



### **Closing the Loop** Utilization of Secondary Resources by Low Temperature Thermal Gasification

Thomsen, Tobias Pape

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# CLOSING THE LCOP

Utilization of Secondary Resources by Low Temperature Thermal Gasification

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Tobias Pape Thomsen

DTU December 2016.























### PhD thesis 2016

### Title:

Closing the Loop - Utilization of Secondary Resources by Low Temperature Thermal Gasification

### Author:

Tobias Pape Thomsen Technical University of Denmark, Department of Chemical and Biochemical Engineering, DTU Risø Campus, Building 313, Frederiksborgvej 399, 4000 Roskilde, Denmark

### Supervisors:

Jesper Ahrenfeldt Technical University of Denmark, Department of Chemical and Biochemical Engineering, DTU Risø Campus, Building 313, Frederiksborgvej 399, 4000 Roskilde, Denmark

Ulrik B. Henriksen Technical University of Denmark, Department of Chemical and Biochemical Engineering, DTU Risø Campus, Building 313, Frederiksborgvej 399, 4000 Roskilde, Denmark

#### Henrik Hauggaard-Nielsen

Roskilde University, Department of Environmental, Social and Spatial Change, Universitetsvej 1, Building 09.2, 4000 Roskilde, Denmark

Jens Kai Holm DONG Energy Thermal Power A/S, Nesa Allé 1, 2820 Gentofte, Denmark

In this online version of the thesis, paper I-IV are not included but can be obtained (when published) from electronic article databases e.g. via www.orbit.dtu.dk or on request from:

Address: DTU Chemical Engineering Department of Chemical and Biochemical Engineering Technical University of Denmark Søltofts Plads 229 2800 Kgs. Lyngby Denmark Phone (reception): +45 4525 2800

Homepage: http://www.kt.dtu.dk/english Email: kt@kt.dtu.dk

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### Author's Note

It seems that the severity of the global challenges associated to anthropogenic pollution and resource use is starting to sink in. More and more people are acknowledging that our modern lifestyle has a cost, and that apparently there was a price on the free lunch after all. But it is already much too late for a quiet settlement. The services have already been delivered and it is time to pay the bill. We talk. And discuss. And while we talk we know that it will be the future generations who will actually pick up the tap. And we know that the price of the bill will increase the longer we postpone the payment. We keep talking. And produce. And consume. While we talk the piles of degraded materials (secondary resources) grow larger and the piles of essential raw materials (primary resources) grow smaller. Both piles are resources. We need to manage them better.

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This study seeks to investigate and identify new ways to improve the current practice related to management of secondary resources. It is in this regard investigated how to apply low temperature thermal gasification in the beneficial utilization of secondary resources to produce non-fossil energy and recover irreplaceable and vital inorganic elements.

The study has been conducted as part of the EUDP financed project "Fuel flexible, Efficient and Sustainable Low Temperature Biomass Gasification" under the work package "WP1: PYRONEER Gasification-fuel variability, Energy Efficiency and Bioash Quality".

Stop talking, start reading.

Best regards

Tobias P. Thomsen, Risø, December 2016

### Acknowledgements

From beginning to end, this work is a melting pot of efforts more than the produce of a single individual. The work will be recorded as my thesis, but it would be no thesis at all without the contribution from so many others. You made this possible, and for that I thank you all. Let us all hope for strong winds of change before we lose what we have not already lost.

First and foremost, thanks to all my supervisors and especially Jesper Ahrenfeldt and Henrik Hauggaard-Nielsen who have guided me through many interesting projects since the summer of 2009. Together with Ulrik B. Henriksen you two have given me the insight, curiosity and expertise I have required to make it to this point.

A special thanks also to my external supervisor Jens Kai Holm at DONG Energy A/S as well as my favorite bonus-supervisors, partners, councilors and co-authors Dorette Sophie Müller-Stöver now at KU PLEN, Peder Stoholm from Danish Fluid Bed Technology Aps, Benny Gøbel from DONG Energy A/S and Zsuzsa Sárossy, Giulia Ravenni, Flemming Frandsen, Maria Puig and Helge Egsgaard from the Biomass Gasification Group. The contributions you have made to this work are nothing less than paramount. And thank you Raimon Parés Viader from DTU BYG, Xiaoxi Li and Peter Sørensen from Aarhus University and Jessica E. Mackay from the University of Adelaide for inviting my work into yours and allowing me to contribute to your highly interesting and very relevant articles.

This project would have led nowhere if it was not for the support of the groups technical team. No technicians, no game. Thank you Hanne Wojtaszewski, Kristian Estrup, Freddy Christiansen and Erik Hansen! And thank you Rasmus Gadsbøll for putting up with me, it is a delight to share office with you! Thank you also; Marvin, Peter, Sønnik, Alexander as well as former colleagues and students at the Biomass Gasification Group. You contributed more than you are aware of. And to all those employed or studying at the now former Biosystems Division at the National Laboratory for Sustainable Energy at Risø; Thank you for great inspiration and great times! All your interdisciplinary input and good company made work feel like a hobby. A special thanks to Sune T. Thomsen, Mads V. Markussen, Andreas Kamp, Morten Jensen and Stefan Heiske for fruitful discussions, strong opinions, help, exercise and academic guidance.

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I would also like to express my sincere gratitude to the appropriate representatives of the Danish Energy Agency for their belief in our technology and expertise and for financing the study via the EUDP program.

And more important than all else – thank you dear family and friends for your interest, love and support. Rikke, Gry and Liv, I love you very, very much! I did my best. For you.

### **English summary**

This study addresses certain issues related to unsustainable management of secondary resources like organic waste, sewage sludge and residues from agriculture and industry with a focus on losses of non-fossil energy potential and valuable elements. In this context it is investigated how suitable application of low temperature thermal gasification could be applied to reduce the environmental impact of such management systems and increase the value and positive awareness of the resources in question.

In the first part of this study, the Low Temperature Circulating Fluidized Bed (LT-CFB gasifier) is described. The LT-CFB gasifier is a technology originally developed for pre-processing of biomass fuels like cereal straw. In popular terms, the LT-CFB gasification process separates the inorganic and organic fractions of the straw. The majority of the inorganic material is extracted in one or several different ash fractions and the organic material is converted into a hot combustible gas product, which is subsequently combusted in an adjacent boiler. This substantially reduces the influence of the fuels inorganic composition on the combustion properties. When combining LT-CFB gasification with existing dust-fired coal boilers, fossil fuels can be directly substituted with renewable fuels while reusing existing energy infrastructure. Currently, two operational LT-CFB gasifiers exist: A pilot scale facility with a thermal capacity ( $_{TH}$ ) of 100 kW and a demonstration unit of 6 MW<sub>TH</sub>. Both units are involved in the present study. Many different fuels have previously been tested in LT-CFB gasifiers and previous results from these experiments are described and evaluated with focus on the energy efficiency of the process and the quality of LT-CFB ashes for use as fertilizers. The general benefits and drawbacks of low temperature gasification compared to anaerobic digestion and incineration are briefly discussed in this regard.

Development and implementation of a method to screen for new fuel candidates for LT-CFB gasification is conducted, and 22 new potential fuel candidates are characterized and compared to 4 previously proven LT-CFB fuels. The investigated fuel candidates are categorized by their apparent suitability as LT-CFB fuels and various positive characteristics as well as potentially problematic issues are discussed. The overall conclusion from the fuel screening is that in a Danish context it is highly 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, two animal meat and bone meal samples and wood pruning from Italian vineyards. The problems mainly relate to the proximate composition, ash sintering, char deposit formation and corrosion of steel surfaces during thermal tests. The fuel screening also includes 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. The fuel screening also involves 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 is 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 is 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. Four experimental campaigns with gasification and co-gasification of sewage sludge in LT-CFB gasifiers are conducted and the results on process performance and the quality of the gas product are compared to results from other studies on thermal gasification of sludge. The overall conclusion is 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 is found to yield the highest hot gas efficiency, carbon conversion rate and total system electrical efficiency of the assessed systems.

Examination of the fertilizer quality of ash substrates from thermal conversion of sewage sludge is a central part of this study. Fertilizer quality is 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. 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 are also included in the investigation. From the investigation of ash fertilizer quality it is 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 is found to have a remarkable effect on P fertilizer quality while co-gasification of sludge and straw in LT-CFB gasifiers in general seem to provide a better ash fertilizer than mono-sludge gasification. Assessment of the influence of the thermal process on the fertilizer quality of the ashes is studied with chemical sequential extraction 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 is also discussed.

In the last part of the study, the results from the previous chapters are combined in an assessment of the possibilities to produce controlled release fertilizers and context-specific designer fertilizers in systems encompassing thermal conversion of secondary resources. A discussion about burden shifting in such management systems is also introduced and results are 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 it is concluded that there is a profound potential for optimizing the management of sewage sludge – and most likely also 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. 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 is found to produce very high quality thermally purified P fertilizers, and the potential benefits of fuel mixing needs to be further examined.

### Dansk sammenfatning

I denne afhandling adresseres nogen af de problemer der i adskillige tilfælde afstedkommes af bearbejdning og afskaffelse af sekundære ressourcer som organisk affald, spildevandsslam og diverse organiske restfraktioner fra jordbrug og industri. I dette studie fokuseres der i denne forbindelse primært på potentielle tab af ikke-fossilt energipotentiale og forskellige værdifulde uorganiske elementer. For at imødegå disse problemer undersøges det om lavtemperatur termisk forgasning kunne bruges i udviklingen af en mere optimal og bæredygtig behandling af sekundære ressourcer med det formål at reducere miljøpåvirkningen fra det samlede system samt øge udnyttelsen og værdien af ressourcerne.

I den første del af studiet beskrives Lav Temperatur Cirkulerende Fluid Bed (LT-CFB) forgasseren. Denne teknologi er oprindeligt udviklet til at forbehandle halm og lignende ressourcer i en proces hvor de uorganiske komponenter koncentreres i en fast askefraktion mens de organiske komponenter i gasform samfyres med f.eks. kul i en tilstødende kedel. Når eksisterende kulkraftværker udbygges med LT-CFB forgasning af biomasse på denne måde, kan fornybar energi direkte substituere fossil energi alt imens næringsstofferne i brændslet genindvindes og den eksisterende energiinfrastruktur bibeholdes og udnyttes. Der findes i dag to operationelle LT-CFB forgassere: Et pilot-anlæg med en termisk kapacitet på 100 kW og et demonstrationsanlæg med en termisk kapacitet på 6 MW. Begge anlæg er inkluderet i det eksperimentelle arbejde i dette studie. Adskillige forskellige brændsler er tidligere blevet testet med stor succes i LT-CFB forgassere og dette studie samler op på de eksisterende erfaringer i en kort gennemgang af tidligere resultater med fokus på energieffektivitet og produktkvalitet. De overordnede styrker og svagheder ved LT-CFB forgasning diskuteres kort i forhold til to konventionelle teknologier til omsætning af lavkvalitetsbrændsler – bioforgasning og forbrænding.

I studiets anden del præsenteres resultater fra udvikling og test af en metode til at screene efter nye brændsler til LT-CFB forgasning. 22 nye brændsler bliver karakteriseret og vurderet ved at sammenligne med analyser af 4 tidligere afprøvede brændsler. De nye brændsler karakteriseres efter deres umiddelbare egnethed til omsætning i LT-CFB forgassere og både fordelagtige og potentielt problematiske karakteristika fremhæves og diskuteres. I en dansk sammenhæng er det i denne forbindelse fundet yderst relevant at overveje LT-CFB forgasning af spildevandsslam og diverse gyllefibre mens det i en international sammenhæng også bør overvejes at omsætte sukkerrørbagasse, diverse fraktioner fra produktion af olivenolie samt risavner i denne type anlæg. Kun fem af de undersøgte brændsler bliver vurderet som potentielt meget problematiske at omsætte ublandede i LT-CFB forgassere: Fedt fra spildevand, rester af palmekerneskaller, to typer af kød- og benmel samt afklippet vinplantemateriale. De potentielle problemer i denne sammenhæng relaterer primært til fedtets manglende indhold af svært nedbrydelige kulstof, gyllefibrenes høje vandindhold samt de uorganiske bestanddele i brændslerne som i nogle tilfælde kan risikere at føre til sintring af aske, aske- og koksbelægninger og/eller korrosion. Brændselsscreeningen indebærer også analyse af gødningskvaliteten af asker og koksprodukter med fokus på plantetilgængeligheden af fosfor (P), og betydelige forskelle på kvaliteten af aske- og koksprodukter er blevet afdækket og diskuteret. Endelig indebærer arbejdet med brændselskarakterisering også en kort analyse af hvordan det påvirker forskellige karakteristika når brændsler blandes inden de omsættes termisk. Det konkluderes at mens de fleste karakteristika kan forudsiges ved en lineær sum af data fra analyse af de blandede brændsler, så er der mulighed for at opnå en positiv synergieffekt vedrørende askesmeltning og –sintring, samt P gødningsværdien af koks og askeprodukter.

Af de 5 mest lovende brændsler konkluderes det at spildevandsslam er en relevant - og både lokalt og globalt tilgængelig, case at undersøge nærmere. Det begrundes med et meget højt potentiale for miljøforbedringer i forhold til nuværende praksis, kombineret med et rimeligt energipotentiale og et ekstremt væsentligt potentiale for at genindvinde P. På den baggrund gennemføres fire eksperimentelle kampagner med det formål at afdække hvor egnet spildevandsslam er til forgasning, og samforgasning med halm, i LT-CFB anlæg. Resultaterne fra de fire forsøg er blevet sammenholdt med resultater fra et litteraturstudie og det konkluderes at adskillige forgasningsdesigns har vist sig at kunne omsætte spildevandsslam men at LT-CFB forgasseren sandsynligvis er den optimale teknologi til at opnå høj varmgasvirkningsgrad, kulstofomsætning og total elvirkningsgrad i systemet.

Studiets tredje del omhandler analyse af gødningsværdien af asker og koksprodukter fra termisk omsætning af spildevandsslam med fokus på næringsstofindholdet, toksicitet samt plantetilgængelighed af P. Forskelle og ligheder mellem adskillige asker og koksprodukter fra forgasning, samforgasning af spildevandsslam og halm, samt forbrænding og pyrolyse af spildevandsslam undersøges og sammenlignes på tværs og med de oprindelige slam-prøver og en mineralsk P reference. Derudover er der udviklet en proces til efteroxidering af asker og koks fra forgasning og pyrolyse og disse prøver er også inkluderet i analysen. Det konkluderes at der kan produceres god P gødningsaske ved både forgasning, forbrænding og pyrolyse så længe processerne designes målrettet dertil. Efteroxidationsprocessen har generelt en stærkt positiv effekt på P kvaliteten, og samforgasning af spildevandsslam og halm i LT-CFB forgassere giver en mærkbart forbedret gødningsaske i forhold til forgasning af ren spildevandsslam. En vådkemisk sekventiel ekstraktion og mikroskopi med et Scanning Electron Microscope er i dette arbejde blevet anvendt til at undersøge hvordan de termiske processer forandrer P-kemien under omsætningen fra spildevandsslam til aske eller koks. Desuden er det også blevet undersøgt hvordan P plantetilgængeligheden ændrer sig over tid i jorden og som funktion af partikelstørrelsesfordelingen af askesubstraterne.

I studiets fjerde og sidste del sammensættes delresultater fra de forskellige undersøgelser i en analyse af mulighederne for at designe gødningsasker med en kontrolleret P afgivelse for at øge den totale gødningseffektivitet. Derudover bruges resultaterne i en diskussion af hvordan det undgås at flytte miljøog ressourceproblemerne fra et område til et andet. Denne diskussion baseres på resultaterne fra to livscyklusanalyser hvor den eksisterende praksis med direkte udbringning af spildevandsslam på landbrugsjord sammenlignes med det foreslåede system med LT-CFB forgasning af slammet og efterfølgende udbringning af asken på landbrugsjord. Resultaterne indikerer muligheder for stærkt reduceret påvirkning af klima, miljø og menneskelig sundhed i det foreslåede system i forhold til referencesystemet.

Baseret på det foreståede arbejde konkluderes det at der foreligger et meget stort potentiale for at optimere nuværende praksis med behandling af spildevandsslam – og sandsynligvis også af andre sekundære ressourcer, ved implementering af optimerede termiske processer. Ved at kombinere de rigtige processer vil dette kunne medføre fuld udnyttelse af energipotentialet i brændslerne samt genanvendelse af værdifulde uorganiske elementer, herunder P. Designprocessen vil kræve et indgående og tværfagligt kendskab til brændselskarakteristika, termisk procesdesign og slutanvendelsen af både aske og energiprodukter. LT-CFB forgasseren kan blive en meget væsentlig proces i denne sammenhæng i kraft af processens fleksibilitet og høje effektivitet, og samforgasning af f.eks. spildevandsslam og halm vil kunne bidrage med højeffektiv produktion af termisk oprenset P gødning af høj kvalitet i en Dansk sammenhæng.

### Structure and content of the thesis

The thesis is composed of two parts. The first part is an introduction and summary of the work conducted in report form. The second part consists of four scientific papers. The four papers are presented below, and referred to in the report as [1]-[4].

Paper I, reffered to as [1] (Provided as pre-press version in Appendix 1)

**Tobias Pape Thomsen**, Giulia Ravenni, Jens Kai Holm, Jesper Ahrenfeldt, Henrik Hauggaard-Nielsen and Ulrik B. Henriksen: *Screening of various low-grade biomass materials for low temperature gasification: Method* development and application. Published in: Biomass and Bioenergy (2015) vol. 79, p. 128–44

Paper II, reffered to as [2] (Provided as submitted version in Appendix 2)

**Tobias Pape Thomsen**, Zsuzsa Sárossy, Benny Gøbel, Peder Stoholm, Jesper Ahrenfeldt, Flemming Jappe Frandsen, Ulrik Birk Henriksen: *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

Paper III, reffered to as [3] (Provided as submitted version in Appendix 3)

**Tobias Pape Thomsen**, Henrik Hauggaard-Nielsen, Benny Gøbel, Peder Stoholm, Jesper Ahrenfeldt, Ulrik B. Henriksen and Dorette Sophie Müller-Stöver: *Low Temperature Circulating Fluidized Bed gasification and co-gasification of Municipal Sewage Sludge. Part 2: Evaluation of ash materials as phosphorus fertilizer*. In review in: Waste Management

Paper IV, reffered to as [4] (Provided as submitted version in Appendix 4)

**Tobias Pape Thomsen**, Zsuzsa Sárossy, Jesper Ahrenfeldt, Ulrik Henriksen, Flemming Frandsen and Dorette Sophie Müller-Stöver: *Changes imposed by pyrolysis, thermal gasification or incineration on elemental composition and phosphorus fertilizer quality of municipal sewage sludge*. In review in: Journal of Environmental Management

The report is composed as follows:

Chapter 1: Definition of secondary resources. General introduction and purpose of the study
Chapter 2: Presentation of the Low Temperature Circulating Fluidized Bed (LT-CFB) gasifier
Chapter 3: Screening of secondary resources for LT-CFB gasification. Expands on the work of Paper I.
Chapter 4: Proof-of-concept operation of LT-CFB gasifiers on selected secondary resources. Expands on the work of Paper II.

**Chapter 5:** Investigation of the fertilizer quality of solid residues from thermal processing of secondary resources. Expands on the work of **Paper III** and **Paper IV** 

Chapter 6: Presentation of the broader perspectives of the work

### Publications not included in the thesis

Several scientific contributions have been made during the course of the project in addition to those composing the thesis. The most relevant of these are presented below, and a few references to the outcome of these works are included in the citations and bibliography of the report.

### Manuscripts in scientific journals

Jessica E. Mackay, Timothy R. Cavagnaro, Iver Jakobsen, Lynne M. Macdonald, Mette Grønlund, **Tobias P. Thomsen** and Dorette S. Müller-Stöver: *Evaluation of phosphorus in thermally processed sewage sludge: P pools and availability to wheat.* In review in: Plant and Soil

Xiaoxi Li, Gitte H. Rubæk, Dorette S. Müller-Stöver, **Tobias P. Thomsen**, Jesper Ahrenfeldt and Peter Sørensen: *Plant availability of phosphorus in five gasification biochars*. In review in: Geoderma

Raimon Parés Viader, Pernille Erland Jensen, Lisbeth M. Ottosen, **Tobias P. Thomsen**, Jesper Ahrenfeldt and Henrik Hauggaard-Nielsen: *Comparison of phosphorus recovery from incineration and gasification sewage sludge ash.* Published in: Water Science and Technology (2017) vol. 75, Issue 5, p. 1251-1260

### Conference and workshop contributions:

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

Rhys Thompson, **Tobias Pape Thomsen** and Dorette Müller-Stöver: *Plant phosphorus availability in thermally treated sewage sludge*. Poster presentation at: 8th International Phosphorus Workshop at Leibniz ScienceCampus for Phosphorus Research, 12-16 September 2016, Rostock, Germany.

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

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

### Co-supervision of bachelor- and master student projects during the study

Giulia Ravenni: *Screening method and selection of marginal feedstocks as fuel for a LT-CFB gasifier*. Msc project conducted in 2014 at the Faculty of Engineering, Università degli Studi di Firenze, Italy.

Emil Lundager Jørgensen: *Energianalyse af Rensningsanlæg med Integreret Termisk Konvertering af Slam*. Bsc project conducted in 2015 at the Technical University of Denmark in the Department of Mechanical Engineering.

Camilla Nygaard: *Gasification of sewage sludge in a two-stage gasifier*. Msc project conducted in 2015 at the Technical University of Denmark in the Department of Chemical and Biochemical Engineering.

Lærke Wester Larsen: *Biogasfibre til jordforbedring – Sammenligning af forskellige efterbehandlingsmetoders indflydelse på næringsstofindhold*. Bsc project conducted in 2016 at Copenhagen University in the Department of Geosciences and Natural Resource Management.

Rhys Thompson: *Plant phosphorus availability of thermally treated sewage sludge*. Msc project conducted in 2016 at Copenhagen University in the Department of Plant and Environmental Sciences.

Christian Loft Bonde: *Detailed Chemical Speciation and Bioavailability of Biomass Ashes*. Msc project conducted in 2016 at the Technical University of Denmark in the Department of Chemical and Biochemical Engineering.

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**Chapter 1** introduces the problem addressed in the thesis: Unsustainable management of secondary resources like organic waste, sewage sludge and hard-to-handle organic residues from agriculture, industry etc. Several case-specific problematic issues are discussed. Based on this introduction, the central questions of the thesis and study are raised, and it is hypothesized that the application of low temperature thermal gasification would be able to substantially reduce the environmental impact of some of the described management systems and increase the value and positive awareness of secondary resources.

### 1 Secondary resources

This study seeks to investigate the potential for optimized management of secondary organic resources (referred to as secondary resources) by low temperature thermal gasification. This work includes 1) identification and characterization of these resources and, 2) Investigation of process stability and product quality and identification of benefits and potential problems related to thermal gasification hereof.

Secondary resources refer in this work to a category of organic residues and degraded organic materials that have a low or negative price due to undesirable circumstances and characteristics e.g.:

- It may be that the resource is very difficult to collect, transport, store or handle
- The resource in question may have very low energy density per unit of mass or volume due to a high moisture content or ash content or due to a very low bulk density
- The composition may be very inhomogeneous requiring very flexible, resource consuming handling
- The resource can be highly polluted, polluting and/or harmfull
- The resource may be very volatile, difficutl to contain and generate local odor or dust problems

If a resource is sufficiently problematic, management of the resource will be costly and in many cases the price of the resource will be low. A low price does not necessarily entail a low value of a given resource. In the modern economy, price and value are often decoupled, and the price of a resource is therefore not necessarily a sufficient representation of the real value [5]. All secondary resources may have undisclosed values that can be realized if they are properly managed. The drivers for realizing such value can include continuous depletion of virgin stock materials that contain the same elements, the global requirements for substitution of fossil energy or the acknowledgement of environmental costs associated to the current management practice [6–11].

The category of secondary organic resources includes many different sub groups. Some of the most important groups are described below and examples are given in Figure 1:

- Agricultural by-products and residues: E.g. Crop residues (stalk, leaf, cob etc.), manure fibers, muck and bedding and fibers from biogas slurry
- Municipal by-products and residues: E.g. Source segregated organic waste, used textiles, grass and cuttings from road and park maintenance, beach cleaning waste and sewage sludge
- Industrial by-products and residues: E.g. Residues from breweries, food packaging, food retail, food preparation, food ingredient production, or residues from production of non-food products based on the partial conversion of animal- and vegetable raw materials



Figure 1: Examples of secondary resource management: A) Municipal waste landfill, India [12]; B) Large scale composting, US [13]; C) Intensive pond fish farming, Israel [14]; D) Sargassum seaweed wash up, Florida, US [15]; Solid slaughterhouse waste [16]; F) Ocean dumping of sewage sludge [17]; G) Sewage sludge landfill, Mexico [18]; H) Bagasse burned during sugar cane harvest, Brazil [19]

Optimized management of secondary resources is important for three main reasons:

**Reason 1: Sub-optimal management of secondary resources can be highly polluting:** When a resource has no apparent value, the main management goal will often be volume reduction or relocation to make room for more of the material. Without proper reduction and disposal systems this can lead to severe pollution. This is exemplified in Figure 1 in the following cases: A) Large scale landfilling lead to severe emissions to air and leaching to soil and ground water, as well as local odor and dust problems [20–23]; c) Intensive pond production of fish and shrimp lead to production of sludge, which is often landfilled or dumped into oceans, rivers or fjords [24]; D) When rotting, large piles or wet seaweed will have anaerobic compartments and with the organic composition of sea weed, severe amounts of methane and other greenhouse gases could be expected to develop and subsequently emit into the atmosphere [25]; F) Ocean dumping of sewage sludge can lead to local oxygen depletion by emissions of organic material as well as pollution from organic and inorganic toxins and eutrophication from emission of nutrients [26]; H) Open air burning of sugar cane bagasse lead to harmful emissions to air [27].

All organic material will inevitably decompose under influenced of biotic and abiotic factors. The rate of decomposition is controlled by the characteristics of the material and the characteristics of the deposit or the environment to which it is emitted. Inorganic material can also decompose during long term deposition and emit gases or leach soluble compounds to the surroundings [20–22,28]. Mechanic degradation during long term deposition can potentially increase the environmental impact of harmful substances by size minimization and increased spreading. This could be the case with e.g. micro-plastic or asbestos fibers.

#### Reason 2: Sub-optimal management of secondary resources can lead to a loss of energy potential:

Deposition and/or thermal mass and volume reduction without proper energy recovery will lead to a loss or reduction of the energy potential in the organic resource. Regardless of the deposition system and the type of material, organic fractions will degrade and decompose during deposition, and ultimately the calorific value of the material is lost as the organic fraction is converted into greenhouse gases and water. The speed of the process will vary substantially with the type of material and the management system as will the composition of the produced greenhouse gases. But the final result will be a complete loss of energy potential and related harmful emissions. This is obviously sub-optimal when there is a high demand for non-fossil energy in the world. This is exemplified in Figure 1 in all cases: A, B, D, E & G) Degradation of waste and residuals in landfills, open air storage and in composting systems leads to production of greenhouse gases and a related reduction in the total energy potential of the resources [23,29]; C and F) When sludge is dumped into water compartments it is dissolved and the energy content in the organic fraction completely scattered and lost; H) Burning bagasse, maize- or cereal straw and other agricultural residues directly in the field without energy recovery or exhaust gas cleaning will completely waste a very high energy potential and lead to massive emissions [27].

**Reason 3: Sub-optimal management of secondary resources can lead to a loss of elemental value**: Many valuable elements can be present in degraded materials. Nutrients and various groups of metals are among those most commonly found in larger quantities [30–36]. If these materials are improperly deposited, polluted or diluted the value of the element is severely reduced, and new virgin material may be required to replace it. This is especially problematic if the element is scarce or in risk of becoming so, or if the costs (monetary or environmental) of replacing the elements are high. This is exemplified in Figure 1 in the following cases: A) Various elements leach from waste landfilling into soil and groundwater [20,21]; C, D &

F) Sewage sludge and sludge from intensive ponds contain many valuable nutrients and also various metals. These are lost in the ocean when the sludge from wastewater treatment and onshore fish farming is dumped or they are leached slowly into soil and ground water when the sludge is landfilled; H) The contents of nitrogen (N) in crop residues like straw and bagasse are largely lost when burning in open fires.

In Denmark the loss of valuable elements from management of secondary resources is very high. This is an effect of an overall strategy of mass- and volume reduction by incineration and use of process residuals in various types of construction. This strategy is exemplified in Figure 2. Left: At Lynetten in Copenhagen, Denmark, sewage sludge is incinerated in a fluid bed oven, and the heat is used in the near-by wastewater treatment plant. The ash from the incineration process is used in the production of mineral insulation [37]. In this way the energy potential is utilized and the ash is re-used. However, the most valuable element in sludge ash is phosphorus (P), which is an essential, irreplaceable nutrient. When sludge is burned and the ash used in the production of mineral insulation then the value of the large P fraction is lost. Right: A similar concern can be relevant in the case of cement production. Sewage sludge as well as animal meat and bone meal have been used in co-firing systems in cement production [38]. Both resources contain very high levels of P, which in this way is locked in construction elements. The energy potential in the resources is utilized and the mineral content is re-used, but the value of the P is lost. Center: The third case is waste incineration, here exemplified by KARA/Noveren in Roskilde, Denmark. In modern waste incineration in Denmark, the energy potential in the waste is used to produce electricity as well as district heating, with relatively high total thermal efficiency. However, the waste contains many valuable nutrients and metals not fully valorized in this process. Large metal pieces are removed from the ashes and slag from the incineration, but the residual material is used mainly in the construction of roads, harbors or other types of construction [39]. In this way, the Danish strategy has solved two of the three challenges towards valorization of secondary resources, but increased focus on the strategic importance of securing e.g. P supply may require another approach in the future.



Figure 2: Various ways to reduce the mass and volume of secondary resources by incineration and co-incineration. Left: Lynetten sludge incineration facility [40]; Middle: Kara/Noveren municipal waste incineration facility [41]; Right: Aalborg Portland cement production facility [42]

#### 1.1 Linear material flows produce more residues

The initial production of secondary resources can have many different reasons, but in general it is largely related to the fact that our current lifestyle requires a constantly increasing flow of energy and materials through society. There is a range of hidden external costs (externalities) related to these flows and thereby

to the services provided within the society. These costs can include degradation, pollution or severe dilution of various valuable elements and materials, depletion of virgin resources and pollution of the surrounding ecosystems – locally as well as globally. The magnitude of the flow grows with the complexity of the society and the level of service, while the magnitude of the secondary resource production also relies on the linearity of the flow [43,44].

An example of this linearity is provided in Figure 3. 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 [45,46]. The story of P is discussed further in section 4.2.



Figure 3: 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. A widely used alternative to direct or indirect deposition of sewage sludge is to spread it directly onto farm soil or compost it and spread it subsequently. However, this practice is associated with increasing risks related to the complex composition of modern sewage sludge. A more precautious alternative is to incinerate the sludge and subsequently refine the ashes and recover the P. This practice is associated with substantial additional costs but the awareness and implementation is increasing nonetheless. These matters are discussed further in chapter 4.

### **1.2** The central question and purpose of the study

With this introduction and background, the main research question of this study is formulated as follows:

## How suitable is Low Temperature Circulating Fluidized Bed (LT-CFB) gasification to procure non-fossil energy and valuable minerals from secondary resources of varying quality and origin?

To answer this question a step-by-step investigation of the following sub-questions has been conducted:

- How broad is the range of suitable fuel candidates for LT-CFB gasification within the group of organic secondary resources?
- How energy efficient is the conversion of new LT-CFB fuel candidates into useful secondary resources?
- How good is the quality of the secondary mineral resources produced?
- Is the LT-CFB gasifier the optimal thermal technology for resource management in this regard?
- How is the environmental impact of LT-CFB gasification of a given secondary resource compared to a representative reference scenario?

The study thus aims at determining if the LT-CFB gasifier could be applied to reconnect some of the linear material flows in society and thereby recover more non-fossil energy and recycle more materials approaching the fundamental cycling of matter we know from all ecosystems. With regard to the linear flow of phosphorous illustrated in Figure 3, closing these loops with optimized management of secondary resources by proper thermal gasification could look as in Figure 4.



Figure 4: An illustration of a society with an ideal, closed phosphorus loop facilitated by flexible thermal gasification. CHP: Combined Heat and Power.

In the illustrated example, the procurement of secondary resources is focused on recirculation of the irreplaceable and strategically critical nutrient phosphorus. However, recirculation of other micro and macro nutrients in the ashes may also prove to be very valuable in the long run. In addition to direct use of ashes from the thermal management as substitutes for virgin resources (as in the case with P fertilizer ashes), it could also be considered what benefits and drawbacks that would be related to further processing and refining of these resources within the concepts of technosphere mining and industrial ecology [30,47]. Extraction and concentration of e.g. precious metals, rare earth metals or other elements present in sufficiently high concentrations may in this regard compete with procurement of the same elements from virgin resources. However, such measures are outside the scope of the present work.

It is a limiting assumption behind the study that optimized management of secondary resources will encompass thermal treatment. The driver behind this assumption is the high level of pathogens, organic toxins and xenobiotics often found in secondary resources combined with an acknowledgement of the robustness of many thermal processes and the potentially high level of energy utilization. There is already an ongoing development taking place in the utilization of the energy potential in secondary resources by thermal processes, and various thermochemical processes are being investigated to optimize the energy efficiency of such processes and in some cases also the recovery of valuable elements [48–55]. It also speaks in favor of a thermal process that there is extensive experience and readily available technology to control emissions from thermal conversion of many different types of materials [26,56–61]. However, it may very well be that with this limitation the study fails to identify relevant non-thermal processes that may be part of the optimal management solution for certain or several secondary resources.

The research questions are addressed in the report as follows:

**Chapter 2 and 3:** Presentation of the Low Temperature Circulating Fluidized Bed (LT-CFB) gasifier and screening of secondary resources to answer the questions: How broad is the range of suitable fuel candidates for LT-CFB gasification within the group of secondary resources?

**Chapter 4 and 5:** Proof-of-concept operation of LT-CFB gasifiers on selected secondary resources to answer the three questions i) How energy efficient is LT-CFB gasification of selected secondary resources? ii) How good is the quality of the minerals recovered? And iii) Is the LT-CFB gasifier the optimal thermal technology for resource management in this regard?

**Chapter 6:** A short description of the broader perspectives of the work and a preliminary investigation of the life cycle environmental impact of LT-CFB management of selected secondary resources to answer the question: How is the environmental impact of LT-CFB gasification of a given secondary resource compared to a representative reference scenario?

**Chapter 2** presents the central thermal technology of the current study: The Low Temperature Circulating Fluidized Bed (LT-CFB) gasifier. The description includes a brief overview of the current LT-CFB plants, a short description of the processes taking place during LT-CFB gasification as well as a summary of previously established operational experience. The many different fuels that have been tested in LT-CFB gasifiers are also presented and the influence of the fuel on the quality of the gas and ash products for use in energy production and as fertilizers respectively, is discussed. General benefits and drawbacks of low temperature gasification compared to anaerobic digestion and incineration are proposed based on the technology description in the last section of the chapter.

### 2 The LT-CFB gasifier

The Low Temperature Circulating Fluidized Bed (LT-CFB) gasifier is a process developed mainly by Danish Fluid Bed Technology A/S, The Biomass Gasification Group under the Technical University of Denmark and DONG Energy A/S. The technology has been under development for almost 20 years and is today commercialized under the registered alias Pyroneer [62]. The LT-CFB process and operation has been described several times in previously published articles and [1,63–70].

The LT-CFB gasifier is originally developed for pre-processing of cereal straw in Combined Heat and Power systems based on dust-fired coal boilers. In popular terms, the LT-CFB separates the inorganic material from the organic fraction of the straw. The inorganic material is extracted in one or several different ash fractions and the organic material is converted into a hot combustible gas product, which is subsequently combusted in an adjacent boiler. The system is illustrated in Figure 5, as it is installed at the Danish power plant Asnæsværket in Kalundborg where a LT-CFB with a thermal capacity of 6 MW can convert straw and other biomass residues and supply a hot combustible gas to the boilers in unit 2 to substitute coal [62].



Figure 5: Illustration of the Low Temperature Circulating Fluidized Bed (LT-CFB) gasifier at Asnæsværket power plant in Kalundborg, Denmark. Re-make from [1]. C: Carbon, K: Potassium. The ash also contains small amounts of phosphorus (P) [71].

The overall thermal efficiency of LT-CFB gasification of straw is around usually around 95% from straw to gas [72] and the net electrical efficiency of the steam cycle and boiler at Asnæsværkets unit 2 is 42.7% based on Higher Heating Value (HHV) [73]. The total net electrical efficiency from straw via LT-CFB gasification and the boiler + steam cycle at Asnæsværket power plant is thereby approximately 41% based on HHV. According to data from the Danish Energy Agency, the best available technology for electricity production in advanced dust fired boilers of >250 MW<sub>TH</sub> can deliver electricity with an efficiency from straw to grid via LT-CFB gasification would become close to 50%. In comparison, the best available technology for direct combustion of straw can deliver electricity with 29-30% efficiency, which is not expected to increase significantly in the near future [74].

### 2.1 Current LT-CFB plants

Currently, two operational LT-CFB gasifiers exist: A pilot scale facility with a thermal capacity ( $_{TH}$ ) of 100 kW and a demonstration unit of 6 MW<sub>TH</sub>. The 100 kW<sub>TH</sub> unit has been used for several years for research and development at the Technical University of Denmark. It is located at the Biomass Gasification Group of the Department for Chemical and Biochemical Engineering in Risø near Roskilde. The gas from the 100 kW<sub>TH</sub> unit is flared after passing through a candle filter for hot gas filtration of particles. The 6 MW<sub>TH</sub> unit is a demonstration plant that was commissioned in 2012. It is owned and operated by DONG Energy A/S and located at Asnæs Power Plant in Kalundborg, Denmark. The hot product gas from the 6 MW<sub>TH</sub> LT-CFB can be fed directly to the adjacent coal fired boiler of Asnæs Power Plant Unit 2 [62]. Pictures of these two existing LT-CFBs are shown in Figure 6 (the picture of the 6 MW unit is from before the gas connection to the boiler was established). Two earlier LT-CFB units have been used extensively for research and development over the years. These units had thermal capacities of 50 kW and 500 kW but are now decommissioned [64,68,75].

### 2.2 Process design and characteristic operation parameters

The LT-CFB gasifier basically consists of a pyrolysis reactor, a recirculating cyclone and a char conversion reactor. A large mass of hot bed material (mainly inorganic particles) circulates internally in the system carrying heat from the char reactor to the pyrolysis reactor. The movement of the circulating particles is made possible by fluidization and particle entrainment due to a high upwards gas velocity in the upper part of the pyrolysis reactor. Hence, entrainment carries the particles – including char produced in the pyrolysis, from the pyrolysis reactor to the cyclone from, which gravity takes the separated particles down into the char reactor. Fluidization of the char reactor is done by adding air and potentially also steam or water, and this makes the particles flow freely like a boiling liquid in the lower sections of the char and pyrolysis reaction chambers as well as through the duct connecting the two. An illustration of the general process schematic of the LT-CFB design is provided in Figure 7 and more details on the system design and behavior are provided in the following section.



Figure 6: Existing LT-CFB gasifiers. Left: Pilot scale gasifier with a thermal capacity around 100 kW used by the Technical University of Denmark and located at Risø near Roskilde, Denmark. Right: Demonstration scale gasifier with a thermal capacity of 6 MW located at Asnæs Power Plant in Kalundborg, Denmark [62].



Figure 7: General process design of a Low Temperature Circulating Fluidized Bed gasifier. From [1,3]

Fuel is fed to the lower part of the pyrolysis reactor (Figure 7, #1). The fuel immediately undergoes a fast drying and pyrolysis by close contact to a large mass of vigorously fluidized hot particles in an essentially inert gas. The temperature in the pyrolysis reactor is usually around 650 °C when operating on straw or crushed straw pellets [64]. The bottom of the pyrolysis reactor is fluidized by adding a small amount of air (Figure 7, #2). Higher up in the reactor, the gas velocity increases dramatically due to the combination of liberation of pyrolysis gases from the fuel undergoing pyrolysis and a large gas volume entering the pyrolysis reactor from the top of the char reactor (Figure 7, #3). Addition of these two gas volumes shifts the fluid dynamics in the upper part of the pyrolysis chamber into the fast bed regime [76]. In this regime, the upwards entrainment of particles - and therefore also the overall particle circulation in the loop - depends on the amount of particles added to the bottom of the fast bed zone, which again depends on the amount of particles in the loop and the addition of air to the bottom of the pyrolysis chamber. Hence, the temperature in the pyrolysis chamber can be controlled by adding/extracting bed particles to/from the loop (slow adjustment mechanism), and by adjusting the amount of air to the bottom of the pyrolysis chamber (fast adjustment mechanism).

When operating on straw, the solid residual char from the fast pyrolysis in the LT-CFB contains approximately 20% of the fuel mass on dry, ash-free basis and around 30% of the fuel heating value [64]. This char is entrained by the gas together with the hot circulating inert particles and carried to the primary cyclone (Figure 7, #4). In the cyclone, most of the heavy inert material and char particles are separated from the exiting raw gas and directed into the char reactor by gravitation (Figure 7, #5). The separation in the cyclone exploits the fact that the size and density of the sand and char particles is usually higher than the size and density of the ash. In the straw system, the (cold) bulk density of the straw ash is around 1500 kg/m<sup>3</sup> while the bulk density of the straw char is around 550 and the bulk density of the straw ash is around 160 kg/m<sup>3</sup> [1]. The sand is thereby approximately a factor of 3 and 9 heavier than the char and ash per volume. At the same time, the char is approximately a factor 3.5 heavier per volume than the ash. These differences in bulk densities of char and ash vary substantially with the fuel as discussed later in section 3.4. Differences between bulk densities can be used as an approximation for differences between real particle densities but do not provide the full explanation for the particle behavior in the system cyclones. However, Investigation of bulk densities of char, ash and sand can be used in first hand estimation of potential changes in the cyclone performance [77].

The circulating particles are cooled in the pyrolysis reactor as energy is used for heating and drying the incoming fuel particles as well as for the predominantly endothermic reactions in the pyrolysis. The particles are re-heated in the char reactor. In this reactor, the main part of the carbon is converted in a set of predominantly exothermal reactions with oxygen from the supplied air. This releases heat to the bed particles in the reactor. The char reactor is a bobbling fluidized bed and the bed material is usually composed of sand, 1-10 wt% carbon and ash. The variations in the carbon content in the bed depend mainly on fuel characteristics, thermal load and the supply of air and water to the reactor [64]. Air is supplied for oxidation of char, and to a lesser extent oxidation of combustible gases, while water or steam can be supplied to control the temperature and to increase the production of mainly H<sub>2</sub> and CO during the char conversion. From the char reactor, the gas produced will leave through the upper section and carry fine ash and char particles to the middle section of the pyrolysis reactor (Figure 7, #3). Sand and large, heavy char and ash particles will flow through the bottom connection between the char reactor and the pyrolysis reactor (Figure 7, #6).

Proper fuel preparation and optimal contact conditions in the pyrolysis chamber should allow for a fast and nearly complete pyrolysis to convert as much of the organic material in the fuel as possible at the chosen pyrolysis temperature. Operation of the char reactor should allow for optimized char conversion and an optimal production of combustible gases (mainly CO and H<sub>2</sub>) while generating sufficient heat to re-heat the bed material for the subsequent pyrolysis. From this starting point it can then be chosen to reduce the carbon conversion rate in order to produce ash with a higher content of unconverted carbon and more pronounced biochar characteristics if this should become a higher priority than energy efficiency [78,79]. The temperature in the char reactor can be precisely controlled by varying the supply of air. If an increased char conversion rate is desired at a given temperature, water or steam can also be added. Increasing the flow of water will reduce the temperature in the reactor by cooling and by endothermic reactions with the carbon in the char. The cooling effect of the water allows for increased air flow while maintaining a fixed temperature. In this way the water has a double effect on the carbon conversion rate. The drawback of this mechanism is a reduction in the heating value of the product gas due to increased levels of CO<sub>2</sub> and N<sub>2</sub>.

During operation of fluidized bed gasifiers, it is important to avoid temperatures near the agglomeration temperature of the bed material throughout the entire system. The bed agglomeration temperature depends on several factors including the fuel ash content, the melting point of the ash, the type of fresh bed material and the rate with which fresh bed material is added. When gasifying straw and other herbaceous biomasses, it is especially the content of silicon, potassium (K), calcium (Ca) and chlorine (Cl) that may dictate the upper temperature limit, and one of the critical temperatures in this regard is the melting point of potassium chloride (KCl) at 773°C [64]. However, due to potential co-formation of Kcompounds with even lower melting temperatures it is often not regarded as safe to operate too close to the KCl threshold. Bed agglomeration may occur as a result of excessive ash melting in the bed, making the bed difficult to fluidize and thereby making it similarly difficult to maintain a proper circulation within the system. In this process, ash species in the fuel can form a viscous melt, which stick to the surface of bed particles, and make the particles adhere to each other and build agglomerates. In a study by Narayan et al. (2016) on bed agglomeration in straw-fired LT-CFB systems it was found that in a hypothetical system with only KCl and silica sand, agglomeration and de-fluidization could occur when the sand particles were bound together by KCl melts at temperature between 756 and 766 °C depending on the mass fraction of KCl in the bed (2-6.5 wt%, highest K content giving the lowest de-fluidization temperature) [67]. In this system there was no widespread reaction between the synthetic ash and the bed sand. However, in two other experiments with a sand+K<sub>2</sub>CO<sub>3</sub> mixture and LT-CFB bed material from a campaign with straw conversion on the 6 MW<sub>TH</sub> unit, the agglomeration was largely attributed to viscous silicate melts formed from reaction of alkaline and alkali earth species in the ash with silica from the bed sand particles. The de-fluidization temperatures in the sand+K<sub>2</sub>CO<sub>3</sub> system were 728-737 °C for bed mixtures with 1.5-6.5 wt% K<sub>2</sub>CO<sub>3</sub> while it was as high as 780-785 °C in the test of actual LT-CFB bed material (4.2-4.8 wt% K). In both cases an increased K content lead to lower de-fluidization temperatures. The relatively high de-fluidization temperature in the real LT-CFB bed sample was ascribed to the content of Ca and Mg in the real straw ash, which was proposed to shift the formation of the eutectic melts to higher temperatures. All experiments were conducted with a relatively low velocity of the fluidizing gas at only twice the minimum fluidization velocity, and de-fluidization was determined by sudden drops in the pressure difference across the bed [67]. Despite the concerns related to K chemistry in circulating fluidized bed gasifiers, LT-CFB gasifiers have a very high K tolerance. During a 106 hour campaign on the 6 MW<sub>TH</sub> LT-CFB gasifying shea nut residues, a

bed K-concentration of 16% was obtained without inducing operational problems [62]. Finally, in a controlled de-fluidization test with gasification of wheat straw on a 50 kW<sub>TH</sub> LT-CFB, Stoholm et al. (2002) observed ash sintering and bed agglomeration in the char reactor when reaching 825 °C. Steady operation at 800 °C was obtained during the experimental campaign, and 730 °C was subsequently suggested as a completely safe char reactor operation temperature. A high carbon content in the char reactor was subsequently suggested as one of the reasons why it was possible to operate at such elevated temperatures [68].

### 2.3 Gas product

Results from three different campaigns conducted on a 500 kW<sub>TH</sub> LT-CFB are provided in Table 1 [64].

 Table 1: Overview of LT-CFB gas product composition from three campaigns with only a hot cyclone for gas cleaning [64]. HHV:

 Higher Heating Value.

		Straw	Dry pig manure pellets	Digested pig manure fibers
CH <sub>4</sub>	Vol%	3	3	2
СО	Vol%	14	11	7
CO <sub>2</sub>	Vol%	15	17	16
H <sub>2</sub>	Vol%	7	7	6
HHV, hot*	MJ/Nm <sup>3</sup>	6.9	7.1	6.6
HHV, cold, dry, tar- & particle-free**	MJ/Nm <sup>3</sup>	3.9	3.5	2.4

\* Estimated based on mass- and enthalpy flow of the hot product gas [64]

\*\* Estimated based on the heat of combustion of CO,  $CH_4$  and  $H_2$  in the gas [80]

The gas composition and heating values are quite comparable across the different campaigns, except for the content of CO. There is generally a very large difference between the determined energy content of the hot and cold product gas from the LT-CFB gasifier. First and foremost, the difference between the energy content of the hot and cold gas products lies in the temperature difference as well as the content of tar and combustible particles in the hot gas. Tar can be a critical parameter in this regard and make up as much as 10-60 % of the total energy content in the hot gas [2]. The energy contribution from the particle content is on the other hand expected to be relatively small (digested pig manure fiber campaign, [75]). The thermal energy in the hot gas has been found to account for up to 30% of the total energy content in the gas when evaluated at temperatures around 600 °C [64]. In addition to these differences, it is also important to acknowledge that the energy contents of the two gas products are usually estimated with very different approaches. The energy content of the hot gas is usually based on mass and energy balances, while the energy content of the cold gas is usually calculated based directly on the determined composition. Calculating the cold gas energy content based on composition requires full knowledge about the composition. This can be problematic as the content of simple hydrocarbons (in addition to methane) is often not quantified and accounted for, and such compounds have been found to constitute as much as 40% of the total energy content [2]. In some cases the cold gas energy content is therefore found to be lower than it actually is, and this can be expected to account for a substantial part of the difference in the estimations of the energy content in the hot and cold gas product.

### 2.3.1 Particles in the LT-CFB gas product

The secondary cyclone removes the vast majority of solid material (mainly small particles of ash and unconverted char) from the product gas, but not all particles are separated out. When LT-CFB gas is burned directly in an adjacent dust-fired boiler, the particulate material in the gas is relatively a small concern. In this case it is mainly important to remove particles to prevent potentially problematic ash species from reaching the boiler and downstream equipment. Some of the escaping ash species may cause corrosion and problematic depositions, but when co-fired with coal, the composition of the coal ash has an inhibiting effect on the melting and corrosion properties of the biomass ash. Another concern in this regard could be the loss of valuable elements in the particulate material. To mitigate the potential issues with particulate material in the LT-CFB product gas, campaigns have been conducted with different types of filters. During the ForskEL project 10730 – Gasolution, a hot gas bag house filter was tested at temperature up to 370 °C and a set of inorganic candle filters were tested at temperatures up to approximately 600 °C. The filtration efficiency was subsequently estimated to be up to 99% [81].

### 2.4 Ash products

The ash product from the LT-CFB gasifier is of outmost interest in this study, as this is the product fraction where most of the wanted – and unwanted, inorganic elements in the fuel can be expected to be recovered. There are three main options for extracting solid ash products from the LT-CFB (Figure 7):

- Ashes separated by the secondary cyclone (SC ash). This is usually the main ash product, and cyclone efficiencies around 90-95% have been reported for three different LT-CFB campaigns [64,68,75]. It is generally desirable to extract as much ash as possible through the cyclone compared to bed draining as the cyclone ash fraction will contain only little or no sand. However, the potential rates of cyclone ash production vary with the fuel and operation parameters. From a series of LT-CFB campaign on the 100 kW<sub>TH</sub> and 500 kW<sub>TH</sub> units, total recovery rates of fuel ash in the secondary cyclone ash between 45 and almost 100% have been accomplished [2,64].
- 2) Extraction of bottom ash from the char reactor (CR bottom ash). It is possible to drain bed material from the char reactor during operation. The bed material will contain a mixture of sand, ash and unconverted char. The temperature of the extracted bed material will be the same as the temperature of the char reactor. To reduce the need for adding fresh bed material as well as unnessesary loss of thermal energy associated with extraction of hot bed material in this way, the extracted bed material should either have a very high concentration of the drain should be designed for selectively draining ash particles
- 3) Filter ashes. If the gas product is filtered, the ash and char collected in the filter can by regarded as a product. However, this product is likely to have elevated concentrations of heavy metals if filtration occurs at reduced temperatures. In this case certain elements may re-condense in the filter after being volatilized in the gasifier [3]. Filtering the gas can be a good way to remove particles as well as various heavy metals (e.g. cadmium) prior to combustion. Optimizing the efficiency of the secondary cyclone will reduce the production of filter ashes.

The distribution of inorganic elements between the LT-CFB products (gas phase, filter ash, cyclone ash and char reactor bottom ash) varies with the composition of the fuel and the operation parameters. During a

campaign with dry pig manure fibers it was determined that 54% of the total amount of the nutrients K, P and Ca in the fuel could be recovered in the SC ash while 30% could be extracted from the bed material and the last 16% was present predominately in dust most of which probably could have been separated by a proper filter. In addition, it was found that 72% of the chlorine in the fuel was recovered in the SC ash. This is important as Cl as well as K is usually unwanted in boiler systems [64]. During operation of the LT-CFB on straw, Stoholm et al. (2002) recovered 73-98% of the important nutrient K as well as 23-75% of Cl in the SC ash product [68].

Recovery of valuable elements is not the only parameter for ash product quality. When considering application of the ashes as fertilizer and/or soil enhancer it is also essential to optimize other ash characteristics including: Organic/inorganic toxicity; pH; fertilizer quality; carbon content and biochar related characteristics.

The content of organic pollutants in LT-CFB ashes in the form of Polycyclic Aromatic Hydrocarbons (PAHs) have been investigated several times. Total PAH content in cyclone ashes during operation on straw fuels have been found to range from 3.5-6.2 mg/kg [64,68]. In cyclone ashes from operation on dry chicken manure, dry pig manure fibers and anaerobically digested pig manure fibers a total PAH content of 2, 2.5 and 0.2-0.7 mg/kg respectively have been identified [64]. The PAH content in all the assessed SC ashes was found to be well below the legal threshold for use in Danish agriculture (12 mg/kg [82]).

The content of heavy metals in ashes from the LT-CFB varies primarily with the composition of the fuel. However, the operation parameters also have significant influence as does the type of ash product (Filter, CR or SC [3]). Heavy metal concentrations in five LT-CFB SC ashes are provided in Table 2.

	LT-CFB unit	Cadmium	Lead	Zinc	Chromium	Nickel	Copper	Mercury
	kW <sub>TH</sub>	mg/kg & mg/kg P	mg/kg & mg/kg P	mg/kg	mg/kg	mg/kg & mg/kg P	mg/kg	mg/kg & mg/kg P
Wheat Straw [83]	100	0.07 6.4	<10 910	160	<u>100</u>	<u>48</u> 4350	31	-
Citrus peel fiber residues [83]	100	0.04 10.8	20 5400	60	<100	<u>34</u> 9200	12	- -
Dry pig manure [64]	500	<0.06 <1	6.8 131	-	32	<u>30</u> 577	-	0.3 6
Digested pig manure fibers [64]	500	<u>2.0</u> 30	13 197	1900	22	<u>57</u> 864	350	0.07 1
Wheat straw [84]	6000	<0.09 22.5*	3.9 975*	-	17	5.6 1400*	-	< 0.001 0.3*
Legal threshold [85]	mg/kg mg/kg P	0.8 100	120 10000	4000	100	30 2500	1000	0.8 200

Table 2: Content of selected heavy metals in ashes from the secondary cyclone from various LT-CFB campaigns. Db: Dry basis. Underlined values violate legal thresholds.

\* Calculated using 4.0 g P/kg ash, db (6 MW LT-CFB gasification of wheat straw [71]).

To be applied as fertilizer in agriculture, the ashes have to comply with the regulations per unit of dry mass or per unit of total P. The results from Table 2 show that the dominating problems in this regard are related to complying with the legal threshold for Nickel. An investigation into this matter indicated a substantial net increase in the total Nickel content leaving the gasifier compared to the amount entering in the fuel. This Ni surplus can originate either from the fresh sand used as bed material or from the inner surface of the LT-CFB. The 100 kW<sub>TH</sub> unit does not have a refractory lining and thereby allows for direct contact between the bed material and the steel alloys used in the construction throughout the system [3,64]. The 500 kW<sub>TH</sub> and 6 MW<sub>TH</sub> units have an inner refractory lining of the reactors, but parts of the system does not (feeding, cyclones, ash handling etc.), and direct contact between bed material and steel will still occur. As the problem with overrepresentation of Ni in the ashes seem to be biggest in the 100 kW unit, this could indicate that leaching from the steel alloy could be at least part of the reason. This issue should be further examined to determine the Ni (and to some extent Cr) source, and secure a high ash quality.

In addition to toxicity, the fertilizer quality of the ashes is also very important. Fertilizer quality of ashes relates to the mobility and plant availability of the nutrients in the ashes. This is usually determined by plant growth experiments in pots, small field plots or large field plots. Approximations of the mobility of nutrients can also be attempted by various incubation and extraction procedures. Plant based investigations of the P and K fertilizer quality in ashes from LT-CFB gasification have been carried out by Kuligowski (2009), Müller-Stöver et al. (2012) and Hansen et al. (2016). In general, the results from assessment of LT-CFB ash fertilizer quality are influenced largely by the type of fuel gasified and the type of soil used. SC ash from straw gasification was found to increase shoot growth 40-165% on a coarse sandy soil compared to unfertilized controls. In the same experiment no effect - or even negative effect, on yield was observed when applying the ash to sandy loam [71]. In another study with a low-P soil classified as Typic Hapludalf, SC ashes from gasification of straw and citrus peel residue fibers were compared in an incubation study, a greenhouse pot experiment and an outdoor lysimeter experiment. The study showed that straw ash increased levels of extractable P and K (Olsen-P and acetate/acetic acid extractable K) in the soil and improved the yield of barley and maize. The ashes from the citrus peel fiber gasification did not increase neither the level of extractable nutrients in the soil nor the plant yield. Faba bean did not react positively to any of the ashes [83]. Finally, the effect of thermally gasified pig manure ash as P fertilizer has also been studied in two experimental campaigns. In the first experiment, the effect of SC ashes on growth and elemental uptake of ryegrass (Lolium rigidum Gaudin) in an acidic, sandy soil (pH 4.5) was investigated in a greenhouse setup. In the second, larger scale field experiment, barley and ryegrass was grown in sandy and loamy Danish soils for 1.5 years. It was found that on acidic, sandy soil, the SC ash was an effective liming agent, which increased electrical conductivity, water holding capacity and bicarbonate-extractable P in the soil and at large P application rates it gave almost the same maximum plant growth yields as monocalcium phosphate (MCP). Heavy metal uptake in the plants fertilized with ash were minor and within regulatory limits [86]. The effect of ash amendment on growth yields was very limited and no response to increasing doses was observed. A small increase in the P-uptake (15%) from the first to the second year was observed. Despite low control P-values it was concluded that P was not the limiting factor and therefore increased dosing had no effect on the yields [87].

The ash from low temperature gasification also holds the potential to sequester carbon for a very long time, and in this way contribute further to the mitigation of climate change. In a LCA study by Nguyen et al. (2013) on LT-CFB gasification of straw it was proposed that 85% of the carbon amended to soil with the

ashes would remain there for the temporal scope of the study (usually >100 years but not stated in the article) and that the beneficial contribution of the carbon sequestration on the total greenhouse gas balance was larger than the contribution from the heat production in the downstream CHP combustion of the product gas [70]. The results were generally supported by another LCA study on SC ashes from LT-CFB gasification of straw conducted by Sigurjonsson et al. (2015). In this study it was concluded that due to the fertilizing effect and content of recalcitrant carbon in the SC ash, a system with straw gasification and recycling of the ashes to soil could deliver carbon neutral and even carbon negative energy in certain settings with a high level of carbon sequestration. It was also concluded that the carbon sequestered with the ashes play a very significant role in the greenhouse gas balance, and it is proposed to prioritize additional carbon in the ashes over thermal efficiency [79]. The stability of carbon in SC ashes from LT-CFB gasification of straw was investigated in a study by Hansen et al. (2014). It was found that after 110 days of incubation of ashes and dry straw in soil, about 3% of the ash carbon was respired as CO<sub>2</sub>, while 80% of the carbon from the straw was respired. The structure of the ash was also investigated and was found to have a high porosity and specific surface area, which was proposed as key quality parameters in regard to improvements of soil structure and the soil ability to retain nutrients and water [78].

### 2.5 LT-CFB gasification compared to anaerobic digestion and incineration

The LT-CFB gasifier has several characteristic features that could make it a very suitable platform for conversion and valorization of secondary resources. The technology has been proven to operate successfully on various problematic fuels including straw, various biogas- and manure fibers and different organic residues from industry [1,64,65]. The technology is also very scalable and efficient in small as well as large scale. Upscaling by a factor of 10 from 50 kW<sub>TH</sub> to 500 kW<sub>TH</sub> and another factor of 12 from 500 kW<sub>TH</sub> to 6 MW<sub>TH</sub> has proved to be relatively straight forward and revealed no apparent limitations in the scalability of the design. In addition, the design of the circulating fluidized bed and use of simple cyclones for hot ash separation reduce the requirements for internal heat exchange surfaces and mechanic parts, which in combination with low operation temperatures reduce plant construction- and maintenance costs and increase robustness [64,75]. However, other conversion platforms may also be relevant to consider when proposing optimized management of secondary resources. Two of the most conventional conversion technologies in this regard are anaerobic digestion and incineration.

### 2.5.1 Thermal or biological gasification?

Anaerobic digestion (AD) and production of biogas is a mature and commercially available technology applied for production of biogas from especially very wet fuels. It is commonly applied to digest organic food waste, sewage sludge, manure and various organic residues from industry and agriculture [28,88,89]. Some of the strengths of anaerobic digestion of such resources compared to LT-CFB gasification include:

- No requirements for drying: Most AD systems operate with a very wet mixture while the gasifier requires a relatively dry fuel (< 30% moisture [64]).
- Very clean gas product with high calorific value: Biogas is mainly composed of 45-70 vol% methane (CH<sub>4</sub>) and the rest mainly carbon dioxide (CO<sub>2</sub>) and the lower heating value can range from around 16 MJ/nm3 in landfill gas to 23 MJ/nm3 in biogas from anaerobic digesters [90,91]. The gas is easily

upgraded to bio-methane of natural gas quality using commercially available technology with small net losses around 3-5% of the energy [92].

- Well known process: AD systems can be extremely simple and have been applied for centuries in rural parts of the world while state-of-the-art AD systems are more complicated, more robust and give higher biogas yields [93].
- Recovery of nutrients: With no requirements for mechanical de-watering and production of a clean gas product, the total content of all nutrients in the feedstock is largely preserved during anaerobic digestion [94].
- Plant availability of nutrients: In general, the plant availability of nutrients in AD slurry is very high and the anaerobic digestion even increases the fertilizer quality of some organically associated nutrients by mineralization [95,96]. In regard to P fertilizer quality in e.g. sewage sludge, this has been found to decrease with 50-70% during LT-CFB gasification compared to the fertilizer quality of the slurry from the AD process [3]. However, no studies have been conducted with LT-CFB gasification of sewage sludge that was not initially digested in an AD system.

The LT-CFB gasification process also has some strong advantages compared to the anaerobic digestion:

- Practically complete utilization of energy potential. During most anaerobic digestion processes, the majority of the lignin and a substantial part of the cellulose will not be converted as these constituents are largely indigestible to common microorganisms. In the case of primary sludge from waste water treatment, up to 65% of the total calorific value of the sludge may be expected to be recovered as biogas/methane [97]. However, the degree of utilization depends largely on the feedstock composition and the design of the anaerobic process and the total efficiency from feed to biogas can be expected to vary from at least 30 to 85% [90,92]. The thermal gasification process will convert practically all organic material in all cases.
- Less influenced by external factors: As the AD system uses living microorganisms to convert the fuel and operate with large volumes and large retention times, many different types of external disturbances in the AD environment can reduce yields for very long periods of time [98]
- Reduced volume and mass of fertilizer product: The ash from the LT-CFB is either completely dry or wetted slightly to make the subsequent handling easier. Organic material in the ash is almost exclusively carbon, and the content can be varied to match desired ash characteristics. The slurry from the AD system contains large amounts of water and nearly half of the organic material. The ash from the LT-CFB thus requires much less transport to be used as fertilizer in agriculture.
- Emissions from management of digestate or ash: Emissions of especially methane and N containing greenhouse gases from anaerobic digestors and the subsequent storage and management of the process digestate have been shown to significantly influence the greenhouse gas balance of the AD process. Even in the best case with little or no emissions from the AD process, the degradation of the digestate in the field will lead to substantial emissions of various greenhouse gases [99,100]. The carbon left in the LT-CFB ash is highly recalcitrant and the vast majority is expected to remain sequestered in the soil much longer than untreated organic carbon [78]. This difference will greatly decrease the on-field greenhouse gas emissions when spreading gasification ashes compared to fibers in the slurry from anaerobic digestion.
- Complete destruction of pathogens, organic xenobiotics and reduction of heavy metal content: Polluted resources like municipal waste or municipal sewage sludge may contain pathogens, heavy

metals and organic pollutants (e.g. antibiotics, fragrances, UV-filters, antiseptics, micro plastics, phthalates, flame retardants, hormones etc. [101–104]). The thermal gasification will most likely destroy practically all organic components in the fuel while also removing mercury, large amounts of cadmium and smaller amounts of other heavy metals [3]. The effect of anaerobic digestion on the pollutants will vary depending on the specific compounds. However, many emerging xenobiotics can be expected to persist through even thermophilic AD processes, and many of the persisting substances can be expected to concentrate in the sludge [105]

- Mineralization of organic P: The P bound in organic molecules (e.g. unconverted lignin and various microorganism) after the AD process is not directly available to plants if applied as fertilizer. During the gasification process, the organic material is decomposed and the P is mineralized. The fertilizer quality of the mineralized P depends largely on the inorganic composition of the fuel and the process conditions [4,32].
- Much lower retention times, facilitating much smaller units.

There can also be several potential benefits of combining AD and LT-CFB. With a downstream thermal conversion of the slurry fibers, the requirements for expensive pretreatment and long retention times in the AD system can be decreased and the process can be optimized to convert only the most labile parts of the fuel. If placed in close proximity of each other, the thermal gasification can provide the heat required in the AD process. This is especially important when the plant is operated at elevated temperatures compared to the ambient (mesophilic plants in cold season and thermophilic plants during the whole season). It has also been proposed that the microorganisms may convert tars in the product gas from the thermal process [106], and/or use H<sub>2</sub> in the product gas to increase the methane yield and carbon efficiency of the total process [107]

### 2.5.2 Thermal gasification or incineration?

Incineration is the most widely applied thermal process for conversion and management of complex, secondary resources like waste and sludge [108,109]. The benefits of incineration includes: Reduction of volume; destruction of pathogens and organic xenobiotics; low-risk and odor free operation and handling; and utilization of the energy potential in the fuel [110,111]. In large scale application the heat released from sludge incineration may be used to produce electricity, but the low operation temperature reduces the electrical efficiency substantially. Currently the best available technology (BAT) mono-sludge incineration plants can convert mechanically dewatered sludge with zero net consumption of electricity and fuels and a heat surplus supplied as district heating of up to 40% of the sludge HHV [112,113]. In these systems there is still a potential for further optimization with additional high pressure steam turbines, and it is expected that optimal BAT mono-sludge incineration of sludge based on combined belt drying, grate stoker furnace and micro gas turbines have also been tested with a successful production of electricity corresponding to approximately 6-8% of the sludge HHV [115]. Thermal gasification has been suggested to possess some of the same benefits as incineration while adding new beneficial characteristics with regard to the following:

 Thermal gasification may enable a larger flexibility in the product range by production and coproduction of electricity, heat, liquid and gaseous fuels and several different potentially valuable ash products [2,3,49]
- When the gasifier is constructed as an add-on to existing boilers, fuels that are only available in relatively small quantities and/or unsuitable for direct co-firing can still be converted with high thermal efficiency.
- Thermal gasification systems can provide high energy efficiency in general and much higher electric efficiency than incineration plants in small and medium scale [72,116,117].
- Thermal gasification plants can run fully automated with full heat integration and optimal thermal efficiency from very small to very large scale [49,72]
- Some gasifiers, including the LT-CFB concept, are more flexible in regard to fuel composition and co-conversion of e.g. sludge and biomass than most sludge-incineration plants [1,4,72]
- With gasification there are an improved potential for reduced emissions compared to incineration since the concentrated and fuel specific gas can be efficiently treated <u>before</u> it is combusted. Thereby, total emissions and/or gas treatment costs from the process related to the emissions of e.g. NO<sub>x</sub>, SO<sub>x</sub>, CO, dioxin and heavy metals can be substantially reduced [26,59,60]
- The flexible operation of the LT-CFB allows for an increased content of recalcitrant carbon in the ashes, which may contribute positively to the overall greenhouse gas balance of the process if the ashes are used in agricultural systems [79]
- Finally, as discussed in chapter 1, ashes from incineration are often used in construction or deposited due to toxicity or low fertilizer value. As discussed in section 2.4, ash from LT-CFB gasification can have a very high fertilizer value. This topic is discussed further in chapter 5.

There are also a few strong points to incineration compared to gasification:

- Reduced requirement for pre-drying (and in some cases pre-grinding) of the fuel
- Grate fired incineration systems involve quite simple and highly robust processes and are tolerant to highly heterogeneous fuels also including large, hard particles like metal and stones
- The technology is fully matured and commercially available and the operational experience on e.g. municipal waste and sewage sludge is substantial
- Due to the maturity, level of commercialization and the simplicity of the incineration process, the infrastructure and plant costs are relatively low.

**Chapter 3** relates strongly to the work presented in Paper I [1], and the purpose of this work is to answer the first sub-question of the thesis by investigating how broad the range of suitable fuel candidates for LT-CFB gasification is within a selection of secondary resources. The overall conclusion of the work is that there are many relevant fuel candidates within this category of resources that may be suitable for LT-CFB gasification, and that sewage sludge and manure fibers are among the most interesting in a Danish context.

The chapter describes the process of developing and implementing a method to screen for new fuel candidates for LT-CFB gasification. The general fuel requirements for LT-CFB fuels are described and 22 new potential fuel candidates are characterized and compared to 4 previously proven LT-CFB fuels and one fossil fuel (coal). The investigated fuel candidates are categorized by their apparent suitability as LT-CFB fuels and various positive characteristics as well as potentially problematic issues are discussed. Chapter 3 expands on the work of Paper I by determination of the elemental composition of ashes and pyrolysis chars of the expanded dataset it is attempted to correlate differences in the elemental composition of ashes and chars to differences in various ash and char characteristics e.g. ash deposit formation and ash and char P fertilizer quality. In the last part of the chapter, it is examined how the analytically determined characteristics of three fuel mixes differ from the expected linear sum of the involved fuels. The results indicate profound possibilities for optimizing fuel characteristics by fuel mixing especially with regard to ash deposit formation and sintering as well as ash and char P fertilizer quality.

# 3 Screening fuel candidates for LT-CFB gasification

The LT-CFB design has been described as fuel flexible, and previously published results have proved that the gasifier can operate on cereal straw (loose or as crushed pellets), citrus peel fibers, wood, dry pig manure fibers, digested pig manure fibers, chicken manure, one sample of dry sewage sludge granules and shea nut residues [1,64,68,72,75,81,83]. To this date, the only published results with technically unfeasible operation of an LT-CFB gasifier has been with dry beet seeds as a fuel. This fuel was gasified in the 6 MW<sub>TH</sub> unit in 2014 and operation was stopped after just 9 hours at full temperature. However, it has not been fully determined if the operational problems were related only to the fuel (and specifically the combination of high content of K, Na and Cl) or it was also related to problems with operation of a new feeding system in the 6 MW<sub>TH</sub> unit [81].

Based on previous experience and a characterization of the LT-CFB gasifier, several desirable fuel characteristics have been identified, which are expected to contribute positively to stabile, efficient operation of the gasifier:

- Small fuel particles with a diameter around 3-4 mm [72]
- Low moisture content, preferably not higher than 20-30 wt% [72]
- High energy density in the fuel to reduce transportation and increase thermal capacity [1]
- Sufficient char content to and char reactivity to supply heat for the pyrolysis when oxidizing char in the char reactor [1]
- Little or no agglomeration of char particles in pyrolysis at temperatures below 650 °C [1]

- Little or no ash sintering and agglomeration of ash particles and ash-sand particles during char conversion in air or air/steam at temperatures below 750 °C [1]
- Low volatilization of inorganics at the conditions in the system. An exception may the heavy metals if the ash is to be applied as fertilizer or soil enhancer. In this case, it may be desirable to release heavy metals in the process and thereby reduce the content in the ash [1]
- Suitable bulk densities and particle size ranges of char and ash in the system to allow for optimal separation of these in the primary cyclone and settling of ash in the secondary cyclone [1]
- An ash composition suitable for reuse or recycling. In case of valuable nutrients P and K, this relates to fertilizer quality of the elements, elemental composition and toxicity [3]

These characteristics can be used to group potential problems with new fuels into the following categories:

- Problems related to practical handling and fuel feeding. Can including low bulk density, high moisture content, high dust content or tendencies of the fuel to create bridges during feeding
- Problems related to ash content. Can be related to total ash content as well as ash composition.
   Unsuitable fuels may have ashes that form viscous eutectic melts at low temperatures and coat or react with the silica sand, forming particle agglomerates. This can lead to de-fluidization and reduced circulation and can bring the gasification process to a stop. The ash composition can also be problematic if large quantities of inorganics are released and cause problems with corrosion or fouling in downstream gas cleaning or boilers. Loss of valuable ash elements (e.g. nutrients) may be another concern related to the ash composition.
- Problems with ash and char densities and particle size distribution: Can occur if the cyclones are not capable of separating ash from char and sand in the primary cyclone, and/or ash from gas in the secondary cyclone.
- Problems related to the proximate composition of the fuel: Very low char content in the fuel combined with low char reactivity may make it difficult to supply enough energy in the char reactor to the pyrolysis. Very low char content in the fuel combined with very high char reactivity could lead to exposure of ash and hotspots. Very high char content combined with very low reactivity may lead to a low thermal efficiency of the process.

In addition to the gasification related characteristics, it can also be relevant to address if the fuel is abundant, if it is generally available, what type of potential value that lies in the conversion of the fuel and how it is currently used. A few examples are provided in Table 3. The results show a great variation among the total fuel energy potentials, potential value and current use. Resources like municipal organic waste and manure fibers have a very large energy potential, whereas a resource like sewage sludge has a much lower total energy potential but a large potential for recovering P, and generally optimize the management compared to the current situation.

Resource	Geographical scope	Global Potential	Potential value	Current use	Reference
Sewage sludge	Global	1-5 EJ HHV <sup>1,2</sup>	Low-Medium energy content & high P potential	Dumping, landfilling, incineration, compositing, direct use as fertilizer	[26,109,118]
Municipal organic waste	Global	23 EJ HHV <sup>1</sup>	Low-Medium energy content and mixed ash	Landfilling, incineration, composting/digestion	[21,22,119,120]
Manure fibers	Global	18 EJ HHV <sup>1</sup>	Low-Medium energy content and high P and K potential	Direct discharge to the environment, use as fertilizer, anaerobic digestion, fibers used as fuel for cooking	[46,121,122]
Sugarcane bagasse	100 + countries	7-10 EJ HHV	Very high energy content and some K potential	Energy production, mulching and on-site torching	[1,123–125]
Rice husks	Mainly Asia	2 EJ HHV	content and some P and K potential	Mainly burning in rice mills or dumped	[1,126–129]

Table 3: Examples of important secondary resources to consider for optimized thermal management systems. HHV: Higher Heating Value. EJ: ExaJoule (=10<sup>18</sup> Joule)

1: Scaled from the resource potential in EU 27+China and re-calculated from biogas potentials reported in [63] 2: The conservative range estimate is based on estimated global production of dry mass and an average heating value of undigested sludge from [130,131]

With these criteria in mind, it is proposed that the selection of secondary resources for optimized thermal management should address the following three potential benefits simultaneously:

- 1) Utilize the energy potential in the resource: Increase the level of long term sustainability in the energy system as well as the local security of supply and substitute energy with higher net levels of pollution and greenhouse gas emissions
- 2) Recover valuable elements: Increase security of supply of valuable elements (e.g. P and other nutrients) and substitute production of (virgin) materials procured from stock taking into account resource scarcity, value and the levels of pollution and greenhouse gas emissions associated with the procurement
- 3) Avoid the alternative: Many secondary resources are presently handled in a ways with unnecessary high impacts on human health, the environment and climate.

It is possible that only relatively few abundant resources are available where a proper thermal treatment can accommodate all these benefits. More resources will be available where a proper thermal treatment can accommodate two of the three benefits and numerous secondary resources are expected to be available where a proper thermal treatment can accommodate one of the listed benefits.

# 3.1 Initial characterization of new fuel candidates for LT-CFB gasification

The fuel candidates that have been screened for LT-CFB gasification in the present study are presented in Figure 8. The samples are categorized as follows: 4 proven<sup>1</sup> references (1 high quality bio-fuel, 2 residues from food production and 1 sludge sample), 9 unproven residues from production of vegetable food, 4 unproven residues from production of animal-based food, and 5 unproven mixed waste fractions predominately from wastewater treatment. Several samples were also collected from separated municipal solid waste. These samples were included in the first few experiments, but were subsequently omitted due to problems with reproducibility and confidentiality of the results. Many fractions of source segregated waste may be highly relevant to address in a future study, using a method dedicated for characterization of highly heterogeneous fuel candidates.

To answer the questions of the fuel screening, the following experiments have been carried out:

- Proximate analysis (content of moisture, volatile organics, recalcitrant carbon and ash)
- Heating value assessment of fuel and char
- Bulk density assessment of fuel, char and ash
- Grinding energy assessment
- Char reactivity measurements and corrosion assessment
- Char sticking and agglomeration assessment
- Ash sticking, sintering/agglomeration and vaporization assessment.

Methods and results from the experimental work are described in detail in Thomsen et al. (2015) [1] and the master thesis by Giulia Ravenni [132]. Additional remarks to the study can be found in the visual presentation from the 22<sup>nd</sup> European Biomass Conference and Exhibition, Milano Italy 2014 [133].

The overall conclusion from the fuel screening was that Bagasse, Olive Kernels, Olive wood pruning material, Rice husks and the new sewage sludge sample were the most promising candidates with little or no apparently problematic characteristics. These resources all have high heating values and energy densities and generally good fuel characteristics. Main concerns about LT-CFB conversion of these resources are potential loss of carbon and thereby thermal efficiency due to very low char bulk density (Bagasse), potential dust issues (Rice husks), ash deposition on reactor surface during char conversion in steam (Olive kernels) and sintering of ashes during prolonged exposure to air at 750 °C (Olive Kernels, Olive wood pruning material and sewage sludge). However, several of the references exhibited comparable behavior and for this reason the practical impact of these concerns is expected to be minimal. Rice husks have additional benefit for LT-CFB valorization compared to some of the other samples as it also contains a sizable amount of P and K and is unused or misused in some systems (Table 3). However, sewage sludge was found to be the optimal candidate as it contains a large amount of P, is globally available and is often poorly managed in present systems (Table 3). One sample of sewage sludge has already been proven as fuel in the LT-CFB. However, sewage sludge varies enormously in composition and characteristics depending on geography, demography, wastewater treatment plant design etc. [101,118]. It is therefore important to further investigate and validate the potential benefits of sewage sludge gasification in LT-CFB systems. This work is described in chapter 4,5 and 6.

<sup>&</sup>lt;sup>1</sup> The fuels have been tested in successful proof-of-concept campaigns on pilot- or demonstration scale LT-CFB gasifiers



Figure 8: Secondary resource samples included in the original screening of LT-CFB fuel candidates [1].

Manure based fuels represented by manure fibers from mechanically de-watered cattle manure and the solids from passively de-watered pig muck and manure was also found to be highly promising fuels. The primary concerns with these resources are a very low density of cattle manure char as well as the high moisture content and the related low energy density in both samples. However, in thermal systems with excess heat availability, optimized management of these resources in systems with LT-CFB gasification could prove to be highly relevant.

The only fuel candidate that was found unsuitable for conversion in LT-CFB gasifiers was the fat fraction from the wastewater treatment plant. This fuel contained almost no recalcitrant carbon, and nearly all organic material can therefore be expected to convert to gas in the pyrolysis. This would result in very low carbon content in the bed material, and generation of heat in the char reactor would be insufficient to dry and pyrolyze the fuel in the pyrolysis reactor. This resource is on the other hand found to be a very good fuel candidate for dedicated fast pyrolysis as well as incineration processes. The sand fraction from the wastewater treatment plant was found to have a somewhat comparable problem with very low content of recalcitrant carbon in the pyrolysis char. However, this resource is not ideal for incineration as it contains a large pool of valuable P, which may become polluted, diluted and immobilized in large scale incineration processes. The high heating value of the fat as well as the large volatile fraction and high content of P in the sand fraction from wastewater treatment could very likely contribute positively to a good LT-CFB fuel by mixing with other secondary resources with the right characteristics.

Four fuel candidates were considered as potentially problematic due to several significant concerns with one or several assessed characteristics. These include the Palm kernel shell sample that sintered completely during exposure to hot air, the two samples of animal meat and bone meal where the char stuck to the pyrolysis reactor sides and subsequently sintered completely during char conversion in steam and finally the wine wood where the ash sintered in air while the char severely corroded the steel surface of the reactor during char conversion in steam. A series of pictures of problematic results from the fuel screening are provided in Figure 9. The images in Figure 9 D and E illustrate how small modifications of the process that produce secondary resources may lead to substantial improvements in the fuel characteristics. The primarily investigated sample of palm kernel shells contained a large amount of NaCl induced during the processing of the palm kernels. This resulted in very high char reactivity, a very low ash melting temperature and a severe tendency of the ash to melt in environments relevant for LT-CFB gasification (Figure 9 A and D). After simple washing and drying of the sample, the char reactivity and ash melting tendencies had been significantly reduces as seen in Figure 9 image E.

The remaining fuel candidates were placed in an intermediate group. This includes the beet seeds, the empty fruit bunches, the lignin pellets, the beach cleaning waste and the grate material from the wastewater treatment plant. Some concerns are related to LT-CFB gasification of these fuels, as they exhibit problematic characteristics in ash and char behavior and some of them also in regard to energy density. A failed attempt to gasify beet seeds in a 6 MWTH LT-CFB gasifier could be interpreted as a validation of the identified potential problems with this fuel. However, as discussed in the introduction to chapter 3 the failure could be due to operational issues as well as the fuel characteristics. In general, the practical impact of the identified concerns is difficult to predict without additional proof-of-concept experiments and more analysis is therefore required to qualify or disqualify these resources.



Figure 9: Pictures from fuel screening showing problematic characteristics of several different fuels. The included pictures show; Complete ash melting pf palm kernel shell ash after exposure to air at 750 °C (A); firmly sticking char depositions after pyrolysis of animal meat and bone meal in N<sub>2</sub> at 600 °C (B); a clean reference crucible (C); the residual from char conversion in steam at 750 °C of the original sample of palm kernel shells (D) and a washed and dried version of the same sample (E); completely sintered and agglomerated ashes from conversion of animal meat and bone meal char in steam at 750 °C (F); close-up of steel reactor surface after conversion of wine wood char (G) and beet seed char (H) in steam at 750 °C; clean reference steel reactor surface (I).

During analysis of the results from the fuel screening it became evident how important screening of proven references and known unsuitable fuels can be. The results from the proven references generate a span of values for a given parameter that has been proven in the LT-CFB gasifier while the set of failed fuels will provide a span of characteristic values that can be expected to fail. However, it may be just as important that a large reference data set also provide information about how the different characteristics influence each other. For instance, it could potentially pose a problem if the ash from a certain fuel is likely to sinter in air at 750 °C, representing the situation in the char reactor close to the air inlet or in situations with improper fluidization. However, if, at the same time, the content of ash is very low and/or the content of recalcitrant carbon in the char is high and the reactivity of the carbon relatively low, then ash sintering may not pose any practical problems after all. In this case, the ash may never be exposed to an oxidizing environment and the residual carbon will protect it from sintering as described by e.g. Kurkela et al. in 1996 and Skrifvars et al. in 1996 who found a relation between the completeness of the fuel carbon conversion and the rate of ash deposit formation [134,135].

More complex studies of the existing references with e.g. de-fluidization tests as well as proof-of-concept operation on currently unproven fuels will strengthen the evaluation criteria of subsequent fuel screenings. Step by step, this will improve the evaluation process, and especially if proof-to-fail operation would be attempted on fuel samples that for one or the other reason look unlikely to succeed. This could help determine the severity of various presumably problematic fuel characteristics and thus slowly improve the method – and potentially decrease the set of experiments required in the analysis.

## 3.2 Screening ash composition

Several of the concerns identified during the fuel screening related to the behavior of ash and/or char and can be expected to be related to the total content of fuel ash as well as the inorganic composition of the fuel [67,136–141]. In addition to potentially problematic issues, the inorganic composition also holds potential benefits in regard to the recovery of valuable nutrients and metals. The inorganic composition of the fuels from the screening have been determined and analyzed for three main reasons: 1) To directly identify potential positive and negative characteristics of the fuels related to the inorganic composition, 2) Supply composition data required for a subsequent screening of P fertilizer quality, and 3) To be able to make a subsequent investigation of potential correlations between LT-CFB relevant fuel characteristics and the inorganic composition of the fuel.

The work conducted on ash screening expands on the work of the primary fuel screening presented in section 3.1 [1]. In addition to the fuels previously investigated, the work with the ash screening also includes the following new fuel candidates: Fish manure from on-shore fish farming in Billund, Denmark; Shrimp waste from shrimp production in Greenland; Tomato residues from production of tomato concentrate in Italy and; Miscanthus grass pellets (commercial fuel pellets from a dedicated energy crop).

#### 3.2.1 Inorganic composition of LT-CFB fuel candidates

The inorganic composition of the fuel candidates was determined by analysis of ashes produced during the determination of the proximate composition of the various fuels [1]. The results from the proximate analysis were then used to estimate the inorganic composition in the char and dry fuel. A pre-test of the method on ash, char and fuel had shown that the best results were obtained by measuring the composition in the ashes and scale these results afterwards. Benefits of this approach include higher concentrations and more comparable concentrations, in the investigated samples reducing uncertainties and errors related to the calibration of the method and analysis. The main drawbacks of this approach are the influence of uncertainties related to weight loss during preparation of the ash samples as well as a potential release of inorganic elements during the thermal treatment. The procedure for the production of the ashes follows the Danish standard for determination of ash in solid biomass (DS/EN 14775 (2009)).

A sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer (Supermini200, Rigaku, USA) was used to obtain a distribution of main elements in the ashes. Determination was made with dry, crushed samples prepared in plastic crucibles covered with polypropylene film. Measurements were conducted in triplicates in a Helium atmosphere. The XRF measurements were calibrated with results from samples of sewage sludge, wheat straw and shea nut with known inorganic compositions. These had been determined in advance by FORCE Technology using a combination of the standards DS/EN ISO 11885 (2009), DS/EN 15290 (2011), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Cl was determined using the standard DS/EN 15289 (2011). Highlight results showing content of the main fertilizer components (P and K) in the dry composition and ash of the different fuel candidates are provided in figure 10. A complete data-set is provided in Appendix 5 with the determined concentrations of main inorganic elements in ash, char and dry material.





The results illustrate a huge variety in the P and K content of various secondary resources. The P content varies from almost zero to more than 4 wt% of the dry samples and to more than 16 wt% of the ash. K content in the dry samples varies slightly less than the P content – from around 0 to 3 wt%, but in the ashes

it varies a lot more – from close to 0 to almost 40 wt%. These reverse relationships express a pattern with relatively low total ash content but very high K content in the ashes from some of the samples of biomass residues (tomato residues, empty fruit bunches, olive kernels and shea nut residues).

If ashes from the thermal processing of the investigated fuel samples were to be used as fertilizer, it will be relevant to determine the P-K relationship as well. P fertilization with ashes from thermal conversion of animal meat and bone meal will only contribute very little to K supply while P fertilization with ashes from thermal conversion of empty fruit bunches (EFB) will contribute unreasonably much to the K supply. The P/K ratio among the ashes vary from <0.1 in EFB to exactly 1 in rice husks and on to almost 30 in shrimp waste. The majority of the vegetable samples have quite low P/K relationships (0.05-1, average around 0.3) while the animal- and waste-samples have quite high P/K relationships (0.7-30, average around 7.3). The P/K relationship in rice husk (exactly 1) stands out in the biomass samples, as does the manure samples in the animal and waste fractions due to the high content of biomass fibers in these samples. As different soils and plants require different P/K ratios, it will usually be relevant to mix either ashes or fuels. Fuel mixing is discussed further in section 3.5.

# 3.3 Screening P fertilizer quality of chars and ashes

A high content of P in a residue applied as P fertilizer does not necessarily mean a good P fertilizer. If the P in the residue is associated to organic and inorganic material in a way the prevent uptake in plants then the P fertilizer quality – and value, of the substrate will be low regardless of the P content. Proper quantification of P fertilizer quality is a very complex issue, and several factors influence the results of the assessment. These factors include (but are not limited to):

- The chemical composition and P speciation in the substrate (discussed in Paper III and 5)
- The liming effect of the substrate [142,143]
- The structure, composition and pH of the soil (discussed in chapter 5)
- The particle size distribution of the substrate (discussed in chapter 5)
- The type of plant applied (plant growth experiments) [144,145]
- The type of P extraction method used (incubation studies without plants) (discussed in chapter 5)
- The temporal scope of the investigation (discussed in chapter 5)
- P dosage ([3,83,143,146,147]
- Limiting effects of deficient levels of other macro- and micronutrients (N, K, S, Mn, Mg, Cu etc.) [148–150]

Despite the complexity of plant-substrate-soil-climate interactions, it is possible to obtain useful indications about a substrates P fertilizer quality with relatively simple measures. In the extended LT-CFB fuel screening, this is done by incubating substrate/soil mixtures for one week with high moisture levels and subsequently extract P from the incubated mixture using anion-exchange resin (AER) strip in bicarbonate form. Several other studies have been published using similar techniques to characterize P fertilizer quality, but since the method has some severe limitations, the quality of the results depend largely on how they are used [146,151–153]. This matter is also discussed further in chapter 5.

The procedure and method for the incubation study and subsequent extraction of P is similar to the method used and described in Paper IV [4]. The experiment with the char samples was conducted in June 2015 while the experiment with the ashes was conducted in January 2016. The soil used for the incubation study was obtained from the upper layer of an agricultural field located at DTU, Risø Campus near Roskilde, Denmark (55°41′N, 12° 05′E). The soil contained 10 % clay, 12% silt, 46% fine sand and 30 % coarse sand. The soil was air-dried and sieved to  $\leq 2$  mm. The soil contained; 12 g kg<sup>-1</sup> total carbon (C), 1.1 g kg<sup>-1</sup> total N, 6 mg kg<sup>-1</sup> bicarbonate-extractable P (Olsen-P) and 69 mg kg<sup>-1</sup> extractable K. pH of the soil in a water solution was determined to be 5.9.



Figure 11: Anion-exchange Resin extractability of phosphorus in incubated char and ash samples from the LT-CFB fuel screening

The AER extractability (Figure 11) of P from the mineral P reference was 50-65% of total P added (soil P subtracted) after one week incubation. Mineral P is 100% AER strip extractable in its pure form, but when incubated, a large fraction of the solubilized P is relatively quickly immobilized in the soil, which reduces the extractability – as well as the plant availability, of the P fertilizer after a very short period of time. By this mechanism, the initial plant uptake of P from mineral fertilizers may be as low as 10-25%. However, recent studies indicate that the residual P pool will become available again as the immediately available P pool is consumed by the crops, and it has been suggested that as much as 50-70% or more of the applied P can be recovered in plant biomass in subsequent growth seasons [154].

The results from the AER strip extraction of the incubated ash and char samples (Figure 11) show a very high variability in P fertilizer quality. Coal from a coal pile at the Danish powerplant Avedøreværket was included in the assessment and showed AER strip extractability of P around zero, regardless of whether it was as a char or an ash. The slightly negative values in coal ash – as well as shrimp waste ash, originate from the adjustment of the results by subtracting the extractability of P in control soil/sand sample.

Several other substrates than coal (ash/char) and shrimp waste ash had very low AER P extractability as well. Ashes from beach cleaning waste (sea weed), the grate and sand fraction of wastewater treatment and fish manure as well as chars from pyrolysis of shea nut residues, olive kernel residues and both types of animal meat and bone meal had P extraction rates around or below 5% of total P.

Beet seed ashes stands out as an exceptionally AER extractable P resource after one week of incubation. As the only substrate, the beet seed ashes had 80% higher relative P extractability than the mineral P reference. The experiment has been repeated with two contrasting soils, and water extraction instead of AER strip extraction. In this study it was also found that in both soils, two of four samples of beet seed ashes had higher P extractability than the mineral P reference. In one soil (Crucial, pH 6.1) the beet seed ashes produced at annealing temperatures 550 °C and 750 °C had 4 and 25% better extractability than the reference P. In the other soil (LTNDT, pH 5.2) the ashes produced at annealing temperatures 750 °C and 850 °C had respectively 2 and 17% better P extractability than the mineral P reference [155]. Both of the soils applied in the study originate from test fields in Taastrup, Denmark operated by scientists from the University of Copenhagen. The soils have comparable textures, and the Crucial soil is described in more detail in Paper IV [4]. Despite differences among the results, both studies support the conclusion that under the proper conditions, ashes from thermal conversion of beet seeds are as good a P fertilizer (or better) than mineral P.

No other substrates performed as well as the beet seed ashes in the AER P extraction experiment (Figure 11). However, several other substrates achieved very high extractability results. The ashes from tomato residues were as extractable as the P reference, while ashes from shea nut residues and empty palm fruit bunches and chars from beet seeds and shrimp waste all had extractability rates higher than 50% of the mineral P reference.

A large difference between ashes and chars of the different substrates was observed in several occasions. When comparing the results relative to the mineral P reference it was found that P in the incubated shea nut ashes was almost 10 times as extractable as the P in the shea nut char. In the empty palm fruit bunches the difference was a factor 8 and in the tomato residues it was around a factor of 5. The opposite was the case with the shrimp waste where the P in the char was more than 30 times as extractable as the P in the ashes. In general there were more samples where the ash had more extractable P than the char (16 samples) than the opposite (9 samples). In one sample (the wastewater sludge from Randers Centralrenseanlæg, "RC dried") the P extractability of ash and char was the same when comparing to the two respective mineral P references. The chars and ashes were produced at comparable temperatures (600 °C and 550 °C). Temperature alone can therefore not be expected to explain the differences between P extractability of ashes and chars. However, in two studies with focus on beet seeds, shrimp waste and sewage sludge, the authors found that temperature in general had a bigger influence on P extractability than the reaction atmosphere (reducing >< oxidizing) [155,156].

Combining the results in Figure 10 and Figure 11 will provide an estimate of the total amount of extractable P per unit of residual mass. These results are provided in Figure 12.



Figure 12: Anion Exchange Resin extractable phosphorus in char and ash from LT-CFB fuel screening

From Figure 12 it is evident that there is a huge potential for recovery of extractable P in ashes from tomato residues and beet seeds. It should be noted once more that these ashes are produced by annealing pyrolysis chars at 550 °C, which is not representative for commercial incineration. A commercial incineration process would not have two separated stages of conversion, and would also occur at much higher temperatures (e.g. 800-1200 °C [157,158]). It is therefore very likely that the P speciation and extractability of commercially available ashes from such fuels would differ significantly. A study and discussion about the influence of process design and operation parameters on P fertilizer quality is given in chapter 5.

During gasification and pyrolysis, the fuel is converted in a reducing atmosphere, and when screening new fuels for such systems, with a focus on the P quality of the solid residuals it makes sense to focus on char characteristics rather than ash characteristics. Pyrolysis chars are produced at 600 °C, which is quite representative for the operation temperatures of commercial pyrolysis units and the temperature in the pyrolysis reactor of LT-CFB gasifiers. However, the very low heating rate and very long retention times applied in the analytical pyrolysis are not generally representative for commercial pyrolysis systems nor the LT-CFB pyrolysis reactor [4,72,159,160]. Of the chars included in Figure 12, the largest fractions of AER extractable P is found in char from pyrolysis of shrimp waste and the new sewage sludge sample. The substantial difference among the two sewage sludge samples and the fact that the new WWTP sludge sample was among the most optimal fuel candidates in the screening, support the previously identified relevance of investigating LT-CFB gasification of sewage sludge further.

#### 3.3.1 Critical reflections

There are two very relevant sources of uncertainty related to the results from the specific AER strip experiments. The first source of uncertainty relates to the P content of the substrates. The main issue in this regard is the quality of the XRF analysis. As previously mentioned, the XRF analysis was calibrated with only three samples, and for samples with very different characteristics than these three, significant uncertainties could be expected. The second very relevant source of uncertainty is the particle size distribution (PSD) of the substrates [32]. Especially with just one week of incubation, it is expected that the incubation could have different effects on large and small particles. All samples were grinded prior to the experiment using identical grinding settings on a Mahlkönig Kenia Disc grinder (MAHLKÖNIG GmbH & Co. KG, Hamburg, Germany). However, the actual PSDs of the different samples were not determined prior to the experiments. Instead, the PSDs were examined after the incubation study on the remaining substrate. This was done using a combination of a Retch Vibro Sieve (Retsch GmbH, Haan, Germany) and a Retsch/Jenoptik Camsizer (Retsch GmbH, Haan, Germany). PSD by camsizing gives high resolution results and is quick to perform. However, it was not possible to make reproducible results with the Camsizer on 16 of the 29 ash samples. The particles from these samples stuck together and formed agglomerates of varying sizes. PSD determination by sieving was performed on these samples instead. In the remaining 13 ash samples and all 29 examined char samples there were no problems, and 8 reproducibility tests gave vary convincing results. Average particle sizes of the different samples are provided in Figure 13 with indications of the reproducibility of selected measurements (error bars indicate standard deviation but are hardly visible). The full dataset with the determined particle size distributions of the different samples is provided in Appendix 6.



Figure 13: Average particle diameters (d<sub>p, average</sub>) of chars and ashes used in phosphorus extractability experiment

The mean and median of the determined dp, average values for ash and char series are quite comparable. In general, there is a much larger variation in the ash series average particle diameter than in the char series. Despite a relatively narrow band of absolute average particle sizes around 0.1-0.3 mm, the relative difference can be more than several hundred percent. In addition, there is a significant variation in the allocation between different size fractions as well as in the determined maximum particle diameter in the different samples (Appendix 6).

There is no straight forward correlation between P extractability and PSD. This is illustrated in Figure 14 by plotting the AER P extractability of incubated chars and ashes as function of 1) average particle size in the investigated samples and 2) Average size of the largest 25% of particles. However, as the variation in the AER strip results also originates from differences in composition, no final conclusion can be made on the potential influence of differences in the particle size distribution of the substrates. This issue is investigated and discussed further in chapter 5. To reduce the potential influence of PSD differences on results from P extractability studies with incubation, it is proposed to align PSDs of the investigated samples before the incubation. Alignment should as a minimum include comparable average particle sizes as well as maximum particle size allowing for a narrow total span of size ranges. Ideally, the PSD curves should be comparable and examined to identify deviations from the average PSDs.



Figure 14: Anion Exchange Resin (AER) extractability of phosphorus (P) as function of: 1) average particle size in the investigated samples and 2) Average size of the largest 25 vol% of particles

## 3.4 Data correlations in LT-CFB fuel screening

Many of the potentially problematic issues as well as the potential benefits regarding thermal conversion of secondary resources relates to the ash chemistry. In the fuel screening it was found important to characterize fuel candidates with regard to risk of ash sintering, char sticking, ash vaporization, corrosion of reactor steel surfaces and ash and char densities. Under comparable conditions, variations within these characteristics can be expected to relate strongly to the inorganic composition of the ash [67,136–141]. In addition, the ash chemistry relates strongly to the potential of a given ash or char as P and K fertilizer – with regard to the total content as well as the quality of the nutrients (Figure 12).

In this section, it is attempted to relate the inorganic composition of the investigated fuels and fuel candidates to characteristics that may be important when screening new fuel candidates. Such relations may improve the intuitive judgement of new fuel candidates and save time and resources in the fuel screening process as well as improve the understanding of how ash chemistry relates to the investigated characteristics. Some correlations are straight forward like the correlation between the total inorganic

content and Higher Heating Value of ashes and chars produced at temperatures between 550 and 600 °C (Figure 15).



Figure 15: Linear correlation between total inorganic content and Higher Heating Value of various ashes and chars

This correlation is very strong, and the significance of the contribution of the assessed parameter (total inorganic content) on the result (Higher Heating Value) seems to describe the full variation in the results. From this correlation it can be validly assumed that the average organic fraction of the assessed ashes and chars has a Higher Heating Value close to 34 MJ/kg, which is slightly above that of pure carbon (32.8 MJ/kg [161]). However, it cannot be expected than many correlations are this simple. As an example, the results in Figure 16 show that the correlation between bulk density of chars and ashes is much weaker, and it is clear from the deviation among the samples that the correlation does not fully describe the variation between the two sets of data.



Figure 16: Linear correlation between char and ash densities. Samples with high content of sand (sea weed collected as beach cleaning waste and the sand fraction collected from wastewater treatment) have been taken out of the data set.

In other cases there will be no evident correlation at all. This can be the case, even with intuitively coupled phenomena. An example is provided Figure 17 showing results from a double experiment with ash deposit sticking and ash vaporization during heating of the same ash samples to 750 °C in air [1].



Figure 17: Illustration of the lack of correlation between data on ash deposit sticking and ash vaporization during heating of ash samples to 750 °C in air [1].

In the following, a series of potential correlations in biomass characterization involving the ash (and char) composition are investigated based only on data from the fuel screening. The investigation involves determination of best-fit correlations between elemental composition of fuels and the following characteristics [1]: Ash: Ash deposit sticking, ash vaporization, ash bulk density and P extractability. Char: Char deposit sticking, char reactivity, char bulk density and char P extractability.

Simple correlations between the inorganic compositions and the different ash and char characteristics are investigated by determining the Pearson's correlation coefficient (R) for linear correlations between a given characteristic and the best-fit sum of one to five of the main inorganic elements in the ash or char.

The highest positive and negative Pearson's correlation coefficients are identified for each assessed char/ash characteristic by analyzing all possible sums (637) of one to five of the ten elements Na, Mg, Al, Si, P, S, Cl, K, Ca and Fe. The robustness of the strongest correlation is determined by examining and evaluating the linear Person's correlation coefficient (R), the visual correlation and R<sup>2</sup> fit of the data to a simple trend line as well as the structure of the correlation matrix (example in Table 4). Finally, the robustness can be tested by conducting the same analysis on a sub-group of categorized or randomly selected samples.

Results from the assessment of a possible correlation between the inorganic composition of ashes and the tendency of the ashes to form firmly sticking deposits at 750 °C in air are provided in Table 4 and Figure 18. Results from test of robustness by investigation of differences in single element correlations of the entire sample population and three sub-groups are included in Figure 19. The ashes from Palm Kernel Shells have been excluded from the investigation of ash deposition as this sample exhibited an extreme behavior compared to all other samples (Relative difference larger than a factor of 10).

Table 4 shows the sum of one to five elements that gave the strongest positive and negative R correlation to the ash deposition data. K and Fe are the single elements with the strongest positive and negative correlations to the formation of firmly sticking ash deposits respectively. This means that ashes with a high content of K are likely to form ash deposits at 750 °C in air whereas a high content of Fe is likely to inhibit the formation of ash deposits. If the combination of two elements is considered in this regard, the best positive correlation is to the sum of K and S in the ashes while the best negative correlation is to the sum of P an Al. In the positive correlation matrix, one new element is added in each layer and the remaining

elements persist. In the negative correlation there is some shuffling of the elements in the first two layers. This could indicate that the positive correlation is more robust than the negative correlation. However, it can also indicate that several elements have almost similar influence on the results.

								РС				
Most influential elements									Positive	Negative		
1 compound	Na	Mg	Al	Si	Р	S	Cl	К	Ca	Fe	0.77	-0.38
2 compounds	Na	Mg	Al	Si	Р	S	Cl	К	Ca	Fe	0.78	-0.50
3 compounds	Na	Mg	Al	Si	Р	S	Cl	К	Ca	Fe	0.79	-0.62
4 compounds	Na	Mg	Al	Si	Р	S	Cl	К	Ca	Fe	0.75	-0.69
5 compounds	Na	Mg	Al	Si	Ρ	S	Cl	К	Са	Fe	0.69	<u>-0.75</u>

Table 4: Maximum Person's correlation (PC) coefficient between ash deposition formation and the aggregated concentration of one to five main elements in the ash. Light gray elements contribute to formation of sticking ash deposits. Dark grey elements inhibit this formation.

The results in Table 4 show that the overall best positive correlation to the ash deposit data is from the sum of Mg, S and K in the ashes, while the best negative correlation is from the sum of Na, Si, P, Ca and Fe in the ashes. In general it is desirable to investigate sums of as few elements as possible as the uncertainty is expected to increase with the number of elements. Therefore only sums of one to five elements are considered in the investigation. This is due to aggregated uncertainty of the composition results as well as the increased influence of hidden, complex mechanism and the risk of identifying false correlations. A visual representation of the best-fit correlations determined in Table 4 is provided in Figure 18.



Figure 18: Best-fit correlation between ash deposit formation at 750 °C of all ashes from biomass screening [1] and the content of elements in the ashes that are Left) Major contributors to formation of sticking ash deposits or Right) Major inhibitors of ash deposit formation of sticking ash deposits

The correlations are visually evident, but with several deviating data points. The general robustness of the correlations can be validated or challenged by re-doing the investigation with one or more data subsets. This is illustrated in Figure 19 with a plot of the single-element correlation coefficients of all 10 assessed elements obtained from investigation of the full dataset as well as three subsets. Two of the subsets are selected by random (I and III) and the last is selected as samples of recent biologic origin only (thus not

including the coal sample and the five samples collected from wastewater treatment). The results indicate a very robust correlation of the data, but it also shows how different sample groups can have different characteristics (the BIO subset vs. the full data and random subsets).



Figure 19: Person's coefficients of correlation between content of various elements in ashes and the tendency of the ashes to form sticking ash deposits.

The single element correlation coefficients from the investigation of ash vaporization, ash bulk density, ash and char P extractability and char reactivity are provided in Table 5. Visual representation of the best-fit correlations between the characterization data and sums of one to five elements in the ashes are provided in Figure 20 to Figure 25.

Table 5: Person' Correlation coefficient of single ash elements to various ash and char characteristics [1]. 25-27 samples included. Samples excluded due to irregular behavior: i) Palm Kernel Shells, ii) Beet seeds, iii) WWTP fat and bone meal C2. Light grey: Best-fit positive correlation of single element. Dark grey: Best-fit negative correlation of single element.

Element	Ash deposits <sup>i</sup>	Ash vaporization <sup>i</sup>	Ash bulk density	Ash P AER <sup>ii</sup>	Char P AER	Char reactivity <sup>i</sup> *	Char deposits <sup>iii</sup>	Char bulk density
Na	-0.34	-0.23	0.46	-0.11	-0.10	0.37	-0.13	0.25
Mg	0.44	0.42	-0.19	0.40	0.36	0.15	0.02	-0.06
Al	-0.28	-0.29	0.10	-0.31	-0.22	-0.05	-0.39	0.35
Si	-0.30	-0.55	-0.06	-0.20	-0.32	-0.13	-0.34	0.19
Р	-0.34	-0.25	0.29	0.03	0.12	-0.03	0.00	0.65
S	0.15	-0.13	0.30	-0.18	-0.07	0.18	-0.20	0.35
Cl	-0.06	-0.10	0.30	0.10	-0.07	0.33	-0.12	0.11
К	0.77	0.22	-0.55	0.77	-0.22	-0.30	0.30	-0.25
Ca	-0.11	0.56	0.14	-0.40	0.51	0.23	0.06	0.37
Fe	-0.38	-0.31	0.37	-0.30	0.00	0.15	-0.37	0.47

\* Char Reactivity: Point reactivity after 50% conversion, R<sub>50</sub> [1].

Table 5 shows how different elements influence different characteristics, and how some of the correlations are much more significant than others. K and Ca are found to be the two elements that have the highest influence on most of the investigated characteristics. These two elements also exhibit some of the strongest single element correlations.



Figure 20: Ash vaporization at 750 °C as function of elemental composition of ashes. Left: Best-fit positive correlation with sum of K, Ca and Mg content in ashes. Right: Best-fit negative correlation with sum of Si, P, Cl, S and Fe content in ashes.



Figure 21: Ash bulk density (produced at 550 °C) as function of elemental composition of ashes. Left: Best-fit positive correlation with sum of Na, Fe, P and S content in ashes. Right: Best-fit negative correlation with sum of K, Si, Ca and Mg content in ashes.



Figure 22: Char bulk density (from slow pyrolysis at 600 °C) as function of elemental composition of chars. Left: Best-fit positive correlation with sum of Al and P content in chars. Right: Best-fit negative correlation with K content in content chars.



Figure 23: AER strip extractability of P in ashes as function of elemental composition of ashes. Left: Best-fit positive correlation with sum of K, P and Mg content in ashes. Right: Best-fit negative correlation with sum of Si, Al, Fe and Ca content in ashes.



Figure 24: AER strip extractability of P in char as function of elemental composition of chars. Left: Best-fit positive correlation with sum of Ca and Mg content in chars. Right: Best-fit negative correlation with sum of Si, K and Na content in chars.



Figure 25: Char reactivity (in superheated steam) as function of elemental composition of ashes. Left: Best-fit positive correlation with sum of Na, S, Cl, Ca and Fe content in ashes. Right: Best-fit negative correlation with sum of Si, K, and P content in ashes.



Figure 26: Char deposition during slow pyrolysis at 600 °C as function of elemental composition of chars. Left: Best-fit positive correlation with K content in chars. Right: Best-fit negative correlation with sum of Si, Fe and Al content in chars.

The strongest correlation was found to be between the ash content of K, Mg and P and the AER strip extractability of P from the ashes after one week incubation in soil (Figure 23). The AER strip extraction experiment was described in detail in section 3.3. The best-fit negative correlation between AER P extractability and ash content of Fe, Al, Si and Ca (Figure 23) is also quite evident, and the strongest negative correlation identified. In general the correlations involving ash characteristics are stronger than the correlations involving char characteristics. This makes sense in terms of the diluting/interfering element of the carbon matrix when investigating char characteristics. The positive correlation of char bulk density to the content of Al and P in the char (Figure 22) is the best char correlation identified.

In a comparable study by Moilanen et al. (2006) the correlation between char reactivity and ash elemental composition was also investigated. However, the conclusions from this study differed substantially from the presented results. Moilanen et al. found the best-fit single element correlations to be between char reactivity and Ca & Mg (positive correlation) and Si & Al (negative correlation) [136]. The corresponding best-fit (single element) correlations of the present study were found to be Na & Cl (positive correlation) and Si & K (negative correlation). Ca was found to be the 3<sup>rd</sup> most positively correlated element while Al was found to be the 3<sup>rd</sup> most negatively correlated element. There is thus some agreement between the results from the two studies, but also significant differences. Part of the explanation is expected to be that Moilanen et al. measured reactivity at 95% conversion where it was measured at 50% conversion in the present work. In addition, Moilanen et al. converted char at 850 °C while the conversion in the present work was done at 750 °C. Most importantly, all samples included in the work by Moilanen et al. were primary biomasses or biomass residues. The samples were thereby all of plant origin, and this can be expected to make a significant difference compared to the mixed samples of the present study. As seen in Figure 19, significant differences to single element correlations were observed when including only samples of plant- and animal origin. Despite these differences and the obvious shortcomings of the investigation (section 3.4.1), a set of useful conclusions has been extracted for use in future screening of LT-CFB fuel candidates:

- The Higher Heating Value of carbon rich chars and ashes can be estimated by:
   HHV [MJ/kg] = -0.38x + 34, with x being the total inorganic content in the char or ash [wt%].
- The average bulk ash density is roughly 2/3 of the average bulk char density
- K, Ca and Mg are generally amongst the most influential ash elements, and K and Mg content in ashes seem to play a significant role in regard to increase P fertilizer quality, increase volatility and deposition tendencies of the ashes and decrease ash bulk density
- Al, Fe and Si species seem to play a significant role with regard to increasing ash and char bulk densities, inhibiting ash vaporization and deposition but also decreasing the ash P fertilizer quality
- The behavior of Ca is complex and seem to rely heavily on the ash composition and the reaction atmosphere (oxidizing >< reducing). While Ca inhibits ash melting and deposition it contributes positively to ash vaporization. Similarly, Ca seems to decrease the ash P fertilizer quality but greatly improve char P fertilizer quality.

#### 3.4.1 Critical reflections

Many significant differences among the samples make it very difficult to obtain strong correlations, and make it impossible to use the currently identified correlations for reliable prediction of fuel characteristics. It is a huge challenge for this work, that it is attempted to include many different types of secondary resources, and the limitation is clearly illustrated by the need to remove data points from samples with irregular behavior to obtain significant correlations. If correlations in fuel characteristics are to become a useful tool when screening for fuels for LT-CFB gasification, it is required that even samples with uncommon behavior are represented in the correlations. With more data, the results can be arranged in sub-groups with more comparable compositions and characteristics e.g. plant biomass residues, animal residues and mixed fractions (e.g. sludge and waste). This will most likely increase the robustness and the predictive quality of the identified correlations. The number of sub-groups can be continuously increased with the amount of available data.

With the currently used method there may be shortcomings related to the concentrations and relevance of some elements, which could be released in the preparation of the ash sample used for XRF analysis. Which elements that are susceptible to release at these low temperatures depend on the total composition of the ash samples in question. However, preliminary results indicate that S and Cl is released during the initial pyrolysis and the subsequent annealing. This corresponds well to the findings of Saleh et al. in a study from 2014 on the release of Cl and S during biomass torrefaction and pyrolysis [162].

The uncertainty of the results is expected to increase with the number of elements included in the simple correlations. Hidden interactions between various compounds as well as multiple different mechanisms related to a single element may lead to expression of false oversimplified correlations, especially when many different elements are aggregated. To strengthen the results and address the issue with complex multi-layered interactions between elements, a series of preliminary tests with application of an Artificial Neural Network (ANN) model have been conducted with Maria Puig Arnavat from DTU KT. The overall conclusion from these tests was that there could a potential for predictive biomass characterization using ANNs, but data from a lot more samples is required. In addition, before starting this work, the quality of the characterization results and ash composition data applied in the model has to be further validated.

An important limitation in regard to general application of the described fuel screening method is that there are severe differences between the thermal processes involved in the screening and mature thermal processes commercially available for real life operation. Some of the thermal processes included in the fuel screening have been designed to approximate LT-CFB conditions to the extent possible. This is important to acknowledge when considering the conclusions of the study for other thermal processes. However, even though the method was designed for screening LT-CFB fuels, there are still severe differences to account for and acknowledge. It is therefore important to include behavior and characteristics of reference fuels that have previously been proven in real LT-CFB systems.

## 3.5 Fuel mixing

With the huge variation in fuel characteristics among potential LT-CFB fuel candidates, it may become useful – or necessary, to mix two or more different fuels. In this way, the practical impact of problematic

fuel characteristics can be reduced, and new benefits obtained. Many different potential benefits could be obtained from proper fuel mixing:

- Reduced requirement for drying by mixing wet and dry fuels
- Optimized ash composition for fertilizer use by mixing fuels with e.g. high P content with fuels with e.g. high K content
- Efficient utilization of fuels with high content of volatiles and low content of recalcitrant carbon.
   Such fuels includes the WWTP fat and sand fraction from the LT-CFB fuel screening [1]. These fuels are not applicable for mono-gasification, but could be a good way to boost the gas product ratio when co-gasifying them with other fuels.
- Potentially increased P fertilizer quality and decreased heavy metal content in ashes by cogasification of P rich secondary resources with fuels with high K, Na, Cl or Mg content [53,55,163– 166]

A small study on this topic has been conducted in collaboration with Giulia Ravenni from the Department of Chemical and Biochemical Engineering at DTU. The work is described in a master thesis report [132]. Three mixed fuels were screened using the same method as described in Thomsen et al. (2015) [1] to see if the characteristics of the mixes were linear combinations of the characteristics of the individual fuels, or if there were significant deviations from such linearity. The fuel mixes are described briefly in Figure 27.



Figure 27: Fuel mixes included in LT-CFB fuel screening. Left) Mix 1 – Palm Kernel Shells & Rice husks, 50/50 w/w, Center) Mix 2 - Palm Kernel Shells & Animal meat and bone meal C1, 50/50 w/w, Right) Rice husks & Animal meat and bone meal C1, 50/50 w/w. All weights on As Received basis.

The screening included proximate composition; higher heating value of fuels and chars; bulk density of fuels, ashes and chars; char reactivity; char deposition and formation of char agglomerates during pyrolysis; ash deposit sticking and vaporization and AER P extractability of incubated ash and char samples. Results showed that there was a good agreement between measured and calculated values of proximate composition, higher heating values (fuel and char) and fuel bulk densities.

In regard to char reactivity there were less linear correlations. The reactivity of Mix 1 char was 20% higher than predicted whereas the reactivity of Mix 2 and Mix 3 chars were 50 and 33% lower than predicted. Unmixed bone meal (BM) char had been found to have an extremely high reactivity, but there was no linear transfer of this to the mixture. However, in all cases, fuel mixing significantly increased the reactivity of the least reactive fuel component.

Char and ash bulk densities of the mixes were quite consequently lower than predicted by linear sums of the char and ash bulk densities of the involved fuels. The difference was highest in Mix 1 and 2 containing Palm Kernel Shell (PKS) ashes. The bulk density of Mix 1 and Mix 2 chars were 20 and 25% lower than

expected while the bulk density of the Mix 3 char was exactly as predicted. The difference was even more pronounced in the ashes where the bulk densities of the ashes from Mix 1, Mix 2 and Mix 3 were respectively 35, 25 and 5% lower than expected from linear sums of the involved fuels.

Char deposition during pyrolysis was also reduced in all three mixes compared to linear sums of the involved fuels. The same was the case for char agglomeration. This was very positive, especially for the Bone meal sample involved as un-mixed bone meal was categorized in the fuel screening as a problematic fuel due to potential problems with char deposition and formation of hard char agglomerates. Bone meal char agglomerates were classified as hardness \*\*\* in a qualitative assessment of ash sintering increasing from 0 to \*, \*\* and \*\*\* [1] while the two mixes involving bone meal were categorized as \*\* and \*(\*) respectively. In a similar classification of the residues from thermal conversion of char in steam at 750 °C, the benefits of fuel mixing were even more pronounced. The bone meal resides were classified as \*\*\* while residues from all mixtures were classified as 0.

Ash deposit sticking and ash vaporization were also significantly improved by fuel mixing. The problem of ash deposit sticking was severe for palm kernel shell ashes, but when mixed with rice husk and bone meal the problem was reduced severely. Compared to linear predictions, ash deposit sticking from Mix 1, Mix 2 and Mix 3 ashes was reduced with 96, 93 and 30% respectively. A significant improvement was also observed by examining the hardness of the residues from heating of ashes to 750 °C. In a qualitative assessment of ash sintering increasing from 0 to \*, \*\* and \*\*\*, palm kernel shells was classified as a \*\*\* sintering [1] while all fuel mixes were categorized as 0.

The mixed fuels were also included in the AER strip experiment described in section 3.3, where the extractability of P in the substrate is quantified after incubation of the substrates in soil for one week. Predicted and measured AER strip results from the Mix substrate chars (600 °C pyrolysis) and ashes (550 °C annealing of the pyrolysis ashes) are provided in Figure 28.



Figure 28: Predicted and measured results of AER strip P extractability of mixed fuels chars and ashes. Results show the level of P extractability in % of total P in the incubated substrate. Predictions are based on linear sums of the P extractability of the involved fuels combined with the contribution of the individual fuels to the total P pool in chars and ashes.

The predicted values were calculated by linear sums of the P extractability of the individual fuels using previously determined contribution to the total mix P pool by the individual fuels on char or ash basis. The AER strip experiment with the mixed chars and ashes was conducted at the same time as the experiment with the single fuel ashes.

The investigation of P extractability showed a tremendous increase in the Mix 1 sample (PKS+RH) compared to the predicted values. The increase was 140% for ash and 70% for char. In the other samples the pattern is less consistent. For Mix 2 and 3 there were increases in the extractability of P from the incubated chars of 60 & 115% compared to the predicted values but reductions in extractability of P from the incubated ashes of 30 & 25%. In all cases where the measured P extractability was higher than the linear prediction, the measured P extractability of the mix is also higher than that of the best performing fuel involved in the mix. For instance, Mix 1 consists of Palm Kernel Shells and Rice husks. The P extractability of the incubated ashes from these two samples was 18 and 13% respectively. When mixing the two fuels, the extractability of P in the mixed ashes became 30-35%, which is almost a factor of two higher than the best individual fuel involved (the Palm Kernel Shells). It makes the synergetic effect even more clear when considering that only 7% of the total P in the ashes from Mix 1 originated from the Palm Kernel Shells and the remaining 93% came from the rice husks. A detailed investigation into the mechanisms behind these differences between measured and predicted values have not been undertaken in the course of this project. However, mixing biomass into animal meat and bone meal before pyrolysis has previously been found to increase extractability of bone meal char P [32]. Similarly, positive experiences has been obtained in studies with thermochemical treatment of waste and sludge with Na and Cl rich additive, and it is therefore expected that the high Na and Cl content of the palm kernel shell sample could have a positive influence on the P extractability of the mixed chars and ashes [163,164].

From this preliminary investigation into the linear and potentially symbiotic effects of fuel mixing and thermal co-conversion, it is expected that continued research and development within this topic could lead to substantial benefits with regard to the initial problems discussed in chapter 1 and the requirements for improved management of secondary resources. More information on this topic can be gathered from analytical and experimental studies in the published literature [32,49,61,138,158,167–175].

"[W]e may be able to substitute nuclear power for coal, and plastics for wood, and yeast for meat, and friendliness for isolation —but for phosphorus there is neither substitute nor replacement" Asimov I. **1974**. Asimov on Chemistry. New York: Doubleday

**Chapter 4** describes several experimental campaigns with sewage sludge gasification and co-gasification in LT-CFB gasifiers and compares the process performance and the quality of the gas product to results from other thermal gasifiers using data from a literature study. The aim of this chapter is to answer the subquestion of the thesis on how energy efficient the conversion of the selected LT-CFB fuel candidates is as well as to provide part of the answer to the two sub-questions related to the quality of products from the gasification process as well as the performance of the LT-CFB gasifier compared to other thermal platforms. In the first part of the chapter, sewage sludge as a resource and fuel is introduced and the story of P is used to identify a relevant dilemma related to sludge management and sludge P recovery. This chapter includes several results from Paper II and III, but detailed descriptions and analysis of the experimental work with gasification and co-gasification of sewage sludge in LT-CFB gasifiers should be obtained by consulting the manuscripts [2,3]. The overall conclusion of chapter 4 is that many different gasification designs have been proven successfully on sewage sludge and LT-CFB gasification was found to be very well suited for gasification of sewage sludge as well as co-gasification of sewage sludge and cereal straw. Substantial differences were found among the energy efficiency and gas product characteristics of the different gasifiers. The described LT-CFB gasification system obtains the highest hot gas efficiency, carbon conversion rate and electrical efficiency of the investigated systems.

# 4 A local and global LT-CFB fuel case: Municipal Sewage Sludge

Of the top-5 best candidates identified in the primary screening of LT-CFB fuel candidates (section 3.1), only sewage sludge was found to be locally as well as globally available, have a profound potential for recovery of valuable elements, recovery of non-fossil energy and reduced environmental impact compared to several of the current management options used. In the screening of ash and char characteristics (section 3.2) it was determined that proper management of sewage sludge holds a substantial potential for recovering of especially P and that the amount of plant available P that can be recovered in char and ash was among the highest in the screening per unit of mass (Figure 12). Based on these findings it has been 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. As the composition of sewages sludge is known to vary significantly [28,101,108,176], it is also an important part of the investigation to determine the influence of variations in the sludge composition on the performance of the gasification process as well as on the quality of the products (ash and gas). The potential benefits of sewage sludge management by LT-CFB gasification are expected to contribute positively to long term sustainability of modern society by recovering P in purified ashes and utilize sludge energy potential to substitute the use of fossil energy. An illustration of this study is provided in Figure 29, expanding on the proposed solution described in Figure 4 to the general problem with improper management of residual products presented in Figure 3. The arrow directing material and P from food production directly to thermal gasification represents agricultural residues particularly straw, as straw is the reference fuel of the LT-CFB gasifier and co-gasification of sludge and straw can be expected to improve ash fertilizer quality [32] and reduce the requirements for thermal drying by mixing de-watered sewage sludge and dry straw.



Figure 29: The role of sewage sludge gasification and co-gasification in an idealized society's closed phosphorus loops

# 4.1 About sewage sludge

Municipal sewage sludge (MSS) is produced when municipal wastewaters are cleaned in modern wastewater treatment plants (WWTP). Depending on the design of the plant, sludge can be extracted as a primary sludge settled directly from the wastewater, as secondary sludge consisting largely of microorganisms grown in an active sludge cycle after initial removal of primary sludge or as a mixed fraction of organic material from the wastewater and microorganisms grown in the active sludge cycle [177,178].

The production of municipal sewage sludge (MSS) from municipal wastewater treatment in Europe, North America and Japan amounts to around 30 million ton dry matter annually, while the annual global production has been estimated to around 50 million tons of dry matter [130,179]. There is an ever increasing global production of municipal sewage driven by improved wastewater cleaning techniques, a growing global population, increasing wealth in developing parts of the world, and more strict regulations on emissions from wastewater treatment to the environment [28,60,109]. The main increases in global sludge production are expected in the developing countries, but even in the European Union, an increase of almost 20% is expected from 2010 to 2020 [60]. In China 9.2 million tons of dry sludge solids were produced in 2008 and it is expected that the annual increase in sludge production will be up to 4% [180]. MSS composition and characteristics are influenced by the design and surroundings (geography, demography and climate) of the specific wastewater collection and treatment system. Even at a single wastewater treatment plant under normal conditions, the variations in sludge characteristics from one month to the next can be substantial [101,179]. Variations in sludge composition are illustrated in Table 6 with data from 61 different sewage sludge samples recorded in the Phyllis2 database. The samples contain primary sludge, secondary sludge, mixed sludge, anaerobically digested sludge, aerobically digested sludge and dried sludge [181].

	Property	Unit	Minimum	Maximum	Mean	Std dev	Samples
	Moisture content	wt% (ar)	0.2	83.9	24.0	30.1	56
Proximate	Ash content	wt% (dry)	18.2	63.6	39.4	9.9	54
Analysis	Volatile matter	wt% (daf)	56.6	101.2	86.7	7.3	40
	Fixed carbon	wt% (daf)	-1.2	43.4	13.4	7.3	40
Calorific	Net calorific value (LHV)	MJ/kg (daf)	12.7	31.9	21.0	3.0	49
Values	Gross calorific value (HHV)	MJ/kg (daf)	14.1	33.2	22.4	3.0	47
	Carbon	wt% (daf)	34.9	85.0	51.1	6.5	56
	Hydrogen	wt% (daf)	5.0	9.3	7.3	0.9	57
Applysis	Nitrogen	wt% (daf)	2.3	12.2	6.9	1.7	57
Allalysis	Sulphur	wt% (daf)	0.2	5.3	2.1	0.8	54
	Oxygen	wt% (daf)	2.6	49.4	32.4	7.4	54
	Chlorine (Cl)	mg/kg (daf)	449	82329	4502	13118	42
Halides	Bromine (Br)	mg/kg (daf)	52	64	57	6	3
	Fluorine (F)	mg/kg (daf)	173	500	256	118	11
Major elements	Aluminum (Al)	mg/kg (dry)	8600	87705	20732	17553	20
	Potassium (K)	mg/kg (dry)	600	20000	5172	4827	21
	Sodium (Na)	mg/kg (dry)	600	20000	2622	4181	21
	Calcium (Ca)	mg/kg (dry)	22111	150000	58494	37189	18
	Silicon (Si)	mg/kg (dry)	10159	85732	34851	26048	11
	Magnesium (Mg)	mg/kg (dry)	3100	15536	5784	2821	18
	Iron (Fe)	mg/kg (dry)	5400	93039	37311	25220	21
	Phosphorus (P)	mg/kg (dry)	16000	115814	35543	23579	15
	Titanium (Ti)	mg/kg (dry)	311	4800	1457	1512	11
	Arsenic (As)	mg/kg (dry)	3	50	12	10	19
	Cadmium (Cd)	mg/kg (dry)	0	20	4	6	21
	Chromium (Cr)	mg/kg (dry)	20	34000	1646	6144	31
Heavy	Copper (Cu)	mg/kg (dry)	100	15000	1103	2675	31
metals	Nickel (Ni)	mg/kg (dry)	18	5400	376	1072	27
	Lead (Pb)	mg/kg (dry)	35	1700	262	374	29
	Zinc (Zn)	mg/kg (dry)	400	12000	2396	2940	32
	Mercury (Hg)	mg/kg (dry)	1	6	2	2	12

 Table 6: Composition and heating value of sewage sludge. Values from 61 different samples extracted from the Phyllis2 database

 [181]. Ar: As Received. Daf: Dry, ash-free basis. Std dev: Standard deviation.

As a sink of many different compounds from modern society, sewage sludge can contain significant amounts of inorganic as well as organic pollutants and xenobiotics. In addition to heavy metals (Table 6) and various well-known organic pollutants e.g. Polycyclic aromatic hydrocarbons (PAH), Linear alkyl sulfonates (LAS), Nonylphenol and –ethoxylates (NPE), Di(2-ethylhexyl)phthalates (DEHP), dioxins and Polychlorinated biphenyls (PCB) sewage sludge has also been found to contain increasing amounts of emerging organic pollutants including antibiotics, fragrances, UV-filters, flame retardants, micro plastics, phthalates, hormones and many more [101–104].

Sewage sludge can take several different forms depending on the sludge handling- and management systems associated with the wastewater treatment plant. Three examples of sewage sludge products from Danish wastewater treatment plants are provided in Figure 30. All three sludge samples are examples of anaerobically digested sludge from Danish WWTPs.



Figure 30: Samples of sewage sludge from three Danish wastewater treatments plants. 1) Mechanically de-watered sludge from Stegholt WWTP, Aabenraa, Denmark (2013). 2) Dry sludge granules from Randers Centralrenseanlæg, Randers, Denmark (2012). 3) Dry sludge pellets from Bjergmarken WWTP, Roskilde, Denmark (2015).

#### 4.1.1 Handling and management of sewage sludge

To reduce problems with the pathogens, xenobiotics and toxins in the sludge as well as greenhouse gas emissions and foul odor from the decomposition, sewage sludge requires immediate handling. Several different management options and strategies exist, and the choice of one or the other can depend on different factors including environmental and legal issues, culture and tradition, practical restrictions, economy, technical development, demography and geography [28,49,109,182].

Most commonly, sewage sludge is disposed of by one of the following methods: Incineration, landfilling, land application or composting. Land application can be of untreated as well as dried or composted sewage sludge with the purpose to utilize the nutrients in the sludge as fertilizer and/or use the organic material in the sludge for soil improvement. Incineration of sludge can occur in mono-incineration systems or by co-firing coal and sludge in coal boilers, by co-firing sludge and waste in municipal waste incinerators or by co-firing sludge and various fuels (biomass as well as fossil fuels) in CHP plants or in the production of e.g. cement or mineral insulation products [101,110,183–186].

As seen in Table 6, MSS contains significant amounts of N, P, organic matter as well as some K, Ca and Mg. These nutrients make the sludge in many regards a cheap fertilizer and soil enhancer [187]. For this reason,

composting or direct application of sludge on farm soil or in landscaping has been practiced intensively [109]. In 2012 it was reported that in the EU-27, around 53% of the MSS production was reused in agriculture either directly or after composting while in Canada and USA, more than 40% and 50% respectively was spread on land [177]. Despite many similarities between EU countries, the differences among the member countries in this context are substantial. In a recent assessment from the EU based on data from 2005-2009, it was found that Portugal distributes almost 90% of MSS directly in agricultural systems, while the rate in Demark, the UK, Ireland and Spain was 60%-70%, in Germany, Italy, Sweden and Poland 20-30%, and in Romania, The Netherlands, Slovenia, Slovakia, Finland, Estonia, Greece and Malta it was < 5% [28].

Despite a long tradition with use of sludge and composted sludge as fertilizer and soil enhancer in e.g. Denmark and Germany, the overall share of sludge being managed in this way is decreasing in many countries. The decrease is often a consequence of a growing concern about known as well as unknown risks associated to this practice in regard to human health and environmental safety, leading to an increasingly restrictive political attitude towards direct application of sewage sludge [179,188]. In areas with rapidly declining landfilling rates and growing concerns about direct application of sludge in agriculture, it is often incineration that is the primarily preferred alternative.

The possible benefits of incineration – and other thermal conversion processes, compared to e.g. direct application of sludge as fertilizer includes energy recovery, mass- and volume reduction, odor reduction, sterilization, purification, and, a general reduction of product variations [60,109,110]. In EU15, the share of sludge that is being incineration has doubled from 11% to 21% in the years from 1992 to 2005, while it is expected that sludge incineration will increase from 27% to 32% in EU-27 from 2010 to 2020 [28,60]. In Germany, the share of sludge being incinerated has increased from 14% in 2004 to 55% in 2015 [179,189]. In other developed nations sludge incineration is also widely practiced e.g. in USA where there are more than 170 incineration plants [190]. The world's largest sludge incineration plant was commissioned in Hong Kong in 2013, with a thermal capacity of more than 500.000 tons sludge dry matter per year [110].

In other areas of the world, the sludge management strategies face other challenges and other paths are chosen than most often seen in the western world. In China the sludge production is increasing rapidly, and the sludge management system is undergoing fast development to keep up with the sludge production. In the present system a relatively small amount of the sludge is being incinerated while the majority is either landfilled or applied in agriculture. However, even with widely used landfilling of sludge in China, a very large amount (>13%, 2006) of the annually produced sludge is unmanaged and waiting for disposal [180]. In Korea the management system is also undergoing rapid development to keep up with increasing sludge production. From 1997 to 2010 landfilling decreased rapidly from 72% in 1997 to 15% today. Ocean dumping has been a widely used management alternative peaking around 2010 with almost 90% of the sludge being dumped in the oceans. Ocean dumping has been banned from 2012, and in present day, around 8.800 t MSS is produced per day and around 15% of this is landfilled, 15% is incinerated, 27% is used directly on land and 42% is still dumped in the ocean [26,191].

## 4.2 The story about phosphorous

Sludge is normally used as fertilizer mainly for its content of N and P. Both nutrients are essential for plant growth, but while N is an omnipresent element, which can be captured via the Haber-Bosch process directly from the surrounding air where it constitutes roughly 78 vol% (dry), P is concentrated primarily as phosphate rock in very few areas of the world. Around 35 countries have reported reserves of phosphate rock, but just six countries control more than 90% of the globally known high-quality phosphate rock reserves. Morocco controls around 74% of the known reserves, and the majority of the remaining P resides in China, Algeria, Syria, South Africa, United States, and Russia [45]. The uneven distribution of the remaining reserves of virgin phosphate rock is one of the main drivers behind decreasing security of Psupply in the regions without P reserves. Another major driver is a rapidly decreasing total stock of known resources of rock phosphate. There is an ongoing debate about the exact quantity of the global reserves of virgin rock phosphate, and in an assessment of 8 studies on the matter it was proposed that the predicted reserves would suffice to extent the year for peak production of rock phosphate to somewhere between 2025 and 2085. After the peak, the production of virgin rock phosphate will start to decline, and unless severe changes are made in the current management of the P resource, the food production in some parts of the world will rapidly decline [45]. In a study by Rosemarin et al. (2011) it was found likely to extent the year of peak P production from 2060 to 2240 by modifications of the current P use and improved re-use strategies [192]. In 2014 phosphate rock was included in a list of 20 critical raw materials for the European Union [193].

In agricultural production systems with insufficient P supply, the productivity will decline as P is an essential – and irreplaceable, macro nutrient and the availability of P in agricultural systems is often a limiting factor especially in older, nutrient depleted soils as the ones found in mid and lower Africa, Asia and Australia [1–4]. In some parts of the world there is a large P surplus in the soil, which can act as a buffer when the P supply decreases [45]. The development in the quantity and quality of the remaining virgin P resource is already reflected in increasing prices of P fertilizer, which will ultimately lead to increases in the cost of food impacting especially the quality of life of the world's poorer population [194]. P fertilizer prices have increased with more than 300% from 2007 to 2013 and are expected to continue to increase with another 3-500% compared to present day prices before year 2100 [45,195]. In 2008-2009, the price of phosphate fertilizer unexpectedly increased more than 800%, due partly to food stock depletions, oil price increases and the growing demand for biomass for biofuels, showing how P fertilizer price volatility in the future can be another critical challenge for farmers around the world [45].

## 4.2.1 The sludge P dilemma

Increased P recycling and reuse is required to stretch the remaining resources of phosphate rock and postpone the occurrence of *peak phosphorus*. Using wastewater or sewage sludge directly in the food production system is the simplest way to close this part of the P cycle, but in recent years, concerns related to the use of sludge on farm land have increased with developing knowledge about the potential harmful effects of this practice related to food production and ground water quality [101,109,196,197].

In Denmark, the official recommendation of the national trade organization for WWTPs and water producers (DANVA) is now to avoid the use of sludge in agricultural systems in areas with ground water reservoirs and in the long term to avoid the use of sludge in agricultural systems in general. The concern of the trade organization is related to the thousands of industrial chemicals, antibiotics, hormones etc.

present in modern wastewater, and the many unknowns related to hazardous impacts of these compounds, their degradation products and potential cocktail effects. Instead, DANVA propose to go by the precautionary principle and convert the sludge in thermal systems producing electricity, heat, concrete or cement as this would at least reduce the impact from WWTPs on energy use and related greenhouse gas emissions [198]. This recommendation is in sharp contrast to current practice in Denmark where the use of wastewater sludge on Danish farm soils has increased to more than 77% of total sludge in 2012, which is the highest level recorded in official statistics [199]. The dilemma between recovery of sludge nutrients and the potential risks related to direct application is complicated. On one hand there is a growing political demand for increased P-recycling. On the other hand there is an increasing knowledge about the potential risks related to spreading of sludge on farmland as well as an awareness of the potential problems related to increased concentration of heavy metals and loss of P plant availability often associated with thermal processing of sewage sludge [101,142,157,200,201].

In Germany, the Sludge P dilemma has been addressed recently, and a new sludge P-recycling ordinance has been sent to the European Commission after 10 years of revision of the previous sewage sludge ordinance. The new ordinance is likely to enter into force from the 1<sup>st</sup> of January 2018. In short, the new ordinance prohibits spreading of sewage sludge on farmland from WWTPs larger than 50.000 Person Equivalents (PEs). The WWTPs larger than 50.000 PE currently treat wastewater with approximately 2/3 of the total P in German wastewaters. For these plants it will become mandatory to recover P either directly from the sludge or from the ashes from mono-incineration of the sludge. If the P content in the sludge is low (<2 wt%, dry) then the WWTP will be allowed to co-incinerate the sludge and recover P from the ashes from the co-incineration. Another new ordinance will set up more strict demands for the quality of the sludge being spread on farmland from the WWTPs smaller than 50.000 PEs. It is expected that the two new ordinances will reduce the current level of direct spreading of sewage sludge on farmland by 50% or more [202].

The increasing knowledge and awareness concerning these potential risks have spawned public resistance towards application of sludge in parts of the general population in especially USA and Europe [203–206]. Concerns on the matter are also developing within governmental organs, and several European countries now have more strict regulations related to sludge management than those dictated on EU level [28].

The focus on P scarcity and the issues with direct P recycling in wastewater and sewage sludge has also led to many initiatives within academia [166,207–211], governmental organizations, and NGOs investigating alternative ways to recover P without the potential risks associated to the direct application of sewage sludge. Many of such initiatives have been presented at scientific conferences during the last year<sup>2</sup> and several national and international projects have provided new results and revealed new opportunities within this topic<sup>3</sup>.

<sup>&</sup>lt;sup>2</sup> e.g. the 2nd IWA Conference on Holistic Sludge Management in June 2016 [266], the 8th International Phosphorus Workshop (IPW8) in September 2016 [267] and the DAKOFA "Phosphorus a Limited Resource - Closing The Loop" conference in October 2016 [268]

<sup>&</sup>lt;sup>3</sup> e.g. the Danish project "Innovationspartnerskab for anvendelse af fosfor fra spildevand og spildevandsslam fra spildevandsforsyninger" [269] and the large European full-scale demonstration project for advanced phosphor recovery from wastewater and sludge "P-REX" [270]

From the current development within sludge and P management it is concluded that the optimal process for efficient and sustainable sludge handling would fully utilize the energy potential of the sludge while preserving P and other nutrients in a plant-available form in an easily manageable fertilizer by-product. The fertilizer product would have a reduced volume and weight compared to the original sludge, heavy metals would be removed, and all pathogens and organic xenobiotics would be destroyed. Finally, the process would be cheap and reliable.

Thermal conversion of MSS can potentially meet several of the requirements listed for the optimal sludge management process: Utilization of the energy potential; production of ashes with high content of P potentially applicable as P fertilizer; substantial reduction of weight and volume and destruction of pathogens and organic xenobiotics. However, to fully solve the sludge P dilemma, it is required to determine how efficiently a given thermal process will utilize the energy potential in the sludge to produce useful energy products, how the process will influence P fertilizer quality, and whether or not the thermal process can reduce the content of heavy metals.

Generally speaking, sludge can be thermally converted by incineration, pyrolysis or thermal gasification [49,60,109,212]. During conventional incineration of sewage sludge, nearly 100% of the energy potential is released as heat around 850-900 °C and the solid residual (ash) has practically no energy potential left [101]. During thermal gasification of dry sludge, up to 80-90% of the energy potential in the sludge can be recovered as chemical energy in the cold gas while it is expected that up to 95% can be recovered as heat and chemical energy in the hot gas [72,191,213]. The majority of the remaining energy potential resides as unconverted carbon in the solid residual (ash) from the process. However, the degree of conversion during thermal gasification of sludge varies substantially [60,191,214,215]. Finally, when pyrolyzing sludge, 50 to 80% of the energy potential can be recovered as energy products (oil or gas) while the rest remains in the solid residual as a recalcitrant carbon matrix [97].

## 4.3 Gasification and co-gasification of municipal sewage sludge

In this study the potential of thermal gasification is studied as an alternative thermal platform for sludge conversion to approach the sludge P dilemma. There is substantial experience with sludge incineration and a growing focus on this technology, while thermal gasification of sludge is still in a phase of research, development and maturing. A rapid acceleration of the development within research on sewage sludge gasification has been taking place in recent years, which can be seen in Figure 31. It shows the number of annual publications in the Scifinder database containing the phrase "sewage sludge gasification". Searh was conducted in November 2015. The data has not been corrected for general increases in digital indexing and publications rates which can be expected to account for part of the recent development.


Figure 31: Histogram showing the development in annual publications containing the phrase "sewage sludge gasification" and recorded in the Scifinder database. Search conducted November 2015.

As a thermal platform for energy production, gasification is often considered for achieving a clean product gas that can be utilized efficiently even in small scale [49]. Within research on sludge gasification, many different process designs have been proposed. Several examples are presented in Table 7.

Type of gasifier	Sludge fuel	ge fuel Gasification Maximum agent temperatures		Reference
Open Top Down-draft gasifier (P)	Briquettes with 15 wt% moisture	Air	800 °C	Arjharn et al. (2012) [216]
Fixed bed Up-draft gasifier (L)	Two types of dry sludge granules (spherical and elongated) with 5 wt% moisture	Air and oxygen enriched air	N.A.	Werle et al. (2015) [214]
Fixed bed Down-draft gasifier (P)	Dry sludge pellets (21 wt% moisture)	Air + steam	1000 °C in oxidation zone	Nygaard et al. (2015) [217]
Fixed bed Down-draft gasifier (L)	Co-gasificaiton of dry and wet sludge (6-9 & 80 wt% moisture) and wood chips (8 wt% moisture). Mixing ratios 0 to 33 wt% sludge.	Air	1000 °C in combustion zone	Ong et al. (2015) [170]
Fixed bed Up-draft gasifier (P)	Co-gasificaiton of sludge pellets (20 wt% moisture) and wood pellets (8 wt% moisture). 0, 30, 70 and 100 wt% sludge.	Air	>1100 °C in char oxidation zone. Ash sintering with high sludge content	Seggiani et al. (2012) [172]
Single stage fluidized bed gasifier (L)	Particles up to 0.2 mm and 8 wt% moisture	Air	850 °C	Calvo et al. (2013) [218]
Single stage fluidized bed gasifier (L)	Dry sludge granules with 6 wt% moisture	Air	860 °C	Kang et al. (2011) [26]

Table 7: Examples of recent studies on thermal gasification and co-gasification of sewage sludge. P: Pilot scale plant. L: Lab scale plant. D/F: Demonstration-/Full scale plant.

Two single stage Bubbling fluidized bed gasifiers (D/F)	Dry sludge granules of 1-4 and 1-7 mm (3-8 wt% moisture)	Air + steam	820 and 870 °C	Judex et al. (2012) [215]
Single stage fluidized bed gasifier (L)	Particles of 0.25–0.5 mm and 9 wt% moisture	Air or air + steam	800 °C	Roche et al. (2014) [117]
Three-stage gasifier with an auger reactor, a fluidized bed and a fixed bed (L)	Particles of 0.6-3.35 mm with 2-10 wt% moisture	Air	830 °C	Choi et al. (2016) [213]
Two-stage gasification with a bubbling fluidized bed and a fixed bed (L)	Particles of 0.2-0.85 mm and 4 wt% moisture	Air	800 °C	Mun et al. (2013) [191,219]
Dual Fluidized Bed system w. gasifier and char combustor (P)	Particles up to 4 mm and 16 wt% moisture	Air	900 °C (char combustor)	Xiaoxu et al. (2012) [220]
Low Temperature Circulating Fluidized Bed gasifier (P+D/F)	Mono-gasification of 2 types of dry sludge granules (moisture content 5 and 12 wt%). Co- gasification of 2 sludge/straw mixtures (30 wt% de-watered sludge + 70 wt% straw and 20 wt% dry sludge pellets + 80 wt% straw. Moisture content in mixed fuels was 30 wt% and 13 wt% respectively)	Air or air + steam	740 °C in mono- sludge campaigns and 750 °C in co- gasification campaigns	Thomsen et al. (2016 I, II and III) [2,3]

On a commercial or near-commercial level, it is primarily fluidized bed gasifiers that are in focus for sludge gasification. Three of the major commercial players in this regard are:

- SÜLZLE Kopf SynGas, full scale bubbling fluidized bed gasifier [215]
- Outotec's full scale dual-circulating fluidized bed gasifier [221]
- DONG Energy's demonstration scale Low Temperature Circulating Fluidized Bed (LT-CFB) gasifier, Pyroneer [2,3,62]

The sludge gasifier developed by SÜLZLE Kopf is part of a stand-alone system with a gas engine for Combined Heat and Power (CHP) production and a boiler to deliver additional heat for sludge drying [215]. Outotec's dual-circulating fluidized bed gasifier as well as DONG Energy's LT-CFB gasifier are developed to produce gas for existing CHP boilers [62,221]. Application of LT-CFB systems for gasification of sludge using existing fossil fuel energy infrastructure is illustrated in Figure 5. Such setup is used for the 6 MW LT-CFB gasifier constructed at Asnæs powerplant [62].

Gas composition, gas product heating value, process efficiency and ash characteristics vary between the mentioned studies on sludge gasification with the design and operation of the process as well as the characteristics of the fuels. Various experimental results from these studies are presented in the following section to illustrate similarities and differences among the processes. The first results relates to the gas composition and heating value of the gas product (Figure 32).

#### ♦CO ▲CO2 ◎H2 □CH4 ×LHV



Figure 32: Composition and Lower Heating Value of cold, dry gas from LT-CFB gasification of sludge compared to product gas from previously published sludge gasification studies. [2,117,170,172,191,213–216,218].

Regarding the composition, the smallest relative variations are in the CO<sub>2</sub> content, which is quite comparable while all of the other investigated gas components vary substantially. There are also significant variations in the Lower Heating Value of the gas, ranging from around 2 MJ/Nm<sup>3</sup> to more than 10 MJ/Nm<sup>3</sup>. This value is often calculated based on the composition of cold, dry gas, and will vary substantially with the number of species accounted for in the analysis. In many cases, the heating values of simple hydrocarbons as well as heavier tar species present in the hot product gas are not accounted for. This can be misleading when comparing different gas products as these compounds can account for a very large share of the total chemical energy in the hot product gas. Content of tar and simple hydrocarbons measured before cooling and condensation in some of the gas products from gasification of sewage sludge are shown in Table 8 with a short description of the tar reduction initiatives used in the respective systems.

The measured content of simple hydrocarbons varies from almost nothing to 7 vol% of the gas. These compounds can therefore be expected to have a largely varying, but potentially very high impact on the actual heating value of the gas product. It has been examined how much simple hydrocarbons contribute to the total gas heating value in an experimental campaign with gasification of straw on a LT-CFB gasifier. In this investigation it was found that a total of 2.3 vol% of 10 simple hydrocarbons with compositions  $C_{2-6}H_{4-10}$  contributed as much as 40% of the determined total Higher Heating Value of the gas [2]. This could explain some of the differences in gas heating values seen in Figure 32. To make consistent investigations of the gas

product quality and process performance it can therefore be very important to quantify such simple hydrocarbons.

Study	Simple hydrocarbons Vol%	Tar content mg/Nm <sup>3</sup>	Tar reduction initiatives (excl. cyclones)
Arjharn et al. (2012) [216]	N.A.	70-80 and 0-5 before and after gas cleaning	Water scrubber + chilled-water scrubber + biomass filter containing wood chips + bag house filter
Werle et al. (2015) [214]	N.A.	N.A.	Scrubber + drop separator
Nygaard et al. (2015) [217]	N.A.	< 26	None
Ong et al. (2015) [170]	N.A.	N.A.	Unknown filter
Seggiani et al. (2012) [172]	4-5	N.A.	Two scrubbers and a packed bed filter
Calvo et al. (2013) [218] Kang et al. (2011) [26]	N.A.	600-850	None
	1-3	N.A.	Hot filter + cooled condensers
Judex et al. (2012) [215]	N.A.	90% tar reduction in sludge bed, final gas composition suitable for gas engines	Gas cooling + granular sludge bed filter + ceramic filter + condenser + two scrubbers.
Roche et al. (2014) [117] Choi et al. (2016) [213]	1-2	3400-9800	None
	0.1-3	22	Heated fixed bed of activated carbon
Mun et al. (2013) [191,219]	0.5-7	170-6060	None or Heated fixed bed with activated carbon, calcined dolomite, calcined natural zeolite or calcined olivine and/or use of calcined dolomite as bed material
Xiaoxu et al. (2012) [220]	N.A.	N.A.	None
Thomsen et al. (2016) [2]	N.A.	26000-245000	None or hot gas candle filter

Table 8: Content of simple hydrocarbons and tar measured in product gas from thermal gasification of MSS before cooling and/or condensation. A short description of related tar reduction systems has been included.

The tar contents in the different sludge gasification gas products (Table 8) vary much more than the contents of simple hydrocarbons. The large variations originate from variations in fuel characteristics, gasifier designs, operating conditions and the application of different tar reduction initiatives. Many efficient methods exist to reduce the tar content in the gas, and in the investigated studies scrubbers, various filters (ceramic filters, bag filters, electrostatic filters and a sludge bed filter) as well as catalytic tar cracking in fixed bed stages or in catalytically active beds is applied. With the proper design, very low levels of tar content can even be achieved without any dedicated tar reduction units or processes as seen in the results from the TwoStage down-draft gasifier converting sludge pellets (< 26 mg/Nm<sup>3</sup> [217]). Tar levels can also be extremely high, and gasification of sludge could even be applied for production of tar-based liquid energy products as proposed in an LT-CFB campaign where co-gasification of wet sludge and dry straw led to production of gas with 12 wt% tar of the total gas product. The energy conversion efficiency in this

experiment from fuel to tar was approximately 60%, opening new possibilities for low temperature gasification of sewage sludge [2]. In general it is important to make robust quantifications of the tar content in the product gas. If the gas product is to be used for synthesis or conversion in a gas engine it is important to determine tar contents to avoid negative influence of tar on the downstream processes. If the gas is to be used hot for direct combustion, the tar content can be fully unproblematic but it is still important to quantify to determine the total energy content in the product gas.

Tar content can significantly influence the difference between cold gas efficiency and hot gas efficiency of a process while it has naturally no influence on the level of total carbon conversion in the system whether the gasified carbon is in the form of light gasses or uncondensed tar.

Large variations among the different studies, and even within the results from a single study, are observed in the results in Table 9. The differences in the results on e.g. cold gas efficiency and carbon conversion on a single unit originates from variations of e.g. fuel composition and fuel load, type and temperature of gasification agent, stoichiometric ratios of the gasification agents, process temperature and type and composition of bed material. The highest cold gas efficiencies, hot gas efficiency and electrical efficiency are obtained on multi-stage systems with fluidized bed reactors [4,191,213]. The maximum carbon conversion rates are less evenly distributed among the gasifier designs, and rates above 90% are obtained in single stage fluidized bed gasifiers [26,215] as well as in multi-stage units encompassing fluidized bed reactors [2,213].

Study	Hot gas efficiency % of fuel	Cold gas efficiency % of fuel	Electric efficiency % of fuel	Carbon conversion % of total C
Arjharn et al. (2012) [216]	-	53-62	7-13	-
Werle et al. (2015) [214]	56-68	51-59	-	-
Nygaard et al. (2015) [217]	-	56	-	79
Ong et al. (2015) [170]	-	63 <sup>ª</sup>	-	-
Seggiani et al. (2012) [172]	-	30-60 <sup>b</sup>	-	48-85 <sup>b</sup>
Calvo et al. (2013) [218]	41-70	34-57	-	-
Kang et al. (2011) [26]	-	27-70	-	65-90
Judex et al. (2012) [215]	-	66-70	-	-
Roche et al. (2014) [117]	-	36-45	-	66-81
Choi et al. (2016) [213]	-	63-89	-	70-93
Mun et al. (2013) [191,219]	-	81-87	-	81-87
Xiaoxu et al. (2012) [220]	-	60	-	-
Thomsen et al. (2016) [2]	88-90 (sludge & (sludge+straw)	-	39 <sup>d</sup>	91-95 (sludge & (sludge+straw)

Table 9: Hot and cold gas efficiency, electric efficiency and carbon conversion of various sludge gasification technologies

<sup>d</sup> With 20wt% dry sludge <sup>b</sup> At 30-70 wt% sludge and varying air ratios <sup>c</sup> Estimated based on fuel and ash characteristics <sup>d</sup> Based on bet ge officiancy and pat electrical officiancy of the steam cycle and bailer at Acamerymetricate unit 2 (42, 7%) [72]

<sup>d</sup> Based on hot gas efficiency and net electrical efficiency of the steam cycle and boiler at Asnæsværkets unit 2 (42.7%) [73]

Summarizing from the results in Table 7, Table 8 and Table 9 as well as Figure 32 it is evident that:

- Thermal gasification and co-gasification of sewage sludge is technically possible
- Many different gasifier designs and fuels have been tested successfully
- Gas energy content (lower heating value) can range from 2 to 10 MJ/Nm<sup>3</sup>
- Gas tar content has been found to range from practically zero to more than 12 % of gas product mass and 60% of total gas energy content
- Scrubbers, catalytic fixed beds, in-situ catalysis in active fluidized beds and various filters have been tested successfully for reduction of tar in product gas from sewage sludge gasification
- Cold gas efficiencies from 27 to 89% have been achieved
- Hot gas efficiencies from 41 to 90% have been achieved
- Carbon conversion rates from 48 to 94% have been observed
- The LT-CFB gasifier has proved itself on many different sludge fuels. The calorific value of the gas
  product from the LT-CFB is highly influenced by the content of simple hydrocarbons and large tars,
  and therefore difficult to determine precisely. The LT-CFB setup obtains the highest hot gas
  efficiency, carbon conversion rate and electrical efficiency of the investigated systems.

To further evaluate the potential of thermal gasification and especially LT-CFB gasification as an improved management option for sewage sludge handling, a few additional topics needs to be addressed:

- Potential operational issues during long term commercial operation
- Detailed assessment and validation of the quality of the ashes from the process for use as fertilizer

The first issue is addressed in the following section while the discussion about ash fertilizer quality is undertaken in chapter 5.

## 4.3.1 Potential issues during long term operation

During the four experimental campaigns with LT-CB gasification of sewage sludge described in Paper II, III and IV, extensive operational experience has been gathered. The primary concerns identified during the work related to the following issues:

- 1) Potential accumulation of inert material in the system due to a high content of large and mechanically robust particles in the dry sludge fuels
- 2) Problems with interpretation of heavy metal balances possibly set off by leaching of e.g. Cr and Ni from the steel alloys in the lab- and pilot scale system to the ashes
- 3) Potential problems related to formation of NOx precursors in the product gas

Accumulation of inorganic material was discussed in Paper II and has also been identified as a potentially problematic issue in the study by Calvo et al. (2013). The solution proposed by Calvo et al. was the same as the one applied generally in the LT-CFB campaigns; Continuous bed draining and addition of fresh sand [218]. Bed draining is a simple and efficient mechanism to use, but if large amounts of sand need to be added simultaneously, it could be costly in regard to cost of fresh sand, loss of heat and dilution of the extracted bottom ashes, making them less ideal for subsequent use as fertilizers or for extraction of other valuable elements.

Based on the experimental work related to Paper II it is proposed that co-gasification of sludge and straw significantly reduces the requirement for bed draining as a consequence of the following mechanisms:

- A lower fuel ash content that leads to lower absolute accumulation rates.
- The reduced fuel ash content reduces the requirement for bed draining, and thereby allows for longer potential ash retention times within the system. Prolonged retention within the system will decrease the average particle size due to increased mechanical wear. Smaller particles are more easily entrained and are also more likely to escape the primary cyclone [77].
- Lower average bulk density of chars and ashes from straw based fuels compared to MSS based fuels decrease cyclone efficiency [1,77].

As an interesting alternative to co-gasification it is also proposed to investigate and test if operation on ashonly bed material could be feasible. In such operation no fresh sand would be required and concentrated bottom ashes could be extracted making this a suitable way to maintain bed height and increase long term stability while extracting high quality ashes for fertilizer application. This approach has been attempted with success in the SÜLZLE Kopf SynGas bubbling fluidized bed gasifiers where the sludge ash itself has been used as the only bed material for several years [215].

The second issue of concern is discussed in Paper III, and also addressed in chapter 2. Ash pollution by Cr and Ni leaching and/or degradation of inner reactor surfaces was also identified as a concern by Hernandez et al. (2011) in relation to useful interpretation on the heavy metal balances in sludge gasification systems [222]. However, in large scale application, refractory lining of reactors and supporting systems can contribute to a reduction of this problem as described in section 2.4.

The third concern is discussed briefly in Paper II where it is suggested that formation of NOx precursors can be an issue in commercial application of sludge gasification as NOx cleaning is expensive. However, several potential solutions towards this concern exist, including among others:

- To combust the gas in a burner zone with temperatures and oxygen levels optimized for Selective Non-Catalytic reduction (SNCR). This can utilize the content of NOx-precursors like NH<sub>3</sub> in the gas to reduce existing and produced NOx, but care should be taken as the remaining gas composition will also play a part in the optimization of the SNCR process [223,224].
- To reduce combustion of N-species by condensing and removing tar and NH<sub>3</sub> and convert the residual gas in a gas engine or boiler. The tar produced by LT-CFB co-gasification of MSS and straw has been found to possess beneficial bio-oil like qualities, and if required it could be further deoxygenated to allow for improved removal and applicability of the liquid product. Catalytic tarreforming and upgrading of pyrolysis gas using zeolite catalysts have been shown to have remarkable potential in this regard [225–227].

None of these solutions are expected to work optimally if the vast majority of fuel N persists as HCN in the gas. This should be avoided by keeping the pyrolysis temperatures in the LT-CFB relatively low [228,229].

Ash sintering and agglomeration is also a common problem in gasification, and in certain cases of MSS gasification. Severe sintering and agglomeration of ash particles was observed by e.g. Ong et al. (2015) during co-gasification of sludge and wood in mixtures with more than 33% sludge at temperatures > 1100 °C [170] and by Nygaard et al. (2015) during gasification of dry sludge pellets in a TwoStage Down-draft

gasifier at temperatures above 1100 °C [217]. However, in both cases successful operation was subsequently achieved at lower temperatures around 1000 °C. With maximum operating temperatures around 750 °C no problems with ash melting or bed agglomeration have been encountered during LT-CFB gasification of sludge. Not even during LT-CFB campaigns with co-gasification of sludge and straw have there been any problems with bed agglomeration at the tested operation temperatures [2].

Many different gasification concepts have been proven in recent years to be able to gasify municipal sewage sludge. Multi-stage systems based on fluidized bed technology generally achieve the highest thermal efficiencies, but they also encounter an additional operational issue related to the accumulation of fuel ash particles in the bed. Mixing sewage sludge with cereal straw efficiently reduces – and maybe even resolves, the problem with accumulation of inorganic material. In addition, this approach to co-gasification can ease or omit requirements for sludge drying, level out fuel variations and increase flexibility on the fuel side as well as the product side. The low operation temperatures of the LT-CFB gasifier provide the possibility to operate on sludge-straw mixtures, and this type of co-gasification may be a very distinct advantage compared to alternative thermal MSS gasification platforms. Issues and benefits of co-gasification of MSS in regard to the ash quality is discussed in the following chapter.

In chapter 5, the ashes from thermal conversion and co-conversion of sewage sludge are examined for their potential use as P fertilizers. The chapter introduces the work and results described in detail in Paper III and Paper IV and seeks to answer the two questions "How good is the fertilizer quality of the ashes produced by gasification of sludge and co-gasification of sludge and cereal straw in LT-CFB gasifiers?" and "Is the LT-CFB gasifier the optimal thermal platform for production of fertilizer ashes from conversion of sewage sludge?". These questions are addressed by comparing the elemental composition, PAH<sup>4</sup> content and P fertilizer quality 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. 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 included in the investigation. From the results of this chapter it was concluded that all thermal platforms are applicable for production of P fertilizers by conversion of sewage sludge. Determination of the optimal thermal platform requires a weighing and balancing of pros and cons in relation to reduction in heavy metal content, contents of PAHs, loss of P and P fertilizer quality. Post-oxidation of pyrolysis chars and gasification ashes was found to have a remarkable effect on P fertilizer quality while co-gasification of sludge and straw in LT-CFB gasifiers in general seem to provide a better ash fertilizer than mono-sludge gasification. The chapter also introduces a study on changes in P association induced by different thermal treatments (Paper IV), and expands on the work with an assessment of changes in P fertilizer quality over time. In the last part of the chapter, a series of critical reflections are provided including a brief investigation into the influence of the assessment method and the effect of a given ash fertilizer's particle size distribution on the determined P fertilizer quality.

# 5 Ash fertilizers from sewage sludge gasification

In this study, assessment of ash fertilizer quality includes determination of the nutrient and carbon content, the content of heavy metals, the content of organic pollutants (in this work only PAHs are investigated) and the fertilizer quality of the primary nutrient phosphorus.

Ash characterization is rare in published studies on sludge gasification as the focus is most often on the characteristics of the gas product and the thermal efficiency of the process. Of the 12 studies on sludge gasification described in section 4.3, only three include a compositional analysis of the ashes: Paper III on LT-CFB ashes [3]; the study by Mun et al. (2013) [191]; and the study by Werle et al. (2015) [214], which has been expanded in a second article from 2014 analyzing the composition of the ashes [230]. There are also a few additional studies that describe composition and characteristics of ashes and chars from thermal gasification of sewage sludge. These include a study by Hernandez et al. (2011) on ashes from batch gasification with air or air+steam in a lab scale fixed bed gasifier [222] and as well as Paper IV of the present study encompassing a detailed investigation of ashes from the LT-CFB gasifier and a pilot scale TwoStage Downdraft gasifier [4]. A short overview of the studies on thermal gasification of sewage sludge that include some kind of ash characterization is provided in Table 10.

<sup>&</sup>lt;sup>4</sup> Polycyclic Aromatic Hydrocarbons, a group of persistent organic pollutants (POPs) that is strongly regulated and monitored because of their persistence, possible toxicity and carcinogenic and mutagenic health effects [271].

Study &	Mun et al. , 2013	Werle et al,	Hernandez et	Thomsen et al,	Thomsen et al,
reference	[191]	2014 [230]	al, 2011 [222]	2016 [4]	2016 [3]
Gasifier	Two-stage gasifier w. fluidized bed and fixed bed (L)	Fixed bed Up- draft gasifier (L)	Fixed bed, batch fed gasifier (L)	Two-Stage	Low Temperature
				down-draft	<b>Circulating Fludized</b>
				gasifier (P)	bed gasifier (P/D)
Fuel	Dry sludge	Dry sludge	De-watered sludge	Dry sludge	Dry sludge &
					sludge+straw mix
Max tem-	900 N A	700 8 000	850 (in char	740 750	
perature °C	800	N.A.	700 & 900	bed)	740-750
Gasification	Air	Air and oxygen	Steam or air-	Air I stoom Air or Air stoo	Air or Airtstoom
medium	All	enriched air	steam	All + Stedill	

Table 10: Studies on thermal gasification use to investigate changes in the concentration of P and various heavy metals from fuels to ashes. L/P/D: Lab/Pilot/Demonstration scale gasifier. SC: Secondary cyclone ashes. CR: Char reactor bottom ashes

In addition to the ashes from sludge gasification, several ashes from pyrolysis and incineration of sludge have been investigated in Paper IV. These samples are referred to as the Cross Platform Sludge Experiment (CPSE) substrates, and have been included in this chapter to broaden the perspective on sludge ashes and qualify thermal gasification as a platform for production of ash fertilizer from sewage sludge. Details on the sludge sample and thermal processes are provided in Paper IV [4]. A visual overview of the primary CPSE substrates is provided in Figure 33.



Figure 33: 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 [4]

### 5.1 Content of nutrients and heavy metals in ashes from thermal conversion of sludge

As sewage sludge composition varies substantially, it is difficult to directly compare different ashes to determine the influence of the thermal process on the release and retention of nutrients and heavy metals. To compare the influence of the thermal process on release of such elements it can therefore be an advantage to compare the differences between elemental concentrations in fuels and ashes as well as investigate changes in relevant elemental relationships. In the present case where the ashes are considered to be used as P fertilizers, it makes sense to compare changes in elemental composition on basis of total P. To illustrate the changes on elemental composition induced by different thermal treatments, the concentrations of the nutrients P and K and various heavy metals in several LT-CFB fuels and ashes from sewage sludge gasification and co-gasification as well as substrates from the CPSE campaign are provided in Figure 34 and Figure 35.

By simultaneous investigation of the sub-charts in Figure 34, it becomes clear that the presumable very different thermal technologies have a very comparable (and minimal) influence on the P/K ratio in the ashes. In most cases the P/K ratio in the ash or char is identical or almost identical to the P/K ratio in the fuel. The major part of the apparent variations in the concentrations of the fertilizer elements P and K are related to the diluting influence of organic material. The most deviating samples from this general pattern is the SC ash from LT-CFB gasification of dry sludge granules (Figure 34, #6) and the pyrolysis chars from fast pyrolysis of sewage sludge pellets (Figure 34, #12). The reason behind this difference in the pyrolysis char has been found to originate from pollution of the ashes by straw material in the pyrolysis plants (picture 4 of Figure 33 and Paper IV [4]) while the reason behind the change in the LT-CFB ash has not been fully identified. In this regard it is intriguing how the P/K ratio in ash sample #6 differs from ash sample #8 despite the fact that they are both SC ashes from LT-CFB gasification of dry sludge granules and the sludge fuels have very comparable P/K relationships. Calculating the recovery of P and K in the total mass of the two SC ashes relative to the P and K in the converted fuels it becomes clear that while both SC ash fraction contain approximately 44% of the K in the fuel, there is a difference in the P recovery between 34% in the SLU-BJ SC ash and 44% in the SLU-RA SC ash. Full mass balance data is not available for the SLU-RA experiment, but the total P recovery in the SLU-BJ experiment was found to be slightly above 100% [3]. It is proposed that differences in the operation parameters (reactor temperature, air ratios etc.) combined with variations in the concentrations of other elements than P and K leads to a higher P retention in the bed of the SLU-BJ experiment where approximately 56% of the total fuel P was found after the experiment. However, this has not been verified as composition data from the final bed of the SLU-RA campaign have not been produced. Finally, it could also be expected that part of the difference between the two P/K ratios could relate to influences of the silica sand used as bed material. From the bed material product sheet it is found that there may be as much as 1.6 wt% K in the sand and no P [231]. During the SLU-RA experiment 800 kg sludge dry matter was converted while only 270 kg was converted in the SLU-BJ experiment. The K in the sand could therefore constitute as much as 56% of total K into the SLU-BJ system while it only constituted around 34% of total K into the SLU-RA system. If more of the K from the fresh bed material leaves during the first hours of operation (the entire fraction of small particles in the fresh sand may escape with the gas product through the primary cyclone relatively quickly), then it could be expected to increase K content in the total bulk mass of SLU-BJ SC ash more than in larger bulk mass of SLU-RA SC ash and in this way reduce the P/K ratio.



**Figure 34: Content of P and K as well as P/K relationship in various sludge-based fuels and the related ashes.** 1) Mun et al. (2013) [191], 2-3) Werle et al. (2014) [230], 4) Hernandez et al. (2011) [222], 5) TwoStage gasifier [4], 6) LT-CFB SC ashes "SLU-BJ" [3], 7) LT-CFB CR ashes "SLU BJ" [3,4], 8) LT-CFB SC ashes "SLU-RA" [3], 9) LT-CFB SC ashes "MIX-ST" [3], 10) LT-CFB SC ashes "MIX-BJ" [3], 11) Slow pyrolysis char [4], 12) Fast pyrolysis char [4], 13) Fluid bed incineration ashes [4] & 14) Fixed bed incineration ashes, 850 °C [4]. SC: Secondary Cyclone. CR: Char reactor. Db: Dry basis. \*: Insufficient data for complete assessment of standard deviation. Error bars represent standard deviation.



**Figure 35: Content of selected heavy metals per unit of P in various sludge-based fuels and the related ashes.** 1) Mun et al. (2013) [191], 2-3) Werle et al. (2014) [230], 4) Hernandez et al. (2011) [222], 5) TwoStage gasifier [4], 6) LT-CFB SC ashes "SLU-BJ" [3], 7) LT-CFB CR ashes "SLU BJ" [3,4], 8) LT-CFB SC ashes "SLU-RA" [3], 9) LT-CFB SC ashes "MIX-ST" [3], 10) LT-CFB SC ashes "MIX-BJ" [3], 11) Slow pyrolysis char [4], 12) Fast pyrolysis char [4], 13) Fluid bed incineration ashes [4] & 14) Fixed bed incineration ashes, 850 °C [4]. SC: Secondary Cyclone. CR: Char reactor. Db: Dry basis. \*: Insufficient data for complete assessment of standard deviation. Error bars represent standard deviation. Dotted lines: Danish legal limits for distribution on farm soil [82,85].

In general, the results from Mun et al. (2013) and Werle et al. (2014) differ from those from Hernandez et al. (2011), the study on ashes from LT-CFB gasification of sludge in Paper III, and the CPSE study in Paper IV. In the studies by Mun and Werle, there is an almost constant increase in the concentration of heavy metals per unit of P in the ashes compared to the fuels. In some cases the increase is more than a factor of 2, and the reason must be a severe up-concentration of heavy metals in the examined ash or a substantial loss of P from the same ashes. From the results in Figure 34 it is evident that the concentration of P in the ashes from the Werle study increase very little compared to the concentrations in the sludge. As the sludge samples are quite comparable with regard to the proximate composition, it would be expected that the P concentration in the ash should increase by at least a factor of 2 in the ashes. However, missing details on the gasifier design, operation temperature etc. makes it difficult to say if the inconsistency is due to severe losses of P or an error in the determination of the P concentration in the ashes [214,230]. The ash composition is hardly discussed in the study by Mun et al. (2013), but it is briefly mentioned that some inconsistencies in the form of increasing concentrations of e.g. Ca and Mg could relate to degradation of the different bed materials and additives tested in the study [191]. As the relative increase in the P concentration looks reasonable (Figure 34), it is proposed that the severe increase in heavy metal concentrations observed could also originate from degradation of bed material and/additives or leaching from construction material. Leaching of especially Cr and Ni from steel alloys to ash materials during thermal gasification have been discussed previously in section 2.4, in Paper III as well as in the study by Hernandez et al. (2011) [222].

In general, the samples from Hernandez et al. (2011) (Figure 35, #4), the samples from LT-CFB gasification and co-gasification of sludge (Figure 35, #6-10) and the samples from the CPSE study (Figure 35, #5, 7 and 11-14) show comparable behavior. From fuels to ashes there is a small average decrease in the content of Zn and Cu per unit of P, a generally higher decrease in the content of Cd per unit of P and a more unstable pattern in the Ni and Cr concentrations due to the potential leaching of these elements from the steel. In addition, all samples with measurement of Hg revealed a complete release hereof in the thermal process (measurements below detection limits, results not shown). Comparable results were obtained in a study conducted by Reed et al. (2001) on ashes from co-gasification of 75 wt% coal and 25wt% dry sludge pellets at temperatures around 960 °C in a pressurized pilot scale single stage Fluidized bed gasifier with a thermal capacity of 2 MW [232]. In this study it was found that only around 0-1% of Hg and Cd was recovered in bed, bottom ashes and cyclone ashes while the remaining 99-100% was captured in the hot gas filter (Cd) or emitted with the gas product (Hg). For Cr, Cu, Ni, Pb and Zn the recovery in ash products was 85%, 95%, 90%, 40% and 85% respectively. The release of Cd in this study was higher than that observed in any of the samples in Figure 35 and Paper III where the levels of total Cd release were around 70-85%. High temperatures combined with a reducing atmosphere were found in Paper IV to facilitate severe release of Cd [4]. However, the composition of the fuel, especially the content of Cl [53,201,233], is also very important in this regard, and the contribution of elements from the coal could be significant.

The overall impression is that thermal gasification has a large potential to reduce the content of cadmium and mercury in ashes compared to the original sludge fuels, especially when regarding the heavy metal content per unit of P. Mercury is almost completely released, and concentrations in the ashes are usually below the detection limits. Disregarding the samples from the study be Werle et al. (2014) the concentration of Cd per unit of P is reduced with 10-93% (average 63%) in all ashes from thermal gasification of sludge compared to the sludge fuel. For the two pyrolysis processes the reduction was 2530% while there was no significant reduction seen as function of the two incineration processes. The largest reductions are seen in ashes from TwoStage gasification, cyclone ashes from co-gasification of straw and sludge in the LT-CFB gasifier, and bottom ashes from mono-gasification of sludge in the LT-CFB gasifier. This pattern speaks in favor of the previously proposed strategy of operating the LT-CFB on ash-only bed material. If the bed consists of only ash and char, then highly concentrated bottom ashes could potentially be extracted with extremely low content of cadmium. In co-gasification systems the Cd content may be even lower, but co-gasification of sludge and straw may also make operation with ash-only bed material more problematic due to the high content of K in the straw. One of the conclusions from Paper III was that the higher temperatures in the char reactor made bottom ash extraction ideal for production of low-Cd P fertilizer. It was also proposed that reduced filter temperatures could increase the levels of Cd captured in the filter substantially. During the SLU-BJ LT-CFB campaign described in Paper II, a hot gas filter was operated at temperatures between 400 and 550 °C. Analysis of the bulk ash from the filter after the experiment showed Cd concentrations in the filter 3-7 times higher than those in the cyclone and bottom ashes per unit of mass and 4-13 times higher per unit of total P [3]. A strong correlation between filter temperature and the content of lead in the product gas was found in the study by Reed et al. (2001), and it was proposed to operate hot gas filters at temperatures below 450 °C to avoid lead in the product gas [232]. However, widespread release of lead during sewage sludge gasification is usually not a concern at temperatures much lower than 900 °C [234].

In Denmark, there are currently no specified regulations for use of char and ash from thermal conversion of sewage sludge as fertilizers. However, there are legal limits on the content of heavy metals (as well as some organic pollutants) in sewage sludge and bio-ashes to be spread on farm soil. For heavy metals, these legal thresholds are set per unit of dry mass (Cu, Zn, Cd, Ni, Cr, Pb and Hg) and for some heavy metals (Cd, Ni, Pb and Hg) also per unit of P [82,85]. The application of thresholds per unit of dry mass is a disadvantage for thermal residues compared to untreated materials as many heavy metals are concentrated in the residues when the organic fraction is converted. For thermal residues it is instead more advantageous to have regulations per unit of P as P and many heavy metals are concentrated alike in the process. In several cases the thermal process even reduces the content of specific heavy metals in ashes when accounted for per unit of total P and compared to the original fuel. In Paper III it was discussed how ashes from sludge gasification in numerous occasions breach the legal thresholds for heavy metal content per unit of dry mass, while almost no legal limits per unit of total P were breached. It is generally agreed that reduction of weight and volume in sludge management is a benefit to avoid excessive transportation. However, in regard to the heavy metal regulations for use of sludge and bio-ash in agriculture it is currently a big disadvantage to reduce weight below the dry-sludge level. To facilitate the continued development and future use of purified, concentrated sludge ashes as P fertilizer it is very important that all pollutants in sludge and sludge ash for use in agricultural systems are regulated per unit of total P instead of per unit of dry mass. It is therefore proposed to enact new, specified regulations of organic and inorganic toxins per unit of P in ash and char from thermal conversion of sewage sludge as the current regulation in Denmark and surrounding regions is an illogical preclusion and obstacle in the development of improved sewage sludge management systems encompassing thermal conversion.

## 5.2 Polycyclic Aromatic Hydrocarbons in ashes from thermal conversion of sludge

Like heavy metals, the content of Polycyclic Aromatic Hydrocarbons (PAHs) in fertilizer substrates is also generally regulated. The Danish legislation on PAH content in sludge and ash for use on agricultural soil has two thresholds for total PAH content i.e. 3 mg/kg dry sludge or waste and 12 mg/kg dry bio-ash [82,85]. No data on PAH content in ashes from mono-gasification of sewage sludge have been found in published literature. However, a single study by Rong et al. (2015) on co-gasification of sewage sludge and wood chips included investigation of PAHs in the bottom ashes from the fixed-bed down-draft gasifier. Despite positive identification of several alcohols, alkenes, carboxylic acids and esters in extract from the bottom ashes, no PAHs were found in concentrations above the detection limits [171]. To build a more comprehensive data-set for investigation of PAHs in other types of gasification ashes, PAH quantification has been conducted in ashes from LT-CFB gasification of four different sludge-based fuels (described in Paper III) as well as ashes from gasification, pyrolysis and incineration of a single sludge sample (the CPSE study, described in Paper IV). These results are provided in Figure 36.

Contents of PAH in samples from MIX-ST and MIX-BJ were determined by an external laboratory (Eurofins GfA Lab Service GmbH, Germany, internal method "LRMS, GLS OC 302" using acetone+toluene extraction and GC-MS). Contents of PAH in samples from SLU-BJ and all CPSE substrates were determined in-house using a GC-MS system with a Hewlett Packard HP 6890 gas chromatograph and a HP5973 Mass Selective Detector (Agilent, Denmark). Prior to analysis, the fuel and ash samples were treated in a Soxhlet extractor using acetone and cyclohexane. A mix of deuterium labeled PAHs was used as internal standard and quantification aid.



Figure 36: PAH content in one sludge fuel and selected char and ash samples. SC: Secondary cyclone. CR: Char reactor. CPSE: Cross Platform Sludge Experiment [4]. MIX-ST and MIX-BJ are ashes from co-gasification of sludge and cereal straw [3]. Error bars represent standard deviations. \*: 1 replicate only, standard deviations not quantified. Dotted lines are Danish legal limits for total PAH content in sewage sludge (3 mg/kg dry sludge) and bio-ash (12 mg/kg dry matter) [82,85].

From the results it is evident that all ashes from LT-CFB gasification and co-gasification of sludge comply with regulation on total content of PAHs in sewage sludge as well as in bio-ash. The ashes from fluid bed incineration do not comply with the sewage sludge regulation while the slow pyrolysis chars and ash from TwoStage gasification violates both sets of legal limits. The content of PAHs could most likely be reduced partly or completely by oxidizing these chars and ashes after the pyrolysis and gasification respectively. Such a process has been proposed in Paper IV to increase the fertilizer quality of the P in the ashes, but it might also prove to be very valuable in regard to PAH content.

As previously discussed with the heavy metal regulation, it should also be considered to expand the current legal limits for PAHs with threshold values on basis of total P content with the same arguments.

## 5.3 P fertilizer quality in ashes from thermal conversion of sludge

Except for results on LT-CFB ashes (Paper III) and the CPSE study (Paper IV), no results have been found in the published literature on the fertilizer quality of P in ashes from thermal sludge gasification. However, there has been a lot of debate about the P fertilizer quality and potential issues with heavy metals when applying ashes from sludge incineration or when applying sewage sludge directly. In addition, a few studies on the fertilizer quality of char from sewage sludge pyrolysis have been published. A few examples of studies on the use of sewage sludge as well as ashes and chars from incineration and pyrolysis of sludge as fertilizers have been collected in the following.

In a study from 1982, Mellbye et al. found that application of sewage sludge ash from incineration would increase the yield of mature corn ears in a 2 year field study with sweet corn. There was no immediate effect the first year, but in the 2<sup>nd</sup> year the ear yield increased up to 30% while there was no increase in total above ground biomass yield [235].

In 1994 Bierman & Rosen published a study with a 4 year field trial with field corn and sweet corn grown on plots fertilized with SSA or triple superphosphate. Annual application rates were 35, 70 and 140 kg P ha-1 based on the ammonium-citrate soluble amount of P in the ashes and P fertilizer. In this way, the effect of slow-release P from the ash was not accredited in the particular study. No effect on field corn yield was evident in the first two years from either treatment, but in the third year there was a 14% increase in the TSP plots and a 16% increase in the SSA plots compared to the unfertilized controls. In both treatments it was the 70 kg P ha-1 application rate that gave the highest yields in the 3<sup>rd</sup> year. In the 4<sup>th</sup> year the crop was changed to sweet corn with increased yields of fresh sweet corn ears of 27% in the SSA plot and 37% in the TSP plot – both with application rates of 70 kg P ha-1 [236].

In a study from 1986, Jakobsen & Willet compared the fertilizing effect of dried lime-treated sludge with its incineration product. Two sets of plots were used – one with ryecorn and ryegrass on relatively fertile soil and one with Lucerne on a highly acidic and P deprived soil. Similar total P levels were provided to the two plot sets corresponding to 0, 5, 10 and 20 t sludge ha-1 in the first and 0, 10, 20 and 40 t sludge ha-1 in the second. The sludge was chemically treated with CaO and FeCl<sub>3</sub>. The authors conclude that the sludge is a source of readily available N and P while the ash contains no N and the P was not available to the crops. Increased yields in the ash plots are found to be very small and the effect is ascribed mainly to the high liming potential of the ash [142].

Kumpiene et al. (2016) evaluated and compared the impact of two different sewage sludge and sewage sludge incineration ashes for use as fertilizers with regard to the content and plant availability of P and Cd, the influence on plant growth and the P and Cd plant uptake. Incineration was found to reduce the content of Cd per unit of P with a factor of 2-5 compared to the sludge. Incineration greatly improved the content of plant available P in the substrates (measured by extraction with 0.1 M ammonium lactate and 0.4 M acetic acid) compared to untreated sludge. Addition of K and Ca to the sludge as well as the incineration temperature (800 to 950 °C) was found to make a substantial impact on P extractability. With regard to biomass yield from plant growth experiments, Kumpiene et al. found that sludge amendment substantially decreased the yield compared to the unfertilized control. In the ash fertilized plots there was substantial variation. In some cases there were no response to the ash amendment, but in two out of 6 cases with the best ash substrate there were clear and significant yield increases of around 70%. The P application rate varied substantially among the treatments and was in general very high (around 800-5800 mg P per kg soil), making it difficult to compare the results to other studies. In addition, no mineral P control was included, and it was not determined if the plant growth was limited by P deficiency. As an explanation behind some of the differences between sludge and sludge incineration ash, the authors pointed towards a potential negative influence on plant growth of elevated concentrations of chlorine and ammonium nitrate in the sludge amended soils related again to the very high application rates [237].

In a recent study by Hossain et al. from 2015, it was found that application of sewage sludge and sewage sludge biochar had a very limited effect on plant (cherry tomato) growth measured as plant height (5-10%). However, there was a significant benefit from both treatments related to number of fruits and total fruit weight increasing yields with 35% and 64% for sludge and sludge biochar treatment respectively. Both treatments were 10 t/ha and no compensation were given for differences in P and N content [238].

A study by Song et al. (2014) with cultivation of garlic in biochar amended soils, the researchers found an increase in total biomass yield of >250% when amending soil with slow pyrolysis sewage sludge biochar produced at 550 °C and applied in soil:biochar ratios of 5:1. In another test with similar biochar produced at 450 °C, the optimal mixing ratio was found to 4:1, which provided just 30% increase in the total biomass yield compared to the soil-only control plant. These application rates are in general very high, and the focus of the study was not specifically on P fertilizer effects [239].

The differences among the studies are many and distinct, and no clear picture is given about the P fertilizer quality of sludge ash or sludge char. The currently available studies on sludge pyrolysis char were not designed as P fertilizer assessments, and the variation in the results from the sludge incineration studies range from no or negative yield to sizeable yield increases. One of the important lessons from several of the studies on incineration ash is that in several cases where no immediate ash fertilizer effect was observed, sludge incineration ash was found to have a slow-release fertilizer effect and a positive impact on yields in the second or third crop season.

Three studies on P fertilizer quality of ashes from thermal gasification and co-gasification of sludge have been carried out doing the course of the current study. The goal has been to expand on the existing data with a detailed investigation on ashes from thermal gasification and co-gasification of sludge - and also to include ashes from thermal gasification in a direct comparison with sludge, sludge incineration ashes and sludge pyrolysis char. The three studies conducted in this regard were:

- Water extractability of P in soil samples incubated for 1 week after amendment with 11 different substrates including sludge and ashes from LT-CFB gasification of sludge and co-gasification of sludge and cereal straw.
- Anion-Exchange Resin strip extractability of P in soil samples incubated for 2 weeks after amendment with 12 different substrates including sludge, ashes and chars from incineration, gasification and pyrolysis of sludge.
- Diffusive Gradients in Thin films extractability of P in soil samples incubated for 14 weeks after amendment with 6 different substrates including sludge, ashes and chars from incineration, gasification and pyrolysis of sludge.

With these studies it has been attempted to evaluate the influence of fuel composition, thermal process design and the effect of incubation time on the plant P availability of ash and char substrates compared to the original fuel samples.

Different soil tests for quantifying plant available P have been applied. The reason has been mainly a desire to develop experience and a knowledgebase within this field and investigate similarities and differences among the methods and results. Investigations of P availability using Anion-Exchange Resin (AER) extraction have been conducted for more than 50 years, and the extractability results have been proven to have a generally good relationship with plant growth and P uptake irrespective of soil properties. In modern AER-P extraction membrane strips are applied, which makes the method very simple and robust [151]. Water extractability of P from soil is the most fundamental P extraction technique, and was recently shown to be among the two best methods out of 14 to correlate soil test P and plant P uptake over one growing season [153,240]. Diffusive Gradients in Thin films (DGTs) is a relatively new P extraction technique developed since 1998 for use in water streams and used since 2005 to extract P from soils [240]. The method has been proved as highly suitable to predict plant fertilizer requirements in several occasions, and in a recent study by Six et al. (2012) it was found that while most conventional soil tests extracted a fraction of P in the soil samples, which was not available to the applied test-crop (maize), the DGTs extracted only P from the plant-accessible pool [146,240]

## 5.3.1 Influence of fuel composition on P extractability of fuels and ashes

The influence of fuel composition on P extractability has been evaluated by comparing ashes from several different sewage sludge based fuels converted on a single thermal platform (LT-CFB) while ensuring that the same soil and setup was used for the soil incubation and subsequent analysis. P extractability was determined by water extraction of the incubated samples. This work is described in detail in Paper III, and highlight results are provided in Figure 37.

The investigated P substrates include four dry sewage sludge samples and cyclone ashes from LT-CFB gasification or co-gasification hereof. The SLU substrates are from mono-sludge experiments while the MIX substrates are from co-gasification of sludge and cereal straw. An SC ash sample from gasification of straw alone has also been included.



Figure 37: P water extractability results from the investigation of fuel composition on the P fertilizer quality of ashes from LT-CFB gasification and co-gasification of sewage sludge [3]. Control soil subtracted. Error bars represent standard deviation. SC: Secondary cyclone. CR: Char reactor (bottom ash). Abbreviations SLU-BJ, SLU-RA, MIX-ST and MIX-BJ refer to different experimental LT-CFB campaigns described in Paper II & III.

The study did not include the mixed fuels in their final composition, because the mixed fuels have a very low P content and dosing with the same amount of P in all incubations would lead to a much higher substrate:soil ratio in the mixed fuel samples. This would make the results difficult to compare as there could be a risk of significant influence on the P extractability from increased substrate-soil interactions. The same is the case for the SC ash from straw gasification. However, this sample was included to improve the interpretation of the co-gasification results (Figure 38).

In general, the results indicate reduced P water extractability in all sludge samples compared to the mineral P fertilizer as well as reduced extractability in the ashes compared to their parent sludge samples. The ash from straw gasification had the highest extractability, but due to a very low P content in this sample compared to the other samples, other factors (e.g. adjustment of soil pH) may play a significant role, and it is difficult to conclude isolated on the P quality. The low extractability of the P in the sludge from Randers WWTP (SLU-RA) and the related SC ash is expected to originate from a very high dosing of especially iron based P precipitation chemicals at this plant. The content of iron in the sludge from Bjergmarken WWTP (SLU-BJ/MIX-BJ) and Stegholt WWTP (MIX-ST) is almost identical, and the P extractability from these sludge samples and their related ashes is also very comparable despite significant differences in the content of aluminum. Pettersson et al. (2008) also reported reduced extractability in sewage sludge ashes where iron had been used in the P precipitation compared to the use of aluminum [168]. There are no clear differences in the composition to explain the difference in extractability of P from the two sludge samples from Bjergmarken WWTP (SLU-BJ and MIX-BJ). However, the compositions of these two samples have been determined at different laboratories using comparable but not similar methods, and the related uncertainties are therefore expected to play a considerable role in this regard.

The ashes from co-gasification of sludge and straw generally perform better than the ashes from gasification of sludge alone. The primary differences in the composition between ashes from sludge gasification and ashes from co-gasification of sludge and straw are severely elevated contents of carbon as well as alkali and earth alkali species in the ashes from co-gasification. The SLU-BJ filter ash also performs better than the related SC ash and also contains slightly larger amounts of C, K and Ca than the SC ash when measured per unit of P. In two studies by Li et al. (2013) and Ren et al. (2015) it was found that when co-firing wheat straw and sewage sludge in fluid bed incinerators, reactions between the P-rich sludge and alkali metals in the straw lead to the formation of K-Ca–P and K-Ca-Mg-P compounds. Evidence of transformation of Ca-phosphates to Ca-K-phosphates during the co-incineration process was also presented [138]. In a study by Zwetsloot et al. (2015) it was found that co-pyrolysis of slaughterhouse waste with wood and corn residues also lead to a beneficial modification in the P species and an increase in the P mobility and P fertilizer quality [32]. Based on the findings of these studies and the results in Figure 37 it is suggested that the identified differences in the water extractability of P from the different gasification ashes are related to content of alkali and earth alkali species and interactions of these with the P in the ash.

To validate these benefits during co-gasification of sludge and straw on the LT-CFB gasifier, it has been attempted to clean the MIX results from the influence of the straw ash to see if the results indicate an improvement of the sludge P by co-gasification with straw. Determining the amount of straw-based P compared to sludge based P in the mix ashes, deducting the availability of the straw based P from the total mix P and finally scaling the remaining sludge based P availability to match the 80 mg total P kg<sup>-1</sup> soil ("SC ash mod.") leads to the following modified results showing the extractability of the P in the ash in % of the extractability of P in the parent sludge:



Figure 38: Modified results on water extractable P in LT-CFB SC ash samples. The "mod" results have been modified to account for the influence of the extractability of straw P on the mix result. Error bars represent standard deviation.

With these modifications the differences between the ash from gasification of sludge and co-gasification of sludge are reduced substantially. Based on the modified results it is therefore not possible to conclude if there is a positive effect on the sludge P by co-gasification compared to gasification. However, as the comparison is made across different sludge samples and some of the composition analysis are conducted at different laboratories these results are not enough to make a final conclusion on this matter. To determine if there is a positive effect of co-gasification of straw and sludge on the extractability of sludge P in the ashes, an experimental campaign has to be conducted where the same straw, sludge, gasifier and laboratory is used to produce and analyze samples from mono-gasification of sludge and straw as well as co-gasification of these same fuels. Such a campaign has been conducted at the 100 kW LT-CFB unit at Risø DTU, but the analysis of the samples and the P plant availability of the ashes has yet to be performed.

However, even with the preliminary set of results there seem to be substantial benefits of co-gasification of sewage sludge and cereal straw in relation to the P/K ratio in the ashes, reduced contents of heavy metals and increased carbon content with potential improvement of biochar related characteristics [78,79,241,242].

## 5.3.2 Influence of the thermal process on P extractability of ashes and chars

The influence of process design on plant P availability has been evaluated by comparing ashes from conversion of a single sewage sludge sample on several different thermal platforms (two pyrolysis plants, two thermal gasifiers and two incineration plants + several post-oxidized ash samples) while ensuring that the same soil and setup was used for the soil incubation and subsequent analysis. In this study, the available soil P was determined using Anion-Exchange Resin (AER) strips. Details on the sludge sample and the thermal processes as well as description of the analysis method and detailed results are provided in Paper IV, while highlight results are provided in Figure 39.



Figure 39: AER strip P extractability results from the investigation of process design on the P fertilizer quality of ashes from thermal conversion of a single sewage sludge sample on several different thermal platforms (Paper IV, [4]). Control soil subtracted. Error bars represent standard deviation.

The investigation includes one sludge sample and several residues from thermal conversion of this sludge. The involved thermal processes were a lab scale slow pyrolysis (600 °C), a pilot scale fast pyrolysis (varying, 550-750 °C), a pilot scale LT-CFB gasifier (750 °C), a pilot scale TwoStage gasifier (850 °C), lab scale fixed bed incineration (two temperatures, 750 and 850 °C) and a full scale fluid bed incineration (850 °C). In addition, the investigation included samples from slow pyrolysis and the two gasifiers that were oxidized for 30 minutes after the thermal conversion. The oxidation was carried out at the same temperatures as the initial thermal process. The OX2 sample also received air during heating and cooling while the OX samples received N2 during heating and cooling.

The best performing thermal residual was the oxidized slow pyrolysis char, and the extractability of P in this sample was found to be as high as the extractability in the dry sludge. In general the post-oxidation process

substantially increased the P availability in the materials, but it was especially effective on LT-CFB ash where the AER-extractable P was more than doubled. There was no significant difference between the P extractability of the TwoStage OX and the TwoStage OX2 sample.

The two pyrolysis chars and the ash from fixed bed incineration at 750 °C performed best among the unoxidized substrates while the extractability of P was the lowest in the gasification ashes and the fluid bed incineration ash. The Fixed inc 850 sample was positioned in between these two groups.

Across all samples it seems that increasing temperature has a negative influence on the P extractability. This is supported by the findings of Qian et al. (2014) [156]. However, the substantial influence of postoxidation on P extractability show that temperature differences alone does not provide the full explanation behind the variations in the results. Other process parameters e.g. heating rate, retention time and reaction atmosphere are also expected to play an important role with regard to P availability in the residual product.

The influence of the different thermal processes on the composition and P extractability was investigated in Paper IV using sequential extraction (SE) with full composition analysis of the different extraction pools combined with Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy.

The analysis provided many results with regard to the chemical differences in the substrates as well as to the beneficial effect of the post-oxidation process. Some examples of the results obtained on this matter are provided in Figure 41 to Figure 43. The first two charts show how P is transferred from SE pools containing soluble P to SE pools containing insoluble P during all thermal processes, and subsequently how the opposite is the case during the post-oxidation process. To be able to make conclusions on potential changes in P plant availability from the differences in substrate chemistry determined in the analysis, the total content of P in the mobile SE pools ( $H_2O$ ,  $C_2H_3O_2NH_4$ ,  $NaHCO_3$  and NaOH) was initially found to be strongly correlated to the AER extractability of P from the same samples (Figure 40).



Figure 40: Correlation between results from incubation studies and sequential extraction (SE). Primary axis is the total P recovered in the soluble SE pools (H<sub>2</sub>O, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>NH<sub>4</sub>, NaHCO<sub>3</sub> and NaOH). Secondary axis is the share of P extracted from the incubated substrates using anion-exchange resin (AER) strip extraction. All results in % of total P in the sample. Error bars represent standard deviation.



Figure 41: Transfer of P between Sequential extraction (SE) pools as function of thermal treatment. Results provided as the net transfer in- or out of a given SE pool in % of total P in sample. Error bars represent standard deviation.



Figure 42: Transfer of P between Sequential extraction (SE) pools as function of post-oxidation. Results provided as the net transfer in- or out of a given SE pool in % of total P in sample Error bars represent standard deviation.

In total, pyrolysis, incineration and gasification led to a net transfer of 40-55% of total P from soluble P pools to less soluble pools. In the case of incineration as well as gasification, this movement can be expected to relate to concentration of P in various sparingly soluble calcium phosphates [110,210,243,244]. During post-oxidation of the produced ash and char substrates there was a net transfer of 10-30% of the total P in the opposite direction. To elaborate on the results of the P transfer assessment, the investigation was expanded with results on the transfer of several other inorganic elements in addition to P. A result



from this investigation is provided in Figure 43. The chart shows how the content of different elements increased in the SE pools with soluble P as a consequence of the post-oxidation process.

Figure 43: Net increase in the content of selected ash elements in accumulated SE pools H<sub>2</sub>O, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>NH<sub>4</sub>, NaHCO<sub>3</sub> and NaOH as function of post-oxidation. Results as mole of element transferred from immobile to mobile pools per kg of substrate oxidized. Error bars represent standard deviation.

The results show how the post-oxidation moves substantial amounts of especially P, Al and Mg but also Ca and S from the immobile to the mobile pools. These results were combined with a surface structure analysis that showed the development of a highly porous crystalline structure on the surface of the oxidized samples.

Based on the analysis conducted in Paper IV, several mechanisms were identified and suggested to drive the differences in P extractability among the CPSE samples. The proposed mechanisms that reduced P extractability during the thermal conversion of sludge related mainly to a severe concentration of P in the immobile SE pool alongside high concentrations of Ca, Al and Fe as well as some Mg. This behavior was most severe in the ashes from fluid bed incineration, TwoStage gasification and LT-CFB gasification, which were also the samples that had the lowest P AER extractability. Concentration of P in insoluble Ca-P, Ca-Fe-P, Ca-Al-P and Ca-Mg-P compounds during thermal sludge conversion was supported by several other studies [110,210,243].The mechanisms that were proposed to increase P extractability were most evident in the post-oxidized samples and the ash from fixed bed incineration. These mechanisms involved increased association of P to Mg, S and Ca in mobile SE pools, complete transfer of P out of the residual SE pool as function of post-oxidation and fixed bed incineration, oxidation of Fe-phosphates, volatilization of P species and formation of a porous crystalline particle surface structure during post-oxidation and fixed bed incineration. Formation of Mg-P species during sewage sludge conversion at temperatures between 750 and 850 °C have also previously been observed and proposed to be a driver behind increased P plant availability [55].

In addition to changes in the P plant availability, the thermal processes were also found to have substantial differences with regard to utilization of the energy potential in the fuel and the release of Cd, S, N and P to the gas product. Most of the processes released 95-100% of the energy from the fuel, but during slow pyrolysis without oxidation, approximately 30% of the heating value of the sludge remained in the pyrolysis char. The Cd content in the gasification ashes was a factor of 4-6 lower than in the other ashes and the sludge per unit of P. The highest content of Cd per unit of P was found in the sludge and the incineration ashes. Stabilization of Cd by interaction with Al and Si oxides at high temperatures were suggested as one

of the drivers behind the high thermal stability of Cd in the incineration ashes. The S content in the gasification ashes was similarly a factor of 3-5 lower per unit of P than in the remaining samples. Losses of P were quantified for the lab scale processes and it was found that up to 12% of the P was released from the ash during fixed bed incineration while up to 10% was released in the post-oxidation processes. No P was lost during slow pyrolysis. Similar losses of P in high temperature oxidation were observed by Matinde et al. (2008) [245].

**5.3.3** Influence of incubation time on the extractability of P from soil/ash mixtures The influence of the incubation time on the P extractability has been investigated in a 14 week incubation of selected ashes from the CPSE study. This investigation provides important information about how the P plant availability of the different ashes changes in soil over time, and revealed an increased P plant availability over time that was not identified in the short term incubation studies. In this study, the P extractability was measured by Diffusive Gradients in Thin films (DGTs). The method used in the DGT based incubation study is described in Appendix 7 and highlight results are provided in Figure 44.



Figure 44: DGT P extractability results in % of mineral P from the investigation of the influence of incubation time on the P fertilizer quality of ashes from thermal conversion of a single sewage sludge sample on several different thermal platforms (description of sludge sample, thermal processes and scientific method in Paper IV and Appendix 7). Control soil subtracted. Error bars represent standard deviation. 8 out of 68 data points removed as outliers from original dataset.

From 2 to 7 to 14 weeks, a steady increase of available P from all substrates is observed when compared to the mineral P treatment, with a higher increase in the first period than after week 7. The highest rate of increase in the extractability of P from the different ashes over time is observed for the TwoStage gasification ash and the lowest in in the fluid bed incineration ash. For the TwoStage ashes, the influence of incubation time is higher on the un-oxidized substrates compared to the oxidized versions. It is interesting to notice, that there is only a very small increase in the P extractability from the fluid bed incineration ash. As ash from sludge incineration has previously been suggested to have increased fertilizer effects in the second or third growing season, therefore it may be worthwhile to investigate the development of P plant availability for longer than only 14 weeks [235,236]. This would allow for an assessment of the slow-release P fertilizer potential of the different substrates.

## 5.4 Critical reflections

#### 5.4.1.1 Influence of substrate elemental composition analysis

In the study on ashes from multiple LT-CFB campaigns on different sludge based fuels (Paper III), the elemental analysis of fuels and ashes have been conducted by three different laboratories. All methods involved ICP OES analysis, but the digestion procedure differed and HF as well as HNO3 was applied. As no material was analyzed at all three laboratories it is not possible to quantify the potential influence of the different methods on the results. In general all substrate analysis for a single study should be conducted at the same laboratory with the same method.

In the case of the CPSE study it was found that the commonly applied method used for analysis of soils and biomasses was not optimal for analysis of ashes. It was concluded by the technical and scientific staff at the University of Copenhagen that due to many strongly bound compounds and generally higher concentrations of elements in ashes than in soils, an improved method with higher concentrations of HF and different dilutions of the extract for determination had to be implemented. The improved method generally identified increased concentrations of several elements in the ashes compared to the previously applied method. The difference in the Cd results was especially pronounced as illustrated in Figure 45 where the results from the original ICP HF analysis and the improved analysis are compared.



Figure 45: Relative difference between original ICP HF and improved ICP HF method used for determination of the elemental composition of sludge and ash substrates. Error bars indicate average standard errors among the two measurements.

In addition to Cd, there were also significant differences in the estimation of the P concentration (6-14%) as well as the concentration of Na, Mg and Fe in the sludge (25-30%). The study is based on the optimized results. However, on the basis of these recent findings it is proposed to further validate, and potentially further optimize, the analysis method to make sure that the best possible procedure is used. Knowing the exact P concentration is essential for soil incubation and plant growth experiments, while the content of all elements is relevant in regard to the kind of investigation on P association conducted in the CPSE study.

## 5.4.2 Verification of sample quality

In general very large samples of several kilos of fuels and ashes have been procured. For analysis large subsamples hereof have been taken at multiple places in the original sample and these have been ground and mixed to obtain good overall representation.

As the sludge sample used for the CPSE study was very large (28 tons) and extracted across several days, as well as in three different forms (dry pellets, dry granules and mechanically de-watered) it was deemed necessary to validate the comparability of the different subsamples. The dry sludge was produced in 14 bags with 3-500 kg in each, and from each bag a sample of around 1.5 kg was collected for subsequent analysis. 22 ton of de-watered sludge was transported directly by truck from the extraction to the incineration plant, and just one sample of 30 kg of de-watered sludge was taken prior to the production of the sample for incineration. All sub-samples were dried for 24 hours at 104 °C. The 15 sludge samples were compared with regard to the proximate composition and the elemental composition of the ash to determine consistency in the sample. Results from this consistency assessment of the sludge sample are shown in Figure 46 and Figure 47.



Figure 46: Proximate composition of CPSE sub-samples

Figure 46 indicates a slight deviation in dry based composition of the de-watered sludge sample compared to the pellets and granules as the dry base ash content is a bit higher while content of volatiles and fixed carbon is lower. This is examined further by comparing the chemical composition of the ashes from the different sub-samples (Figure 47).



■Na ■Mg ■Al □P ⊠S ■K ■Ca ⊠Fe

Figure 47: Bulk ash elemental analysis X-ray fluorescence (XRF)

The elemental analysis indicates a small shift in the sludge inorganic chemistry from the granules and pellets to the de-watered sludge sample. A small decrease in the Al concentration is observed, while the other elements are either directly comparable or within the uncertainty range. Dosing of aluminum at Bjergmarken WWTP is dependent of the season, and is decreased during the spring, summer and autumn. The sludge sample was extracted in March, and it is suspected that the apparent changes in the sludge sample could originate from a decrease in the dosing of Al-based precipitation chemicals at the WWTP. The compositions of the samples were overall very similar and the difference in the ash content and Al concentration were very small. Therefore it was concluded that the differences were not large enough to exclude the sample from the analysis. However, to validate these results more samples should ideally have been taken as the identified difference could be an initiated shift in the composition that lead to larger differences among the last sludge extracted.

## 5.4.3 Uncertainty related to incubation studies

During the incubation studies four potentially very significant sources of uncertainty were determined. These sources are 1) The composition analysis, 2) The choice of soil type, 3) Differences between the P extraction methods and 4) the homogeneity of the particle size distribution of the investigated substrates. The last three topics are briefly investigated and discussed in the following

#### 5.4.3.1 Influence of soil type and P extractability assessment method

The choice of the soil type used in studies of P fertilizer quality is known to have a very high influence on the results [86,153,246,247]. In this work, one acidic and one slightly acidic (pH 5.2 and 5.9) soil have been used, and the results could be very different using alkaline soils as e.g. observed by Nanzer et al. (2014) [164]. To strengthen the results of similar studies, it would be beneficial to include at least two contrasting soil types in all incubation experiments.

The influence of the method used to assess P extractability and thereby approximate P plant availability is also very important. Many different methods exist and in a detailed study by Wünscher et al. (2013 & 2015) 14 different methods were tested on 50 agricultural soils from Austria and Germany. The authors found that the combination of soil type (pH, organic carbon content and clay content) and extraction method was important to obtain robust results and concluded that a single method often would not be enough to provide a robust estimation of both current and potential plant available P. For best estimations of the P available to plants in one growing season, weaker extraction agents like water correlated best with the uptake by wheat [153,240]. In a study by Erik Sibbesen (1983) it was concluded that Anion Exchange Resin extraction was the best method to provide a reasonable estimate of the amount of soil P that could be released to a crop or plant root under optimum growth conditions. Water extraction was found by Sibbesen to be the 2<sup>nd</sup> or 3<sup>rd</sup> best option [152]. These two methods have been applied in the current study together with the more recent method diffusive gradient in thin films (DGT), which has been thoroughly tested in recent years and found to be a highly applicable method to predict plant P uptake and response [248,249].

To be able to compare the P extraction rates of the different extraction methods applied in the study, the six CPSE substrates used for the 14 weeks incubation experiment with DGT extraction were also extracted using AER strips. The results are provided in Figure 48.



Figure 48: Correlation between DGT results (x-axis) and Anion Exchange Resin strip extraction results (y-axis). DGT results after 2, 7 and 14 weeks. AER results after 2 weeks. All results given as extractability in % of mineral P extractability results to investigate the fit of the linear correlation to the identity line (X=y). Error bars indicate standard deviation.

Substantial differences are observed between the results from the two methods after 2 weeks incubation. These differences are expected as the applied methods extract different pools of P from the incubated samples. In general the AER P extraction is higher than the DGT extraction, and several data points are placed far from the linear correlation between the results ( $R^2$ =76). However, it is interesting to see how the pattern changes abruptly after 7 weeks of incubation. When comparing AER results from 2 weeks incubation with DGT results from 7 weeks incubation, the linear correlation between the two data sets is almost perfect, and has even moved much closer to the identity line (x=y). After 14 weeks the pattern is the same as after 7 weeks, but now the linear correlation between the DGT and AER results is placed on top of the identity line. Additional conclusions cannot be drawn from the current results on differences and similarities of the P pool extracted with AER after two weeks and DGTs after 2-14 weeks. For the present work, the most important conclusion is that both methods rank the approximated results for P plant availability of the different substrates in the same order. This strengthens the conclusions. However, as both methods are mere approximations of P plant availability, a full set of plant growth experiments is required to fully validate the results. The correlation between results from incubation studies and plant growth experiments can be expected to vary with the characteristics of the investigated soils and substrates. For this reason, the quality of incubation study results obtained with the tested methods should be validated against plant growth data on identical or comparable substrates.

In general, the standard deviations of both sets of results from the incubation studies are significant, and measures should be taken to reduce them in future studies. More experience with the analysis methods as well as an increase in the number of replications is expected to contribute positively to the reproducibility of the results in this regard.

#### 5.4.3.2 Potential influence of substrate particle size distributions

During the incubation studies it was questioned and discussed how the particle size distribution of the substrates could influence the results of the subsequent extraction of P from the incubated samples. No published literature has been found on this topic, but the matter is discussed in a comprehensive review on the application of phosphate rock from 1996 and several studies on ashes applied in forestry. In these publications it is evident that particle size distribution has a significant influence on the P plant availability of phosphate rock and that there is a significant inhibiting effect of increased particle sizes on the solubility of P in ashes applied in forestry [250–253]. From the results from these studies and the experience with wet extraction and analysis of ashes gathered, it was regarded as a potential risk of increased uncertainty if the particle size distribution varied among the substrates.

The particle size ranges of all CPSE substrates were therefore aligned to reduce the impact of particle size variations on the results from the incubation studies. The cut off rule for the alignment was that all particles had to be smaller than 0.25 mm and 90% of the total mass of the substrate had to be particles smaller than 0.125 mm. This is obviously not a perfect alignment, but it was expected to at least decrease the potential influence of variations in the particle size distributions on the final results. This alignment was performed for the substrates used in the incubation studies with LT-CFB ashes described in Paper III as well ash the study on the CPSE substrates described in Paper IV.

There were small differences in the final substrates, and in general the sludge samples had more large particles than the other substrates. However, all samples complied with the cut off rule and the relatively small variations were expected to have a similarly small influence on the results of the incubation study. It is not easy to compare particle size distributions, and therefore a simple combination of the applied cut-off rule and a determination of the average particle diameter were used. For the CPSE substrates the variation in the average particle size distribution in Figure 49. As the average particle diameter does not take the actual particle size distribution into account, the method does not fully satisfy an alignment or monitoring of the differences in particle size distribution of the applied substrates.



Figure 49: Average particle size by weight of CPSE substrates as applied for analysis and incubation studies

To determine the influence of the average particle size of the substrates on the extractability of the incubated samples, three subsamples with different average particle sizes were prepared from the LT-CFB CR ash used in the DGT and AER analysis of the CPSE study in Paper IV. The prepared sub-samples were not included in the water extraction experiment included in Paper III. To expand the data-set, annealed carbon-free versions of the three sub-samples were also prepared and included in the AER analysis. Results from the investigation of particle size of LT-CFB CR ash on P extractability by AER strip and DGT methods are provided in Figure 50.



Figure 50: Influence of particle size on P extractability in incubated substrates. Char: LT-CFB bottom ash from CPSE campaign. Ash: Annealed LT-CFB bottom ash from CPSE campaign (550 °C). R<sup>2</sup> values to linear fits between average particle size and P extractability. Error bars represent standard deviations.

The results indicate a declining P extractability with increasing average particle size. However, the standard deviations are very high and dominate the results. Despite the fact that 3 of 4 datasets show a completely linear correlation between average particle size and P extractability, a more robust and reproducible study has to be conducted to verify and characterize the correlation. Future studies should also include other particle size fractions to determine the shape of the correlation in other areas. Finally, a different metric for the particle size distribution than the currently applied average particle diameter should be tested.

Particle size distribution measurements were also performed on three soil/sand mixtures used for the CPSE incubation study to determine if the soil and sand was evenly distributed among the samples. No significant difference was found and the comparability of the sample particle size distributions was very good.

#### 5.4.4 Uncertainty related to the investigation of changes in P chemistry

The overall robustness of the investigation of P association in the CPSE study is reduced by the potential influence of determining the residual pool in the sequential extraction (SE) by balance calculations as well as by the uncertainties related to the composition analysis and the incubation study results since these data are involved in the work.

Determination of the residual pool in the SE analysis by balance calculations is a sub-optimal approach as it makes it impossible to estimate the overall balance gap of the extraction process. Ideally, the residual pool should be determined by analysis of the solids remaining after the HCl extraction. In this way the result on the residual pool would be more robust and it would be possible to assess inconsistencies in the total balances of the different extraction series.

In addition, the sequential extraction itself contains certain elements of error and uncertainty related to the practical and analytical work. In the present work only two samples of each substrate were extracted. To better identify data outliers and improve reproducibility of the study it would be better to have at least three samples of each substrate.

Finally, the point analysis by Scanning Electron Microscopy [3] could benefit greatly from determination of many more points and investigation of more particles from each sample.

Despite the significant uncertainties related to the investigation of P association in the CPSE study, the combination of incubation studies, wet sequential extraction with full elemental composition and SEM-EDS analysis is expected to have a great potential for providing useful data in regard to the future characterization and development of fertilizer ashes from thermal conversion of secondary resources. More experience with the method as well as improvements by the discussed guidelines is expected to further strengthen the work and results of future studies.

**Chapter 6** expands the perspective on the obtained results and seeks to answer the questions "How is the environmental impact of LT-CFB gasification of a given secondary resource compared to a representative reference scenario?". Several results from the previous chapters are combined in an assessment of the possibilities for production of controlled release fertilizers and context-specific designer fertilizers in systems encompassing thermal conversion of secondary resources. A discussion about burden shifting in such management systems is also introduced and results are 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. In the last part of the chapter, some of the apparent challenges related to further development and implementation of new thermal management systems for optimized utilization of secondary resources are discussed.

## 6 The broad perspective

Sewage sludge has been identified as a very interesting fuel candidate for thermochemical processes. Pyrolysis as well as thermal gasification of municipal sewage sludge have been found to be promising alternatives to the current practice with either direct application in agricultural systems or incineration. Analysis of the energy efficiency and the gas and char products from the LT-CFB gasifier has indicated that thermal gasification of sewage sludge could be an efficient way to purify the sewage sludge before spreading it on farm soil by lowering the environmental impact while safely recycle a nonrenewable but essential nutrient like P back to the food production system.

From the investigation of the experimental results produced and presented in the current study (e.g. Figure 35, Figure 37 and Figure 39), it is expected that the current results could be further improved and even greater benefits could be obtained by optimized pyrolysis or gasification of sewage sludge. Well-designed co-gasification and ash extraction systems combined with integration of a post oxidation process (see Paper IV and chapter 5) could possible further reduce the heavy metal content per unit of P as well as increase the P fertilizer quality. In addition to optimizing the post-oxidation process, it is also recommended to optimize the LT-CFB operation to fit the fuel or fuel mix that is to be converted. In regard to monogasification of sewage sludge it should be attempted to operate the gasifier with very high ash content or even ash-only in the bed. Preliminary reduction of the fuel particle size may be required to avoid dramatic increases in the bed particle size distribution and related problems with fluidization. Reducing the fuel particle size may lead to increased losses of unconverted char in the primary cyclone, but the practical impact of this on the operation and product quality needs to be experimentally examined before dismissing this option. Based on the comparative study on different sewage sludge gasification designs conducted (see section 4.3) it could also be attempted to slightly increase the temperature in the char reactor and decrease the temperature in the filter. These initiatives will reduce the thermal efficiency of the process. However, additional services is obtained through extraction of highly concentrated bottom ashes from the char reactor and collection of filter ashes in the filter. It could be a simple way to further reduce the content of heavy metals in the fertilizer ashes and product gas while similarly up concentrating heavy metals content in the filter ash. To avoid a significant increase in the production of toxic filter ashes when

reducing the fuel particle size and filter temperature, the secondary cyclone has to work very efficiently, and it could be considered to employ a tertiary cyclone working at high temperatures as has previously been done with the LT-CFB gasifier [66,75].

From the preliminary results obtained on the benefits of thermal co-conversion, supported by literature findings [e.g. 33,50,141,161,172–181], it is anticipated that further investigations into fuel mixing and thermal co-conversion of problematic residual resources could contribute greatly to increase the level of sustainability in the agricultural and waste handling sectors. In addition to sewage sludge and cereal straw, fuel mixing and co-conversion of e.g. municipal organic waste, biogas fibers, manure fibers, meat and bone residues, fish farming sludge, bagasse, rice husks and various forms of macro algae and beach cleaning waste could become interesting with regard to optimization of fuel characteristics, process efficiency and quality of gas and ash/char products. Profound in-depth knowledge about relevant fuel and ash characteristics and the influence of these when mixed with one or several other fuels should be regarded as a high priority discipline in thermal management of secondary resources.

In this optimization process it is also regarded as highly important to maintain a focus on the complete elemental balance of the proposed systems as several of the obtained results have pinpointed the risk of substantial release of valuable elements like P during the thermal treatment (see Paper IV). In this way, the potential benefits of e.g. the post oxidation process may come at a significant cost. The solid recovery from the post-oxidation processes of the slow pyrolysis char, LT-CFB ash and TwoStage ash (in  $N_2$  & air heating) was 77%, 93.8% and 92.6/93.3% respectively. Combining the solid material recovery rates from the postoxidation experiments, with the elemental composition of the ashes before and after oxidation, indicates a potential loss of fertilizer constituents of around 20-50% of S, 10% of P, 4-5% of N and 1-3 % of Ca, K and Mg during the post oxidation process. A loss of e.g. 10% of P during the thermal treatment should then again be carefully evaluated in relation to the obtained reductions in toxicity as well as to the short and long term efficiency of the produced fertilizer substrate. In many cases the crop P uptake efficiency in the first year after application could be expected to be as low as 10-25% of the total fertilizer P applied due to P fixation caused by reactions with clay particles, iron and aluminum compounds in the soil. However, the total P recovery may very well increase in the following growing seasons [154]. High precision fertilization and use of individual element fertilizers as well as controlled rate release fertilizer have been shown to increase cop yields compared to conventional practice [254]. In addition, soil pH adjustments, soil structural changes and modification of the soil anion and cation exchange capacity may also improve the fertilization effect and growth and may be modified with the proper substrates [71,78,143,241,255,256]. The development of an optimal post oxidation process has just started and these considerations should be taken into account in the coming stages of the development. It has already been found (Paper III and IV) that fuel composition as well as the design of the thermal process have an immense impact on the composition, structure and fertilizer quality of the ash and char substrate produced. Combining knowledge about the fuel, the conversion process, the produced substrate and the potential effects of the substrate on soil characteristics, microbes and plants can be used to produce case optimized fertilizer ash substrates of high quality – in a very efficient process – and with substantially reduced risks – from secondary resources.

The substrate carbon content can be used as one of the controlling factors in this regard. The LT-CFB gasification platform is highly suitable for controlling the carbon content in the procured ashes and a combination of pyrolysis and post-oxidation could possibly be used to obtain even wider ranges for ash

carbon content. With combinations of detailed fuel characterization, thermal process expertise and soil science relevance, the proper carbon skeleton functions of the designed fertilizer substrate can be achieved. The primary idea is to use the absorption capacity and the physical structure of the carbon matrix to control the P release to better match plant P requirements. The carbon matrix will most likely reduce the immediate P plant availability, but at the same time reduce soil P fixation and thereby increase the long term availability of the P in the substrate. In short, the idea is to control P availability to the plant significantly longer than what is currently done when applying rapidly available nutrient fertilizers like superphosphate through manipulation of the carbon content in the ash fertilizer. Ash/biochar production systems could in this way be developed to form designer fertilizers that have specific chemical characteristics matched to selective chemical and/or physical issues to improve local P-use-efficiency. Modifications to the carbon content will influence the carbon conversion rate of the thermal process and thereby the total energy efficiency. However, it will also influence the carbon sequestration potential and biochar characteristics of the substrate, which have previously been shown to have potential for substantial positive effects on soil quality and carbon balance [78,79,241,242]. It could also prove beneficial to mix ashes with different elemental compositions as well as ashes with high immediate P release and long term controlled P release to match the combined nutrient requirements of the plant-soil complex. Ashes from different fuels, ashes from different thermal processes or ashes with different downstream treatment (post-oxidation, particle size management etc.) could be mixed in this regard. As thermal processing in general release the majority of N from the processed fuel, addition of N-rich substrates to the ash mixtures could complete the product from the thermal fertilizer refinery.

To reduce the risk of proposing a solution to one problem by generating another (burden shifting), it is proposed that modeling of the complete lifecycle of the proposed solution can contribute to enlighten otherwise hidden risks and benefits [257]. Two life cycle assessment (LCA) studies have been conducted on LT-CFB gasification of dry sewage sludge from Bjergmarken WWTP near Roskilde, Denmark in the 6 MW LT-CFB located at the Asnæs powerplant in Kalundborg, Denmark. One of the studies was carried out prior to the experimental campaigns to determine potential benefits and problematic issues in the system surrounding the thermal process. This study is described in detail in the Thomsen 2012 master thesis, and the overall conclusion from the initial assessment study was that *"*[*LT-CFB*] gasification of sludge and distribution of the ashes as P fertilizer significantly reduces the environmental consequences compared to distribution of dry or de-watered sludge" [258].

The second study was conducted after the experimental campaign to apply the obtained data in a life cycle context. It was a very simple study compared to the first LCA for three main reasons: i) The second LCA only investigates the present state system with existing infrastructure, ii) Only two scenarios are compared (direct application of sludge >< LT-CFB gasification and application of ash fertilizer) and, iii) several parameters in the life cycle index had been found to have little or no impact on the results in the first LCA and was left out of the second study. Illustrations of the models used in this work as well as the results from the Normalized Impact Assessment are provided in Appendix 8. The overall conclusion from the second LCA generally supported the findings of the first study. The highest positive impact was found to be on Eco-toxicity followed by Human toxicity, Eutrophication and Global Warming Potential. In the first LCA the highest positive impact was found in Terrestrial Eco-Toxicity followed by Freshwater Toxicity, Global Warming Potential, Eutrophication and Human Toxicity if comparing the results from the same two models as those implemented in the second LCA (the reference scenario with direct application of sludge and a
scenario with centralized LT-CFB gasification) [258]. The two studies differ substantially with regard to the level of detail in the life cycle index, the software used for the modeling (Gabi v. 4.4 & EaseTech 2013 respectively) as well as the applied characterization- and impact assessment methods (CML 2001 method, November 2009 update & ILCD recommended 2013 DTU update respectively). It is generally desirable to perform LCA studies with multiple approaches and methods. Due to inclusion of many parameters and assumptions, the uncertainty related to LCA results is often very significant. To verify or challenge LCA results, multiple studies on the same system is therefore an advantage. To compare the two studies, the results were normalized to estimate the relative share of one person's annual sewage sludge production on that person's annual environmental impact [259]. As the impact categories of different impact assessment methods also differ, the two general impact categories Global Warming Potential (GW) and Toxicity (TOX) have been chosen for the comparison (see Hauschild et al. (2013) for more characterization and impact assessment modeling in LCA studies [260]). Toxicity is in this regard used an aggregated impact category that covers Human Toxicity as well as Ecological Toxicity in the environmental compartments water, air and soil. To make the studies even more comparable, the investigated system only includes the life cycle costs and benefits of the sewage sludge from it is produced and dried at the WWTP to the final use-on-land of either sewage sludge (direct) or ash (after conversion). In this way the two studies focus on the potential benefit of the energy production from the thermal conversion as well as the potential benefits of spreading purified ashes compared to unpurified sewage sludge. Differences in sewage sludge and ash composition with regards to contents of e.g. nutrients, carbon and heavy metals are included in the assessment. Losses of P, N and other elements in the thermal gasification are also included and so is the fertilizer quality of the P in the sewage sludge and the ash as well as the stability of the carbon herein. The results from the comparison are provided in Figure 51 as the net change in environmental impact when going from the reference (direct spreading of sewage sludge) to the proposed system with LT-CFB gasification and subsequent spreading of the ashes.



Figure 51: Comparing results from LCA calculations on the benefit of gasifying sewage sludge from Bjergmarken WWTP near Roskilde Denmark in a 6 MW LT-CFB at Asnæs powerplant in Kalundborg, Denmark. Results show the net change in the impact from 1 person when gasifying the sewage sludge produced by that person and spreading ashes instead of spreading sewage sludge directly. Two studies are compared: One study is modeled using GaBi with CML 2001 [258] and the other is modeled using EaseTech with ILCD recommended 2013 DTU Update (model overview in Appendix 8 . GWP: Global Warming Potential. TOX: Aggregated impact category combining Human Toxicity and Ecosystems Toxicity.

The simplified results of the two studies show a very good agreement with regard to the normalized impact of the two investigated impact categories. The results indicate that when sewage sludge is gasified and the ashes spread as P fertilizer instead of spreading the sewage sludge directly, the average person in that specific wastewater treatment system will reduce their impact on global warming potential (GWP) with ½-1 % and reduce their impact on human and environmental toxicity with 20-25%. Despite mentioned assumptions and simplifications it is still evident that thermal purification of sewage sludge prior to spreading it on farm soil has the potential to substantially reduce the toxic impact of the sewage sludge on humans and ecosystems. It should be noted that only the toxicity of heavy metals and PAH are included in this assessment, while the potential impact of emerging organic toxins in e.g. pharmaceuticals, steroids and hormones (destructed by thermal treatment technology) in the sewage sludge has not been included.

As mentioned, the LCA conducted with Gabi and CML characterization [258] is the far most advanced and detailed of the two. It includes the entire treatment process at the WWTP as well as infrastructure and detailed case specific modeling of the power plant. In this study it was also investigated how the processes at the WWTP could be modified to optimize the benefit of the thermal sewage sludge conversion. A series of sewage sludge maximization initiatives were discussed and included in additional scenarios. These initiatives included the following: The anaerobic digestion unit and drying unit are bypassed and the sewage sludge dried at the power plant; the Active Return-sludge Process (ARP) facility at the WWTP is replaced with improved biological P removal; a primary settling tank is included for direct settling and removal of primary sludge; and finally, large particles are now grinded locally and fed to the LT-CFB alongside the sludge and the sand fraction. In the results from the study it was found that these sludge maximization initiatives had a considerable effect on the optimization potential of the sewage sludge gasification process compared to the reference case. In the optimal scenario with sludge maximization and sewage sludge gasification in the 6 MW LT-CFB, the most significant benefits were identified as a 3% decrease in the average citizen's impact on Global Warming and an 8% reduction in impact on terrestrial toxicity alone [258]. A 3% reduction in the GWP of the average Danish citizen (including industry) would prevent emissions of approximately 315 kg CO<sub>2</sub>-equivalents per person per year totaling around 1.8 million tons of  $CO_2$  equivalents per year in Denmark. On top of this should be added the benefits related to reductions in toxicity, eutrophication, fossil fuel depletion and risk reduction.

Several of the resources that could benefit from optimized management with application of thermal processing are likely to be small in quantity and have distinct characteristics. In such cases, designing the optimal management system should take into account case-specific investigations of the local energy system as well as the local resource management and logistics systems. In cases where ashes from the thermal process are to be applied as fertilizers, the system design should determine and embrace fuel characteristics, fuel mixing possibilities, agricultural practice (crop selection and trade of the produce), soil characteristics and climatic conditions. In addition, social norms as well as laws and regulations should be included. The energy system should be analyzed to determine efficient production and consumption of the energy products produced and all these aspects should be matched to the design of the thermal process to provide optimal management processes for complex systems with distinct case-specific characteristics it will often be the case that one-size-fits-nothing and the best solution is found by adapting and designing the management process to comply with the local conditions.

To initiate development of optimized management of degraded materials and secondary resources with increased recovery and recycling of e.g. P it is required to include multiple actors with relevant knowledge on different aspects of the investigated system. Energy producers, energy system operators, waste and residue logistics (incl. WWTP operators), farmers, agronomists, consumers (of energy as well as produce), toxicologist, sustainability assessment experts and politicians all have to work with - and not against, the thermal system designers and operators. This cooperation can be either by active participation in the development process or by working with the same general guidelines towards common goals. This is no simple task, and requires a general transition in the local, national and international society. Such transitions entail a set of interconnected changes that reinforce each other like changes in processes and management influencing routines, perceptions and attitudes. A common acknowledgement of general guidelines for societal development as those proposed by the United Nations via the Climate Change Assessment Reports by the Intergovernmental Panel on Climate Change and the Sustainable Development Goals proposed by the United Nations Department of Economic and Social Affairs is likely to contribute positively to this transition [261,262]. Profound implementation of such common development guidelines on national, regional and local scale would increase the odds of relevant actors working in the same direction to develop new and better systems for management of available resources.

Politicians on all levels are expected to play a vital role in this transition and development. Legal frameworks have to support optimal resource management and prevent systems with large apparent or hidden costs – economically, socially and environmentally. In a Danish context of developing better thermal systems for management of e.g. sewage sludge, it is proposed to initiate the process by changing the current legal framework to comply with the following:

- 1) Secure a stronger implementation of the precautionary principle in regard to the use of complex organic fertilizers, especially in ecosystems with production of food and water procurement [263]
- 2) Adapt new legal thresholds for contaminants in ashes and chars to be used as P fertilizer. In the current framework it is a disadvantage to reduce the weight of P fertilizer substrates, even though such a reduction of weight by thermal measure can lead to a substantial reduction in the content of organic as well as inorganic contaminants if measure per unit of P. Legal thresholds for contaminants in P fertilizer ashes and chars should therefore be given on basis of P content and should include new thresholds for at least the regulated heavy metals and total PAHs [85]
- 3) Modify the existing legislation on heat production to allow generally for the possibility to recovery and supply produced heat (of a suitable temperature) to district heating networks. A declaration of intent on this topic has been included in the newly formed Danish government's general political framework [264]

## Conclusions

This study was initiated to determine how suitable Low Temperature Circulating Fluidized Bed (LT-CFB) gasification is to procure valuable secondary resources in the form of nutrients and non-fossil energy from secondary resources of varying quality and origin.

Many suitable LT-CFB gasification fuel candidates have been identified in a comprehensive screening. The conducted screening does not provide a full catalogue of potential fuel candidates in this regard but serves more as a proposal for an applicable method and an initial test hereof. From the fuel screening results several correlations between fuel and ash characteristics have been identified, and with additional screening data and proof of concept operations some of these correlations may be used to reduce the work required to screen future fuel candidates as well as increase the understanding about various fuel characteristics influence the thermal conversion process and products. One of the most interesting correlations identified was between P fertilizer quality and the elemental composition of chars and ashes from the fuel screening. Profound differences were identified between char and ash P fertilizer quality. In 16 out of 25 cases ashes were found to have significantly higher P fertilizer quality than the chars from which the ashes were produced while the opposite was pattern was observed for the remaining 9 cases. In an assessment of data correlations it was found that different elements seem to contribute to improve the plant availability of the P in the ashes and chars. While ashes seem to benefit primarily from high contents of K and Mg in this regard, chars seem to benefit from high contents of Mg and Ca. However, significant uncertainties are related to these results, and more data is required to make stronger conclusions on the matter. Initial tests with characterization of fuel blends were also conducted and have revealed how some characteristics can be predicted with linear sums of the involved fuel species, while others (e.g. ash deposition and P fertilizer quality) seem to obtain synergetic effects from the co-conversion. Further investigation into this matter can be used to optimize fuel and ash quality and increase the potential value of some hard-to-handle secondary resources in optimized management systems encompassing LT-CFB gasification.

From the results of the fuel screening and a subsequent investigation of currently applied management of municipal sewage sludge it was found that in a Danish context, sewage sludge may be one of the most relevant secondary resources to utilize in systems encompassing optimized thermal treatment. As the currently existing data on this matter relates mainly to incineration and co-incineration of sewage sludge several experimental campaigns with LT-CFB gasification of sewage sludge, co-gasification of sewage sludge and cereal straw as well as campaigns with TwoStage down-draft gasification, thermal pyrolysis and incineration of sewage sludge have been conducted. In addition, a post-oxidation process has been developed to expand the data material and improve fertilizer quality of ashes and chars from pyrolysis and gasification. In general the results showed that it is possible to design thermal systems to fully and efficiently utilize the energy potential in the sludge while recovering P and other elements in fertilizer ashes with reduced weight and volume, little or no PAHs, reduced content of heavy metals (especially Hg and Cd) and an attractable P fertilizer quality. Pyrolysis, gasification as well as incineration have been shown to be able to produce good ash or char P fertilizers with the proper process design, operation settings and posttreatment. Based on the results from these campaigns it is concluded that in regard to P fertilizer quality the performance of ashes from thermal conversion of MSS cannot be generalized just by the category of the thermal process. A striking example of how such a generalization can be wrong was seen among two

different ashes from incineration of the same sewage sludge sample. While one of the incineration ashes had one of the lowest levels of plant available P of all substrates, the other incineration ash sample was among the substrates with the highest level of plant available P.

To increase the understanding about how LT-CFB gasification and other thermal conversion processes influence ash fertilizer quality, a detailed investigation has been conducted on ash and char substrates from selected experimental campaigns. From analysis of the transfer of P and related elements between soluble and insoluble pools it was proposed that high P plant availability was largely related to beneficial association of P to especially Mg, S and Ca as well as to modifications in the association of P to Fe. Structural changes in the particle surface during oxidative treatments with long retention times are also expected to contribute positively to P fertilizer quality. In general, it seems that beneficial P association can be achieved by two opposing pathways. In one pathway, the P quality of the original sludge is largely preserved by minimizing the transfer of P from soluble to less soluble pools during the thermal treatment. Fast and slow pyrolysis seems to be the only thermal processes that prevent excessive re-association of sludge P in this regard. The other option is to facilitate a full set of oxidative modifications to the sludge ash by combining high air excess ratios and long retention times. This was achieved in a fixed bed incineration process and by post-oxidation of pyrolysis chars and gasification ashes. In the investigation it was also found that all thermal processes seem to facilitate a release of mercury while the combination of a reducing atmosphere and high temperatures in thermal gasifiers seem to strip large amounts of cadmium from the ash containing the vast majority of P. Further reduction in cadmium content may be obtained by increasing reaction temperature, by co-gasification of sewage sludge and straw or by prioritizing extraction of bottom ashes over cyclone ashes.

In general, many different factors have been found to have an effect on the process performance and ash product quality, and the study has revealed a profound potential for optimization of the thermal processing of sewage sludge. LT-CFB gasification is in many respects a very promising thermal process for this purpose combining flexibility and very high energy efficiency. In addition, co-gasification of sewage sludge and cereal straw in LT-CFB gasifiers was found to eliminate sludge drying requirements, increase long term operation stability and produce very high quality thermally purified P fertilizers.

The topic of this study is far from exhausted with the currently conducted work, and additional optimization potential is expected within the areas of: i) improving fuel and ash characteristics by mixing and blending fuels ii) LT-CFB gasification with extraction of highly concentrated bottom ashes iii) improving downstream ash processing with further development of the post-oxidation process 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 controlled release P fertilizers v) mixing different ashes and proper N-substrates to provide full nutrient coverage in products from a thermal fertilizer refinery concept.

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.

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# Appendix

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Appendix 1: Paper I. Published in Biomass & Bioenergy 79 (2015) 128-144 (Not included in online version)

Appendix 2: Paper II. Submitted to Waste Management

(Not included in online version)

Appendix 3: Paper III. Submitted to Waste Management

(Not included in online version)

# Appendix 4: Paper IV. Submitted to Journal of Environmental

#### Management

(Not included in online version)

# Appendix 5: XRF composition data (fuel screening)

XRF results with concentrations of various inorganic elements in ash, char and dry matter of the fuel candidates included in the LT-CFB fuel screening [1]

Ash concentrations	Na	IVIg	AI	SI	Р	S	CI	К	Ca	11	Fe
	Average	e result	s, wt%, a	sh from a	annealin	g [1]					
Coal	1.29	1.20	15.06	34.93	0.17	3.16	0.02	2.14	1.52	0.71	5.10
Pine wood pellets	1.09	3.31	0.40	2.02	2.70	1.28	0.18	17.13	15.25	0.02	0.58
Shea nut residue pellets	0.06	3.46	0.75	3.17	3.88	2.16	2.13	39.89	2.51	0.06	0.61
Crushed straw pellets	0.36	1.89	0.28	10.87	1.99	4.89	4.55	21.94	13.49	0.02	0.32
Wastewater sludge (RC dried)	0.37	0.70	4.52	17.85	6.83	2.50	0.05	0.99	8.15	0.49	11.82
Bagasse	0.33	1.10	3.70	39.63	1.01	0.66	0.10	4.32	3.11	0.30	1.40
Beet seeds	3.35	5.78	0.03	0.12	2.89	1.35	3.95	11.60	20.83	0.00	0.10
Empty palm fruit bunches	0.03	2.08	0.96	9.92	1.42	0.87	4.73	33.63	2.71	0.04	0.49
Lignin pellets (Inbicon)	5.71	0.06	0.39	46.33	0.34	0.35	0.10	0.95	2.46	0.03	1.04
Olive kernels	0.10	2.37	0.22	0.89	1.75	0.58	0.22	26.10	14.94	0.01	0.44
Olive prunings	0.90	2.28	0.95	2.53	3.59	1.24	1.08	12.41	23.11	0.04	1.84
Palm kernel shells	26.20	1.16	0.68	13.90	1.71	0.64	41.17	3.81	1.45	0.05	0.39
Rice husks	0.03	1.43	1.56	45.19	6.50	0.07	0.01	6.48	0.60	0.12	0.62
Vine prunings	0.49	5.67	0.18	0.45	2.99	0.79	0.16	16.41	19.48	0.01	0.12
Bone meal C1	7.42	0.83	0.22	1.45	14.33	0.21	2.48	1.60	22.32	0.02	0.53
Bone meal C2	5.02	0.91	0.18	0.85	16.42	0.11	2.53	3.92	23.75	0.01	0.25
Cattle manure	1.90	4.27	0.87	8.41	5.31	1.65	2.23	7.48	20.95	0.05	1.02
Pig manure	3.91	3.28	0.55	10.20	8.48	1.94	7.42	12.98	10.94	0.05	1.27
Sea weed	13.62	5.20	1.44	13.31	0.91	3.51	14.08	2.44	13.14	0.06	0.73
WWTP sludge	0.24	0.92	6.13	11.59	7.71	2.45	0.08	1.02	9.27	0.33	6.07
WWTP fat	0.66	0.28	2.36	4.73	0.49	0.51	0.71	0.53	31.51	0.16	1.25
WWTP Grate	0.96	1.24	2.31	11.86	5.53	1.50	1.02	1.75	21.85	0.61	2.31
WWTP sand	0.53	1.03	1.79	15.76	5.23	4.10	0.65	1.13	18.87	0.18	3.92
Fish manure	13.64	2.71	0.60	2.31	8.63	1.03	16.21	0.70	14.54	0.02	6.95
Tomato residues	0.69	4.84	0.06	0.18	10.90	1.35	6.38	32.60	4.74	0.01	0.24
Miscanthus pellets	0.04	1.09	1.14	38.15	2.38	0.85	0.11	10.11	8.58	0.11	0.72
Shrimp waste	0.53	1.49	0.01	0.20	5.05	0.24	0.44	0.17	29.85	0.01	0.03
Ash concentrations	Na	Mg	Al	Si	Р	S	Cl	К	Са	Ti	Fe
	Span in	results	, (+/-) wt	%, ash fr	om anne	aling [1	]				
Coal	0.12	0.01	0.06	0.08	0.00	0.02	0.00	0.02	0.01	0.00	0.05
Pine wood pellets	0.07	0.03	0.02	0.00	0.05	0.01	0.01	0.12	0.14	0.00	0.00
Shea nut residue pellets	0.00	0.03	0.02	0.10	0.02	0.03	0.02	0.08	0.04	0.01	0.02
Crushed straw pellets	0.06	0.04	0.00	0.00	0.01	0.04	0.06	0.09	0.01	0.01	0.00
Wastewater sludge (RC dried)	0.06	0.01	0.20	0.68	0.33	0.18	0.00	0.06	0.47	0.02	0.59
Bagasse	0.13	0.05	0.08	0.72	0.00	0.03	0.00	0.02	0.05	0.00	0.01
Beet seeds	0.25	0.36	0.00	0.01	0.19	0.00	0.08	0.20	0.12	0.00	0.03
Empty palm fruit bunches	0.01	0.06	0.02	0.06	0.01	0.01	0.00	0.09	0.02	0.00	0.00
Lignin pellets (Inbicon)	0.46	0.01	0.01	1.31	0.02	0.01	0.00	0.00	0.00	0.00	0.00
Olive kernels	0.05	0.09	0.01	0.03	0.05	0.02	0.00	0.36	0.11	0.00	0.01

Olive prunings	0.11	0.03	0.02	0.05	0.05	0.00	0.01	0.17	0.07	0.01	0.02
Palm kernel shells	0.19	0.04	0.04	0.30	0.00	0.01	0.33	0.03	0.01	0.01	0.02
Rice husks	0.02	0.02	0.07	0.34	0.15	0.00	0.00	0.11	0.01	0.01	0.01
Vine prunings	0.01	0.05	0.00	0.02	0.03	0.00	0.00	0.06	0.02	0.00	0.00
Bone meal C1	0.13	0.03	0.01	0.02	0.12	0.00	0.08	0.03	0.36	0.00	0.00
Bone meal C2	0.19	0.02	0.00	0.04	0.39	0.00	0.07	0.08	0.61	0.00	0.01
Cattle manure	0.12	0.21	0.02	0.04	0.12	0.06	0.08	0.26	0.47	0.00	0.06
Pig manure	0.03	0.01	0.01	0.15	0.28	0.08	0.36	0.62	0.41	0.00	0.01
Sea weed	0.22	0.00	0.10	0.70	0.03	0.09	0.23	0.08	1.32	0.01	0.04
WWTP sludge	0.18	0.03	0.01	0.28	0.06	0.22	0.00	0.01	0.09	0.01	0.01
WWTP fat	0.03	0.04	0.03	0.11	0.01	0.01	0.00	0.01	0.53	0.01	0.01
WWTP Grate	0.06	0.10	0.01	0.93	0.14	0.05	0.05	0.02	0.56	0.01	0.10
WWTP sand	0.01	0.10	0.08	2.55	0.30	0.27	0.04	0.03	1.74	0.02	0.60
Fish manure	0.02	0.05	0.00	0.09	0.15	0.01	0.16	0.00	0.06	0.00	0.01
Tomato residues	0.03	0.02	0.00	0.00	0.10	0.02	0.07	0.02	0.07	0.00	0.00
Miscanthus pellets	0.00	0.01	0.00	0.06	0.00	0.00	0.00	0.01	0.03	0.00	0.00
Shrimp waste	0.01	0.03	0.00	0.01	0.04	0.00	0.00	0.00	0.12	0.00	0.00

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Char concentrations	Na	Mg	Al	Si	Р	S	Cl	K	Ca	Ti	Fe
	Averag	e result	s, wt%, (	char from	n slow py	rolysis	[1]				
Coal	0.46	0.43	5.38	12.47	0.06	1.13	0.01	0.76	0.54	0.25	1.82
Pine wood pellets	0.02	0.05	0.01	0.03	0.04	0.02	0.00	0.25	0.23	0.00	0.01
Shea nut residue pellets	0.01	0.59	0.13	0.54	0.66	0.37	0.36	6.79	0.43	0.01	0.10
Crushed straw pellets	0.07	0.37	0.05	2.11	0.39	0.95	0.88	4.26	2.62	0.00	0.06
Wastewater sludge (RC dried)	0.28	0.53	3.42	13.51	5.17	1.89	0.04	0.75	6.16	0.37	8.94
Bagasse	0.07	0.22	0.75	8.02	0.20	0.13	0.02	0.87	0.63	0.06	0.28
Beet seeds	0.59	1.01	0.00	0.02	0.51	0.24	0.69	2.02	3.64	0.00	0.02
Empty palm fruit bunches	0.00	0.24	0.11	1.16	0.17	0.10	0.55	3.94	0.32	0.00	0.06
Lignin pellets (Inbicon)	1.70	0.02	0.11	13.77	0.10	0.10	0.03	0.28	0.73	0.01	0.31
Olive kernels	0.00	0.04	0.00	0.01	0.03	0.01	0.00	0.44	0.25	0.00	0.01
Olive prunings	0.05	0.13	0.06	0.15	0.21	0.07	0.06	0.73	1.36	0.00	0.11
Palm kernel shells	3.03	0.13	0.08	1.61	0.20	0.07	4.77	0.44	0.17	0.01	0.05
Rice husks	0.01	0.54	0.58	16.93	2.44	0.03	0.00	2.43	0.23	0.04	0.23
Vine prunings	0.06	0.64	0.02	0.05	0.34	0.09	0.02	1.86	2.21	0.00	0.01
Bone meal C1	4.46	0.50	0.13	0.87	8.61	0.12	1.49	0.96	13.42	0.01	0.32
Bone meal C2	2.73	0.49	0.10	0.46	8.92	0.06	1.37	2.13	12.90	0.01	0.14
Cattle manure	0.64	1.44	0.29	2.84	1.79	0.56	0.75	2.53	7.08	0.02	0.35
Pig manure	1.67	1.40	0.24	4.37	3.63	0.83	3.18	5.56	4.68	0.02	0.54
Sea weed	11.24	4.29	1.19	10.98	0.75	2.90	11.62	2.02	10.84	0.05	0.60
WWTP sludge	0.18	0.68	4.56	8.62	5.73	1.82	0.06	0.76	6.90	0.25	4.52
WWTP fat	0.49	0.21	1.75	3.52	0.37	0.38	0.53	0.40	23.46	0.12	0.93
WWTP Grate	0.44	0.56	1.05	5.39	2.51	0.68	0.47	0.79	9.93	0.28	1.05
WWTP sand	0.35	0.68	1.19	10.52	3.49	2.74	0.44	0.75	12.60	0.12	2.62
Fish manure	9.17	1.82	0.41	1.56	5.80	0.69	10.89	0.47	9.78	0.02	4.67
Tomato residues	0.10	0.68	0.01	0.03	1.52	0.19	0.89	4.55	0.66	0.00	0.03
Miscanthus pellets	0.00	0.12	0.12	4.12	0.26	0.09	0.01	1.09	0.93	0.01	0.08
Shrimp waste	0.43	1.20	0.01	0.16	4.08	0.20	0.35	0.14	24.16	0.01	0.02

Char concentrations	Na	Mg	Al	Si	Р	S	Cl	К	Ca	Ti	Fe
	Span in	results	, (+/-) wt	%, char f	rom slov	v pyroly	sis [1]				
Coal	0.04	0.00	0.02	0.03	0.00	0.01	0.00	0.01	0.00	0.00	0.02
Pine wood pellets	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Shea nut residue pellets	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Crushed straw pellets	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.02	0.00	0.00	0.00
Wastewater sludge (RC dried)	0.04	0.01	0.15	0.51	0.25	0.14	0.00	0.04	0.36	0.02	0.45
Bagasse	0.03	0.01	0.02	0.15	0.00	0.01	0.00	0.00	0.01	0.00	0.00
Beet seeds	0.04	0.06	0.00	0.00	0.03	0.00	0.01	0.03	0.02	0.00	0.00
Empty palm fruit bunches	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Lignin pellets (Inbicon)	0.14	0.00	0.00	0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Olive kernels	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Olive prunings	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Palm kernel shells	0.02	0.01	0.01	0.04	0.00	0.00	0.04	0.00	0.00	0.00	0.00
Rice husks	0.01	0.01	0.02	0.13	0.05	0.00	0.00	0.04	0.00	0.00	0.00
Vine prunings	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Bone meal C1	0.08	0.02	0.00	0.01	0.07	0.00	0.05	0.02	0.21	0.00	0.00
Bone meal C2	0.11	0.01	0.00	0.02	0.21	0.00	0.04	0.04	0.33	0.00	0.00
Cattle manure	0.04	0.07	0.01	0.01	0.04	0.02	0.03	0.09	0.16	0.00	0.02
Pig manure	0.01	0.01	0.00	0.06	0.12	0.04	0.15	0.27	0.18	0.00	0.01
Sea weed	0.18	0.00	0.08	0.58	0.02	0.08	0.19	0.07	1.09	0.01	0.04
WWTP sludge	0.14	0.02	0.01	0.21	0.05	0.17	0.00	0.00	0.07	0.01	0.01
WWTP fat	0.02	0.03	0.02	0.08	0.00	0.01	0.00	0.00	0.39	0.01	0.01
WWTP Grate	0.03	0.05	0.01	0.42	0.07	0.02	0.02	0.01	0.26	0.00	0.04
WWTP sand	0.00	0.06	0.05	1.70	0.20	0.18	0.03	0.02	1.16	0.01	0.40
Fish manure	0.01	0.03	0.00	0.06	0.10	0.01	0.11	0.00	0.04	0.00	0.01
Tomato residues	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00
Miscanthus pellets	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Shrimp waste	0.01	0.02	0.00	0.01	0.04	0.00	0.00	0.00	0.10	0.00	0.00
Dry matter concentrations	Na	Mg	Al	Si	Р	S	Cl	К	Ca	Ti	Fe
	Average	e results	s, wt%, d	ry mater	ial [1]						

Dry matter concentrations	Na	Mg	AI	Si	Р	S	CI	К	Ca	11	⊦e
	Average	e results	, wt%, d	ry materi	ial [1]						
Coal	0.29	0.27	3.35	7.76	0.04	0.70	0.00	0.48	0.34	0.16	1.13
Pine wood pellets	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.07	0.06	0.00	0.00
Shea nut residue pellets	0.00	0.23	0.05	0.21	0.26	0.15	0.14	2.70	0.17	0.00	0.04
Crushed straw pellets	0.02	0.11	0.02	0.63	0.12	0.28	0.27	1.28	0.79	0.00	0.02
Wastewater sludge (RC dried)	0.16	0.31	2.00	7.89	3.02	1.10	0.02	0.44	3.60	0.22	5.22
Bagasse	0.02	0.07	0.22	2.36	0.06	0.04	0.01	0.26	0.19	0.02	0.08
Beet seeds	0.17	0.30	0.00	0.01	0.15	0.07	0.20	0.60	1.08	0.00	0.01
Empty palm fruit bunches	0.00	0.07	0.03	0.31	0.04	0.03	0.15	1.06	0.09	0.00	0.02
Lignin pellets (Inbicon)	0.74	0.01	0.05	5.98	0.04	0.05	0.01	0.12	0.32	0.00	0.13
Olive kernels	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.12	0.07	0.00	0.00
Olive prunings	0.01	0.04	0.01	0.04	0.06	0.02	0.02	0.19	0.36	0.00	0.03
Palm kernel shells	1.41	0.06	0.04	0.75	0.09	0.03	2.21	0.20	0.08	0.00	0.02
Rice husks	0.00	0.19	0.21	6.10	0.88	0.01	0.00	0.87	0.08	0.02	0.08
Vine prunings	0.02	0.20	0.01	0.02	0.10	0.03	0.01	0.57	0.67	0.00	0.00

Bone meal C1	2.25	0.25	0.07	0.44	4.35	0.06	0.75	0.49	6.78	0.01	0.16
Bone meal C2	0.83	0.15	0.03	0.14	2.72	0.02	0.42	0.65	3.94	0.00	0.04
Cattle manure	0.24	0.53	0.11	1.05	0.66	0.21	0.28	0.94	2.62	0.01	0.13
Pig manure	0.61	0.51	0.09	1.59	1.32	0.30	1.16	2.02	1.70	0.01	0.20
Sea weed	6.51	2.49	0.69	6.36	0.44	1.68	6.73	1.17	6.28	0.03	0.35
WWTP sludge	0.10	0.37	2.44	4.63	3.08	0.98	0.03	0.41	3.70	0.13	2.42
WWTP fat	0.02	0.01	0.08	0.17	0.02	0.02	0.02	0.02	1.11	0.01	0.04
WWTP Grate	0.14	0.19	0.35	1.78	0.83	0.22	0.15	0.26	3.28	0.09	0.35
WWTP sand	0.17	0.33	0.57	5.03	1.67	1.31	0.21	0.36	6.02	0.06	1.25
Fish manure	4.33	0.86	0.19	0.74	2.74	0.33	5.15	0.22	4.62	0.01	2.21
Tomato residues	0.02	0.16	0.00	0.01	0.36	0.04	0.21	1.07	0.16	0.00	0.01
Miscanthus pellets	0.00	0.03	0.03	1.11	0.07	0.02	0.00	0.29	0.25	0.00	0.02
Shrimp waste	0.24	0.67	0.00	0.09	2.28	0.11	0.20	0.08	13.50	0.01	0.01
Dry matter concentrations	Na	Mg	Al	Si	Р	S	Cl	К	Ca	Ti	Fe
	Span ii	n results	s, (+/-) w	t%, dry n	naterial [	[1]					
Pine wood pellets	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Shea nut residue pellets	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Crushed straw pellets	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Wastewater sludge (RC dried)	0.03	0.00	0.09	0.30	0.15	0.08	0.00	0.02	0.21	0.01	0.26
Bagasse	0.01	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Beet seeds	0.01	0.02	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.00
Empty palm fruit bunches	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lignin pellets (Inbicon)	0.06	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Olive kernels	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Olive prunings	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Palm kernel shells	0.01	0.00	0.00	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.00
Rice husks	0.00	0.00	0.01	0.05	0.02	0.00	0.00	0.01	0.00	0.00	0.00
Vine prunings	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bone meal C1	0.04	0.01	0.00	0.01	0.03	0.00	0.02	0.01	0.11	0.00	0.00
Bone meal C2	0.03	0.00	0.00	0.01	0.06	0.00	0.01	0.01	0.10	0.00	0.00
Cattle manure	0.02	0.03	0.00	0.00	0.02	0.01	0.01	0.03	0.06	0.00	0.01
Pig manure	0.01	0.00	0.00	0.02	0.04	0.01	0.06	0.10	0.06	0.00	0.00
Sea weed	0.10	0.00	0.05	0.33	0.01	0.04	0.11	0.04	0.63	0.00	0.02
WWTP sludge	0.07	0.01	0.01	0.11	0.02	0.09	0.00	0.00	0.04	0.01	0.01
WWTP fat	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
WWTP Grate	0.01	0.02	0.00	0.14	0.02	0.01	0.01	0.00	0.08	0.00	0.01
WWTP sand	0.00	0.03	0.02	0.81	0.09	0.09	0.01	0.01	0.55	0.01	0.19
Fish manure	0.01	0.02	0.00	0.03	0.05	0.00	0.05	0.00	0.02	0.00	0.00
Tomato residues	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Miscanthus pellets	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Shrimp waste	0.00	0.01	0.00	0.01	0.02	0.00	0.00	0.00	0.05	0.00	0.00

## Appendix 6: Particle size distribution data (fuel screening)

Results from particle size distribution assessment of ashes and chars used in quantification of Anion Exchange Resin (AER) P extractability in section Error! Reference source not found.. A = Ash samples. C = Char samples. Sample numbers and names (randomized for AER experiment): A1) Bone meal C2, A2) Lignin pellets, A3) Coal, A4) Bone meal C1, A5) WWTP Grate, A6) Shrimp waste, A7) Rice husks, A8) WWTP sand, A9) WWTP sludge, A10) Pig manure, A11) Fish manure, A12) Shea nut residue pellets, A13) Pine wood pellets, A14) Olive kernels, A15) Sea weed, A16) Empty palm fruit bunches, A17) MIX 2, A18) Olive prunings, A19) MIX 3, A20) Crushed straw pellets, A21) Tomato residues, A22) Vine prunings, A23) Cattle manure, A24) Wastewater sludge (RC dried), A25) Bagasse, A26) Miscanthus pellets, A27) MIX 1, A28) Palm kernel shells, A29) Beet seeds, C1) sea weed, C2) tomato, C3) fish manure, C4) WWT grate material, C5) wwt sand fraction, C6) mix 3, C7) pig manure, C8) cattle manure, C9) Wastewater sludge (RC dried), C10) WWTP sludge, C11) bone meal C1, C12) bone meal C2, C13) palm kernel shells, C14) vine prunings, C15) shrimp waste, C16) Empty palm fruit bunches, C17) olive kernels, C18) beet seeds, C29) rise husts

Results	from vis	ual asses	sment w	vith Cam	Sizer. Re	sults on	volume	basis					
	A1	A3	A4	A6	A7	A8	A9	A10	A15.1	A15.2	A17	A19	A24
[mm]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
0.038	0	0	0	0	1	1	1	0	0	0	0	0	1
0.045	0	0	1	1	1	1	1	0	0	0	1	1	2
0.053	1	1	2	1	2	3	2	0	0	0	1	2	3
0.063	1	1	3	2	5	5	4	1	1	1	3	3	6
0.075	2	2	5	3	8	8	6	2	1	1	5	5	10
0.09	4	3	8	5	14	13	9	3	2	2	8	8	15
0.106	6	5	13	7	22	19	13	4	3	3	12	13	20
0.125	10	8	18	11	32	26	16	7	5	5	17	18	25
0.15	15	12	27	16	47	36	20	11	9	9	25	26	31
0.18	22	18	36	22	64	46	25	17	16	16	35	36	36
0.212	28	26	44	30	77	54	30	25	26	26	46	47	40
0.25	35	36	52	39	87	62	35	35	39	40	57	58	45
0.3	42	47	60	50	94	69	43	48	55	55	69	70	51
0.355	48	57	66	60	97	75	51	60	67	68	77	79	59
0.425	54	66	72	69	99	81	62	71	76	77	84	86	67
0.5	60	72	78	76	99	85	74	79	81	81	90	91	77
0.6	66	78	83	82	100	90	87	86	84	85	94	95	85
0.71	71	82	88	87	100	93	95	91	86	87	97	97	91
0.85	77	87	92	91	100	95	99	94	89	90	99	99	96
1	82	90	94	94	100	97	100	96	91	92	99	100	98
1.18	86	94	96	96	100	98	100	97	94	94	100	100	99
1.4	90	96	97	98	100	99	100	98	96	96	100	100	99
1.7	93	98	98	98	100	99	100	98	98	98	100	100	99
2	95	98	99	99	100	100	100	99	99	99	100	100	99
2.36	100	99	100	99	100	100	100	99	100	100	100	100	99
2.8	100	100	100	100	100	100	100	100	100	100	100	100	100
	A27	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10.1	C10.2	C11
[mm]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
0.026	0	0	0	0	0	0	0	0	0	0	0	0	1
0.032	0	0	0	1	1	1	0	0	0	1	1	1	1
0.038	0	1	1	1	1	1	1	1	0	1	1	1	2
0.045	0	1	2	3	2	3	1	1	1	2	3	3	5
0.053	1	2	3	5	4	5	3	2	1	5	5	5	9
0.063	1	4	5	9	7	9	5	5	3	9	9	9	16
0.075	2	6	9	15	12	15	8	8	5	16	16	14	24

0.09	3	10	15	24	19	24	12	13	8	26	25	22	34
0.106	5	14	21	33	28	32	17	20	13	37	34	31	44
0.125	7	19	29	44	37	42	22	28	20	49	45	41	53
0.15	12	27	39	56	49	53	28	40	30	64	58	54	65
0.18	19	35	49	69	60	65	34	52	43	78	71	68	77
0.212	29	42	59	80	70	75	39	64	56	88	82	80	86
0.25	42	50	68	88	78	84	44	75	68	95	90	89	93
03	59	58	76	94	85	92	51	84	81	98	96	96	98
0.355	73	66	83	97	90	96	58	91	90	99	99	99	99
0.335	86	73	88	99	94	98	66	95	95	100	100	100	100
0.425	93	79	Q1	100	96	90	73	97	98	100	100	100	100
0.5	98	85	03	100	97	100	21 81	97	90	100	100	100	100
0.0	90	80	95	100	97	100	20	90	100	100	100	100	100
0.71	100	93	96	100	90	100	9 <i>1</i>	99	100	100	100	100	100
1	100	96	97	100	100	100	94	100	100	100	100	100	100
⊥ 1 10	100	00	00	100	100	100	00	100	100	100	100	100	100
1.10	100	90	90 100	100	100	100	33 100	100	100	100	100	100	100
1.4	100	99 100	100	100	100	100	100	100	100	100	100	100	100
1.7	100	100	100	100	100	100	100	100	100	100	100	100	100
	C12 1	C12.2	C12	C14	C1E	C16	C17	C10	C10 1	C10.2	C20 1	C20.2	C21 1
[]	C12.1	C12.2	[0/]	C14	[0/]	[0/]	[0/]	[0/]	[0/]	C19.Z	C20.1	C20.2	CZ1.1
	[70]	[70]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
0.032	1	1	1	0	0	1	1	0	0	0	0	0	0
0.038	2	1	1	0	1	1	1	0	1	1	1	1	0
0.045	5	5	1	1	2	1	1	1	1	1	1	1	1
0.053	0	5	2	1	3	2	2	1	2	2	2	2	1
0.003	10	9	4	1	0	4	4	2	5	3	4	3	2
0.075	15	14	8	2	11	/	/	4	5	0	/	5	4
0.09	22	20	13	3	1/	12	11	6	9	9	11	10	6
0.106	29	27	19	5	25	18	1/	9	12	14	16	14	10
0.125	37	35	27	8	34	26	25	13	18	19	22	20	16
0.15	47	45	37	13	46	38	36	20	25	27	32	29	25
0.18	59	57	48	20	58	52	50	29	36	38	43	41	38
0.212	71	70	60	28	69	65	63	39	48	50	55	53	51
0.25	83	83	72	38	/9	/8	//	51	61	62	67	65	65
0.3	93	93	84	51	87	89	89	64	73	74	79	77	78
0.355	98	98	92	61	93	96	96	74	81	81	87	85	87
0.425	100	100	97	70	96	98	99	82	86	86	91	89	93
0.5	100	100	99	75	98	100	100	86	88	88	93	92	97
0.6	100	100	100	80	99	100	100	90	91	90	95	93	99
0.71	100	100	100	84	100	100	100	92	93	92	96	95	99
0.85	100	100	100	87	100	100	100	94	95	94	97	96	100
1	100	100	100	90	100	100	100	96	97	96	98	98	100
1.18	100	100	100	94	100	100	100	98	98	98	99	99	100
1.4	100	100	100	97	100	100	100	99	99	99	100	100	100
1.7	100	100	100	99	100	100	100	100	100	99	100	100	100
2	100	100	100	100	100	100	100	100	100	100	100	100	100
_	C21.2	C21.3	C22	C23	C24	C25	C26.1	C26.2	C27	C28.1	C28.2	C29.1	C29.2
[mm]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
0.032	0	0	0	0	0	0	0	0	0	1	1	1	1
0.038	0	0	0	1	1	0	1	1	1	1	1	1	1
0.045	1	1	1	1	2	1	1	1	2	2	2	2	2

0.053	1	2	1	2	4	1	2	2	3	4	4	3	4
0.063	3	3	2	4	7	3	4	4	6	7	8	6	7
0.075	5	6	4	8	11	4	7	6	11	12	13	10	11
0.09	8	10	7	12	18	7	12	11	18	18	20	16	17
0.106	12	16	11	17	26	11	18	16	26	25	26	22	24
0.125	19	24	17	24	36	17	25	22	35	31	32	30	32
0.15	29	35	26	31	49	26	34	30	47	39	39	40	42
0.18	42	49	38	39	63	37	44	40	59	46	46	51	53
0.212	56	62	52	45	75	49	53	50	70	52	52	62	64
0.25	69	74	66	52	85	62	63	61	81	58	57	73	74
0.3	81	84	81	60	94	74	73	72	90	64	64	83	85
0.355	89	91	91	66	97	83	79	80	96	70	69	91	91
0.425	95	95	96	73	99	91	85	86	99	76	75	96	96
0.5	97	97	99	79	100	95	89	89	100	81	80	98	98
0.6	99	98	100	85	100	98	91	92	100	87	86	99	100
0.71	99	99	100	91	100	99	93	94	100	93	92	100	100
0.85	100	99	100	96	100	100	95	96	100	97	96	100	100
1	100	100	100	98	100	100	97	97	100	99	99	100	100
1.18	100	100	100	100	100	100	98	98	100	100	100	100	100
1.4	100	100	100	100	100	100	99	99	100	100	100	100	100
1.7	100	100	100	100	100	100	99	99	100	100	100	100	100
2	100	100	100	100	100	100	100	100	100	100	100	100	100
	A2	A5	A11	A12	A13	A14	A16	A18	A20	A21	A22	A23	A25

[mm]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.025	24	18	11	8	6	40	9	23	6	14	27	8	37
0.075	41	57	38	59	82	83	60	89	76	71	86	69	80
0.125	49	71	54	74	92	90	81	98	87	80	95	79	90
0.25	63	86	80	93	98	99	100	100	96	92	99	90	98
0.5	79	94	98	99	100	100	100	100	100	98	100	95	98
1	100	100	100	100	100	100	100	100	100	100	100	100	100
2	100	100	100	100	100	100	100	100	100	100	100	100	100
3	100	100	100	100	100	100	100	100	100	100	100	100	100
5	100	100	100	100	100	100	100	100	100	100	100	100	100

	A26	A28	A29
[mm]	[%]	[%]	[%]
0	0	0	0
0.025	13	35	40
0.075	85	58	67
0.125	96	68	74
0.25	100	81	83
0.5	100	92	93
1	100	100	100
2	100	100	100
3	100	100	100

# Appendix 7: Incubation study method (DGT analysis)

A 2-7-14 week incubation with six selected samples and extraction of P using Diffusive Gradients in Thin films (DGTs). Substrates included the dry sludge, the LT-CFB ash (original and oxidized), the TwoStage gasifier ash (original and oxidized) and the Incineration ashes from the fluid bed incineration facility. The soil used for the incubation study was a sandy loam soil with 16.5% clay that was collected in 2014 from the upper layer of a nutrient depletion trial on the University of Copenhagen's experimental research farm in Taastrup, Denmark. After collection, the soil was air-dried and passed through a 2 mm sieve. The soil had a pH of 5.2 and was mixed with quartz sand in a 50/50 w/w mixture for the incubation study.

All substrates used for the incubation study were pre-dried and the particle size range and average particle sizes were determined and homogenized to reduce the influence of particle size on the P extractability of the different substrates. The process was divided into the following steps: 1) Grinding in a Mahlkönig Kenia Disc grinder 2) Sieving using only a 0.125 mm sieve on a Retch Vibro Sieve 3) The fraction larger than 0.125 mm was then crushed in a FRITSCH Mortar Grinder Pulverisette 2 at maximum load 4) Splitting the crushed fraction as in step 2 and redoing step 2-3 until at least 90% of the total sample mass passed the 0.125 mm sieve and all particles were smaller than 0.25 mm 5) The different fractions are all mixed together and the final particle size distribution of the substrate was determined in the same Retch Vibro Sieve using sieves 25 µm, 75 µm, 125 µm and 250 µm.

Triplicates of 50 g soil/quartz sand mixture and CPSE substrate samples corresponding to 80 mg P kg<sup>-1</sup> soil mixture were prepared. The mixtures were shaken thoroughly and watered to 50% of the soil mixtures water holding capacity with demineralized water. Sustrate-free control mixtures of soil and sand and samples with a mineral P reference  $(KH_2PO_4)$  were included in the study as well. After shaking and watering the samples were incubated in a climate chamber (Memmert Celsius HPP749, Germany) for 2 to 14 weeks. Water content in all samples was monitored by regular weighing and the water content adjusted back to 50% of water holding capacity whenever it was found to be below 40 %. In this way, the water content was adjusted 30 times during 14 weeks of incubation. Temperature of the climate chamber during the incubation was 20.4 ± 0.4 °C. The relative humidity of the climate chamber during the incubation was 93 ±5 %RH

On the last day of incubation, the samples for DGT analysis are watered to 100% of water holding capacity and settled by gentle tapping on a hard surface. The container was closed with a lid to avoid water evaporation during the following equilibration lasting for 24h at room temperature. Subsequently, the soil was mixed and commercially available DGT devices (DGT Research Ltd., Lancaster, UK) were applied to the single samples by smearing some soil paste onto the filter layer of the device and pressing the unit gently onto the soil surface in the incubation container. After 24 h application time at room temperature, the DGT devices were removed from soil, rinsed on the filter paper with Milli-Q water and opened. The ferrihydrite-containing binding gel was eluted in 1 mL of 1 M HNO<sub>3</sub>. After another 24 h, the gel was removed and aliquots of the eluate were diluted in Milli-Q water. Samples were stored refrigerated (5 °C) before PO<sub>4</sub>-P analysis on a Flow Injection Analyser (FIAstar 5000, FOSS, Denmark), connected to an autosampler (5027, FOSS, Denmark). The average interfacial concentration of P (CDGT) was calculated according to Davison and Zhang (2012) [272].

### Appendix 8: EaseTech LCA model illustration and normalized results

Modeling conducted in EaseTech 2013 Version 2.0.0



Reference model with direct application of sewage sludge to local farm soil



Scenario model with LT-CFB gasification of sewage sludge at Asnæs powerplant. The gas is burned in the pulverized coal boiler of the power plant unit 2, and the ashes are subsequently spread on local farm soil.

Normalized results from LCA study. Characterization factors, impact assessment factors and normalization factors from "ILCD recommended – 2013 Prosuit Global NR – DTU Updated".

Reference scenario	SUM	Sludge manufac- turing	Transpor- tation	Gasification process	CHP production	Use on land (sludge)	Fertilizer effect
IPCC 2007, climate change,	0.533	0.388	0.000			0.238	-0.093
GWP 100a_updated PE	0.401	0.072	0.000			0 512	0.004
terrestrial acidification PE	0.491	0.072	0.000			0.513	-0.094
ReCiPe v.1.08 Midpoint (H)		0.045	0.000			4.955	
w/o LT, marine eutrophication	4.273	0.015	0.000			4.266	-0.008
w/o LT, MEP w/o LT PE							
ReciPe V.1.08 Midpoint (H)	0.044	0.005	0.000			0.001	0.025
oxidant formation w/o LT.	0.041	0.065	0.000			0.001	-0.025
POFP w/o LT PE							
Accumulated Exceedance,	1.018	0.112	0.000			0.990	-0.084
terrestrial eutrophication PE							
EDIP w/o LT, environmental							
impact w/o LT, stratospheric	0.000	0.000	0.000			0.000	0.000
w/o LT PF							
USEtox, human toxicity.							
carcinogenic, W/O Longterm,	1.695	0.016	0.000			1.839	-0.160
DTU updated version PE							
USEtox, human toxicity, non-	7 102	0.006	0.000			10 00E	E 707
carcinogenic, W/O Longterm,	7.183					12.005	-3.707
DTU updated version PE							
Particulate matter, updated	0.189	0.044	0.000			0.204	-0.059
II CD 2011) PF							
ReCiPe v.1.08 Midpoint (H)							
w/o LT, ionising radiation w/o	0.008	0.008	0.000			0.000	0.000
LT, IRP_HE w/o LT PE							
ReCiPe v.1.08 Midpoint (H)							
w/o LT, freshwater	-3.762	0.014	0.000			1.316	-5.093
eutrophication w/o LT, FEP							
W/O Longterm. DTU updated	30.314	0.025	0.001			35.987	-5.699
version PE							
CML 2012, resources,	0.000	0.067	0.000			0.001	
depletion of abiotic resources,	0.069	0.067	0.000			0.001	0.000
fossil, 2012 PE							
CML 2013, resources,	0.378	0.508	0.000			0.000	-0.131
(reserve base) PE							

	LT-CFB gasification scenario	SUM	Sludge manufac- turing	Transpor- tation	Gasification process	CHP production	Use on land (ash)	Fertilizer effect
-	IPCC 2007, climate change, GWP 100a_updated PE	-0.134	0.388	0.001	0.062	-0.569	-0.010	-0.007
_	Accumulated Exceedance, terrestrial acidification PE	-0.021	0.072	0.000	0.014	-0.100	0.011	-0.018
	ReCiPe v.1.08 Midpoint (H) w/o LT, marine eutrophication w/o LT, MEP w/o LT PE	0.087	0.015	0.000	0.002	-0.015	0.085	0.000
	ReCiPe v.1.08 Midpoint (H) w/o LT, photochemical oxidant formation w/o LT, POFP w/o LT PE	0.003	0.065	0.000	0.010	-0.071	0.000	-0.003
	Accumulated Exceedance, terrestrial eutrophication PE	0.016	0.112	0.000	0.019	-0.132	0.020	-0.004
_	EDIP w/o LT, environmental impact w/o LT, stratospheric ozone depletion, ODP 100a w/o LT PE	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	USEtox, human toxicity, carcinogenic, W/O Longterm, DTU updated version PE	0.081	0.016	0.000	0.001	0.003	0.205	-0.143
-	USEtox, human toxicity, non- carcinogenic, W/O Longterm, DTU updated version PE	-1.643	0.006	0.002	0.004	-0.004	3.511	-5.161
-	Particulate matter, updated from Humbert 2009 (after ILCD 2011) PE	-0.067	0.044	0.000	0.018	-0.120	0.004	-0.014
	ReCiPe v.1.08 Midpoint (H) w/o LT, ionising radiation w/o LT, IRP_HE w/o LT PE	0.005	0.008	0.000	0.000	-0.004	0.000	0.000
-	ReCiPe v.1.08 Midpoint (H) w/o LT, freshwater eutrophication w/o LT, FEP w/o LT PE	-0.518	0.014	0.000	0.000	-0.010	1.237	-1.760
_	USEtox, ecotoxicity, total, W/O Longterm, DTU updated version PE	14.665	0.025	0.005	0.002	-0.009	19.425	-4.783
_	CML 2012, resources, depletion of abiotic resources, fossil, 2012 PE	-0.677	0.067	0.002	0.089	-0.837	0.000	0.000
_	CML 2013, resources, depletion of abiotic resources (reserve base) PE	0.455	0.508	0.001	0.002	-0.009	0.000	-0.046

# CLOSING THE

Utilization of Secondary Resources by Low Temperature Thermal Gasification


Around the world, human societies consume large amounts of raw materials and energy. As a consequence hereof, the piles of degraded materials (secondary resources) in the world grow larger and the piles of essential raw materials (primary resources) grow smaller.

Both piles are resources. We need to manage them better.

This study therefore seeks to find new ways to substantially improve the current practice related to management of secondary resources. It is in this regard investigated how to apply low temperature thermal gasification in the beneficial utilization of secondary resources to produce non-fossil energy and recover irreplaceable and vital inorganic elements.







**DTU Chemical Engineering** Department of Chemical and Biochemical Engineering

Technical University of Denmark, Department of Chemical and Biochemical Engineering, DTU Risø Campus, Building 313, Frederiksborgvej 399, 4000 Roskilde, Denmark

