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Research article

Possibilities of the utilization of char from the pyrolysis of tetrapak

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ABSTRACT

Since the cellulose used in the production of tetrapak is of very high quality, the char generated during pyrolysis should be influenced mainly by the pyrolysis temperature. This article aims to determine the chemical composition of biochar prepared at the temperatures of 400, 500, 600 and 700 °C and its environmental properties determined by the presence of organic compounds with toxicity and relatively high mobility in the environment. The analytical pyrolysis of char was used to identify the following groups of organic compounds: alkanes, cycloalkanes, alkenes, cycloalkenes, alkynes, alkadiens, ethers, alcohols, nitrogen compounds, nitrils, ketones and aldehydes, compounds containing phenols, furans, benzofurans, PAHs (polycyclic aromatic hydrocarbons), carboxylic acids, compounds containing benzenes and markers indicative of the presence of synthetic polymers (polyethylene layers, a part of dyes, antioxidants, stabilizers), and fragments of cellulose. Concerning the use of char as a soil conditioner, its ecotoxicity was monitored (*Folsomia candida*) by monitoring its addition to the artificial soil (char addition: 0.5, 1, 2.5, 5, 10, 15, 20, 50 and 100%). The lowest reproduction inhibition of *Folsomia candida* is caused by biochar prepared at the temperature of 400 °C and 700 °C, but it is not suitable for the agricultural application, the concentration of PAHs is three times higher than the EBC limit. Low-density polyethylene which is present in the aseptic box in concentration of 6%, can degrade biochar so that it cannot be used as a soil amendment. The results of the char analyses show that the pyrolysis temperature is a decisive factor in the applicability of biochar.

1. Introduction

The packaging of food is essential from the point of view of food quality and also environmental impacts: waste production, global warming, and acidification potential. The production and disposal of aseptic cartons have the lowest environmental impact in the global warming and acidification potential, while the production of PET and HDPE has similar but higher impacts. This impact is only due to the recycling of the carton layer, and it could be improved if the aluminium and plastic layers could also be recycled (Meneses et al., 2012).

The tetrapak beverage carton is made up of about three-quarters of cellulose made of wood, from a renewable natural source; therefore it represents one of the most ecological types of packaging. It is divided into aseptic (for durable products) and non-aseptic (for pasteurized products). Aseptic cartons are made up of 6 layers (1 paper, 4 polyethylene, 1 aluminium), and non-aseptic contain 4 layers (only 1 paper and 3 polyethylene). Paper provides strength to the packaging. Polyethylene does not let through water or micro-organisms. Aluminium protects the packaging from light. Both types of cartons contain an inorganic component - minerals for strengthening, for aseptic packaging it is up to 4.9%. The main component is calcite (3.8%), and the rest is formed by muscovite and talc. For non-aseptic

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boxes, the mineral content is even higher (8.4%). The main components are calcite and kaolinite.

Tetrapak, SIG Combibloc and Elopak manufacture beverage carton for processing, packaging and distribution of food. The Alliance for Beverage Cartons and the Environment produces packing material at 20 plants in Europe. In 2013, recycling worldwide reached just 24%, with 43 billion packaging sorted out. The company TetraPak has committed to 40% recycling of beverage cartons by 2020. The used beverage cartons can be utilized in material and energy processes. Beverage carton can be utilized in the paper mill because the beverage cartons contain high-quality paper fibres. Cellulose fibres (70–90%) are recovered from beverage cartons (Mourad et al., 2008). The paper fibres are then used to produce new paper products. Remaining polyethylene and aluminium are used, for example, directly in the paper mill to produce the steam (for example: by pyrolysis), as fuel to cement works, or it is processed into other products. The aluminium foil has a high economic value due to the expensive production of aluminium from bauxite. The recovery of aluminium foil is not an easy task, but it can be solved by wet separation (flotation or hydrocyclone) or electrostatic separation. The options for separating Al from tetrapak using the hydraulic pulping technique described Yan et al. (2015). The mechanical recycling of residues of aluminium foil is commercially interesting. On the contrary, production of primary polyethylene is very cheap, and this is why mechanical recycling of polyethylene from beverage cartons is not so attractive from the economic point of view. The second possibility of recycling beverage cartons is the production of building and insulation boards. In this case, the beverage cartons are crushed, washed, dried, and then pressed into plates at temperatures of about 200 °C, the resulted construction material is called Flexibuild. These boards have many features similar to plasterboard, and they have similar uses.

A certain alternative to the full use of all the raw materials contained in tetrapak is pyrolysis. When pyrolysis temperature reaches maximum 600 °C, particles of aluminium are chemically not affected (the only change is that carbon enters aluminium along particle rims). PE foil is utilized and decomposed during thermal conversion. The pyrolysis carbon from the cartons (biochar) produced in this process can be used as a sorbent or soil amendment (Bernardo et al., 2014), or possibly as a fuel. Biochar, which is formed at higher temperatures, is very interesting in terms of sequestering carbon because it contains so-called recalcitrant carbon, which remains unchanged in soils (Rehrah et al., 2016).

Adding biochar to soil can increase soil fertility, reduce nutrient leaching, increase water retention capacity (Quilliam et al., 2012), and increase soil respiration, thereby stimulating microbial activity (Han et al., 2016). Biochar can enhance soil water holding capacity and thus plant production under limited water supply (Rizwan et al., 2018). Advantages of biochar utilization as an additive in compost are described by Waqas et al. (2017).

Some authors point to the positive effect of the addition of biochar to soils, but also indicate that environmental hazards that are related not only to biochar quality (IBI Certification Program Requirements, Version 2.1 November 23, 2015) but also to its applied amount are not known (Domene et al., 2015).

Biochar may contain many organic compounds of volatile nature that arise as a result of re-condensation of pyrolysis liquids and gases; their amount depends on production conditions and pyrolysis technology (Buss and Mašek, 2014) and equipment (Spokas et al., 2011). Since there are only a limited number of reported studies on the topic of VOCs (volatile organic compounds) and biochars and to our knowledge no quantitative studies, there is a need to investigate the composition and concentration of organics sorbed to biochar (Buss et al., 2015). Lower pyrolytic temperatures (< 350 °C) produced biochars with sorbed VOCs consisting of short carbon chain aldehydes, furans and ketones; elevated temperature biochars (> 350 °C) were typically dominated by sorbed aromatic compounds and longer carbon chain hydrocarbons (Spokas et al., 2011). Organic compounds present in biochar consist of: aromatic and polyaromatic hydrocarbons, aliphatic hydrocarbons, compounds containing phenols, carboxylic acids, polychlorinated biophenyls and dioxins (Bernardo et al., 2009).

The aim of the paper is to identify the occurrence of organic compounds that originate or decompose in biochar during pyrolysis of tetrapak performed at different temperatures (400, 500, 600, 700 °C). Ecotoxicity of biochar was determined. Parthenogenetic collembolans *Folsomia candida* have been chosen due to their abundance and diversity widely used to assess the environmental impacts of a different range of pollutants in soil. Collembolans *Folsomia candida* play an important role in the functioning of the ecosystem and are sensitive to soil contamination (Meli et al., 2013).

2. Materials and methods

Char samples were obtained by pyrolysis of used beverage cartons (tetrapak) for juice (aseptic boxes). Prior to pyrolysis, aluminium foil was removed from aseptic beverage packaging. The input material for pyrolysis was mechanically crushed below 1 cm. The prepared materials were pyrolyzed at the pilot plant Pyromatic, ENET Centre, VŠB Technical University of Ostrava at 400, 500, 600 and 700 °C.

Parameters of proximate and ultimate analysis of biochar and tetrapak were determined according to EN standards. Organic compounds in the samples of char were analysed using the method of pyrolysis gas chromatography with mass spectrometric detection (Py-GC/MS). The residue samples (100 μg) were inserted into quartz tube sealed at both ends by quartz wool. Each biochar sample was analysed by analytical pyrolysis at the appropriate temperature, which corresponded to the temperature of production of individual chars (400, 500, 600, 700 °C). The analytical pyrolysis conditions: time 10 s, temperature increase rate was 5 °C/ms. The interface between the pyrolytic unit and the gas chromatograph was heated to the temperature of 285 °C in order to prevent condensation of pyrolytic products. The pyrolysate was then separated at the non-polar column HP 5 ms (60 m × 0.25 mm x 0.25 μm). The temperature program for separation: 40 °C (retention time 2 min), 220 °C (retention time 10 min, temperature ramp 10 °C/min). From 220 °C the temperature increases with the rate of 33 °C/min up to 320 °C (retention time 5 min). The sample was injected automatically by the pyrolytic unit into the part of chromatograph at the temperature of 290 °C in the split mode 1:100. Quantification was conducted by comparison of GC peak area with that of co-injected known standard (1,3,5-terc.-tributylbenzene). Relative standard deviation varied for PAHs between 0.1 and 1.0%, for phenols the average value of RSD was 3.3%.

Ecotoxicity testing for soils was performed using 28-days reproduction test (ISO 11267 – Soil quality – Inhibition of reproduction of Collembola (*Folsomia candida*) by soil pollutants) was used to assess ecotoxicity of soils. Standard medium for soil bioassay (*Folsomia candida*) is artificial soil. The artificial soil for ecotoxicity testing was prepared according to the instructions of OECD – Guidelines for Testing Chemicals, Collembolan Reproduction Test in Soil, Test Guideline 232. The artificial soil was prepared by mixing of 5% of peat, 20% of kaolin clay (Stara Role, Czech Republic, content of kaolinite 92%) and sand.

According to the standardized guideline, 10 individuals (10–12 day old) were put into each replicate. Food (dry yeast) was provided at the beginning of the test and after 14 days and aeration was ensured (twice a week). After 28 days vessels were flooded with water to float organisms to the surface and pictures were taken using a digital camera. Ecotoxicity was determined by monitoring of the behaviour of *Folsomia candida* in artificial soil with char addition of 0.5, 1, 2.5, 5, 10, 15, 20, 50, and 100%.

3. Results

Table 1 shows the proximate and ultimate analysis of biochar