Fuels and their influence on the properties of ash in boilers for local heating

K Kryštofová[1, 2], H Raclavská[1, 3], H Škrobánková[1, 4] and V Sassmanová[2]

[1]ENET Centre-Energy Units for Utilization of Non-traditional Energy Sources, VSB-Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic
[2]Department of Power Engineering, Faculty of Mechanical Engineering, VSB-Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic
[3]Institute of Geological Engineering, Faculty of Mining and Geology, VSB-Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic
[4]Institute of Environmental Engineering, Faculty of Mining and Geology, VSB-Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic

Email: helena.raclavska@vsb.cz

Abstract. Local household boilers significantly contribute to the air contamination. The quality of combusted fuel can be monitored by an ash analysis. Cocombustion of waste in local boilers influences the amount of unburned carbon in ash and its distribution into separate grain size classes. The paper is focused on determination of the ash melting point in dependence on the fuel quality.

1. Introduction

Boilers for local heating significantly contribute to air quality. The composition and quality of combusted fuel can be identified from the ash analysis. The fuels, the used equipment – the boiler, as well as the way of heating significantly contribute to the nature of the air pollution from the local heating. Approximately half a million households in the Czech Republic use Class 1 or 2 boilers according to ČSN (Czech National Standard) EN 303-5, which will become unsuitable in the future, and only about 150,000 households have boilers belonging to Class 3 or higher, which are suitable for the future use. In the Czech Republic, a number of measures have been implemented to reduce air pollution from small combustion sources up to the thermal output of 50 kW, so-called boilers for local heating combusting solid fuel and often waste. Reduction of air pollution will be achieved by preventing burning of combustible waste in the existing solid fuel boilers by installing automatic boilers for coal, biomass or both coal and biomass, where combustible waste cannot be batched. Unsuitable Emission Class 1 and 2 boilers can also be used for waste and non-compliant or forbidden fuels. Modern boilers with automatic stoking cannot be stocked with forbidden fuels, or it is very difficult.

The amendment to the Act on the Air Protection of 2012 introduced a mandatory inspection of boilers (Decree No. 194/2013 Coll. [1]) with effect from 1 January 2017. The newer Act No. 369/2016 Coll., which amends Act No. 201/2012 Coll., on the Air Protection, establishes the obligation of the operators of household combustion sources to allow persons authorized by the municipal authority with extended competences access to the source, its accessories and the used fuels [2].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

The inspection of households from the point of view of combustion of fuels and wastes has been legislated by 13 of 22 European countries. The problem of the inspections is the missing methodology for identifying combusted fuel from ash from small combustion sources. The information on the bottom ash chemical composition is used to identify parameters that may be useful for determining the combusted fuel. The presented article deals with the possibility of identifying the combusted fuel based on assessments of ash energy parameters and chemical composition.

2. Chemical composition of fuels

The principal inorganic elements of the biomass i.e. simple inorganic compounds of Si, K, Ca, Mg, Na, P, S, and Cl are also present in coal, but there are some important differences in the way they are bonded to the minor inorganic component (ash) or the organic fuel component (table 1). In coal, some elements display affinity for the inorganic and organic component. The maceral trace element association could have effect on the enrichment of the trace elements in the bottom ash. Ni, As, and Hg have a strong affinity for vitrinite macerals. Inertinite macerals have a high affinity for Sn and Li and partial affinity for Ga and Se [3]. An important component of ash in coal consists of clay minerals that can bind: As, Al, Ba, Bi, Cd, Co, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Ni, P, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, iron sulphides: As, Ba, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb S, Sb, Se, Ti, W, Zn, and carbonates: Ca, Cd, Co, Mn, Zn [4].

The essential or nutritious ash forming elements for plants can be macronutrients, namely K, Ca, Mg, P and S, and micronutrients such as Fe, Mn and Cl. The data from a study related to the composition of 86 varieties of terrestrial biomass show that the major elements are commonly C > O > H > N > Ca > K, while the minor elements normally include Si > Mg > Al > S > Fe > P > Cl > Na, and occasionally Mn and Ti. The reference studies reveal that the contents of major and minor elements in plant ashes are Si > (Mg, P) > S > (Ca, K) > Na > Al > (Fe, Cl) > Mn > Ti [5].

Table 1. Chemical analysis of different kind of ash (normalized to 100%), wt%. [5].

	SiO_2	CaO	K_2O	MgO	P_2O_5	Al_2O_3	SO_3	Fe_2O_3	Na_2O	TiO_2	Mn	Cl^-
Paper plastic fluff	38.5	23.26	3.01	2.76	1.81	17.27	2.67	4.2	5.12	1.4		
Waste paper	28.62	7.63	0.16	2.4	0.2	53.53	1.73	0.82	0.54	4.37		
MSW	37.92	24.66	4.79	3.82	0.74	13.62	3.72	2.93	6.34	1.46	0.1	7.8
Furniture	52.17	13.78	3.74	3.25	0.5	17.14	0.99	5.59	2.34	0.5		
Demolition wood	33.55	20.96	5.17	11.8	3.15	9.66	4.91	5.8	2.26	2.74	0.16	1.72
Wood (conifer)	14.25	42.75	10.42	13.06	5.41	5.8	3.69	2.77	1.32	0.5	1.32	0.5
Pine sawdust	11.16	42.81	7.23	10.92	3.68	2.54	17.93	2.87	0.71	0.15	1.05	0.12
Pine wood	29.56	45.56	6.17	2.48	0.8	7.63	1.57	4.78	0.92	0.53	2.3	0.1
Pine bark	9.2	56.83	7.78	6.19	5.02	7.2	2.83	2.79	1.97	0.19	1.08	0.01
Pine branches	6.28	51.74	10.49	12.35	7.41	4.53	2.37	1.95	2.78	0.1		0.01
Biomass	39.67	19.57	2.6	4.03	2.18	16.15	3.16	6.27	2.62	3.75	0.16	
Coal - mean	54.06	6.57	1.6	1.83	0.5	23.18	3.54	6.85	0.82	1.05	0.049	0.14
Coal - minimum	32.04	0.43	0.29	0.31	0.1	11.32	0.27	0.79	0.09	0.62		
Coal maximum	68.35	27.78	4.15	3.98	1.7	35.23	14.42	16.44	2.9	1.61		
Lignite – mean	44.87	13.11	1.78	2.5	0.2	17.11	8.64	10.8	0.48	0.81	0.055	0.21

In bottom ash (BA) the oxide contents are normally SiO_2 > CaO > K_2O > MgO > P_2O_5 > Al_2O_3 > SO_3 > Fe_2O_3 > Cl_2O > Na_2O > MnO > TiO_2. The elements such as Ca, Cl, K, Mg, Mn, Na, P, and S in BA from natural biomass normally show higher contents than the respective values for coal ashes. On the other hand, elements such as Al, Fe, Si, and Ti in BA commonly reveal lower concentrations than the respective values for coal ashes [5].

Bottom ash from municipal waste incinerators is material rich in SiO_2 (34%) and CaO (22%). Iron as Fe_2O_3 (14%), aluminium as Al_2O_3 (10%), and Na as Na_2O (7%) are present in a smaller

amount [6]. Significantly lower levels of Fe_2O_3 for ashes from municipal solid waste (MSW) incinerators were reported [5]. Iron content may be related to the level of municipal waste separation.

Table 2 lists the contents of the minor elements contained in bottom ash from combustion of biomass, coal and MSW incineration plants. The minimum and maximum contents of the elements mentioned in ashes from the Czech Republic derive from the combustion of brown coal (lignite) from the Most and Chomutov Coal Basins. Ashes from lignite combustion are characterized by higher contents of Co, Ni, and V. Higher contents of As, Cu, Cr, Mo, Sb, Sn, and Zn were found in ashes from MSW incinerators. When reaching a certain concentration, it is therefore possible to consider these elements as indicators for incineration of "undesirable admixtures in traditional fuels – coal and biomass". The sources of these elements in household wastes are:

As is used as a decolourizer and fining agent in the manufacturing of bottle glass and other types of glassware, wood preservative salts, in leather industry, as a paint pigment. Other utilization: doping agent in electro conductive polymers alloys, batteries, semiconductors, herbicides, insecticides [7].

Cu compounds are used as a wood preservative. Textile fibres are blended with copper to create antimicrobial protective fabrics. Copper oxide and carbonate are used to add colour in stain glass works. Integrated circuits and printed circuit boards increasingly feature copper in place of aluminium because of its superior electrical conductivity. Antimicrobial applications.

Cr is responsible for yield yellow, red and green pigments, but in traces it is utilized also for other pigments: from black to blue. Other utilization: wood protection, leather processing, steel.

Sb is utilized in production of paint, ceramic, glass and plastic production, white, yellow and orange pigments, rubber vulcanization.

Mo is used as an alloying element in steel and super alloys. Pigments in anticorrosive paints for steel and aluminium. Less toxic substitute for antimony oxide in flame retardant agents for PVC.

Sn is used in the manufacture of dyes, polymers, and textiles; as a food preservative; as an additive in perfumes used in soaps; and as an anti-gumming agent in lubricating oils. Tin oxide (SnO_2) is used in the manufacture of special kinds of glass, ceramic glazes and colours, perfumes and cosmetics, and textiles. Organotin is the most important compound for stabilising PVC. PVC compounds incorporating tin heat stabilisers are used in a diverse range of applications including sheet, bottles, profiles, injection moulded fittings, credit cards, blister packs, food containers – tin cans and display trays.

Zn in the waste fraction of textile/leather/rubber Zn content varies from around 30 to 18,000 mg/kg and in fraction of waste glass between 0 and 10,000 mg/kg. ZnO is also the main ingredient for the production of a flame retardant. Zinc borate is added to a number of materials and products, such as plastics (15 – 10,000 mg/kg), textiles and rubber (32 – 17.64 mg/kg). Zinc stearate, $Zn(C_{18}H_{35}O_2)_2$ is used as a heat stabilizer in PVC. Variety of PVC based plastics, such as potable water pipes, water bottles, cable covering and PVC toys are stabilized with the Ca/Zn. Cardboard/paper contain only 13 – 160 mg/kg Zn [8].

Table 3 lists the minimum and maximum concentrations for bottom ash and fly ash from biomass combustion and for fly ash from combustion of bituminous coal in the Czech Republic. Ashes from biomass combustion show significantly lower As and Cd contents in bottom ash, comparable content in bottom ash and fly ash is shown by Cr, Pb, and V. Other elements show a slight enrichment in fly ash. The highest contents of Co, Ni, and V were found in bituminous coal combustion products. In BA from biomass combustion, Zn occurs in a concentration about 5 times higher than in ash from coal combustion. In biomass fly ash, Zn concentration may be up to 10 times higher than in fly ash from coal. The highest metal contents were found in bottom ash from MSW incinerators: As, Cr, Cu, Mo, Pb, Sb, Sn, and Zn. These elements can be considered as indicators of combustion processes using waste.

Table 2. Chemical analysis of bottom ash (BA) and fly ash (FA) from biomass and coal combustion (mg/kg dry matter).

	Biomass									
	BA		BA-literature [9]		FA		FA-literature [9]		FA - lignite CR [4]	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
As	2.17	3.19	1.4		2.68	6.98	1.5	24	29.7	126
Ba	802	1400	1600	2200	797	2320	1200	4300	630	1537
Cd	0.15	0.46	<0.2	5.7	7.32	16.3	5.1	34	0.4	3.2
Co	4.23	7.3	6.7	11	5.79	9.69	11	13	37	77
Cu	64.6	111	69	200					87	120
Cr	24.9	69.5	64	220	26.5	62.7	32	290	152	235
Mo	1.06	1.84	1	5.87	1.46	4.29	6.6	9	1.38	11.5
Ni	27.4	38.6	22	200	22.4	52.5	19	54	89.5	190
Pb	4.74	79.8	4	40	10.7	73.8	25	470	25	56
Sb	0.49	3.48	0.86	2.3	0.72	5.83	1.7	3		
Sn	0.3	1	11	16	1.21	6.37	15	22	9.85	23.2
Sr	466	783	610	710	578	1240	750	2100		
Tl	0.12	0.47			0.978	1.98				
V	10.4	18.4	26	64	6.75	18.2	5.1	43	276	309
Zn	73.9	234	65	950	446	1120	370	1860	122	190

Table 3. Bottom ash and fly ash from electrostatic precipitators from MSW incineration plant.

	BA [10]	BA [11]	BA [12] Mean ± S.D.	BA [6] Mean	BA [13] Min - Max	FA[14] Min - Max	MSW ash Max
As			108 ± 42		0.1 - 190	6.4 - 27.9	0.1 - 190
Ba					400 - 3000	700 - 1100	400 - 3000
Cd			7 ± 1		0.3 - 70		0.3 - 70
Co			21 ± 2	47			47
Cu	700-1000	4600	315 ± 22	1801	190 - 8200	820 - 1550	190 - 8200
Cr			252 ± 42	537	23 - 3200	254 - 656	23 - 3200
Hg							
Mo			12 ± 2		2 - 280	10 - 24.7	2 - 280
Ni			48 ± 24	63	7 - 120	51.9 - 60.4	
Pb		550		234	100 - 13700	1370 - 2800	100 - 13700
Sb		9.2			10 - 430	128 - 773	128 - 773
Sn				128			128
V					20 - 120	10 - 35	20 - 120
Zn	1600-2500	3000	1922 ± 33	2357	610 - 7800	4210 - 14400	4210 - 14400
Zr				193			

MSW – Municipal Solid Waste, S.D. - standard deviation

If the identified concentration in ash from local furnaces is higher than: As (126 mg/kg), Cr (235 mg/kg), Cu (120 mg/kg), Mo (12 mg/kg), Sn (23 mg/kg) and Zn (1,900 mg/kg), it can be assumed that waste was combusted in the boiler in addition to the approved fuel.

3. Conclusion

As part of the bottom ash and fly ash analysis from combustion of biomass and coal, elements that clearly originate from coal combustion were defined: Co, Ni and V, or Zn from biomass (figure 1). As, Cr, Cu, Mo, Sn, and Zn will be used to identify waste combustion in local furnaces. The concentration that demonstrates the presence of waste in the combustion process is derived from the maximum occurrence of the given element in fly ash from bituminous coal combustion. These elements can be

easily monitored by the X-Ray fluorescence method used by a number of accredited laboratories. In addition to the majority elements, chlorides and sodium (Na_2O) are of importance in demonstrating possible waste combustion. If the increased content of indicator elements is demonstrated in ash, the analysis can be refined by identifying the organic compounds by pyrolysis chromatography Py-GC/MS. This method will allow accurate identification of combusted waste. In the case of boilers that have a half emission limit for pollutants according to EN 303-5: 2012 – reduced from 150 or 125 mg/m^3 (Class 2 and 3 boilers) to 75 mg/m^3 (Class 4 boilers) or 60 mg/m^3 (Class 3 boilers), higher particulate capture will occur, which will cause an increase in the concentration of the majority and minority elements in ash. The proposed limit concentrations for the indicator elements will have to be increased by about one half. This assumption must be verified on an experimental device.

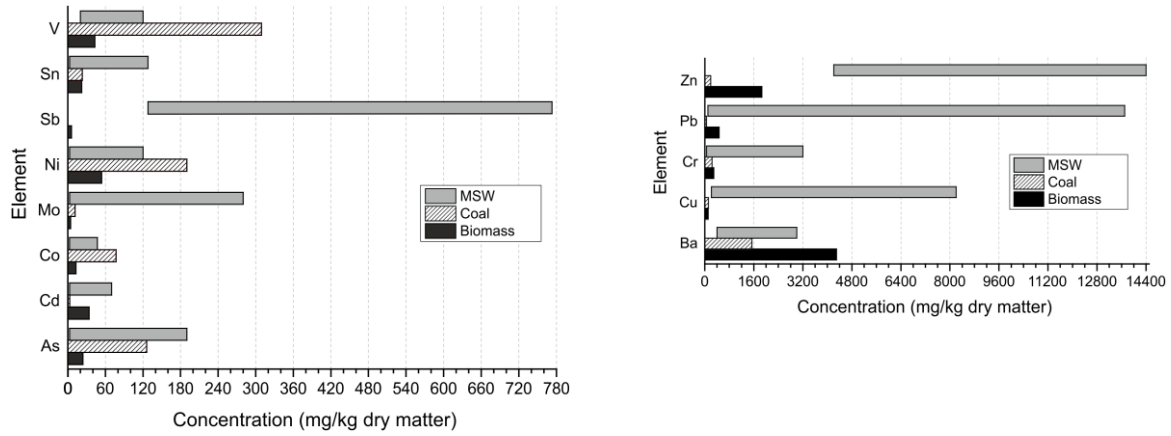


Figure 1. Concentration of elements in ash from biomass, coal and MSW.

Acknowledgement
This study was supported by the research projects of the Ministry of Education, Youth and Sport of the Czech Republic: The National Programme of Sustainability LO1404 – TUCENET, SGS 2017/35 Research in Selected Areas of "Smart Energy" of the 21st Century and the INTER-EXCELLENCE programme “European Anthroposphere as a Source of Raw Materials” LTC 17051

References

[1] Inspection of Boilers and Heat Distribution Decree No 194/2013 Coll *Ministry of Environment*
[2] Air Protection Act No 369/2016 Coll *Ministry of Environment*
[3] Oboirien B O, Thulari V and North B C 2016 *Appl. Energy* **177** 81–86
[4] Dolníčková D, Drozdová J, Raclavský K and Juchelková D 2012 *J. Pol. Miner. Eng. Soc.* **1** 59-68
[5] Vassilev S V, Vassileva Ch G, Song Y C, Li W Y and Feng J 2017 *Fuel* **208** 377–409
[6] Kowalski R F, Kasina M and Michalik M 2017 *Energy Procedia* **185** 56-62
[7] US EPA 1998 *Locating and estimating air emissions from sources of arsenic and arsenic compounds* (Research Triangle Park: EPA-454/R-98-013)
[8] Jones F, Bisaillon M, Lindberg D and Hupa M 2013 *Waste Manag.* **33** 2675–2679
[9] Maresca A, Hyks J and Astrup T F 2017 Recirculation of biomass ashes onto forest soils: ash composition, mineralogy and leaching properties *Waste Manag.* (*In press*)
[10] Xia Y, He P, Shao L and Zhang H 2017 *J. Environ. Sci.* **52** 178 – 189.
[11] Okada T and Tomikawa H 2013 *Waste Manag.* **33** 605–614
[12] Yao J, Qiu Z, Kong Q, Chen L, Zhu H and Long Y 2017 *Ecological Engineering* **102** 577-582
[13] Sabbas T, Polettini A, Pomi R, Astrup T, Hjelmar O, Mostbauer P, Cappai G, Magel G and Salhofer S 2003 *Waste Manag.* **23** 61-88.
[14] Raclavska H, Corsaro A, Hartmann-Koval S and Juchelkova D 2017 *JEMA* **205** 1-9