Fuel Processing Technology 146 (2016) 85–89

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Particle size based recovery of phosphorus from combined peat and wood fly ash for forest fertilization

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ARTICLE INFO

Article history:
Received 9 November 2015
Received in revised form 10 February 2016
Accepted 11 February 2016
Available online 24 February 2016

Keywords:
Phosphorus recycle
Forest fertilizer
Fly ash utilization

ABSTRACT

Correlations between the concentrations of P, K, and As with particle size in fly ash from power plants were examined with a viewpoint to obtain fractions suitable for forest fertilization. Fly ash samples from several CHP plants were fractionated by using four sieves and the five fractions were analyzed by ICP-OES; it was found that both P and K are concentrated in smallest size (<45 μm) fractions. Some fly ash samples were found to contain As in excess of the legal limit of 40 mg/kg, but even in these cases it was possible to obtain size fractions that pass the legal limit while containing useful amounts of P and K. Fractionating fly ash into different sizes is identified as a viable phosphorus recovery method for obtaining legally acceptable fractions for forest fertilization.

1. Introduction

Utilization of forest resources has increased in Finland in recent decades. The total volume of the growing stock for extraction amounts to 2357 million m^3 over bark and 16 million m^3 are utilized annually for energy production [1]. In addition, 9.3 million ha of land area are covered by peatlands and 0.6% of this, 60,000 ha, are used for peat production [2]. Such harvesting removes nutrients from the forest and peatlands and may lead to the acidification of growing sites, affecting tree growth and the chemistry of runoff water [3]. Studies of ash utilization, such as Ref. [4,5], have indicated a deficiency of mineralized phosphorus in Scots pine growing on drained thick-peated mires. It is thus very essential to return the nutrients to these sites to sustain the mineral cycle and tree growth. Combined heat and power plants in Finland produce over 150,000 t of wood ash and 450,000 t of peat ash annually. 30% of their fly ash and 70% of bottom ash are generally utilized in some way. Most of the wood fly ash are being used as forest fertilizer which replaces the nutrients removed in biomass harvesting, counteracts soil acidification and improves tree growth. For example, 27,000 t of wood ash were used as forest fertilizer in 2004 [3]. Experimental studies have reported 3.1–12.1 m^3ha^{-1} a^{-1} of growth increase, and 44–56 years of fertilizer influence when 5000–16,000 kg ha^{-1} were utilized [6]. Thus, refining of wood ash for forest and ground vegetation fertilization has been developed at an industrial scale in Finland during recent years [7].

Typical mineral elements in wood and peat fly ash are silicon (Si), calcium (Ca), potassium (K), phosphorus (P), magnesium (Mg), manganese (Mn), iron (Fe), sodium (Na), aluminum (Al), boron (B) and titanium (Ti). The fertilizing effect of ash depends mainly on its phosphorus and potassium content, while calcium and magnesium exhibit a liming effect [8]. However, it lacks nitrogen, which is lost as flue gas during combustion. According to Väätäinen et al., the fertilizing effect of wood ash lasts for 30–40 years. On the contrary, fertilizing effect for chemical fertilizers with similar phosphorus and potassium concentration has been estimated to last for 15–25 years [5]. The reason for this difference is the different leaching rates of phosphorus between wood ash and chemical fertilizers. The slow leaching rates of phosphorus in wood ash have been attributed to the adsorption of P by Al and Fe [9]. In addition, wood and peat ash contain various heavy metals which are classified as harmful and toxic. Thus, the forest use of ash is regulated by a new Decree on fertilizer products, imposed by the Finnish legislature in 2011. According to the new Decree on fertilizer products the minimum recommended sum of phosphorus and potassium concentrations should be 2% d.w. (20 g/kg) and for calcium 6% by weight or 60 g/kg. Furthermore, the new Decree on fertilizer products imposes no limit values for pH, moisture, dry matter content, neutralizing value or the concentration of chloride [10]. Meanwhile, the same Decree also sets maximum limit values for heavy metals as shown in Table 1.

Fly ash is, in general, an extremely inhomogeneous material. However, its elemental composition seems to be a function of its particle size distribution. A limited number of studies [11,12] have focused upon the correlation of ash mineralogy with its particle size distribution, while Dahl et al., and Lanzerstorfer [13,14] considered heavy metals and found that metals such as As, Cd, Cr, Cu, Ni, Pb and Zn are more concentrated in smaller particle size (<75 μm) fractions than in the larger ones. However, discrete studies on effect of size fractionation of fly ash on the elements with fertilizing qualities like P and K have not yet been conducted. Therefore, this study aims to investigate the dependence of fly ash chemistry on its particle size and the effect of fractionation on the

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http://dx.doi.org/10.1016/j.fuproc.2016.02.016
0378-3820/

Table 1
Physical and chemical properties of fly ash originated from various mixtures of peat (P) and wood based biomass (B) as fuel (subscripts indicate the fuel composition used for combustion).

Parameters	Fly ash samples							Limit value [10] (max.)
	P_{100}	$P_{80}B_{20}$	$P_{70}B_{30}$	$P_{65}B_{35}$	$P_{50}B_{50}$	$P_{30}P_{70}$	B_{100}	
(a) Particle size distribution profile (μm)								
D_{10}	7.1	11.2	13.6	15.2	7	13.9	12	
D_{50}	21.3	72.1	102.9	119.9	46.4	116.7	196.3	
D_{90}	81.2	168.3	230	236.5	148.1	176.4	494.1	
AMD	22	52	70	78	37	71	114	
(b) Weight fraction of sieved samples (wt.%)								
<45 μm	61.3	48.9	28.6	32.2	53.2	29.4	22	
45–63 μm	9.2	14.2	18.3	13.6	16.7	13.7	20.8	
63–125 μm	22.8	24.7	28	23.7	19.4	27	16.1	
125–250 μm	6.8	12.3	20.6	23.9	7.4	25.3	16.6	
>250 μm	0	0	4.4	6.5	3.2	4.6	24.5	
(c) Elements/mineral composition (10^3 mg/kg)								
C	10.8	2.6	8.2	6.8	22.1	20.8	13.6	
H	2.9	–	–	–	1.6	1.1	2	
N	–	–	–	–	–	0.4	–	
Al	79.3	91.4	99.9	86.1	60.1	47.7	33.8	
Ca	304.3	92.2	81.7	86.4	131.1	47.5	154	
Fe	107.3	142.8	106.7	80.3	60.4	31.7	20	
K	14.4	19.8	22.4	19.1	21.7	14.3	31	
Mg	23.5	16.5	13.5	12.6	16.9	8.5	21.6	
Mn	1.3	3.3	2.6	3	6.6	2	8.7	
Na	10.3	11	14.5	11	7.3	6.5	9	
P	10.1	13.3	9	9.5	17.2	4.9	12.1	
Si	145.6	189.1	207.4	190	187.8	296.4	173.1	
Ti	2.1	3.3	3.4	3	2	1.6	1.5	
d) Heavy metal composition (mg/kg)								
As	33.4	78.9	34.5	33.1	61.6	24.3	6.7	40
Cd	1.1	2.7	1.1	2.2	7.4	4	8.6	25
Cr	36.2	67.6	53.7	35.3	57.8	34.7	45.1	300
Cu	84.2	100	93.5	130.4	125.7	112.6	89.6	700
Ni	29	31.8	23.2	28	37.5	26.5	24.6	150
Pb	40.4	82.4	39.6	43.9	69.9	38.2	26.3	150
Zn	114.9	274.7	188.5	224.4	675.7	239.2	1704	4500

AMD = arithmetic mean diameter, (–) = below detection limit.

total phosphorus and potassium concentration of the fractions as an aid in the selection of suitable fraction for potential forest use.

2. Material and methods

Seven samples of fly ash were received from three different combined heat and power (CHP) plants of Finland. The seven fly ash samples originated from different combinations of peat and wood based biomass as a fuel for combustion in the power plants. A large number of ash samples allow us to generalize the correlation between element distribution and particle size of fly ash originating from various fuel mixtures. The fuel composition varies from 100% peat to 100% wood based fuel. The fly ash samples are labeled on the basis of their fuel composition, and are indicated as P_{100}, $P_{80}B_{20}$, $P_{70}B_{30}$, $P_{65}B_{35}$, $P_{50}B_{50}$, $P_{30}B_{70}$ and B_{100}, where P and B indicate the fuel type and refer to peat and woody biomass. In addition, the subscripts indicate the fuel composition percentage by weight. P_{100} is received from Keljonlahti CHP, while $P_{80}B_{20}$, $P_{70}B_{30}$, $P_{65}B_{35}$, $P_{50}B_{50}$ and $P_{30}B_{70}$ are from Rauhalahti CHP, and B_{100} is from Alholmens Kraft CHP.

The particle size distribution profiles (PSDPs) for all seven samples were evaluated with a Fritsch Analysetter 22 Economy particle size analyzer using a wet dispersion method in a saturated sodium chloride solution. The use of saturated solution is presumed to mitigate the problems associated with the dissolution of fly ash particles in water. RETSCH sieve shaker (AS200 basic) was employed for dry sieving with a screening time of 30 min. Samples of 20 g of each fly ash were taken for screening. Then the sieved fractions were collected and weighed. The following five fractions were obtained: [(0–45), (45–63), (63–125), (125–250), (>250)] μm. In the present study, mechanical sieving method has been employed solely for quantitative analysis of element distribution. Sieving may not be an appealing separation method in industrial scale, however methods such as air classification could be feasible.

The elemental composition of the fly ash samples was determined with an Elementar vario EL(III) and an ICP-OES PerkinElmer Optima 8300 instrument. All reagents used were of analytical grade. 0.25 g samples of primary fly ash and fractioned fly ash samples were dissolved in 3 ml of aqua-regia with 3–4 drops of hydrofluoric acid. The digestion was further assisted by ultrasound for 18 min with sonication procedure divided into six equal steps (3 min). All samples were shaken in between and the evolved gas was released. The samples were diluted to 100 ml in plastic volumetric flasks with high purity water produced by a Maxima water purification system provided by Elga. The sample matrices were analyzed with ICP-OES for heavy metals. The same samples were further diluted by a factor of 10 for mineral elements analysis in order to get suitable element concentrations for analysis by ICP-OES. A similar digestion method was employed for a standard reference material, SRM1633c [15], certified by NIST and recovery percentages of >98% for all heavy metals and phosphorus and 82–92% for most mineral elements were achieved, except for Si for which about 80% was obtained. Three replicate analyses were performed resulting in RSDs of about 5–10%. Due to the greater precision in the determination of heavy metals and mineral elements like phosphorus and potassium, this digestion method was adopted in this study. Relative composition of phosphorus and potassium on respective weight fraction (F_1–F_5) is estimated as;

$$M_{F_i} = C_{F_i}^{M} \cdot F_i^{\mathrm{wt.\%}} \text{ and } M_{F_i}\% = \frac{M_{F_i}}{\sum_{i=1}^{5} M_{F_i}}$$

where M_{F_i} is the relative concentration of element in F_i weight fraction, $C_{F_i}^{M}$ is the concentration of element in F_i determined with ICP-OES and $F_i^{\mathrm{wt.\%}}$ is the weight proportion of the F_i fraction.

3. Results and discussion

3.1. Physical and chemical properties of fly ash and its fractions

Seven fly ash samples originated from different fuel mixtures from three power plants of Finland were compared in terms of particle size distribution. Fig. 1 shows the significant variation in their particle size distribution, and the results of their diameter range is listed in Table 1a. According to Dahl et al. [13], the quality of fly ash including PSDPs is also affected by power plant processing conditions and collection system. The sieving of all fly ash samples indicates that a large proportion of the particles belongs to the smallest size range, 0–45 μm. This trend is valid for all seven fly ash samples in Table 1b.

A comprehensive elemental analysis of seven fly ash samples reveal significant variation in the distribution of elements in fly ash originating from different fuel mixtures and the results are listed in Table 1c. The phosphorus composition varies from 4.9 to 17.2 g/kg of ash while the potassium varies from 14.4 to 31 g/kg of ash. Such quantity of P and K in fly ash makes it adequate for forest fertilization. However, the composition of heavy metals in fly ash solely regulates its use as forest fertilizer, according to the Decree on fertilizer products. The heavy metal analysis of seven fly ash samples reveals the unsuitability of $P_{80}B_{20}$ and $P_{50}B_{50}$ for forest use because their arsenic (As) concentration exceeds its limit value of 40 mg/kg. Meanwhile, P_{100}, $P_{70}B_{30}$, $P_{65}B_{35}$, $P_{30}B_{70}$ and B_{100} can be utilized in fulfilling the requirements of the Decree on fertilizer products.