Baltic Forum for Innovative Technologies for Sustainable Manure Management

# **KNOWLEDGE REPORT**

# Thermal Gasification of Manure



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WP6 Energy potentials











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#### PREFACE

This report offers an overview of thermal gasification of manure. Thermal gasification is an emerging technology, not developed on full-scale at the time of writing. However, it holds a promise for a new way to utilise the energy content of manure. Bearing this in mind, the following report is mostly based on the technology developed by Peder Stoholm from DONG Energy, Denmark, in a Low Temperature-Circulated Fluidised Bed (LT-CFB) 500 kW gasifier.

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the authors





#### CONTENT

1	Intro	oduction	4
2	Basi	ic theory of thermal gasification	4
	2.1	Pre-treatment	4
	2.2	Pyrolysis	6
	2.3	Thermal gasification	6
3	Ener	rgy use and advantages over combustion	6
4	Syn	gas purification and use	7
	4.1	Syn gas purification	8
	4.2	Biofuels from syn gas	8
	4.3	Emissions during thermal gasification	8
5	Poss	sibilities and barriers for implementing the technology	9
6	5 Description of the pilot experiments in Denmark10		
	6.1	Description of manure pellets	10
	6.2	Thermal gasification in LT-CFB	11
	6.3	Characteristics and use of the residue from LT-CFB	11
	6.3.1	Ash chemistry	12
	6.3.2	Element mobility and P extraction potential	12
	6.3.3	Application of ash in agriculture	
	6.3.4	Ash spreading techniques on land	14
	6.3.5	Summary of ash reuse	14
	6.3.6	Changes in the residue as compared to original manure	14
	6.3.7	Changes during storage	15
	6.4	Future possibilities	15
7	REFL	ERENCES	





# 1. Introduction

Thermal gasification is a process which converts carbonaceous materials into combustible gases. The resulting gas is called *syn gas* which can be more efficiently converted to high quality energy, such as electricity, than achieved by direct combustion of the fuel. Thermal gasification has been already widely applied to coal and wood, while its application to mechanically separated solid fraction of animal manure has so far been rather limited on a commercial scale. There have been some experiments, either on co-gasification with other biomass fuels or solely for manure carried out in pilot/demonstration plants in Denmark [1-4] and in the USA [31].

In order to solve the challenge of high quantities of agricultural manure and of phosphorus balance in the environment without a necessity to restrict animal production, animal manure must be utilized on site or transported to places with a deficit of phosphorus. Since the transportation of raw slurry with its high water content is expensive and inefficient, farm-scale mechanical separation of the manure (raw or anaerobically digested) into solid and liquid fractions may offer a solution [5, 6]. The liquid fraction can be used as nitrogen fertilizer, whereas the phosphorus-rich solid fraction could be further dried and thermally gasified to recover heat and electricity.

Previous studies have shown that a technological chain consisting of anaerobic digestion in a biogas plant and subsequent thermal gasification of the dried pellets from the manure digestate, recovers up to 60% of the energy contained in the original raw materials. This is only slightly more than anaerobic digestion alone (50-55%), as the calculations take into account the energy loss during the dewatering, drying and pelletizing of the digestate and the loss of nitrogen during the thermal processes [7]. In spite of considerable reduction of the input dry manure mass (2-3 times) during thermal gasification, the energy gain is currently rather insignificantly higher than for biological processes alone (anaerobic digestion). Therefore, this technology is still under development and requires further research and feasibility evaluations.

# 2. Basic theory of thermal gasification

Thermal gasification relies on chemical processes at elevated temperatures (>700°C), contrary to biological processes such as biogas technologies. Depending on the raw materials used, it may require pre-treatment (drying). Then the process proceeds in two phases, i.e. pyrolysis and thermal gasification [1].

#### 2.1 Pre-treatment

The fuel, suitable for thermal gasification, must have a certain heating value. Usual fuels used and/or tested for thermal gasification have a wide range of heating values from 7.5 to 37.6 GJ/t (Tables 1-3). Different fuels can also be mixed and co-gasified, e.g. coal with feedlot and chicken litter biomass (Table 2). The necessity for pre-treatment, mostly involving drying, is mainly dependent on the moisture content of the fuel (dry matter, DM). Additionally, grinding may be needed for fuels with large particles, such as coal, in order to ensure a greater contact area for the





better heat transfer through the fuel. The lower heating value (LHV) is determined by subtracting the heat of vaporizing water vapor from the higher heating value (HHV).

Fuel [Reference]	Dry matter (%)	Higher heating value HHV (GJ/t)	
Coal [17]	85–97	16–32	
Biomass, generally [17]	65–90	13–18	
Waste, generally [17]	40–60	8-10	
Manure, pellets [4]	90	15.3	
Digested manure, pellets [4]	90	11.3	
Poultry litter [31]	80–65	15.3*	
Turkey litter [31]	70	11.8*	
Swine solids [31]	42	19.3*	
*dry basis			

Table 1. Comparative approximate analysis of different fuels.

Table 2. Comparative approximate analysis of coal, biomass and their mixtures [30].

Fuel	Dry matter (%)	Higher heating value HHV (GJ/t), dry basis
Coal	79	27.7
Feedlot biomass	89	16.8
Chicken litter	92.5	10
Coal and feedlot biomass (50:50 w/w)	84	21.9
Coal and chicken litter (50:50 w/w)	86	18.1

Table 3. Lower heating value for different fuels [32].

Fuel	Dry matter (%)	Lower heating value LHV (GJ/t)
Coal	88.5	24.8
Vegetable oils	0.0	37.6
Straw	87.3	14.6
Treated wood	85.4	15.3
Untreated wood	80.2	14.8
Grass/plants	75.8	13.1
Sludge	67.5	8.2
Manure	56.4	7.5





When gasifying manure, the pre-treatment involves solid-liquid separation (mechanical separation, dewatering), drying and pelletizing. The national legislation should be considered when organizing the pre-treatment. For example in Denmark, drying and pelletizing of manure is not allowed at farm-scale due to the vicinity of pig feed. Slurry separation using screw presses, vibration filters or decanters is already practiced e.g. in Denmark and in the Netherlands using mobile, containerized units, easy to relocate from farm to farm (examples of Danish producers: Samson Bimatech, ManuPower, SB Engineering, Vredo; in the Netherlands more high-tech including reverse osmosis and ultra filtration). In Denmark, the separation results in around one (1) million tons of slurry separated each year (3% of total slurry production) [33]. Pelletizing of manure/digestate is still a novel technology, therefore not common on a commercial scale yet.

The drying of the digestate may consume more than 5.3 MJ/kg manure DM, which constitutes almost 50% of the HHV of the resulting pellets from digested manure [25]. Another option is to use solar energy to dry the manure, preferably in a glasshouse and controlled conditions. Such approach is already used for drying sewage sludge. Drying of manure could also be done using the excess of heat from the biogas plant, offering also a valid use for the biogas-based heat. Summing up the overall energy efficiency of the manure handling chain leading to thermal gasification could be strongly improved by appropriate heat management during drying.

#### 2.2 Pyrolysis

After drying, the first process that the fuel undergoes is *pyrolysis*, which initiates at around 230 °C. During pyrolysis, thermally unstable components, such as lignine in biomass are broken down and evaporated with other volatile components. The resulting *pyrolysis gas* consists mainly of *tar* (condensible hydrocarbons or hydrocarbons with C6 and higher, including polycyclic aromatic hydrocarbons, PAH), methane (CH<sub>4</sub>), steam or nitrogen (when using air as gasification agent, see below) and carbon dioxide (CO<sub>2</sub>). The solid residual contains carbon structures (*coke*) and ashes. The *tar* formed during pyrolysis can be sticky like asphalt. It is also known to be highly carcinogenic and represents a great challenge to the machinery — e.g. internal combustion engines and turbines — when the gas produced is transported, stored, and used [1].

#### 2.3 Thermal gasification

The actual gasification happens at temperatures above 700  $^{\circ}$ C when the glowing coke and pyrolysis gas are allowed to react with a *gasification agent*, such as oxygen, air or steam. The gasification agent is normally injected in small amounts. The coke is gradually broken down into gases, such as carbon monoxide (CO), carbon dioxide and hydrogen (H<sub>2</sub> from the steam reaction) or nitrogen (N<sub>2</sub> if air is used as gasification agent). The gasification can take place in a pile of coke — a fixed bed — or e.g. in a fluid bed [1].

### 3. Energy use and advantages over combustion

Thermal gasification has already been widely applied to coal and wood; however its application to the solid fraction of animal manure is still limited on a commercial scale. There have been some research experiments, either on co-gasification with other biomass fuels or solely for manure carried out in pilot/demonstration plants in Denmark [1-4] and in the USA [31].





When comparing thermal gasification and direct combustion of combustible fuels, thermal gasification allows for a broader range of very low grade and difficult biomass and waste fuels to be used. Additionally, no problems regarding agglomeration have been encountered, in spite of using only ordinary silica sand as bed material for many hours of operation (some combustion technologies may also control bed temperature and influence ash behavior).

Thermal gasification uses only a hot cyclone, without prior raw gas cooling, which allows for retaining ash at around 95% efficiency. Partly evaporative ash components, such as potassium and phosphorus can be retained roughly as efficiently as the ash in general. Hence the boiler is protected and ash mixing avoided when using the syn gas for co-firing with coal or waste. Thermal gasification also allows for easy and clean handling of large ash streams, while the lower temperature (<750°C) than that of combustion (>1000°C) makes the corrosive compounds (i.e. potassium chloride KCl) retained in the ash, enriching the fertilizer value of the residues and causing no corrosion in the boiler [1-4].

Before transport, the syn gas of thermal gasification would require an extra cleaning stage to remove tar, as the syn gas cannot be transported hot and the cooled tar would condensate and cause problems, such as clogging. However, when upgraded (purified), the syn gas as an energy carrier, can be transported over long distances. Hence the heat can be recovered even at long distances from the location of the gasifier. This makes the installation of the plant independent of the location (rural, urban) in opposition of the combustion plant, in which some heat is lost while transporting steam or hot water over long distances (urban location more appropriate).

Additionally, more electricity can be produced during thermal gasification than during combustion, which relates to better electricity production rate of a gas engine (40%) than a steam turbine (25%) [7]. These values, however, are given for large-scale power plants, and for small-scale gasifiers the efficiency is likely to be lower.

Thermal gasification results in less gaseous (nitrogen oxides  $NO_x$ ) and dioxin emissions, and as all nitrogen is converted to gaseous nitrogen, none is leached to waterways. Also, ash from combustion of manure is more contaminated with zinc, copper and chromium, and has less potassium (the key macro-element after phosphorus) than ash from thermal gasification [9]. Ash from gasification is also characterized with more readily-usable phosphorus than ash from combustion [16].

### 4. Syn gas purification and use

When it comes to syn gas itself, its further application (i.e. injection into natural gas grid) significantly depends on its content of impurities. The pollutants involved in these processes may include sub-micron particulate matter, tars, ammonia, metals, dioxins, furans and acid gases. The syn gas purification can be achieved with proven, reliable scrubbing (absorption) and adsorption technologies, similar to the processes used in conventional scrubbing of gases from combustion. However, a pre-treatment with tar removal may be necessary.





#### 4.1 Syn gas purification

The syn gas may simply be directed through the thermal process destroying the tar at high temperature without the need for a separate purification step. The trade-off, however, is a lower energy content of the syn gas. Alternatively, the tar may be removed in a separate scrubber. This approach has a lower outlet temperature and results in higher energy content in the purified syn gas, but results in tars that are more difficult to remove. The main challenge of tar removal relates to the fouling that can occur in the initial stages of condensing and collecting the tars. The "tar balls", which are long-chained hydrocarbons, have a tendency to agglomerate and stick together, and subsequently foul the equipment. Tar removal processes also produce liquid wastes with higher organic concentrations, which increase the complexity of subsequent water treatment.

#### 4.2 Biofuels from syn gas

Conversion of syn gas into alkenes is a well-known industrial process using both low temperature Fischer–Tropsch (LTFT) and high temperature Fischer–Tropsch (HTFT) routes. There are several possibilities for modifying the classical Fischer–Tropsch process to yield predominantly alkenes. These are production of alkanes and subsequent steam cracking to lower alkenes, upgrading of Fischer–Tropsch liquids into lower alkenes and modification of Fischer–Tropsch catalyst to achieve higher selectivity for alkene formation. Solid acid catalysts, such as zeolite, can catalyze the conversion of syn gas into methanol, which is subsequently converted into alkenes. Through appropriate choice of process conditions, catalyst formulation and morphology of the catalyst, a product mixture with higher content of lower alkenes can be obtained [19].

The catalytic reforming of methane and naphtha are well-established petrochemical processes, and in recent years gasification technology is becoming increasingly focused on catalytic processing. The specific objective is then to transform the light and heavy hydrocarbons in the syn gas. There are numerous publications in the literature on experimental investigations into the catalytic conditioning of the raw gas obtained in biomass gasification processes. Much of the work in this field has involved commercial reforming catalysts, which for reasons both technical and economic contain nickel as the active element.

The industrial feasibility of such processes depends mainly on the cleaning technologies for the product gas. The aim is to separate dust and convert the condensable tar into permanent gases so that they can be rendered into an acceptable fuel for internal combustion engines, gas turbines, fuel cells or other local utilities, as well as for a chemical feedstock for such processes as methanol synthesis [20].

#### 4.3 Emissions during thermal gasification

Thermal gasification technology practically provides no emissions, apart from the gases (mainly methane and carbon dioxide) emitted with the syn gas. However proper management of the gases with no leakages within the plant (production, storage, upgrading, transport) ensures no emissions. When comparing several technology chains for manure: (i) anaerobic digestion with pre-treatment, (ii) combustion of either raw manure or manure digestate and (iii) thermal gasification of manure digestate, followed by land application of residues from each, they reportedly yield the same savings for carbon dioxide (120–130 kg CO<sub>2</sub> per ton of raw manure





treated). The only scenario with slightly lower savings (about 110 kg CO<sub>2</sub> per ton raw manure treated) was observed for thermal gasification of pellets from raw manure, omitting the anaerobic digestion step. Still, the differences between the scenarios reported are relatively small and changes in the input data therefore may change the relative succession of the scenarios with respect to carbon dioxide balances [7].

## 5. Possibilities and barriers for implementing the technology

Technically thermal gasification is unproblematic and can be fully automated, but manure fibres should, according to the EU Waste Combustion Directive (2000/76/EF), be treated as waste, resulting in regulations for the quality of combustion gases to be released. This results in requirements for detailed measurements and possibly also purification (including commissioning, registering, monitoring), which are not economically applicable for farm-scale gasification. As the result manure fibres should in practice be treated in large gasification units or CHP plants only, and most likely in combination with other biomasses, such as straw, wood chips or household wastes.

Regulations for heating should also be considered. Changes in excise taxation of the heat produced at such plants could be implemented. Alternatively, it could be forbidden via spatial planning to establish own heating plants or heating plants that do not use a prescribed fuel.

Any technologies that result in products that are intended for sale/export out of the farm/region have the drawbacks that the markets do not currently exist or are not yet fully developed for the products.

The technologies are to some extent proven, but their environmental and economic performances are especially researched in case of fibre fractions from pig slurry. Such research would also clarify whether some policy measures could make it more feasible to implement thermal gasification for manure [16].

The gasifier may also be used in the following:

- Co-firing with coal, oil or gas in existing power plant boilers,
- Indirect firing in gas turbines,
- In large Stirling engines,
- Direct firing in gas turbines,
- In combustion engines or fuel cells (with gas cleaning)
- In production of liquid fuels.

The technology for thermal gasification of manure is not presently available as standalone technology at farm-scale. Therefore, economic feasibility studies should be made in all target countries. According to Polish data, the investment cost of an installation running for other biomass fuels than manure is within a range of 1-5 million EUR/MW installed [17]. In general, the technology is still difficult to implement technically, with legislative challenges in relation to the interpretation of the EU Waste Combustion Directive [16].





# 6. Description of the pilot experiments in Denmark

Several experiments in Denmark have been undertaken using the Low Temperature Circulating Fluidized Bed (LT-CFB) pilot gasifier of 500 kW, designed especially for difficult, low grade biomass and waste fuels, such as the agricultural biomass of cereal straw, energy crops and animal manure. The necessary high fuel flexibility is achieved through a novel but simple combination of a preceding fast pyrolysis in a fast fluidized bed chamber and subsequent char gasification in a slowly fluidized bubbling bed chamber. The LT-CFB gasifier allows for an efficient gasification at a very well-controlled maximum process temperature, which is usually below 750°C [3, 4].

#### 6.1 Description of manure pellets

The manure used in the experiments made with the 500 kW LT-CFB gasifier was first digested in the Fangel biogas plant, Denmark (Table 4), then dried and pelletized. The pre-treatment steps of the manure digestate involved mechanical separation (from 4 to 30% DM) and drying with steam or flue gases (from 30 to 90% DM). The owner of the biogas plant is Fangel Miljø- & Energiselskab A.m.b.a. The plant processes mesophilically (37 °C) pig and cattle slurry and small amounts of poultry and mink slurry from 26 animal farms from the area. In addition to slurry, intestinal content and flotation sludge from an abattoir, dairy waste, as well as waste from food processing industry, tannery industry and medicinal industry is supplied. The biomass is heated using a heat exchanger system and sanitised at 60 °C for 3½ hours, before digestion. After digestion, part of the digested biomass is mechanically separated into solid and liquid fractions. The liquid fraction is used in the biological gas purification filter. The main part of the digested biomass is transported to the 23 decentralised storage tanks with a total capacity of 25,000 m<sup>3</sup>, close to the fields. The surplus of digested biomass is sold each year to the crop farmers in the neighbourhood [34].

Main data	Value	Unit
Animal manure	124	tons/day
Alternative biomass	19	tons/day
Biogas production	2.2	mill. Nm³/year
Digester capacity <sup>1</sup>	3750	m <sup>3</sup>
Process temperature	37	°C
Pasteurisation MGRT	3,5	hours at 60 °C
Gas storage capacity	50	m <sup>3</sup>
Utilisation of biogas	CHP-plant/gas boiler	
Biomass transport vehicle	20	m <sup>3</sup> vacuum tanker
Average transport distance	6.5	km
Investment cost <sup>2</sup>	25.3	mill. DKK

Table 4. Main data of the Fangel biogas plant [34].

1) 2 × 1600 m<sup>3</sup> + 550 m<sup>3</sup>, 2) including storage capacity





The resulting pellets (Fig. 1) from dried digestate of Fangel biogas plant (f ( $\phi$  4mm) have been shown to have a rather good HHV, 11.3 GJ/t (15.3 GJ/t s for pellets from raw manure) [4, 8].



Figure 1. Pellets from digested pig manure (90% DM). Photo: Ksawery Kuligowski, POMCERT.

#### 6.2 Thermal gasification in LT-CFB

In the gasification experiments, small fuel particles were entered into the pyrolysis chamber and rapidly pyrolysed at ~650°C due to good thermal contact with the mainly re-circulated sand and ash particles. Due to the low temperature and retention time in the pyrolysis chamber essentially only light tars and no PAH were formed.

The residual char, pyrolysis gases and inert particles were then blown upwards into the primary cyclone, which separated char and inert particles into a bubbling bed char reactor. There the char was gasified at typically ~730°C using air and steam. The char gas and fine ash particles left the top of the char reactor and entered the pyrolysis chamber. Heavier inert particles were re-circulated into the pyrolysis chamber from the bottom of the char reaction chamber while acting as a heat carrier. The heat liberated due to the mainly exothermic reactions in the char reactor was consumed by the mainly endothermic processes in the pyrolysis chamber. Therefore, the exit stream out of the pyrolysis chamber had an even lower temperature compared to the temperature in the char reactor. No extra pressure was applied in the gasifier chamber. Pressurized gasification has so far only been applied to coal, wood, peat, straw and sawdust, as well as in processes of co-gasification of coal with biomass [26-29].

Ash particles formed may have recirculated several times but eventually the main part typically escaped through the primary cyclone and was separated by the more efficient secondary cyclone. A further coarser ash stream may be drained from the bottom of the gasifier, and in these two ways, typically around 95% of the ash was retained.

#### 6.3 Characteristics and use of the residue from LT-CFB

Residues from coal combustion are already widely used in the markets of construction materials as an additive to concrete in cement plants or as a soil filler, e.g. in bridge embankments. The fertilizer value of coal ash is lower than the potential ashes from gasifying biomass due to the lower phosphorus content and contamination with radioactive elements. Wood ashes can normally be used as soil filler in forests and parks, avoiding its application for plants directly consumed by humans and/or animals.





No data on the characteristics of residual ashes from full-scale thermal gasification of manure is, to our knowledge, available, but the results from Danish pilot experiments are described below. Figure 2 shows the ash from thermal gasification of pelletized digested pig manure.



Figure 2. Ash from thermal gasification of pellets from digested pig manure. Photo: Ksawery Kuligowski, POMCERT.

#### 6.3.1 <u>Ash chemistry</u>

The main component of the ash from the thermal gasification experiments using digested pig manure was calcium (Ca, Table 5). The relatively high content of phopshorus (54.4 g/kg) and potassium (34.7 g/kg) made the ash a good candidate for fertilizer. Other elements were iron (Fe), sulfur (S), magnesium (Mg) and sodium (Na). Among heavy metals, the greatest concentrations were recorded for zinc (Zn), strontium (Sr) and copper (Cu). Main minerals found in the ash were calcite and quartz. Ash phosphorus occurred in the form of a mixture of carbonate- and hydroxy-apatite, which form various, irregular crystals with dimensions of up to 100 mm. Table 5 shows the basic chemical composition of the ash from the pilot-gasification experiments.

	Unit			Unit	
Analysis	g/kg	(SD)	Analysis	g/kg	(SD)
Total Ca	311	12.2	Total Na	9.1	0.64
Total P <sup>1</sup>	54.4	4.3	Total Mn	0.7	0.04
P soluble in water <sup>2</sup>	0.1*10 <sup>-3</sup>	0.043*10 <sup>-3</sup>	Total Zn	1.04	0.02
P soluble in					
ammonium citrate <sup>2</sup>	45*10 <sup>-3</sup>	2.4*10 <sup>-3</sup>	Total Sr	0.4	0.02
Total K <sup>3</sup>	34.7	0.36	Total Cu	0.26	0.26*10 <sup>-3</sup>
Total Fe	29.2	1.75	Total Ni	0.02	0.09*10 <sup>-3</sup>
Total S	21.1	0.14	Total Pb	0.93*10 <sup>-3</sup>	0.21*10 <sup>-3</sup>
Total Mg	20.7	1.2	pH (1:25 H₂O)	12	

Table 5. Concentration of chosen elements in the ash (ICP-OES). SD denotes standard deviation.

<sup>1</sup> Measured by UV-VIS spectrometry in H<sub>2</sub>SO<sub>4</sub> extracts [9]

<sup>2</sup> Shown as % of Total P

<sup>3</sup> Measured by Energy Dispersive X-Ray Fluorescence (EDXRF) [9]

#### 6.3.2 <u>Element mobility and P extraction potential</u>

The ashes were leached in order to test the mobility of the elements and especially phosphorus. Leaching with water removed up to 65% of potassium, 48% of sodium, 41% of molybdenum, 21% of sulphur, 14% of aluminum, 10% of selenium and 9% of calcium from the ash using a 1:200 (w/w) ash:water load. However, the water soluble phosphorus in ash was very low (< 0.1% of total





P). The optimal sulphuric acid requirement (measured as mass of acid applied per mass of phosphorus extracted) was 0.98 kg  $H_2SO_4/kg$  ash at an acid concentration of 0.6 M, yielding phosphorus extraction of 94%. This is approximately three times more acid than used in industrial production of phosphorus fertilizer from phosphate rock (acid requirement about 6-7 kg  $H_2SO_4/kg$  P recovered). The use of higher acid concentrations (2 M) did not improve phosphorus dissolution, but increased zinc release. Removal of calcite equivalent to 70% of initial ash mass reduced ash pH from 12 to 6 and concentrated total phosphorus (two times higher), water soluble phosphorus (10 times higher) and citric acid soluble phosphorus (1.5 times higher) [10], [11].

### 6.3.3 Application of ash in agriculture

Ashes from thermally gasified, pre-digested pig manure were also used as fertilizers on fields. In general, leaching of phosphorus from ash-amended soils was very low (<0.5% of phosphorus applied in ash) compared with the inorganic fertilizer used, disodium phosphate (DSP) (97% and 12% of phosphorus applied in soils with low and high phosphorus sorption capacity, respectively). Phosphorus leaching depended on irrigation rate and soil sorption capacity (clay content and organic matter), but did not depend on whether long-term ash-soil incubation had taken place prior to onset of irrigation [10].

On acidic soil, ash was an effective liming agent (2% addition by mass raised soil pH from 4.5 to 7.9). It also increased soil electrical conductivity (20% higher), water holding capacity and soil bicarbonate-extractable phosphorus (available phosphorus; 3-6 times more). Removal of lime prior to ryegrass fertilization on acidic, sandy soil did not have any significant effect on plant yield compared to using ash containing lime, as soil acidity gradually dissolved the lime in ash treatments and enhanced phosphorus availability. However, plant phosphorus uptake from ash with lime removed was three times higher than that of lime-containing ash. For high phosphorus application rate (1066 mg P/kg soil), the yields in ash treatments were almost as good as for using the inorganic fertilizer of monocalcium phosphate (MCP). Heavy metal uptake by plants was minor [14].

The field tests for the growth of barley and ryegrass on two Danish (one sandy and one loamy) agricultural soils over two growing seasons indicated that application of ash for 20 kg P/ha only slightly increased barley DM yield compared to no addition. However, total phosphorus uptake in barley was the same as for addition of 20 kg P/ha DSP during the first year (1.2 g P/m<sup>2</sup>) and 15% higher in a new experiment in the second year. Tripling ash application rate to 60 kg P/ha in both sandy and loamy soil had no significant effect on barley DM yield and phosphorus uptake was comparable to the application of 20 kg P/ha in ash. Performance of neutralized phosphorus containing acid extract from the ash was as good as DSP in sandy soil both in terms of barley DM yield and phosphorus uptake. Despite the low background phosphorus level in both soils, the rye grass crop grew very well and application of extra phosphorus in the form of ash therefore did not produce any significant increase in grass DM yield and phosphorus uptake. Soil pH was noticed to increase from 6.3 to 6.8 in both soils 18 months after ash application [12].





#### 6.3.4 Ash spreading techniques on land

Because the ash from thermally gasified manure was a very fine material with almost 80% w/w of particles ranging in diameter between 75-250  $\mu$ m [9], it is sensitive for wind erosion. In order to prevent its loss after fertilization, several techniques can be recommended:

- 1. Mixing with topsoil this was the case during the field experiments shown in [12] and [14], however on a large scale, rather time consuming and unpractical,
- 2. Injection with water the drawback of ash having a highly hydrophobic nature (big wetting angle) resulting in inhomogeneous distribution in water,
- 3. Granulation (techniques already developed for other kinds of ashes, e.g. wood [21, 22, 23]),
- 4. Mixing with sewage sludge to provide mineral-organic fertilizer.

#### 6.3.5 <u>Summary of ash reuse</u>

In general, ash from thermally gasified manure releases phosphorus in a slower rate than mineral fertilizers, providing lower plant yields but in parallel lower leachability. Therefore it is not recommended as a starter fertilizer; however, its supplementation in later stages of growth may be an option. In spite of lower yields, phosphorus uptake from ash is similar to the uptake from mineral fertilizers. The mismatch between relatively good phosphorus uptake and poorer plant yields is probably due to other factors, such lime content and toxicity from heavy metals. Long-term field studies with ash application and testing of residual effects are needed also to verify the accumulation of phosphorus and heavy metals in the soil.

#### 6.3.6 <u>Changes in the residue as compared to original manure</u>

Thermal gasification of manure concentrates acid-extractable metals in the ash as compared to the original pellets. The other factor which may affect these measurable concentrations is the halforganic nature of the pellets (38-44% ash content) and totally mineral nature of ash. Therefore, in order to compare the chemical characteristics of these two materials, the concentrations were referred to incombustible matter (IM), which in case of pellets denotes the ash content. Even then, most of the measured elements were detected at higher concentrations in the ash than in the pellets. Only phosphorus range was quite similar. Table 6 shows the comparison between basic chemical composition of pellets from digested pig manure and ash from its thermal gasification.

Table 6. Comparison of chemical composition between pellets and ash as measured by UV-VI-	S
spectrometry in $H_2SO_4$ extracts (P) and FAAS (remaining metals). IM – incombustible matter [9	<i>]</i> .

	Pellets	Ash
Analysis	g/kg IM	g/kg IM
Total P	38–57	54.4
Total K	11	15
Total Zn	0.81	1.25
Total Cu	0.07	0.20
Total Cr	0.18	0.09
Total Ni	0.03	0.12





#### 6.3.7 Changes during storage

During storage of ash, the transformation of lime from calcium oxide (CaO) into calcium carbonate (calcite) may occur. The lime in the ash is abundant in two forms; calcium oxide (burnt lime) and calcium carbonate (limestone, calcite) depending on its age. In the beginning of storage, calcium oxide present in the ash can react with water from the atmosphere forming calcium hydroxide (Ca(OH)<sub>2</sub>) and further reacting with carbon dioxide forming calcium carbonate (CaCO<sub>3</sub>, carbonization). This may have a negative effect on ash pre-treatment prior to phosphorus extraction due to limited dissolution of calcium at later ash ages. The reason for low calcium removal from the ash is in fact that calcium oxide rapidly forms calcium hydroxide with a very low water solubility (0.18 g Ca(OH)<sub>2</sub> in 100 ml H<sub>2</sub>O at 0°C), thus only minor amounts of calcium oxide present in fresh ash can be dissolved in water [11, 13, 15].

#### 6.4 Future possibilities

The use of low value fuels for production of electricity at efficiencies around 45% is within the scope of the LT-CFB gasifier, which is expected to be feasible in sizes from around 5 to around 100 MW of fuel input. Based on more intensive purification, the gas can also be used for more demanding applications, and the possibility of producing liquid fuels/products may also be considered [3, 4]. However, production of fuels would require extensive and expensive purification stages as well as most likely a change into steam gasification.

The technology (LT-CFB) presented in this report is now being upgraded in the 6 MW demonstration plant owned by DONG Energy in Kalundborg, Denmark. The demonstration plant is described in more detail in the separate Baltic MANURE report "Examples of existing good practices in manure energy use" (available at http://www.balticmanure.eu).

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# This report in brief

Thermal gasification is an emerging technology for the utilization of manure energy content with proven advantages over conventional combustion.

While the technology is ready for many other fuels (e.g. coal, wood, waste) its development for low calorific problematic (i.e. corrosive) fuels, such as manure, is still work in progress. The economic feasibility is not proven yet, and the environmental legislation still needs to be adjusted for farm-scale installations.

However, thermal gasification holds promise for energy production from manure while also offering reduction of manure-based emissions, providing the energy storage in the resulting syn-gas and reuse options for phosphorous and micronutrients from the ash.

This report on thermal gasification of manure was prepared as part of Workpackage 6 on Manure Energy Potentials in the project Baltic Manure.

# About the project

The Baltic Sea Region is an area of intensive agricultural production. Animal manure is often considered to be a waste product and an environmental problem.

The long-term strategic objective of the project Baltic Manure is to change the general perception of manure from a waste product to a resource. This is done through research and by identifying inherent business opportunities with the proper manure handling technologies and policy framework.

To achieve this objective, three interconnected manure forums has been established with the focus areas of Knowledge, Policy and Business.

Read more at www.balticmanure.eu.









Baltic Sea Region

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