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Low Temperature Circulating Fluidized Bed gasification and co-gasification of Municipal Sewage Sludge. Part 2: Evaluation of ash materials as phosphorus fertilizer

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Abstract

The study is part 2 of 2 in an investigation of gasification and co-gasification of municipal sewage sludge in low temperature gasifiers. In this work, solid residuals from thermal gasification and co-gasification of municipal sewage sludge were investigated for their potential use as fertilizer. Ashes from five different Low Temperature Circulating Fluidized Bed (LT-CFB) gasification campaigns including two mono-sludge campaigns, two sludge/straw mixed fuels campaigns and a straw reference campaign were compared. Experiments were conducted on two different LT-CFBs with thermal capacities of 100 kW and 6 MW, respectively. The assessment included: i) Elemental composition and recovery of key elements and heavy metals; ii) content of total carbon (C) and total nitrogen (N); iii) pH; iv) water extractability of phosphorus after incubation in soil; and v) plant phosphorus response measured in a pot experiment with the most promising ash material. The results showed that co-gasification of straw and sludge in LT-CFB gasifiers gave the best fertilizer qualities across all assessed characteristics. These mixed fuel gasification ashes had a high content of recalcitrant C, phosphorus (P) and potassium (K), a low content of heavy metals (especially cadmium) and an improved plant P availability compared to the mono-sludge ashes. It was also found that bottom ashes from the char reactor contained even less heavy metals than cyclone ashes. It is concluded that LT-CFB gasification and co-gasification is a highly effective way to purify and sanitize sewage sludge for subsequent use in agricultural systems.

Keywords: Municipal sewage sludge; cereal straw; thermal gasification; phosphorus fertilizer ash; heavy metals

1 Introduction

Phosphorus (P) is an essential macro nutrient and the availability of P in agricultural systems is often a limiting factor especially in older soils as the ones found in mid and lower Africa, Asia and Australia [1–4]. The main source for P fertilizer, mined phosphate rock, is a critical non-renewable globally demanded resource and there is an increasing concern about the commercial availability of this resource in the near future (Cordell and White, 2014). Determinations of the P depletion rate and especially quantifications of the remaining P resource have been the subject of a recent scientific debate (Edixhoven et al., 2013; Scholz and Wellmer, 2016, 2013), but it is generally agreed on that the geopolitical importance of the P resource is increasing as is the urgency of developing more efficient P management strategies (Chowdhury et al., 2016; Ott and Rechberger, 2012).

A substantial proportion of P used in agriculture ends up in municipal sewage sludge (MSS) (Kahiluoto et al., 2015), and recycling this fraction via direct application of MSS to agricultural soil has been considered a cheap and efficient way to enhance and fertilize soils (Chowdhury et al., 2016; Fytili and Zabaniotou, 2008; Linderholm et al., 2012). However, the extent of direct MSS soil application varies greatly among countries and regions, and the variation is caused by many different factors including practical alternatives, differences in sludge quality as well as political and cultural restrictions (Fytili and Zabaniotou, 2008; Hukari et al., 2016; Kelessidis and Stasinakis, 2012). In recent years, there has been a growing concern in many countries of the potential risks associated with the content of emerging organic pollutants and xenobiotics in MSS, including antibiotics, fragrances, UV-filters, antiseptics, micro plastics, phthalates, hormones and much more (Choban and Winkler, 2008; Igos et al., 2012; Krüger et al., 2014; Michael et al., 2013). As a consequence of this growing concern, there is an increasingly restrictive political attitude towards direct application of sewage sludge in many countries (Krüger and Adam, 2015), and alternative management options are continuously developed and implemented. Thermal gasification of sludge is one of these alternatives (Qian and Jiang, 2014).

All types of thermal conversion of municipal sewage sludge leads to production of one or more ash- and/or char fractions. The quality and quantity of these products can vary substantially with the quality of the parent sludge and the design of the thermal process (Fericelli, 2011; Jakobsen and Willett, 1986; Li et al., 2015; Qian and Jiang, 2014). Many scientific studies have been conducted to examine the potential application of incineration ashes and pyrolysis chars in agricultural systems as fertilizers and/or soil enhancers. These studies usually involve investigation of one or several of the following characteristics: Content and type of toxins; fate and mobility of heavy metals; determination of eco-toxicity levels; content and availability of macro- and micro nutrients; technical routes for down-stream upgrading and potential long-term carbon sequestration (Fraser and Lum, 1983; Furr et al., 1980, 1979; Hossain et al., 2015; Jakobsen and Willett, 1986; Liu et al., 2014; Lu et al., 2013; Mellbye et al., 1982; Méndez et al., 2012; Song et al., 2014; Sousa and Figueiredo, 2015). However, to this date, no published studies on the fertilizer quality of ashes and chars from thermal gasification of municipal sewage sludge have been identified. Most studies on thermal gasification of sewage sludge are focused on the potential energy recovery, the technical feasibility of the process and the gas quality (Manara and Zabaniotou, 2012; Seggiani et al., 2012; Zhu et al., 2015).

The aim of this study was to test the use of two Low-Temperature Circulating Fluidized Bed Gasifiers (LT-CFBs) to convert MSS focusing on the quality of the solid process residuals and the potential use of these solid products as fertilizers and/or soil enhancers. Gasification ashes were collected from two MSS campaigns, two MSS/straw co-gasification campaigns and a straw reference campaign. Ash analysis included i) Composition and elemental balances of macro nutrients and heavy metals; ii) pH measurements and iii) incubation studies and pot experiments to determine phosphorus fertilizer quality.

This work is part of a larger assessment of the suitability of the LT-CFB gasification technology as a platform to convert municipal sewage sludge to electricity, heat and ash fertilizer. The complete assessment is composed of the following two parts:

- Part 1: Assessment of process feasibility and stability, process performance and energy efficiency, product distribution and gas product characteristics (Thomsen et al., 2016)
- Part 2: Characterization of LT-CFB ashes as P fertilizer and determination of key elemental balances (this study)

2 Materials and Methods

2.1 The LT-CFB gasifier

Two LT-CFB units currently exist; a 100 kWth pilot scale plant at the Technical University of Denmark located at Risø near Roskilde, Denmark, and a 6 MWth demonstration unit at DONG Energy's Asnaes Powerplant in Kalundborg, Denmark. Both plants are involved in the present study. The LT-CFB technology is commercially registered as the Pyroneer Gasifier by DONG Energy and has been described previously (Ahrenfeldt et al., 2013; Narayan et al., 2016; Nguyen et al., 2013; Nielsen, 2007; Thomsen et al., 2016, 2015). A generalized process flow chart of the LT-CFB gasifier is provided in Figure 1.

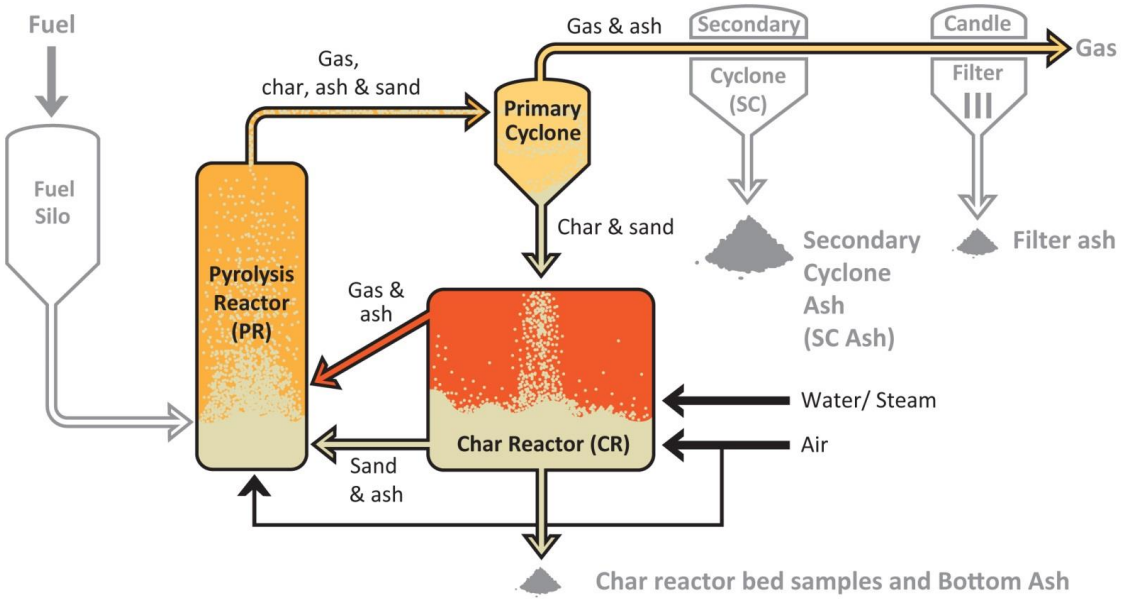


Figure 1: Illustration of a Low Temperature Circulating Fluidized bed (LT-CFB) gasification system with indications of the main input and product streams. Adapted from (Thomsen et al., 2015)

2.2 The sewage sludge fuels and LT-CFB campaigns

The applied MSS samples originated from three different Danish wastewater treatment plants (WWTPs) and the samples were collected at different seasons. The three WWTPs that supplied the sludge samples for the study are characterized as follows:

Stegholt WWTP (Aabenraa, Denmark): Constructed as a Mechanical-Biological (active sludge loop)-Nitrification-Denitrification-Chemical cleaning facility (MBNDC). However, the use of precipitation chemicals for P capture

has been phased out through constant process optimization. Iron chloride is still applied in the clarifiers to optimize the sedimentation of floating sludge. The MSS is treated by thermophilic anaerobic digestion for up to 18 days at the WWTP before it is dewatered mechanically and exported.

Randers WWTP (Randers, Denmark): A representative Danish MBNDC where P is captured approximately 50% biologically and 50% chemically using a mix of iron chloride and aluminum. This estimation is based on the annual use of precipitation chemicals at the time of the LT-CFB experiment and an assumption of a 1:1.8 capturing rate for aluminum and of 1:3 for iron. All sludge goes through the active sludge cycle before it is digested anaerobically in a mesophilic process with a retention time close to one month. The sample for the LT-CFB campaign was dried at the WWTP in a Krüger BioCon dryer with temperatures ranging from 100-175 °C.

Bjergmarken WWTP (Roskilde, Denmark): Another representative Danish MBNDC facility where precipitation chemicals are added before the active sludge cycle and phosphorous is captured approximately 70% biologically and 30% chemically. Iron chloride sulfate and aluminum chloride is used to capture P and precipitate sludge. All sludge goes through the active sludge cycle before it is digested anaerobically for almost three weeks in a thermophilic digestion process. After digestion, the sludge is mechanically dewatered and dried in a Krüger BioCon dryer (100-175 °C). MSS products can be delivered as de-watered sludge, as dry granules or as dry pellets.

The LT-CFB campaigns include a reference campaign on straw (REF campaign), two campaigns on mono sludge fuels (SLU campaigns) and two campaigns with co-gasification of sludge and straw (MIX campaigns). A short description of the campaigns is provided in Table 1. More details and data on fuels and LT-CFB campaigns can be found in part 1 of the study (Thomsen et al., 2016). The fuels applied in the MIX-ST and MIX-BJ experiments have been designed to provide ashes with P:K relationships around 1:2.

Table 1: Overview of Low Temperature Circulating Fluid Bed (LT-CFB) sludge gasification campaigns. WWTP: Wastewater treatment plant. Th: Thermal capacity.

Campaign description	Abbreviation	Fuel type	Sludge origin (WWTP)	LT-CFB plant
Reference campaign	REF	Crushed wheat straw pellets (Denmark)	None	Risø DTU (100 kW_{Th})
Mono-gasification of sludge from Randers	SLU-RA	Dry sludge granules	Randers	Risø DTU (100 kW_{Th})
Co-gasification of mixed fuel with sludge from Stegholt	MIX-ST	Mix: Dewatered sludge + crushed straw pellets	Stegholt	Risø DTU (100 kW_{Th})
Co-gasification of mixed fuel with sludge from Bjergmarken	MIX-BJ	Mix: Dry sludge pellets + crushed straw pellets	Bjergmarken	Asnaes Power plant (6 MW_{Th})
Mono-gasification of sludge from Bjergmarken	SLU-BJ	Dry sludge granules	Bjergmarken	Risø DTU (100 kW_{Th})

Proximate analysis of fuels samples (Thomsen et al., 2016) have shown substantial differences among the different fuels with regard to moisture content (5-30 wt% as received) and ash content (8-43 wt% dry basis) whereas the content of volatile organics (43-69 wt% dry basis) and recalcitrant carbon (14-24 wt% dry basis) as well as the higher heating value (11-16 MJ/kg as received) were more comparable.

Ash samples have been collected from the secondary cyclones (SC, Figure 1) in all campaigns. In addition to the SC ashes, a filter ash sample from the SLU-BJ candle filter as well as a final composition char reactor (CR) bed sample from the MIX-ST and SLU-BJ campaigns and a size separated sand-free char reactor bottom ash sample from the SLU-BJ campaign were collected. 2-5 kg of each ash sample was collected.

2.3 Analytical procedures

Ash samples were examined on dry basis for their content of volatile material, recalcitrant carbon and ash using standards ASTM D3174-73, DS/EN 14775 (2009) and EN 15169 (2007).

Higher Heating values were measured by a calorimetric method using a Parr 6300 Bomb Calorimeter and DS/EN 14918 (2010).

The inorganic compositions of fuels, chars and ashes from REF, MIX-ST and MIX-BJ campaigns were determined by an external laboratory, FORCE Laboratory, using a combination of DS/EN ISO 11885 (2009), DS/EN 15290 (2011), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Cl was determined using DS/EN 15289 (2011) while Hg was determined using EPA 7473 (2007). Samples from the SLU-RA campaign was analyzed at the external laboratory at Kommunekemi A/S using standard DS259 for preparation and digestion of the samples and ICP-MS by the DS/EB ISO 17294-1-2 standard for the subsequent analysis. Samples from SLU-BJ have been analyzed by ICP-OES (Optima 5300 DV, Perkin Elmer, USA) using the procedure described by Hansen et al. (2009) (Hansen et al., 2009) after digestion with HNO_3, H_2O_2 and HF.

Total C and N content was measured at the Center for Permafrost of the Department of Geosciences and Natural Resource Management, University of Copenhagen, by Dumas combustion (1020 ºC) on an elemental analyser (CE 1110, Thermo Electron, Milan, Italy).

The pH was determined by mixing 1 g of dry, grinded ash or sludge with 25 ml of milliQ water before shaking (1 hour), settling of suspended particles and measurement on a pH meter (Mettler-Toledo AG, Switzerland).

Elemental balances have been conducted based on the product distribution determined in part 1 of the study (Thomsen et al., 2016) combined with the fuel and ash compositions.

2.4 Determination of plant available P in ash

Assessment of P fertilizer quality of the ashes was conducted in two experiments: i) a short-term soil incubation study screening sludge and ash samples from all campaigns with subsequent assessment of water extractable P; ii) a plant pot experiment measuring barley aboveground biomass production and P uptake with

SC ashes from the MIX-ST campaign as P fertilizer. The soil selected for the study was taken from the upper layer of an agricultural field at DTU, Roskilde Campus (55°41'N, 12° 05'E) and contained 10% clay, 12% silt, 46% fine sand and 30% coarse sand. The soil was air-dried and sieved to obtain the fraction ≤ 2 mm for the incubation study and ≤ 1 cm for the pot experiment. The soil had a total carbon (C) content of 12 g kg^{-1}, a total nitrogen (N) content of 1.1 g kg^{-1}, a bicarbonate-extractable phosphorus (Olsen-P) content of 6 mg kg^{-1}, an extractable K content of 69 mg kg^{-1} and a pH of 5.9 (water).

2.4.1 Soil incubation study:

All MSS and ash samples were ground in a Mahlkönig Kenia Disc grinder (MAHLKÖNIG GmbH & Co. KG, Hamburg, Germany) and particles larger than 0.125 mm were extracted by sieving on a Retsch Vibro Sieve (Retsch GmbH, Haan, Germany) and subsequently crushed in a FRITSCH Mortar Grinder Pulverisette 2 (Fritsch GmbH, Idar-Oberstein, Germany). Sieving and crushing of the large particle fraction was repeated until at least 90% of the total sample mass passed a 0.125 mm sieve and all particles were smaller than 0.25 mm. Final particle size distribution of the samples was determined using sieves 25 µm, 75 µm, 125 µm and 250 µm.

Triplicates of 50 g soil/quartz sand mixture (50:50 w/w) were mixed with ash samples at a rate of 80 mg P kg^{-1} soil by thorough shaking and watered with demineralized water to 50% of the soil's water holding capacity. Mass fraction of sludge and ashes in the mixtures were: Mono-sludge ashes (SLU) = 0.1%, Dry sludge (SLU & MIX) = 0.2%, Mix ashes (MIX) = 0.3% and straw ash (REF) = 2%. Substrate-free controls and mineral P (KH_2PO_4) dosed reference samples were included. Samples were incubated in a climate chamber at 85 % RH and 20 °C for 1 week. After incubation, 0.75 g sample (dry basis) was shaken with 45 ml of purified water for 1 hour in a 50-ml Falcon tube, centrifuged (1 min, 3500 rpm), and the supernatant was filtered through a Whatman no. 5 filter paper. Extracts were stored at 4°C before analysis of water extractable P on a Flow Injection Analyzer (FIAstart 5000, FOSS, Denmark).

2.4.2 Plant pot experiment

For the pot experiment, the MIX-ST ash material was incorporated into a mixture of soil and quartz sand (50:50 w/w) at a rate of 0, 40, 60, 80, and 100 mg total P/kg dry soil with 4 replicates per treatment. Pots (2.5 kg soil substrate) receiving mineral P-fertilizer (KH_2PO_4) or straw gasification ash from the REF campaign at the same total P rates were set up as positive controls. A negative control not receiving any P fertilizer was also included. K_2SO_4 was added to all treatments except the REF treatment and the MIX-ST treatment at the highest P rate to give a final concentration of 200 mg K kg^{-1} dry soil. $CaCl_2x2H_2O$ (20 mg Ca kg^{-1} soil), $MgSO_4x7H_2O$ (9 mg Mg kg^{-1} soil), NH_4NO_3 (50 mg N kg^{-1} soil) and micronutrients (3 mg Mn, 1.2 mg Zn, 0.5 mg Cu, and 0.07 mg Mo kg^{-1} soil, respectively) were further added to each pot. During the course of the experiment, all pots received another 9 mg Mg kg^{-1} soil and 175 mg N kg^{-1} soil. Pots were randomized and placed in a growth chamber with a 16 h day^{-1} photoperiod and an average temperature of 24 /16 °C (day/night). Six seeds of spring barley (cv. Iron) were sown into each pot, which were thinned to three plants after emergence. Pots were regularly watered to maintain soil moisture at ca. 60% of the soil's water holding capacity. The aboveground biomass of barley plants was harvested after 7 weeks of plant growth, dried in an oven at 70°C for 48 h and weighed. The dry plant material was finely ground and a subsample was wet-digested in a solution of nitric and perchloric acid

(4:1, v/v). Total P concentration in the digest was measured on an AutoAnalyzer 3 (Bran+Luebbe, Norderstedt, Germany).

Statistical analyses were carried out using STATISTICA software (Statsoft Inc. 2010). All tests of significance were conducted at $P \leq 0.05$. When data were not normally distributed or showed heterogeneity of variances, they were log-transformed before analysis. Data was analyzed with a one-way ANOVA and when significant F-tests were obtained, multiple mean comparisons were carried out using Tukey's Honest Significant Difference (HSD) test.

3 Results and discussion

3.1 Proximate analysis of ash samples

Results from the proximate analysis of the ash samples showed much lower ash content in the MIX and REF SC ashes than in the SLU ashes (Table 2).

Table 2: Proximate analysis of dry ash samples. DM: Dry matter. SC: Secondary cyclone. CR: Char reactor.

Campaign	Ash sample	Volatiles % DM	Recalcitrant carbon % DM	Ash % DM
SLU-BJ	SC ash	1.4±0.3	3.0±0.2	95.7±0.2
SLU-RA	SC ash	1.1±0.3	4.3±0.9	94.6±0.9
MIX-ST	SC ash	8.9±0.1	27.6±1.3	63.5±1.3
MIX-BJ	SC ash	5.0±0.2	22.0*	73.0*
REF	SC ash	6.3±0.3	36.7*	57.0*
SLU-BJ	Filter ash	1.6±0.2	3.5±0.1	94.9±0.1
SLU-BJ	CR bottom ash	1.8±0.1	2.6±0.2	95.6±0.2

Likewise, the content of volatile organic material was a factor of 4-8 higher in the MIX and REF SC ashes than in the SLU ashes while the content of recalcitrant carbon was a factor of 5-12 higher. Despite the differences in the total quantity, the ratio between the volatile and recalcitrant carbon was found to be relatively stable (0.2-0.5) among all SC ashes. Applying data on the proximate composition of the fuels as well as product distribution from part 1 (Thomsen et al., 2016) it is estimated that the degree of conversion of volatile organics was around 99% in all campaigns, and that the degree of conversion of recalcitrant carbon varied between 82-86% in the MIX and REF campaigns and 94-95% in the SLU campaigns. The data cannot be used to suggest, which materials will provide the most recalcitrant carbon for soil sequestration, but there will be a much larger potential pool of recalcitrant carbon as well as volatile organics in the ashes from co-gasification than in the ashes from MSS gasification alone.

3.2 Elemental analysis and elemental mass balance

Most of the N originally present in the fuel was transferred to the gas phase while the C content in the ashes varied substantially with the type of fuel (Table 3).

Table 3: C and N content of fuels and ashes. DM: Dry matter. SC: Secondary cyclone. CR: Char reactor.

Campaign	Sample	Total C % DM	Total N % DM
SLU-BJ	Sludge	27.6±0.1	3.9±0.0
SLU-RA	Sludge	28.7±0.4	3.9±0.1
MIX-ST	Sludge	30.6±0.1	4.4±0.0
MIX-BJ	Sludge	27.6±0.1	3.8±0.0
SLU-BJ	SC ash	4.2±0.0	0.4±0.0
SLU-RA	SC ash	6.7±0.1	0.4±0.0
MIX-ST	SC ash	25.5±0.0	0.7±0.0
MIX-BJ	SC ash	23.8±0.2	0.4±0.0
REF	SC ash	44.5±0.3	0.4±0.0
SLU-BJ	Filter ash	5.2±0.0	0.4±0.0
SLU-BJ	CR ash	7.1±0.1	0.4±0.0

Combining data from Table 3 and the ash production rates from the different campaigns (Thomsen et al., 2016), it is determined that in mono-sludge campaigns 1-2 % of the fuel N is recovered in the SC ash and 0-1% is captured in the Filter ash. In the reference campaign and the two mix campaigns, 4-5% of the fuel N is recovered in the SC ashes. From an N-conservation point of view, it seems like there is an advantage from co-gasification in this regard, especially since the N concentration in dry sludge fuels can be expected to be at least 4-5 times as high as in dry mix and straw fuels (ECN, 2016a, 2016b). However, plant availability of N in sewage sludge biochar is reported to be substantially lower than in the feedstock, decreasing with increasing conversion temperature (Wang et al., 2012).

LT-CFB ashes produced from straw have previously been found to be highly suitable for carbon sequestration and provide other soil benefits as well (Hansen et al., 2015). However, the very low carbon content in the mono-sludge SC ashes decreases the potential effect of using these ashes to sequester carbon and increase the content of organic carbon in soils, and could also affect other common biochar characteristics like high cation exchange capacity, water retention etc. In this regard co-gasification of MSS and straw is also found to have an advantage compared to mono-gasification of MSS. Char from MSS pyrolysis as well as ashes from straw gasification has recently been shown to increase these soil fertility parameters significantly, but no studies on the effect of ashes from MSS gasification or co-gasification have been found (Hansen et al., 2016; Sousa and Figueiredo, 2015).

When ash is considered as a fertilizer, the content of major nutrients P and K is especially interesting.

The P content in sludge is substantial while the K content is quite low. In straw, the relationship is the opposite. In mixed fuels it is thereby possible to design a P-K relationship suitable for agricultural use (Figure 2).

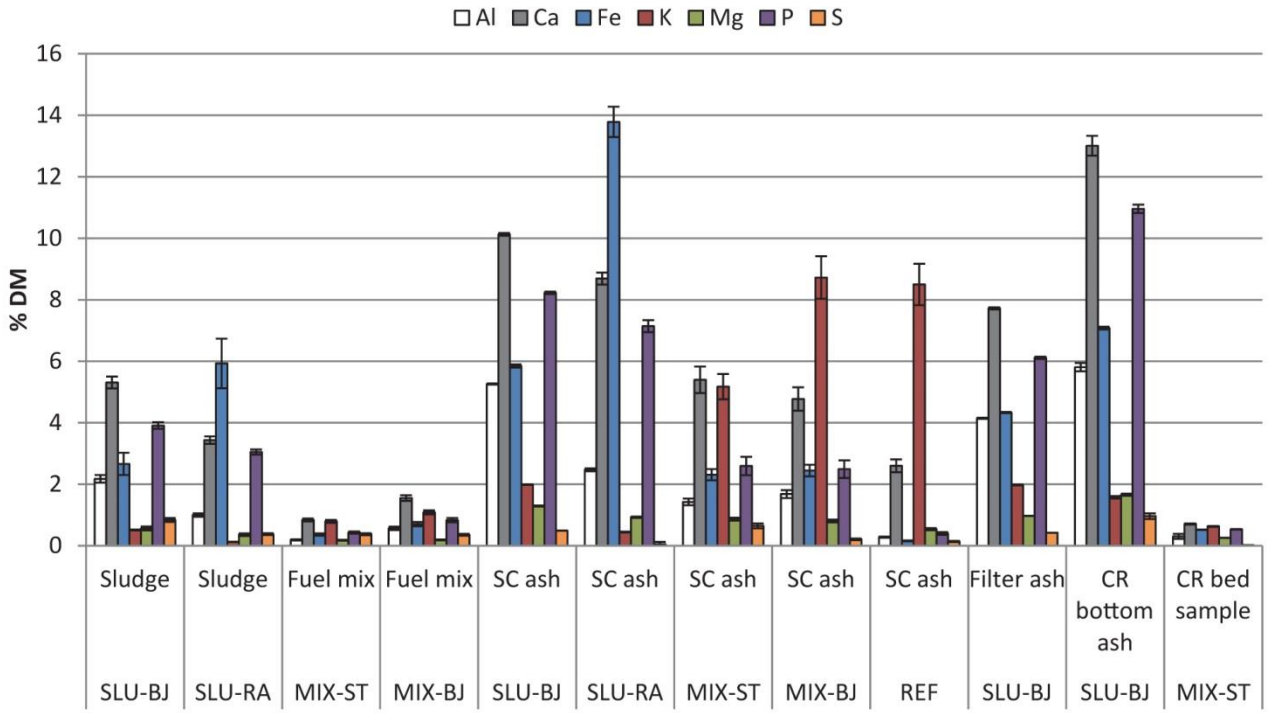


Figure 2: Content of selected elements in fuel and ash samples. Results given in % of dry mass (%DM). SC: Secondary cyclone. CR: Char reactor.

If including the content of recalcitrant carbon as a key characteristic of the ashes, the relationship between carbon, phosphorous and potassium can be expressed roughly as C:P:K = 1:1:0 (SLU-BJ & SLU-RA), 10:1:2 (MIX-ST), 10:1:4 (MIX-BJ) and 110:1:21 (REF). The optimal P:K ratio will vary with soil, plant and climate, but the obtained results clearly indicate that it is possible to design the SC ash fertilizer in a very wide range of compositions depending on the MSS:straw ratio in the fuel. This is very important in regard to optimal utilization of P and K resources and economical value of the fertilizer ashes.

The content of aluminum (Al) and especially iron (Fe) has been found to have a profound negative influence on the plant P availability in sludge and deriving ashes (Krogstad et al., 2005; Pettersson et al., 2008). The ratio between Al and Fe in sludge was largely maintained in the ashes, and concentrations were increased with 100-650% and 50-550% respectively.

Other elements such as magnesium (Mg), calcium (Ca) and sulfur (S) are also valuable plant nutrients contained in ashes (Nieminen et al., 2005). The content of Ca (1-13%) was found to be very high in ashes from mono-sludge campaigns. The concentrations of Ca and Mg in the ashes increased with 50-550% and 50-650% respectively while the concentrations of S in the ashes were 15-170% of those in the corresponding fuel.

However, plant availability of these elements in the ash products might vary, as shown in experiments by Nieminen et al (2005) using wood ash (Nieminen et al., 2005).

When applying sludge or ash as fertilizer or soil enhancer, the content of heavy metals is usually strongly regulated. In Denmark, heavy metals in sludge and ash are regulated either per unit of dry mass or per unit of total P mass. In the European Union, the regulation is per dry mass. Both set of results are included in Table 4.

Table 4: Contents of selected heavy metals in fuels and ashes. Results as mg heavy metal per kg dry matter (DM) and per kg total P. SC: Secondary cyclone. CR: Char reactor. BA: Bottom ash. BS: Bed sample. Grey marks a violation of the legal threshold for use of sludge and waste products in agricultural systems in Denmark (Danish Ministry of the Environment, 2008, 2006)

		Cd		Ni		Pb		Hg	
		mg/kg DM	mg/kg P	mg/kg DM	mg/kg P	mg/kg DM	mg/kg P	mg/kg DM	mg/kg P
SLU-BJ	Sludge	2.5±0.1	63±2	23±2	600±40	N.A	N.A	N.A	N.A
SLU-RA	Sludge	1.0±0.0	34±1	24±2	800±60	41±4	1300±100	1.5±0.1	49±5
MIX-ST	Fuel mix	0.6±0.1	142±4	10±1	2400±0	5±1	1200±100	0.1±0.0	20±2
MIX-BJ	Fuel mix	0.5±0.0	59±0	6±0	680±20	10±1	1300±100	0.0±0.0	1±0
SLU-BJ	SC ash	5.5±0.1	54±4	158±1	1900±0	110±0	1300±0	N.A	N.A
SLU-RA	SC ash	1.5±0.1	22±1	87±7	1200±100	84±2	1200±0	0.2±01	3±1
MIX-ST	SC ash	1.1±0.0	41±0	68±5	2600±900	42±4	1600±200	0.0±0.0	0±0
MIX-BJ	SC ash	0.1±0.0	4±0	15±1	600±40	47±4	1900±200	0.0±0.0	0±0
SLU-BJ	Filter ash	12±0	197±0	153±4	2500±100	83±1	1400±0	N.A	N.A
SLU-BJ	CR BA	1.6±0.1	15±0	67±3	610±30	160±10	1400±100	N.A	N.A
MIX-ST	CR BS	0.0±0.0	6±0	7±1	1300±100	4±1	830±80	0.0±0.0	0±0
Legal limit*		0.8	100	30	2500	120	10000	0.8	200

*(Danish Ministry of the Environment, 2008)

Legal thresholds per basis of dry mass were breached several times for contents of cadmium and nickel and a few times for lead and mercury. The thermal process concentrated thermally stable elements in the ashes as also observed in the assessment of major fertilizer elements (Figure 2), which is a severe drawback in regard to legal thresholds on basis of mass. With the regulation of heavy metals per unit of P, the pattern is different. For nickel and lead, the thermal gasification increased the concentration per unit of P, but the level of increase varied, and in a few cases the concentrations were even decreased. Ni content per unit of P increased substantially in all 100 kW campaigns (SLU-BJ, SLU-RA and MIX-ST). Little or no P is expected to be lost at the low temperatures, and the increase in the Ni/P is expected to be due to leaching of Ni from the CR reactor steel lining as also observed in a study by Hernandez et al. (2011) (Hernandez et al., 2011). The pattern was not expressed in the 6 MW campaign (MIX-BJ), and this is consistent with the hypothesis, as the 6 MW CR reactor has inner refractory lining.

For cadmium and mercury there was a profound reduction per unit of P in all cyclone and bottom ash fractions collected. Mercury was almost completely removed in all ashes while the content of cadmium per unit of P was reduced with 13-96%. These findings are very important as mercury and cadmium are often considered the

most problematic heavy metals when using MSS or ashes in agriculture (Roberts, 2014; Werther and Ogada, 1999). The cadmium content per unit of P decreased significantly in SC ashes but much more in CR ashes. Furthermore, the reduction of Cd per unit P in SC ashes as well as in CR ashes compared to their parent fuels was a lot higher in MIX campaigns than in mono-sludge campaigns. During the thermal process, cadmium is evaporated out of the particulate matter and into the hot gas phase as a result of the temperatures in the pyrolysis and char reactors. Elemental cadmium melts at 321 °C and has a fairly high vapor pressure around 50 kpa at 720 °C. Another relevant Cd-species is cadmium chloride ($CdCl_2$), which melts around 568 °C but has a vapor pressure generally a factor of 10 lower than elemental cadmium (Skudlarski et al., 1987; Stull, 1972). Some of the Cd liberated to the gas phase in the hot CR is probably re-condensed on the surface of particulate matter in the colder secondary cyclone. This explains the elevated Cd-concentration in the SC ash compared to the CR ash. Through the secondary cyclone, the gas temperature drops to around 600 °C. At this temperature the vapor pressure of cadmium has decreased with almost a factor of 5 compared to the char reactor environment. As the gas cools further towards the filter, even more Cd is condensing out on entrained and captured particles. This explains the high Cd/P relationship in the SLU-BJ filter ashes, which was more than three times higher than in the fuel, 4 times higher than in the SC ash and 13 times higher than in the CR bottom ashes. Based on the high toxicity of Cd, it is essential to keep the particle temperatures as high as possible in the separation processes following the gasification. If ash separation and handling is properly addressed, the LT-CFB sludge treatment can in this way be used to recover P for use in agricultural systems where it would otherwise be banned. The hot gas candle filter applied in the SLU-BJ campaign was found to collect more than half of the released cadmium, and this could be an important aspect in relation to downstream treatment of product gas or boiler exhaust gas. Lowering the temperatures in the filter would most likely increase the Cd recovery in this part of the system.

Elemental system balances of the SLU-BJ and MIX-ST campaigns have been established for selected nutrients and heavy metals (Figure 3 and Figure 4).

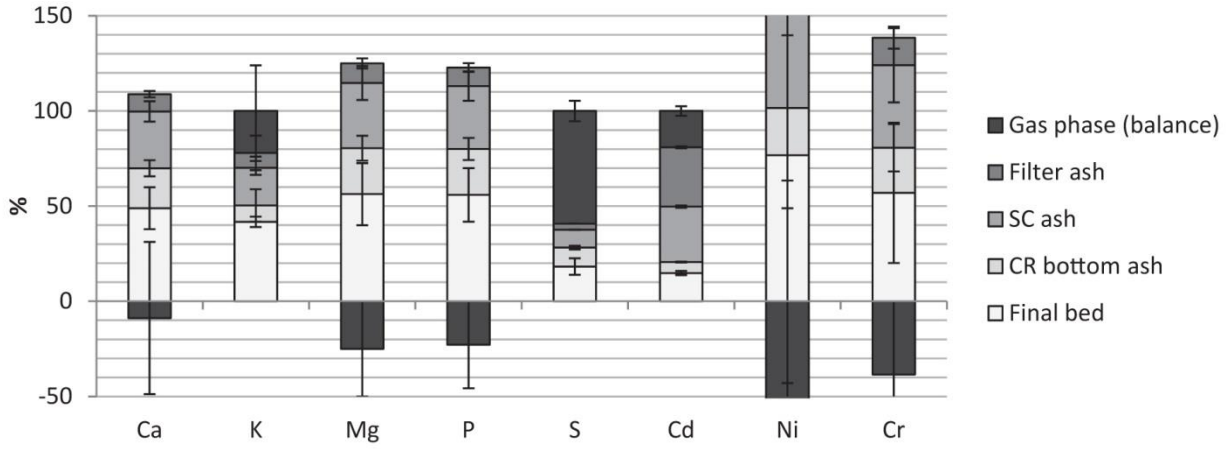


Figure 3: Elemental balance of SLU-BJ. Results given as element recovered in percent of element in fuel + virgin bed material

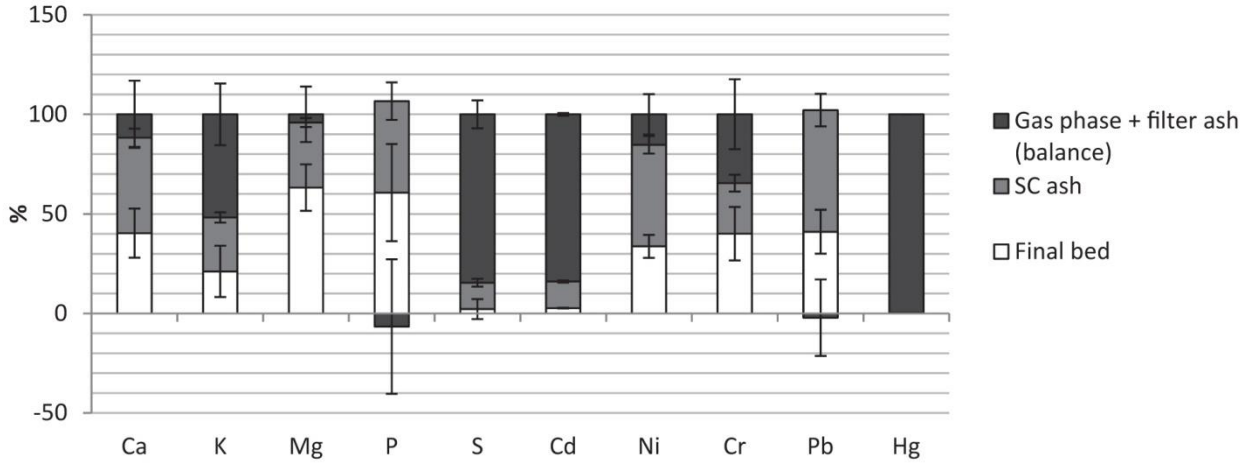


Figure 4: Elemental balance of MIX-ST. All results given as element recovered in percent of element in fuel + virgin bed material

The uncertainty related to the elemental mass balance is significant but a few strong trends can be derived. The substances Mg, P, Ca, K and Cr were allocated quite consistently to the SC ash of both campaigns, but the distribution among the CR accumulation and gas phase was less consistent. In the SLU-BJ campaign the main inconsistency seems to relate to the Ni balance. The Ni-balance gap supports the theory previously presented regarding steel alloy leaching in the 100 kW campaigns. However, this is not supported by the MIX-ST results indicating that there is a big influence of the fuel and ash composition on the release of heavy metals. It is expected that the increase in total system Cl content by co-gasification with straw can facilitate additional release of heavy metals as also seen in Cd and Cr balances. This approach has been studied extensively as a MSS ash upgrading method (Adam et al., 2009; B Nowak et al., 2012; Benedikt Nowak et al., 2012; Vogel et al., 2011). The remaining results of the SLU-BJ campaign are in quite good agreement with the results from a series of tests conducted in a Circulating Fluidized Bed gasifier in Finland in the late 1990's (Kurkela, 2010).

3.3 pH

The pH values of the sludge samples were close to 7 for all materials (Table 5). Gasification consistently increased pH compared to the respective sludge fuels to values between 10 and 11.

Table 5: pH of sludge and ash samples in water. Maximum deviations between duplicates < 0.5%. SC: Secondary cyclone. CR: Char reactor.

	Sludge	SC ash	Filter ash	CR Bottom ash
SLU-BJ	7.3	10.4	10.0	10.5
SLU-RA	6.8	11.1	N.A.	N.A.
MIX-ST	6.9	9.9	N.A.	N.A.
MIX-BJ	6.7	10.4	N.A.	N.A.
REF	N.A.	10.7	N.A.	N.A.

3.4 Ash P fertilizer quality assessment

3.4.1 Soil incubation study

In the incubation study conducted, fuel mixes and straw fuels were not applied as they do not have practical relevance as pure P fertilizers due to very low P contents (Figure 2). The P concentration in the REF SC ash is also too low for use as pure P fertilizer, but it is included for interpretation of the mixed fuel ashes.

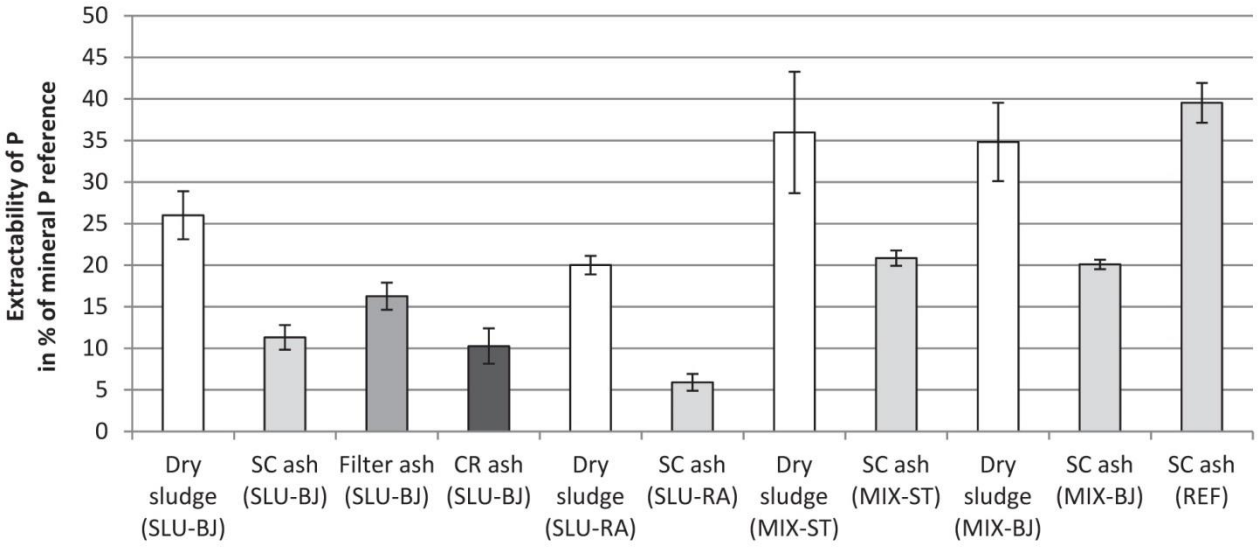


Figure 5: Water extractable P in soil after the amendment with sludge and ash samples, relative to the mineral P reference. Values of the non-amended control soil have been subtracted. SC: Secondary cyclone. CR: Char reactor.

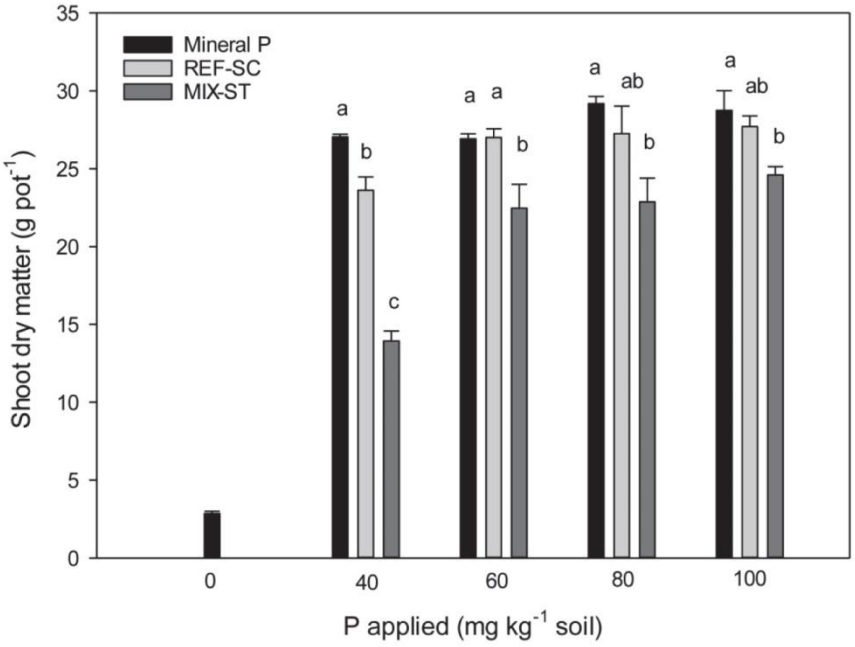
The screening results in Figure 5 show reduced plant P availability in all incubated SC ashes compared to their parent sludge samples. The results also show that MIX ashes perform slightly better than all SLU ashes. In a previous study, co-pyrolysis of slaughterhouse waste with wood and corn residues have been found to lead to a beneficial modification in the P species and an increase in the P solubility and P fertilizer quality (Zwetsloot et al., 2015). It is therefore hypothesized that a similar effect could be part of the explanation behind the improved P availability of MIX ashes in the incubation study. However, with the current set of results, the influence from variations in the sludge composition cannot be distinguished from the influence of the co-gasification with straw to an extent where it is actually possible to conclude if there is a significant improvement in the P quality. The mono-straw SC ash (REF) has a comparatively high plant available P pool, which makes it difficult to conclude on the optic of the potential improvements in the MSS P from go-gasification. The good REF P result could be due to the P speciation alone but might as well be due to influence of other ash characteristics. As the P content of the REF SC ashes is very low, the dosage of REF SC ashes was a lot higher than for the other ashes – by weight as well as volume. Therefore, the potential effects on other soil parameters such as pH are expected to be higher for this ash than for the others.

The MSS sample and SC ash from Randers WWTP (SLU-RA) performed worse than the comparable MSS and SC ash samples. This may be expected from the fact that the dosing of Al and especially Fe-based precipitation chemicals, which have the ability to form highly insoluble aluminum- and iron phosphates, is higher at Randers compared to the other WWTPs (Parés Viader et al., 2015). However, despite the fact that the use of metal based precipitation chemicals is higher at Bjergmarken WWTP than at Stegholt WWTP, no obvious difference between MSS or ash samples from the two MIX-campaigns are obvious. Measured per unit of total P, the Al content in the sludge from Bjergmarken is almost a factor of 1.5 higher than the Al content in sludge from Stegholt. The iron content on the other hand was almost identical in the two sludge samples and exactly the same in the mixed samples. Assuming that the metal-based precipitation chemicals in general have a strong influence on the P-solubility, these results could indicate that the iron content is a more important influence on the P water solubility than the aluminum content. This is corroborated by a study of Pettersson et al. (2008), who reported P extraction from sewage sludge ashes being more difficult when P had been precipitated with Fe than with Al-based chemicals (Pettersson et al., 2008).

The SLU-BJ filter ash performed better than the SC ash and CR bottom ash from the same campaign in terms of P availability. From the data in Figure 2 the main differences in the elemental composition between the ash fractions seem to be an increased content of alkali metals (Ca and K) per unit of P in the filter ash. This is also a general trend in the MIX and REF ashes showing higher P availability compared to the SLU ashes. However, despite the higher amount of available soil P after application of the filter ash compared to the SC ash and CR ashes, the high relative content of heavy metals Ni, Cr and especially Cd makes this ash unsuitable for agricultural application.

3.4.2 Plant pot experiment

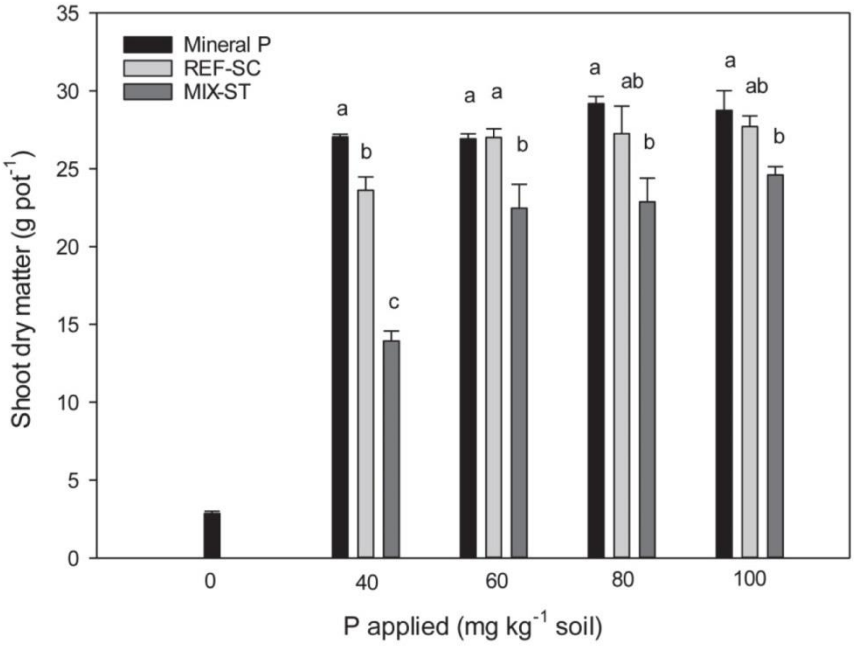
366 Without added P, the growth of the barley plants was extremely restricted (only 2.9 g DM per pot,



367

368 Figure 6) and the addition of mineral P as well as ash greatly improved plant dry matter production already at
369 40 mg P kg^{-1} soil. As observed in previous experiments (Müller-Stöver et al., 2012), REF straw ash was very
370 effective in supplying P to the plants, especially at higher application rates. Only at the lowest dosage applied,
371 REF ash application resulted in a significantly lower dry matter yield compared to mineral fertilizer, while at all

372 other dosages, the same amount of plant dry matter as with mineral fertilizer could be produced with ash.



373 However, plant P uptake (

374 Figure 6) still showed the differences between P availability in the two materials, indicating that P uptake from
375 mineral P at the higher dosages was already beyond a level that still increases biomass production. In contrast,
376 the application of the MIX-ST ash - although also showing a strong positive dose-yield response and an
377 increasing relative effectiveness compared to mineral fertilizer– did never result in the same dry matter
378 production as the mineral fertilizer. However, P uptake was statistically similar at 60 and 80 mg P kg^{-1} soil
379 between REF straw ash and MIX-ST ash, and no statistically significant difference in dry matter production

could be observed between the two ash treatments at the two highest phosphorus levels (

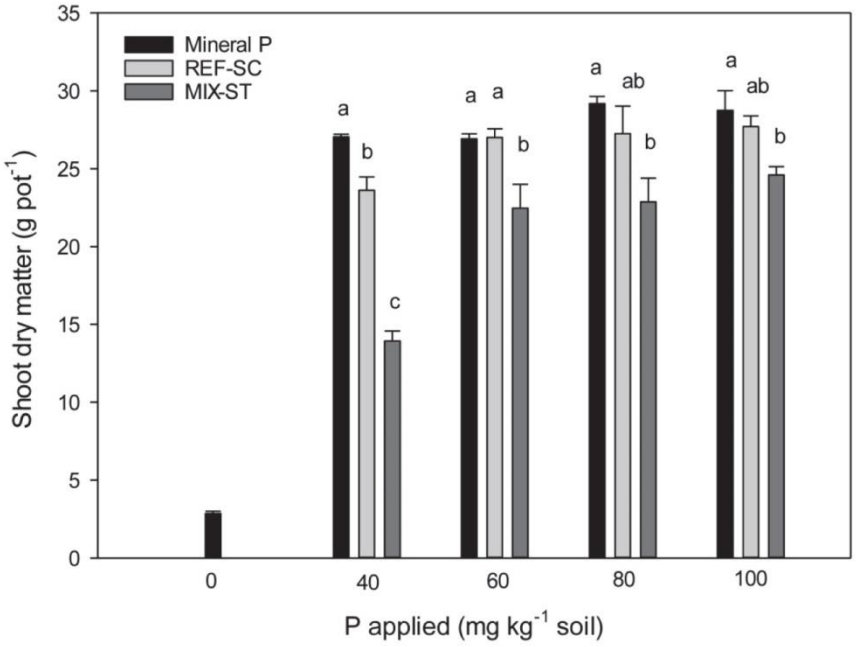


Figure 6 and Figure 7). P originating from both fuel components appeared plant-available in the MIX-ST ash, since taking the fuel mixing ratio and the P content of the straw ash into consideration, at the highest application rate a maximum of 10 mg P kg^{-1} soil could originate from the straw component in the mixed ash.

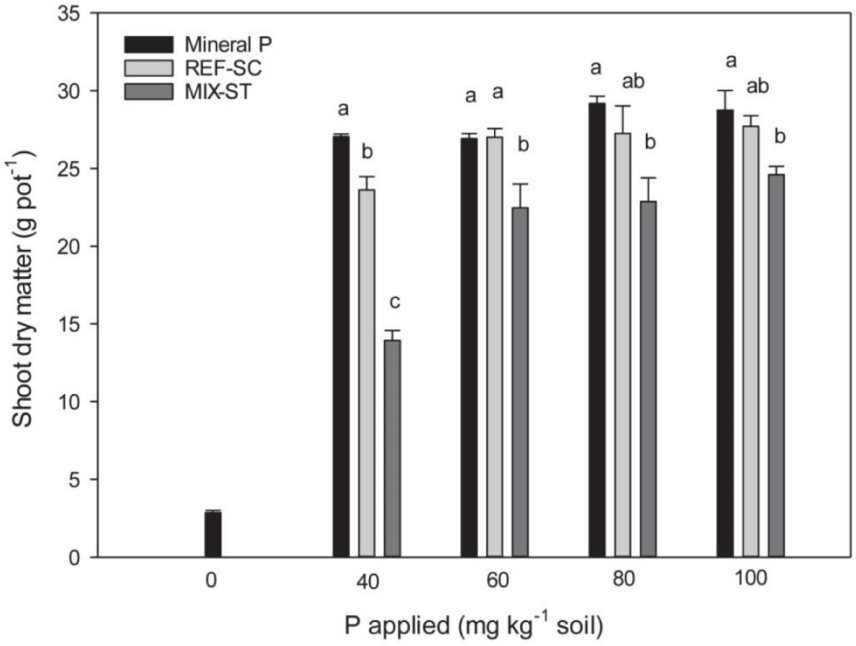


Figure 6: Shoot dry matter in the treatments receiving mineral fertilizer or two different ash materials in various P application rates. Different letters indicate statistically significant differences within the same application rate. Results on basis of total dry matter.

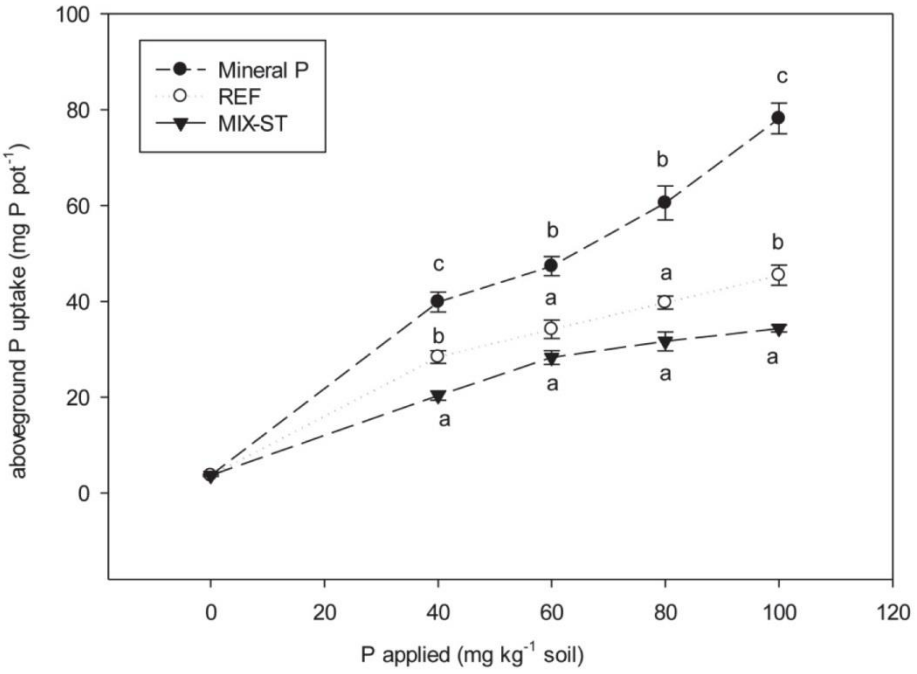


Figure 7: Plant phosphorus uptake in the treatments receiving mineral fertilizer or two different ash materials in various application rates. Different letters indicate statistically significant differences within the same application rate.

Qualitatively, the results of the pot experiment correspond quite well to those of the P screening. However, the performance of the REF and MIX-ST ashes relative to the mineral fertilizer was generally better in the pot experiment than in the simple screening. A weak correlation between water-extractable P and plant P uptake from more complex P sources has been reported previously for rock phosphate (Bationo et al., 1991). Mackay et al. (1984) concluded that although water extraction might be useful to assess relative differences between fertilizer materials such as rock phosphates, it may be misleading when only relying on extraction methods to evaluate their agronomic effectiveness compared to more soluble P sources (Mackay et al., 1984).

Conclusion

Ash product fertilizer quality has been compared across five successful experimental LT-CFB campaigns with different fuels and plant scales. Four of the fuels were municipal sewage sludge or a mix of sludge and cereal straw. The fifth fuel was a reference straw fuel. Results have indicated that it is possible to modify desired characteristics of char and ash products from sludge gasification by co-gasification with straw in different ratios. If the sludge is dry, the mixing ratio can be from 0-100% sludge.

The P fertilizer quality of ash and char samples was examined as water-extractable P after soil amendment and in a plant pot experiment. Qualitatively, the results obtained after 1-week soil incubation corresponded to the

results from the pot experiment. However, fertilizer efficiency of the ash samples had a tendency to be underestimated in the short-term assessment, revealing the need for more comprehensive soil-plant experimentation also including different soil types and plant species. Nevertheless, ashes from co-gasification of straw and sludge had higher plant P availability than ashes from mono-sludge gasification, showing the potential to be developed into alternative P-fertilizer products.

Co-gasifying straw with sludge consistently increased ash fertilizer quality in regard to NPK composition, P plant availability and by a reduced content of heavy metals especially cadmium. In addition, co-gasification led to a higher content of recalcitrant carbon in the ashes increasing potential for beneficial biochar characteristics and long term carbon sequestration. Extracting ashes from the char reactor was found to yield ashes with an even lower content of heavy metals than the SC ashes, but the P fertilizer value was at the same time reduced. It was found that LT-CFB gasification of sludge was an effective way to purify and sanitize sewage sludge for subsequent use in agricultural systems, especially when co-gasifying sludge with cereal straw.

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