

Original Research

Effect of Mineral Additives on Fusion Behavior of Agricultural Residue Ashes during Combustion or Co-combustion with Lignite

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Abstract

In this work, the ash fusibility behaviour of selected agricultural residues and their blends with lignite was studied, by carrying out chemical, mineralogical, fusibility and thermogravimetric analyses and calculating slagging/fouling indicators for predicting deposition tendencies in boilers. Two additives, bauxite, and clinocllore, were used at varying amounts to reduce ash melting, followed by examining their anti-fusion mechanisms. Initial deformation and softening temperatures of biomass materials were low for combustion processes operating above 900 °C due to their high concentration in K, Na, and P compounds. When the additives were mixed with raw fuels or lignite/biomass blends, the initial deformation of ashes started at temperatures up to 340 °C higher, whereas the fluid temperature in most cases exceeded 1500 °C. Bauxite was more effective than clinocllore. The positive impact of additives was attributed to the mineralogical transformations during ashing to phases with a high melting point through reactions with K, Na-bearing minerals, or CaO of fuel ashes.

Keywords

Ash; fusion; additives; fouling; biomass; lignite



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1. Introduction

Renewable energy sources are increasingly being used worldwide to replace the fossil fuel reserves declining rapidly and reduce environmental emissions. Biomass contributes the highest share to heat and power generation because of its widespread availability in nearly all countries, low cost, and carbon-neutral [1, 2]. Although high-quality woody materials have been traditionally used in the energy sector, they are recently preferred to generate liquid biofuels and chemicals [3, 4], thus increasing their prices and reducing their availability for combustion applications. Consequently, residual biomass, such as agricultural wastes or naturally grown energy crops, which are abundantly found globally could meet the European Union Agricultural and Renewables Policy [5, 6], in line with the circular economy concept.

However, compared to woody biomass, agricultural residues have certain properties that make their thermochemical conversion less effective. In addition, their ash content is often 5- to 20 times higher. The ash-forming elements are generally dominated by silicon and potassium, the latter due to the use of fertilizers during crop cultivation. Such alkaline species, other alkaline earth metals, and problematic elements chlorine and sulfur may react with each other and/or with silica compounds through complex mechanisms to produce new chemicals and eutectics with low melting temperatures [7-10]. These compounds can cause ash slagging, fouling, and corrosion of heat exchange surfaces, thereby reducing the efficiency and availability of combustion systems and increasing the power cost [10-15].

To alleviate ash-related operational problems during the combustion of agricultural fuels, several approaches have been used: a) biomass leaching to remove soluble alkaline compounds, b) blending biomass with coal in existing infrastructures that offer simultaneously economic, environmental, and technical (lower ash deposition than stand-alone biomass systems) benefits and c) use of additives principally based on aluminosilicates [3, 8, 14].

Additives can capture problematic ash species by physical or chemical adsorption, or increase ash melting temperatures by altering the ash chemistry during combustion [7, 11, 16, 17]. Kaolin has been proven highly effective in improving the slagging behavior of biomass fuels, such as straws [4, 7, 18], wood pellets [3, 9], and olive cake [9], by decreasing the initial deformation temperature of ashes between 200 and 240 °C. Similarly, Ca-based additives and coal fly ash have been found to mitigate the melting of straws [4, 9, 16], herbaceous biomass [6], wood, and olive cake [9, 16] by lowering the initial deformation temperature of ashes between 40- and 140 °C and 55- and 90 °C, respectively.

Although several studies have determined the characteristic fusion temperatures of biomass ashes and predicted their slagging potential in boilers while using aluminosilicate additives, there is a lack of data on the efficacy of bauxite and clinocllore minerals, mined in large quantities in several countries, when added to different biomass types, such as agricultural wastes and perennial non-food crops. Furthermore, the ash melting behavior of ashes produced by blending biomass materials with lignite and mixing with additives has not yet been studied. Previous investigations focused on high-rank coals [10, 15]. However, the properties of ashes formed during the combustion of a fuel mix cannot be predicted from those of parent fuels. In addition, mutual interactions can occur that may or may not be beneficial. Therefore, knowledge of the behavior of the final ash materials on system performance is important to avoid fuel combinations with unwanted properties.

Based on the above discussion, we studied the ash fusibility behavior of selected agricultural residues and their blends with lignite by performing chemical, mineralogical, fusibility, and thermogravimetric analyses and assessing the slagging/fouling propensities. Two additives, namely bauxite and clinochlore, were used at varying amounts to mitigate ash melting and so the deposition phenomenon in the combustion units. In addition, their anti-fusion mechanisms were explored in detail. Given that the exploitation of waste materials for power production is limited in most countries, current results are expected to offer valuable information to promote these wastes in fueling combustion enterprises. Moreover, the study of the effect of chemistry and mineralogy of inorganic constituents of coal/biomass blends on the fusibility behavior of ashes and determining slagging/fouling phenomena in boilers will provide additional data for the successful operation of fixed-bed biomass fired appliances, such as grate furnaces or underfeed stokers, and coal/biomass co-firing units, such as stokers.

2. Experimental

2.1 Raw Materials

The raw materials of this work were one lignite from Western Macedonia mines in North Greece (ML) and three biomass materials abundantly found in the fields near the area, namely cardoon (*Cynara Cardunculus* L, CY), straw of hard wheat (SW), and peach kernels (PEK) provided by a local juice factory. After homogenization and riffing, all samples were ground and sieved to a particle size $\leq 200 \mu\text{m}$ (lignite in a jaw crusher and ball mill, biomasses in a cutting mill). Each biomass material was mixed with the lignite at a ratio of 30:70, which is typical for co-firing applications in Europe [19]. Representative samples of fuels were characterized in terms of proximate analysis, ultimate analysis, and calorific value, following the ASTM standards (D5142, D5373, D5865) and European CEN/TC335 standards for the lignite and biomasses, respectively.

The additives—bauxite and clinochlore—were selected to reduce the slagging and fouling tendency of ashes during combustion. These are rich in Al and Si, respectively. These were mixed at 3% and 5% mass fraction to each biomass fuel, corresponding to additive/ash ratios of 0.19-0.32:1, 0.26-0.43:1, 0.58-0.98:1, for cardoon, straw, and peach kernels, respectively. In the case of lignite/biomass mixtures, additive/ash ratios were 0.13-0.22:1, 0.14-0.23:1, 0.15-0.25:1, for ML/CY, ML/SW and ML/PEK, respectively. Both additives were characterized by X-ray diffractometry (XRD).

2.2 Analysis of Fuel Ashes and Additive Blends

Raw materials, lignite/biomass mixtures, and their blends with additives were ashed into a muffle furnace at 550 °C and 1200 °C to study the changes in the composition and thermal behavior. The decomposition of additives was assessed by thermogravimetric analysis TG/DTG (accuracy 0.2%wt, sensitivity $< 5 \mu\text{g}$, temperature precision $\pm 2 \text{ }^\circ\text{C}$). The weight loss (TG curves) and the rate of weight loss (DTG curves) were recorded continuously under nitrogen of flow rate of 35 mL/min, up to 1000 °C with a heating rate of 10 °C/min.

Fusibility test was conducted according to the European standard DDCEN/TS 15370-1:2006 using a heating microscope equipped with a high definition video camera, model Leitz Wetzlar EM201 of Hesse Instruments. Ash specimens (produced at 550 °C) were heated up to 1550 °C at a

rate of 5 °C/min in an oxidizing atmosphere. The characteristic fusion temperatures, i.e., the initial deformation IDT, softening ST, hemispherical HT, and fluid FT temperatures were recorded during the test.

The crystalline phases of the ashes were detected using an X-ray diffractometer (XRD), type D8 Advance of Bruker AXS. The scanning range was 2- to 70 2θ°, with increments of 0.02°/s. Minerals were identified using the software DIFFRAC plus Evaluation in conjunction with the JCPDS database.

Chemical analysis of the major inorganic elements of ashes was performed using an X-ray fluorescence spectrometer, model S2 Ranger/EDS of Bruker AXS.

2.3 Slagging and Fouling Indices

The slagging and fouling indices adopted in the present study are widely accepted, in conjunction with a pilot plant testing, to predict the deposition tendency of ashes in boilers and were based on the chemical composition of ashes, according to the standards previously discussed.

For biomass fuels, the alkali index (AI) expresses the amount of alkali oxides in the fuel per unit energy in GJ [20]:

$$AI = \text{kg}(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{GJ}, \quad (1)$$

when AI = 0.17-0.34 kg/GJ, the deposition tendency is low, whereas when AI > 0.34 kg/GJ the deposition tendency is high.

The base-to-acid ratio (B/A) is given by [20]:

$$B/A = \%(\text{Fe}_2\text{O}_2 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O})/(\text{Si}_2\text{O} + \text{TiO}_2 + \text{Al}_2\text{O}_3) \quad (2)$$

when B/A < 0.5, the deposition tendency is low; when 0.5 < B/A < 1, the deposition tendency is medium; when B/A > 1, the deposition tendency is high.

The fouling index (Fu) and Babcock index (Rs) are based on the B/A ratio and are expressed as [12]:

$$Fu = (B/A)(\text{K}_2\text{O} + \text{Na}_2\text{O}) \quad (3)$$

$$Rs = (B/A)S \quad (4),$$

where S is the percentage of sulfur in the dry fuel.

When Fu < 0.6 and Rs < 0.6, the deposition tendency is low; when 0.6 < Fu < 40 and 0.6 < Rs < 2, the deposition tendency is medium; when Fu > 40 and Rs > 2, the deposition tendency is high.

The slag viscosity index (Sv) is calculated as follows [12]:

$$Sv = \text{SiO}_2 \cdot 100(\text{Si}_2\text{O} + \text{Fe}_2\text{O}_2 + \text{CaO} + \text{MgO}) \quad (5),$$

If Sv > 72, the slagging tendency is low; if 65 < Sv < 72, the slagging tendency is medium; and if Sv < 65, the slagging tendency is high.

Finally, the ash fusibility index (Fs) is defined by [12]:

$$F_s = (4IDT + HT)/5 \tag{6}$$

Fusibility is low when $F_s > 1342$, medium when $1232 < F_s < 1342$, and high when $F_s < 1232$.

3. Results and Discussion

3.1 Characterization of Raw Materials

The proximate analysis of raw fuels, shown in Table 1, reveals that the volatile percentage of biomass fuels was considerably higher than that of lignite, ranging between 71 and 81%, whereas the ash content was lower (5 to 15%). According to the ultimate analysis, the higher oxygen content of biomass materials, compared to lignite, in conjunction with their lower carbon content, resulted in a lower calorific value, which nevertheless was significant and comparable to that of lignite. The concentration of nitrogen in cardoon was significantly high, implying undesirable NO_x emissions during combustion. However, the sulfur content of all samples was low to negligible, suggesting insignificant SO_x emissions during combustion.

The XRD spectra of the two additives used are represented in Figure 1. Bauxite consisted largely of diaspore, corundum, and hematite, and small amounts of kaolinite, gibbsite, and anatase. Clinocllore contained traces of quartz and ferrogedrite. Thermograms in Figure 2 show that the peak of bauxite at 535 °C corresponds to the decomposition of diaspore [21], whereas smaller peaks of clinocllore at 649 °C and 800 °C represent the evolution of water as steam [22]. The decomposition of clinocllore occurs above 840 °C.

Table 1 Proximate and ultimate analyses and calorific value of the fuels (% dry weight).

Sample		Volatile matter	Fixed Carbon	Ash	C	H	N	O	S	GCV ^a (MJ/kg)
Cynara Cardunculus (CY)	L	71.5	13.2	15.3	41.4	6.0	2.8	33.9	0.2	19.2
Straw of hard wheat (SW)		80.9	7.5	11.6	46.8	7.0	1.0	33.7	-	23.2
Peach kernels (PEK)		76.0	18.7	5.3	49.5	6.1	1.2	38.1	-	20.0
Macedonia lignite (ML)		57.5	17.1	25.4	49.9	5.5	1.6	26.6	0.5	25.7

^a Gross calorific value

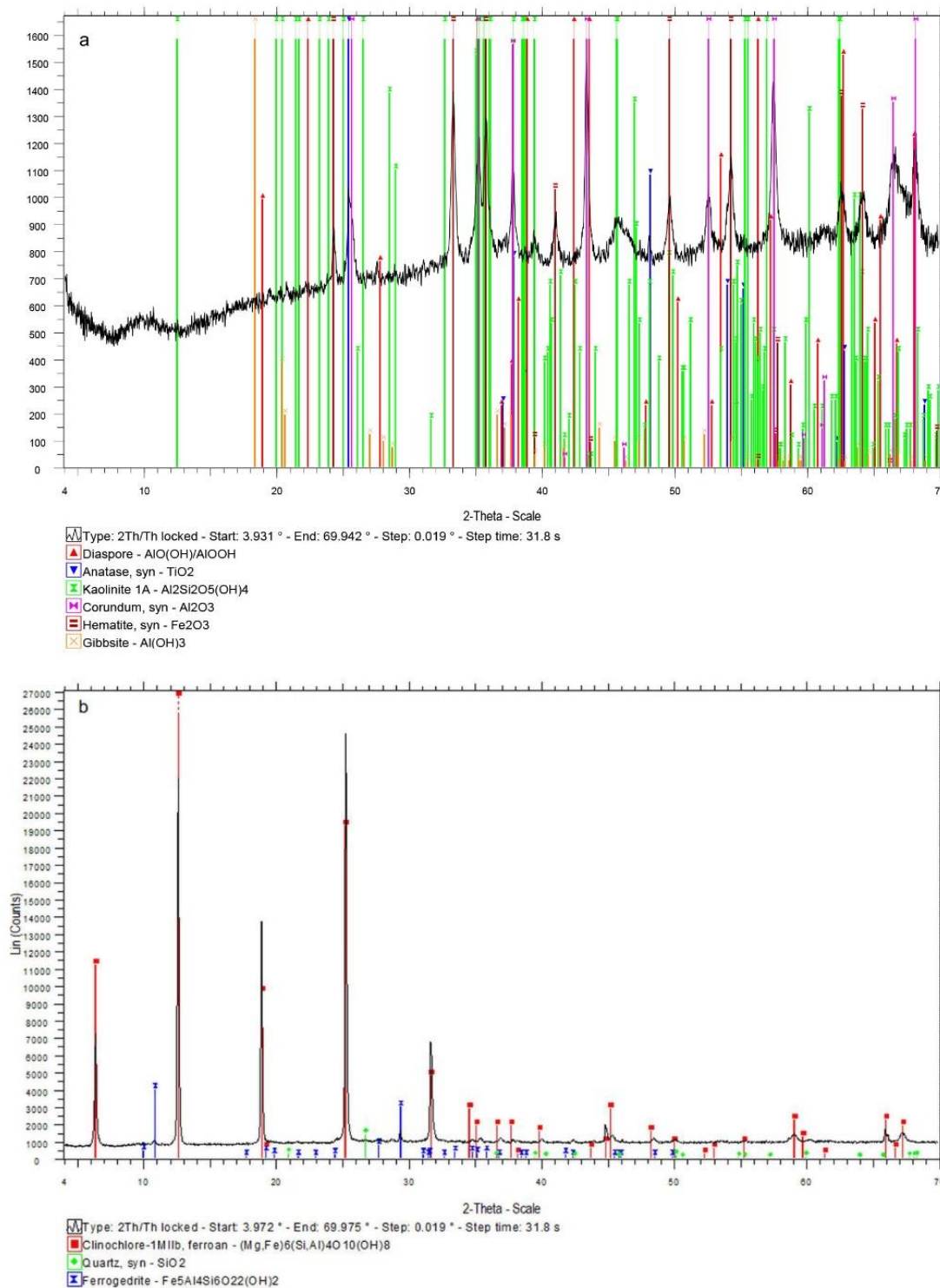


Figure 1 XRD spectra of (a) bauxite and (b) clinochlore additives.

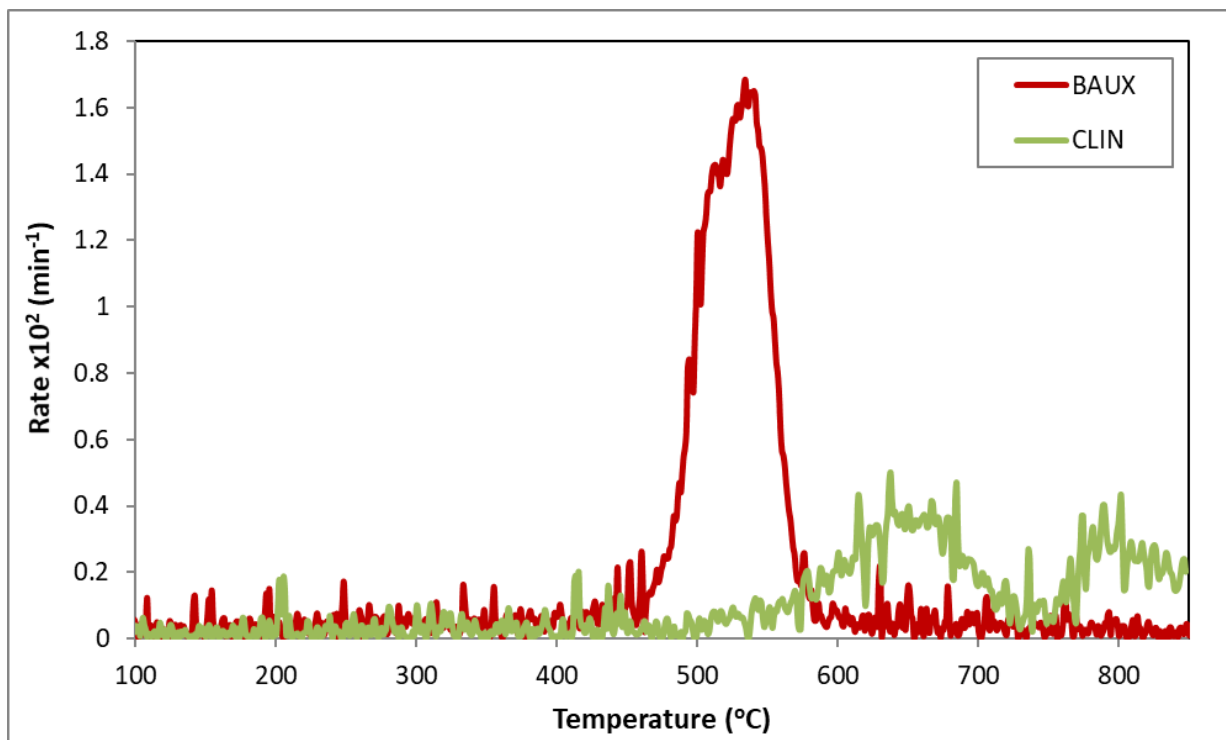


Figure 2 Thermograms of bauxite and clinochlore additives.

3.2 Characterization of Fuel Ashes and Additive Blends

3.2.1 Melting Behavior

The melting behavior of ashes was evaluated by the fusibility test. The characteristic fusion temperatures of biomass materials, with or without additives, as recorded by the heating microscope, are compared in Table 2 and Figure 3. The low IDT of all samples, varying between 867 °C and 1010 °C, implies slagging and fouling effects in the boilers, apart from those operating below 900 °C, such as fluid beds. The FT of PEK was particularly high (1500 °C), inferring that high-temperature molten materials were present or formed in this ash during heating. In contrast, CY presented not only the lowest FT but also the smallest difference between IDT and FT temperatures. This is known [15] to induce a higher fouling rate inside the combustion units, which was found to increase in the following order among the fuels tested: CY>SW>PEK.

Table 2 Fusibility analysis of biomass ashes with or without additives.

Sample	Initial deformation temperature (IDT) (°C)	Softening temperature (ST) (°C)	Hemispherical temperature (HT) (°C)	Fluid temperature (FT) (°C)
CY	867	1120	1178	1190
CY+3% baux	1209	1313	1382	1435
CY+5% baux	1205	1414	1443	>1550
CY+3% clin	1162	1278	1297	1321
CY+5% clin	1177	1366	1450	>1550
SW	1010	1085	1146	1242
SW+3% baux	1209	1362	1375	1515
SW+5% baux	1299	1509	>1550	>1550
SW+3% clin	1146	1308	1312	1404
SW+5% clin	1199	1358	1372	1421
PEK	917	1253	1421	1500
PEK+3% baux	1225	1355	1445	1532
PEK+5% baux	1254	1363	1465	1532
PEK+3% clin	1223	1338	1361	1420
PEK+5% clin	1250	1359	1392	1470

CY: Cynara Cardunculus L, SW: Straw of hard wheat, PEK: Peach kernels

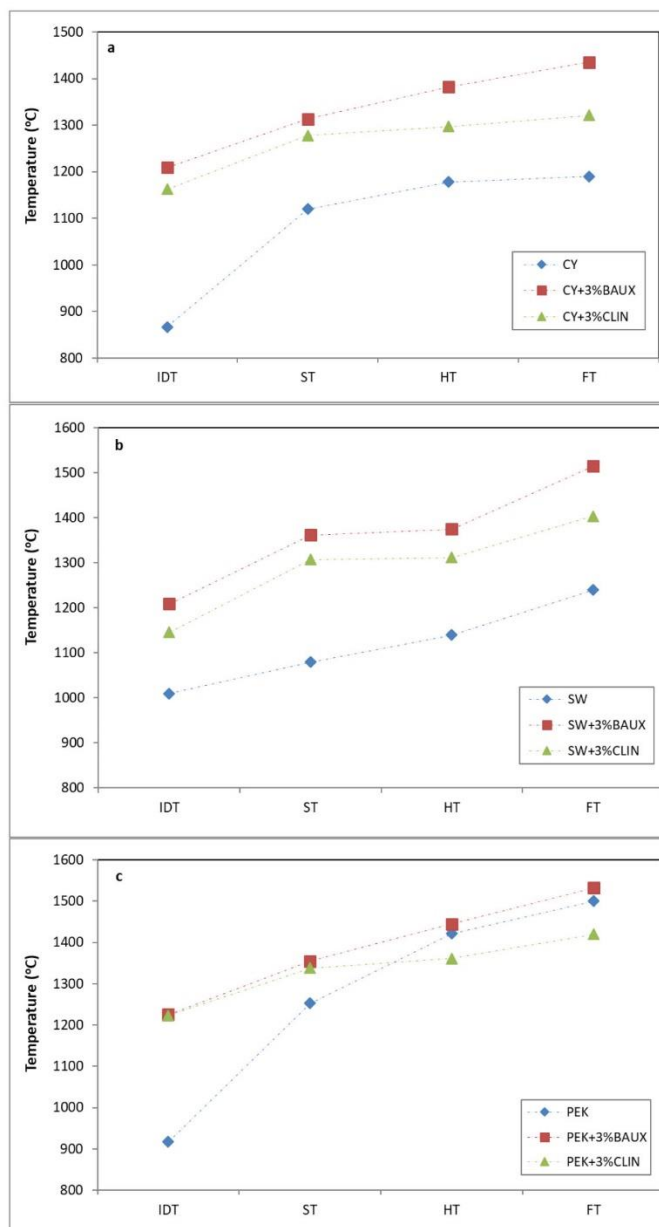


Figure 3 Characteristic fusion temperatures of (a) CY, (b) SW, and (c) PEK ashes with or without additives.

Furthermore, these results demonstrated that when bauxite or clinochlore, which consisted of high melting point (MP) minerals of Si, Al, Fe, and Mg, were added to biomass materials at percentages of 3% and 5%wt, all characteristic fusion temperatures were significantly increased. IDT of ashes commenced at temperatures ~140- to 340 °C higher, whereas FT in most cases exceeded 1500 °C. As compared to the available literature, both bauxite and clinochlore are superior additives than kaolin or calcium oxide, which were found to lower the IDT of straws, wood and olive cake by 200-240 °C and 40-140 °C, respectively [4, 6, 9]. In the case of mixtures with 3% additive, fusion temperatures were increased as follows: PEK>SW>CY, whereas the expected fouling rate followed the reverse order, as in the case of raw fuels. Clinochlore was shown to be less effective in preventing the melting of ashes than bauxite. Moreover, from Table

2, it can be noticed that the higher amount of additive did not affect the melting data. Thus, a proportion of 3% of raw fuel was satisfactory for most combustion processes.

Regarding the blends of lignite with each biomass material, Table 3 shows that characteristic fusion temperatures were intermediate to each blend component and higher in comparison to each biomass fuel, except for HT and FT of PEK. The lower melting temperatures were recorded when CY was mixed with the lignite. However, the fouling rate of the blends was lower than that of lignite. The addition of either bauxite or clinochlore to fuel mixtures produced an enhancing effect on the fusion temperature values, as for raw fuels. The increase in IDT temperatures was between 190 °C and 250 °C, whereas it was lower between 30 °C and 180 °C for FT. Bauxite performed better than clinochlore, especially for the ML/SW mixture (Figure 4). Thus, the fusion temperature of blends increased in the order: ML/SW+baux>ML/CY+baux> ML/PEK+baux.

Table 3 Fusibility analysis of lignite/biomass ashes with or without additives.

Sample	Initial deformation temperature (IDT) (°C)	Softening temperature (ST) (°C)	Hemispherical temperature (HT) (°C)	Fluid temperature (FT) (°C)
ML	1120	1220	1335	1360
ML/CY	1059	1200	1295	1315
ML/CY+3% baux	1269	1290	1343	1350
ML/CY+5% baux	1267	1380	1398	1423
ML/CY+3% clin	1238	1249	1310	1332
ML/CY+5% clin	1251	1326	1334	1345
ML/SW	1015	1200	1290	1368
ML/SW+3% baux	1187	1360	1397	1508
ML/SW+5% baux	1265	1492	1550	1550
ML/SW+3% clin	1180	1275	1293	1392
ML/SW+5% clin	1240	1328	1333	1410
ML/PEK	1069	1200	1362	1400
ML/PEK+3% baux	1253	1440	1448	1490
ML/PEK+5% baux	1276	1452	1460	1499
ML/PEK+3% clin	1230	1319	1332	1354
ML/PEK+5% clin	1254	1323	1332	1360

CY: Cynara Cardunculus L, SW: Straw of hard wheat, PEK: Peach kernels, ML: Macedonia lignite

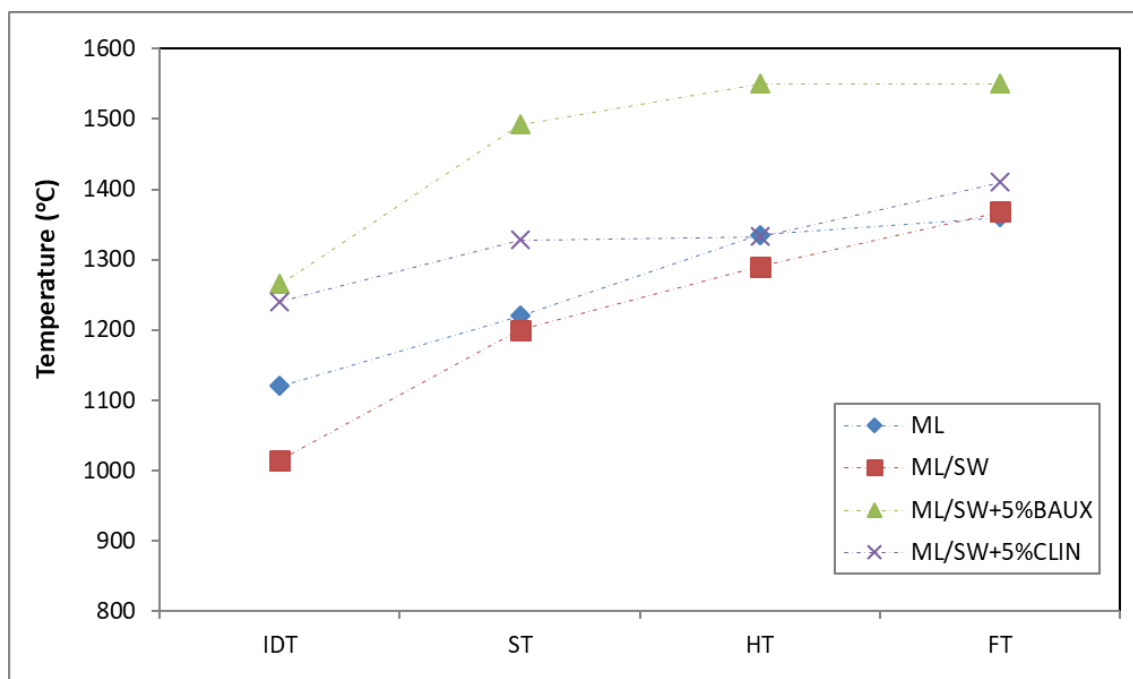


Figure 4 Characteristic ash fusion temperatures of ML/SW mixture with or without additives.

3.2.2 Influence of Chemical Composition on Melting Behavior of Ashes

No Additives Present. The results of XRF analysis of fuel ashes are represented in Figure 5a. The biomass ashes produced at 550 °C contained significantly higher concentrations of K, Na, and P with respect to lignite, whereas comparable to increased concentration of Mg. The ash of lignite was richer in Si, Al, Fe, and Ca. An exception was the Si of straw, the total content of which reached 53%wt in the ash. With an increase in the ashing temperature to 1200 °C, Figure 5b shows that the amounts of K, Na, and P were reduced by 82- to 94%, 11- to 80%, and 29- to 82%, respectively, among biomass samples. This suggests that these elements were present as volatile compounds in the ashes. In contrast, the proportions of Si, Al, Fe, Mg, and Ca increased at a higher temperature, revealing the association of these elements with more stable or less volatile compounds.

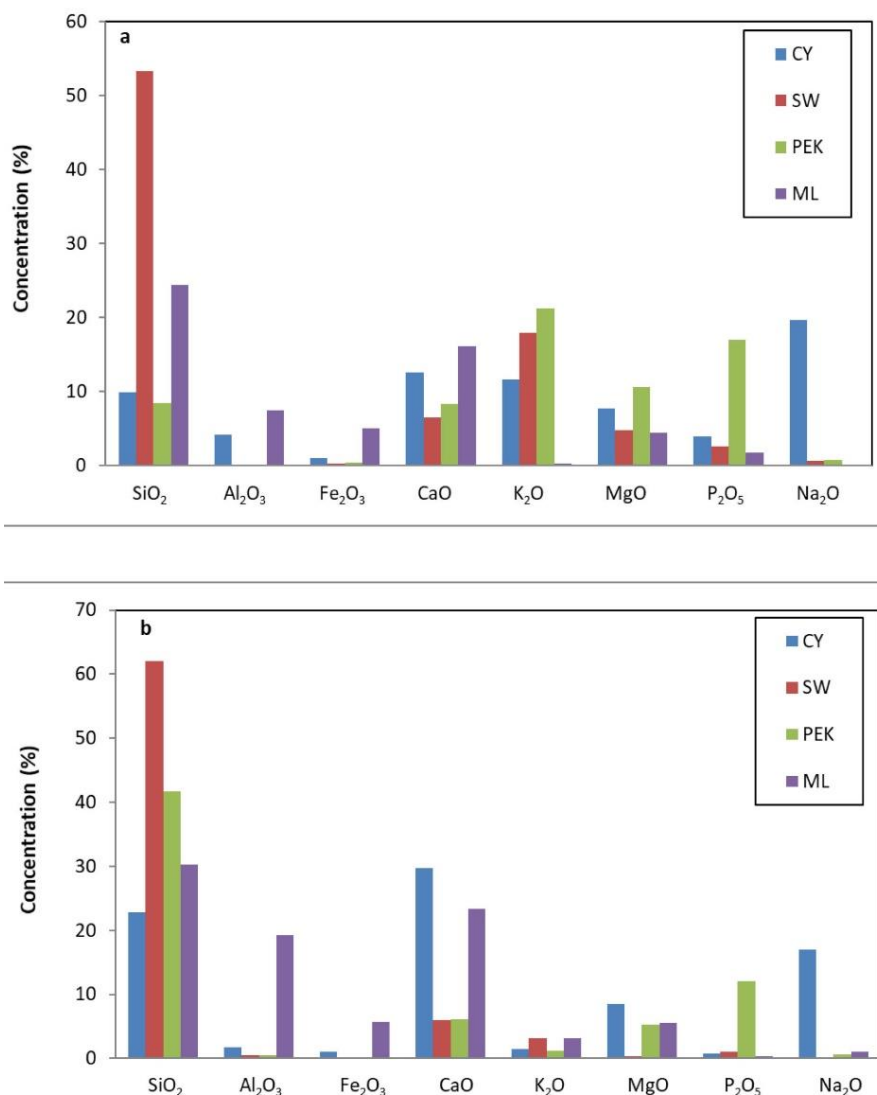


Figure 5 Chemical analysis of fuel ashes in major elements produced at (a) 550 °C and (b) 1200 °C.

In Presence of Additives. When fuels were mixed with additives bauxite or clinocllore and ashed at 1200 °C, according to the XRD results discussed below, the majority of new phases formed incorporated K. Thus, the concentration of K in the ashes was compared to that determined with the addition of bauxite (Figure 6) for all biomass materials to investigate the K captured in the solid phase. The results showed that when the ashes were enriched with additive, the fraction of K retained in the ash was higher than in the raw fuels. The effect was less pronounced in peach kernel ash, implying that the additive decreased the volatility of K at high temperatures by promoting ash-fixing reactions between K and aluminosilicate minerals. The positive effect of kaolin additive on K capture ability was reported in previous studies [7, 23]. The chemical composition of lignite/biomass ash mixtures varied between that of component fuels.

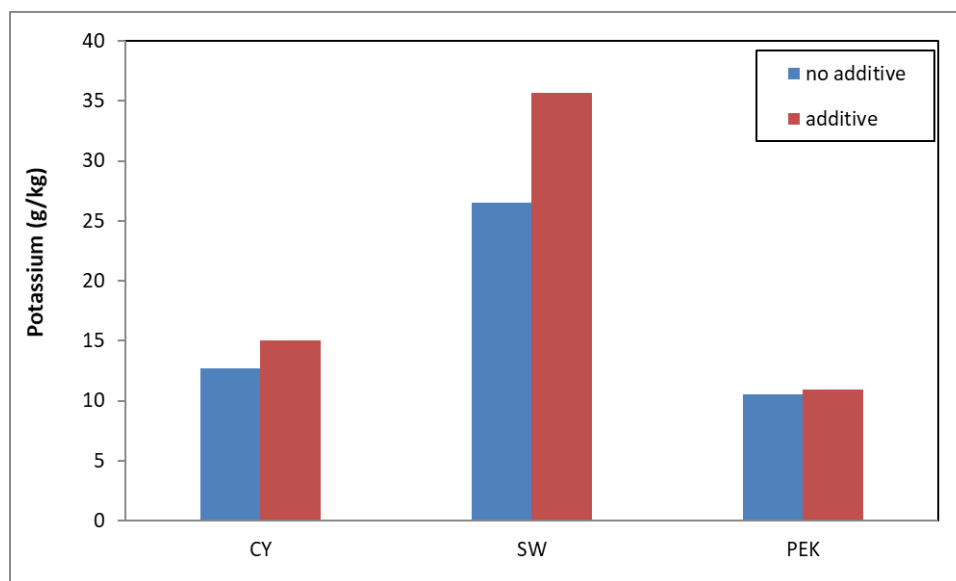


Figure 6 Concentration of potassium of fuel ashes produced at 1200 °C, with or without bauxite additive (5% of biomass fuel).

The empirical slagging/fouling indices calculated based on the chemical composition of fuel ashes (equations 1 to 6) are compared in Table 4. These indices could be a useful tool in providing a quick pre-evaluation of deposition problems in boilers. In addition, these indicate that the fusion of ashes is a synthetic result of both acidic (Si, Al, Ti) and basic oxides (K, Na, Ca, Mg, Fe).

Table 4 Empirical slagging/fouling indices of fuels and blends.

Sample	Al	B/A	FU	RS	SV	FS	Deposition tendency
CY	2.55	3.73	116.37	0.74	31.83	929.2	High
SW	0.92	0.56	10.36	-	82.25	1036.0	Medium to high
PEK	0.56	4.80	105.12	-	30.39	1017.8	High
ML		0.80	0.19	0.40	48.90	1163.0	Medium
ML/CY 70:30		0.94	3.57	0.38	43.57	1106.0	Medium to high
ML/SW 70:30		0.73	4.23	-	57.33	1070.0	Medium to high
ML/PEK 70:30		1.22	8.21	-	45.35	1128.0	Medium to high

CY: Cynara Cardunculus L, SW: Straw of hard wheat, PEK: Peach kernels, ML: Macedonia lignite

With reference to the Al index, all biomass materials have certain fouling potential. The B/A ratio confirmed the high deposition tendency of the fuels, except for straw, due to the dominance of basic oxides in ashes in relation to acidic ones. The high content of Si of straw was responsible for its medium fouling propensity, expressed by this index. Furthermore, Table 4 shows that the fouling index Fu was high for cardoon and peach kernels and medium for straw; however, it was low for lignite due to the low percentages of K and Na in the lignite ash. The Babcock index could not be applied to straw and peach kernel ashes as the content of sulfur in these was not measurable. According to this index, although cardoon had an extremely low concentration of sulfur, its slagging/fouling tendency is characterized as “medium: because of a high value of B/A

ratio. In contrast, this tendency for lignite is characterized as “low,” revealing that the significant amount of SiO₂ in lignite ash could prevent the formation of deposits enriched in sulfur. The slag viscosity index Sv indicates that fuels with an elevated percentage of silica present a low ash deposition propensity was low only for straw and high for all other fuel ashes. Finally, regarding the fusibility index (Fs), the risk of ash melting in combustion boilers was considered high for all fuels studied, and ash-related problems should be expected in the following order: CY>PEK>SW>ML. For lignite/biomass blends, Table 4 shows that the deposition tendency remained unaltered with respect to lignite and was low-to-medium in relation to alkali and sulfur, whereas high in relation to slag viscosity and fusibility.

3.2.3 Influence of Mineralogical Composition on Melting Behavior of Ashes

No Additives Present. The melting behavior of ashes can be predicted by their mineralogical composition, as analyzed by XRD. During the heating of ashes at different temperatures, changes in the crystalline structure can occur, and mineral components might interact with each other causing variations in ash composition. The XRD analysis results of fuel ashes at ashing temperatures 550 °C and 1200 °C are shown in Table 5.

Table 5 Mineralogical analysis of fuel ashes at different temperatures.

Mineral phases	ML		CY		SW		PEK	
	550 °C	1200 °C	550 °C	1200 °C	550 °C	1200 °C	550 °C	1200 °C
Quartz SiO ₂	+++	+++	++		+++	+++	+	+++
Anhydrite CaSO ₄	++	++			+	+		
Halite NaCl			++					
Calcite CaCO ₃	+		++	+	+		+	
Microcline max K(Si ₃ Al)O ₈	+						+	+
Fairchildite K ₂ Ca(CO ₃) ₂					+	+		
Archerite K(H ₂ PO ₄)							+	
Hydroxyapatite Ca ₅ (PO ₄) ₃ (OH)				+	+		++	+
Fluorapatite Ca ₅ (PO ₄) ₃ F			+					
Gehlenite Ca ₂ Al(AlSi)O ₇		++				+		
Hematite Fe ₂ O ₃	+	+	+	+				
Muscovite	+	+						
KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂ /H ₂ KAl ₃ Si ₃ O ₁₂								
Periclase MgO	+	+	+	+				
Albite calcian (Na,Ca)(Si,Al) ₄ O ₈	+				+	+	+	+
Sylvite KCl			+		++			
Aphthitalite K ₃ Na(SO ₄) ₂			+					
Krausite KFe(SO ₄) ₂ H ₂ O			+					
Hatrurite Ca ₃ (SiO ₄)O				++				
Portlandite Ca(OH) ₂				+				
Nyererite Na ₂ Ca(CO ₃) ₂			+					

Whitlockite $\text{Ca}_3(\text{PO}_4)_2$		+	+	+	+	+
Mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$				+		+
Tridymite SiO_2		++				
Brownmillerite $\text{Ca}_2\text{FeAlO}_5$	+	+				
Dolomite $\text{CaMg}(\text{CO}_3)_2$					++	
Orthoclase KAlSi_3O_8			+	+		
Anorthite sodian	+					
$\text{Ca}_{0.66}\text{Na}_{0.34}\text{Al}_{1.66}\text{Si}_{2.34}\text{O}_8$						
Rokhinite $\text{FeCl}_2 \cdot \text{H}_2\text{O}$					+	
Albite $\text{NaAlSi}_3\text{O}_8$			+			
Niter $\text{K}(\text{NO}_3)$					+	
Buetschliite $\text{K}_2\text{Ca}(\text{CO}_3)_2$					+	+
Maghemite Fe_2O_3						+
Arcanite K_2SO_4			+	+	+	
Lime CaO	+					
Diopside $\text{Ca}(\text{Mg,Al})(\text{Si,Al})_2\text{O}_6$						+
Larnite Ca_2SiO_4	+	++				

+++ : high intensity ++ : medium intensity + : low intensity

CY: Cynara Cardunculus L, SW: Straw of hard wheat, PEK: Peach kernels, ML: Macedonia lignite

Cardoon ashed at 550 °C was dominated by chlorides, sulfates, and carbonates of K and Na, in agreement with the chemical analysis. Ca and Si were present in moderate amounts as calcite and quartz, whereas the concentrations of Mg as periclase and P as fluorapatite were smaller. Therefore, the low IDT 867 °C and FT 1190 °C of cardoon (Table 2) can be assigned to the fusible forms of sylvite (MP 790 °C), halite (MP 801 °C), apthitalite (MP 900 °C), krausite (MP 156.6 °C), and nyererite (MP 815 °C) [13, 24-26]. With an increase in the ashing temperature to 1200 °C, as can be observed, chlorides, sulfates, and carbonates of K and Na were not identified as they were evaporated into the gas phase or decomposed. In addition, Table 5 implies that calcite was partially decomposed to lime, forming new phases with SiO_2 (larnite, hatrurite) and Fe_2O_3 (brownmillerite) and absorbing moisture after ashing (portlandite).

For straw ash of 550 °C, Table 5 shows that silicon was incorporated in high amounts as quartz, which is consistent with the XRF analysis (Figure 5a) and in lower amounts in feldspars (albite, orthoclase). In addition, K was present in a high proportion as arcanite, sylvite, and fairchildite. Ca and P were detected in the forms of calcite, anhydrite, and hydroxyapatite, whitlockite, respectively. As for the cardoon ash, the fusible forms of arcanite (MP 1070), sylvite, and fairchildite (MP 815 °C) [13, 24-26] minerals were responsible for the relatively low IDT and ST (1010-1080 °C) of this biomass material. Sylvite and hydroxyapatite were found to volatilize at a higher temperature of 1200 °C, whereas calcite was decomposed to lime and transformed to gehlenite, most probably by reacting with an aluminosilicate. Moreover, Table 5 shows that mullite in the 1200 °C ash was generated from albite.

The XRD pattern of peach kernels ash at 550 °C shows that this biomass ash consisted primarily of K and P crystalline phases, in accordance with its chemical analysis previously presented, which appeared in the form of arcanite, niter, buetschliite, and phosphates archerite, hydroxyapatite and whitlockite. Mg, Ca, and Si were also incorporated in considerable amounts in dolomite,

calcite, quartz, and feldspars (albite, microcline). Iron was detected in a smaller quantity as rookhite. The low IDT of peach kernels 917 °C (as shown in Table 2) was attributed to the low melting point minerals arcanite (MP 1070 °C), niter (MP 334 °C), and buetschliite (MP 815 °C) [25, 27]. Increasing the ashing temperature to 1200 °C led to the evaporation of sulfate, nitrate, and phosphate phases of K. In addition, rookhite was oxidized to maghemite, and albite was partially converted to mullite. Furthermore, calcite and dolomite were decomposed at this temperature to lime and periclase, forming a new phase through a reaction with SiO₂, diopside (MP>1300 °C) [24]. These mineralogical transformations during the heating of peach kernels ash to phases with high melting point (between 1300 °C and 1910 °C), combined with the loss of fusible forms of K, explain the high FT of this material (1500 °C).

The ash of lignite, which was found by XRF analysis to be consisting of higher proportions of Si, Al, and Ca than those in biomass ashes, presented significant amounts of quartz, aluminosilicates, calcite, and anhydrite. The contributions of Fe and Mg were small, in the forms of hematite and periclase, respectively. Accordingly, the higher fusion temperatures of lignite than those of biomass fuels reflect its composition in minerals with a high melting point (>1300 °C). When the ashing temperature was increased to 1200 °C, Table 5 shows that calcite decomposed to lime, which reacted with quartz, hematite, and an aluminosilicate to form the new phases of larnite, brownmillerite, and gehlenite, respectively.

In Presence of Additives. The crystalline mineral phases identified in the XRD spectra, in the presence of additives, are listed in Table 6. As shown in Figure 2, diaspore in bauxite decomposed at 535 °C to corundum, explaining the absence of diaspore phase at 1200 °C. Furthermore, clinocllore was decomposed above 840 °C to forsterite, spinel, enstatite, and fayalite. When bauxite was added to cardoon, several new phases were formed. Gehlenite (MP 1593 °C) and merwinite (MP 1553 °C) [26] were generated by lime and periclase of cardoon ash with the aluminosilicate additive as follows:

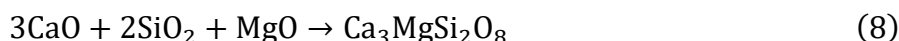
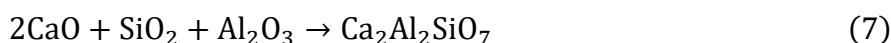


Table 6 Mineralogical analysis of fuel ashes (1200 °C) in the presence of additives.

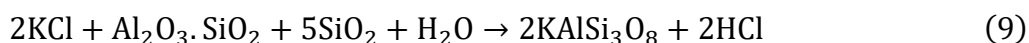
Mineral phases	CY		SW		PEK	
	Bauxite	Clinocllore	Bauxite	Clinocllore	Bauxite	Clinocllore
Quartz SiO ₂				++	++	+++
Anhydrite CaSO ₄				+	+	
Merwinite Ca ₃ Mg(SiO ₄) ₂	++		++			
Leucite KAlSi ₂ O ₆			+	++	+	+
Microcline max K(Si ₃ Al)O ₈	++				+	+++
Nepheline Na ₃ KAl ₄ Si ₄ O ₁₆	+		+			
Merrihueite K ₂ Mg ₅ Si ₁₂ O ₃₀			+			

Hydroxyapatite Ca ₅ (PO ₄) ₃ (OH)			+		+	+
Gehlenite Ca ₂ Al(AlSi)O ₇		++	+++	+	++	
Hematite Fe ₂ O ₃	++	+	+	++		+
Goethite FeO(OH)			+			
Periclase MgO		++	++			
Albite calcian (Na,Ca)(Si,Al) ₄ O ₈						+
Monticellite CaMgSiO ₄			+			
Forsterite ferroan Mg _{1.8} Fe _{0.2} (SiO ₄)		+++	++		++	+++
Enstatite aluminian (Mg _{0.9} Al _{0.04})(Al _{0.04} Si _{0.9} O ₃)		++	+		++	++
Spinel (Mg _{0.64} Al _{0.36})(Al _{0.82} Mg _{0.18}) ₂ O ₄		+		+		+
Gibbsite Al(OH) ₃	+		+	+		+
Hatrurite Ca ₃ (SiO ₄)O		++				
Tridymite SiO ₂			+			
Whitlockite Ca ₃ (PO ₄) ₂			+			+
Mullite 3Al ₂ O ₃ .2SiO ₂	++	+		++	++	++
Brownmillerite Ca ₂ FeAlO ₅		++				
Kalsilite KAl(SiO ₄)		+				
Orthoclase KAlSi ₃ O ₈				+	+	
Corundum Al ₂ O ₃	+++			+++		+++
Limenite FeTiO ₃	+			+		
Albite NaAlSi ₃ O ₈				+	+	
Fayalite Fe ₂ SiO ₄		+			+	+
Buetschliite K ₂ Ca(CO ₃) ₂						+
Maghemite Fe ₂ O ₃						+
Anatase TiO ₂	+					+
Wollastonite CaSiO ₃						+
Diopside Ca(Mg,Al)(Si,Al) ₂ O ₆						+
Larnite Ca ₂ SiO ₄		+++	++			

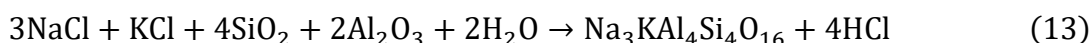
+++: high intensity ++: medium intensity +: low intensity

CY: Cynara Cardunculus L, SW: Straw of hard wheat, PEK: Peach kernels

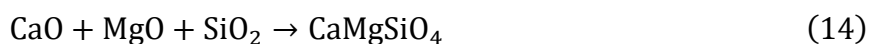
Sylvite and arcanite, which were liberated during ashing at 1200 °C, reacted with bauxite to produce microcline (MP 1150 °C):



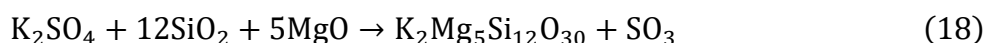
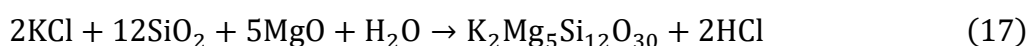
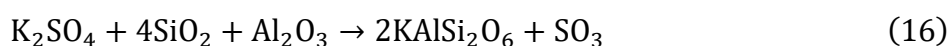
Furthermore, bauxite promoted the reactions with K-and Na-bearing minerals of cardoon evaporated at 1200 °C (as shown above) to form new phases kalsilite (MP 1500 °C) [4] and nepheline (MP 1550 °C) [28]:



In the presence of clinochlore additive, gehlenite, merwinite, and nepheline were generated according to equations (7), (8), and (13), respectively. Goethite was produced due to the absorption of moisture by hematite after ashing, whereas monticellite (MP 1503 °C) [26] was synthesized following the reaction of lime of cardoon ash with Mg and Si incorporated in clinochlore:



Leucite (MP 1600 °C) [4] instead of kalsilite was found in this case and, additionally, the new phase merrihueite (MP>1300 °C) [26], through the reaction of sylvite and/or arcanite volatilized from cardoon ash up to 1200 °C with the magnesium silicate additive. The possible formation mechanisms are:



In conclusion, these results show that the FT of cardoon with additives of either bauxite or clinochlore increased above 1500 °C due to the high melting point mineral phases produced upon ashing.

Regarding the straw ash, Table 6 shows that when bauxite or clinochlore was added, one new crystalline phase was generated, leucite, according to equations (15) and/or (16). Tables 5 and 6 show that sylvite and arcanite of straw evolved in the gas phase at 1200 °C and subsequently reacted with quartz and alumina. Thus, the FT of straw, 1515-1550 °C and 1404-1421 °C in the presence of bauxite and clinochlore, respectively, was attributed to the high sintering components of the additives, as well as those of straw, such as quartz (MP 1700 °C), mullite (MP 1910 °C), and gehlenite (MP 1593 °C) [26, 29].

For peach kernels ash (Table 5 and Table 6), leucite was formed that upon addition of bauxite via equations (15) and/or (16), or:



In contrast, in the presence of clinocllore, lime produced from the decomposition of calcite and dolomite reacted with quartz to form wollastonite (MP 1510 °C) [24], which could be partly responsible for the lower FT with respect to raw ash:



The effect of additives, in this case, was to increase IDT and ST of peach kernels ash, as previously discussed.

The mineral phases of ashes, produced by the co-combustion of lignite with each biomass material at blending ratios 70:30, were the same as those identified in component fuels. Those in small amounts could hardly be detected. An example is shown in Figure 7. Apart from the complex reactions occurring during ash heating with mineral additives, the melting behavior of the ashes was affected by the dilution effect.

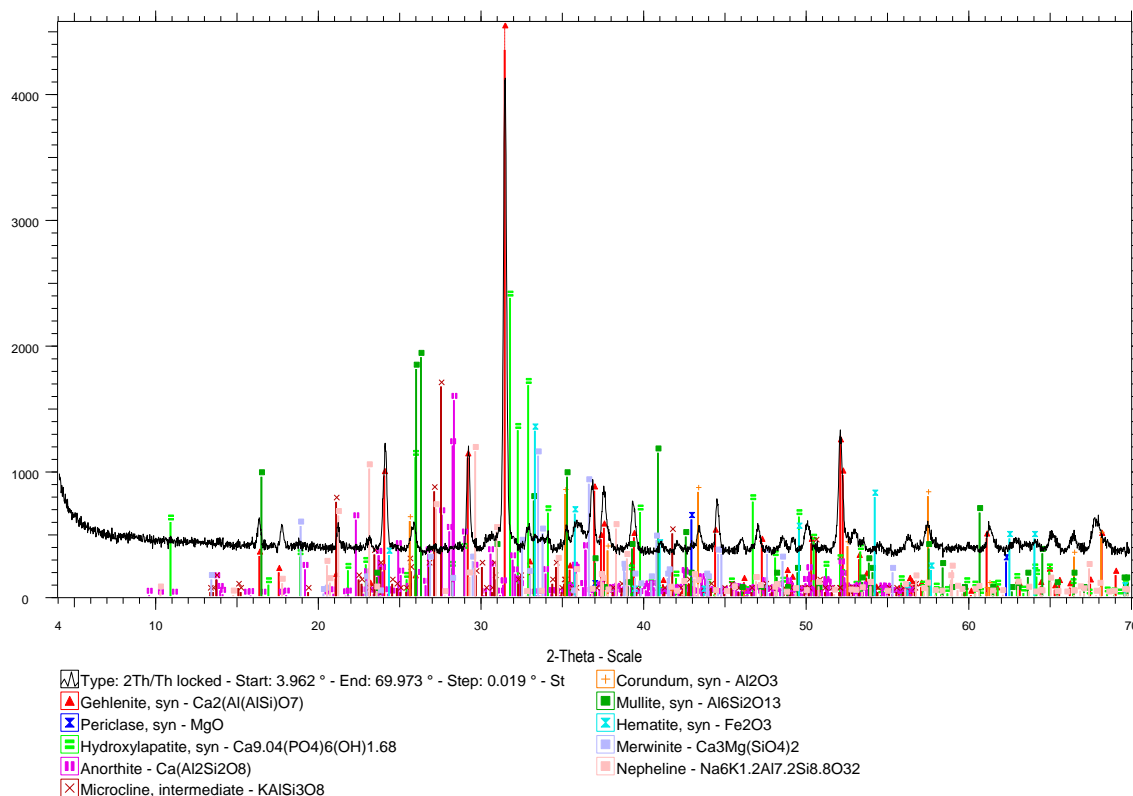


Figure 7 XRD spectra of ML/CY ash produced at 1200 °C in the presence of bauxite additive.

4. Conclusions

According to the ash fusibility test, the initial deformation and softening temperatures of biomass samples, ranging between 867 °C and 1253 °C, were low for boilers operating above 900 °C due to their significantly higher concentration in K, Na, and P compounds. The deposition tendency increased as follows: CY>PEK>SW>ML. The behavior of lignite was reflected in its mixtures with the biomass materials.

When the additives were mixed with raw fuels or lignite/biomass blends at percentages 3- to 5% and heated at a high temperature, the initial deformation temperature of ashes initiated at temperatures up to 340 °C higher, whereas the fluid temperature in most cases exceeded 1500 °C. Clinocllore was less effective than bauxite. The positive impact of the additives was attributed to the mineralogical transformations during ashing to phases with a high melting point through reactions with K, Na-bearing minerals, or CaO of fuel ashes. Both bauxite and clinocllore could be used for reducing slagging/fouling propensity of these or similar fuels in combustion applications.

These results provide valuable information for the operation of lignite/biomass co-firing units relevant to the control of ash deposition in boilers. Although the mineralogical and chemical compositions of these ashes are linked to a low environmental impact following land disposal, further leaching tests and scaling-up of the process are required before any application.

Acknowledgments

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Additional Materials

The following additional materials are uploaded at the page of this paper.

1. Figure S1: XRD spectra of (a) CY, (b) SW, (c) PEK and (d) ML ashes produced at 550°C and 1200°C.

Author Contributions

D. Vamvuka: concept, writing, evaluation; M. Deli: experiments; A. Stratakis: XRD analysis and evaluation.

Competing Interests

The authors have declared that no competing interests exist.

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