ASH AND SLAG HANDLING

3.6. Handling solid by-products from combustion of other fuels

3.6.1. Possibilities of utilisation of ashes from biomass

E. J. Bielińska[1], E. Meller[2], S. Stankowski[2], CZ. Wołoszyk[2]
Live Sciences University, Lublin, Poland (1)
Westpomeranian University of Technology, Szczecin, Poland (2)

ABSTRACT

In the paper the chemical composition of ashes from combustion of different kind of biomass and co-firing of coal and biomass was presented. Ashes from biomass, in general, have high content of macro elements as Ca and K. Increase of some macro elements in ash from co-firing of coal and biomass was relatively low, even share of biomass was 30%. Primary results of experiments indicate positive effect of ashes from biomass on yielding and some other parameters of chosen species of plants.

1. BIOMASS AS ENERGY SOURCE

Increasing the use of renewable energies offers significant opportunities for Europe to reduce greenhouse gas emissions and secure its energy supply. Within European Union in particular, biomass is seen as the most relevant renewable energy source besides hydropower.

For this purpose we can divided the stream of potential sources for agriculture, forestry and biowaste products. The main biowaste streams contributing to this potential are solid agricultural residues (e.g. straw), wet manures, wood processing residues, the biodegradable part of municipal solid waste. At country level, Germany and France have by far the largest potential for bioenergy from waste. Their combined potential level accounts for about one third of the EU-25 total. Other countries with large populations and land area also have significant resources (such as the United Kingdom, Italy, Poland).

The thermal utilization of solid biomass is expected to play a major role in future concepts for the reduction of greenhouse gas emissions from heat and electricity production. In general, three different technologies for thermal biomass conversion can be applied, namely pyrolysis, gasification and combustion. Combustion is the most advanced and market-proven application, while pyrolysis and gasification are still in the development or demonstration stages. A broad spectrum of biomass combustion technologies for different types of biomass fuels (woody biomass fuels, herbaceous biomass fuels, biodegradable wastes and residues) covering a wide range of plant capacities are currently available. Finally it should be mentioned that co-firing of biomass fuels in large scale coal fired power stations also offers an interesting option for biomass utilisation.

2. CHEMICAL COMPOSITION OF ASHES FROM BIOMASS AND CO-FIRING WITH STONE COAL

Biomass ashes could be use as a fertilizer or soil improver or row material for fertilizer production. Utilisation of ashes in all this purposes is possible but limited. For plants the most important are three elements as N, P and K. In ashes there are no nitrogen. From the next two mentioned above potassium could be more useful. Phosphorus is present in lower amount and sometimes in poor solubility in soil. From other elements ashes could contain significant amount of Ca, Mg or S. The amount of ash and basic elements in ash from biomass and co firing are in table 1 and 2 [8]

Table 1. **Share of ash and content (%) of macro elements in ash of some kind of biomass**

Kind of biomass	Ash	Ca	P	K	Mg
Stone coal	22.0	1.4	0.3	2.6	1.0
Mallow	2.6	32.0	0.6	11.3	2.8
Willow	1.5	21.6	6.8	19.2	3.4
Miscanthus	3.7	4.2	1.4	22.4	2.6
Rape straw	5.2	17.8	1.8	10.8	2.6
Millet hulls	9.1	0.1	7.0	7.6	3.1
Sunflower huls	3.7	9.4	2.6	27.6	3.1
Cereals (plants)	-	3.1	3.9	12.0	1.5
Wood wastes	-	30.0	1.1	4.8	3.0
Alcohol distillery waste	5.0	1.2	20.4	19.9	6.3
Municipal waste	27.5	18.6	0.8	3.2	1.1
Poutry litter	-	3.0	5.0	3.0	1.7

Average content of ash in stone coal was 22% and generally was higher than ash content for most of investigated sources of biomass. The lower ash content was observed for mallow and willow the highest for millet hulls and municipal wastes – for this kind ow waste ash content was even higher than for stone coal. Concentration in ash of main element, which are necessary for plant growth, was differentiated. A lot of potassium was observed in sunflower hulls , miscanthus and willow as well as in distillery wastes. Analyse of dates indicate that P content was on lower level but in most cases was higher than for ash from stone coal. The biggest content from all elements was noticed for Ca, also the biggest differences were noticed – from 32% for mallow to 0,1 to millets hull.

Differentiation in ash content and investigated element concentration is strong connected not only with the kind of biomass but also with the environmental (soil and weather) conditions and agrotechnical factors – like fertilization.

Actually more popular in great power plants is co-firing of coal with biomass. Addition of organic product is not very high and amount from several percent until about 20-30 percent. Chemical compositions of ash from co-firing were more similar for ash from stone coal. It resulted from small share of of ash in most kind of biomass and not very high amount of it for co-firing.

Table. 2. **Content (%) of macroelements in ash from some mictures**

Mixture	Ca	P	K	Mg
Stone coal	1.4	0.3	2.6	1.0
Mallow (M)	32.0	0.6	11.3	2.8
Stone coal + 10% of M	1.9	0.3	2.8	1.0
Stone coal + 20% of M	2.4	0.3	2.9	1.1
Stone coal + 30% of M	3.0	0.4	3.0	1.1
Willow (W)	21.6	6.8	19.2	3.4
Stone coal + 10% of W	1.6	0.3	2.8	1.1

Stone coal + 20% of W	1.8	0.4	2.9	1.1
Stone coal + 30% of W	2.0	0.5	3.1	1.1

3. EFECT OF BIOMASS ASHE USE AS K FERTILIZATION

3.1. Metodology

In the pot experiment, realized in 2008, the effect of 4 fertilization variants (3 kinds of ashes - ash from wheat grain, from wheat straw, from wooden briquettes and mineral NPK fertilization) and 2 doses of fertilization on growth of *Festulolium* cv. Felopa was examined. The doses were balanced using potassium content in ashes. Total content of P and K, doses of ashes, P, K were presented in Table 3. Ashes were applied to the soil (mixed with half of the soil volume). On every variant with ashes nitrogen fertilization (0.30 g per pot as urea 46%) was given. Half of the dose was applied before sowing and second part after the first harvest of plants. In experiment were also used 2 control variants (without fertilization and with mineral N fertilization). The doses were presented in Table 4.

Phosphorus fertilization was given as Ca $(H_2PO_4)_2$ H_2O before sowing. Potassium (potassium salt 60%) dose was divided in 2 parts (first part before sowing, second after first harvest). Every mineral fertilizer were applied in water solution. The samples were analyzed for the pH in 1 mol·dm^{-3} KCl by means of the potentiometer method, calcium carbonade ($CaCO_3$) by means of the Scheibler method, the losses on ignition by means of a sample burning in the temperature 550^0C. The contents of macroelements (P, K, Mg, Ca, Na) and heavy metals (Zn, Cu, Mn, Fe, Ni, Co, Pb) in the soil and vegetation samples was determined after the mineralization of the material in the mixture of the concentrated acids HNO_3 + $HClO_4$, with the Unicam-Solar 929 atomic absorption spectrophotometer, while that of phosphorus was determined colorimetrically. Moreover the soil samples were analyzed for the content of soluble phosphorus and potassium using Egner-Riehm method and soluble magnesium using Schachtschabel method. The chlorophyll content, using analyzer SPAD-502 (Minolta) was measured 2 times – before first and second harvest on 14 leaves from each pot. After each of 3 harvests the green matter of plants was determined. The analysis of variance was used for statistical description of results in 2-way complete randomized design. $LSD_{0.05}$ was calculated using Tukey test.

3.2. Research results

The reaction of investigated ashes was alkaline (Table 3). The highest pH_{KCl} was obtained in ash from wheat grain (delivered from Austria). Concentration of $CaCO_3$ was different in compared ashes. It ranged from 4.0 to 17.5 %. Content of organic mater, determined by sample burning in the temperature 550^0C, amounted from 15.76 to 20.42%. That indicate for not sufficient burning process. Abundance of soluble elements in investigated ashes was generally good (Table 5). The highest content of soluble macro-elements was observed in ashes from wheat grain. According to IUNG classification [3], used for describing content of macro- and micro-elements in soils, could be described as very high.

Ashes from straw and briquette had medium abundance of soluble form of phosphorus and very high of potassium and magnesium. The total content of macro-elements (Table 6) was different in ashes. The most rich in phosphorus, potassium and magnesium was ash from wheat grain. The highest content of calcium and sodium was observed in ash from briquette.

Usability of waste product, including ashes, is strongly connected with the amount of heavy metals in them [4, 5; 7]. The highest concentration of heavy metals was noticed in ashes from briquette (Table 7) but in all products used in experiment was not very high. They did not create impendence to soil environment.

Green matter yield of *Festulium* was presented in Table 8. In the first harvest the highest yield of green matter was obtained after application of ash from wheat grain. The effect of ash from straw, ash from briquette and mineral NPK fertilization was similar. Giving only N fertilization resulted in lower yield than for ash from wheat grain. Yields for the remaining fertilization variants were similar. The lowest yield was obtained for control without any fertilization. In the second harvest, significant difference was observed between variant with straw ash and NPK fertilization. The lowest yield was obtained in control variant - without fertilization. At last harvest yield of *Festulolium* was very low – about 13.3 grams per pot. Better results were obtained for ashes than for mineral fertilization. The sum of yields from 3 harvests was bigger after application of ashes from wheat grain and straw than for NPK fertilization. Lower value was obtained after N application and the lowest or control without fertilization. Increase of dose of ashes or NPK fertilization resulted in higher yield only in 2 harvest time – first and second. In the third harvest time there was no significant difference. There was no interaction between kind of fertilization and dose. Increasing of the dose had similar effect on the yield independently to the kind of fertilizer.

Application of different kind of fertilizer (ashes, NPK) had no strong effect on chlorophyll content (Table 9). Only one significant effect was observed at first time of measurement (before first harvest). Higher values were obtained for variants with ash from briquette and NPK fertilization than for ash from grain and straw. The fertilizer dose did not affect this trait. The biggest difference in this trait was noticed between all variants and control in the second time of measurement.

3.3. Conclusions

In the nearest future utilization of biomass for combustion will increase very strong. Actually about 4% of the whole energy production is covered by biomass and up to 2020 will probably tripled. The production of biomass requires reutilization of residues of the bio-energy processes in order to realize a nutrient cycling. Ashes from different sources probably could be used as fertilizer or component for multi component fertilizers [1, 2]. But we have to know if this material is free from heavy metals and take to consideration every additionally aspect including economical aspects.

The results of this experiment indicate that content of heavy metals in ashes from wheat grain and straw is not very high.

Table 3. **Total content of P and K (g·kg^{-1} DM), dose of ashes and P, K applied with ashes (g per pot^{-1})**

Kind of ash	Total content (g kg^{-1} d.m.)		Ash dose (g pot^{-1})		Dose of P and K (g pot^{-1})			
					P		K	
	P	K	I	II	I	II	I	II

Grain	3.39	49.0	10.17	20.34	0.0346	0.0692	0.498	0.996
Straw	2.59	32.7	15.23	30.46	0.0396	0.0792	0.498	0.996
Briquette	0.69	13.4	37.27	74.53	0.0149	0.0298	0.498	0.998

Table 4. **Doses of mineral fertilization N and NPK**

Treatment	Dose of pure component					
	N		P		K	
	g pot^{-1}	kg·ha^{-1}	g pot^{-1}	kg·ha^{-1}	g pot^{-1}	kg·ha^{-1}
N	0.30	100	-	-	-	-
NPK I	0.30	100	0.0297	9.90	0.498	83
NPK II	0.30	100	0.0594	19.80	0.998	166

Table 5. **Reaction, loss in ignition, content of $CaCO_3$ and soluble forms of P, K, MG in ashes**

Kind of ash	pH_{KCl}	$CaCO_3$	Loss in ignition	P	K	Mg
		%		[g·kg^{-1}]		
Grain	12.78	4.00	19.63	0.10	11.08	0.247
Straw	10.23	7.38	20.42	0.06	13.15	0.189
Briquette	9.63	17.51	15.76	0.05	4.23	0.235

Table 6. **Total content of macro-elements in ashes (g·kg^{-1})**

Kind of ash	P	K	Ca	Mg	Na
Grain	3.39	49.00	134.84	43.79	0.43
Straw	2.59	32.66	58.17	8.00	1.29
Briquette	0.69	13.37	177.12	20.27	6.99

Table 7. **Total content of microelements in ashes (mg·kg^{-1})**

Kind of ash	Fe	Mn	Zn	Cu	Pb	Ni	Co	Cd
Grain	835	808	424	102.0	14.58	8.17	0.22	0.163
Straw	5615	2027	212	36.1	5.99	5.45	2.49	1.195
Briquette	9415	5988	361	450.5	80.68	46.77	34.70	2.265

Table 8. **Effect of fertilization with ashes and NPK and dose on green matter yield (g pot^{-1}) of *Festulolium***

Harvest	Fertilization variant (F)				Doze (D)		$LSD_{0,05}$	
	A	B	C	D	I	II	F	D
1	76.7	71.6	71.3	71.4	70.5	75.0	5.05	3.06
	Control variants: N - 69.5; O – 48.2							
2	44.5	46.8	42.6	40.8	42.4	45.0	4.02	2.11
	Control variants: N - 37.9; O – 14.3							
3	13.6	14.4	14.5	11.8	13.6	13.5	1.79	r.n.
	Control variants: N - 9.8; O – 7.6							
1-3	134.8	132.8	128.4	124.1	126.5	133.5	7.54	3.95
	Control variants: N – 117.2 ; O – 70.1							

Table 9**. Effect of fertilization with ashes and NPK and dose on chlorophyll content (SPAD units) of *Festulolium***

Harvest	Fertilization variant (F)				Doze (D)		$LSD_{0.05}$	
	A	B	C	D	I	II	F	D
1	24.4	23.3	26.2	26.6	25.5	24.7	2.55	ns
	Control variants: N -21.4 ; O – 21.3							
2	22.6	23.3	23.9	23.3	23.4	23.2	ns	ns
	Control variants: N – 23.1 ; O – 16.4							

The highest content of soluble macro-elements was observed in ash from wheat grain. Application of ash from wheat grain and straw resulted in higher yield of *Festulolium* than yield obtained after NPK. Yield of green matter obtained at N fertilization and control (without fertilization) was relatively lower. Reaction for increasing dose of fertilization was similar independently to the kind of fertilizer (ashes, mineral NPK). The effect of different fertilizers on chlorophyll content was similar.

LIST OF DESIGNATION

A – ash from grain; B – ash from straw; C – ash from briquette; D- NPK

REFERENCES

1. **Codling, E.E., Chaney R.L., Sherwell J.** Poultry litter ash as a potential phosphorus source for agricultural crops. J. Environ. Quality 31. 2002. 954-961.
2. **Eichler-Loeberman B., Lopez R., Steinbrecht D., Koppen D.** Pozytywne skutki nawożenia popiołami z biomasy w rolniczej produkcji roślinnej. W. Popioły z energetyki. Red. Myszkowska A, Szczygielski T. Wyd. Ekotech Sp. z o.o. 2006. 229-236.
3. **IUNG.** Zalecenia nawozowe. Cz. I. Liczby graniczne do wyceny zawartości w glebach makro i mikroelementów, Seria P(44), Puławy. 1990. 1-26.
4. **Kabata-Pendias A., Piotrkowska M.** Pierwiastki śladowe jako kryterium rolniczej przydatności odpadów. IUNG Seria P(33), Puławy. 1987. 1-39.

5. **Niedźwiecki E., Meller E., Meller J.** Możliwości wykorzystania popiołów ze spalania węgla kamiennego w Elektrowni "Dolna Odra" w rekultywacji wysypisk odpadów komunalnych. Mat. Konf. Nauk.-Tech. nt. "Rekultywacja terenów zdegradowanych w województwie szczecińskim", 18 września 1995, Nowe Czarnowo. Rozwój Szczecina i Regionu – Technika i Ekologia.1995. 109-117.
6. **Niedźwiecki E., Meller E., Kęsek S., Jakubiec A.** Właściwości fizyko-chemiczne popiołów powstałych ze spalania odpadów drzewnych w zakładzie Kronopol w Żarach oraz możliwości i sposoby ich zagospodarowania. Zesz. Probl. Post. Nauk Roln., z. 518. 2007. 119-125.
7. **Protasowicki M., Niedźwiecki E., Brucka-Jastrzębska E.** Oddziaływanie składowiska popiołów z węgla kamiennego na środowisko w świetle wieloletnich badań stężeń metali w odciekach. Zesz. Probl. Post. Nauk Roln., z. 476. 2001. 251-258.
8. **Przewodnik** metodyczny Procedury bilansowania i rozliczania energii wytwarzanej w procesach współspalania. Red. Ścieżko M., Zuwała J., Sobolewski A. Instytut Chemicznej Przeróbki Węgla, Towarzystwo Gospodarcze Polskie Elektrownie. Warszawa, Zabrze -2007.

Paper text could be published in the open press.