [1–3] leads (among others) to increased number of spontaneous heating incidents caused by biomass. E.g., in the Czech Republic, spontaneous combustion incidents of coal clearly prevailed ten years ago over these of biomass (by a factor of 5), however, since the year 2015, the ratio is quite inverse [4], see Fig. 1.

To deal with the spontaneous heating of biomass, experience with self-heating of coal matter is usually applied [5–8]. Evolution of carbon monoxide has thus been taken as a generally recognized criterion of self-heating both of coal and biomass [1,5,8,9]. For early detection of coal, ratios between evolved gases (including consumed oxygen) are also often used. Among them, traditional Graham’s ratio $CO/\Delta O_2$ is best known and still valid in “spon-com” prevention of coal [1,7,9–11]. Furthermore, *indication (index) gases*, which appear in developed stage of self-heating process only when so called *threshold* temperature T^{th} of the hot spot is reached, are of important practical use [1,5,9–11]. Specifically, unsaturated hydrocarbons represent well recognized indication gases frequently applied in the prevention of spontaneous heating of coal [9,10]. Finding the ethylene in the gaseous mixture should thus indicate temperature of the hot spot ca. 100 °C [12], 130 °C

[13] and/or 140 °C [10]. Similarly, propylene should appear only when threshold temperature reached 120–140 °C [11] or 150 °C [10]. Presence of the acetylene then indicates temperature of the hot spot exceeding value of 200 °C [9,11]. However, oxidation behaviour of biomass differs from coal oxidation, mainly due to possible microbial activity of the microorganisms in the initial, low temperature stage of the biomass heating, up to ca 80–90 °C [3,14,15]. Thus, evidently, knowledge of the oxidation behaviour of coal can hardly be directly transferred to the spontaneous heating of biomass.

This paper is aimed at analysing gases evolved during oxidation of lignocellulosic biomass in view to consider suitable indicator(s) of spontaneous heating. It will be shown that unsaturated hydrocarbons holding principal role in the “spon-com” detection of coals can hardly be applied for indication of the self-heating process of lignocellulosic biomass. For the purpose, ethane is here presented as a promising index gas.

2. Material and methods

2.1. Samples

Three samples of lignocellulosic biomass (denoted as “LS”, “KC” and

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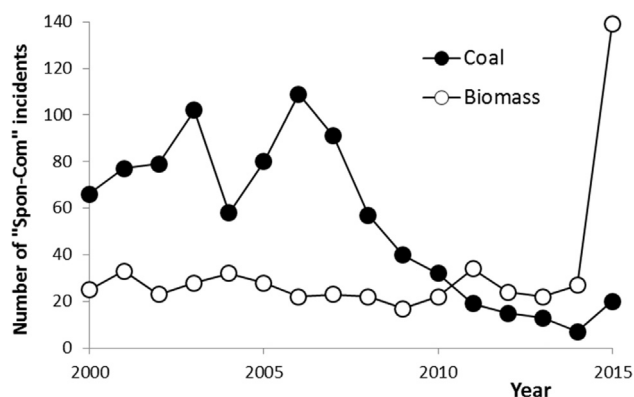


Fig. 1. Development of spontaneous combustion incidents of coal and biomass in the Czech Republic.

Table 1
Proximate and ultimate analyses of the studied samples.

Sample	Description	Moisture (as received,%)	Ash (dry,%)	Carbon (daf,%)	Hydrogen (daf,%)
LS	Forest chips	26	7.8	56.4	6.5
KC	Spruce bark	36	4.1	53.4	5.8
EDE	Straw-wood pellets	9	8.9	49.1	6.4
HUK	Subbituminous coal	25	29.5	69.1	5.6

daf – dry, ash-free basis.

“EDE”) were studied. Samples “LS” and “KC” represent “crude” biomass of forest chips and spruce bark, respectively, that are mainly used as alternative energy source. Sample “EDE” represents pellets made of straw-wood mixture that are commercially supplied as additive fuel preferable for co-firing with coal. As a “reference” basis, a sample of subbituminous coal (“HUK”) of North Bohemian basin was applied. The basic analytical characteristics of the samples are given in Table 1.

To compare structural aspects of the studied samples, method of infrared spectroscopy was used (Nicolet 6700, Thermo scientific, USA). ATR technique with single bounce diamond crystal was applied for the measurements. Total of 256 scans were collected for every spectrum with the resolution 4 cm^{-1} and Happ-Genzel apodization.

2.2. Pre-treatment of the samples

Before the IR measurements, the samples were diminished below 0.5 mm grain size and pre-dried under vacuum at $60\text{ }^{\circ}\text{C}$ for 5 h.

Before gas evolution experiments, the samples were diminished and sieved for size lower than 4.0 mm in diameter. Samples were measured both in wet (as received) and dried states. Drying of the samples was performed under vacuum ($60\text{ }^{\circ}\text{C}$ for ca. 5 h) to avoid pre-oxidation. Before drying, the oven to be evacuated was repeatedly flushed with nitrogen. When dried, sample was cooled under nitrogen atmosphere to room temperature and sealed in an airtight bag. Residual moisture of the samples was about 1 wt%.

2.3. Measurements of gases evolution

The gases evolved during aerial oxidation of the samples were monitored using a continuous flow reactor operating under air at temperatures of $40\text{--}160\text{ }^{\circ}\text{C}$ (method of thermal oxidation [16,17]). A weighed sample (20–40 g (biomass), 60–70 g (coal)) was packed in the reactor and the temperature was set at a starting level of $40\text{ }^{\circ}\text{C}$, with air flowing at a rate of ca. 20 ml min^{-1} . After a “stabilisation” period of 20 min, the gas stream at the reactor’s exit was collected in a tedlar bag for 30 min. Then the temperature was set at a level $20\text{ }^{\circ}\text{C}$ higher,

followed again by the stabilisation and gas collecting periods. The cycle was repeated until a temperature of $160\text{ }^{\circ}\text{C}$ was reached. During the measurements, the air flow was repeatedly checked both at the entry and exit of the reactor using a bubble flow meter. The collected gas samples were immediately analysed. The content of CO_2 and CO were measured by infra-red analysers (Unor, Maihak), concentration of O_2 was determined by paramagnetic analyser (Servomex OA 250). Other (minor) gaseous compounds were analysed using gas chromatograph Master GC (Dani Instruments) equipped with QS-BOND column (Restek) and flame ionization (FI) or thermal conductivity (TC) detectors. The following compounds were chromatographically determined: methane, ethane, propane, ethylene, propylene, acetylene, methanol, acetaldehyde, dimethyl ether and hydrogen. Isomers of the butanes/butenes could not be determined separately because of coincidence between retention times of n-butane/2-butene and isobutene/1-butene. Thus, butanes were evaluated together with butenes as a sum.

Detection limits of CO and CO_2 analyses were 1 ppm and 0.03%, respectively. Detection limits of the chromatographically determined compounds using FI detector were better or equal to 0.05 ppm. However, detection limit for hydrogen analysed by TC detector was ca. 10 ppm only.

The repeatability of the gas evolution measurements was evaluated from five subsequent tests with coal sample, and mean relative deviation was found to be $\pm 4\%_{\text{rel}}$ for analyses of CO , CO_2 and O_2 , while $\pm 15\%_{\text{rel}}$ was evaluated as mean relative deviation of the chromatographically determined compounds.

The amount of the evolved gases was expressed as the rate of production ($R_{(x)}$) in volume per sample mass and time units, preferably in ml per tonne of dry biomass and minute (from the practical point of view). Fig. 2 displays typical record of the gases measurement experiment as obtained for biomass sample EDE.

3. Results

Fig. 3 compares infrared spectra of the samples thus proving quite similar structural aspects of all the biomasses.

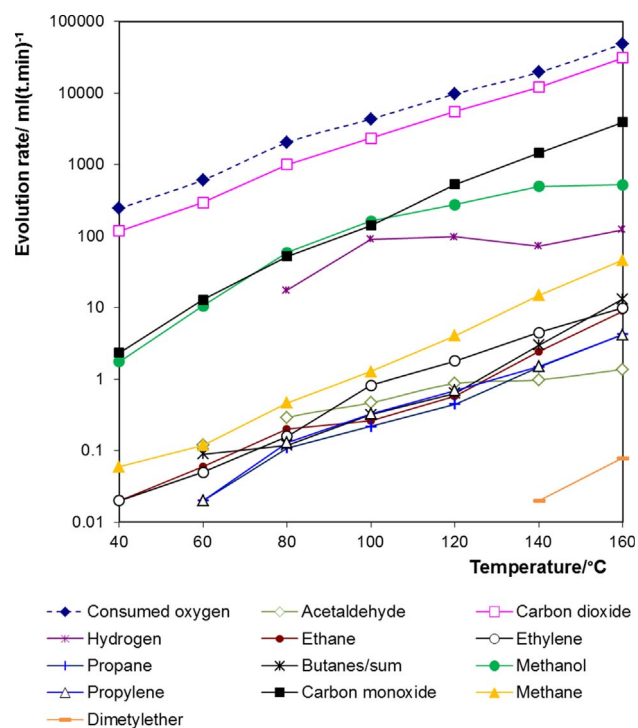


Fig. 2. Evolution rates of gases released during aerial oxidation of wet (as received) sample EDE as a function of temperature.

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