



CO₂ capture and storage by carbonation of beech wood chips ash

Улавяне и съхранение на CO₂ чрез карбонатиране на пепели от букови стърготини

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Introduction

Carbon dioxide is a primary agent of global warming among the greenhouse gas emissions as CO₂ constitutes 72% of the total anthropogenic greenhouse gases and causes 9–26% of the greenhouse effect (Oke, Olatiilu, 2011). More than 38 Gt of CO₂ emissions are released globally to the atmosphere each year due to use of fossil fuels and particularly their combustion in power plants (Samanta et al., 2012). Therefore, special countermeasures on worldwide scale are necessary to diminish CO₂ level in the atmosphere. The use of low carbon fuels and especially renewable energy sources, as well as CO₂ capture and storage (CCS) through different approaches are considered to be among the most actual strategies to diminish CO₂ in the atmosphere. The main focus of the present study is related to these two options, specifically biomass use and CCS by biomass ash (BA). Biomass is a renewable and carbon-neutral energy source with respect to the greenhouse gas balance and the bioenergy attracts a huge attention at present as the most promising among all renewable energy sources. About 15% of the world bioenergy nowadays are based on biomass (Saidur et al., 2011), and it is expected that up to 50% of the world's primary energy consumption would be met by biofuels in 2050 (McKendry, 2002). The direct combustion of biomass is the dominant conversion process currently used for bioenergy production and about 476 Mt of biomass ash (BA) are probably generated annually worldwide (Vassilev et al., 2013a). BA is a waste product normally dumped near CO₂ emission sources, namely to disposal sites of power plants. This product has high reactivity and exhibits promising CO₂ fixation capability because CCS is a result of interaction between flue gas or atmos-

pheric CO₂ and BA. Therefore, one of the most prospective and economically feasible technique is the direct CCS by carbonation of ash during combustion and post-combustion. The major purpose of the present study is to use a systematic approach and a combination of methods to identify: (1) composition and properties of BA; and (2) mechanism of CCS by carbonation of BA.

Material and methods

A beech wood chips sample representing a traditional biofuel was supplied from the JRS Company (Rosenberg, Germany). The beech wood chips ash (BCA) was laboratory produced in an electric oven with static air at 500 °C for 2h. The above temperature fits to the minimum temperature for complete biomass combustion. The generated BCA was stored in a plastic envelope for a couple of months at room temperature and then the sample was studied to definite its composition, phase transformations, carbonation-decarbonation behavior, and CCS potential. Methods such as light microscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and differential-thermal (DTA), thermo-gravimetric (TGA) and chemical analyses, as well as water leaching procedures were used to realize the above listed specific purposes (Vassilev et al., 2013c, 2014).

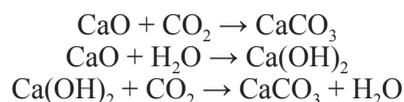
Results and discussion

The chemical composition and some properties of BCA produced at 500 °C include: CaO 62.6%, K₂O 18.0%, MgO 7.5%, SiO₂ 5.5%, P₂O₅ 2.5%, SO₃ 0.8%, Al₂O₃ 0.5%, Fe₂O₃ 0.4%, Na₂O 0.1%, pH of leachate 12, and water-soluble components

20%. The important sum of alkaline-earth and alkaline oxides for BCA is 88.2%. The phase-mineral composition of BCA consists mostly of inorganic amorphous matter and calcite, and to a lesser extent, whitlockite and quartz (Fig. 1A). The ash formation and specific phase and mineral transformations during combustion of the present beech wood chips at 500–1300 °C have been studied in detail earlier (Vassilev et al., 2013c). It was found that the biomass combustion and ash formation at 500 °C consist of: (1) burning of combustible gases and char; (2) formation of calcite as a result of oxidation and carbonation of organically bound Ca and Ca oxalates by CO₂; (3) crystallization of whitlockite due to a reaction between organically bound Ca and P; (3) opal transformation to quartz; and (4) formation of non-glass inorganic amorphous material. These newly formed inorganic phases are mostly originated during biomass combustion; however, some post-combustion calcite crystallization may also occur during storage of BCA. The present study focuses on the carbonation and decarbonation of BCA because these processes are responsible for CCS.

The data show that calcite in BCA is newly formed mineral because it was not identified as original mineral in beech wood chips (Vassilev et

al., 2013c). The formation of calcite is a result of solid-gas and solid-liquid reactions between Ca oxyhydroxides and CO₂. For instance, there is decomposition and oxidation of original organic matter and oxalates abundant in Ca and consequent carbonation of the newly formed oxyhydroxides by the flue CO₂ gases during biomass combustion. Subsequently, additional post-combustion calcite may be formed by reactions between the unreacted Ca oxyhydroxides in BCA and CO₂ occurring in air and water during BCA storage. However, the differentiation of calcite formed during combustion and post-combustion is problematic. The general carbonation reactions in BCA can be simplified as follows:



It is interesting to note that the mass of dry water-soluble residue for BCA increases with 10 % after one-month room storage. This observation also confirmed the post-combustion hydration, hydroxylation and carbonation of some minerals in BCA by moisture and CO₂ in the air through storage of BAs even for a relatively short period of time.

The results reveal the intensive formation of calcite at 500 °C (Fig. 1A) and its complete decomposition at 900 °C (Fig. 1B). The decarbonation of calcite was determined by DTA and TGA curves, namely: (1) endothermic peak at 743 °C and mass loss of 28% (550–900 °C) for BCA (Fig. 1B). Hence, the mass loss measured by TGA in the temperature range between 550 and 900 °C will approximately determine the CO₂ volatilization from calcite in BCA. This calculation reveals that the CO₂ uptake per ton BCA is 280 kg.

Biomass ashes are especially prospective for CCS among other sorbents because the contents of alkaline-earth and alkaline oxides in specific BA varieties can reach very high contents, namely up to 83.5% of CaO, 63.9% of K₂O, 28.7% of Na₂O, and 21.6% of MgO (Vassilev et al., 2017). The present data reveal that BA captures CO₂ from flue emissions or air and stores this gas by chemical reactions as newly formed carbonates. The CO₂ mineral carbonation is similar to a natural rock weathering process and an effective method for both capturing and permanent storing of CO₂. Additionally, this is a geological process and a special monitoring of CCS is not required due to the long-term (for years) carbonation reactions in ash disposals. Biomass, in contrast to fossil fuels, is a renewable and carbon-neutral energy source because the CO₂ released during combustion or other conversion processes of biomass is recaptured by the regrowth of the biomass during photosynthesis. Furthermore, the

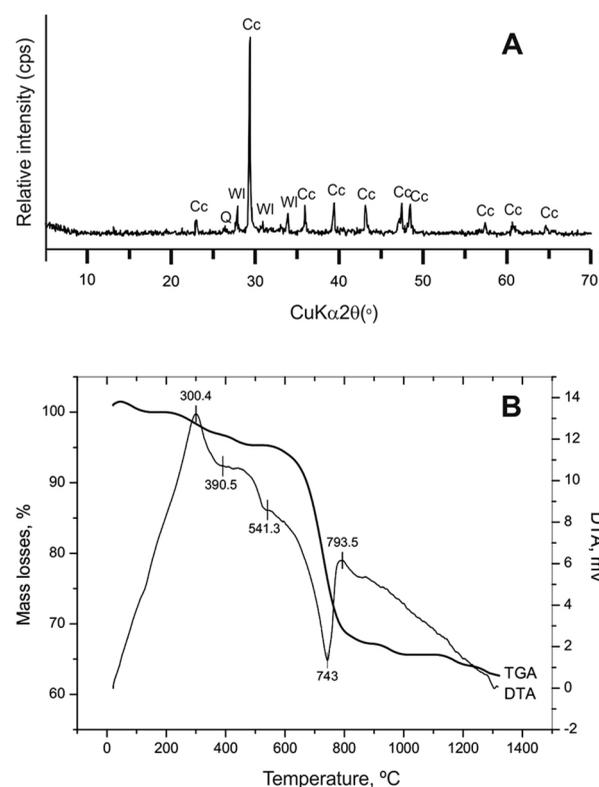


Fig. 1. A, XRD pattern of beech wood chips ash (BCA) generated at 500 °C/2h. Abbreviations: Cc, calcite; Cps, counts per second; Q, quartz; Wl, whitlockite (Ca₃(PO₄)₂); B, DTA and TGA profiles of beech wood chips ash (BCA) generated at 500 °C/2h.

data show that the bioenergy can be not only carbon-neutral, but also with some extra CCS potential due to the additional fixation and immobilization of atmospheric CO₂ as carbonates during BA storage (Vassilev et al., 2013b).

The theoretical CO₂ sequestration capacity (TCSC) of different waste products can be calculated according to the Steinour equation (López et al., 2018), namely $CO_2 (\%) = 0.785 (CaO - 0.7 SO_3) + 1.09 MgO + 0.71 Na_2O + 0.468 K_2O$. TCSC calculated for BCA is 65.4% or the CO₂ uptake is 654 kg per ton BA. On the other hand, the present TGA data for CO₂ emission from the decomposition of calcite in the studied BCA show that the CO₂ uptake capacity is 2.3 times less than the calculated TCSC. Another calculation shows that TCSC of BA produced worldwide (476 Mt per year) is 162 Mt of extra CCS annually based on the mean chemical composition of 141 BA varieties (Vassilev et al., 2017). It is well known that solely one ton of mineral lime has the theoretical capability to sequester up to 799 kg of CO₂ as calcite according to the chemical formula of this mineral. However, there are also supplementary active phases in biomass combustion residues such as other Ca-, Mg-, K- and Na-bearing oxides, hydroxides, inorganic amorphous material, silicates, phosphates, sulphates, and char that are capable of capturing and storing additional CO₂ during biomass combustion and storage. For example, 178 (totally among 291) minerals and mineral groups containing alkaline and alkaline-earth elements have been identified in BAs worldwide (Vassilev et al., 2013c). Unfortunately, the mechanisms of CCS by BA and specific minerals in BA are at an initial stage of research and future detail studies are required. Despite such limitations, it is clear that BA can be used as a novel CO₂ sorbent and shows an actual extra CCS phenomenon. Hence, the future large-scale bioenergy production (especially from combustion and gasification) can contribute enormously for reducing CO₂ emissions and can decrease or eliminate the application of expensive technologies for CCS. Therefore, bioenergy has a huge potential for reduction of harmful CO₂ emissions generated from fossil fuels. As pointed above about 15% of the world energy supplies at present are based on biomass and it is expected that up to 50% of the world's primary energy consumption would be met by biofuels in 2050. It is well known that each ton of biomass fired in a power plant directly reduces the fossil CO₂ emissions by 1 t (Tillman, 2000). Hence, about 13 Gt of CO₂ emissions could be reduced from the present 38 Gt of fossil-

fuel CO₂ emissions (Samanta et al., 2012) by 35% increasing of bioenergy application. This prognosis indicates that a huge amount of CO₂ emissions can be reduced by bioenergy produced by sustainable second (non-edible) and third (algae) biofuel generations, as well as by the extra CCS of BA. Hence, the use of sustainable bioenergy together with the extensive afforestation of abandoned, low productive, degraded or contaminated land, as well as with the sustainable forest management, and soil C manipulation may contribute for solving the global warming problem.

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