A COMPREHENSIVE ANALYTICAL CHARACTERIZATION OF GREEK LIGNITE BOTTOM ASH SAMPLES

by

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Bottom ash samples were collected from four lignite power plants of Greece. Granulometric analysis was executed and after homogenization four distinct fractions (>1.25, 0.63-1.25, 0.18-0.63, <0.18 mm) were obtained. The samples were analysed by X-ray diffraction and energy dispersive system, while thermogravimetric and stereomicroscope viewing were applied for the coarse fractions. Furthermore, proximate analysis (moisture, ash, volatiles, fixed carbon) was undertaken and loss on ignition and calorific values were determined. The particle size distribution revealed that bottom ash satisfies the gradation criteria for concrete and geotechnical applications. The mineral composition included mainly amorphous matter, quartz, plagioclase, calcite and gehlenite and minor amounts of pyroxene, portlandite, hematite, micas, etc. The chemical analysis showed Si, Ca, Al, Mg, Fe, S as major and Ti and K as minor chemical elements, indicating high slagging, and fouling potential within the thermal chambers. Based on the chemistry and mineralogy of the bottom ash samples, a potential utilization in concrete manufacturing is discussed, taking into account certain limitations. Based on loss on ignition, proximate analysis, calorific values and thermogravimetric profiles of the coarse fractions (>1.25 mm), certain differences in the characteristics of the bottom ash of the younger and the three older power plants were observed. High amounts of unburnt carbon were determined in the coarse fraction (>1.25 mm) of all plants except the younger one, indicating a problematic combustion within the chambers and a potential of reburning these coarse material in a waste to energy application.

Keywords: lignite bottom ash, grain size distribution, mineralogy, geochemistry, thermogravimetric, energy dispersive system, X-ray diffraction, calorific value, proximate analysis, energy recovery

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Introduction

Bottom ash (BA) is a coal combustion by-product derived from the thermal chambers of a thermoelectric power plant and generally preserves a high proportion of unburnt carbon. Huge amounts of BA are produced in coal-consuming countries worldwide [1, 2]. Approximately 700000 tones per year of BA were produced in the lignite-fired power plants of Greece during the previous decades [3, 4]. The BA is used globally in concrete industry, road constructions, geotechnical, and environmental applications, *e.g.* as aggregate in lightweight concrete, as fine aggregate in cement mortars, as a raw material in the cement clinker raw meal, as a soil amendment, in asphalt mixes *etc.* [5-11].

In Greece, it is entirely deposited in abandoned lignite mine sites and/or in landfills. It should be noted however that due to recent political decisions, lignite production will be dismissed until the end of 2030, since the use of fossil fuels is considered highly polluting and releases GHG. Thus, the amounts of coal combustion by-products will be inevitably limited. Nevertheless, excessive quantities of BA have already been dumped, since there was an intensive exploitation of lignite deposits the last fifty years.

The analytical characterization of BA samples is a prerequisite in order to suggest any potential utilization. Likewise, useful information could be derived regarding the combustion parameters within the thermal chamber, which could be used in order to improve the energy efficiency of the power plant. The potential utilization of the relatively high contents of unburnt carbon, in an attempt to evaluate their energy recovery, is also an asset. The X-Ray fluorescence (XRF), X-Ray energy dispersive spectrometer (EDS), and X-Ray diffraction (XRD) are the state of the art techniques for chemical and mineralogical studies of such material [7, 12, 13]. Thermo-analytical methods may also provide a rapid, cost-effective assessment of the fuel quality or mineral composition of several materials and thermogravimetric (TG) is one of the most widespread technique for an initial evaluation of such materials [14-16].

The assessment of the morphological, physicochemical, mineralogical, and thermal characteristics of selected Greek, lignite BA samples is the aim of the present study, in order to discuss their potential applications and assess the efficiency of the thermoelectric power stations.

Material and methods

The BA samples were collected from four lignite power plants, *i.e.* Agios Dimitrios (DIM), Kardia (KAR), Meliti (MLT) (Western Macedonia, northern Greece), and Megalopoli (MGL) (Peloponnese, southern Greece). Kardia's thermoelectric plant was founded in 1975 and has a capacity of 1200 MW, while Agios Dimitrios's and Megalopoli's plants, with a capacity of 1600 MW and 850 MW, respectively, were founded in 1980's and the newest Meliti's power plant was founded in 2003 and has a capacity of 330 MW.

All samples were dried in oven at 100 °C for 24 hours. Dry sieving was applied in order to obtain the particle size distribution. Four distinct fractions (>1.25 mm, 0.63-1.25 mm, 0.18-0.63 mm, <0.18 mm) of each sample were obtained after homogenization and ground for further analyses. Moreover, a Euromex stereo-microscope coupled to CMEX-1 digital camera and the IMAGE FOCUS software was employed in order to study the microscopic features of the coarse fraction (>1.25 mm) of all samples, before grinding. Proximate analysis, moisture, ash, volatile matter (VM), fixed carbon (FC), and loss on ignition (LOI) determination were performed with the LECO TGA 701 device, based on the ASTM D 5142-09 ASTM D 7348-13 standards respectively [17, 18]. The determination of the calorific value was made with the

lordanidis, A., et al.: A Comprehensive Analytical Characterization of	
THERMAL SCIENCE: Year 2021, Vol. 25, No. 3A, pp. 1879-1889	1881

LECO AC-500 isoperibol bomb calorimeter, using the ASTM D 5865-13 standard [19]. Samples were also analyzed by thermogravimetry (TG/DTG), using the LECO TGA701 apparatus, according to the following procedure: approximately 500 mg of each sample was heated from room temperature (25 °C) up to 1000 °C, with a heating rump of 10 °C per minute, under air atmosphere, with a flow rate of 3.5 L per minute. For the XRD, a Phillips PW1710 diffractometer was used with a CuK α radiation source. The XRD patterns were obtained by step scanning from 3° to 63° in scan speed 0.020° 20 per second. The Oxford INCA 250 EDS coupled to the JEOL JSM-840A SAM was used for the chemical analysis.

Results and discussion

Granulometry and Minerochemical composition

The particle size distribution of the analyzed BA samples is shown in fig. 1. It is evident that coarse fractions with a size greater than 1.60 mm prevail for MLT sample, while in the other samples (DIM, KAR, and MGL), the fractions with a size ranging between 0.18 and 1.25 mm have the highest proportions. In particular, 43 wt.% of MLT sample exhibit a size >2.5 mm, whereas the most abundant grain size fraction in DIM, KAR, and MGL samples is below 0.63 mm and above 0.18 mm, with a percentage of 45 wt.%, 47 wt.%, and 59 wt.%,



Figure 1. Particle size distribution of the four analyzed BA samples; DIM – Agios Dimitrios, MLT – Meliti, KAR – Kardia, and MGL – Megalopoli

respectively. It is well known that the mechanical and durability properties of concretes depend on the grain size distribution of BA [6, 8, 10]. Since the grain size of BA particles of this study resembles the grain size of fine aggregates with low percentage of silt-clay, it could be concluded that BA can successfully replace the fine aggregates in the manufacturing of concrete [9, 10]. Moreover, the particle size distribution satisfies the gradation criteria for utilization as strengthened/reinforced soil (backfill material) [8].

The chemical composition of BA samples is shown in tab. 1. The analysis of major oxides ascertains a differentiation in the chemical composition of MLT sample. Thus, while DIM, KAR, and MGL samples are composed of elevated contents of CaO were found for all samples, ranging between 12.70 wt.% (MLT > 1.25) and 43.74 wt.% (DIM < 0.18), while the MLT > 1.25 sample reveal the highest contents of SiO₂ (46.43 wt.%), and the range of SiO₂ content in all the other samples is between 26.96 wt.% (DIM < 0.18) and 45.30 wt.% (MGL > 0.63). The MgO content ranges between 2.61 and 5.86 wt.%, Al₂O₃ between 10.97 and 19.52 wt.% and Fe₂O₃ between 5.12 and 8.41 wt.%. The SO₃ amounts are rather high, especially for

the coarse fractions of MGL samples (21.33 wt.%), a fact that is related to the high sulphur contents of the MGL lignite deposits. This fact inhibits a potential application in concrete industry, since the high sulphur contents may cause loss in the compressive strength and increase drying shrinkage in concrete applications [2]. Minor amounts of TiO₂ (up to 2.31 wt.%) and K₂O (up to 2.72 wt.%) were also found in some samples, while Na₂O was absent. The high amounts of silica and alumina contents, apparently in a glassy-amorphous state, are indicative for pozzolanic properties, while the high calcium contents suggest hydraulic/self-cementing properties [2, 8-11]. Regarding potential hazardous heavy metals, low amounts of copper (<2 wt.%) were only detected in the fine fractions (<0.63 mm) of KAR sample (not included in tab. 1). Therefore, the possibility of leaching of potential toxic heavy metals in the environment should be investigated by employing chemometric methodologies suitable for trace element identification [2, 13].

Table 1. Chemical composition (major oxides, wt.%), slagging (Rs), fouling (Fu), and slag viscosity (Sr) indices of all fractions of the BA samples

						r î					-
SAMPLES	MgO	Al_2O_3	SiO ₂	SO_3	CaO	Fe ₂ O ₃	TiO ₂	K ₂ O	Rs	Fu	Sr
DIM > 1.25	3.07	14.62	28.77	7.68	39.33	6.53	—	١	2.2553	0	37.0270
DIM > 0.63	3.48	14.70	38.51	2.79	32.67	5.13	_	2.72	0.6946	2.2492	48.2641
DIM > 0.18	3.96	14.96	30.12	9.05	32.05	7.09	-	1.44	2.7565	1.4227	41.1363
DIM < 0.18	4.27	11.94	26.96	7.20	43.74	3.78	_	2.11	2.7573	2.9236	34.2349
MLT > 1.25	4.21	19.52	46.43	5.94	12.70	8.41	2.31	0.49	0.8583	0.1852	64.7108
MLT > 0.63	2.98	22.36	44.35	6.10	16.60	5.40	_	2.22	0.7706	0.9051	63.9694
MLT > 0.18	4.14	12.91	27.58	16.13	39.24	-	_	-	4.6176	0	38.8669
MLT < 0.18	4.62	18.15	32.03	8.16	33.41	3.63	_	_	2.0589	0	43.4658
KAR > 1.25	5.86	10.97	28.97	9.13	39.35	5.12	_	1	2.6013	0	36.2578
KAR > 0.63	4.52	13.53	32.24	6.73	35.70	4.74	_	2.55	1.8891	2.6469	41.7616
KAR > 0.18	3.29	17.39	37.49	5.46	27.18	6.41	_	1	1.1625	0	50.4101
KAR < 0.18	3.97	12.18	27.03	5.30	41.79	5.34	_	1.04	1.9148	1.3829	34.5961
MGL > 1.25	3.47	11.94	32.44	21.33	20.32	7.10	1.28	2.10	4.3466	1.5162	51.2237
MGL > 0.63	3.26	16.33	45.30	11.38	15.73	6.91	_	1.08	1.6810	0.4727	63.6235
MGL > 0.18	2.61	18.13	41.16	6.61	16.25	12.61		2.63	1.3918	1.5126	56.6707
MGL < 0.18	4.11	17.34	41.76	3.67	17.99	12.16	1.03	1.94	0.7525	1.1679	54.9329
Average	3.86	15.44	35.07	8.29	29.04	6.69	1.54	1.85	2.0318	1.0241	47.5720

The calculation of the Rs, Fu, and Sr indices is based on Yang *et al.* [20] (and references therein), according to:

$$\frac{B}{A} = \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}$$
(1)

$$Rs = \frac{B}{A}XS$$
 (2)

$$Fu = \frac{B}{A}X(K_2O + Na_2O)$$
(3)

$$Sr = \frac{\text{SiO}_2 X100}{\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}}$$
(4)

The results are shown in tab. 1. The average value of Rs index was 2.0318, while Fu and Sr indices had values of 1.0241 and 47.5720, respectively. Since Rs values between 2 and 2.6, Fu values between 0.6 and 40, and Sr values <65 are related to high Rs, Fu, and Sr potential [20], the BA samples of the present study could be considered harmful for the thermal chambers of the lignite-fired power plants.

The semi-quantitative mineralogical results of the analyzed BA samples are shown in tab. 2. It is evident that amorphous matter is prevailing in all samples, with concentrations ranging between 26 and 43 wt.%. This amorphous material is attributed either to carbona-

Table 2. Mineralogical composition (wt.%) of all fractions of the BA samples

SAMPLES	Am	Qz	Ca	Pl	Ge	Mi	Ру	Ро	Hm	Kf	Ma	Do	Cr	Mg	La
DIM > 1.25	27	10	60	-	_	2	_	_	_	_	_	_	1	_	_
DIM > 0.63	36	27	33	2	1	1	1	1	-	1			-		-
DIM > 0.18	40	33	15	5	7	-	I	I	-	-	I	-	-	I	
DIM < 0.18	32	18	29	4	11		-	-	-	-	-	-	-	3	3
MLT > 1.25	33	22	15	16			8	1	6	1			-		-
MLT > 0.63	41	15	14	9	4	-	I	11	-	6	I	-	-	I	
MLT > 0.18	37	23	16	6	4	-	1	14	-	-	-	-	-	-	-
MLT < 0.18	43	11	20	5	6	1	1	14	-	1			-		-
KAR > 1.25	30	14	33	4	5	2	8	I	4	-	I	-	-	I	
KAR > 0.63	29	18	33	7	1	2	1	1	1	8	1	3	-	I	-
KAR > 0.18	26	34	19	15	5	1	I	I	-	-	I	-	-	I	
KAR < 0.18	35	16	34	5	8	-	I	2	-	-	I	-	-	I	
MGL > 1.25	27	30	27	2		3	1	1	9	1			-		-
MGL > 0.63	33	39	12	7	I	1	8	I	-	-	I	-	-	I	
MGL > 0.18	36	23	5	9	7	1	6	_	-	_	13	_	_	_	-
MGL < 0.18	38	21	7	7	8	_	6	_	_	_	13	_	_	_	_

Am = amorphous, Qz = quartz, Ca = calcite, Pl = plagioclase, Ge = gehlenite, Mi = micas, Py = pyroxene, Po = portlandite, Hm = hematite, Kf = K-feldspar, Ma = maghemite, Do = dolomite, Cr = cristobalite, Mg = magnetite, La = larnite

ceous matter or to the inorganic fused ash material [2, 21]. The presence of unburnt carbon has frequently been considered beneficial for an overall improvement in concrete manufacturing [9]. Calcite [CaCO₃] was the most dominant mineral, with concentrations ranging from 5% to 60 wt.%. Quartz [SiO₂] was the next most common mineral, showing contents of 10-39 wt.%. Plagioclase [anorthite, CaAl₂Si₂O₈], ranging between 2 and 16 wt.% and Gehlenite [Ca₂Al₂SiO₇], ranging between 1 and 11 wt.% were the additional main crystalline mineral phases that were identified in all samples. Substantial amounts of Portlandite [Ca(OH)₂] were found mainly in MLT samples (2-14 wt.%), Pyroxene [Augite, (Ca,Na)(Mg,Fe,Al,Ti) (Si,Al)₂O₆] mainly in MGL samples (6-8 wt.%) and iron-rich phases, such as Hematite $[Fe_2O_3]$ (4-9 wt.%), Magnetite $[Fe_3O_4]$ (3 wt.%), and Maghemite $[\gamma$ -Fe₂O₃] (13 wt.%) in a few samples. Micas [muscovite, KAl₃Si₃O₁₀(OH,F)₂] were also identified in very low amounts (≤ 3 wt.%) in several samples, while Dolomite [CaMg(CO₃)₂], K-Feldspar [KAlSi₃O₈], Cristobalite [SiO₂] and Larnite [Ca₂SiO₄] were also sporadically assigned with concentrations up to 3 wt.%. The prevalence of amorphous phases, along with the presence of aluminosilicate minerals, portlandite and calcite suggest a beneficial pozzolanic activity in concrete manufacturing,

although certain upper limits do occur for definite concrete applications [1, 2]. Therefore, a careful grinding and processing of the BA material may provide BA categories adapted for specific applications.

Proximate analysis and thermal characteristics

Proximate analysis, LOI, total weight loss (based on TG analysis) and gross calorific values (GCV) of all samples are shown in tab. 3. The ash content is generally high, as it is anticipated for BA material. However, the coarse fraction (>1.25 mm) samples of the DIM,

weight loss (based on 1G prome) and GC v or an mactions of the DA samples									
SAMPLES	Moisture	Ash	VM	FC	LOI	Total weight loss	GCV (MJ/kg)		
DIM > 1.25	6.83	41.77	37.51	13.89	58.22	58.11	9.82		
DIM > 0.63	4.11	70.13	19.03	6.73	30.26	30.31	3.31		
DIM > 0.18	3.40	78.75	15.05	2.80	20.99	20.48	1.85		
DIM < 0.18	4.27	72.68	23.00	0.05	27.88	28.02	2.28		
MLT > 1.25	2.35	81.92	7.29	8.44	17.74	18.23	3.05		
MLT > 0.63	2.38	82.31	10.05	5.26	17.24	17.76	2.65		
MLT > 0.18	2.78	78.80	12.72	5.70	21.36	21.88	3.72		
MLT < 0.18	4.62	68.81	16.84	9.73	30.35	31.13	5.64		
KAR > 1.25	7.52	36.90	33.94	21.64	62.17	64.24	12.71		
KAR > 0.63	4.28	61.35	21.51	12.86	39.04	39.24	7.16		
KAR > 0.18	2.60	78.84	13.79	4.77	19.91	18.36	2.99		
KAR < 0.18	3.83	67.92	26.92	1.33	31.62	31.81	5.38		
MGL > 1.25	8.74	46.01	32.98	12.27	53.87	53.66	10.26		
MGL > 0.63	4.42	74.00	14.39	7.19	26.00	25.72	4.99		
MGL > 0.18	1.26	92.45	6.01	0.28	6.88	7.20	0.43		
MGL < 0.18	2.05	87.79	9.67	0.49	10.79	9.06	1.17		

Table 3. Proximate analysis (moisture, ash, VM, FC), LOI,

All values are in wt.%, except GCV

KAR, and MGL BA reveal rather low ash contents (down to 36.90 wt.%), a fact that implies high proportions of unburnt carbon in their composition. Nevertheless, this is not the case for MLT sample. The range of VM is between 6.01 wt.% (MGL > 0.18) and 37.51 wt.% (DIM >1.25). Once more, MLT samples present the lowest VM values, while the coarse fractions of the other three BA samples retain the highest VM contents. The FC content ranges from 0.05 wt.% to 21.64 wt.%. In general, the fine fractions (<0.63 mm) present low FC values, except MLT samples, which differentiate form this trend. The LOI values range between 6.88 wt.% (MGL > 0.18) and 62.17 wt.% (KAR > 1.25), resembling the trend of VM content. The exceptional high LOI values limit the use of a BA in cementitious materials due to possible future durability problems and may lead to discoloration, weak air entrainment, segregation and low compressive strength [2, 6]. It should be noted however that LOI values are usually determined by XRF methodology and not by thermal techniques, which is the case in our study. Therefore, based solely on LOI contents, no secure conclusions could be derived regarding the application of BA in concrete materials. Accordingly, the total weight loss values range from 7.20 wt.% (MGL > 0.18) to 64.24 wt.% (KAR > 1.25). Finally, the GCV ranges between 0.43 MJ/kg (MGL > 0.18) and 12.71 MJ/kg (KAR > 1.25).

Consequently, MLT sample, showing high ash content (up to 81.92 wt.%), low VM (down to 7.29 wt.%), FC (down to 5.26 wt.%), LOI (down to 17.24 wt.%), total weight loss (down to 17.76 wt.%), and GCV (down to 2.65 MJ/kg) values, clearly differs from the other samples (DIM, KAR, and MGL), which have lower ash contents (down to 36.90 wt.%) and

lordanidis, A., et al.: A Comprehensive Analytical Characterization of	
THERMAL SCIENCE: Year 2021, Vol. 25, No. 3A, pp. 1879-1889	1885

higher VM (up to 37.51 wt.%), FC (up to 21.64 wt.%), LOI (up to 62.17 wt.%), total weight loss (up to 64.24 wt%), and GCV (up to 12.71 MJ/kg) values. It is evident from the proximate analysis and the LOI, total weight loss and calorific value determinations that the coarse fraction (>1.25 mm) of three BA samples (DIM, KAR, and MGL) have adequate combustible matter and can be re-utilized for energy production. Therefore, their combustion characteristics are further discussed in the next section. Besides, a problematic combustion is inferred for the older DIM, KAR, and MGL power plants, while the characteristics of MLT samples indicate a better combustion performance within the younger MLT power plant.

The correlation of the proximate analysis data with the mineralogical and chemical composition provided significant information. For example, the regression plot between calcite and VM contents ($R^2 = 0.74$) indicates that a great amount of volatiles is attributed to the calcite decomposition and not the organic material itself, while the regression of ash *vs.* amorphous matter ($R^2 = 0.32$) indicates a medium positive correlation and therefore provides evidence for the existence of both organic and inorganic matter in the amorphous phases found by XRD, fig. 2. The MLT samples exhibit indeed a clear differentiation in their characteristics when compared to the other three BA samples and thus it is noticeable that when MLT samples are excluded from the calculations, the above mentioned correlations are becoming stronger.



Figure 2. Regression plots of ash vs. amorphous matter (Am) contents (a) and calcite vs. VM contents (b) for all the analyzed bottom ash samples

The TG/DTG profiles of the coarse fractions (>1.25 mm)

The stereo-microscope viewing of the coarse fractions (*i.e.* >2.5 mm, 1.6-2.5 mm, and 1.25-1.6 mm) of all BA samples revealed char particles of several dimensions and shapes, showing a black or brown colour, a porous/vesicular structure and a spherical or elongated morphology, fig. 3. Additionally, inorganic (some partially fused) particles of several dimensions, having round, angular or irregular shapes and showing mostly a grey colour, have also been observed, fig. 3.

Figure 4 illustrates the compiled TG/DTG profiles of the coarse fraction (>1.25 mm) of the four BA samples of this study. Three distinctive regions are shown in these profiles. The first region on DTG curves (<150 °C) corresponds to the moisture loss. The second region (200-700 °C) is due to oxidation and removal of VM and the oxidation of the remaining char [16, 21]. Moreover, there are peaks in rather high temperature (>800 °C), which are

probably attributed to calcite decomposition or to transformation of the inorganic matter to neo-minerals at such high temperatures. [15, 16].



Figure 3. Microphotographs of characteristic aggregates of coarse particles (>1.25 mm) from MGL (a) and MLT (b) bottom ash samples

The combustion characteristics of the coarse fraction (>1.25 mm) of all the analyzed samples are illustrated in tab. 4. Thermal parameters such as ignition temperature, T_i , maximum rate of weight loss, R_{max} , peak and burnout temperatures, T_{max} , T_{b} , were determined from the thermogravimetric (TG/DTG) profiles. Definitions are explained by Vamvuka et al. [14, 15] and in our previous work [16]. The total weight loss, as determined by the TG methodology, tab. 3, varies between 18.23% (MLT) and 64.24% (KAR). The ignition temperature, T_i , ranges between 204 °C (MGL) and 295 °C (MLT). The burnout temperature, T_b, displays values between 849 °C (MLT) and 970 °C (KAR), while the peak temperature, $T_{\rm max}$, varies between 576 °C (MLT) and 903 °C (DIM). The maximum rate of weight loss appears with values up to 2% per minute (DIM sample) and mostly occurs in the temperature range of 730-950 °C, fig. 4. However, MLT sample reveals a rather low maximum rate of weight loss (0.4 % per minute and in a different temperature range (330-770 °C). It is evident that the sample with enhanced value of FC (MGL) generally ignite at lower temperatures and these lower, T_i , values usually correspond to better combustibility [15, 16]. A clear association of the maximum weight loss rate, R_{max} , with the VM content is also found, *i.e.* samples with high VM content, such as DIM exhibit high R_{max} .

the coarse mactions (> 1.25mm) of the analyzed Dri samples							
SAMPLES	$T_{\rm i} [^{\rm o} \rm C]$	$T_{\rm b} [^{\rm o} {\rm C}]$	$T_{\rm max} [^{\rm o} {\rm C}]$	<i>R</i> _{max} [%/min]			
DIM > 1.25	228	910	903	2.00			
MLT > 1.25	295	849	576	0.40			
KAR > 1.25	220	970	858	1.48			
MGL > 1.25	204	955	881	1.06			

Table 4. Combustion characteristics of	
the coarse fractions (>1.25mm) of the analyzed H	BA sample

Overall, the determined combustion characteristics (ignition temperature, maximum rate of weight loss, peak and burnout temperatures) indicate the high potential of the coarse particles of BA samples for energy production (except MLT sample). Therefore, the reburning of the carbon-rich coarse fraction of BA, which could be easily recovered after careful screening, is an attractive option regarding the beneficial utilization of Greek BA [3, 12, 22, 23]. This combustible material could be considered as a renewable, low cost energy source,

which can be co-fired with miscellaneous solid wastes and/or coal, minimizing the coal waste load in general and reducing the dependency on fossil fuels [24].



Figure 4. The TG/DTG profiles of the coarse fractions (>1.25 mm) of the analyzed bottom ash samples

Conclusions

Several fractions of BA samples from four Greek lignite-fired power plants were analyzed in this study. Definite differences in the characteristics of the BA samples collected from the younger MLT power plant comparing to the older (>30 years) DIM, KAR, and MGL plants were found. The thermal characteristics (proximate, LOI, GCV, TG/DTG) and the chemical (EDX) and mineralogical (XRD) composition of the analyzed BA samples provided important information regarding the efficiency of the power plants (unburnt carbon, Rs, and Fu indices) as well as the potential utilization of this lignite combustion by-product.

The analytical results witness for the poor combustion in the older power plants, comparing to the higher efficiency and the improved coal combustion technologies in the younger power plant. In particular, high amounts of unburnt carbon (enhanced values of FC, LOI, and weight loss) were determined in the samples from DIM, KAR, and MGL plants, while Meliti's samples revealed low amounts of carbonaceous matter. The results imply a problematic combustion and a low energy efficiency for the older thermal plants compared to the higher efficiency of Meliti's plant. High Rs and Fu potential were calculated based on the abundance of specific chemical elements, a fact that provokes inevitable detrimental effects in the thermal chambers of the thermoelectric stations.

The presence of glassy/amorphous aluminosilicate phases in the ingredients of the BA samples along with their calcareous nature suggested a possible utilization in concrete and other geotechnical applications, taking into the account specific limitations. A careful processing of the BA could provide material that satisfies specific geotechnical needs.

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Nomenclature

$R_{\rm max}$	– maximum rate of weight loss [% min ⁻¹]	DIM	 Agios Dimitrios power plant
FC	- fixed carbon [wt.%]	Do	– dolomite
Rs	 slagging index 	EDS	- X-ray energy dispersive system
Fu	– fouling index	Ge	– gehlenite
Sr	 slag viscosity index 	Hm	– hematite
Tb	– burnout temperature [°C]	KAR	 Kardia power plant
GCV	– gross calorific value [MJkg ⁻¹]	Kf	– K-feldspar
Ti	– ignition temperature [°C]	La	– larnite
$T_{\rm max}$	- peak temperature at the maximum rate	MGL	 megalopoli power plant
	of weight loss [°C]	Mi	– micas
VM	– volatile matter [wt.%]	MLT	 meliti power plant
		Ma	– maghemite
Acrony	<i>yms</i>	Pl	– plagioclase
Am	– amorphous	Ро	– porltandite
BA	– bottom ash	Ру	– pyroxene
Ca	– calcite	Qz	– quartz
Cr	– cristobalite	XRD	– X-ray diffraction

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