Science of the Total Environment 593–594 (2017) 406–417

Contents lists available at ScienceDirect

Science of the Total Environment

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

A study of torrefied cardboard characterization and applications: Composition, oxidation kinetics and methane adsorption

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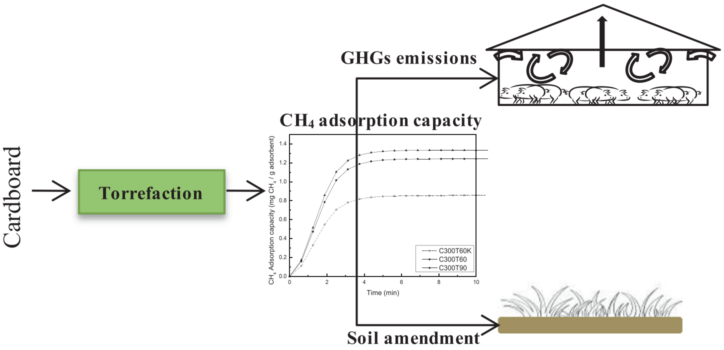
HIGHLIGHTS

- Torrefaction of cardboard is proposed as a valorization process.
- Effect of torrefaction temperature and residence time on the physico-chemical properties and thermal stability.
- Torrefied cardboard could be valorized as CH_4 adsorbent in agriculture.
- Freundlich isotherm fitted the CH_4 adsorption capacity of cardboard torrefied.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 September 2016
Received in revised form 9 March 2017
Accepted 11 March 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Torrefaction
Biochar
Modeling
CH_4 adsorption
Agriculture greenhouse gases
Waste valorization

ABSTRACT

Torrefaction is proposed as a valorization process for non recycled cardboard. Torrefied cardboard was physically and chemically characterized and it was proposed for energy production and methane adsorption. The surface area and pore volume obtained were among 3.0–6.0 m^2/g and $5.7 \cdot 10^{-3}$–$2.3 \cdot 10^{-2}$ cm^3/g, respectively. The carbon content increased with temperature and residence time of torrefaction. Oxidation kinetics of torrefied cardboard at different temperatures (250–300 °C) and at different plateaus (60–120 min) were tested. Torrefied cardboard was chemically treated with KOH in order to study the effect of K on thermal oxidation kinetics. It was observed that high torrefaction temperatures and residence times lead to a more stable char. Furthermore, kinetic parameters were obtained by iso-conversional methods and Coats and Redfern method. Attending to iso-conversional method, a decrease of E_a was observed with both, temperature and residence time of torrefaction. Whereas chemically treated presented highest E_a values than torrefied cardboard. In addition, regarding Coats and Redfern method, the oxidation model was not highly modified by torrefaction temperature and residence time. However, for chemically treated samples the oxidation model was modified by K presence. Finally, CH_4 adsorption capacity of torrefied cardboard was studied at 30 °C and atmospheric pressure. CH_4 partial pressures tested were lower than 0.45 kPa. It was observed that CH_4 adsorption capacity increased with torrefaction time and decreased with chemical treatment. Thus, for the tested samples, the highest adsorption capacity observed was 5.70 mg CH_4/g of sample.

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http://dx.doi.org/10.1016/j.scitotenv.2017.03.119
0048-9697/

1. Introduction

Nowadays, the management of organic residual biomasses (ORB) from municipal and industrial origin is a subject of debate in several countries. In this regard, their disposal in landfills contributes, among other issues, to the emission of greenhouse gases (GHGs) paper and cardboard cover a large part of them. The municipal solid wastes (MSW) in European Union (EU-27) were 78 million tons in 2012. Around 66 million tons were recovered and about 64.6% belonged to packing wastes from which 40% were paper and board (Eurostat Statistics Explained, 2015). In United States (USA), the total MSW generation in 2012 was 251 million tons, being around 87 million tons recovered (paper and paperboard accounted for over 51%) (United States Environmental Protection Agency, 2014). In Canada, 25 million tons of MSW were generated in 2012, which 8.8 million tons were recyclable. Among recyclable materials, paper, cardboard, and packaging cover the 41% of the total (Statistics Canada, 2012). However, non-recyclable and non-recovery paper and cardboard finished in the landfills. In EU-27, about 20% of the total ORB (12 million tons) corresponded with paper and cardboard packaging (Eurostat Statistics Explained, 2015). In USA, 164 million tons of ORB were discharged after recovery, where paper and cardboard represented about 15% (United States Environmental Protection Agency, 2014). In Canada, cardboard and boxboard represented about 17% of the total ORB discharged (Statistics Canada, 2012). Since stricter legislations that will ban the ORB disposal are coming up, the valorization of paper and cardboard are getting more interest of research for the years to come (Directive 2008/98/EC, 2015; ISD-318, 2014).

One of the most feasible solutions would be to treat or transform the ORB (especially packaging and paper materials) into value added compounds or energy. In this regard, the valorization of biomass by biochemical or thermochemical processes is one of the most promising fields of research. Among them, it is of special interest the thermochemical valorization of ORB, such as gasification, oxidation, pyrolysis or torrefaction due to the fact that these processes are easy to scale-up and they are already mature technologies (López-González et al., 2014a; Tumuluru et al., 2011). For instance, cardboard, which is mainly constituted by hemicellulose, lignin and cellulose, could be revalorized for its energetic application. In this sense, Phan et al. (2008) almost doubled the calorific value of cardboard from 15.17 MJ/kg to 24.60 MJ/kg by pyrolysis at 350 °C.

In this work, the cardboard torrefaction has been proposed as a valorization process in order to be used as CH_4 adsorbent. Torrefaction is a thermal pretreatment at temperatures ranged from 200 to 300 °C and residence time lower than 2 h is suitable, under an inert atmosphere or under a low oxygen concentration (Acharya et al., 2012; Basu, 2013). Torrefaction can be considered as a mild or incomplete pyrolysis. The main product from torrefaction would be a high-energy density solid product called biochar, which is similar to the pyrolytic product. Torrefaction, is mainly divided into 4 steps depending on the temperature: (1) Regime A, among 50 and 120 °C, it is associated to moisture loss; (2) Regime B, between 120 and 150 °C, the structural modifications such porosity reduction takes place due to moisture loss; (3) Regime C or reactive drying happens at temperatures between 150 and 200 °C. In this regime, irreversible structural modifications on biomass begin with the breakage of hydrogen and carbon bonds (depolymerization of hemicelluloses). Finally, (4) the regime D takes place between 200 and 300 °C, this regime is also called destructive drying, and it consists in the carbonization and devolatilization of the biomass sample. At these temperatures, the breach of inter- and intramolecular hydrogen bonds, a C—C and C—O bonds take place. As result, biomass structure is completely destroyed as well as the total devolatilization and carbonization of hemicellulose (from 125 to 300 °C). Furthermore, lignin (from 250 to 750 °C) and cellulose (from 280 to 625 °C) are partially devolatilized and carbonized (Basu, 2013; López-González et al., 2013; Tumuluru et al., 2011). Torrefaction allows to overcome the challenges associated with thermochemical biomass valorization, such as high moisture content, low energy density, high bulk density, and irregular shape and size of biochar. Torrefaction objectives are to maximize energy and mass yields by increasing the fixing carbon density, changing their structural properties.

In literature, biochar can be used as a combustible, in the agricultural sector as a soil amendment (organic and inorganic pollutants), catalyst support or adsorbent in chemical and environmental sectors (Cao and Harris, 2010; Nanda et al., 2015; Nowicki et al., 2012; Qian et al., 2015). The benefits of the use of biochar as soil amendment are the high C and mineral content, their capability to adsorb organic and inorganic pollutants, reduce the soils acidity and retain nutrients (Beesley et al., 2011). We proposed to use the torrefied cardboard as adsorbent of gaseous pollutants, which are retained by adsorption on biochar surface. In this regard, biochars have been used as adsorbents for different types of compounds in aqueous solutions (Pb, atrazine (Cao and Harris, 2010), and NH_3 (Gai et al., 2014)), and in gaseous effluents (NO_2 (Nowicki et al., 2012), CO_2, N_2O (Cornelissen et al., 2013), and CH_4 (Sadasivam and Reddy, 2015a)). In all cases, biochars were prepared via torrefaction (300 °C) or pyrolysis (400 to 800 °C) varying the residence time (1 to 6 h). A chemical treatment of biochar can modify its structure and properties. The chemical treatment (i.e. KOH) can increase the surface area and microporosity acting as pre-activation agent (Azargohar and Dalai, 2006; Unur, 2013). In addition, it can also modify the chemical composition of the biochar surface by hydrolysis of biomass compounds (Feng et al., 2012). These factors affect the thermal stability and morphological properties of the biochar material determining its sorption properties.

The aim of this work was to study the properties of torrefied cardboard in order to be valorized and used as fuel and CH_4 adsorbent. Torrefied cardboard could be used as soil amendment in agriculture or in landfill stabilizing CH_4 concentration, which favors the methanotrophic activity and as a consequence may reduce the CH_4 emissions from landfills and increase the CH_4 sink capacity of soils (Reddy et al., 2014; Syed et al., 2016). Therefore, the effect of the torrefaction temperature (250–300 °C) and the residence time (60, 90, 120 min) on the physico-chemical properties and thermal stability were analyzed. Firstly, the samples were characterized by X-ray diffraction (XRD), N_2 adsorption-desorption isotherms, scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR) and also their chemical composition in order to correlate their physical and chemical properties with their reactivity in an oxidative environment and its potential to be used as adsorbent. Secondly, the thermal stability under oxidative atmosphere of torrefied cardboard samples was evaluated by thermogravimetric analysis (TGA). Furthermore, the kinetic parameters were calculated by two methods: Starink and Coats-Redfern. Similarly, the effect of KOH as a promoter over torrefied cardboard was also evaluated. Finally, the CH_4 adsorption at 30 °C and atmospheric pressure was evaluated over selected torrefied cardboards. Their adsorption capacities were compared with those of a chemical treated sample.

2. Methods

2.1. Torrefied cardboard

Compressed cardboard in form of densified particles was torrefied in a screw reactor supervised by LoggerNet software (Campbell Scientific Software). It was connected to an automatic control unit (Campbell Scientific Inc. CR10, Logan, USA). The reactor working volume was 2000 ml, and its temperature was increased using a heating rate of 10 °C/min under a N_2 flow rate of 2000 ml/min. 150 g of cardboard was heated electrically to different operating temperatures (250 and 300 °C) and residence times (60, 90 and 120 min).