

Study on char recovery from bottom coal ash

Mihai Cruceru, Bogdan Diaconu, Lucica Anghelescu, and Traian Alexandru Abagiu

Abstract — Although Romania has developed electricity generation technologies, the lignite-fired power plants still play a significant role, covering approximately 25% from electricity consumption in Romania. For many years in the past, the lignite-fired power plants used to cover over 40% of power consumption.

The major drawback is the generation of large amounts of coal ash. There are 108 ash coal landfills in Romania occupying an area of 2823 ha, the volume of stored coal ash representing several thousand million cubic meters.

It is true that a part of coal ash may be reintroduced into the economic circuit by using it in building materials industry. The coal ash presents a valuable oxide composition, a suitable fine grain size, which is a major advantage in the production of building materials by excluding the energy required for grinding. However, despite a large-scale production, only small amounts of coal ash is used currently in Romania in building materials industry. One of the reasons for restricted use of the coal ash is its high carbonaceous content. The coal ash contains appreciable quantities of carbon residues in various forms. The carbon residues may be unreacted coal particles, or char as a result of the chemical transformation of coal in poor oxygen environment.

The coal ash used in building material industry must have a low carbon content, usually less than 3,5%, so the carbon residues have to be separated. The carbon residues recovered from the coal ash are currently considered as valuable precursors for absorbents, graphite substitutes or active coal.

The paper presents the method that we used for separating and enriching the char by sequentially removing the inorganic matter from bottom coal ash. Very high fixed carbon content in the final product is necessary in order to obtain a valuable graphite precursor.

Keywords— fixed carbon content, bottom coal ash, dimensional separation

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M. Cruceru is with the Department of Automation, Energy, Environment and Sustainable Development, Faculty of Engineering, University “Constantin Brancusi” from Targu-Jiu, Eroilor 30, Targu Jiu, Gorj, RO 210152, Romania, (phone: +40 766567521, fax: +40 253 218222, e-mail: cruceru.mihai@gmail.com)

T.A. Abagiu is with the RESENERG Research Centre, University “Constantin Brancusi” from Targu-Jiu, Eroilor 30, Targu Jiu, Gorj, RO 210152, Romania

L. Anghelescu is with the Department of Automation, Energy, Environment and Sustainable Development, Faculty of Engineering, University “Constantin Brancusi” from Targu-Jiu, Eroilor 30, Targu Jiu, Gorj, RO 210152, Romania

B. Diaconu is with the Department of Automation, Energy, Environment and Sustainable Development, Faculty of Engineering, University “Constantin Brancusi” from Targu-Jiu, Eroilor 30, Targu Jiu, Gorj, RO 210152, Romania

I. INTRODUCTION

ACCORDING to the International Energy Agency and the World Coal Association, coal provides about 30% of the global primary energy needs. The total coal production in 2012 reached 7830 Mt and it has been estimated that current coal reserves are sufficient to meet at least 100 years of supply at this level of production [1].

The carbon content in ash differs depending on the quality of the coal, the efficiency of the combustion plant etc. Considering the most favorable case, where the average carbon residues content in ash would be 1%, it would result in about 8 million tons of carbon residues per year. Since the carbon content in ash is generally higher (often 3-5%), and given that the use of modern low-NOx burners rather complicates the effort to decrease it, the annual carbon residues in ash is estimated to be of tens of millions of tons [1].

In addition to the priority aspect of energy loss due to incomplete coal combustion, there are two main areas of research to be given special attention today:

- The higher level of carbon content in ash prevents the subsequent use of these ashes as an addition in Portland cements and in building materials industry, also involving increased cost of waste transporting and / or storing. From this point of view, the carbon residues from the ash is an unwanted component whose percentage should be reduced by an optimized combustion process or by efficient separation techniques.
- Because of the promising characteristics of unburned carbon, there is a strong tendency to find a feasible use of this material, for example, for the preparation of efficient absorbents, graphite substitutes, and so on.

The separation of unburned coal from ash can be done for various purposes - to reduce the unburned coal content before its use (eg for cement production), to collect uncharged coal to further study its characteristics or to prepare some absorbents, graphite materials, etc. The choice of the separation procedure is therefore given by the purpose of the separation, the properties required for unburned carbon, or by the subsequent intended use [2].

The coal ash storage raises concerns in terms of economy and environment (e.g. a 330 MW pulverized fuel unit consumes around 1,000 ton/h of coal and generates ca. 400 tons of ash and slag at the same time). It is true that a part of fly ash that may be reintroduced into the economic circuit by using it in cement industry. However, only 5-8% of the coal ash generated is used currently in Romania, the rest being stored in large landfills, usually built through major changes of

the natural landscape and containing tens or even hundreds of millions tones of ash [3]. Therefore, several actions are being taken in Romania in order to decrease the amount of ash landfilled, and to raise awareness concerning the need to revise legal provisions (e.g. actually the use of ash in road construction is still banned, without distinguishing between fly ash (chemically active ash that can generate important secondary phenomena by hydration processes) and bottom ash (chemically inert and with physical-chemical properties very close to those of natural granular aggregates, like sand) [5].

The University "Constantin Brancusi" of Targu Jiu (UCB) is actively involved since 2011 in an research effort to detect efficient directions to recover the coal ash generated by thermal power plants, prevalent in the Oltenia industrial area, particularly for using them as alternative raw material in the building industry [6]. Therefore, UCB continue and widens the efforts to recover coal ash through its participation in the European Project CHARPHITE consortium under the scope of the "Third ERA-MIN Joint Call (2015) on Sustainable Supply of Raw Materials in Europe.

The main goal of the project is to use the carbonaceous solid residue (char) from Oltenia bottom ash as substitution material for natural graphite in cutting-edge energy technologies, such as catalysts for electrochemical reactions in cell batteries or hydrogen and oxygen production by water electrolysis [6].

The UCB's research team contribution in this project mainly aims the separation of the char from fresh and landfilled bottom ash, and further assessment and utilization of the "char-free" coal ash.

II. METHODOLOGY AND PROCEDURES

A. Procedures used for char separation. A literature review

Generally, the carbon residues (char) fractions can be separated from other fractions using wet processes (gravimetric separation, froth flotation and hydrophobic agglomeration in the upper hydrocarbon medium) or dry techniques (sieving, incipient fluidization and tribo-electrostatic separation). Compared to wet separation procedures, dry separation techniques do not pose a risk of leaching of soluble or contamination specimens, which may be problematic if, for example, the chemical composition is studied.

Gravimetric (sedimentation / float) separation is based on the fact that char particles usually have a lower density than ash particles. Typically, a gravimetric separation reservoir uses water as medium to separate the material through the density difference. The tank is filled with water (density 1 g / cm^3). Depending on the needs, additives can be added to slightly increase or decrease water density. The material introduced into this tank with a density greater than 1 g / cm^3 will sink, while materials with a density of less than 1 g / cm^3 will float.

Thus, char particles are more numerous in the floating fraction, while the heavier ash particles are sinking. Choosing the liquid medium is important because, depending on its

density, the particles are separated into "light" and "heavy" fractions [8].

Froth flotation is based on the separation of hydrophobic materials from hydrophilic materials. In the case of the flotation processes applied for the separation of ores, it is necessary to add foaming agents in order to reduce the superficial tension and to facilitate the formation of stable foam. Foaming agents are surface-active, polar or non-polar substances that reduce surface tension due to the accumulation trend at the liquid-gas interface. The added substances are adsorbed to the surface of air bubbles, covering them with a very thin film that makes the bubbles flexible and stable. The basic conditions for the separation of solid impurities by flotation are: adhesion of particulate impurities to the air bubble and displacement of particle-bubble-particle assembly at the surface of the liquid.

Typical additives used in column flotation are kerosene (petroleum lamp) or Orfom (group of organic solvents and solvents), methyl isobutyl carbinol or coniferous oil, sodium metasilicate (ion exchanger) and butyl alcohol (typically buoyancy of carbon particles) [9].

The major problem in flotation separation is that even if high concentrations of reagents are used, it is often difficult for carbonized particles to float due to their oxidized surface and reduced hydrophobicity [9]. Therefore, if the original ash sample has low carbon content (10-15%), the purity of the char concentrate usually does not exceed 40-50% (for simple flotation, without combination with other techniques). However, a 84-91% purity of was achieved by froth foaming, but it should be noted that the purity of char before flotation was 61-85% [10].

Separation in the flotation column is an important method in mineral processing technology. It is a process considered mature and offers some advantages over conventional flotation. Advantages of the flotation column include: less space for placement, less energy required, and greater capacity to recover valuable minerals to a better degree by minimizing or preventing hydraulic traction of unwanted fractions [11-13].

The introduction of the cyclonic circulation method is one of the most important developments in column flotation technology in recent years. Yalcin [14] indicated that the application of centrifugal force to the flotation device is able to provide a high rate of bubble-particle contact and allows the process to take place in a very short column. FCSMC technology, in which column flotation and centrifugal field are combined, is a method developed by the University of Mining and Technology in China, and related studies indicate that it has some advantages over conventional flotation plants. Because of the high mixing speed and the large contact surface in the zone of mineralization, there is rapid contact and efficient particle collection [15-16].

Maroto-Valer et al. [17] separated unburned carbon, with only 3.6% ash content, by combining froth flotation with acid demineralization, but high purity in this case is undoubtedly

due to acid digestion (almost total dissolution of the mineral matter).

Acid digestion is certainly a very efficient process for removing mineral substances from unburned carbon. However, severe conditions must be provided for the dissolution of silicates or other poorly soluble minerals (eg chromite). Moreover, such treatment using strong oxidizing agents can change the characteristics of unburned carbon; for example, new functional groups may be created or the sample may be contaminated. [18]

With respect to dry separation procedures, dimensional sorting is commonly used as part of the sequential separation procedure for preparing the ash sample for additional separation. The efficiency of this separation is given by the granulometric distribution of unburned coal in the ash and can yield very good results (if there are carbon-rich fractions) or rather poor results (if char is evenly distributed in most fractions, regardless of size). However, this technique is widely used because of its simplicity and the fact that it does not involve any liquid media.

Incipient fluidisation is a dry separation method, typically using a glass tube in which a small amount of the ash sample is placed inside. A gas is introduced in short jets at the bottom, which trains the ash sample upwards, after which the ash is successively allowed to sediment. Heavier ash particles will settle at the bottom of the tube, while the lightest (unburned carbon) floats. A great advantage of this technique is that there is no danger of leakage or contamination; In addition, high carbon purity (75% C) can be obtained [19].

In industry, tribo-electrostatic separation is widely used. The tribo-electrostatic separator is usually formed from two vertical electrode plates and an ejector. The ash particles are electro statically charged and injected into an electric field (made up of two plate electrodes) and collected separately according to their load (char is attracted to the negative electrode) [20]. However, ash humidity can lead to undesirable equipment behavior.

A comparison between the efficiency of separation methods by granulometric separation, gravimetric decantation / floating separation and electrostatic separation is presented in [21]. Compared with the other methods of separation studied (gravimetric and electrostatic), the granulometric separation method was the most technically and economically efficient.

B. The proposed procedure for char separation

Under the scope of CHARPHITE project, 350 samples of bottom ash were collected from two coal ash and slag landfills belonging to Turceni Power Plant and Govora Combined Heat and Power Plant. In a previous paper [7], we described in detail the procedure of ash sampling.

Once collected, the ash samples were immediately closed in plastic boxes, to preserve their original properties until the laboratory testing to determine the moisture concentration, bulk density and granulometry. Moisture was determined by drying the sample in an electric oven (150 liters capacity) at a

temperature of $110 \text{ }^{\circ}\text{C} \pm 2 \text{ }^{\circ}\text{C}$ by holding the maximum temperature for 10 hours.

Bulk densities (freely settled and tapped) and granulometry were determined after samples drying. The bulk density was determined following gravimetric method of STAS 1913/3-76 by weighting a known volume of bottom ash sample and using a graduated cylinder and an analytical balance.

To determine the bottom ash samples granulometry on mass basis, a mechanical sieving trial was conducted using a set of standard R20 sieves with the following nominal sieve opening in mm: 4, 2; 1, 0.5, 0.25, 0.125, 0.09, and 0.063.

In order to assess the char characteristics of the samples, the partner research team of University Politehnica Bucharest (UPB) [6] conducted a preliminary observation of the char under reflected light optical microscopy using glycerin immersion objectives with a combined magnification of $\times 350$.

In addition, the samples were sieved using a set of sieves (nominal sieve opening in mm: 3, 2; 1, 0.4, 0.2, 0.1), and conducted a proximate analysis (moisture, ash, volatile matter), which included also the fixed carbon content (Table 1).

Table 1. Proximate analysis: bottom ash from compartment 1, Turceni PP; selected ash samples (0,4-3 mm)

Grain size [mm]	Proximate analysis (%)			
	M _a	A _{db}	V _{db}	FCC
2-3	3.57	74.66	9.65	11.75
1-2	4.26	72.76	8.52	15.18
0,4-1	3.13	81.42	6.59	8.16
0,2-0,4	1.63	90.78	4.03	1.31
0,1-0,2	1.47	93.34	2.68	0.14
< 0.1	1.62	92.66	3.43	0.06
100 samples average	4.08	93.49	4.89	1.63
Selected ash samples (0,4-3 mm)				
Turceni	3.34	84.26	6.87	8.87
Govora	1.92	85.56	4.62	9.82

M_a moisture as received basis; db dry basis; A - ash; V - volatile matter; FC - fixed carbon.

The fixed carbon content (FCC) results range from 0.06% to 15,18 % for the size fractions analyzed, and it is clear that the char is concentrated in the large size fractions since the FCC is much higher than in the lower size fractions and also in relation to the average value.

We focused on the bottom ash provided by Govora CHPP and we developed a char enrichment procedure by repeatedly removing the inorganic matter through various processes such as sieving, flotation, magnetic separation (figure 1).

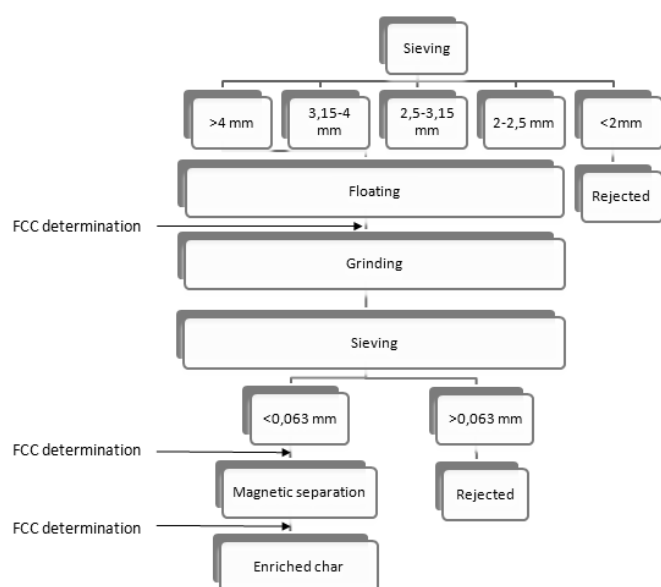


Figure 1. The proposed procedure for enrichment of char

The procedure has several stages of char enrichment. The first stage is sieving and dimensional separation. Taking into account the preliminary results, we used only the large fractions, with high FCC, respectively: sample G1 >4mm, sample G2 3,15-4 mm, sample G3 2,5-3 mm and sample G4 2-2,5 mm. Next, each sample was individually subjected to flotation in water, the separated char being grinded and sieved again on a 0,063 mm sieve. The particle larger than 0,063 mm was rejected.

The magnetic matter was separated from the fraction smaller than 0,063 mm, the rest resulting in the final product.

III. RESULTS AND DISCUSSIONS

The amount of char in bottom ash and its properties are affected by the chemical composition of the coal, the coal petrography, coal preparation and by the combustion conditions (combustion temperature, air preheat, excess air, residence time, boiler output, etc).

The bottom coal ash from Govora CHPP was used. The particle size distribution after the first stage of sieving and dimensional separation is presented in table 2.

Table 2. Size distribution of Govora bottom ash

Sample	Sieve opening size [mm]				
	4	3,15	2,5	2	< 2
1	2,2	2,8	3,9	5,5	85,6
2	2,8	3,3	4,3	5,8	83,9
3	2,6	2,9	3,8	5,5	85,3
4	2,7	3,4	4,2	6,2	83,5
5	2,7	3,3	4,1	6,1	83,7
Average	2,83	3,14	3,80	5,18	84,40

The mechanical sieving trial was conducted using a set of sieves with the following nominal sieve opening in mm: 4;

3,15; 2,5 and 2. One can see that 15,6% from the bottom is larger than 2 mm. The explanation for this is due to the xylite fragments that, in the power plants boilers, are subjected only to a partial combustion due to their higher weight (caused by low milling capacity). Therefore, xylite remains in the coal powder suspension too short time for complete combustion, and end up in the bottom ash.

Usually, the carbonaceous char residue that remains after the coal is devolatilized burns slowly by surface reactions. If the char particle is too large, mixing in the combustion is poor, or heat is transferred too quickly, char particles may not be fully consumed.

Technical analysis of the bottom ash after dimensional separation and density separation by floating confirms a relatively high fixed carbon content. The results are shown in table 3.

Table 3. Technical analysis of bottom ash

Sample (Govora)	Size [mm]	Moisture M^0 (%)	Technical analysis		
			A, %	V, %	FC, %
G1	>4	9,55	34,51	35,58	29,91
G2	3.15-4	9,46	32,41	28,77	38,82
G3	2.5-3.15	9,79	42,05	21,1	36,85
G4	2-2.5	7,79	53,84	14,89	31,27
G5	<2	3,21	79,55	79,55	14,42

The samples G1..G4 having some chunks of semi-sintered material was subjected to size reduction to enhance liberation of char by using a laboratory fan mill which strikes the particles, shattering the friable ones.

A new mechanical sieving trial was conducted using only a sieve with the nominal sieve opening of 0,063 mm. The particles larger than 0,063 mm were rejected.

The particles smaller than 0,063 mm were subjected to a technical analysis, the results being shown in table 4.

Table 4. Technical analysis of bottom ash after second sieving

Sample from	A, %	V, %	FC, %
G1	15,72	43,79	40,49
G2	14,88	35,23	49,89
G3	21,76	28,09	51,15
G4	34,14	21,14	44,72

These samples were introduced in a strong magnetic field. Even if we used niobium magnets, the mass of the particles attracted by the magnets was less than 0,3%, the ferromagnetic particles being found in the rejected fraction.

IV. CONCLUSIONS

The separation of carbonaceous solid residue (char) from bottom coal ash can be achieved by physical methods based on size distribution and density differences. By such methods, the properties of the char correspond to characteristics of semi-coked coal (no oxide components).

The proposed procedure for enrichment of char content by sequentially removing the inorganic matter leads to a high fixed carbon content of the final product.

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