Chemical Engineering Journal 163 (2010) 1–9

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

# The composition and dissolution in citric extractants of ash from the thermal gasification of pig manure

Kuligowski Ksawery[a,*], Gilkes Robert John[b], Poulsen Tjalfe Gorm[a], Yusiharni Baiq Emielda[b]

[a] *Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Sohngaardsholmsvej 57, 9000 Aalborg, Denmark*
[b] *School of Earth and Environment, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia*

ARTICLE INFO

*Article history:*
Received 10 April 2010
Received in revised form 15 June 2010
Accepted 16 June 2010

*Keywords:*
Animal manure ash
Citrate extraction
Phosphate fertilizer
Apatite
X-ray diffraction
Scanning electron microscopy

ABSTRACT

Ash derived from the thermal gasification of anaerobically digested, dried and pelletized pig manure (GA) was characterized by standard Association of Official Agricultural Chemists (AOAC, 1990) methods of chemical analysis for phosphorus soluble in citric acid ($P_{CA}$), neutral ammonium citrate ($P_{NAC}$) and alkaline ammonium citrate ($P_{AAC}$) for several extraction times. Concentrations of other elements in the three extracts were measured by inductively coupled plasma with optical emission spectroscopy (ICP-OES). The ash had 54.4 g/kg total P (TP), 28.2 g/kg $P_{CA}$ after 6 h extraction and 48.7 mg/kg water soluble phosphorus ($P_{H_2O}$) and is therefore suitable for use as a P-fertilizer. The very high pH (12) of the ash indicates its strong acid neutralizing ability when applied to acidic soils, although the very high lime content of the ash may reduce P bioavailability in soils. Lime-free gasifier ash (lf-GA) was obtained by treating GA with buffered sodium acetate solution (pH 5) for periods up to 120 h. Removal of calcite equivalent to 70% of initial GA mass reduced pH to 6, increased TP (about 2 times), $P_{H_2O}$ (10 times) and $P_{CA}$ (1.5 times). X-ray powder diffraction (XRD) patterns of lf-GA indicate that P is mostly present as intermediate hydroxyl-apatite/carbonate-apatite. Apatite grains of various Ca (20.2–48.5%) and P (8.4–17.8%) concentrations were determined by scanning (SEM) and transmission (TEM) electron microscopy with energy dispersive X-ray spectrometry (EDS). Other elements in lf-GA are: Fe (5–15%), Si (<10%), S (<3%) and Na, Mg, Al, Cl, K, Ti (<1% each). The ash contained minor quartz, feldspar and ilmenite.

## 1. Introduction

Acidic soils are commonly P-deficient and consequently require both P-fertilization and liming. In regions with concentrated livestock farming (e.g. Netherlands, Germany, Denmark) the P present in animal manure applied to soil often exceeds the local crop requirement, and leaching or surface runoff of manure causes environmental problems such as eutrophication of water bodies. Recycling manure P to P-deficient regions is especially attractive because of increasing P-fertilizer costs (Van Kauwenbergh [1]). Long distance transport of the raw manure is costly due to its high water and organic matter contents so that the development of on-site liquid–solid separation involving thermal treatment of separated manure (pig, poultry, turkey) dry matter for energy extraction (Buckley and Schwarz [2]; Babu [3]; Stoholm [4]; Poulsen et al. [5]) and export of the P-rich ash as a fertilizer (Yusiharni et al. [6]; Kuligowski et al. [7]) is of interest. Thermal gasification is a technology that is well suited for use at the farm scale for producing a combustible gas that may subsequently be sold for further energy production. The technology is also able to extract more energy from the manure compared to anaerobic digestion. During the period 1990–2007, global pork production increased by approximately 2.5% annually exceeding 100 million tons in 2005 (Pig International [8]). This corresponds roughly to a global pig manure production of 1.5 billion metric tons (about 1.5 $km^3$) with a total potential energy content of $1.4 \times 10^{18}$ J and a total P content of 1.5 million metric tons. It is projected that pig production will continue to grow in response to increasing demand. Animal manure is therefore increasingly being regarded as an industrial waste that needs to be managed in an environmentally sound manner.

Ash from gasified pig manure has relatively high plant nutrient concentrations (typically 5.4% P, 3.6% K) (Rubæk et al. [9];

---

*Abbreviations:* GA, gasifier ash; lf-GA, lime-free gasifier ash; IA, incinerator ash; GAw1, gasifier ash washed with sodium acetate buffered solution after first extraction step; GAw2, gasifier ash washed with sodium acetate buffered solution after second extraction step; GAw2 < 100 μm, gasifier ash washed with sodium acetate buffered solution after second extraction step, screened through 100 μm sieve; AOAC 1990, Association of Official Agricultural Chemists; CA, citric acid; NAC, neutral ammonium citrate; AAC, alkaline ammonium citrate; $P_{CA}$, phosphorus soluble in citric acid; $P_{NAC}$, phosphorus soluble in neutral ammonium citrate; $P_{AAC}$, phosphorus soluble in alkaline ammonium citrate; TP, total phosphorus; $P_{H2O}$, water soluble phosphorus; $TP_{H2O}$, total water soluble phosphorus; EDS, energy dispersive X-ray spectrometry.

* Corresponding author. Tel.: +45 9940 8493; fax: +45 9940 0558.
*E-mail address:* ksawerykuligowski@o2.pl (K. Ksawery).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.06.024

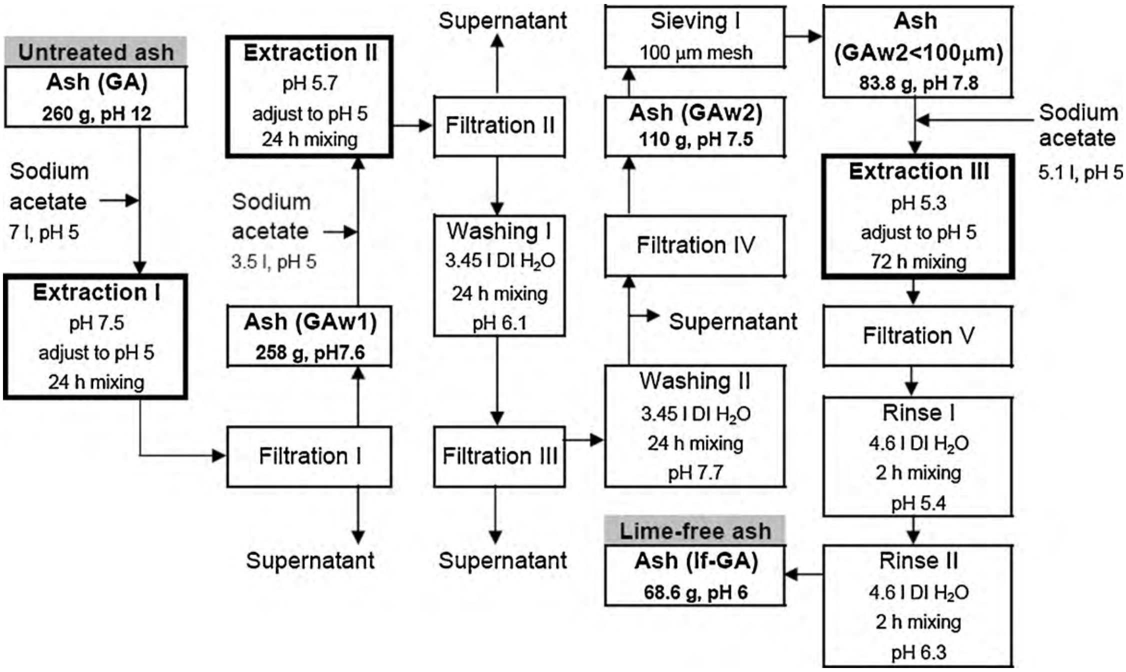


**Fig. 1.** Process schema for stepwise dissolution of carbonates and soluble salts from the gasifier ash (GA). Modified from (SSSA [19]).

Kuligowski et al. [7]), and its high alkalinity (due to considerable amounts of Ca) could be used to raise the pH of acidic soils. The net alkalinity of the ash depends largely on the sulphur (decreases pH) and calcium (increases pH) concentrations of the ash (Jala and Goyal [10]). The high neutralizing value of other ash by-products such as wood fly ash (Cavaleri et al. [11]; Soon et al. [12]) and coal fly ash (Pathan et al. [13]; Jala and Goyal [10]) has been already proven, however their nutrient concentrations are usually much lower than for animal manure ashes (Pathan et al. [13]; Yusiharni et al. [6]). Raising soil pH through adding liming agents eliminates Al and Mn toxicity, supplies Ca, increases Mo availability and increases the biological activity of the soil (White [14]). The availability to plants of P in ash depends on its chemical form and on the lime content of the ash as dissolution of P compounds is reduced at high pH. To assess the P availability and lime content of ash, the mineralogy, morphology and chemical composition of the ash must be examined. Ashes from the combustion of coal, wood and animal litter have been studied by several authors including Vamvuka and Zografos [15] and Yusiharni et al. [6]. The bioavailability of elements in ash is determined by associations of these elements with particular compounds, so that information of the identity and composition of compounds in ash is useful for predicting agronomic effectiveness (El-Mogazi et al. [16]). Yusiharni et al. [6] found that calcite, apatite and quartz were the most abundant compounds in chicken litter ash, but knowledge of the compounds in other animal manure ashes is rather limited.

The aim of this study was to investigate the composition of ash from thermally gasified pig manure with respect to P solubility and P compounds. Dissolution of P in various extractants (water, citrate solutions) according to standard AOAC fertilizer analysis procedures was used to evaluate plant available P for both raw ash and ash from which lime had been removed. Both P speciation and lime content of the ash affect interactions in the ash–soil–plant system and must be determined in order to assess the likely agronomic effectiveness of ash compared to conventional mineral fertilizer.

## 2. Materials and methods

### 2.1. Thermal treatment of pig manure

Pig manure ash (GA) was obtained by thermal gasification of anaerobically digested, dewatered, thermally dried and pelletized pig manure (90% dm) supplied by the Fangel Biogas Plant, Denmark. The gasification process was conducted in a 500 kW Low Temperature Circulating Fluidized Bed (LT-CFB) pilot scale gasifier developed by Danish Fluid Bed Technology and its partners at the Technical University of Denmark in Lyngby. The gasifier operates at 700–750 °C and is designed especially for low-grade biomass and waste fuels including agricultural biomass such as cereal straw, energy crops and animal manure. Details of the gasification process can be found in Babu [3], Stoholm [4], Stoholm et al. [17] and Carlsen [18]. The ash from the gasifier was analyzed in this research. Additional pelletized, dried, anaerobically digested manure was incinerated at 1000 °C for 24 h and the resultant ash (IA) was analyzed for comparison purposes. For a complete description of the chemical composition of materials and analytical methods see Kuligowski et al. [7].

### 2.2. Removal of lime from the ash

It was necessary to remove free lime from the ash in order to identify the P compounds in ash. GA was treated with 0.5 M sodium acetate ($CH_3COONa$) solution adjusted to pH 5 with acetic acid ($CH_3COOH$) according to the modified ASA method (SSSA [19]) by which carbonates in soil are dissolved in buffered sodium acetate solution (pH 5).

An ICP-OES analysis of an acid digest was initially used to determine an approximate elemental composition to be used for estimating the amount of ash required for the carbonate dissolution procedure so as to obtain a sufficient amount of the P compound(s). The approximate mineral composition of GA determined by XRD was: calcite (∼70%), quartz (∼15%), apatite (∼10%), halite (1%) and others (4%) (w/w). A schematic of the stepwise carbonate removal procedure is shown in Fig. 1. The three largest frames in the figure (extraction I, II and III) denote the main extraction processes with buffered sodium acetate solution, each extraction required fresh solution adjusted to pH 5 with acetic acid. Each extraction took place in a 10 l bucket with perforated lid (to allow $CO_2$ to escape) placed on a mechanical shaker. The five smaller frames in Fig. 1 identify all ash residue materials, i.e. the initial material (untreated ash; GA), intermediate products (ashes with lime partially removed; GAw1, GAw2, GAw2 <100 μm) and final product (lime-free ash; lf-GA). The intermediate products were sampled for determination of their lime content after extraction I (GAw1), extraction II (GAw2) and after sieving through a 100 μm mesh (GAw2 < 100 μm). After each extraction in sodium acetate solution, the ash suspension was filtered with a vacuum pump and filter paper to remove exhausted sodium acetate solution and minimize loss of ash materials. The suspension was sieved through a 100 μm mesh after extraction II to remove the largest quartz grains. The ash collected on the filter paper was washed two times with 3.45 l of DI water and then dried at 60 °C for 24 h prior to further analyses. All of the above five ash materials were analyzed by XRD to determine the presence and intensity of calcite peaks in the diffractograms which provided an indication of the effectiveness of the lime dissolution procedure. pH was measured in a 1:25 solid:DI water extract. The treatments were carried out in duplicate for all materials. The total extraction time for the ash was 172 h (120 h in sodium acetate and 52 h in DI water).

### 2.3. Ash chemical composition

Total element concentrations in GA and lf-GA were measured using a PE ELAN 600 inductively coupled plasma with optical emission spectroscopy (ICP-OES) instrument (Perkin-Elmer, Norwalk, CT, USA) after concentrated perchloric acid ($HClO_4$) digestion. Because untreated ash (GA) contained high amounts of carbonates, samples of 0.2 g had been pretreated with dropwise (0.75 ml) addition of concentrated nitric acid ($HNO_3$) until the reaction was less vigorous. Next, 2 ml of $HClO_4$ was added and stepwise digestion was performed for 70 min at temperatures of 130–190 °C. Final extracts were diluted with MilliQ water to a final volume of 20 ml.

Total P (TP) concentrations were determined on sulphuric acid digests, as this method had been previously found to be most reliable for this type of sample (Kuligowski et al. [7]). Material samples of 0.1 g were treated with 25 ml of 0.04 M $H_2SO_4$ and 5 ml of peroxodisulphate solution ($K_2S_2O_8$), autoclaved at 120 °C for 30 min, filtered through 0.22 μm Millipore filter and diluted with 0.04 M $H_2SO_4$ to concentrations measurable by molybdate blue colorimetry (0.1–1 mg/l). Additionally TP was measured for ash after partial removal of lime (GAw2 < 100 μm) to check the effect of sodium acetate extraction on P loss. To determine water soluble elements in ash leachates, 1 g of ash was mixed with 200 ml of DI water and placed on a mechanical shaker for 24 h. Extracts were then filtered through 0.22 μm Millipore filter. Water soluble P was measured by two methods. The first method allowed measurement of total water soluble P ($TP_{H_2O}$): 40 ml of the filtered extract was digested with 40 ml of 0.04 M $H_2SO_4$, and 16 ml of $K_2S_2O_8$ solution was added to oxidize organic particles in ash which could have passed the filter. Next extracts were autoclaved at 120 °C for 30 min, cooled to room temperature and used for colorimetric analysis. For the second method of measuring water soluble P ($P_{H_2O}$), a 9.5 ml subsample was taken from 200 ml filtered water extract, digested with 0.5 ml of concentrated hydrochloric acid (HCl) and analyzed by colorimetry. Other dissolved elements in the 20 ml water extract digested with 1 ml of concentrated HCl were measured by ICP-OES. All extractions were performed in duplicate.

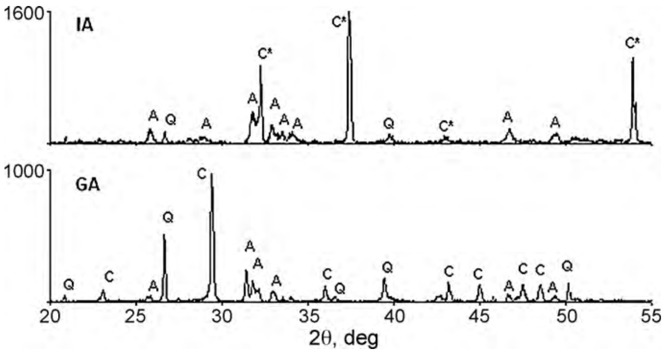


**Fig. 2.** XRD patterns of incinerator ash (IA) and untreated gasifier ash (GA). A – apatite, C – calcite, C* – calcium oxide, Q – quartz.

### 2.4. Ash compounds

The crystalline compounds in ash samples were identified by XRD using a Philips PW3020 diffractometer with Cu radiation and curved graphite crystal monochromator. Diffractograms were processed by Traces V6 computer software. The particles were examined by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and transmission electron microscopy (TEM). Samples for SEM and EDS analyses using a JEOL 6400 electron microscope were placed on metal stubs. A total of 23

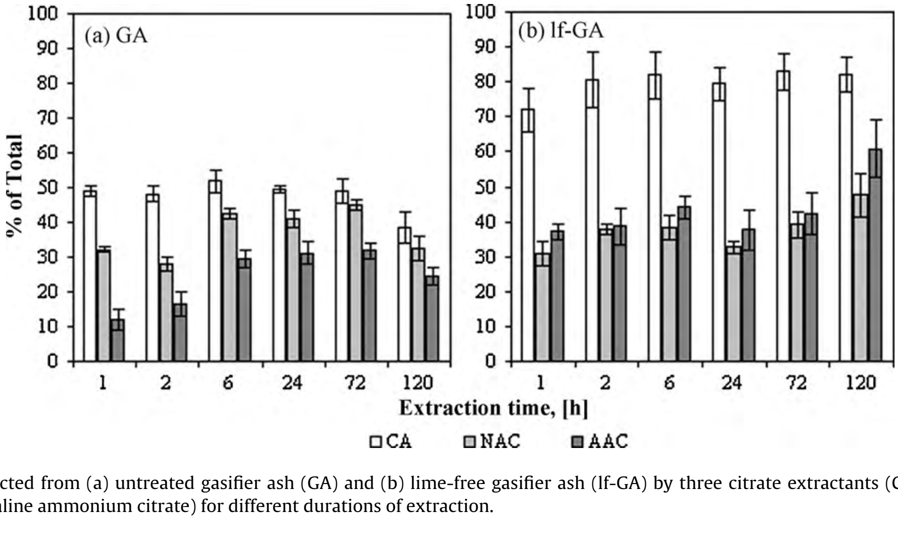


**Fig. 3.** Percentages of P extracted from (a) untreated gasifier ash (GA) and (b) lime-free gasifier ash (lf-GA) by three citrate extractants (CA – citric acid, NAC – neutral ammonium citrate, AAC – alkaline ammonium citrate) for different durations of extraction.

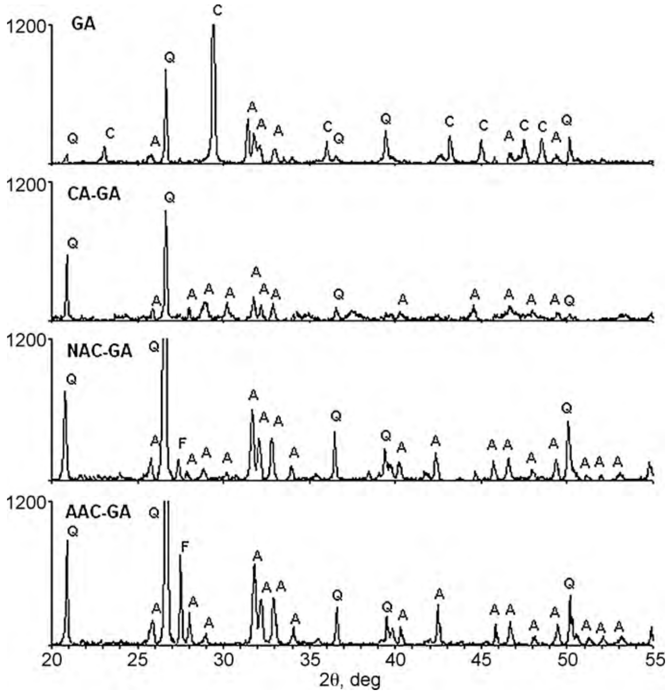


**Fig. 4.** XRD patterns of gasifier ash (GA) and its residue after extraction for 120 h in citric acid (CA), neutral ammonium citrate (NAC) and alkaline ammonium citrate (AAC). A – apatite, C – calcite, Q – quartz, F – feldspar.

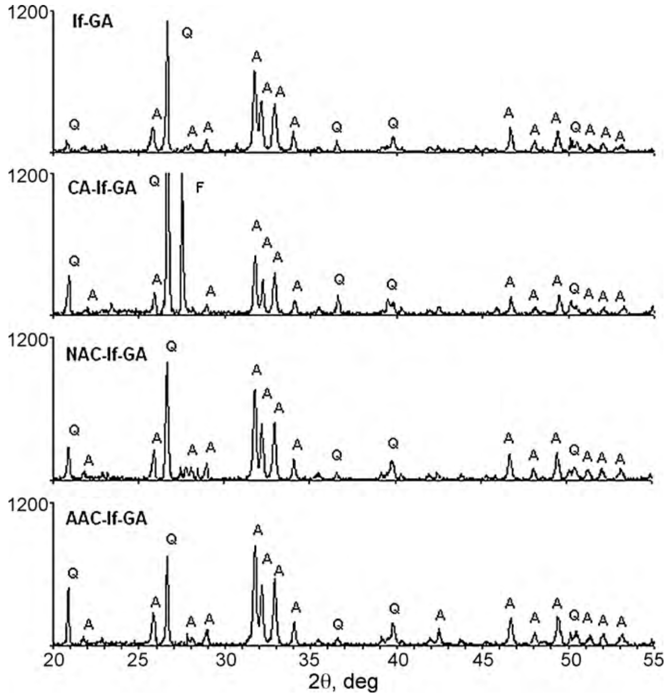


**Fig. 5.** XRD patterns of lime-free gasifier ash (lf-GA) and its residue after extraction for 120 h in citric acid (CA), neutral ammonium citrate (NAC) and alkaline ammonium citrate (AAC). A – apatite, C – calcite ($CaCO_3$), Q – quartz, F – feldspar.

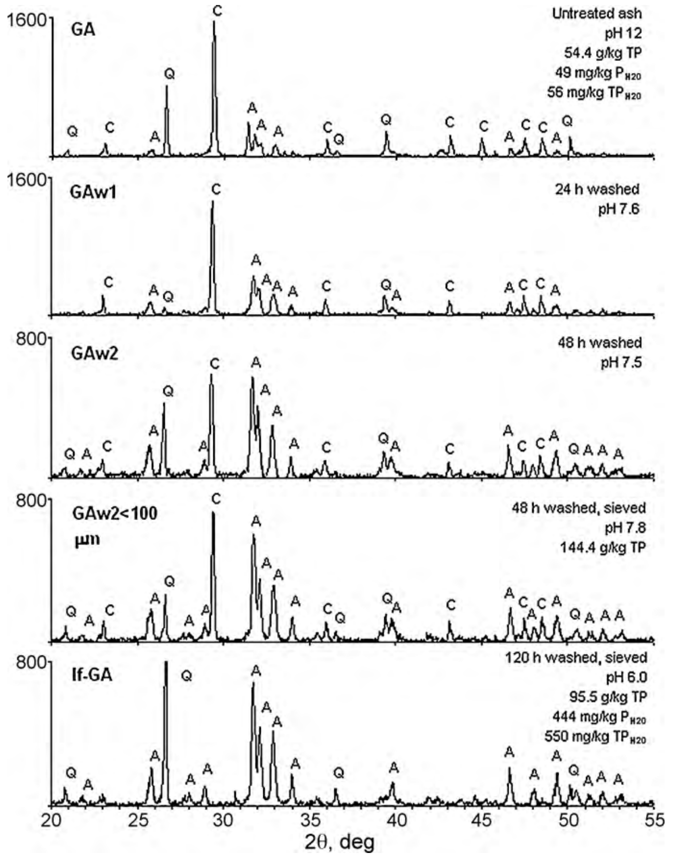


**Fig. 6.** XRD patterns of untreated gasifier ash (GA), intermediate products: ashes with lime partially removed (GAw1, GAw2, GAw2 <100 µm) and final product: lime-free gasifier ash (lf-GA) after stepwise extraction in sodium acetate buffer solution pH 5. A – apatite, C – calcite ($CaCO_3$), Q – quartz, F – feldspar.

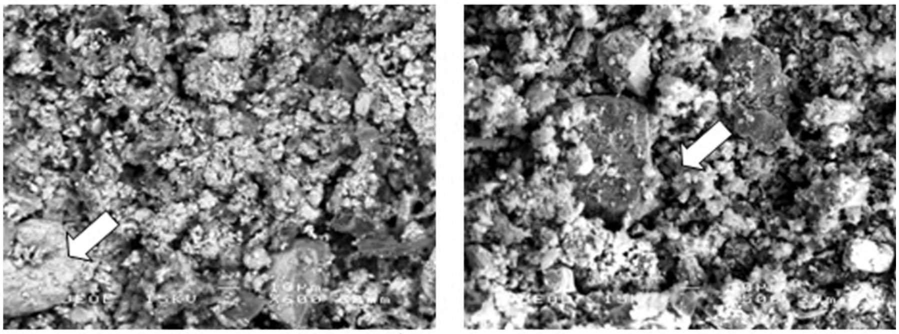
SEM images were obtained and 55 EDS spectra of particles to determine their chemical composition. SEM element maps were used for the calculation of approximate average element concentrations using image processing software (ImageJ 1.32j). Image processing analyses were performed for randomly chosen areas. TEM specimens were prepared by ultrasonically dispersing the sample in MilliQ water and then a drop of the very dilute suspension was placed onto a carbon coated grid and left to dry. The TEM studies were performed on a JEOL 2011 electron microscope operated at 200 kV. EDS spectra were obtained for the determination of the chemical composition of ash particles.

### 2.5. *Determination of P by standard AOAC methods for fertilizers*

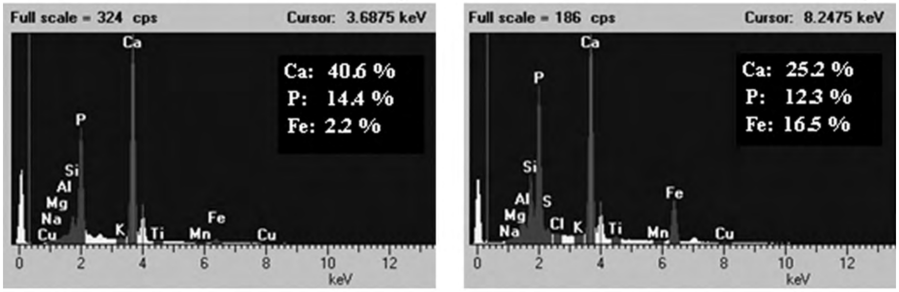
Association of Official Agricultural Chemists (AOAC) standard methods (AOAC [29]) were used to determine available P in the both untreated (GA) and lime-free (lf-GA) ash. The methods involve extractions in water, citric acid ($P_{CA}$), neutral ammonium citrate ($P_{NAC}$) and alkaline ammonium citrate ($P_{AAC}$). Three different citrate extractants were used to best describe P availability simulating the conditions in alkaline, neutral and acidic soils. Normally $P_{NAC}$ is commonly used as a P availability index, but it cannot predict the P availability of all P compounds. Apatite is almost insoluble in water so that when apatite in ash is applied to soil, dissolution of apatite is the consequence of a chemical reaction between soil acidity and apatite, thus an acidic extractant (CA) is most likely to predict the dissolution of apatite in acid soils (Khasawneh and Doll [20]). To evaluate the kinetics and congruency of dissolution of the phosphate compounds, several extraction times were used. This approach, which enables optimum extraction times to be identified, was developed by Gilkes and Palmer [21] for calcined rock phosphate fertilizers and applied by Yusiharni et al. [6] to chicken litter ash, wood ash and slag.

2% citric acid (CA) solution was produced by dissolving 100 g of pure citric acid in 5 l of DI water. Neutral ammonium citrate (NAC) solution was prepared as in the standard procedure, AOAC 963.03 (AOAC [29]). Alkaline ammonium citrate (AAC) solution was pre-

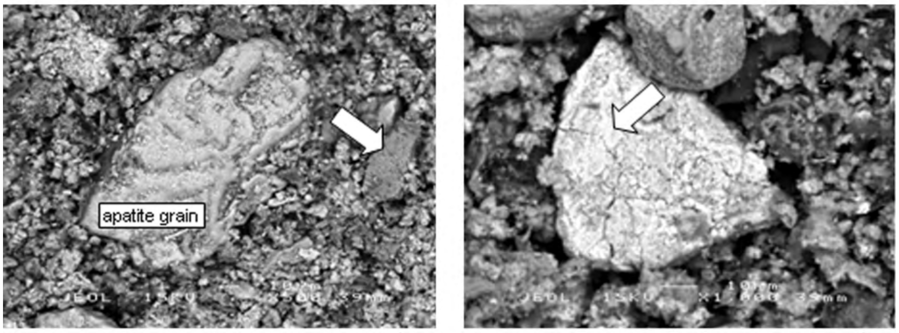
(a) SEM : coarse fraction (b) SEM: fine fraction



(c) Analyzed area (apatite) (d) Analyzed area (apatite)



(e) SEM: grain other than apatite (f) SEM: grain other than apatite



(g) Analyzed area (K-feldspar) (h) Analyzed area (Fe, Ti-rich mineral)

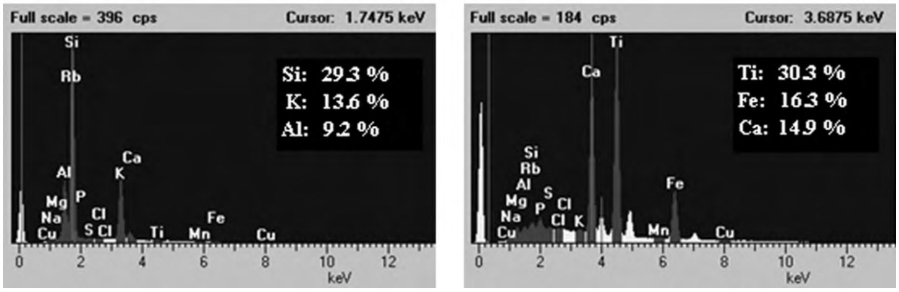


**Fig. 7.** SEM analyses of lime-free gasifier ash (lf-GA), (a, b, e, f) scanning electron micrographs and (c, d, g, h) X-ray spectra of indicated (a) apatite grain, (b) fine fraction, (e and f) a grain of ilmenite. Element concentrations are displayed as percentages (w/w).

pared by dissolving 865 g citric acid in 2 l of DI water to which 3 l of 5 M $NH_4OH$ was added (Boxma [30]). The pH was adjusted to 9.35 and the specific gravity to 1.08. The ash material to extractant ratio was 1:100 (w/v) and the extraction was conducted at 65 °C for NAC and AAC and at 25 °C for CA. Each ash sample was mixed with extractant, shaken in a temperature-controlled mechanical shaker and aliquots of the suspension were sampled at 6 times; at 1, 2, 6, 24, 72 and 120 h. The 0.5 ml aliquots were immediately quenched with pure ice (NAC, AAC) and diluted with DI water (CA) to 10 ml to prevent further dissolution during filtering through a 0.22 μm Millipore filter. 1 ml of solution was diluted 100 times with DI water and acidified with 0.5 ml HCl. The solid residue after 120 h extraction was washed with DI water and analyzed by XRD. The extractions were performed in triplicate.

Phosphorus concentrations (TP, $TP_{H2O}$, $P_{H2O}$, $P_{CA}$, $P_{NAC}$, and $P_{AAC}$) in the extracts were measured using the molybdenum blue method with colorimetric analysis. Absorbance was read at 820 nm on a Hitachi U-1100 spectrophotometer.

## 3. Results and discussion

Total and water soluble element concentrations for untreated ash (GA) and lime-free ash (lf-GA) are presented in Table 1. Both materials contain considerable amounts of macro- and micro-

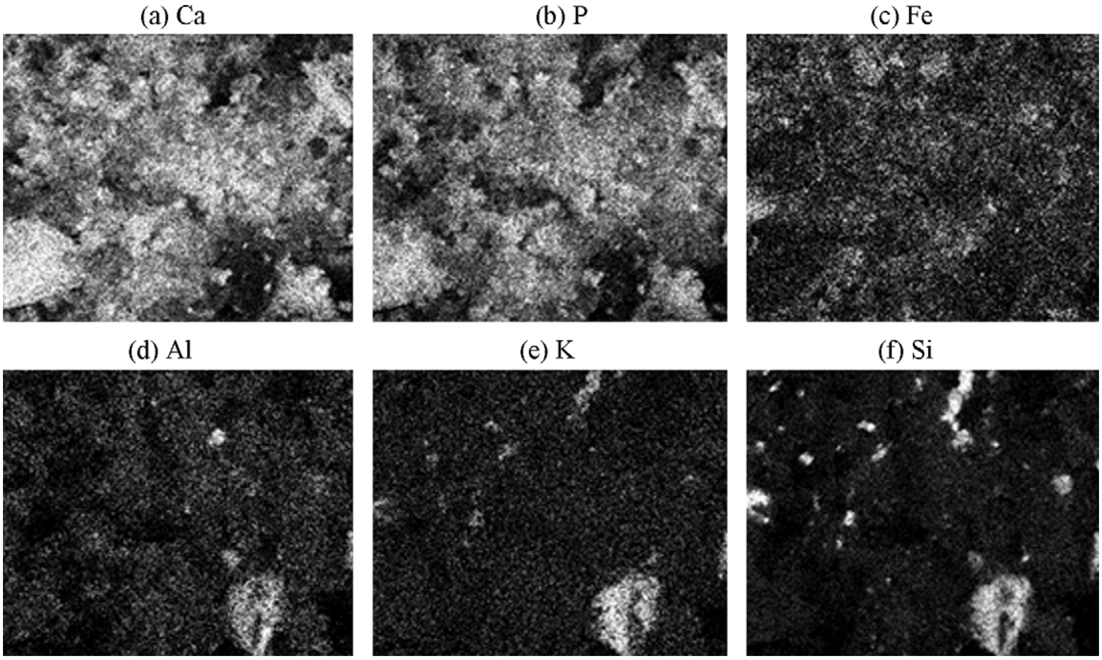


**Fig. 8.** SEM results of elemental mapping for lime-free gasified ash (lf-GA). Mapped area is shown in Fig. 7a.

nutrients with Ca, P, K, S, Mg and Fe being the most abundant. Removal of carbonates from GA with sodium acetate solution concentrated some elements in lf-GA, but considerable amounts of some elements were removed (Ca, K, Na). All of the heavy metal (Cd, Cr, Cu, Pb, Hg, Mo, Ni, Zn) and As and Se concentrations in the ash materials, comply with standards for forest fertilization (Pitman [22]), agricultural field fertilization (Vesterinen [23]) and AAPFCO (Association of American Plant Food Control Officials) and limits for phosphate fertilizers (Van Kauwenbergh [1]) for GA. However Cu and Zn concentrations in lf-GA (Cu 662, Zn 1916 mg/kg) exceed limits for field fertilization (Cu – 600 mg/kg and Zn – 1500 mg/kg). Concentrations of toxic elements in the ash are mostly much lower than for phosphate rocks with Se (in both materials) and Cr (in lf-GA) being higher (Van Kauwenbergh [1]).

### *3.1. Compounds in untreated ash*

X-ray diffraction patterns for IA and GA are presented in Fig. 2. Both ashes contain apatite and quartz. The lime in incinerator ash is calcium oxide (burnt lime) whereas gasifier ash contains calcium carbonate. The reason for this difference is the age of IA (2 weeks) is much less than GA (18 months) so that CaO that was present in GA has reacted with $CO_2$ in the atmosphere to form $CaCO_3$. The quantity of quartz is higher for GA than IA, because sand is used as a heat carrier material in the gasifier chamber.

### *3.2. Availability of P in citric extractants*

Fig. 3 shows the percentage dissolution of P in citric extractants for GA and lf-GA for various extraction times. The reason for the difference between $P_{CA}$, $P_{NAC}$ and $P_{AAC}$ is mostly due to pH of the ash extracts which is a function of the pH of the ash material (high for GA and low for lf-GA) and the pH of the extractant, which is mostly responsible for differences in the dissolution of P from the ash. In general CA was the most efficient extractant (for both materials) followed by NAC (for GA) and AAC (for lf-GA). Values of $P_{CA}$ (70–80% of TP) and $P_{AAC}$ (40–70% of TP) for lf-GA were higher than for GA, for which $P_{CA}$ and $P_{AAC}$ were 40–50% and 10–30% of TP, respectively, for all extraction durations. This

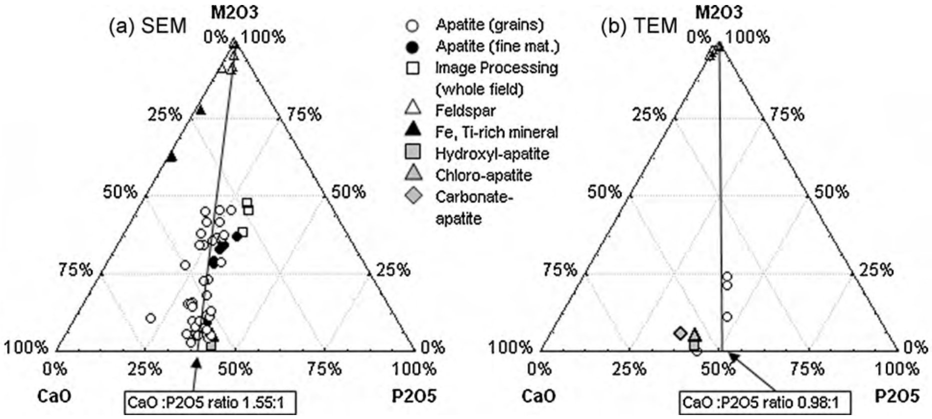
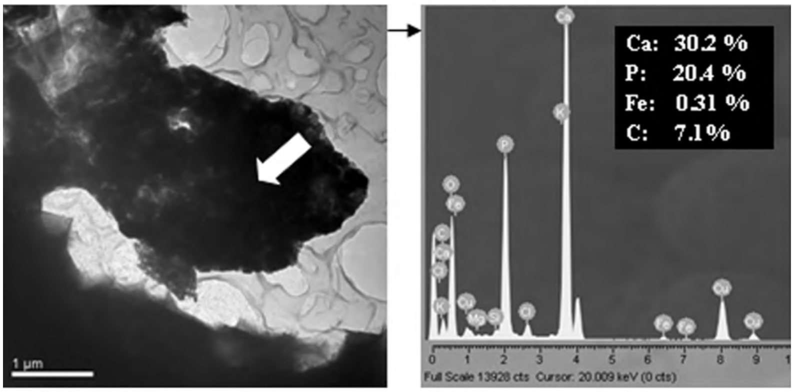
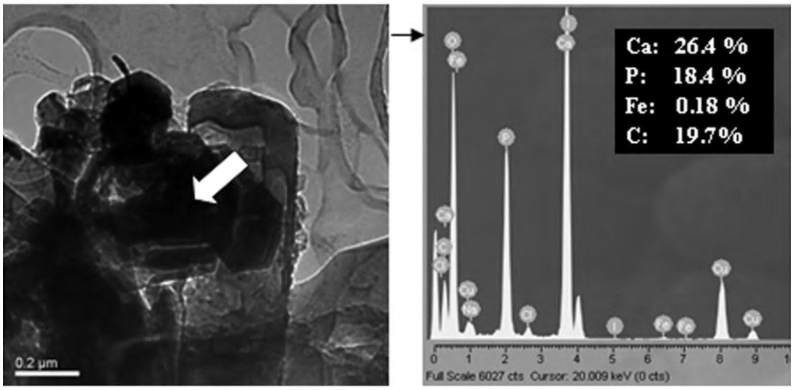
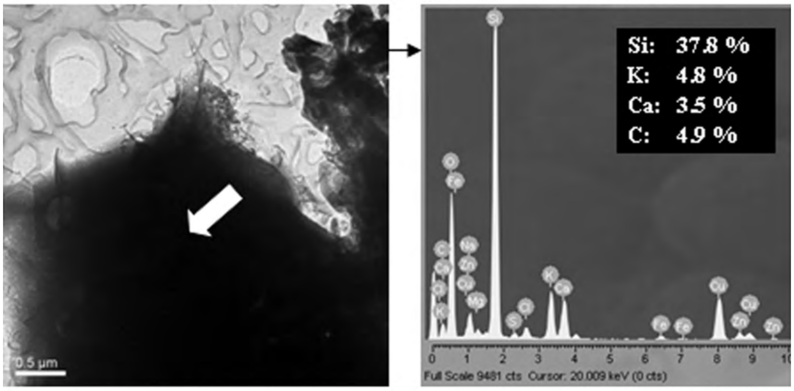


**Fig. 9.** Mineral composition of lime-free gasifier ash (lf-GA) presented on ternary plot based on EDS from (a) SEM and (b) TEM analyses. Concentrations are presented as oxides; $M_2O_3$ symbolizes the sum of elements other than CaO and $P_2O_5$. Additionally results from element mapping followed by image processing are displayed. The composition of three ideal apatites is shown for reference. A straight line in each plot indicates the average CaO: $P_2O_5$ mass ratio (1.55:1 for SEM and 0.98:1 for TEM).


(a) TEM: apatite
(b) Analyzed area (apatite)


(c) TEM: apatite
(d) Analyzed area (apatite)


(e) TEM: grain other than apatite
(f) Analyzed area (feldspar)

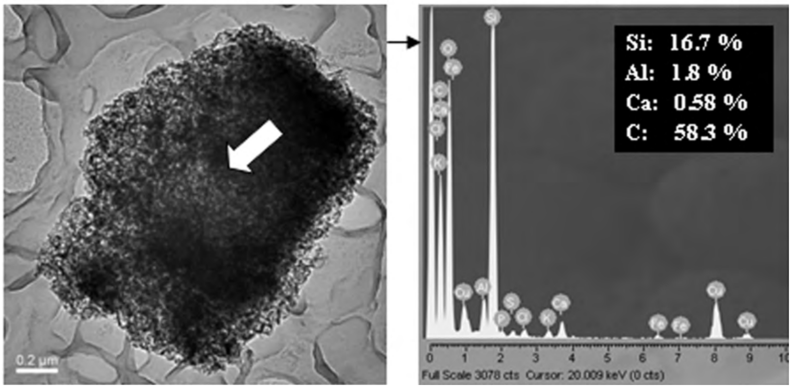

(g) TEM: grain other than apatite
(h) Analyzed area (carbon + Al-silicate)

**Fig. 10.** TEM analyses of lime-free gasifier ash (lf-GA), (a, c, e, g) transmission electron micrographs and (b, d, f, h) X-ray spectra of (a, c) apatites and (e, g) other minerals. Element concentrations are displayed as percentages (w/w).

difference in percentage extraction between materials is because during extraction of GA, a major part of the citric acid (CA) was consumed in dissolving the high content of lime, thus dissolution of P was reduced. Dissolution of P in NAC was slightly less for lf-GA than in GA. Maximum $P_{CA}$ extraction was 82% of TP for lf-GA and 52% for GA after 6 h extraction. For longer reaction times (24–120 h) the solubility of P in GA decreased somewhat for all three extractants. This could have been caused by presence of soluble iron (as indicated by the yellow color of the solutions), which may react with dissolved P, causing precipitation of iron phosphate. An opposite effect occurred for lf-GA, where P dissolution at 120 h had increased by about 10% in NAC and 20% in AAC compared to shorter extraction times. The dissolution kinetic of lf-GA is similar to that of ash derived from incineration of chicken litter (CLA) at 750 °C (Yusiharni et al. [6]). Lehr [24] found that release of P from apatitic phosphate fertilizers is greater for CA, followed by NAC and AAC which is the same sequence as for GA. Adam et al. [25] recovered only 30% of P from sewage sludge ash with CA, but after thermo-chemical treatment with $MgCl_2$ at 1000 °C, $P_{CA}$ extractability reached almost 100%. The technology is used by ASH DEC Umwelt AG to manufacture a fully licensed P-fertilizer (Hermann [26]). Rubæk et al. [9] achieved a solubility of P in NAC of 11% of TP for pig slurry ash and 40% for poultry manure ash.

XRD patterns of residues of 120 h citrate extractions of GA and lf-GA are shown in Figs. 4 and 5. By comparing the height of apatite peaks relative to a quartz peak (i.e. internal standard) in diffractograms, it can be seen that much less apatite is left in the CA residue than in NAC and AAC residues for both GA and lf-GA. Quartz and feldspars have been concentrated in the insoluble residues after dissolution of apatite and calcite (for GA). Yusiharni et al. [6] found similar results for the residues of citrate dissolution of CLA.

### 3.3. Effect of lime removal on mineralogy, pH and ash P content

XRD patterns of GA, intermediate products (GAw1, GAw2, GAw2 <100 μm) and the final product (lf-GA) of pH 5-sodium acetate extraction are shown in Fig. 6. The extraction method is designed to dissolve calcite from the ash, leaving apatite in the residue due to its much lower solubility than calcite in this reagent. It is possible to evaluate the amount of calcite removed at each step by comparing heights of calcite reflections to the apatite reflections as apatite acts as an inert internal standard. Calcite peaks become relatively weaker with every extraction step as is well demonstrated by the strongest calcite peak at $29.4° 2\theta$ (spacing $d = 3.035$ Å). A relatively short dissolution time (24 h) removed about half of the calcite so the 3.035 Å reflection for GAw1 is much weaker relative to apatite peaks than for untreated GA. After 48 h of extraction most calcite had been removed (~50% based on material mass balance). Screening of the residue through 100 μm mesh sieve removed around 25% of the quartz according to the intensities of quartz reflections for GAw2 and relative to apatite reflections. Screening to remove quartz and continuing extraction of the screened sample with fresh sodium acetate for another 72 h (extraction III) removed up to 30% (10% removed by screening and 20% by extraction) more calcite as compared to the initial content. At the conclusion of the extraction, all the lime (about 70% of mass) had been removed from the untreated ash (GA) by the extraction process. In general, removal of lime from the ash considerably improved P extractability both in $H_2SO_4$ (2 times) and water (10 times). TP concentration in screened ash (GAw2 < 100 μm) after extraction II was 1.5 times higher than in the final product (lf-GA) indicating that some P was dissolved by sodium acetate.

### 3.4. Identification of apatite

The XRD pattern of the final product (lf-GA) indicates that no calcite was left in the material after 120 h extraction. Based on measurements of diffraction line broadening and the Scherrer equation (Klug and Leroy [27]), the mean crystal dimension of apatite for several reflections ranges from 40 to 50 nm. Based on accurate spacing measurements for the seven strongest apatite peaks ($d = 3.449$, 2.817, 2.784, 2.721, 2.636, 1.945 and 1.844 Å) accurate apatite cell dimensions (a, c) were calculated and are listed in Table 2 (Holland and Redfern [28]). The calculated cell dimensions are close to carbonate-apatite. This was also the case for chicken litter ash (Yusiharni et al. [6]).

SEM micrographs of lf-GA (Fig. 7) show that most of the material consists of particles with sizes <10 μm and with irregular shapes. A few larger grains with dimensions ranging from 10 to 100 μm are also present. EDS spectra of many large grains (Fig. 7a) and the finer particles around them (Fig. 7b) shows them to be Ca and P-rich which indicates that these materials are apatite. Sand-size grains of quartz, K-feldspar ($KAlSi_3O_8$) (Fig. 7e) and grains with high concentrations of Ti and Fe (ilmenite) were also observed (Fig. 7h).

SEM element maps of lf-GA are shown in Fig. 8. Mapping was done for the same area as in Fig. 7a and it covers a rectangle with dimensions of 196 μm × 147 μm. Most of the material consists of Ca/P compounds with a few Al, K, Si-rich grains (feldspar, quartz). Fe is sometimes associated with Ca/P-rich grains.

The results for 55-point analyses by SEM of lf-GA are shown in Fig. 9a in the form of a ternary diagram. Data points from image processing based on semi-qualitative SEM elemental mapping of an entire field of view are also shown. CaO and $P_2O_5$ concentrations in grains were 28–68% and 19–41%, respectively. Fig. 9a indicates that there is a quite constant $CaO:P_2O_5$ mass ratio for all 43 SEM analyses of apatites – the composition at any analyzed point simply representing apatite of constant composition diluted by various amounts of $M_2O_3$ (mainly $Fe_2O_3$). The calculated average $CaO:P_2O_5$ mass ratio (1.55:1, SD = 0.35) indicates that the apatite in lf-GA is most probably carbonate-hydroxyl-apatite ($CaO:P_2O_5$ mass ratio 1.58:1). No fluorine or chlorine were detected so that the mineral is not fluoro – nor chlorapatite. Impurities associated with apatite grains contributed between 2.5 and 45%, of the analyses obtained by SEM-EDS, where $Fe_2O_3$ was the most abundant impurity (up to 24%). $SiO_2$ accounted for up to 15%, $SO_3$ up to 10% whereas, $Na_2O$, MgO, $Al_2O_3$ accounted for <2% each and Cl, $K_2O$ and $TiO_2$ <1% each. The P concentrations calculated by the image processing method for whole fields of view in the SEM are quite comparable with results obtained from EDS of single grains. Data points of other minerals such feldspars (7) and Fe, Ti-rich minerals (3) are also displayed in the tertiary diagram (Fig. 9a).

Results of TEM analyses of single particles are presented in Fig. 10a–h. Apatite grains seen in Fig. 10a and c are irregular and subrounded. Other particles include a glassy silicate (Fig. 10e) and carbon-rich ash (Fig. 10g). Fig. 9b shows data points from 11 particles analyzed by TEM. CaO and $P_2O_5$ concentrations in four apatite grains determined by TEM were 36–56% and 40–47%, respectively.

## 4. Conclusions

Ash produced by thermal gasification of dried and pelletized pig manure has high nutrient concentrations and minor heavy metals contents, Zn and Cu were most abundant. Removal of lime and soluble salts from the ash increased concentrations of total P, citric acid soluble P, water soluble P, total Zn, Cu, Pb and most other trace elements in the residue. In general, the solubility of P in citric extractants increased with extraction time and the maximum extractability of P as a percentage of TP in untreated gasifier ash followed the trend: CA > NAC > AAC and in lime-free gasifier ash CA > AAC > NAC. XRD and SEM analyses indicate that most P in the ash occurs in carbonate-apatite. Quartz, feldspars and Fe, Ti-rich sand grains also occur in ash. Untreated ash (pH 12) could be used as a combined liming agent and phosphate fertilizer on acidic soils, where soil acidity would dissolve both the lime and apatite.

## Acknowledgments

Authors would like to thank to Nattaporn Prakongkep and Naoko Zwingmann for their help with SEM and TEM analyses, Saowanuch Tawornpruek for assistance with the UnitCell computer program, Elizabeth Halladin for her advice on analytical chemistry and finally to Michael Smirk for advice on acid digestion of ash and ICP-OES analysis.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.06.024.

## References

[1] S.J. Van Kauwenbergh, Overview of phosphate fertilizer production alternatives, phosphate rock production and quality factors, in: Proceedings from Phosphate Fertilizer Production Technology Workshop, Brussels, June 18–22, 2007.

[2] J.C. Buckley, P.M. Schwarz, Renewable energy from gasification of manure; an innovative technology in search of fertile policy, Environmental Monitoring and Assessment 84 (2003) 111–127.

[3] B.S. Babu, Perspectives on biomass gasification, in: Proceedings of the IEA Bioenergy Agreement workshop, Task 33: Thermal Gasification of Biomass, Vienna, May 3, 2004, pp. 5–7.

[4] P. Stoholm, Gasification of problematic biofuels, Bioenergy Research 20 (2007) 8–10.

[5] T.G. Poulsen, T. Prapaspongsa, J.A. Hansen, Energy and greenhouse gas balances for pig manure using alternative treatment options, in: Proceedings of the ISWA/WMRAS World Congress, Singapore, November, 2008.

[6] B.E. Yusiharni, H. Ziadi, R.J. Gilkes, A laboratory and glasshouse evaluation of chicken litter ash, wood ash and iron smelting slag as liming agents and P fertilizers, Australian Journal of Soil Research 45 (2007) 374–389.

[7] K. Kuligowski, T.G. Poulsen, N. Pind, J. Laursen, Nutrients and heavy metals distribution in thermally treated pig manure, Waste Management and Research 26 (2008) 347–354.

[8] Pig international world market review, Pig International 38 (2008) 6–10.

[9] G. Rubæk, P. Stoholm, P. Sørensen, Availability of P and K in ash from thermal gasification of animal manure, in: Proceedings of the 12th International Ramiran Conference: Technology for Recycling of Manure Organic Residues in a Whole-Farm Perspective, vol. II, Aarhus, Denmark, September, 2006, pp. 177–179.

[10] S. Jala, D. Goyal, Fly ash as a soil ameliorant for improving crop production – a review, Bioresource Technology 97 (2006) 1136–1147.

[11] M.A. Cavaleri, D.W. Gilmore, M. Mozaffari, C.J. Rosen, T.R. Halbach, Hybrid poplar and forest soil response to municipal and industrial by-products: a greenhouse study, Journal of Environmental Quality 35 (2004) 1055–1061.

[12] Y.K. Soon, M. Arshad, A. Azooz, N. Lupwayi, Effects of wood ash vs. agricultural lime on crop production and soil chemical and physical properties, in: Proceedings from ASA–CSA–SSSA International Annual Meetings, New Orleans, November 4–8, 2007.

[13] S.M. Pathan, L.A.G. Aylmore, T.D. Colmer, Properties of several fly ash materials in relation to use as soil amendments, Journal of Environmental Quality 32 (2003) 687–693.

[14] R.E. White, Soil acidification – and overview for Australia and New Zealand, in: Proceedings of the Joint Conference of the Australia and New Zealand Societies of Soil Science – Soil the living skin of Planet Earth, Massey University, Palmerston North, New Zealand, December 1–5, 2008.

[15] D. Vamvuka, D. Zografos, Predicting the behavior of ash from agricultural wastes during combustion, Fuel 83 (2004) 2051–2057.

[16] D. El-Mogazi, D.J. Lisk, L.H. Weinstein, A review of physical, chemical, and biological properties of fly ash and effects on agricultural ecosystems, The Science of the Total Environment 74 (1988) 1–37.

[17] P. Stoholm, J. Ahrenfeldt, U. Henriksen, A. Gómez, J. Krogh, G.R. Nielsen, B. Sander, Danish Fluid Bed Technology ApS (DFBT), c/o CAT, Technical University of Denmark (DTU-Risø), University of Castilla – La Mancha, Anhydro A/S, DONG Energy A/S, The Low Temperature CFB Gasifier – 500 kW test on biogas fiber residue, in: Proceedings of the 16th European Biomass Conference, Valencia, 2–6 June, 2008.

[18] H. Carlsen, Biomass Gasification Group, What is gasification? Available at: http://www.bgg.mek.dtu.dk/About%20BGG.aspx (accessed 06/10/2009).

[19] A. Klute, Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods, Nr 9, Agronomy, 2nd ed., ASA, SSSA, Madison, Wisconsin, USA, 1986.

[20] F.E. Khasawneh, E.C. Doll, The use of phosphate rock for direct application to soils, Advances in Agronomy 30 (1978) 159–206.

[21] R.J. Gilkes, B. Palmer, Calcined Christmas Island C-grade rock phosphate fertilizers: mineralogical properties, reversion and assessment by chemical extraction, Australian Journal of Soil Research 17 (1979) 467–481.

[22] R.M. Pitman, Wood ash use in forestry – a review of the environmental impacts, Forestry 79 (2006) 563–588.

[23] P. Vesterinen, Wood ash recycling state of the art in Finland and Sweden, VTT Processes, Research Report Number PRO2/6107/03, PRO2-6107-03, 2003, unpublished results.

[24] J.L. Lehr, Phosphate raw materials and fertilizers: Part I-a look ahead, in: The Role of Phosphorus in Agriculture, 1st ed., Soil Science Society of America, Madison, WI, 1980.

[25] C. Adam, G. Kley, F.G. Simon, Thermal treatment of municipal sewage sludge aiming at marketable P-fertilisers, Materials Transactions 48 (2007) 3056–3061.

[26] L. Hermann, Nutrient recovery from ash after incineration of organic residues, in: Proceedings of the 12th International Ramiran Conference: Technology for Recycling of Manure Organic Residues in a Whole-Farm Perspective, vol. II, Aarhus, Denmark, September, 2006, pp. 213–215.

[27] H.P. Klug, E.A. Leroy, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd ed., Wiley–VCH, 1974.

[28] T.J.B. Holland, S.A.T. Redfern, Unit cell refinement from powder diffraction data: the use of regression diagnostics, Mineralogical Magazine 61 (1997) 65–77.

[29] Association of Official Agricultural Chemists, Association of official agricultural chemists, official methods of analysis, 15th ed., AOAC, Virginia, 1990.

[30] R. Boxma, Evaluation of phosphate in fertilizers by means of the alkaline ammonium citrate extraction according to Petermann, Netherlands Journal of Agricultural Research 25 (1977) 42–50.