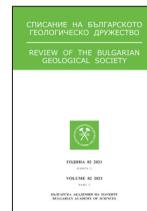




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CO₂ capture and storage by carbonation of biomass ashes

Улавяне и съхранение на CO₂ чрез карбонатиране на пепели от биомаса

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Abstract. The CO₂ capture and storage by carbonation of eight short-term stored, long-term stored and weathered biomass ashes was studied. It was found that the CO₂ uptake by BAs is up to 2–32% (mean 16%). Hence, the future large-scale sustainable biomass production and combustion can contribute greatly for reducing CO₂ emissions in the atmosphere.

Keywords: CO₂ capture; CO₂ storage; biomass ash; mineralogy; carbonation.

Introduction

The major gas that contributes for the global warming is CO₂ and it constitutes 72% of the total anthropogenic greenhouse gases in the atmosphere (Oke, Olatilu, 2011). More than 38 Gt of CO₂ emissions, especially from fossil fuels burning in power plants, are released worldwide to the atmosphere annually (Samanta et al., 2012) and urgent actions are required to reduce CO₂ level. The application of renewable energy resources and various CO₂ capture and storage (CCS) methods are among the most prospective strategies to diminish CO₂ in the atmosphere. Therefore, the present study focusses on biomass use and CCS by biomass ash (BA). Biomass is the most promising renewable and C-neutral energy source; however, only about 15% of the world energy are produced from biomass (Saidur et al., 2011). The prognosis shows that up to 50% of the world's primary energy consumption would be met by biofuels in 2050 (McKendry, 2002). The combustion of biomass is the leading conversion process recently used for bioenergy production and about 480 Mt of BA are probably generated annually worldwide (Vassilev et al., 2013). This waste product is commonly stored in disposal sites near CO₂ emission sources such as power plants. On the other hand,

BA reveal significant CO₂ fixation capability because CCS is due to the interaction between flue gas or atmospheric CO₂ and BA. Hence, some of the most forthcoming approaches for CO₂ sequestration are to enhance the biomass combustion and to apply direct CCS by carbonation of BA during combustion and post-combustion. The major purpose of the present study is to identify: (1) the composition and properties of different BAs; and (2) the mechanism of CCS by carbonation of BAs.

Material and methods

Eight BAs, namely beech wood chips ash (BCA), corn cobs ash (CCA), marine macroalgae ash (MMA), plum pits ash (PPA), rice husks ash (RHA), switchgrass ash (SGA), sunflower shells ash (SSA), and walnut shells ash (WSA), were produced in an oven at 500 °C for 2h under static air. Three types of ash samples were studied, namely: (1) short-term stored BAs kept in open plastic envelopes under ambient conditions for a couple of months; (2) long-term stored BAs kept under the above conditions for 10 years; and (3) weathered BAs subjected to induced weathering and produced from the long-term stored BAs following 30 hydration (1:20 ash-distilled water mass ratio) and dehydration cycles

at ambient conditions for 4 months; before their characterization. Methods such as light microscopy, powder X-ray diffraction (XRD), differential-thermal (DTA) and thermo-gravimetric (TG) analyses, as well as differential scanning calorimetry (DSC), evolved CO₂ profiles and chemical analyses were used (Vassilev et al., 2021).

Results and discussion

The chemical composition of BAs is highly variable as the contents of oxides fluctuate in large ranges, particularly for SiO₂ (1–90%), CaO (1–63%), K₂O (4–50%), SO₃ (1–28%), Na₂O (0.1–14%), and MgO (Vassilev et al., 2021). The phase-mineral composition of BAs (Table 1) consists mainly of inorganic amorphous matter, carbonates and bicarbonates, and to a lesser extent, silicates, chlorides, hydroxides, phosphates and sulphates, plus some char.

It was found that the biomass combustion and ash formation at 500 °C include: (1) burning of combustible gases and char; (2) formation of carbonates as a result of oxidation and carbonation of organically bound Ca, K and Mg, and carbonation of oxalates by CO₂; (3) crystallization of phosphates, hydroxides, sulphates and chlorides due to reactions among organically bound Ca, K, Mg, Na, P and S; (4) opal transformation to quartz; and (5) formation of non-glass inorganic amorphous material (Vassilev et al., 2013). The present study focuses on the carbonation and decarbonation of BAs because these processes are responsible for CCS.

The data show that carbonates in BAs are mostly newly formed minerals because they were identified only as traces in the biomass samples (Vassilev et al., 2013). Their formation is a result of both solid-gas and solid-liquid reactions between alkaline-earth and alkaline oxyhydroxides and CO₂ during biomass combustion, as well as post-combustion

Table 1. Phase-mineral composition detected for 8 biomass ashes according to XRD data

Phase, mineral	Formula
<i>Inorganic amorphous matter</i>	
<i>Carbonates and bicarbonates</i>	
Calcite	CaCO ₃
Kalicinite	KHCO ₃
Fairchildite	K ₂ Ca(CO ₃) ₂
Butschliite	K ₂ Ca(CO ₃) ₂
Baylissite	K ₂ Mg(CO ₃) ₂ ·4H ₂ O
<i>Oxides and hydroxides</i>	
Portlandite	Ca(OH) ₂
<i>Chlorides</i>	
Sylvite	KCl
Halite	NaCl
<i>Sulphates</i>	
Anhydrite	CaSO ₄
Gypsum	CaSO ₄ ·2H ₂ O
Arcanite	K ₂ SO ₄
Picromerite	K ₂ Mg(SO ₄) ₂ ·6H ₂ O
<i>Phosphates</i>	
Apatite	Ca(PO ₄) ₃ (Cl,F,OH,CO ₃)
Struvite	KMg(PO ₄) ₆ ·H ₂ O
Archerite	K(H ₂ PO ₄)
<i>Silicates</i>	
Quartz	SiO ₂
Plagioclase	NaAlSi ₃ O ₈ -CaAl ₂ Si ₂ O ₈
Leucite	KAlSi ₂ O ₆
Kalsilite	KAlSiO ₄

hydration, hydroxylation and carbonation of some minerals by moisture and CO₂ in the air through storage of BAs. It was found that the mineral composition of the short-term stored, long-term stored and weathered BAs is similar; however, there are

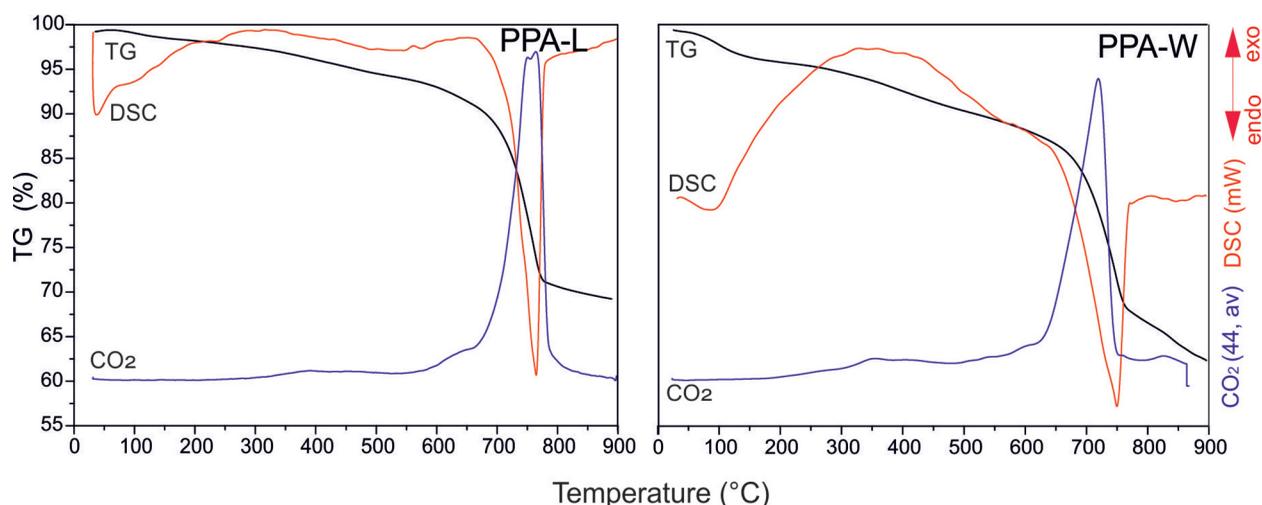


Fig. 1. TG, DSC and evolved CO₂ profiles of long-term stored (denoted as L) and weathered (denoted as W) PPA

Table 2. Mass loss of 8 biomass ashes (BAs) determined at 600–900 °C, %

BAs	Short-term stored BA	Long-term stored BA	Weathered
BCA	27	32	32
CCA	6	9	8
MMA	11	21	27
PPA	10	24	26
RHA	1	2	2
SGA	3	6	4
SSA	8	11	12
WSA	18	16	18

increased proportions of carbonates and especially bicarbonates in the long-term stored and weathered BAs (Vassilev et al., 2021). The DTA, TG, DSC and evolved CO₂ data show the complete decomposition of carbonates in BAs according to the endothermic effects and mass losses at 600–900 °C (Vassilev et al., 2021). An example of this decarbonation is illustrated herein for long-term stored and weathered PPA in Fig. 1.

Therefore, the mass loss measured by TG in the temperature range between 600 and 900 °C can approximately determine the CO₂ volatilization from carbonates (excluding the partial decarbonation of bicarbonates) or respectively CCS in BAs. This measurement (Table 2) reveals that the CO₂ uptake by BAs is as follows: 1–27% (mean 11%) for short-term stored BAs; 2–32% (mean 15%) for long-term stored BAs; and 2–32% (mean 16%) for weathered BAs (Vassilev et al., 2021).

Hence, the results 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 long-term storage and weathering of BAs. These data reveal that BAs are very prospective for CCS among other sorbents because the contents of alkaline-earth and alkaline components, which are responsible for the carbonate formation in BA, can reach very high contents (Vassilev et al., 2013). Solely one ton of mineral lime has the theoretical capability to sequester about 800 kg of CO₂ as calcite according to the chemical formula of this carbonate. On the other hand, there are also additional active phases in BA such as other Ca-, Mg-, K- and Na-bearing oxyhydroxides, silicates, phosphates, sulphates, inorganic amorphous material, and char

that are capable for CCS during biomass combustion and BA storage.

CCS by carbonation of BA is similar to a natural rock weathering process. BA captures CO₂ from flue emissions or air and stores this gas permanently and safely by chemical reactions. Even more, a special monitoring of CCS is not required due to the long-term (for years) carbonation reactions in ash disposals. The calculation shows that 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. Hence, the future large-scale bioenergy production, particularly from combustion and gasification, can contribute greatly for reducing CO₂ emissions and can decrease or eliminate the application of expensive technologies for CCS. However, the mechanisms of CCS by BA and specific minerals in BA are still not well known and future detail studies are required in this topic.

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