

Project details

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Project partners	Technical University of Denmark (DTU), Copenhagen University (KU), Aarhus University (AU), Roskilde University Centre (RUC), SEGES, Danish Technological Institute (DTI), DONG Energy and Hededanmark A/S.
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Table of contents

1	Short description of project objective and results	3
2	Executive summary	6
3	Project objectives and development	7
3.1	Project development	9
4	Project results	11
4.1	WP1: PYRONEER Gasification – Fuel Variability, Energy Efficiency and Bio-ash Quality	11
4.1.1	WT 1.1 PYRONEER Biomass Gasification & WT 1.2 Fuel and Bio-ash Analyses	11
4.1.2	WT 1.3 Testing of Bio-ash Material in Short-term Studies	15
4.2	WP2: Bio-ash Characterization and Method Development for Removal of Heavy Metals and Unwanted Organic Substances	17
121	WT 2.1 Lab Analysis Heavy metal content in the produced bio-ashes using standard methods	
	WT 2.2 Electrodialytic Removal of Heavy Metals	17
	WT 2.3 Testing of Bio-ash Material in Short-term Pot Experiments	19
	WT 2.4 Feedback to Task 1.1	19
4.2.4	WP3: Bio-ash Amendment to Agricultural Soils – Logistics and Handling	20
	WT 3.1 Investigation of the Agglomeration Properties of Selected Bio-ash Materials	20
	WT 3.2 Screening of the Agglomerated Bio-ash Material for Potential Fertilizer use	21
	WT 3.3 Micro-plot Field Experiments with Bio-ash and Bio-ash Granules	22
	WT 3.4 Larger-scale Field Experiments and Demonstration Experiments with Straw Bio-ash	23
4.4	WP4: The Market, the Business, the Legislation and the Guidelines	26
	WT 4.1 Farmers' Attitude, Market Potential, Pricing	26
	WT 4.2 Bio-ash Business Plan	28
	WT 4.3 Legislation	28
	WT 4.4 Guidelines	29
5	Utilization of project results	30
6	Project conclusion and perspective	31
•	Troject conclusion and perspective	J _
7	Dissemination of project results	33
7.1.1	Scientific peer reviewed publications:	33
7.1.2	Other publications:	34
7.1.3	Conference and workshop presentations:	34
7.1.4	Others:	36
7.1.5	PhD Thesis:	37
7.1.6	Master Thesis:	38
7.1.7	Bachelor Thesis:	38
7.1.8	External visiting PhD students	38
7.1.9	Patent applications	38
8	Annex (Not to be published)	39
8.1	Market development material from Work Package 4	39
8.2	Scientific peer reviewed publications	39

1 Short description of project objective and results

The project aims at testing the low temperature circulating fluidised bed (LT-CFB aka. PYRONEER) gasification technology as a platform for improved utilisation of a variety of low-value, difficult biomass and waste fuels from different sectors of society. The goal is to produce electricity and heat with a high efficiency to increase security of supply and reduce the environmental impact of the energy sector. Furthermore, a substantial part of the work relates to investigations and demonstrations on handling, utilisation and marketing of bio-ash fertilizer from gasification of such resources to add to the economic feasibility and long-term sustainability of the process.

The goal of the project is thus to demonstrate the potential application of the Pyroneer gasification platform to enforce a more circular economy by co-production of energy and fertilizers from low-cost organic residues and wastes (secondary resources). This is regarded as a crucial measure to increase security of supply of energy and critical non-renewable nutrients, especially phosphorus, as well as to reduce the environmental impact of the energy sector and the agricultural sector. The potential role of the Pyroneer gasification technology in this regard, is illustrated in an example with a circular phosphorus economy in Figure 1.

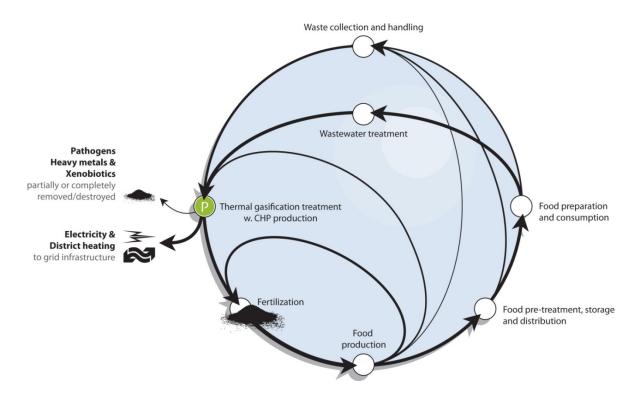


Figure 1: An illustration of a society with an ideal, closed phosphorus loop facilitated by flexible thermal gasification. CHP: Combined Heat and Power.

To optimize the project resource efficiency, the investigation and demonstration has been carried out with complementary activities on laboratory scale, pilot scale and demonstration/full scale. Laboratory screening of new potential fuel candidates, fertilizer ash characteristics and eletrodialytic P extraction from ashes have been conducted at the Technical University of Denmark and Copenhagen University. Pilot scale gasification of selected fuel candidates has been conducted at the Technical University of Denmark while Copenhagen University and Aarhus University have conducted numerous pot plant

experiments on these to investigate ash fertilizer quality. Demonstration scale gasification of optimal fuel candidates was performed by DONG Energy at Asnæs Power Plant in a 6 MW Pyroneer gasifier. With ashes from demonstration scale gasification, field plant trials were conducted in cooperation between Copenhagen University, Agrotec, DONG Energy and the Technical University of Denmark.



Figure 2: Investigation of Pyroneer fuel flexibility in laboratory scale (left), pilot scale (center) and demonstration scale (right).



Figure 3: Investigation of Pyroneer ash quality in laboratory scale incubation studies (left), pilot scale pot plant experiments (center) and demonstration scale field trials (right)

The results from the experimental part of the study show that the Pyroneer gasifier is a versatile and highly flexible technology capable of converting a very wide range of secondary resources including highly problematic organic residues and waste water sludge. In a large experimental campaign it was found that ashes from Pyroneer gasification of sewage sludge – especially if extracted from the char reactor, have a much lower concentration of heavy metals and Polycyclic aromatic hydrocarbons per unit of Phosphorus than all other technologies investigated (two pyrolysis platforms, TwoStage gasification and two incineration technologies). The fertilizer quality of Pyroneer ashes measured by phosphorus plant availability is severely influenced by the quality and characteristics of the fuel, as well as the soil type and to some extent by the assessment method and range from very low to almost

commercial P fertilizer quality. In a comparison with other technologies converting the same sewage sludge fuel, phosphorus in Pyroneer gasification ashes was found to be less plant available than phosphorus in the sludge and pyrolysis chars and incineration with high air equivalence ration and long retention times. However, Pyroneer gasification ashes performed better than commercial fluid bed incineration ashes and ashes from TwoStage gasification. Development of a simple process for thermal oxidation of Pyroneer ashes almost doubled plant availability of the phosphorus in the ashes, placing the ashes in the best half of the assessed substrates.

Doing excessive research with electrodialytic treatment of Pyroneer gasification ashes, a highly improved next generation process has been developed. In the course of this work it was found that ashes from gasification of sewage sludge are much better suited for electrodialytic upgrading than ashes from sludge incineration.

As a natural part of the project, legal and practical issues related to marketing and handling of bio-ashes for use as fertilizers in the Danish agricultural system has been evaluated. Farmers and farming consultants are largely positive towards the potential option to use bio-ashes for phosphorus fertilization - especially within the organic farming community. However, there is currently no demand for bio-ash products in the Danish agricultural sector that would justify a business plan and a satisfactory price. This may change with legislation (Danish or on EU level) on the use of organo-fertilizers (including manure and sewage sludge), and for the organic farming community, the demand can be expected to increase towards 2022 where the use of straw and manure from conventional farming will be banned. For a reasonable development in the use of bio-ashes in Danish agriculture the current legislation needs to be adapted to encompass this new type of fertilizer.

The bio-ash research area (production, optimization and end-use) is complex and comprehensive, but a significant step to improve relevant knowledge and applicability has been taken with this project. The results of the project indicate a huge optimization potential and has already sparked new research and development activities by the consortium, by project partners as well as by other stakeholders in Denmark and abroad.

More than anything else, this project has identified remarkable potentials and benefits from application of Pyroneer gasification and use of gasification bio-ashes in agriculture. Increased security of supply of energy and irreplaceable nutrients, reduced environmental impact and improved economy of energy producers and farmers may be some of the positive consequences. Proper management of secondary resources will be vital in the future, and Pyroneer gasification is a very strong asset in this regard. The results from the current project have sparked a new interdisciplinary research area into the optimized thermal management of organic resources. Many new research and development activities have already been initiated related to the design and implementation of optimized systems where fuels with the proper characteristics are identified or produced by blending and pre-treatment and matched to the thermal process design and operation, the downstream ash treatment and the end-use of the final ash and energy products to increase economic feasibility and long term sustainability of the systems. In addition to new effort to increase the general understanding of these systems, specific Pyroneer related research and development projects are also conducted to improve applicability of this unique process in new settings with smaller, de-centralized units.

2 Executive summary

English summary:

The goal of the project is to demonstrate the potential application of the Pyroneer gasification platform to enforce circular economy by co-production of energy and fertilizers from organic residues and wastes. The project involves a comprehensive screening for new fuel candidates, proof-of-concept operation on selected fuels in pilot and demonstration scale, development of downstream ash treatment, market analysis and development and investigation of ash fertilizer quality in laboratory and field scale. It was found that a system with a good match between fuel characteristics, thermal process design and end-use of the products can co-produce electricity, heat and ash fertilizer with very high efficiency. Pyroneer gasification and co-gasification is in many respects a very promising platform for this purpose combining flexibility in fuels and products and high energy efficiency.

Dansk sammenfatning:

Projektet demonstrerer hvorledes implementering af Pyroneerforgasning kan styrke den cirkulære økonomi ved at samproducere energiprodukter og gødning fra termisk omsætning af organiske rest- og affaldsprodukter. Projektet inkluderer en omfattende screening af nye brændsler, proof-of-concept forgasningforsøg i pilot- og demonstrationsskala, udvikling af teknologier og processer til askeopgradering, udvikling og analyse af markedet for bio-aske samt undersøgelser af udvalgte bio-askers gødningskvalitet i laboratorie- og markforsøg. Resultaterne viser at det er muligt at designe systemer der effektivt kan samproducere el, varme og god askegødning, såfremt der er et godt match mellem brændselskarakteristika, den termiske proces og slutanvendelsen af produkterne. Pyroneerforgasning er en meget lovende teknologi i denne sammenhæng, på grund af dennes høje brændsels- og produktfleksibilitet og effektivitet.

3 Project objectives and development

The project aims at testing the low temperature circulating fluidised bed (PYRONEER) gasification technology as a platform for improved utilisation of a variety of low-value and difficult biomass fuels from different sectors of society, with the goal of producing electricity and heat with a high efficiency to increase security of the national energy supply. Furthermore, a substantial part of the work relates to investigations and demonstrations on handling, utilisation and marketing of the bio-ash as high value fertiliser to add significantly to the profitability and long-term sustainability of the process. The objectives of the project, as it was originally formulated, were:

- Investigate and demonstrate the performance and feasibility of improved PYRONEER process operations while utilising alternative fuels, also with regard to bio-ash quality.
- Remove heavy metals from the obtained ash fraction to favour its applicability to agricultural soils
 using the electrodialytic remediation method.
- Increase bio-ash applicability by agglomeration and demonstrate its use as a fertiliser.
- Investigate legal status and market aspects for PYRONEER bio-ash, with respect to origin of the feedstock and to the expenses connected with the upgrading of PYRONEER bio-ash to a commercial product.

A successful project will contribute to increased enforcement of a circular economy by co-production of energy and fertilizers from low-cost organic residues and wastes (secondary resources). In this way, the project will contribute to the mitigation of environmental impacts related to current linear consumption flows in modern society.

An example of this linearity is provided in Figure 4. The figure illustrates a conceptual linear flow of phosphorous (P) through society via a food production and consumption chain. Linear flows of P can increase the vulnerability of the agricultural sector as the global stock of the P fertilizer raw material (rock phosphate) is rapidly decreasing while consumption is increasing. Without proper recycling and reuse, the agricultural sector could face periods with P fertilizer deficiency in the future. Unlike fossil-fuel energy there is no biological or technological substitute for P.

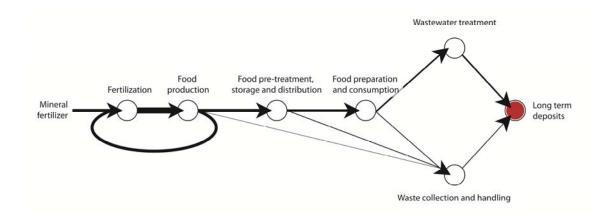


Figure 4: Example of a linear material flow, illustrating the movement and degradation of phosphorous through a food production and consumption chain.

In the case of P, a large fraction is accumulated in organic waste and sludge, and the associated long term deposition in the illustrated system can be directly to compartments of soil or water, or following treatment by e.g. incineration. In any regard, the P flowing into the society in this linear process would end up completely detached from the original purpose of the element. The linear flow is largely unsustainable, and an enormous optimization potential regarding society's net utility of these materials could lie in more holistic handling and management strategies.

The role of the Pyroneer gasification technology in this regard, is illustrated in Figure 5.

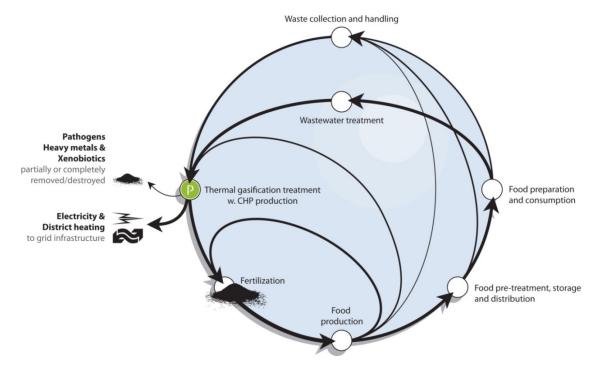


Figure 5: An illustration of a society with an ideal, closed phosphorus loop facilitated by flexible thermal gasification. CHP: Combined Heat and Power.

In the illustrated system, P circulates from use as fertilizer via food and food consumption to sewage sludge and waste. During the cycle, the P is heavily polluted with organic and inorganic toxins and xenobiotics from the surrounding society. In the present Danish system a large part of the P circulating is distributed directly in agricultural systems carrying many unwanted substances. In the proposed system, all recollection of P rich resources is directed through a thermal purification stage where practically all organic compounds are destroyed and the content of several problematic heavy metals severely reduced. If the thermal purification is conducted using highly efficient thermal gasification (e.g. the Pyroneer gasifier), then a substantial amount of electricity, heat or other energy products are produced in the process. This project aims to validate this approach by proving the technical feasibility of Pyroneer gasification of various secondary resources and investigating the potential benefits and challenges hereof.

3.1 Project development

Overall, the project has been a great success. There have been a number of severe challenges to engage during the course of the work, but the project consortium has pulled through it all and provided a comprehensive set of highly relevant and interesting results.

Two PhD students were hired; Tobias Pape Thomsen enrolled at DTU KT worked primarily on task 1.1 activities, including both theoretical and experimental investigations; and Raimón Parés Viader, enrolled at DTU Byg, worked in central experimental activities in WP2, i.e. developing of treatment schemes for electrodialytic removal of toxic elements from gasified waste biomass from different sources, and physico-chemical characterization of the ash prior to and after treatment with focus on toxic elements and nutrient speciation (tasks 2.1 and 2.2). Both PhD thesis have been submitted and defended and both candidates have been granted the PhD degree.

There have been several significant changes to the project consortium, project description and objectives throughout the course of the project period. The most essential are described in the following:

- In October 2014, DONG Energy decided to shut down development of gasification technology and the activities related to the 6 MW Pyroneer plant in Kalundborg. According to the management at New Biosolutions at DONG, the technology worked very well and the business case of a 65 MW plant at Kalundborg was good. However, it had proved impossible to find a global partner to co-develop and construct full-scale plants (http://www.biopress.dk/PDF/dong-dropper-termisk-forgasning).
- In November 2014, a two-day project meeting with all the project partners was therefore held and it was concluded that the LT-CFB/Pyroneer technology was as strong and relevant as it had ever been. The development of the technology was still going on at DTU, and new perspectives especially at smaller scale were emerging. Therefore, it was found relevant to continue the project activities in the same general direction, but with some relevant changes.
- Up until October 2014, the project had a strong commercial focus in the selection and analysis
 of new fuels for PYRONEER gasification. New fuels were characterized by their fuel
 characteristics, market value, total quantity, energy production potential and potential ash
 quality and value.
- After the meeting in November 2014 it was decided to increase focus on fundamental aspects of ash fertilizer quality and application. This led to a shift in the project objectives:
 - With no large scale ash production, no large scale ash fertilizer handling test or ash fertilizer quality investigation (field trials) could be conducted
 - o Reduced focus on large scale energy production
 - o Focus on good small and medium scale business cases (e.g. sewage sludge gasification) and the future value of phosphorus recovery
 - A stronger focus on ash chemistry and a more fundamental understanding of ashes from the PYRONEER gasifier as well as ashes from thermal conversion in general
 - Development of a large study (the Cross Platform Sludge Experiment) to examine differences in the fertilizer quality of ashes produced from the same fuel on multiple gasifiers, pyrolysis systems and combustion/incineration plants.

After DTU KT took over facilities and employees of the former Biosystems Division at Risø National Laboratory for Sustainable Energy, there was a continuous reformation of the capacities. This led to the following changes in the project consortium:

- Senior scientist Henrik Hauggaard-Nielsen left ECO (DTU KT) in August to 2014 to accept a new position as professor at Roskilde University (RUC), Department of Environmental, Social and Spatial Change. Dorette Müller-Stöver (DTU KT) took over Henrik's responsibilities in the project, while Henrik stayed on affiliated to the project as co-supervisor for the two Ph.d. students.
- Later on, Dorette Müller-Stöver moved to University of Copenhagen (KU) as a result of a
 company transfer between DTU and KU. A group of three researchers and three PhD students
 focusing on the development of solutions for a sustainable use of the limited phosphorus
 resources in agricultural production were transferred to the Institute for Plant and
 Environmental Sciences (PLEN) at KU. The group is now integrated in PLEN's basic research on
 soil fertility and plant nutrition.

Other relevant changes in the consortium included:

- In 2015 Videncentret for Landbrug merged with the Videncenter for Svineproduktion, changed the name and became SEGES, and the project responsible at SEGES later changed.
- AgroTech is since the first of January 2016 a division of Danish Technological Institute (DTI).

All these changes affected the project consortium that was initially formed by: Danmarks Tekniske Universitet (DTU KT and DTU Byg), DONG Energy A/S, Aarhus Universitet, Agrotech A/S, Videncentret for Landbrug and Hededanmark A/S. By the end of the project, the project consortium was formed by DONG Energy A/S, Danmarks Tekniske Universitet (DTU KT and DTU Byg), KU PLEN, Roskilde University, Aarhus University, DTI, SEGES and Hededanmark A/S

4 Project results

The results of the project are described for the different work packages. An overview of the related dissemination activities of the entire project is provided in the final chapter (chapter 7).

4.1 WP1: PYRONEER Gasification – Fuel Variability, Energy Efficiency and Bio-ash Quality

4.1.1 WT 1.1 PYRONEER Biomass Gasification & WT 1.2 Fuel and Bio-ash Analyses

The first set of results from WT 1.1 and 1.2 related to the development and implementation of a method to screen for new fuel candidates for LT-CFB gasification. 22 new potential fuel candidates were collected and characterized and compared to 4 previously proven LT-CFB/PYRONEER fuels (see Figure 6). The fuels included residues from vegetable production, residues from animal production as well as wastewater sludge and waste fractions. Samples were collected from Denmark, Italy, Brazil, Malaysia and Mali to achieve a wide span in the assessed characteristics. The work focused on the technical feasibility related to potential conversion of the new fuels in Pyroneer systems, but also included assessment of practical issues related to handling and feeding as well as estimations of overall energy yield ratios and ash fertilizer phosphorus quality. The investigated fuel candidates were categorized by their apparent suitability as LT-CFB fuels and various positive characteristics as well as potentially problematic issues have been identified and discussed.

The overall conclusion from the fuel screening was that the PYRONEER technology is highly fuel flexibility and applicable within a wide range of settings. In a current Danish context it was found to be most relevant to consider low temperature gasification of especially sewage sludge and manure fibers while the international perspective includes especially sugarcane bagasse, various residues from olive oil production and rice husks. Only five fuel candidates are considered as potentially very problematic for single fuel LT-CFB gasification: Fat separated from wastewater treatment, palm kernel shell residues with high NaCl content, two animal meat and bone meal samples from DAKA Biodiesel and wood pruning from Italian vineyards. The problems mainly relate to the proximate composition, potential ash sintering, ash/char deposit formation and corrosion of steel surfaces during thermal tests.

The fuel screening also included a screening of P fertilizer quality of ashes and chars produced from thermal treatment of the different fuels, and significant differences were identified between the P fertilizer quality of ashes and chars. Finally, the fuel screening also involved an investigation of how analytically determined characteristics of three fuel mixes differ from the expected linear sum of the involved fuels' individual characteristics. The results indicate profound possibilities for optimizing fuel and ash characteristics by fuel mixing with regard to ash deposit formation and sintering as well as ash and char P fertilizer quality.

Of the 5 best candidates identified in the fuel screening, sewage sludge was found to be one of the most interesting as it is a locally as well as globally available resource with a large potential for optimized management compared to several of the currently applied management options. Proper management of sewage sludge holds a substantial potential for recovery of highly concentrated phosphorus (P) with good plant availability in ashes and chars from the thermal conversion. It was therefore decided to progress with sewage sludge in a series of experimental campaigns to provide a detailed investigation of potential benefits and problematic issues related to sewage sludge management by LT-CFB gasification.



Figure 6: Secondary resource samples included in the original screening of LT-CFB fuel candidates [1].

Four experimental campaigns with gasification and co-gasification of sewage sludge in LT-CFB gasifiers have been conducted and the results on process performance and the quality of the gas product were compared to results from other studies on thermal gasification of sludge. The overall conclusion was that many different gasifier designs have been proven successfully on sewage sludge fuels and LT-CFB

gasification is very well suited for gasification of sewage sludge as well as co-gasification of sewage sludge and cereal straw. The LT-CFB gasifier was found to yield the highest hot gas efficiency, carbon conversion rate and total system electrical efficiency of the assessed systems.

Detailed examination of the fertilizer quality of char and ash substrates from thermal conversion and coconversion of sewage sludge was a central part of this work task. Fertilizer quality was addressed by comparing the elemental composition, PAH content and P plant availability of LT-CFB ashes from different gasification and co-gasification campaigns to ash and char samples from incineration and pyrolysis of sewage sludge as well as to their respective untreated sludge samples and a mineral P reference (the Cross Platform Sludge Experiment, CPSE). In addition to the conventional thermal platforms, a process for post-oxidation of pyrolysis chars and gasification ashes has been developed and the oxidized substrates were also included in the investigation. Pictures of fuels and ash samples are provided in Figure 7. From the investigation of ash fertilizer quality it was concluded that all of the investigated thermal platforms are applicable for production of P fertilizers by conversion of sewage sludge with the proper design and operational settings. Post-oxidation of pyrolysis chars and gasification ashes was found to have a remarkable effect on P fertilizer quality – especially on the LT-CFB ashes. In addition, co-gasification of sludge and straw in LT-CFB gasifiers in general seem to provide a better ash fertilizer than mono-sludge gasification. Many different people within DTU and cooperative companies participated in the preparation and execution of the CPSE experiments including DTU KT, DTU BYG, DTU CEN, DTU ENV, KU PLEN, KU IGN, DONG Energy, Frichs A/S, FORS A/S, BIOFOS and WERKSTÄTTEN heating-systems.



Figure 7: Pictures from the CPSE study of sludge fuel variants (1-3) obtained from the Danish WWTP Bjergmarken Renseanlæg in Roskilde as well as of ash and char substrates from pyrolysis (4-5), gasification (7,9), and incineration (12-14) of the sewage sludge samples. Post oxidized samples of slow pyrolysis char (6), LT-CFB bottom ashes (7) and TwoStage gasifier ashes (10-11) were also included in the study

Assessment of the influence of the thermal process design on the fertilizer quality of the ashes was studied with a new adapted method combining short term incubation studies, chemical sequential extraction with full elemental mass balance and scanning electron microscopy to identify changes in P association induced by different thermal treatments. Changes in P fertilizer quality as function of incubation time and as function of changes in the particle size distribution of the ash substrate was also investigated. The results indicate vast possibilities to produce optimized ash fertilizers and context-specific designer fertilizers in systems encompassing thermal conversion of e.g. sewage sludge or custom fit mixes of multiple low value residues and wastes. A discussion about burden shifting in such management systems has been introduced and results were analyzed from two life cycle assessment case studies comparing sewage sludge gasification in centralized LT-CFB gasifiers with the current practice of direct application of sludge on farm soil. The results indicate a substantial improvement of the LT-CFB scenario compared to the reference case with regard to a reduced impact on climate change and reduced toxicity of the P fertilizer.

Based on this work in WT 1.1. and 1.2 it is concluded that there is a profound potential for optimizing the management of sewage sludge, straw and many other types of residues and wastes, by applying the proper thermal processes. With a good match between fuel characteristics, process design and end use of the produced ash and gas products, such a system can be setup to encompass full utilization of the energy potential in the resource and simultaneously produce high quality fertilizers. LT-CFB gasification is in many respects a very promising platform for this purpose combining flexibility in fuels and products and high energy efficiency. Co-gasification of sewage sludge and cereal straw has been found to produce very high quality thermally purified P fertilizers, and the potential benefits of fuel mixing needs to be further examined.

Highlight results from WT 1.1 and 1.2 includes the following:

- New method for fuel screening developed and tested, allowing for effective characterization of relevant fuel and ash characteristics
- Illumination of some of the potential benefits and perspectives of fuel blending
- Identification of many new relevant fuels for PYRONEER gasification as well as a suitable fuel for TwoStage gasification
- Contribution to development of a Danish focus on thermal treatment of sewage sludge within the wastewater treatment companies, technology providers and farmers
- Test and development of a new method for fertilizer ash characterization and analysis
- Initial development of a simple thermal method for post-process optimization of the P fertilizer quality of pyrolysis chars and gasification ashes
- Identification of co-gasification of sewage sludge and cereal straw (e.g. wheat) as a highly beneficial way to manage sewage sludge
- Determination of several relevant mechanisms promoting or inhibiting P fertilizer quality in ashes and chars
- Potential development of PK ash fertilizers for organic farming
- Life cycle analysis of PYRONEER systems for sewage sludge gasification indicate substantial benefits for society with regard to climate change mitigation, reduced eutrophication and especially reduced eco- and human toxicity

The perspectives of these results are many and highly positive. From a commercial as well as a societal stand point. Reduced environmental impact, improved public health, reduced dependence on fossil fuel and phosphorus import, improved economy for wastewater treatment plants and energy producers, increased export of energy technology and potentially increased turnover and employment within organic farming.

Problems and delays (their consequences and corrective actions taken):

As previously mentioned, the discontinuation of the 6 MW Pyroneer induced substantial changes on these tasks, but the changes were used positively to expand the perspectives of the work.

4.1.2 WT 1.3 Testing of Bio-ash Material in Short-term Studies

The main objective of this task was to test ash materials deriving from the low-temperature gasification process for their P fertilizer value. It was a further aim of the screening process to identify ash or soil parameters that might predict the fertilizer value of the material to be able to avoid time-consuming and labour-intensive pot experiments.

The first pot experiments on the fertilizer value of ashes were mainly focused on ash material from the gasification of wheat straw and sewage sludge. Later, other materials such as shea nut gasification ash and ashes from a mixture of straw and sewage sludge were investigated as well. In the last phase of the project, the P plant availability of the different substrates deriving from the CPSE experiment was in the focus of the investigations.

Generally, two-month pot experiments were carried out in 2-3 kg pots with spring barley as a test plant, incorporating the ash materials into a low-P soil and comparing their effects on plant biomass and P uptake with the effect of a mineral P fertilizer. In-depth studies were carried out by labelling the soil phosphorus pool with the radioactive isotope 33P, which allows determining the proportion of plant P derived from an external P source more precisely. Furthermore, selected ash materials were investigated in a three-month soil incubation study, where at regular intervals sub-samples were sequentially extracted to assess the dissolution of the different ash materials and their distribution into soil P pools of different availability.

Various soil test methods (Olsen-P, anion exchange resin-extractable P, water-extractable P, Diffusive Gradient in Thin films (DGT) – P) were used and correlated to the plant P uptake observed in pot experiments.

The results showed that straw gasification ash contains considerable amounts of plant-available phosphorus, but availability might be delayed compared to water-soluble mineral P. Furthermore, soil application of straw ash increased the level of exchangeable potassium to about 80% of what was the level achieved with the application of K_2SO_4 . Soil pH was also increased throughout the experiments, especially at high doses of straw ash applied. Ash from low-temperature gasification of shea nuts showed a similar P fertilizing effect as straw ash, although it was less efficient at lower dosages. In contrast, the application of sludge ash derived from sludge from Randers WWTP did not cause an increase in P uptake of barley, independent of the dosage applied, which might be due to high amounts

of Fe and Al-phosphates present in the material. The results of the sequential extraction of soil P pools corresponded well with the plant availability observed in the pots. It could further be concluded that the addition of ashes did not exert indirect effects on soil or plants that caused a markedly increased P uptake from the soil P pool.

Two ashes from a mixture of straw and sludge also proved to be suitable as P-fertilizing materials, with a P:K ratio well adapted to plant demand and a lower content of heavy metals compared to pure sludge ash.

All tested CPSE materials increased plant biomass compared to the untreated control. The pyrolysis chars and the incineration ash had a fertilizer value comparable to that of sludge and mineral fertilizer and better than the gasification ashes. However, applying a final oxidation step increased P availability in low-temperature gasification ash to an extent that plant biomass became comparable to that in the treatments receiving pyrolysis char or incineration ash. Generally, a smaller particle size of the materials resulted in a higher P availability of the materials.

In the soil tests conducted, water-extractable P and DGT-P showed the overall best availability to reflect plant P uptake from thermally treated materials, but still not to an extent that renders plant pot experiments unnecessary.

Problems and delays (their consequences and corrective actions taken):

The first sludge ash showed no plant P availability which among other reasons lead to the experiments on mixing sludge and straw as a fuel. Furthermore, the CPSE study was initiated to obtain more in-depth knowledge about the change of P plant availability when thermally treating sewage sludge.

WP 1 Milestones:

All milestones of WP1 were met timely despite changes in the project disposition.

M1.1 (M 20) Determination of the gasification characteristics for the different biofuels.

An initial screening let to selection of relevant candidates for pilot- and demonstration scale testing, and provided new information about fuels, ashes and processes.

M1.2 (M 23) Selected bio-ashes are tested regarding their fertiliser value.

A comprehensive bio-ash characterization campaign was conducted with multiple different methods to accommodate the objectives of the current WP and develop the related knowledge and methods for future studies.

M1.3 (M 25) Bio-ashes to be further investigated in WP2 and WP3 are selected.

Proof-of-concept operation in pilot and demonstration scale of selected fuel candidates provided ash samples for the remaining WPs and in-depth bio-ash characterization.

4.2 WP2: Bio-ash Characterization and Method Development for Removal of Heavy Metals and Unwanted Organic Substances

4.2.1 WT 2.1 Lab Analysis Heavy metal content in the produced bio-ashes using standard methods

The aim of this task was to measure the heavy metal content, and nutrients like phosphorus, in the Pyroneer gasification ashes provided by the project partners from WP1. This would confirm the need to separate these toxic elements from the ashes using a remediation technique like electrodialysis, in order to recover the fertilizer value of gasification ashes.

Three different Pyroneer gasification ashes were analyzed in terms of heavy metal content:

- One resulting from the gasification of a mixture of sewage sludge (Stegholdt) where P was totally precipitated with biological methods (30%) and wheat straw (70%).
- Another one produced from gasifying sewage sludge where P was precipitated in a 50% with Fe salts (Randers).
- The third one produced from gasifying sewage sludge where P was precipitated in a 30% with Fe salts (Bjergmarken) and Al flocculants were used.

In addition, ash resulting from the incineration of Bjergmarken sewage sludge was also analyzed. The elements measured were the ones existing in the Danish legislation for sewage sludge and bio-ashes: Cd, Cr, Cu, Ni, Pb and Zn. The concentration of these elements, P and other major elements like Al, Ca or Fe, was measured using an ICP-OES after pre-treatment following the Danish Standard DS259 (digestion with 7.3 M HNO₃). The results were compared to Danish legislation limits and values in commercial fertilizers.

The heavy metal concentration in the four ashes, and its ratio to P, was compared to Danish legislations for sewage sludge application, and bio-ashes, into agricultural soils. The results showed that the limits were exceeded only for Pb in Bjergarken ashes, and Ni/P in Stegholdt ashes. From this perspective, the content in heavy metals was not a major issue.

However, the results also showed that the heavy metal to phosphorus ratio was clearly higher to the ones found in commercial fertilizers, except for Cd and Cr. Therefore, there was still a need to separate the heavy metals from the ashes to avoid its accumulation in agricultural soils.

4.2.2 WT 2.2 Electrodialytic Removal of Heavy Metals

The objective of this task was to separate P from heavy metals in the four studied ashes using electrodialysis (ED). The technology is briefly described in Figure 8.

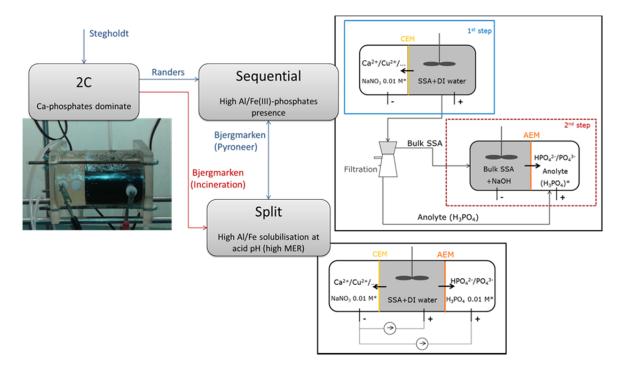


Figure 8: ED setups used in the research in WP2, WT 2.2. *Initial solutions.

Prior to the electrodialytic removal of heavy metals, solubilisation of Al, Fe, Ca, P and heavy metals at different pH values (using solutions of HNO₃ and NaOH) was studied. This would give a first approach about how the ashes should be treated. Once the pH release experiments were completed, the electrodialytic experiments were executed starting with a 2-compartment setup.

pH release experiments showed that heavy metals or P were not soluble in water, and either an acid or alkaline extraction of (some of) the heavy metals involved a solubilisation of P at the same time. Therefore, a removal of the heavy metals in the different ashes using electrodialytic methods was also entailing a solubilisation of P. The focus was then to recover P in a different solution than the heavy metals, which could have potential in the fertilizer industry.

Moreover, pH release results showed a high amount of alkaline soluble P for Randers and gasification Bjergmarken ashes. The reason was the high content of Al/Fe(III)-P bindings in these two ashes. Using an acid extraction in them, P was simultaneous released with Fe and Al, which would complicate its separation using ion exchange techniques. A methodology which enabled a proper separation of P from Al, Fe and heavy metals in these two ashes was a two-step extraction, using HNO₃ in the first step and NaOH in the second one.

For each ash, a different electrodialytic method was needed to achieve a separation of P from the bulk ash as well as Al, Fe and the heavy metals. Thus, a 2-compartment setup (or similar) was enough to recover P from Stegholdt and incineration Bjergmarken ashes at a rate of 80%. For Randers and gasification Bjergmarken ashes, the combination of a couple of 2-compartment setups sequentially was needed to recover around 70% of P. In this two-step electrodialtyic process, ashes were acidified in the first step, and alkalinised in the second, emulating the two-step extraction with HNO₃ and NaOH. Highlight results are presented in Figure 9.

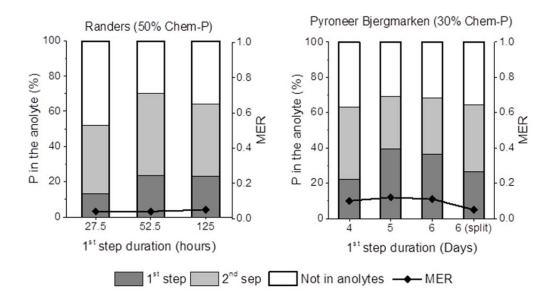


Figure 9: P recovered (%) and MER in each analyte using the sequential ED setups for Randers and Pyroneer Bjergmarken SSAs. MER: Minor Element Ratios - a common parameter to evaluate the suitability of wet process phosphoric acid WPA in the fertilizer industry.

The final P products were P-acidic solutions, and therefore H_3PO_4 , which had a ratio of AI, Fe and heavy metals to P comparable to wet process phosphoric acid (WPA), a P raw material used in the production of P fertilizers nowadays. This ensured the recovery of the fertilizer value for all the ashes.

Problems and delays (their consequences and corrective actions taken)

Some minor adaptations in the electrodialytic setups had to be made to Bjergmarken ashes, as Al and Fe were more soluble than for Randers and Stegholdt ashes. High Al and Fe content in H_3PO_4 solutions are inconvenient for the production of commercial fertilizers.

4.2.3 WT 2.3 Testing of Bio-ash Material in Short-term Pot Experiments

As explained in the previous work task, the research focused in the P extraction in a liquid solution as heavy metal could not be separated without solubilizing P at the same time. Also, as explained in Task 2.2 results, the solution produced was comparable in terms of purity to WPA, widely used in the fertilizer industry. Therefore, no pot experiments were found necessary.

4.2.4 WT 2.4 Feedback to Task 1.1

Partners from WP 1 were informed of the results obtained from Stegholdt and Randers samples as soon as they were obtained.

WP 2 Milestones:

M2.1 (M 20) Heavy metal content in bio-ashes is identified.

The heavy metal concentration in the four ashes, and its ratio to P, was compared to Danish legislations for sewage sludge application, and bioashes, into agricultural soils. The results showed that the limits were exceeded only for Pb in Bjergarken ashes, and Ni/P in Stegholdt ashes. From this perspective, the content in heavy metals was not a major issue.

M2.2 (M 23) Toxic elements are experimentally removed from bio-ashes with high levels of these.

The final P products were P-acidic solutions, and therefore H3PO4, which had a ratio of Al, Fe and heavy metals to P comparable to wet process phosphoric acid (WPA), a P raw material used in the production of P fertilizers nowadays. This ensured the recovery of the fertilizer value for all the ashes.

M2.3 (M 29) Treatment cycle and operational parameters are evaluated.

For each ash, a different electrodialytic method was needed to achieve a separation of P from the bulk ash as well as Al, Fe and the heavy metals.

M2.4 (M 30) Bio-ash fertilizer value is documented.

The research focused in the P extraction in a liquid solution as heavy metal could not be separated without solubilising P at the same time. Since the solution produced was comparable in terms of purity to WPA, no pot experiments were found necessary.

4.3 WP3: Bio-ash Amendment to Agricultural Soils – Logistics and Handling

4.3.1 WT 3.1 Investigation of the Agglomeration Properties of Selected Bio-ash Materials

The objective of this task was to use bio-ashes selected from task 1.2 for agglomeration experiments in the laboratory and pilot size agglomeration reactors. The aim was to study the pelletization using a single pellet press unit, a bench scale pellet mill and test the compression strength and abrasion properties of the pellets produced.

A number of methods for production of ash pellets were tested. A single pellet press was used to test the pelletizing properties of bio-ash samples. The diameter of the press channel was 8 mm, and the temperature of the die was controlled using a thermo-couple connected to a control unit. A first bio-ash sample with 50% moisture content was pelletized at different die temperatures (29 and 81°C) under different pressing pressures (195-585 MPa) and different pelletizing sequences (stepwise and one time). It was found that increasing the temperature didn't ease the pelletization, and the static friction in the press channel was very high (>4000 N). Therefore in the second stage, sodium laureth sulfate and water were mixed with the bio-ash sample as a lubricant. The static friction was reduced to less than 800N, which means possible production in bench-scale pelletizers. In the next step, different kinds of additives such as lignin by product were tested. However, it was concluded that no suitable method could be identified for these carbon-rich ashes without addition of high amounts of extra material to the ash, and

such amendments would be unrealistic (M3.1). In the meantime, experience showed that when about 50% water is added to the ash, the material is spreadable avoiding problems with dust emission during storage, transport and spreading, and at the same time self-ignition of carbon-rich ash can also be avoided. Therefore water addition to the ash was considered the most realistic method of ash handling.

Problems and delays (their consequences and corrective actions taken):

No pellets could be produced with the bio-ashes and water addition to bio-ash from gasification was the most suitable method of ash treatment. Therefore, the effects of water addition on the availability of P and K for fertilization were studied.

4.3.2 WT 3.2 Screening of the Agglomerated Bio-ash Material for Potential Fertilizer use

The objective of this task was to study the extractability of P and K in bio-ash granules/pellets of different quality selected from task 3.1 after application to different soil types in soil incubation experiments and compared with untreated bio-ash. P and K dynamics in soil should have been followed by measuring water-, Olsen- and resin-extractable P and exchangeable K in soil compared with soil treatments receiving traditional P and K fertilizers.

Potassium (K) availability of a range of biomass ash and gasification biochar (GB) products was tested across three contrasting soils (i.e., acid clayey, acid coarse sand and alkaline coarse sand) in a 16-week laboratory incubation experiment. Soil exchangeable K was measured over time to represent the K availability. The recovery of K in soils from applied residue products was compared with that of potassium chloride (KCI) to calculate the mineral fertilizer equivalent (MFE). To determine the potential effect of residue storage on K availability, one straw GB was subject to different wetting-drying schemes before the experiment. No clear difference was seen between ash and GB in K recovery after soil application. However, a direct comparison between straw ash and straw GB indicates lower K availability in the ash. Some variance in K recovery among the applied residues was found, e.g., 31-86%. In the KCl and the majority of the ash/biochar treatments, higher K availability was found in soils with lower clay contents. All products displayed high K fertilizer effects, 50-86% MFE eight weeks after application to all three soils, except lower MFE when two GBs from sewage sludge-straw mixture applied to an alkaline coarse sand soil (35 and 45%). After 16 weeks not all K in the residue products was available, and very little extra release occurred between 1 and 16 weeks in the current experimental setup without plants. Water-soluble K in waste products gives an indication of K availability but not very precisely. Storage of GB with water showed no significant effects on K availability except for a tendency of increased K availability in the acid sandy soil after wet storage. This study indicated high K fertilizer value of various ash/biochar products in three different soil types during a 16-week period, and adding water will provide new possibilities for practical handling of such waste products without reducing their K availability. Results from laboratory studies of P availability are described under Task T3.3.

Problems and delays (their consequences and corrective actions taken)

Due to the failure of production of pellets the effects of water addition to ash were instead studied.

4.3.3 WT 3.3 Micro-plot Field Experiments with Bio-ash and Bio-ash Granules

The objective of this task was to measure the fertilizing value of selected bio-ash granules/pellets under natural conditions in soil-collar experiments on P-depleted soils on two contrasting locations. The idea was to plant plots with a commonly grown cereal and to measure the nutrient uptake to compare it to the uptake on plots receiving mineral fertilizers. Effects of the bio-ash granules/pellets on P availability would be measured in the year after application by measuring Olsen- and resin-extractable P in soil.

Two Micro Plot trials with four selected ashes were established in spring 2014 at two different locations with different soil types with a low P level. Unfortunately one of the experiments (at DTU Risø Campus) had to be abandoned due to problems with crop establishment despite of repeated re-sowing of the experiment. In the remaining experiment, P fertilizing effects of ashes from gasification of straw, sewage sludge + straw and shea nut were tested. Effects of different application rates and ash placement in soil on P uptake in spring barley were investigated and compared with reference treatments with increasing amounts of mineral P applied as liquid fertilizer. Effects of ash application on soil pH and soil P tests in autumn 2014 and spring 2015 were investigated (M3.2).

Phosphorus (P) availability was tested in gasification biochars (GBs, 730°C) of different origin: wheat straw (STR), shea nut shells (NUT), poultry manure (POUL) and two sewage sludges mixed with wheat straw (SSA and SSB). GBs were mixed with a loamy sand in a field mini-plot experiment with spring barley and compared with a mineral P fertilizer (KH₂PO₄) and applied at 30 and 60 kg P ha-1. An accompanying 16-week laboratory incubation study was carried out with three contrasting soils. The field experiment showed only tendencies of increased yield and P uptake in barley after application of biochar or KH₂PO₄, indicating non-limiting P status in this soil. During the 16-week incubation, all GBs increased pH markedly, especially in STR- and NUT-amended soils and in acid soils. Of the P applied as STR, NUT and POUL 21–29% was recovered as resin-extractable P (available P) in the two acid soils after 16 weeks, while in the alkaline soil the recovery from STR (49%) almost matched that from triple superphosphate (52%). Recoveries from SSA and SSB were similar and constantly low (<14%) throughout the incubation. A significant positive relationship was identified between the resin-P concentration and the resulting pH in soils amended with some GBs with low P contents. These results showed a varying P availability after biochar amendment depending on the feedstock and a different ability of GBs to substitute mineral P fertilizer for crops. The initial soil pH had a significant effect on the P availability in GB-amended soils. A few results from this study are supplied in Figure 10.

Problems and delays (their consequences and corrective actions taken):

Identical Micro-plot experiments were established at two locations with different soil types. Due to poor establishment of plants one location no reliable results from this location are available. The result from the other location are presented in a scientific paper submitted to Geoderma

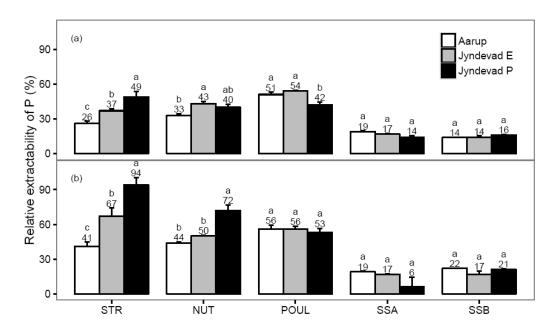


Figure 10: Plant availability of P in gasification biochars relative to P in triple superphosphate fertilizer measured as relative extractability (%) of P by resins in soils amended with gasification biochars after 1 week (a) and 16 weeks (b) in a laboratory experiment with three soils with variable clay content and pH (gives a measure of. It is calculated as the ratio (%) of recoveries of the applied P as soil resin-P between the GB and corresponding TSP treatments. The values and bars are means and standard errors (n = 3). Same letters above each GB indicate no significant differences among the soils (p > 0.05). Treatments were STR: gasification biochar from wheat straw; NUT: gasification biochar from shea nuts; POUL: gasification biochar from poultry manure; SSA: gasification biochar from mixture of sewage sludge (Stegholt)and straw; SSB: gasification biochar from mixture of sewage sludge (Bjergmarken)and straw. (Li et al. Unpublished results, see dissemination results in chapter 7).

4.3.4 WT 3.4 Larger-scale Field Experiments and Demonstration Experiments with Straw Bio-ash

This task was dedicated to field experiments on plant nutrient availability from bio-ash applications. Field trials on low P soil were initially planned with two types of bio-ash (fine dust bio-ash and bio-ash pellets/granules) and two levels of bio-ash in order to test crop P utilization. Demonstration experiments on spreading techniques of the granules/pellets of two different bio-ash types were also initially planned.

Field trials with ash applied to spring barley were established in spring 2014 and 2015 on a soil with a very low P status at DTU Risø Campus. In 2015 the trial included both plots with new application of ash and plots where ash was applied in 2014 in order to quantify residual effects. As in the 2014 experiment, the fertilizing effect of P in two selected ashes and one raw sludge material was tested at two different application rates, which have been increased in 2015 due to the minor plant response in 2014. The plant response in dry matter yield and P uptake was compared to reference treatments receiving 0, 30, 60 and 90 kg P/ha in triple-superphosphate fertilizer. Soil samples were taken for analysis of phosphorus status

in soil after application of ash and again after harvest. Plant samples were taken during the growing season and at harvest for analysis of nutrient uptake and finally yields were recorded (M3.3).

In 2014, no clear plant response to P supply could be observed, not even in the superphosphate treatments. Part of the explanation might be the very dry spring and general retarded plant growth in the whole experiment. Plant response to the increased phosphorus dosages in 2015 was, however, much more pronounced. In 2015 the measured plant response to the increased phosphorus dosages was much clearer than that observed in 2014. In the superphosphate treatments, the yield of the treatment fertilized with 90 kg P/ha was significantly increased compared to the treatments receiving 0 or 30 kg/ha, which was also reflected in a higher P status in soil (Olsen-P value). The plots receiving the highest ash dosages also produced the overall highest grain yields, being significantly different from all other treatments except superphosphate at 90 or 60 kg P/ha. The soil P status (Olsen-P values) in the ash plots, however, were not increased to the same extent as those in the mineral fertilizer treatments, thereby confirming the results from the previous pot experiments. Furthermore, available K in soil was greatly increased especially in the plots receiving the high straw ash dosage. The applied sludge granules (not gasified) did not show a P fertilizing effect compared to the untreated control indicating that the P fertilizer effect of the sludge was increased by the gasification. In the 2014 plots, no residual fertilizer effect of the ash application was observed. A few results from the study on K fertilizer quality are supplied in Figure 10.

Problems and delays (their consequences and corrective actions taken):

Spreading technique of bio ash was prepared and relevant equipment was investigated. A demonstration activity with machines for spreading of ash was planned to take place in August/September 2014. Due to the shutdown of the Pyroneer gasifier it was not possible to get enough ash for the demonstration and thereby it had to be cancelled. Excess resources were completely channeled into the field trial which made it possible to include both first and second year residual effect in 2015 year's field trial. In the field trials bio-ash was spread by hand. In the first field experiment carried out in 2014, no plant response to P fertilization could be observed. It was therefore decided to increase P dosages in the following season, which lead to increased yields in the high-P plots.

WP 3 Milestones:

M3.1 (M 17) Bio-ash granulation methods to be used/compared are identified

No suitable granulation method was identified. Instead it was found that the bio-ash could be stored and spread in a moist form without affecting the availability of nutrients.

M3.2 (M 25) Micro-plot field studies on fertilizing effects of differently pre-treated bio-ash are performed.

Micro-plot experiments were established at two locations (Risø and Foulum) but had to be abandoned on one location (due to un-foreseen problems with plant establishment). The study showed that bioashes had variable P fertilizing effect, but lower than for mineral P fertilizers. Laboratory experiments showed a K fertilizing effect of 50-85% relative to KCl fertilizer.

M3.3 (M 32) Field and demonstration studies on the fertilizer value and spreading technique of bioash/bio-ash granules are carried out.

Field studies of fertilizer values of bio-ash was performed in two years. A demonstration study of spreading technique had to be abandoned due to lack of bio-ash after cut down of the Pyroneer facility in Kalundborg. Instead additional measurements of fertilizer value in the year after application was made. In the field study bio-ash had a P effect but lower than that of mineral P fertilizer. The applied sludge granules (not gasified) did not show a P fertilizing effect compared to the untreated control indicating that the P fertilizer effect of the sludge was increased by the gasification. No detectable residual fertilizer effect of the ash application was observed in the following year after the application.

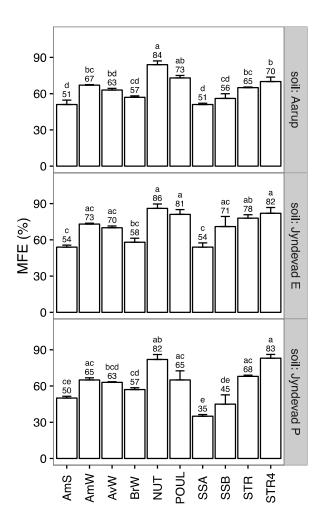


Figure 11: 2. The mineral fertiliser equivalent of K applied as biomass ashes/gasification biochars after 8 weeks in three soils relative to KCl fertilizer. Error bars and values over each column are standard errors and means, respectively (n = 3). Different letters over columns indicate significant differences among treatments (p < 0.05). Treatments: first four treatments were different combustion ashes (AmS, AmW, AvV, BrW from Amager and Avedøre powerplants and Brande Varmeværk); STR, STR4: gasification biochar from wheat straw; NUT: gasification biochar from shea nuts; POUL: gasification biochar from poultry manure; SSA: gasification biochar from mixture of sewage sludge (Stegmarken) and straw; SSB: gasification biochar from mixture of sewage sludge (Bjergmarken) and straw. (Li et al. Unpublished results).

4.4 WP4: The Market, the Business, the Legislation and the Guidelines

The decision by DONG Energy to shut down Pyroneer related activities influenced the work in WP 4 substantially. The product and market became hypothetical and large scale investigations were no longer possible. However, important preliminary work has been conducted in this WP to prepare commercialization of bio-ash from thermal gasification in a future scenario where production is restarted.

4.4.1 WT 4.1 Farmers' Attitude, Market Potential, Pricing

A descriptive analysis of the Danish and selected European markets as well as interviews with market participants was to be performed in this task in order to assess the evolution and the present appearance of the markets for the ash products, as well as potential risks associated with market opportunities. Price sensitivity and price elasticity needed to be analyzed along with farmers' attitudes (interests, expectations, concerns) towards the potential products.

<u>Progress:</u> The terminology and potential fertilizer value of the ash has been discussed in the project group comparing it to other recirculation products as incineration ash and sludge.

Agricultural advisers have been consulted on the farmers expected response to bio-ash.

The bio-ash has been presented as an option on a seminar (09-04-2014) for organic farmers and other professionals on the theme Recirculation of nutrients to organic farming. A common statement from the seminar has been enclosed in Appendix..

Information and interview material was prepared for the Danish Organic Convention 2013 (Økologikongres 2013) in Bredsten, Denmark. The work included a series of 2 new posters and exhibition design and execution (Figure 12). The main purpose of the work was to get in dialogue with organic farmers and try to determine (quantitatively as well as qualitatively) their willingness and desire to use Pyroneer fertilization ashes from conversion of waste water sludge as P fertilizer when the current use of conventional manure is banned in a few years' time. Results were very positive and indicated that the vast majority of the organic farmers would consider using Pyroneer ash fertilizer from conversion of waste water sludge as P source in future organic farming systems. Bio-ashes were presented again and discussed on a stand at the Congress for organic farmers in November 2015. It is estimated, that about 150 persons visited the stand during the two days of the congress.

<u>Results:</u> By interviews and discussion it was concluded that the best option is to refer to ashes from thermal gasification of organic residues as bio-ash.

The responses from farmers and advisers have shown that bio-ash has a strong competition from other residues that can be used in agriculture.

The lack of nitrogen in the ash is seen as a drawback and regarding pricing other residues as sludge and incineration ash can be received for free or even with a premium.



Figure 12: Picture of EUDP project exhibition at Danish Organic Convention 2013

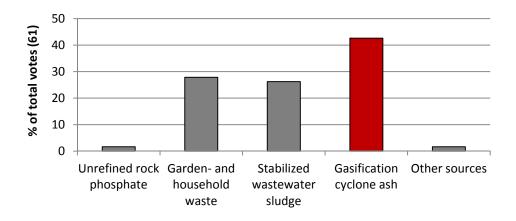


Figure 13: Main result from the audience vote to the question "How should organic Farmers replenish the P stock of their soils in future farming systems?" at the Danish Organic Convention 2013

Even if bio-ash from waste water sludge can be produced with reduced content of heavy metals and no organic harmful substances there is a fear for the reputation when using it for fertilizing and soil improvement. It is therefore concluded that it will be very difficult to get a profitable price for bio-ash in the current situation.

For future commercialization, the ability to store and handle the bio-ash in a simple way will be of prime importance. Some kind of standardization of the product will be necessary if the bio-ash should enter the market as a commercial fertilizer. The present scenario points towards a distribution of the bio-ash resembling the distribution of bottom ash from straw fired combustion plants.

4.4.2 WT 4.2 Bio-ash Business Plan

In this task, a business plan should be prepared containing a description of different PYRONEER bio-ash fertilizers (depending on the fuel), the market, pricing, financial analysis, possible strategies and a concise executive summary. The business plan regarding the gasification technology is covered by the ForskEL (PSO) project, B4C - Biomass for Combustion (2010-1-10445).

<u>Progress:</u> The project group collected relevant information for a business plan.

Results: Results from Task 4.1 as the main factor supplied with performance factors as the following:

- Bio-ash needs controlled storage and wetting.
- The ash should be made in pellets (like commercial fertilizers) but this has shown to be difficult to achieve.
- Mixing of bio-ash with other components to get a well balanced fertilizer requires a company taking the liability on the product.

It was therefore concluded that the current situation do not make basis for a business plan for bio-ash as fertilizer.

Problems and delays (their consequences and corrective actions taken):

The recognition of a low demand, strong competition from other products and difficulties in handling bio-ashes caused a decision to drop formulation of a business plan.

The analyses of the challenges have however given important clues on how bio-ashes should approach the market in the future.

4.4.3 WT 4.3 Legislation

In WT 4.3, the current legislation concerning recirculation of the residual products to conventional and organic agriculture is described and possible uses of each type of residual product in different conventional or organic cultures determined in dialogue with the National Authorities, as bio-ashes are not yet well-defined in the National legislation. Furthermore, it was to be assessed which – if any – changes to the existing laws will be necessary to cover the tested types of bio-ash (incl. evaluation of the feasibility and possible timescale of these changes as well as the authorities to be involved).

<u>Progress:</u> The Danish authorities have been consulted on the regulation of bio-ashes and their use. Needs for regulatory changes have been discussed in the project group and at the seminar mentioned in task 4.1.

<u>Results:</u> It has been established that bio-ash from straw and unpolluted wood is regulated under the "Bio-ash Order" (Bioaskebekendtgørelsen). If the bio-ash consists of any other products it will be regulated after the "Sludge Order" (Slambekendtgørelsen).

Organic farmers can only use bio-ash derived from pure wood.

There will be a need to improve the regulation – especially for use in organic farming – to improve the use of bio-ash as a tool for recirculation of nutrients.

Bio-ashes – or biochar - are not yet well-defined in the EU legislation. Therefore the products might not easily go through the EOW (End OF Waste) criteria, which could result in a more limited use and income.

4.4.4 WT 4.4 Guidelines

In the final WT of WP 4, each type of bio-ash is allocated a recommended use according to composition, legislation, application techniques, practical aspects, farmer attitude and pricing. The guidelines will be elaborated with the goal of optimizing the combination of energy and fertilizer output from the process chain, while minimizing the workflow and the risk of producing unwanted substances.

<u>Progress:</u> Realizations and results from the whole project have been summarized in a guideline (in Danish) published at LandbrugsInfo where advisers, farmers and companies are used to find technical information on the use of fertilizers in agriculture.

Results: The guideline consists of the following:

- Description of the characteristics of bio-ash
- The content of nutrients and heavy metals in two types of bio-ash
- Experiences from fertilizer trials.
- Regulatory claims on the use of bio-ash
- Summarizing recommendations

WP 4 Milestones:

M4.1 (M 15) An analysis of price sensitivity and price elasticity are performed.

Achieved

M4.2 (M 30) The business plan is elaborated.

Concluded not relevant under current conditions.

M4.3 (M 36) All available information is gathered, and guidelines are elaborated.

Achieved. "Forgasningsaske som gødning og jordforbedringsmiddel" (https://www.landbrugsinfo.dk/Energi/andre-teknologier/Sider/LI-artikel_om_vejledning_Bioaske.aspx)

5 Utilization of project results

The potential utilization of project results shifted radically when DONG Energy's Pyroneer related activities were put on hold. The project was expected to push application of the Pyroneer gasifier into new markets and substantially improve the economic feasibility of the process by valorization of the ash product as well as by increasing the national and global Pyroneer fuel potential. The project related activities at Asnæsværket would lead to large gasification bio-ash quantities being available to Danish agriculture, and the results and new product availability was expected to spark a new market for ash fertilizers in conventional and organic agriculture with several related business developments.

As the technological and commercial focus of the project changed, utilization of results was instead directed into development of new knowledge and research disciplines as well as dissemination of project results and potentials. The project has led to application of several new research projects including "Microbial biofertilizers for improved crop availability of phosphorus from soil and waste (MiCroP)" co-funded by The Danish Council for Strategic Research, PCP phase 2 project "Omsætning af spildevandsslam ved damptørring og pyrolyse til biokoks med plantetilgængeligt fosfor" supported by The Market Development Fund and one ERC project application and two MUDP project applications currently under preparation. The project has kick-started research and development of bio-ash production, quality and application from thermal gasification, pyrolysis and incineration of secondary resources of various origin and quality. In addition, the project has strengthened the co-operation between many actors within this area of knowledge including DTU, RUC, KU, AU, DONG Energy, FORS, BIOFOS, SEGES etc. During the project, SEGES has collected important information on the bio-ash value as fertilizer and will utilize this in the future recommendations on fertilizing with recirculation products also compared with fertilizers from biogas plants. The results from the project are not expected to give SEGES commercial opportunities but are expected to become important for farmers in their future fertilizer planning. The results may also contribute to the choice between thermal gasification and biogas production.

The result of the work also generated a patent application which has been filed internationally (Patent number: WO2017055341). The invention is an electrodialytic setup, which can be used to recover P from sewage sludge ashes produced in reductive thermal processes (like gasification or pyrolysis). No other methods focus on P recovery from gasification/pyrolysis ashes with high content of Fe. However, currently these thermal processes have not been commercially extended to treat sewage sludge, which reduces the developed technology's marketability. A report including an economical assessment of this setup, and some future scenarios considering a higher presence gasification/pyrolysis of sewage sludge, will be produced in the coming months. This report will be the base of future commercial activities related to this invention. To explain this invention and the other results of the PhD work under WP2, the PhD student attended to several conferences including 13th symposia on Electrokinetic Remediation (EREM) in September 2014 in Malaga in Spain, 1st IWA Resource Recovery Conference in August and September 2015 in Gent in Belgium and 2nd IWA Holistic Sludge Management (HSM) Conference in June 2016 in Malmö in Sweden.

Finally, the project has fostered massive dissemination activities (chapter 7), and the influence of the scientific papers produced during the project as well as the teaching, lobbying and conference activities conducted are expected to spread and expand slowly throughout the coming months and years.

6 Project conclusion and perspective

The project has fostered numerous conclusions in the different work packages. In WP 1 it was found that the fuel and product flexibility of the Pyroneer gasifier in a Danish context is immense and the potential application of the technology would lead to substantial societal benefits.

In WP 2 it was found that by using different electrodialytic methods, including a setup for which a patent was filed, at least 70% of phosphorus was recovered from Pyroneer gasification of sewage sludge ashes; some of which had a high presence of alkaline-soluble aluminium- and iron-phosphates. Moreover, the product was a solution with impurity levels of iron, aluminium and heavy metals comparable to wet process phosphoric acid, widely used in the manufacturing of fertilizers. This result is crucial if gasification and/or pyrolysis are chosen as future thermal processes to treat e.g. sewage sludge, as the immediate P plant availability in the resulting ashes in certain cases may be expected to be low.

In WP 3 and 4, it was attempted to develop the bio-ash market and validate the agronomic effect of Pyroneer bio-ashes in field conditions and thereby investigate the commercial value of this by-products. The market was generally positive and the nutritional value of phosphor from the ash was generally good on test locations with very low soil phosphorus content. The project has demonstrated that bioash from gasification of different biomasses can be returned to soil and utilized as P and K fertilizers in agriculture. After some weeks in soil P availability in bio-ash from straw, shea nuts and poultry manure were 40-90% relative to triple superphosphate. Bio-ash from a mixture of sewage sludge and straw had a lower relative P availability around 20%. The relative availability of K in bio-ash varied between 50 and 86% in agricultural soils with normal pH and was slightly lower in a more alkaline sandy soil. As a commercial fertilizer, marketing of the ash in a current Danish content may be difficult since the logistics and handling is challenging, the long term effects have not been fully investigated, the level of variation in the product quality is high, current soil phosphorus levels are very high, and the farmers are currently not in demand for alternative phosphorus fertilizer substrates. However, a shortcut to the market may be to get approval for use of certain bio-ashes in organic farming as organic farmers will face a severe phosphorus deficit after 2022 where the current use of manure and straw from conventional farming is phased out by law.

Based on this work it is an important general conclusion that there is a profound potential for optimizing the management of sewage sludge and many other secondary resources, by applying the proper thermal processes. With a good match between fuel characteristics, process design and end use of the produced ash and gas products, such a system can be setup to encompass full utilization of the energy potential in the resource and simultaneously produce high quality fertilizers. Pyroneer gasification is in many respects a very promising platform for this purpose combining flexibility in fuels and products and high energy efficiency. Co-gasification of sewage sludge and cereal straw is found to produce very high quality thermally purified P fertilizers, and the potential benefits of fuel mixing needs to be further examined.

From the results of this work it is thus expected that additional optimization potential exist within the areas of: i) improving fuel and ash characteristics by mixing and blending fuels ii) extraction of highly concentrated and purified bottom ashes from Pyroneer gasification with ash-only beds iii) improving downstream ash processing with further development of post-oxidation and electrodialytic separation processes iv) improving the total growth season P efficiency of fertilizer ashes by modification of the P

speciation, carbon matrix and particle size distribution to design case-specific P fertilizers v) mixing different ashes and proper N-substrates to provide full nutrient coverage in products from a thermal fertilizer refinery concept and vi) develop politics, the market and the target groups attitude towards the multiple societal benefits that can be associated with optimized use of bio-ashes in agricultural systems.

To fully utilize the potential for sustainability improvements by thermal conversion of secondary resources like sewage sludge, it is essential to acknowledge the importance of the interdisciplinary benefits related to the efficient substitution of fossil energy, the recovery of valuable elements and the reduced toxicity related to the recycling of nutrients to food production systems. To identify and implement new and better management systems of this type will require a strong cooperation between the owners and producers of the relevant resources, politicians, thermal process specialists, chemists, agronomists and farmers.

This project reinvented the multidisciplinary approach required to solve multifaceted problems, and the results show examples of profound potential benefits which would not have been identified and developed without this approach. Fuel characteristics, technology design, residual quality and end use application of products and by-products all need to be taken into account when designing optimized management of resources – primary as well as secondary. This effort requires a strong co-operation between many stakeholders with very different abilities and responsibilities. In the current project this was accomplished. The consortium has worked as a group pulling different topics and tasks in the same direction.

Development of the Pyroneer technology did not stop with DONG Energy's deactivation of Pyroneer related activities. The current status is that the technology has proven itself in demonstration scale and was found to work and perform as foreseen even after a factor 10 scaling of the thermal capacity. With DONG Energy's temporary abandonment of very large scale application of Pyroneer gasification, the development has taken a new – or several new, directions with the overall goal to foster new settings and applications for this forceful technology. Today, Pyroneer related research and development therefore also aims at medium and small scale application of decentralized units. The development is carried out by the Biomass Gasification Group at DTU Chemical Engineering and supported by KU, RUC, DTU MEK, DTU BYG, DTU MAN, AU, DONG Energy, DGC and several agricultural stakeholders, municipalities and supply companies. Currently, two large R&D projects are under way to facilitate new application of the Pyroneer technology:

- Innovation Fund Denmark, project 4106-00006B "SYNFUEL Sustainable synthetic fuels from biomass gasification and electrolysis"
- ForskEL 12454 "PolyGas Polygeneration of bio-oil, electricity, heat and bio-ashes from thermal gasification of biomass and waste"

In addition, the Pyroneer technology is expected to play an essential role in future project applications on advanced thermal fertilizer refineries, waste gasification and gasification of manure and biogas fibres. The awareness of the technology within agriculture and agriculturally related business has increased substantially since the project was initiated.

7 Dissemination of project results

7.1.1 Scientific peer reviewed publications:

Parés Viader, R., Jensen, P. E., Ottosen, L. M., Ahrenfeldt, J., & Hauggaard-Nielsen, H. (2015). *Electrodialytic extraction of phosphorus from ash of low-temperature gasification of sewage sludge*. Electrochimica Acta, 181, 100-108. DOI: 10.1016/j.electacta.2015.05.025

Thomsen, T. P., Ravenni, G., Holm, J. K., Ahrenfeldt, J., Hauggaard-Nielsen, H., & Henriksen, U. B. (2015). *Screening of various low-grade biomass materials for low temperature gasification: Method development and application.* Biomass and Bioenergy, 79, 128-144. DOI: 10.1016/j.biombioe.2014.12.019

Parés Viader, R., Jensen, P. E., Ottosen, L. M., Ahrenfeldt, J., & Hauggaard-Nielsen, H. (2017). Sequential electrodialytic recovery of phosphorus from low-temperature gasification ashes of chemically precipitated sewage sludge. Waste Management, vol. 60, pp 211-218. DOI: 10.1016/j.wasman.2016.11.030

Parés Viader, R., Jensen, P. E., Ottosen, L.M., Thomsen, T. P., Ahrenfeldt, J., Hauggaard-Nielsen, H. (2017) *Comparison of phosphorus recovery from incineration and gasification sewage sludge ash*. Water Science and Technology, vol. 75, issue 5, pp. 1251-1260; DOI: 10.2166/wst.2016.620

Mackay J.E., Cavagnaro T.R., Jakobsen, I., Macdonald L.M., Grønlund, M., Thomsen, T.P. and Müller-Stöver D.S. (2016) *Evaluation of phosphorus in thermally processed sewage sludge: P pools and availability to wheat.* Plant & Soil (Submitted)

Li, X., Rubæk, G.H., Müller-Stöver, D.S., Thomsen, T.P., Ahrenfeldt, J., Sørensen, P. (2016) *Plant availability of phosphorus in five gasification biochars.* Geoderma (Submitted)

Müller-Stöver, D.S., Jakobsen, I., Grønlund, M., Rolsted, M., Magid, J., Hauggaard-Nielsen, H. (2016) *Phosphorus bioavailability in straw and sewage sludge ashes from low-temperature biomass gasification*. Soil use and management (Submitted)

Li, X., Rubæk, G.H., Sørensen, P. (2016) K availability in biomass combustion ash and gasification biochar: an incubation study. Geoderma (In preparation)

Davide Tonini, Panagiotis G. Kougias, Charlotte Scheutz, Zsuzsa Sárossy, Tobias P. Thomsen, Jesper Ahrenfeldt, Ulrik B. Henriksen, Thomas F. Astrup (2016) *Chapter 8 - Energy recovery from water and food sector residual resources.* Chapter in peer-reviewed report. Published in: DTU International Energy Report 2016.

Thomsen, T. P., Sárossy, Z., Gøbel, B., Stoholm, P., Ahrenfeldt, J., Frandsen, F. J., Henriksen, U. B. (2017) Low Temperature Circulating Fluidized Bed gasification and co-gasification of Municipal Sewage Sludge. Part 1: Process performance and gas product. Accepted for publication in: Waste Management

Thomsen, T. P., Hauggaard-Nielsen, H., Gøbel, B., Stoholm, P., Ahrenfeldt, Henriksen U. B., Müller-Stöver, D. S. (2017) Low Temperature Circulating Fluidized Bed gasification and co-gasification of

Municipal Sewage Sludge. Part 2: Evaluation of ash materials as phosphorus fertilizer. Accepted for publication in: Waste Management

Thomsen, T. P., Sárossy, Z., Gøbel, B., Stoholm, P., Ahrenfeldt, J., Henriksen, U. B., Frandsen, F. J., Müller-Stöver, D. S. (2017) Changes imposed by pyrolysis, thermal gasification or incineration on composition and phosphorus fertilizer quality of municipal sewage sludge. Accepted for publication in: Journal of Environmental Management

7.1.2 Other publications:

Skøtt, T. (2015) *Med forgasning kan bioenergi bliver CO2-negativt*. FiB nr. 51, March 2015 http://www.biopress.dk/PDF/med-forgasning-kan-bioenergi-bliver-co2-negativt/view

Jesper Ahrenfeldt, Tobias Pape Thomsen, Dorette Sophie Müller-Stöver and Henrik Hauggaard-Nielsen (2015) *Forgasning og fremstilling af halmkoks*. Published in: Proceedings of the Plantekongres 2015, 14-15 January 2015, Herning, Denmark.

Tobias Pape Thomsen, Giulia Ravenni, Jens Kai Holm, Jesper Ahrenfeldt, Henrik-Hauggaard-Nielsen and Ulrik B. Henriksen (2015) New Marginal Biomass Resources for Medium and Large Scale Low Temperature Gasification in Denmark – Characterization and Feasibility assessment. Published in: Proceedings of the 22nd European Biomass Conference and Exhibition, 23-26 June 2015, Hamburg, Germany. Page 81-90.

Henriette Lemvig and Jesper Ahrenfeldt (2015) *Forgasning af halm bidrager til energi og værdifuldt restprodukt*. Published in Effektivt Landbrug, April 2015, special issue *TEMA: HALM OG HALMHÅNDTERING*.

Erik Fog (2016) Vejledning om forgasningsaske som gødning og jordforbedringsmiddel. Published online on Landbrugsinfo.dk (https://www.landbrugsinfo.dk/Energi/andre-teknologier/Sider/Ll-artikel om vejledning Bioaske.aspx)

7.1.3 Conference and workshop presentations:

Oral:

Müller-Stöver, D.S., Grønlund, M., Jakobsen, I., Hauggaard-Nielsen, H. (2013) *Suitability of gasification biochar as a renewable phosphorus fertilizer* // *The future of biochar*. Final Conference for the Interreg project "Biochar: Climate saving soils", 10 December 2013, Groningen, The Netherlands

Müller-Stöver, D.S., Hansen, V., Ahrenfeldt, J., Holm, J.K., Hauggaard-Nielsen, H. (2014) *Gasification biochars as alternative P fertilizer*. Workshop: Closing nutrient cycles via integration of biochar and composting, 18-June 2014, Leeds, UK

Parés Viader, R., Jensen, P. E., Ottosen, L.M., Hauggaard-Nielsen, H., Ahrenfeldt, J. (2014) *Electrodialytic extraction of phosphorus from ash of low-temperature gasification of sewage sludge*. 13th Symposium on Electrokinetic Remediation. 7-10 September 2014, Málaga, Spain. Proceedings p. 47-48.

Ahrenfeldt, J., Thomsen, T.P., Müller-Stöver, D.S., Hauggaard-Nielsen, H. (2015) *Forgasning og fremstilling af halmkoks*, Plantekongres 2015, 14th-15th January 2015, Denmark

Hauggaard-Nielsen, H., Hansen, V., Ahrenfeldt, J., Holm, J.K., Henriksen, U.B., Müller-Stöver, D.S. (2015) *Potential use of low-temperature gasification biochar as nutrient provider and soil improver - field evaluation*. International Biochar Symposium: Biochar Contribution to Sustainable Agriculture. 28-29 May 2015, Potsdam, Germany.

Müller-Stöver, D.S., Bruun, E., Hansen, V., Hauggaard-Nielsen, H. (2015) *Danske udbytteforsøg* and *Biochar og rodvækst*. Two oral presentations, Tema dag om biochar i planteproduktion, 6 October 2015, Askov forsøgsstaion, Vejen, Denmark

Thomsen, T. P., Ravenni, G., Holm, J. K., Ahrenfeldt, J., Hauggaard-Nielsen, H., & Henriksen, U. B. (2015). *Screening of various low-grade biomass materials for low temperature gasification: Method development and application*. 22nd European Biomass Conference and Exhibition (22nd EUBC&E) 23-26 June 2014, Hamburg, Germany.

Parés Viader, R., Jensen, P. E., Ottosen, L.M., Thomsen, T. P., Ahrenfeldt, J., Hauggaard-Nielsen, H. (2016) *Comparison of phosphorus recovery from incineration and gasification sewage sludge ash.* 2nd IWA Conference on Holistic Sludge Management (HSM2016), 7-9 June 2016, Malmö, Sweden.

Dorette Sophie Müller-Stöver, Jesper Ahrenfeldt, Veronika Hansen, Tobias Pape Thomsen & Henrik Hauggaard-Nielsen (2013) *Biochar and Ash from straw and sludge*, full conference exhibition booth with information, samples, questionnaires and target group interviews at Økologi-Kongres 2013, 27-28 November 2013, Bredsten, Denmark.

Poster:

Müller-Stöver, D.S., Jakobsen, I., Hauggaard-Nielsen, H. (2013) *Plant phosphorus availability in low-temperature gasification ashes*. 7th International Phosphorus Workshop, 9-13 September 2013, Uppsala, Sweden

Tobias Pape Thomsen, Jesper Ahrenfeldt, Ulrik Henriksen, Jens Kai Holm, Henrik Hauggaard-Nielsen & Dorette Sophie Müller-Stöver (2013) *Pyroneer ASKEPROJEKT - Brændselsfleksibel lavtemperatursforgasning til fosforgenindvinding og effektiv produktion af bæredygtig el og varme.* Økologi-Kongres 2013, 27-28 November 2013, Bredsten, Denmark.

Dorette Sophie Müller-Stöver, Jesper Ahrenfeldt, Jens Kai Holm, Ulrik Henriksen, Tobias Pape Thomsen & Henrik Hauggaard-Nielsen (2013) *Pyroneer ASKEPROJEKT - ASKE fra termisk biomasse-forgasning som et væsentligt element af bæredygtige dyrkningssystemer.* Økologi-Kongres 2013, 27-28 November 2013, Bredsten, Denmark.

Müller-Stöver, D.S., Jakobsen, I., Ahrenfeldt, J., Holm, J.K., Hauggaard-Nielsen, H. (2014) *Char from low-temperature gasification as a sustainable phosphorus fertilizer?* 22nd European Biomass Conference, 23-26 June 2014, Hamburg, Germany.

Müller-Stöver, D.S., Grønlund, M. Jakobsen, I., Ahrenfeldt, J., Hauggaard-Nielsen, H. (2014) *Ashes from low-temperature gasification as sustainable phosphorus fertilizer*. Sustainable Phosphorus Summit 2014, 1-3 September 2014, Montpellier, France

Müller-Stöver D.S., Jensen, L.S., Rolsted, M.; Grønlund, M., Jakobsen, I., Ahrenfeldt, J., Hauggaard-Nielsen, H. (2015) *Understanding Biochar Mechanisms for Practical Implementation*. Joint International Biochar Symposium 2015, Final EU-COST Action "Biochar" & 76. Symposium ANS e.V. 28-30 September 2015, Geisenheim, Germany

Müller-Stöver, D.S., Jensen, L.S., Rolsted, M., Grønlund, M., Jakobsen, I., Ahrenfeldt, J., Hauggaard-Nielsen, H, (2015) Return of phosphorus in agricultural residues and sewage sludge to soil using biochar from low-temperature gasification as fertilizer product. Joint International Biochar Symposium 2015, Final EU-COST Action "Biochar" & 76. Symposium ANS e.V. 28-30 September 2015, Geisenheim, Germany

Parés Viader, R., Jensen, P. E., Ottosen, L. M., Ahrenfeldt, J., & Hauggaard-Nielsen, H. (2016). *Electrodialytic recovery of phosphorus from chemically precipitated sewage sludge ashes.* 1st IWA Resource Recovery Conference, Ghent, Belgium.

Li, X., Rubæk, G.H., Müller-Stöver, Sørensen, P. (2016) *Plant availability of phosphorus in biomass gasification biochars*. 8th International Phosphorus Workshop (IPW8), 12-16 September 2016, Rostock, Germany

Thompson, R., Thomsen, T.P., Müller-Stöver, D.S. (2016) *Plant phosphorus availability in biochar and ashes from sewage sludge processed by different thermal conversion technologies*. 8th International Phosphorus Workshop (IPW8), 12-16 September 2016, Rostock, Germany

7.1.4 Others:

Müller-Stöver, D.S., Hansen, V., Ahrenfeldt, J., Holm, J.K., Hauggaard-Nielsen, H. (2014) *Gasification biochars as alternative P fertilizers*. Oral presentations at Institute of Soil Science, Chinese Academy of Science and at Nanjing Agricultural University, 9-10 October 2014, Nanjing, China (scientific visit to explore future collaboration possibilities).

Pape Thomsen, T. (2014) Integration af Lav-temperatur Termisk Forgasning I Dansk spildevandsrensning – et case studie af samfundsorienteret optimeringspotentiale indenfor spildevandsrensning. Oral presentation at a leader group seminar at Roskilde Forsyning (FORS A/S).

Parés Viader, R., Jensen, P. E., Ottosen, L.M., Ahrenfeldt, J., Hauggaard-Nielsen, H. (2015) *Electrodialytic separation of phosphorus and heavy metals from sewage sludge ash.* / Poster session presented at EMS Summer School 2015, Liberec, Czech Republic.

Pape Thomsen, T. (2015) New Marginal Biomass Resources for Medium and Large Scale Low Temperature Gasification in Denmark - Characterization and Feasibility Assessment. Oral session on Gasification and Pre-treatment, Annual CHEC Day 2015, Department of Chemical and Biochemical Engineering, Technical University of Denmark.

Pape Thomsen, T. (2015) Experimental Investigation Of

Trends And Correlations In Ash And Char Characteristics. Oral presentation, CHEC seminar on Pyrolysis and Gasification, Department of Chemical and Biochemical Engineering, Technical University of Denmark.

Pape Thomsen, T. (2016) LT-CFB gasification of municipal sewage sluge

- Results from four experimental campaigns. Oral presentation, CHEC seminar on Pyrolysis and Gasification, Department of Chemical and Biochemical Engineering, Technical University of Denmark.

Pape Thomsen, T. (2016) Pyroneer ASH PROJECT Fuel Flexible Low Temperature Gasification to close phosphorus cycle, poster presented at DTU poster competition.

Teaching in the DTU Master Course 28231 Laboratory in chemical and biochemical engineering

Teaching in the DTU Master Course 28271 Bioenergy and Sustainability – Recycling of ash fractions from thermal gasification

Teaching in the DTU special Master course Gasification of sewage sludge in a TwoStage gasifier

Teaching in Copenhagen University master course Plant Nutrition and Soil Fertility

Theme-day for RUC master students at DTU Risø "Thermal conversion of biomass and waste"

Interviews, teaching and training of interns and project students from different Danish elementary schools

7.1.5 PhD Thesis:

Parés Viader, R. (2016) *Upgrading and recovery of fertilizer value of ash from PYRONEER gasification* (PhD thesis), Technical University of Denmark (DTU), Lyngby, Denmark (ISBN: 9788778774538)

http://orbit.dtu.dk/en/projects/upgrading-and-recovery-of-fertilizer-value-of-ash-from-pyroneer-gasification-of-lowvalue-an-difficult-biomass-feedstock(a831b752-e7af-4705-86b3-20faf62e3a6d).html

Pape Thomsen, T. (2016) Closing the Loop - Utilization of Secondary Resources by Low Temperature Thermal Gasification (PhD thesis), Technical University of Denmark (DTU), Lyngby, Denmark

http://orbit.dtu.dk/files/131573789/Tobias P Thomsen 2016 Closing the Loop phd thesis Online v ersion.pdf

7.1.6 Master Thesis:

Giulia Ravenni (2014) Screening method and selection of marginal feedstocks as fuel for a LT-CFB gasifier. Master thesis, the Technical University of Denmark in the Department of Chemical and Biochemical Engineering & the Faculty of Engineering, Università degli Studi di Firenze, Italy.

Camilla Nygaard (2015) Gasification of sewage sludge in a two-stage gasifier. Master thesis, the Technical University of Denmark in the Department of Chemical and Biochemical Engineering.

Rhys Thompson (2016) Plant phosphorus availability of thermally treated sewage sludge. Master thesis, Copenhagen University in the Department of Plant and Environmental Sciences.

Christian Loft Bonde (2016) Detailed Chemical Speciation and Bioavailability of Biomass Ashes. Master thesis, the Technical University of Denmark in the Department of Chemical and Biochemical Engineering.

7.1.7 Bachelor Thesis:

Emil Lundager Jørgensen (2015) Energianalyse af Rensningsanlæg med Integreret Termisk Konvertering af Slam. Bachelor thesis, the Technical University of Denmark in the Department of Mechanical Engineering.

Lærke Wester Larsen (2016) Biogasfibre til jordforbedring – Sammenligning af forskellige efterbehandlingsmetoders indflydelse på næringsstofindhold. Bachelor thesis, Copenhagen University in the Department of Geosciences and Natural Resource Management.

7.1.8 External visiting PhD students

Kamil Adem, Addis Ababa University, Ethiopia. Duration of the stay: January-March 2017

Jessica Mackay, University of Adelaide, Australia. Duration of the stay: April 2015 – February 2016

7.1.9 Patent applications

"Sequential electrodialytic extraction of phosphorus compounds" (European Patent application number WO2017055341 (A1)), which is an invention destined to recover P from char/ashes produced from the gasification/pyrolysis of sewage sludge.

8 Annex (Not to be published)

8.1 Annex 1: Scientific peer reviewed publications:

- 1) Parés Viader, R., Jensen, P. E., Ottosen, L. M., Ahrenfeldt, J., & Hauggaard-Nielsen, H. (2015). *Electrodialytic extraction of phosphorus from ash of low-temperature gasification of sewage sludge*. Electrochimica Acta, 181, 100-108. DOI: 10.1016/j.electacta.2015.05.025. **9 pages.**
- Thomsen, T. P., Ravenni, G., Holm, J. K., Ahrenfeldt, J., Hauggaard-Nielsen, H., & Henriksen, U.
 B. (2015). Screening of various low-grade biomass materials for low temperature gasification: Method development and application. Biomass and Bioenergy, 79, 128-144. DOI: 10.1016/j.biombioe.2014.12.019. 17 pages.
- 3) Mackay J.E., Cavagnaro T.R., Jakobsen, I., Macdonald L.M., Grønlund, M., Thomsen, T.P. and Müller-Stöver D.S. (2016) *Evaluation of phosphorus in thermally processed sewage sludge: P pools and availability to wheat.* Plant & Soil (Submitted). **27 pages.**
- 4) Li, X., Rubæk, G.H., Müller-Stöver, D.S., Thomsen, T.P., Ahrenfeldt, J., Sørensen, P. (2016) *Plant availability of phosphorus in five gasification biochars*. Geoderma (Submitted). **35 pages.**
- 5) Müller-Stöver, D.S., Jakobsen, I., Grønlund, M., Rolsted, M., Magid, J., Hauggaard-Nielsen, H. (2016) *Phosphorus bioavailability in straw and sewage sludge ashes from low-temperature biomass gasification*. Soil use and management (Submitted). **30 pages.**
- 6) Li, X., Rubæk, G.H., Sørensen, P. (2016) *K availability in biomass combustion ash and gasification biochar: an incubation study.* Geoderma (In preparation). **19 pages.**
- 7) Davide Tonini, Panagiotis G. Kougias, Charlotte Scheutz, Zsuzsa Sárossy, Tobias P. Thomsen, Jesper Ahrenfeldt, Ulrik B. Henriksen, Thomas F. Astrup (2016) *Chapter 8 Energy recovery from water and food sector residual resources*. Chapter in peer-reviewed report. Published in: DTU International Energy Report 2016. **20 pages.**
- 8) Parés Viader, R., Jensen, P. E., Ottosen, L.M., Thomsen, T. P., Ahrenfeldt, J., Hauggaard-Nielsen, H. (2017) *Comparison of phosphorus recovery from incineration and gasification sewage sludge ash.* Water Science and Technology, 75.5, 1251-1260. DOI: 10.2166/wst.2016.620. **10 pages.**
- 9) Parés Viader, R., Jensen, P. E., Ottosen, L. M., Ahrenfeldt, J., & Hauggaard-Nielsen, H. (2017). Sequential electrodialytic recovery of phosphorus from low-temperature gasification ashes of chemically precipitated sewage sludge. Waste Management, 60, 211–218. DOI: 10.1016/j.wasman.2016.11.030. 8 pages.
- Thomsen, T. P., Sárossy, Z., Gøbel, B., Stoholm, P., Ahrenfeldt, J., Frandsen, F. J., Henriksen, U.
 B. (2017) Low Temperature Circulating Fluidized Bed gasification and co-gasification of Municipal Sewage Sludge. Part 1: Process performance and gas product. Accepted for publication in: Waste Management. 35 pages.
- 11) Thomsen, T. P., Hauggaard-Nielsen, H., Gøbel, B., Stoholm, P., Ahrenfeldt, Henriksen U. B., Müller-Stöver, D. S. (2017) Low Temperature Circulating Fluidized Bed gasification and cogasification of Municipal Sewage Sludge. Part 2: Evaluation of ash materials as phosphorus fertilizer. Accepted for publication in: Waste Management. 30 pages.
- 12) Thomsen, T. P., Sárossy, Z., Gøbel, B., Stoholm, P., Ahrenfeldt, J., Henriksen, U. B., Frandsen, F. J., Müller-Stöver, D. S. (2017) Changes imposed by pyrolysis, thermal gasification or incineration on composition and phosphorus fertilizer quality of municipal sewage sludge. Accepted for publication in: Journal of Environmental Management. **33 pages.**

8.2 Annex 2: Market development material from Work Package 4

- Common statement from WP4 seminar "Recirculation of nutrients to organic farming" By SEGES, 1 page
- 2) Guidelines from WP4 "Forgasningsaske som gødning og jordforbedringsmiddel Vejledning for jordbruget". By SEGES, **9 pages**