



CO₂ capture and storage by carbonation of plum pits ash and walnut shells ash

Улавяне и съхранение на CO₂ чрез карбонатизиране на пепели от сливови костилки и орехови черупки

Stanislav Vassilev, Christina Vassileva, Nadia Petrova
Станислав Василев, Христина Василева, Надя Петрова

Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 107, 1113 Sofia, Bulgaria; E-mails: vassilev_stan@yahoo.com; ch_vassileva@yahoo.com

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Introduction

Carbon dioxide is a major agent of global warming as CO₂ constitutes 72% of the total anthropogenic greenhouse gases (Oke, Olatilu, 2011). More than 38 Gt of CO₂ emissions, particularly from fossil fuels combustion in power plants, are released worldwide to the atmosphere each year (Samanta et al., 2012) and special countermeasures are required to diminish CO₂ level. The use of renewable energy sources and diverse CO₂ capture and storage (CCS) approaches are among the most actual strategies to reduce CO₂ in the atmosphere. The main focus of the present study is connected with biomass use and CCS by biomass ash (BA). Biomass is a renewable and C-neutral energy source, and bioenergy attracts a huge attention as the most promising renewable energy sources. About 15% of the world bioenergy currently 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 presently used for bioenergy production and about 480 Mt of BA are probably generated annually worldwide (Vassilev et al., 2013). BA is a waste product normally dumped near CO₂ emission sources, namely to disposal sites of power plants. This product exhibits promising CO₂ fixation capability because CCS is a result of interaction between flue gas or atmospheric CO₂ and BA. Therefore, some of the most prospective and economically feasible techniques for CO₂ reducing are: (1) to increase the biomass combustion, and (2) 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 BAs, and (2) the mechanism of CCS by carbonation of BAs.

Material and methods

Plum pits (weathered) and walnut shells samples were collected from the Debnevo area, Bulgaria. The plum pits ash (PPA) and walnut shells ash (WSA) were produced in an oven at 500 °C for 2h under static air. The generated ashes were stored in open plastic envelopes for a couple of months at room temperature and then the samples were studied to define their 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 for that purpose (Vassilev et al., 2013).

Results and discussion

The chemical composition of PPA and WSA (Table 1) is variable; however, the important sum of alkaline-earth and alkaline oxides is very high (65–91%). The water leachates of these BAs have alkaline to highly alkaline pH values and brine character.

The phase-mineral composition of PPA and WSA (Table 2) consists mostly of inorganic amorphous matter, carbonates and bicarbonates, and to a lesser extent, silicates, phosphates and sulphates.

It was found that the biomass combustion and ash formation at 500 °C include: (1) burning of

Table 1. Chemical composition of plum pits ash (PPA) and walnut shells ash (WSA), wt%

Characteristic	PPA	WSA
SiO ₂	12.01	2.84
CaO	43.95	38.11
K ₂ O	16.29	49.33
P ₂ O ₅	10.17	2.37
Al ₂ O ₃	2.57	0.52
MgO	4.18	3.80
Fe ₂ O ₃	1.75	0.40
SO ₃	7.72	2.03
Na ₂ O	0.79	0.12
TiO ₂	0.16	0.05
Cl ₂ O	0.27	0.38
MnO	0.14	0.05
Sum	100.00	100.00
CaO+MgO+K ₂ O+Na ₂ O	65.21	91.36
pH of leachate	8.9	10.5
Dry water-soluble residue	9.4	41.1

combustible gases and char; (2) formation of carbonates as a result of oxidation and carbonation of organically bound Ca and K, and carbonation of oxalates by CO₂; (3) crystallization of apatite due to a reaction between organically bound Ca and P; (3) opal transformation to quartz, and (4) 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 newly formed minerals because they were not identified as original minerals in the biomass samples (Vassilev et al., 2013). Their formation is a result of both solid-gas and solid-liquid reactions between Ca and K oxyhydroxides and CO₂. For instance, there is decomposition and oxidation of original organ-

ic matter and oxalates abundant in Ca and K and consequent carbonation of the newly formed oxyhydroxides by the flue CO₂ gases during biomass combustion. Subsequently, additional post-combustion calcite, fairchildite, butschliite, and particularly kalicinite may be formed between the unreacted Ca and K oxyhydroxides in BA and CO₂ occurring in air and water during BA storage. The general carbonation reactions in BA can be simplified as follows:

- $MO + CO_2 \rightarrow MCO_3$ (M = Ca or Mg)
- $R_2O + CO_2 \rightarrow R_2CO_3$ (R = K or Na)
- $R_2O + MO + 2CO_2 \rightarrow R_2M(CO_3)_2$ (M = Ca or Mg and R = K or Na)
- $MO + H_2O \rightarrow M(OH)_2$ (M = Ca or Mg)
- $M(OH)_2 + CO_2 \rightarrow MCO_3 + H_2O$ (M = Ca or Mg)
- $R_2CO_3 + H_2O + CO_2 \leftrightarrow 2RHCO_3$ (R = K or Na)

It should be stated that the mass of dry water-soluble residues for PPA and WSA increases with 1% and 18%, respectively, after one-month room storage. This observation also confirmed the post-combustion hydration, hydroxylation and carbonation of some minerals in BAs by moisture and CO₂ in the air through storage of BAs even for a relatively short period of time.

The XRD data reveal the intensive formation of carbonates at 500 °C (Table 1), while the DTA and TGA results show their almost complete decomposition at 900 °C (Fig. 1), namely: (1) endothermic effect at 737 °C for calcite and mass loss of 10% in the temperature range 600–900 °C for PPA (Fig. 1a); and (2) endothermic effects at 777 °C for calcite and 896 °C for K-Ca carbonates, and corresponding mass loss of 18% in the range 600–900 °C for WSA (Fig. 1b). Hence, the mass loss measured by TGA in the temperature range between 600 and 900 °C will approximately determine the CO₂ volatilization

Table 2. Phase-mineral composition of plum pits ash (PPA) and walnut shells ash (WSA) according to XRD data, wt%

Phase, mineral	Formula	PPA	WSA
1. Inorganic amorphous matter		F	F
2. Inorganic crystalline matter		F	F
2.1. Carbonates and bicarbonates		F	F
Butschliite	K ₂ Ca(CO ₃) ₂		Ma
Fairchildite	K ₂ Ca(CO ₃) ₂	Mi	F
Calcite	CaCO ₃	F	Ma
Kalicinite	KHCO ₃		Mi
2.2. Sulphates		Mi	Mi
Anhydrite	CaSO ₄	Mi	Mi
2.3. Phosphates		Mi	
Apatite	Ca(PO ₄) ₃ (Cl,F,OH,CO ₃)	Mi	
2.4. Silicates		Mi	
Quartz	SiO ₂	Mi	

Abb.: F, forming (>20%); Ma, major (10-20%); Mi, minor (1–9%) mineral or phase.

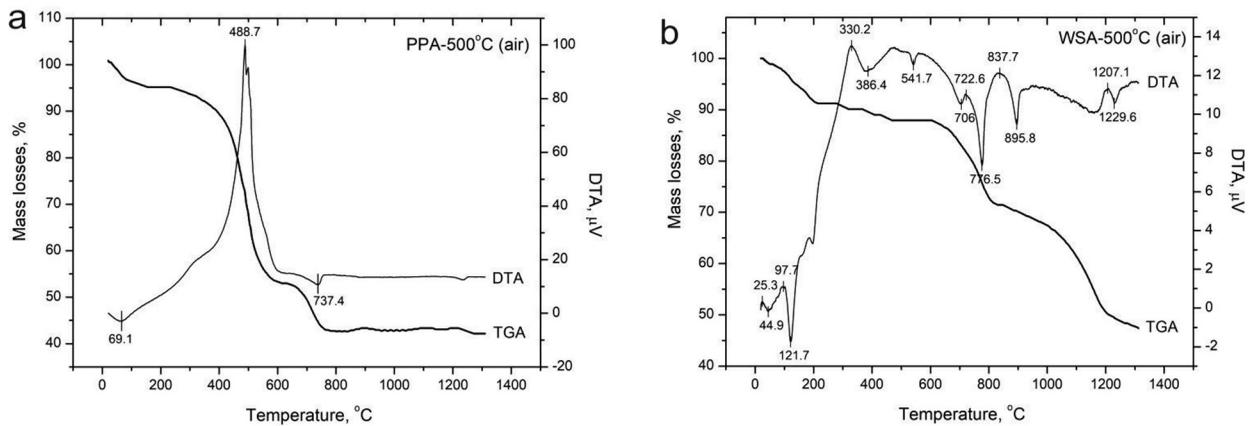


Fig. 1. DTA and TGA profiles of: *a*, plum pits ash (PPA); *b*, walnut shells ash (WSA), generated at 500 $^{\circ}\text{C}/2\text{h}$

from carbonates or CCS in BAs. This measurement reveals that the CO_2 uptake per ton PPA and WSA is 100 kg and 180 kg, respectively. However, CCS of WSA seems to be about 8% more than the determined CO_2 volatilization at 600–900 $^{\circ}\text{C}$ because this ash contains K bicarbonate and it is much more abundant in K-Ca carbonates than calcite (Table 2). It can be speculated that there is some kalicinite decarbonation ($\sim 5\%$) at 100–200 $^{\circ}\text{C}$ and additional fairchildite-buttschliite decarbonation ($\sim 3\%$) in the range 900–1000 $^{\circ}\text{C}$ for WSA (Fig. 1b).

BAs are very 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 84% of CaO, 64% of K_2O , 30% of Na_2O , and 16% of MgO (Vassilev et al., 2013). It is well known that solely one ton of mineral lime has the theoretical capability to sequester up to 799 kg of CO_2 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, silicates, phosphates, sulphates, inorganic amorphous material, and char that are capable of capturing and storing additional CO_2 during biomass combustion and storage. 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.

The results show that CCS by carbonation of BA captures CO_2 from flue emissions or air and stores this gas permanently and safely by chemical reactions. This BA carbonation is similar to a natural rock weathering process and an effective method for both capturing and permanent storing of CO_2 . 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. Furthermore, the 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 CO_2 as carbonates during BA storage. The calculation reveals that about 13 Gt of CO_2 emissions could be reduced from the present 38 Gt of fossil-fuel CO_2 emissions (Samanta et al., 2012) by 35% increasing of bioenergy application. This prognosis indicates that a huge amount of CO_2 emissions can be reduced by bioenergy produced by sustainable second (non-edible) and third (algae) biofuel generations. Hence, the future large-scale bioenergy production (especially from combustion and gasification) can contribute enormously for reducing CO_2 emissions and can decrease or eliminate the application of expensive technologies for CCS.

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