

# Nutrients and Heavy Metals Distribution in Thermally Treated Manure

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### Among pigs...



1 Do you know that there is already 25mln of us in Denmak?

2 WOW, that's 5 per 1 Danish citizen! Why so much?

5 Do you know that we produce 11.6 t of manure dry matter per year?

6 SO MUCH?!? How do humans deal with our wastes?

7 They store it, apply on agricultural land and burn to get energy.

8 If I was a human, I would try to use ashes as fertilizers.

3 To feed 3 times more people than population of Denmark.



4 And improve the economy!



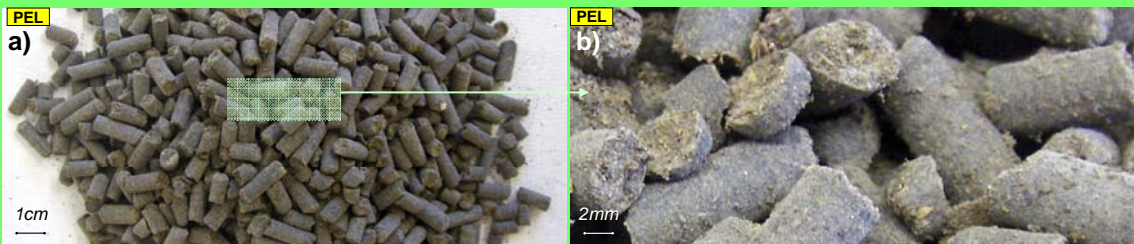
9 To protect the environment and improve the economy!



## ABSTRACT

Ashes from pig manure treated by combustion (IA) and thermal gasification (GA) are characterized and compared in terms of nutrient, i.e., potassium (K), phosphorus (P) and heavy metal, i.e., cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn) contents. Total nutrient and metal concentrations were measured using energy dispersive X-ray fluorescence (EDXRF) analysis. Acid ( $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ) and water extractable concentrations were also measured both in non-classified ash and in selected ash particle size fractions using flame atomic absorption spectrometry (FAAS) and colorimetric spectrometry. Ash from gasified manure contains more water soluble K compared to combusted manure whereas the opposite is the case with respect to P. Heavy metals Ni, Cr and Cd were present in higher concentrations in the fine particle size fractions ( $<30\mu\text{m}$  of particle diameter), whereas K, P, Zn and Cu exhibited higher concentrations in the coarser particle size fractions ( $>30\mu\text{m}$ ).

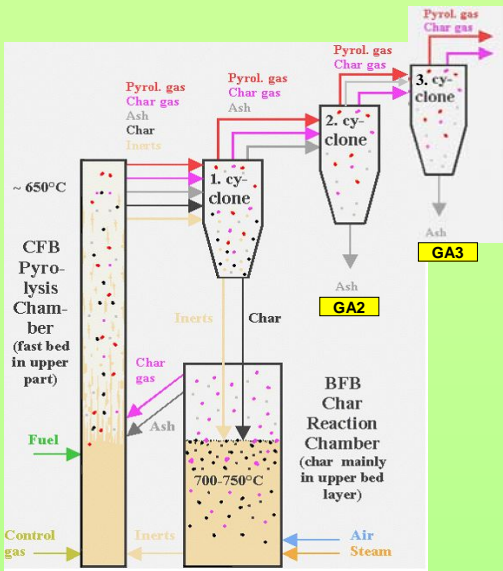
## Materials & Methods



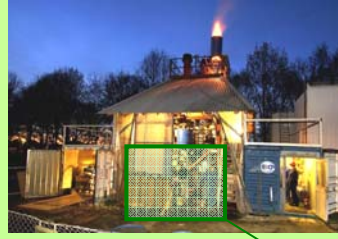
**Fig. 1** Untreated, dewatered, thermally dried (90% DM) and pelletized pig manure from Fangel Biogas Plant, Denmark – fuel for LT-CFB gasifier (a)...

...and its magnification (b).

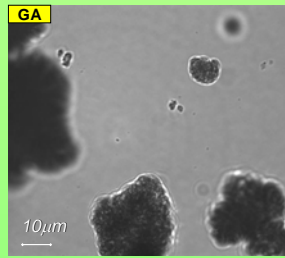
# THERMAL TREATMENT



**Fig. 2** Schematic of LT-CFB gasifier with arrows indicating the composition of material streams. Numbers 1, 2, 3 denote primary, secondary and tertiary cyclones.



**Fig. 3** Picture of LT-CFB gasifier at DTU, Copenhagen and the view of the 5m long tank for 2<sup>nd</sup> and 3<sup>rd</sup> ash.

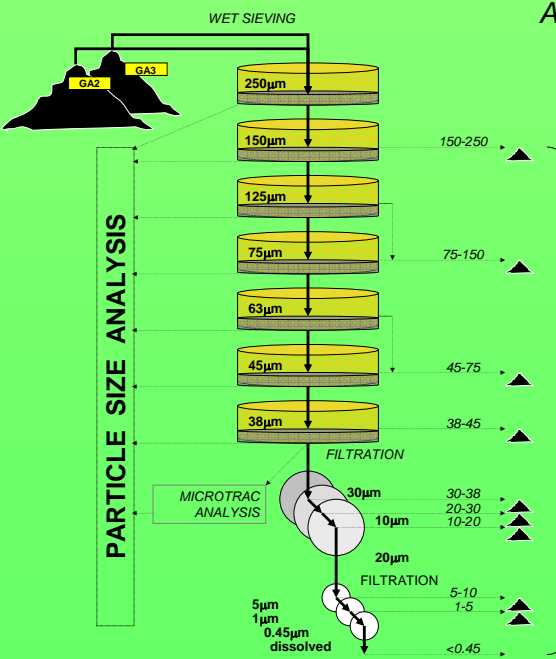


**Fig. 4** Ash from thermal gasification of pig manure (a) and its particles seen under the microscope (b) (GA).



**Fig. 5** Ash from incineration of pig manure at 1000°C after 24h (IA).

## SAMPLE ANALYSIS



Additionally

- Ash (mixed, non-classified) from gasification
- Ash from incineration
- Dried and pelletized manure (gasifier fuel)

ANALYTE

METHOD

**P**

H<sub>2</sub>O extraction, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> digestion (120°C, 30min) + colorimetric spectrometry, EDXRF

**K**

H<sub>2</sub>O extraction, HNO<sub>3</sub> digestion (120°C, 30min) + FAAS, EDXRF

**Zn**  
**Cu**  
**Cr**  
**Cd**  
**Ni**

HNO<sub>3</sub> digestion (120°C, 30min) + FAAS, EDXRF

# Results

## PARTICLE SIZE ANALYSIS

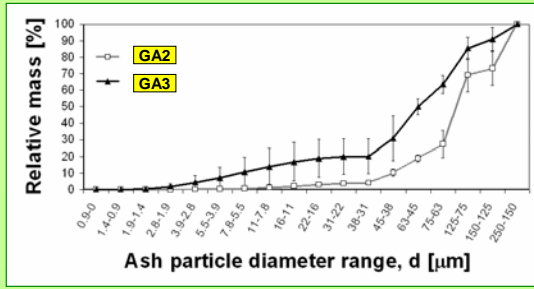


Fig. 6 Cumulative particle size distributions of gasified fiber residue ash from the secondary and tertiary cyclones of the LT-CFB gasifier.

## NUTRIENTS

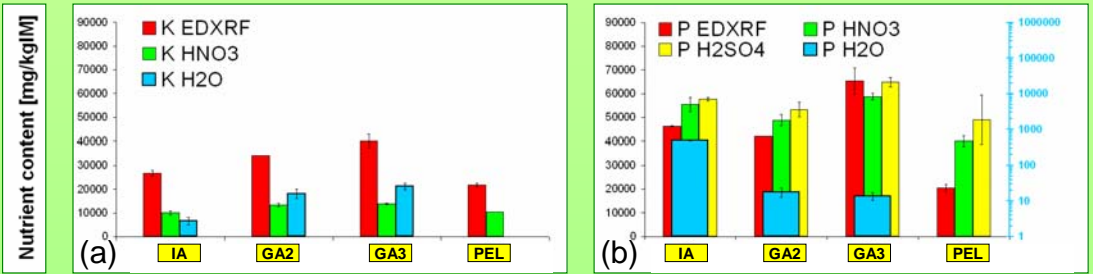


Fig. 7 Concentration of; (a) K and (b) P in combusted (IA), thermally gasified (GA2, and GA3) and dewatered fiber residue (PEL) in reference to incombustible matter (IM). Data measured using different methods are shown. Note that values for P measured by  $H_2O$  extraction refer to the secondary logarithmic axis.

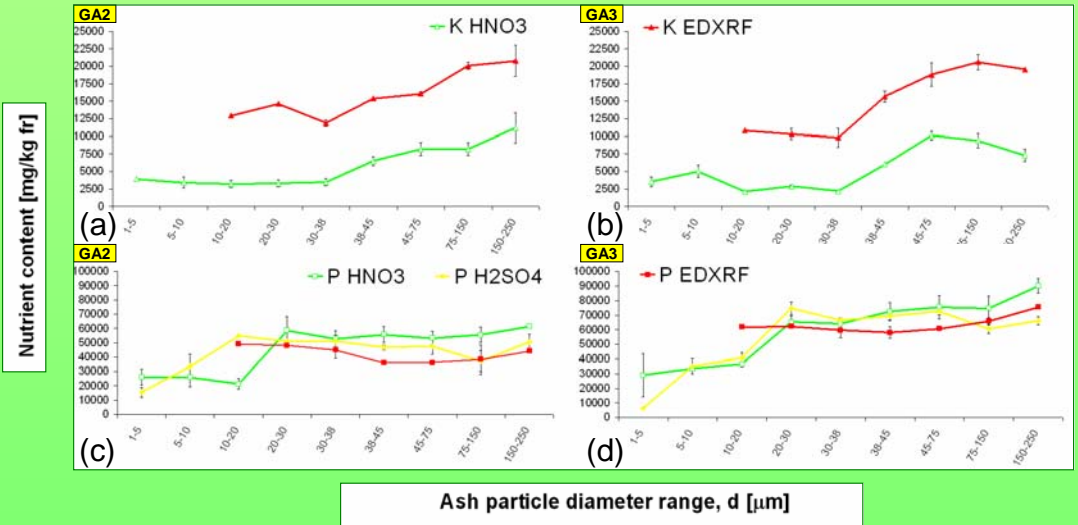


Fig. 8 Nutrient (total K and P) concentrations in ash particle size fractions from thermally gasified fiber residue; a, c) – secondary cyclone ash and b, d) – tertiary cyclone ash. Data measured using different extraction methods are shown. Concentrations refer to the particular fractions (fr).

## HEAVY METALS

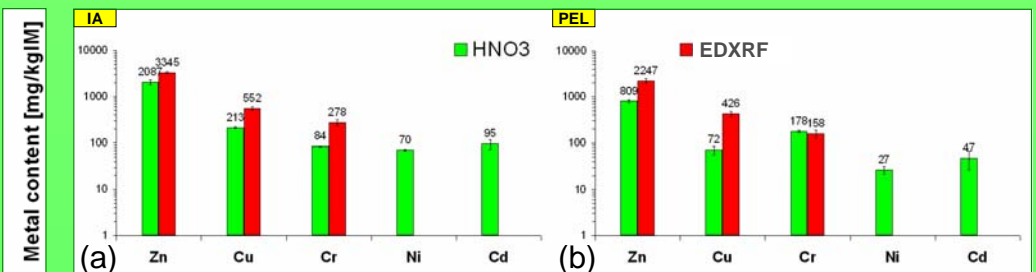
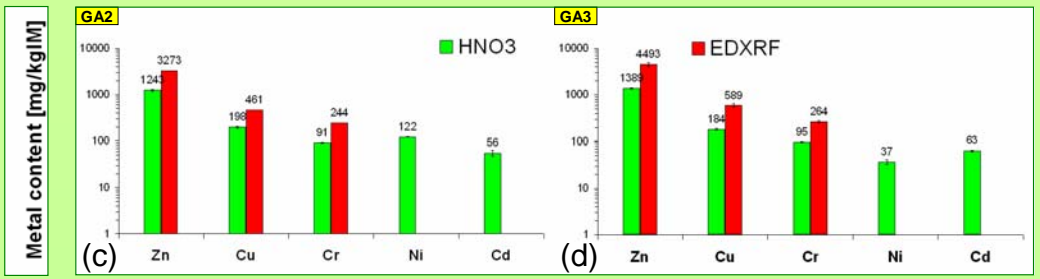
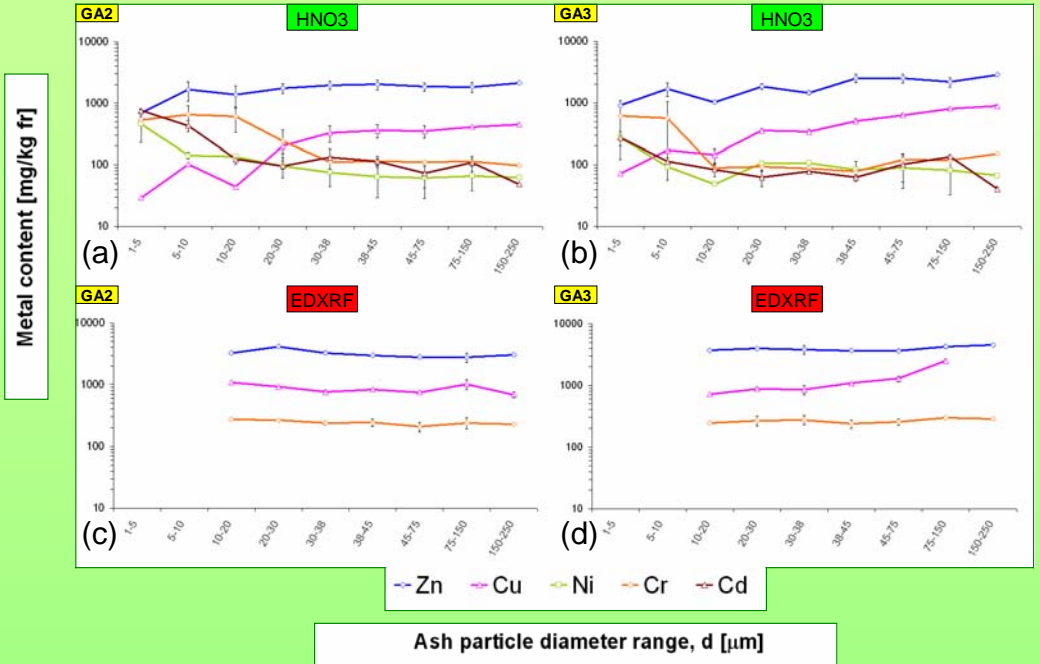


Fig. 9 Total heavy metal (Zn, Cu, Cr, Ni, and Cd) concentrations in thermally treated fiber residue; a) IA and b) PEL in reference to incombustible matter (IM). Data measured using different extraction methods are shown.



**Fig. 9** Total heavy metal (Zn, Cu, Cr, Ni, and Cd) concentrations in thermally treated fiber residue; c) GA2, d) GA3. Data measured using different extraction methods are shown.



**Fig. 10** Distribution of total heavy metal concentrations in ash fractions from thermally gasified fiber residue; a), c) – secondary cyclone ash and b), d) – tertiary cyclone ash. Data measured using different extraction methods are shown. Concentrations refer to the particular fractions (fr).

## CONCLUSIONS

Incinerated manure ash contained **27g/kg K**, whereas gasified ash had **25%** more of K. Both ashes contained about **55g/kg P**. Water and acid extractable K in both ashes was **30-50%** of the total amount. Water extractable P was about **1%** of the total in ash from combustion but **only 0.04%** in ash from gasification. This indicates that P availability for plant growth may be lower in the gasified ash. Acid extractable P was about **100%** in both ashes.

Both ashes contained about **3000-4500mg/kg Zn**, **450-600mg/kg Cu** and **240-280mg/kg Cr**. Acid extractability of these metals was **30-40%** in both ashes, for Cd and Ni the values were **50-100mg/kg** and **30-120mg/kg**, respectively. Concentrations of acid extractable Ni, Cd, and Cr in the gasified ash increased with decreasing particle size. **Removal** of some of the smallest particle fractions could therefore **improve** ash quality with respect to these metals. Cu and Zn concentrations increased with increasing particle size, so did P and K.

The total concentrations of nutrients and heavy metals **do not necessarily** reflect the potential risk of leaching to the groundwater of these compounds in connection with utilization of the ash as fertilizer on farmland. It is likely that fine ash particles which can move easily through soil may function as carrier for nutrients and metals adsorbed to the particles. To evaluate the leaching potential, leaching and mobility experiments should be conducted.

### References:

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