

REUSE OF COAL COMBUSTION ASH AS SORBENT: THE EFFECT OF GASIFICATION TREATMENTS

Marco Balsamo*, Francesco Di Natale*, Alessandro Erto*, Amedeo Lancia*,
Fabio Magri**, Fabio Montagnaro** and Luciano Santoro**

marco.balsamo@unina.it

* Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli Federico II,
Piazzale Vincenzo Tecchio 80, 80125 Napoli (Italy)

** Dipartimento di Chimica, Università degli Studi di Napoli Federico II,
Complesso Universitario di Monte Sant'Angelo, 80126 Napoli (Italy)

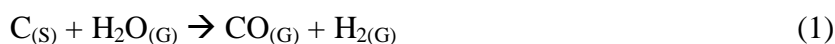
Abstract

Beneficiation through gasification of coal combustion ash coming from an industrial power plant aimed at its reuse as adsorbent is dealt with. The raw ash was gasified in a tubular reactor at 850°C for times ranging from 10 to 60 min, using either steam or CO₂ as gasifying agents. The relationships among ash properties, gasification treatments and properties of the gasified ashes deserve investigation. Therefore, ash characteristics (such as carbon content, porosimetric, diffractometric and granulometric properties) were correspondingly determined. In the light of a critical analysis of the obtained results, gasification conditions able to make the parent ash a potentially better adsorbent material were defined, with a particular emphasis on similarities and differences between steam and CO₂ gasification.

Overview

Adsorption is a consolidated technique widely used in many environmental applications. Activated carbon is the most commonly employed sorbent, but there is a critical concern about the high unit cost of virgin material and the disposal/regeneration of exhausted one. In this scenario, non-conventional materials like industrial residues, natural materials, agricultural by-products and other biomasses can be used as cheaper alternatives to activated carbon [1]. This work deals with *coal combustion ash* (CCA), an industrial residue whose disposal must be limited in accordance with the issuing of recent specific regulations. Apart from construction materials industry [2,3] and other possible environmental processes [4], adsorption applications are interesting possibilities for CCA reuse, due to CCA moderately porous structure and the presence of both an inorganic matrix and unburnt carbon which can contribute to the pollutants capture [5–11].

The CCA reutilization as adsorbent can take advantage from proper beneficiation techniques (such as chemical modification, demineralization, gasification, mechanical sieving, pyrolysis) aimed at improving the physical, chemical and morphological characteristics of the raw material [1,5,7,9,11,12]. *Gasification* is the activation treatment on which this paper is focused: it can be carried out in *steam* or *carbon dioxide* [13], and involves the conversion of the ash unburnt carbon into gaseous products according to the following endothermic reactions, respectively:



Gasification, generally carried out at temperatures in the range 700–900°C, is very effective in the development of ash porosity, as reported by other authors in the literature [14–

16]. Nonetheless, issues concerning close relationships among ash properties, gasification treatments and properties of the gasified ash surely deserve further investigation. For example, in a recently-published work [11] in which demineralization and mechanical sieving have been employed as ash beneficiation treatments, it has been qualitatively and quantitatively underlined the significance that exposed contact surface and porosity do have on ash adsorption performances.

Following the path drawn in that paper, in this work CCA has been gasified by either steam or CO₂ for different activation times, and ash characteristics (such as carbon content, porosimetric, diffractometric and granulometric properties) have been determined. The aim is to define gasification conditions to make CCA suitable as sorbent material, while a parallel investigation is currently being carried out to characterize the gasified ash adsorption behaviour, whose results will be published in a forthcoming paper.

Experimental

The coal combustion fly ash (CCA) adopted in this work was generated in an Italian power plant operated by Enel, and it was characterized in a former work by Balsamo *et al.* [11]. CCA was gasified by either steam (Eq. (1)) or CO₂ (Eq. (2)) in an electrically-heated tubular reactor (Nabertherm R60/750/13, i.d.=60 mm). The reactor was kept, in any case, at the temperature of 850°C. Samples (1 g) of CCA were charged into the reactor and kept in contact with a stream of steam or CO₂: steam was generated by feeding liquid water (flow-rate at room temperature equal to 60 mL h⁻¹) through a pump (Stepdos 03RC) to the reactor, while CO₂ was fed at a flow-rate of 80 L h⁻¹ (at room temperature). It is highlighted that both steam and CO₂ flow-rates at the operating temperature (850°C) assume the value of about 300 L h⁻¹. Steam gasification (SG) or carbon dioxide (so-called ‘dry’) gasification (DG) were carried out for times equal to 10, 30 and 60 min, giving rise to the following two terns of samples: *SG10*, *SG30*, *SG60* and *DG10*, *DG30*, *DG60*.

Solid materials were characterized by the following techniques: (a) carbon content determination by means of a Leco CHN-2000 analyzer; (b) porosimetric analysis, carried out by a mercury intrusion Thermo Finnigan Pascal 240/140 porosimeter operated in the pore size range 3.7–500 nm; (c) X-ray diffraction (XRD), performed by a Bruker D2 Phaser diffractometer operated at diffraction angles ranging between 10 and 60°2θ with a scan velocity equal to 0.05°2θ s⁻¹; (d) laser granulometric analysis, carried out by a Malvern Instruments Master Sizer 2000 granulometer operated down to a minimum particle size of 0.02 μm.

Results and Discussion

The raw ash was characterized by a carbon content (wet basis) equal to 23.3%. The evolution of the gasification process was followed by weighing the ash sample before and after reaction, and by determining the C-content of the gasified ash. This allowed to calculate the burn-off degree:

$$\xi = \frac{m^{CCA} X_C^{CCA} - m^{SG(DG)} X_C^{SG(DG)}}{m^{CCA} X_C^{CCA}} \quad (3)$$

where m is the sample mass and X_C is the mass fraction of carbon. The results reported in Table 1 show that steam gasification was practically complete after 30 min, and that $\xi=48\%$ even after 10 min (for the *SG10* sample, it was $X_C=0.144$). Moreover, it can be observed that the CO₂ gasification treatment gave qualitatively similar results; nonetheless, CO₂ gasification was slightly less effective, with $\xi=98\%$ for *DG60* and $\xi=45\%$ for *DG10* (having $X_C=0.151$).

Table 1. Relevant parameters for gasified ashes and (for comparison) raw CCA.

	X_C [-]	ξ [-]	ψ [mm ³ g ⁻¹]	δ [μm]	d_s [μm]	d_{50} [μm]
CCA	0.233	–	30	45	10	25
SG10	0.144	0.481	63	42	6	12
SG30	n.d.	~1	47	–	–	–
SG60	n.d.	~1	45	–	–	–
DG10	0.151	0.446	49	42	6	19
DG30	0.011	0.966	37	–	–	–
DG60	0.008	0.976	37	–	–	–

Table 1 also reports the values of ψ , the specific cumulative pore volume in the pore size range investigated, for the gasified ashes and (for comparison) raw CCA. Steam and dry gasification produced similar results in terms of: (a) with respect to $\psi^{CCA}=30 \text{ mm}^3 \text{ g}^{-1}$, each gasification treatment was able to increase the ash porosity; (b) the ψ -versus-time trend was non-monotonic, since ψ reached a maximum after 10 min ($\psi=63$ and $49 \text{ mm}^3 \text{ g}^{-1}$ for SG10 and DG10, respectively) to decrease thereafter down to a nearly asymptotic value for treatment times of 30 min. While the feature (a) was expected and proved the effectiveness of the ash beneficiation treatment, the interesting feature (b) should be ascribed to a competition between the porosity development during gasification (see ξ -values) and thermal sintering effects due to the longer ash residence time at 850°C. In particular, sintering seemed to exert a prevailing role in the time range 10–30 min, where the gasification process showed a burn-off increase up to very high values. Results obtained under the present operating conditions suggested to limit the gasification time both for the highest development of the sample porosity and for a simultaneous presence of residual C in the sorbent. Differences when comparing steam and CO₂ gasification arose for total pore volume, at each gasification time, as it resulted $\psi^{SG} > \psi^{DG}$. This result resembled the observations already made when discussing about ξ , leading to the conclusion that steam gasification (Eq. (1)) was slightly faster than carbon dioxide gasification (Eq. (2)). This was already observed in the literature, for different operating materials [13,17,18], and was commonly ascribed to the larger dimensions of the CO₂ molecule that would imply a slower gas-solid diffusion than in the case of steam diffusion.

On the basis of the previous results, further experiments were carried out on SG10 and DG10 samples. Figure 1 shows XRD patterns for the gasified ashes and (for comparison) raw CCA. It can be observed that the inorganic crystalline structure of the raw ash (mainly silico-aluminous and based on quartz and mullite) was fully retained upon gasification, thus underlining that the only chemical process to take into consideration is, for practical purposes, the steam (or dry) carbon gasification.

Figures 2 and 3 report the absolute and cumulative, respectively, particle size distributions for the gasified ashes and (for comparison) raw CCA. Relevant parameters are again listed in Table 1. From the absolute values (Figure 2), while it is recalled that CCA was characterized by a unimodal distribution having a peak (δ) at 45 μm and a mean Sauter diameter (for X_i mass fraction of particles having diameter d_i):

$$d_s = \frac{1}{\sum_i \frac{X_i}{d_i}} \quad (4)$$

of 10 μm , and that particles coarser than 150 μm were substantially absent, the following results for the gasified ashes can be underlined: (a) the absolute distributions for *SG10* and *DG10*, though still unimodal, appeared more polydisperse with respect to CCA; (b) a non-negligible fraction of very fine (smaller than 0.7 μm) particles was now detectable; (c) both δ and d_s decreased (down to 42 and 6 μm , respectively) and no differences in these values were observed when comparing *SG10* and *DG10* (therefore, the exposed contact surface $-6/d_s-$ is the same for both *SG10* and *DG10*). While quantitative differences between gasified ashes will be highlighted looking at the cumulative distributions, it is here noted that the feature (a) should be ascribed to dishomogeneities in particle size induced by the gasification treatment, and the feature (b) is due to fragmentation following gasification. Moreover, the very interesting feature (c) should be analyzed in the light of the results published in the recent work by Balsamo *et al.* [11], where it was observed that the demineralization treatment (associated with a decrease in the inorganic fraction) ended up in an increase of the mean particle size. In this scenario, and apart from the contribution given by the already-noted fragmentation phenomena, gasification should be considered as the opposite treatment, since it led to a decrease of the mean particle size. Apparently, C-rich particles in the ash are the coarser ones, and this is also in line with the consideration that these char particles were not able to undergo significant combustion in the industrial plant. From the cumulative distributions (Figure 3) the following values for d_{50} (*i.e.*, the particle diameter for which 50wt% of the material is finer and 50wt% is coarser) can be observed: 25, 12 and 19 μm for CCA, *SG10* and *DG10*, respectively. Thus it is underlined that, coherently with data concerning gasification evolution (burn-off) and cumulative porosity, the more extensive steam treatment was able to give a gasified ash characterized by finer particle sizes.

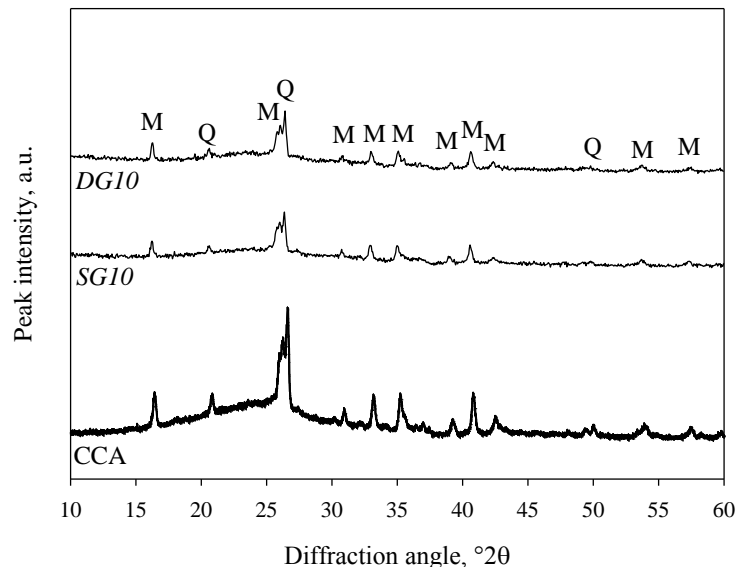


Figure 1. XRD patterns for gasified ashes (*SG10* and *DG10*, treated at 850°C for 10 min using steam and carbon dioxide, respectively) and (for comparison) raw CCA. M=mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; Q=quartz, SiO_2 .

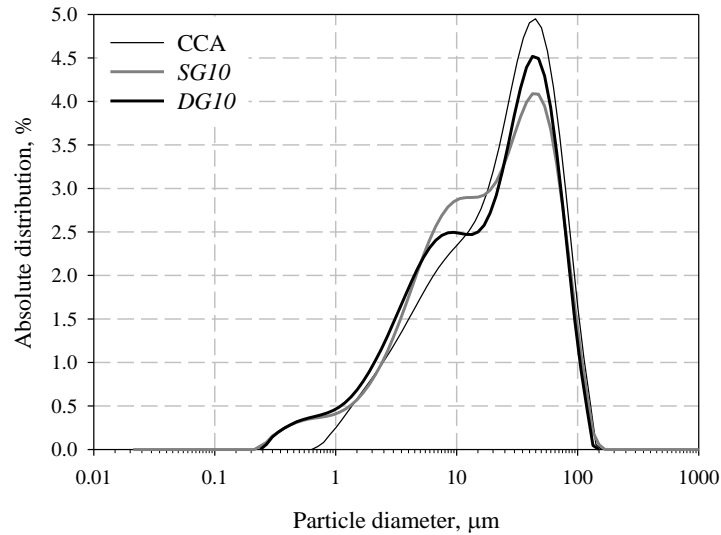


Figure 2. Absolute particle size distributions for gasified ashes (*SG10* and *DG10*, treated at 850°C for 10 min using steam and carbon dioxide, respectively) and (for comparison) raw CCA.

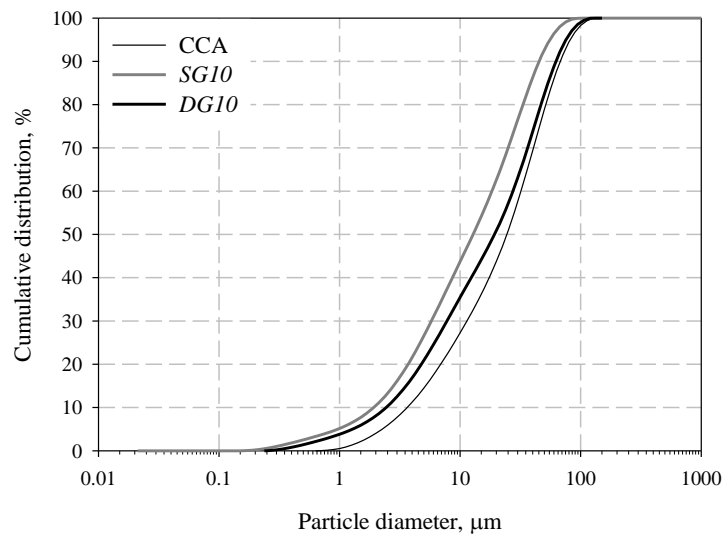


Figure 3. Cumulative particle size distributions for gasified ashes (*SG10* and *DG10*, treated at 850°C for 10 min using steam and carbon dioxide, respectively) and (for comparison) raw CCA.

The considerations hitherto developed should make the steam gasified ash as the more interesting sorbent for future applications, even if issues concerning sorbent/sorbate chemical affinity suggest to investigate both materials (*SG10* and *DG10*) as sorbents for reference pollutants, and to interrelate their adsorption properties with the characteristics of the materials as obtained in this study.

Conclusive Remarks

In this work, the gasification of a coal combustion ash, as beneficiation treatment for sorptive properties development, has been investigated. Steam gasification resulted, under comparable operating conditions, slightly more effective than carbon dioxide gasification as far as burn-off degree is concerned: while the former showed a burn-off of 48% after 10 min-gasification and was practically complete after 30 min, the latter was characterized by a burn-off of 45% after 10 min and 98% after 60 min. This was related to differences in gaseous molecule size which would make the CO₂ diffusion into the solid matrix slightly slower.

Both gasification treatments were able to increase the ash porosity (from 30 mm³ g⁻¹ to 63 and 49 mm³ g⁻¹ for steam and CO₂ treatment, respectively), but it was observed a competition between porosity development upon gasification and thermal sintering effects. This suggested to limit the gasification time to 10 min in order to maximize porosity also retaining a residual carbon content in the sorbent.

Particle size distribution analyses revealed, in particular, that gasification ended up in a decrease of the mean particle size with respect to the raw ash (this was related to the coarser size of C-rich particles in the parent material) and that, coherently with previous data, the more extensive steam treatment was able to give a material with finer particle sizes.

The results obtained in this study will be critically considered in a forthcoming paper where gasified ashes will be used in adsorption processes for reference pollutants, to interrelate the adsorption properties with the sorbent characteristics.

Acknowledgements

The authors thank Enel Produzione Ricerca (Italy) for having supplied the raw ash, and are indebted with Dr. Massimo Urciuolo (IRC-CNR, Italy) and Dr. Antonio Telesca (University of Basilicata, Italy) for their help in some solid characterization.

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