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Application News

EDX-8100 Energy Dispersive X-ray Fluorescence Spectrometer

Analysis of Combustion Ash from Biomass Power Generation by EDXRF

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User Benefits

- EDXRF enables analysis of Na and K, which cause fluidization problems (agglomeration) in circulating fluidized bed boilers in biomass power generation.
- Simple qualitative/quantitative analysis of elements is possible with minimal sample preparation.
- Comparative analysis of heterogeneous samples in the as-received condition and in the homogenized condition after crushing is possible.

■ Introduction

In biomass power generation, electricity is generated by using bioresources (biomass) derived from animal and plant sources as a carbon neutral fuel. Biomass power is expected to contribute to reducing total CO_2 emissions, and in recent years, the number of woody biomass power plants using wood chips, pellets, and palm kernel shells (PKS) has increased.

Circulating fluidized bed (CFB) boilers used in woody biomass power generation generate power by circulating and burning biomass fuel together with silica sand, which is as a fluidized bed medium. However, alkali metal elements (Na, K) contained in the fuel adhere to the surface of the silica sand and combustion ash, causing the particles to stick together and form agglomerates (lumps, coarse particles), which are considered to cause boiler damage and fluidization problems (agglomeration) in the fluidized bed [1].

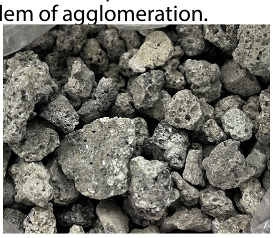
In this article, a Qual-Quant analysis of PKS combustion ash and its coarse particles was conducted using an EDX-8100 energy dispersive X-ray fluorescence spectrometer (EDXRF). Since adhesion of alkali metal elements was detected on the surface of agglomerated lumps, which are considered to cause the problem of agglomeration, analysis of combustion ash by EDXRF can contribute to operational management of combustion furnaces by monitoring the conditions in the combustion furnace.

■ Samples

Four samples of combustion ash (① to ④) resulting from the combustion of PKS fuel were prepared. Samples ① and ② consisted of coarse particles in the form of lumps of combustion ash (bottom ash), which are thought to cause agglomeration in the bottom of the combustion furnace. Sample ③ was fly ash from the combustion furnace, and sample ④ was combustion ash (bottom ash) that remained in the bottom without agglomerating.

① Bottom ash, coarse particles, gray
② Bottom ash, coarse particles, white
③ Fly ash
④ Bottom ash

Fig. 1 shows photographs of the lumps (coarse particles of bottom ash) of samples ① and ②, which are thought to cause the problem of agglomeration.



(Long diameter: 2 cm to 5 cm)

Fig. 1 Lumps Considered to Cause Agglomeration
(Mixture of Gray and White Coarse Particles of Bottom Ash)

■ Elements

$_{6}C$ - $_{92}U$

■ Sample Preparation

Sample preparation for samples ① to ④ was carried out as follows.

① Bottom ash, coarse particles, gray and ② Bottom ash, coarse particles, white: Samples in the as-received condition, without sample preparation ("untreated"), and samples which were pressure-molded after homogenization by crushing using an agate mortar and ball mill ("crushed") were prepared. Fig. 2 shows photographs of sample ① before and after treatment.

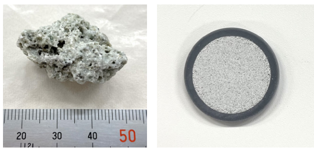


Fig. 2 Sample ① Bottom Ash, Coarse Particle, Gray: (Left) Untreated, (Right) After Crushing

③ Fly ash: Because fly ash is a fine powder, the sample material was pressure-molded using a vinyl chloride ring in the as-received condition without crushing.

④ Bottom ash: After crushing with an agate mortar, the sample was pressure-molded using a vinyl chloride ring.

Table 1 shows the treatment conditions (with/without crushing and pressure-molding) of the respective measurement samples.

Table 1 Sample Treatment Conditions
(With/Without Crushing and Pressure-Molding)

Sample	Crushing	Molding	Measurement sample
①	No	No	①-a Coarse gray untreated
	Yes	Yes	①-b Coarse gray crushed
②	No	No	②-a Coarse white untreated
	Yes	Yes	②-b Coarse white crushed
③	No	Yes	③ Fly ash
④	Yes	Yes	④ Bottom ash

■ Qualitative Analysis Results: Sample ①-a, ①-b

Fig. 3 shows the overlay of the profiles of samples ①-a and ①-b. In the profile of Na (lower right), the profile of a quartz (SiO_2), which does not contain Na, was overlaid. As a result, differences could be seen in Na, P, K, Ca, and Zn.

In comparison with ①-b, large amounts of Na and K were detected in ①-a, suggesting that Na and K adhered to the surface of untreated sample ①-a. This result is consistent with agglomeration caused by alkali metal elements (Na, K) on the surface of combustion ash [2].

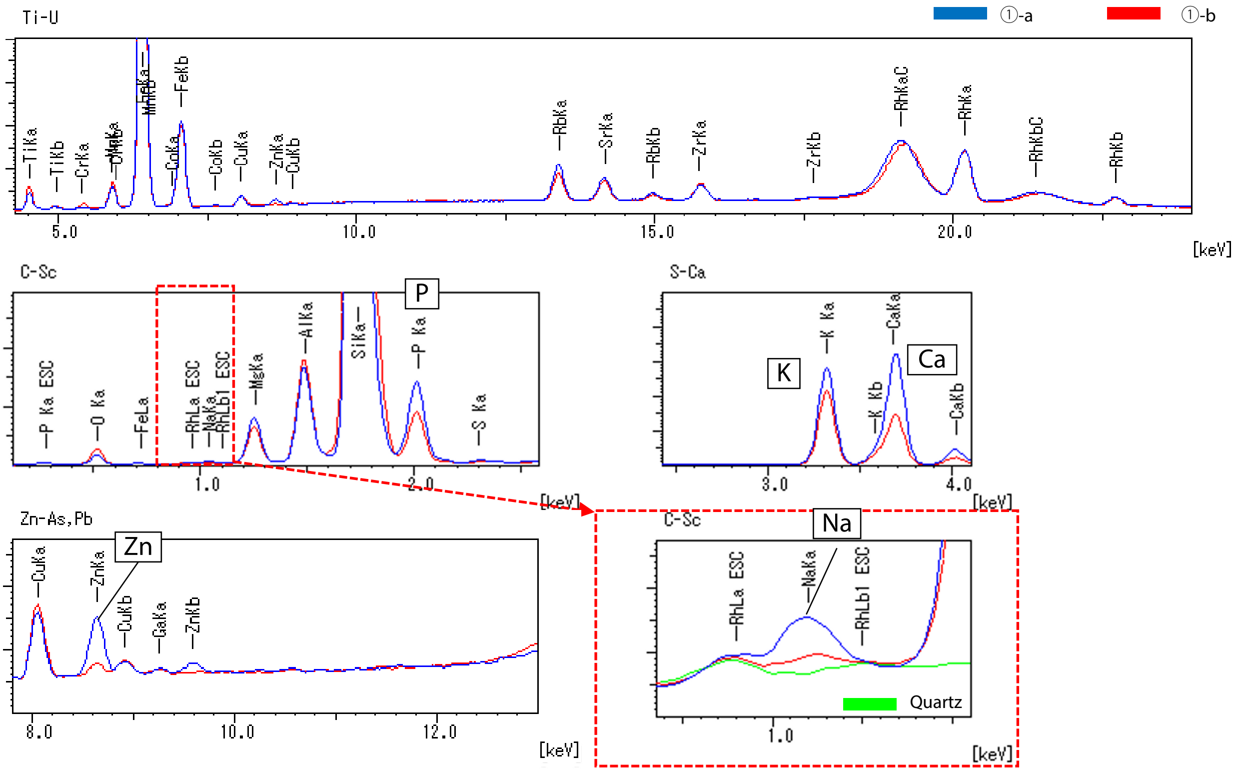


Fig. 3 Overlay of Profiles of Samples ①-a and ①-b and Enlargement of Area Around NaKα

■ Quantitative Analysis Results

Table 2 shows the quantitative analysis results by the fundamental parameter (FP) method for the measured samples, and Fig. 4 shows the cumulative bar graphs for the main components in each of the samples. Fig. 5 shows the enlarged cumulative bar graphs of Na and K, which are thought to be the cause of agglomeration. The total content of Na and K is lower in ④ bottom ash than in the coarse particle samples of ①-b and ②-b obtained by crushing coarse particles. Unlike the coarse particles from ①-a to ②-b and the bottom ash of sample ④, the results ③ fly ash showed that the total content of Na and K was low.

Since fly ash has a large content of Ca, this suggests that Ca (calcium carbonate), which causes a reduction of the melting point, was discharged properly as fly ash. In addition, the high volatility elements Cl and S were also detected.

■ Conclusion

Based on the results of a qualitative analysis of lumps (coarse particles of bottom ash), which are thought to cause agglomeration (defluidization) of the fluidized bed, in the combustion ash of PKS, it was found that alkali metal elements (Na and K) had adhered to the surface of the particles.

Since EDXRF enables Qual-Quant analysis of elements with only simple sample preparation, it is considered a useful technique for monitoring the progress of agglomeration and deterioration of the silica sand in the power generation using PKS or woody biomass. Periodic measurements by EDXRF can also be expected to prevent damage and deterioration in combustion furnaces and equipment stops due to defluidization.

■ Measurement Conditions

Instrument	: EDX-8100
Elements	: $_{6}$C - $_{92}$U
Analysis group	: Qualitative/quantitative analysis
Detector	: SDD
X-ray tube	: Rh target
Tube voltage	: 50 [kV] (Ti-U), (Zn-As, Pb), 15 [kV] (C-Sc) (S-Ca)
Tube current	: Auto [µA]
Collimator	: 10 [mmφ]
Primary filter	: Non (Ti-U), Non (C-Sc), #2 (S-Ca), #4 (Zn-As, Pb)
Atmosphere	: Vacuum
Integral time	: Non (Ti-U) 100 [s], Non (C-Sc): 300 [s], #2 (S-Ca): 100 [s], #4 (Zn-As, Pb): 100 [s]
Dead time	: Max. 30 [%]

<Acknowledgement>

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<References>

1) Tomoo Yamashita, Tatsunori Shibata: Development of Combustion Technology in CFB Boilers, Sumitomo Heavy Industries Technical Review, No. 177, Dec. 2011, pp. 5-8.
2) H.J.M. Visser: The influence of fuel composition on agglomeration behavior in fluidized-bed combustion, ECN-C-04-054, 2004, pp. 1-43.

Table 2 Quantitative Analysis Results

Quantitative value [wt%]

Analysis sample	①-a Coarse gray untreated	①-b Coarse gray crushed	②-a Coarse white untreated	②-b Coarse white crushed	③ Fly ash	④ Bottom ash
SiO_2	56.6	76.2	55.2	69.7	45.7	64.6
CaO	12.9	4.23	16.7	10.2	31.2	16.2
SO_3	0.055	-	0.049	-	4.81	-
K_2O	11.9	7.92	10.7	8.32	4.69	6.89
Al_2O_3	4.84	3.85	2.34	1.60	3.11	5.00
Fe_2O_3	4.30	2.43	2.34	1.45	3.03	2.12
MgO	4.28	2.51	6.11	3.72	2.76	2.29
P_2O_5	3.94	2.11	5.36	4.52	2.74	1.92
Cl	-	-	-	-	1.12	-
Na_2O	0.236	0.095	0.508	0.032	0.394	0.518
CuO	0.044	0.025	0.045	0.029	0.027	0.020
ZnO	0.024	0.002	0.021	0.005	0.018	0.017
Cr_2O_3	0.020	0.041	0.052	0.059	-	0.085
Other	0.901	0.683	0.635	0.464	0.420	0.401

" - " indicates not detected.

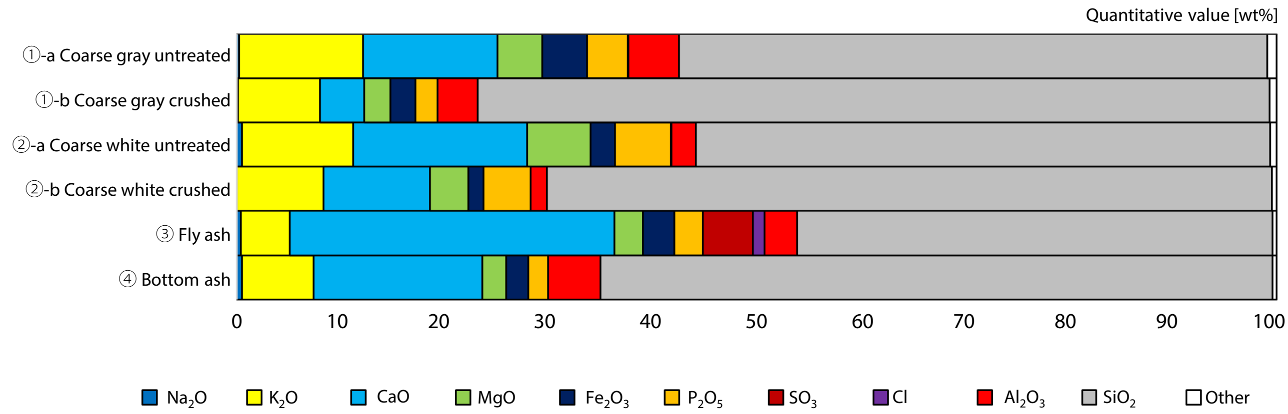

Fig. 4 Cumulative Bar Graphs of Main Components

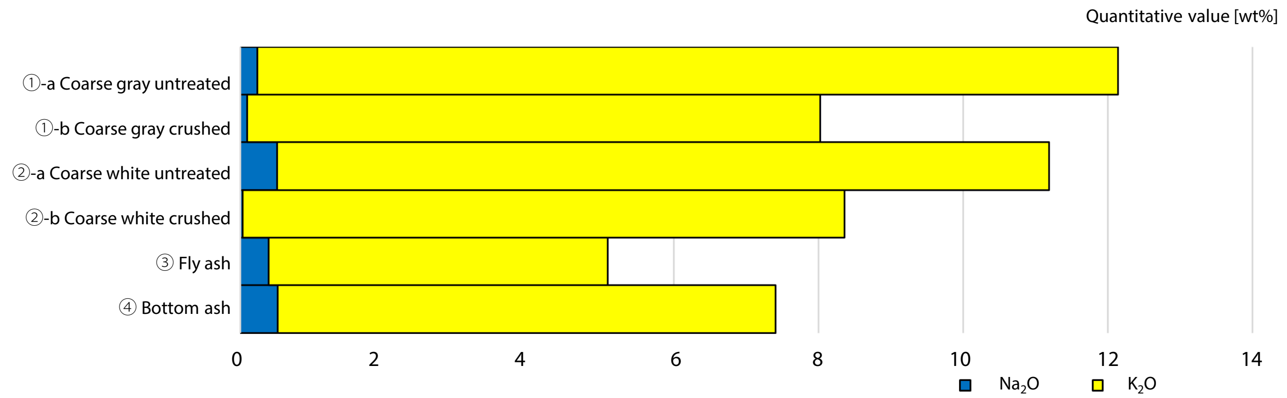

Fig. 5 Enlarged Cumulative Bar Graphs of Na and K

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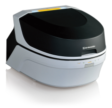

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