Optimization of the Separation of Unburned Coal from a Selected Fly Ash

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Abstract

Unburned coal grains often hinder the economic utilization of fly ash and also represent energy loss of the fuel. This paper addresses the possibility of separating unburned coal from a selected fly ash with typical mineralogical and chemical characteristics. To assess the possibility of separating the unburned coal, the analysis of the grain density and composition of ash was used. The unburned coal was separated using one wet gravity and three dry methods. The highest amount of unburned coal, 62% in the concentrate, was obtained using the fluidized bed method with separation. The largest weight yield of concentrate equal to 17.8% was obtained using the electrostatic method.

Introduction

By-products like fly ash and furnace slag (CBP) are generated during the coal gasification and coal combustion process in a power plant or in a combined heat and power plant. CBP has been increasingly seen not as waste, but as a valuable raw material, as its industrial use in cement is possible if the fly ash contains a low content of unburned coal (Bahadori 2010). The unburned coal content in CBP is an indicator of the inefficiency of the combustion process and is most often an obstacle to its economic use (Dindarloo and Hower 2015).

Unburned coal which has been separated from fly ash and suitably enriched has significant potential as a high-value product with many possible applications (Cabielles et al. 2008, Rubio et al. 2008). The unburned coal grains, due to good sorption properties, may be used to remove B, As Cu, Pb, Zn, Mn, Cr and Ni from wastewater, or to capture CO_2, SO_2 or NOx from exhaust gases (Cabielles et al. 2008, Rubio et al. 2008, Bartonova 2015, Camean and Garcia 2011). In the simplest case, the separated coal may be used for re-combustion, or be a substitute for natural graphite-bearing raw materials (Bartonova 2015). Recovering unburned coal and using it as a substitute for natural graphite in "green energy" technologies is a new and important direction of research.

In the literature there is a series of reviews on the origin (Bartonova 2015, Bartonova et al. 2011), the purification (Cao et al 2012, Gray et al. 2002, Kim et al.2001, Deng et al.2015,Maroto-Valer et a. 1999, Sung et a. 2016, Ucurum et al. 2011, Yamik and Dogruoz 2008, Rui et al.2019, Yaowen et al. 2019), the characteristics (Baltrus et al. 2001,Bartonova et al. 2007, Cabielles et al. 2008, Hurt et al. 1995, Kulaots et al. 2004, Yan and Li 2009) and the use of char (Bartonova 2015, Wu et al. 2010, Yaowen et al. 2019). A number of methods (wet and dry methods) have been developed for the recovery of unburned carbon from coal fly ash, and there are various options for the beneficiation of coal fly ash to reduce the LOI value. Most of the current methods for separating unburned carbon from fly ash use sieving, gravity separation, electrostatic separation, froth flotation, and oil agglomeration (literature). The above-mentioned methods have their advantages and disadvantages, and their possible use must take into account the properties of fly ash as well as the requirements for separation products. This applies especially to the purity level of the products and the carbon recovery. Froth flotation and oil agglomeration methods often cannot be used due to the harmful adsorption of hydrocarbons. The screening method is usually inefficient and cumbersome due to the small size of the separated grains. In such cases, gravity or electrostatic methods and their combination are available.

The paper presents the results of research on the possibility of separating unburned coal from fly ash using gravity methods and the electrostatic method. One two-step wet gravitational separation method and two dry gravitational separation methods were applied.

Materials And Methods

The material used for testing was fly ash from pulverized coal boilers, taken from a power plant located in southern Poland. The power plant utilizes a blend of energy coal, classified according to ISO 11760 (2005) as subbituminous coals. The coal contained 20.7% ash, and its calorific value was 21300 kJ/kg. The ash sample was collected and prepared in accordance with EN 14899 (2005).

The chemical and phase composition of the fly ash was determined on the basis of tests carried out using:

- X-ray fluorescence spectrometer (XRF),
- X-ray diffractometer (XRD),
- scanning electron microscope (SEM / EDS).

The main chemical components of the ash sample were determined using the XRF X-ray fluorescence spectrometry using a Philips PW 2400 spectrometer and SuperQ software. The results are expressed as a percentage of the main oxides of the elements.

X-ray tests have been carried out using X-ray powder diffractometry with the help of a PANalytical Empyrean diffractometer with Co K_{α} radiation. The quantitative content of individual phase components was determined using the Rietveld method.

The ash characteristics, determined using the SEM scanning electron microscope, included the determination of the morphology and size of grains and the elemental composition based on the observation of grain surface and X-ray microanalysis. The SEM / EDS analysis was performed with the help of the Hitachi SEM SU3500 variable pressure scanning electron microscope, with the use of an X-ray spectrometer with energy dispersion of the EDD UltraDry from Thermo Scientific NORAN System 7. The BSE (Backscattered Electron) detector was used for analysis because of its ability to illustrate contrast in the composition of multiphase samples.

The size distribution of ash was determined using a wet sieving method according to ISO 1953 (1994). The measure of the amount of unburned coal was loss on ignition (LOI). The amount of unburned coal (LOI) was determined in accordance with the procedure described in EN 196-2 (1994) at 900^{o}C.

The float and sink analysis was performed according methodology of standard ISO 7936 (1992). Organic liquids with densities of 1.4 to 2.0 g/cm^3, every 0.1 g/cm^3 were used for the tests.

Ash samples with a grain size above 0.1 mm were used to study the recovery of unburned coal from ash. The distribution of the unburned coal content, in relation to the grain size in the total ash sample (Fig. 1), and the technical requirements of some separators, was the basis for this selection.

The unburned coal extraction with the wet gravitational method was carried out in two stages. In the first stage, cenospheres were separated which float on the surface of the suspension. In the second stage, the technique of separation in a rising current of water was used. The methodology of the above technique was described by Bialecka et al. (2020).

Two different gravitational separation techniques were also applied using the dry method. One of them was the traditional fluid bed method, the other was a fluid bed method with vibrations and a classifier.

Separation fluid bed method was carried out in a laboratory fluid bed separator, which was a properly instrumented quartz tube with a diameter of 100 mm and a height of 500 mm. Quartz sand with a grain size of 0.3 - 0.385 mm was used as a fluid-forming agent. The separation ash was gradually dosed in portions to ensure the required pressure drops over the deposit. After the end of the ash dosing and the setting of the pressure over the deposit at a stable level, the air flow velocity was reduced in order to arrange the grains in characteristic layers. In the upper layer of the deposit, unburned coal grains formed, and in the lower layer, ash grains and a layer of quartz sand grains formed.

Fluid bed separation method with vibrations was carried out in a device consisting of a separator with a flat nozzle bottom and a classifier with vertical air flow. This is a combination of the classification method with vertical air flow and elutriation. Furthermore, vibrations were used to loosen the grains at the fluid deposit forming stage.

Electrostatic enrichment tests were carried out using the Boxmag-Rapid Limited device from England. The main variable was the voltage between the electrodes regulated within 10-25 kV. Increasing the voltage between the electrodes to above 25 kV caused a spark and prevented separation.

The separation products of individual tests were dried (in the case of wet methods), the losses on ignition (LOI) were determined as a measure of unburned coal content, and a mass balance was prepared. The recovery of unburned coal in the separation process products were calculated from the dependence:

$$\varepsilon = \frac{\beta}{\alpha} * \gamma$$

Where: ε - unburned coal recovery ,

β - loss on ignition value in the product

α - loss on ignition value in the enrichment feed,

γ - product weight yield.

Results And Discussion

The results of the mineral analysis of ash compositions are presented in Table 1. The dominant ash component is the amorphous - Am (glassy) phase. The content during this phase was 75.46%. The second quantitatively mineral component is mullite – Mu with a content of 13.90%. The last quantitative significant component is quartz - Q, and its content is 9.04%. All three phases (amorphous - Am, mullite - Mu and quartz - Q) account for over 90% of the mineral composition of ash, which indicates an insignificant share of other minerals such as: anhydrite - Ah, hematite - He, magnetite - Mgt, maghemite – Mgh and periclase - Pe.

Table 1.
Mineral composition of fly ash

Mineral composition	Q	Mu	Ah	He	Mgt	Mgh	Pe	Am	Sum
Weight yield, %	9.04	13.90	0.20	0.10	0.10	0.60	0.60	75.46	100.00

Table 2.
The main chemical components of fly ash

Chemical components	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Mn_3O_4	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	LOI	Sum
Weight yield, %	51.68	0.99	22.19	6.16	0.11	2.56	3.36	1.05	2.70	0.17	0.10	8.93	100.00

The results of the chemical analysis are presented in Table 2. The dominant components of the ash are silicon and aluminum oxides (Table 2). The share of SiO_2 is 51.68%, while Al_2O_3 is 22.19%. Together, these two components account for over 70% of the total share. An important element of ash is unburned coal (LOI), whose content is 8.93%. The chemical components which are present in amounts ranging from approximately 1% to 6% are: Fe_2O_3 (6.16%), CaO (3.36%), K_2O (2.7%), MgO (2.56%), Na_2O (1.05%) and TiO_2 (0.99). The average content of other remaining oxides (Mn_3O_4, P_2O_5 and SO_3) does not exceed 0.50%. It should be noted that the above-mentioned mineralogical and chemical characteristics are typical for fly ashes produced in coal power plants (Bialecka et al. 2020, Hurt and Gibbinost 1995, Harja et al. 2008, Bartonova 2015, Hower et al. 2017).

Yield in each ash fraction and respective content of unburnt coal (LOI) is shown in Figure 1. The content of unburned coal for whole sample was 9,4 %.

This shows that the content of unburned coal in the ash increases with the increasing grain size. The grain composition of the ash and the increase in the content of unburned coal along with the increase in ash graining is consistent with the data given in the literature (Bialecka et al.2020, Hurt et al.1995, Harja et al.2008, Bartonova 2015, Hower et al.2017).

The float and sink analysis of the grain class +0.1 mm ash are presented in Table 1.

Table 3.
Float and sink analysis

Fraction	Sum of the yield, %	Yield, %	LOI in fraction, %	LOI in concentrate, %	LOI in waste, %
- 1.4	17.2	17.2	2.69	2.69	18.96
1.4 – 1.5	9.4	26.6	18.44	8.25	19.03
1.5 – 1.6	6.9	33.5	16.15	9.87	19.32
1.6 – 1.7	4.9	38.4	15.11	10.54	19.66
1.7 – 1.8	7.2	45.6	30.06	13.64	18.27
1.8 – 1.9	16.7	62.3	39.05	20.45	9.08
1.9 – 2.0	7.4	69.7	31.75	21.65	3.57
+ 2.0	30.3	100	3.57	16.16	
Sum	100		16.16		

The float and sink analysis indicated that the two extreme fractions, i.e. the lightest (- 1.4 g/cm^3) and the heaviest (+ 2.0 g/cm^3) together constituted approximately 47.5%. The lightest fraction was virtually pure cenosphere, found floating on the water surface. The unburned coal content in the lightest and heaviest fractions was 2.69% and 3.57%, respectively. The yield of the other fractions are 4.9 - 16.7%, and the contents of unburned coal are in the range of 15.11 - 39.05%. These characteristics indicate that the emission of unburned coal using gravity methods is very difficult, because the undesirable fractions in the concentrate are the two extreme fractions, ie -1.4 and + 2.0 g/cm^3. This characteristics require the use of two-stage gravity enrichment, using the wet method. In the first stage, the lightest density fraction, ie cenospheres floating on the surface of the suspension, should be separated. In the second stage, grains with a density above 2.0 g / cm^3 should be separated.

This is also confirmed by the results of calculations of unburned coal in concentrate and wastes (Table 3). Separating the lightest fraction will increase the LOI to 18.96%. On the other hand, separating only the heaviest fraction will result in the LOI in the remaining concentrate being equal to 21.65%. For the aforementioned reasons, unburned coal remove by wet gravity was carried out in two stages. The results of the selected unburned coal exuding tests using specific methods are presented in Table 4.

Table 4.
Characteristics of unburned coal obtained in individual separation methods

Separation methods	Value of loss ingnition of the product	Mass yield of the product	Carbon recovery
	β,%	γ,%	ε,%
Separation in a rising water stream	30.30	12.9	24.2
Fluid bed separation	55.95	2.4	8.3
Fluid bed separation with vibration	62.00	5.6	21.5
Electrostatic separation	45.90	17.8	50.5

The content of unburned coal in concentrates separated by individual methods varies considerably between the range of 30.30 - 62.00%. The product with the highest coal content is concentrate from fluidized separation with vibration, and the smallest concentrate is from two-stage wet separation. The second parameter characterizing the separated coal concentrates is their yield. This fluctuates widely between 2.4 - 17.8%. The largest yield of coal concentrate was obtained by electrostatic separation, and the smallest by the fluid bed separation method. Using the above parameters and the coal content in the distribution feed, the coal recovery in the individual separation methods were calculated. The highest recovery, equal to 50.5%, was obtained by the electrostatic method and the smallest, 8.3%, by the fluid bed method. In the other two distribution methods, coal recovery are similar and amount to 24.2% in the wet method and 21.5% in the fluid bed separation with vibration.

Figure 2 presents an image from an electron microscope of one of the concentrates, including the point analyzes of the chemical composition of selected grains. For the other concentrates, the grain views were very similar. The vast majority of grains have an irregular shape, as well as grains of an elongated shape and grains in the shape of plates or stripes. The very large porosity of dark coalaceous grains, with bright shiny areas that constitute mineral inclusions, is noteworthy. The content of elemental coal in points 1 and 2, designated as coal monoxide, is over 92%. The elemental coal content in bright shiny areas is much lower and amounts to around 40% (point 3). This is a typical picture of the grain, referred to as the false middlings. In the tested case, it is not possible to increase the LOI in the separation products without prior grain grinding. The crushing releases coal from the false middlings. However, crushing the grains will reduce their dimensions, making it more difficult to separate them.

Conclusion

The possibility of separating unburned coal from a selected fly ash was evaluated in this paper. Recovering unburned coal with one wet method and 3 dry methods was proposed. These methods included:

- fluid bed separation,

- fluid bed separation with vibration,

- electrostatic separation

From fly ash with grain size above 0.1 mm and unburned coal content of 16.16%, it was possible to obtain a concentrate containing 30.3 - 62% of unburned coal. The highest amount of unburned coal in the concentrate, equal to 62%, was obtained using a fluid bed method with separation. The largest yield of concentrate, equal to 17.8%, was obtained using the electrostatic method. Further cleaning of the concentrate is impossible without crushing the grains in order to release the carbon grains from false middlings.

Declarations

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Conflicts of interest/Competing interests:

Not applicable

Availability of data and material:

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Code availability:

Not applicable

Authors' contributions:

Conception or design of the work. – Wierzchowski K., Białecka B.

Data collection. – Klupa A., Całus-Moszko J.

Data analysis and interpretation. Wierzchowski K., Całus-Moszko J.

Drafting the article. – Klupa A., Białecka B.

Critical revision of the article. Wierzchowski K., Całus-Moszko J.

Final approval of the version to be published. – Białecka B.

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Figures

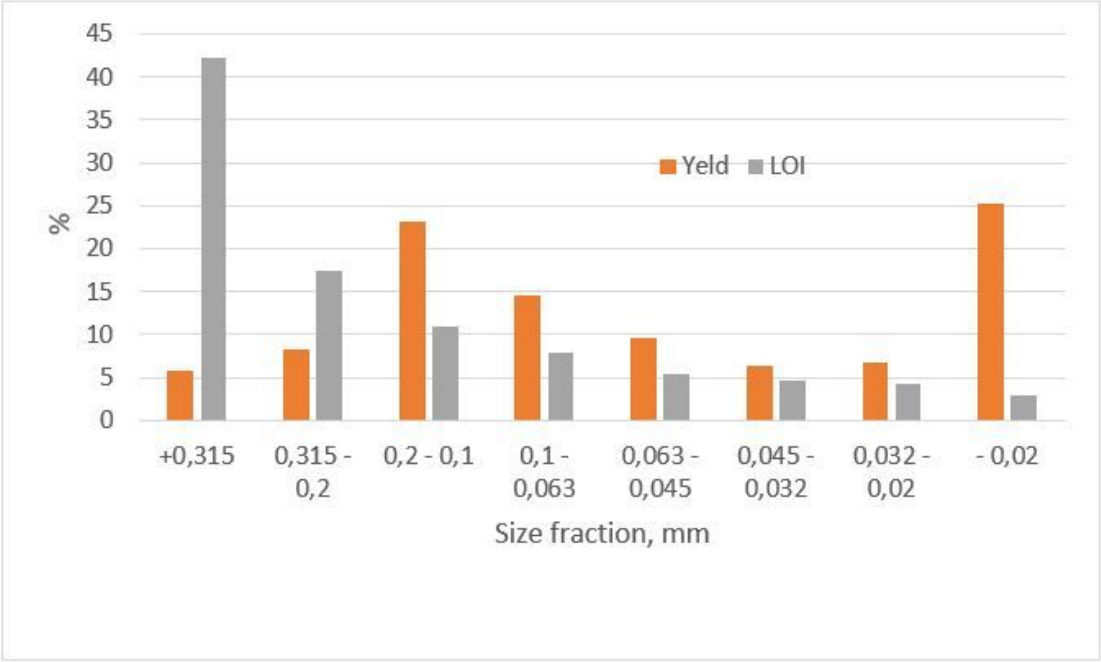

Figure 1

The grain composition of the ash sample and unburned coal content (LOI) in the function of the size of fly ash particles

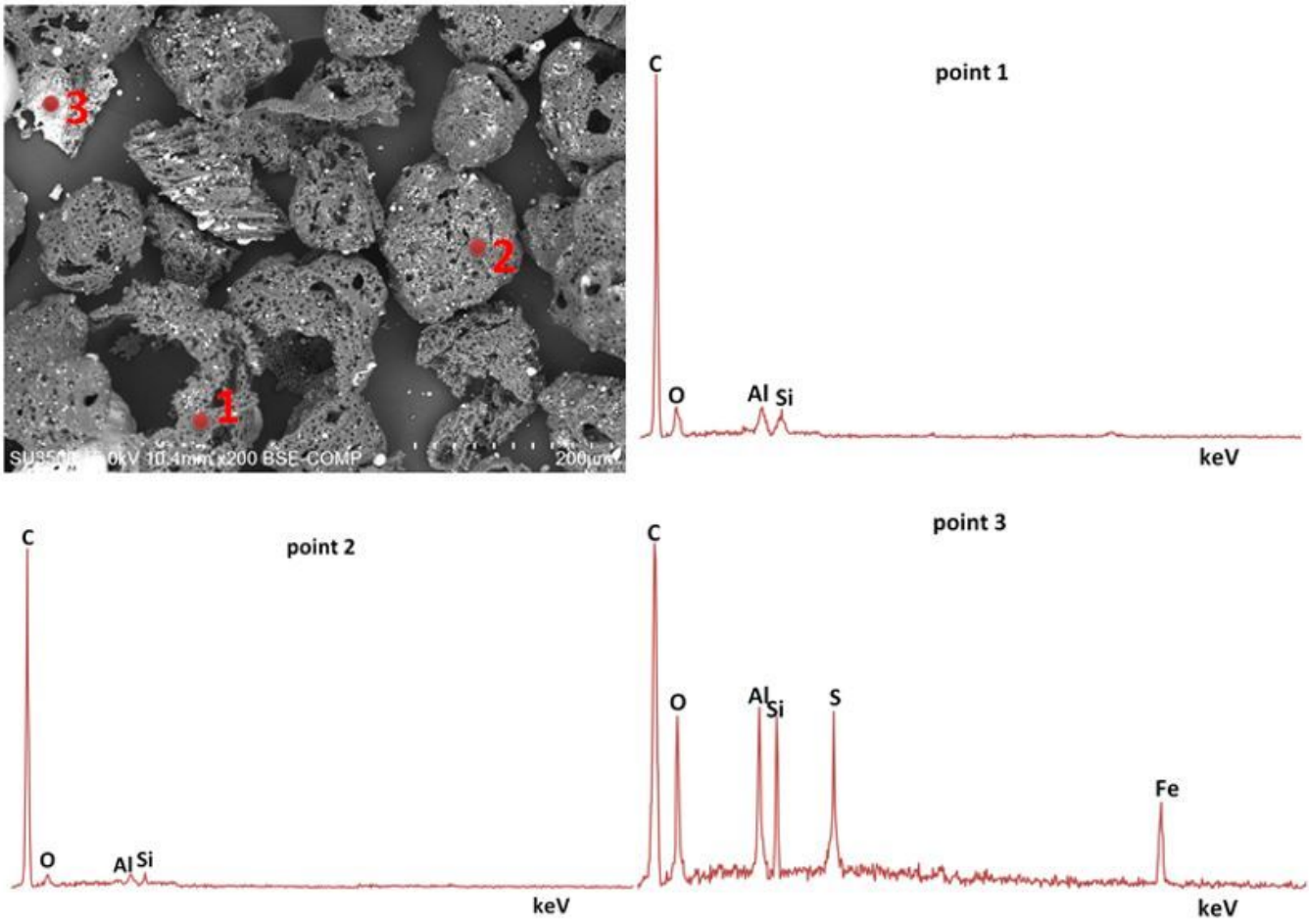

Figure 2

The view of the seeds of one of the concentrates including point analyzes of the chemical composition of selected seeds