7. HTP-Fachforum

Hydrothermale Prozesse zur stofflichen und energetischen Wertschöpfung

27./28. SEPTEMBER 2022 | LEIPZIG, DBFZ

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HTP
Hydrothermale Prozesse

IMPRESSUM

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*Sehr geehrte Referent*innen und Teilnehmer*innen des HTP-Fachforums 2022,*

zuerst möchten wir uns bei allen bedanken, die zum Erfolg unseres 7. Fachforums Hydrothermale Prozesse beigetragen haben. Nach einem pandemiebedingten Fachforum als Online-Konferenz war es eine besondere Freude, wieder so viele Interessent*innen persönlich begrüßen zu können. Allen war das Bedürfnis, sich persönlich auszutauschen, anzumerken.

Wir konnten gemeinsam inhaltlich an vieles anknüpfen, was bereits traditionell Thema unserer Veranstaltungen ist. Dabei haben uns die in letzter Zeit forcierten Bemühungen um den Klimaschutz und die aktuellen politischen Ereignisse mit ihrem Einfluss auf den Rohstoffmarkt wie nie zuvor die Bedeutung und die Dringlichkeit unserer Arbeiten aufgezeigt.

Inhaltliche Schwerpunkte stellten neben der Herstellung und Anwendung von festen Kohlenstoff-materialien der Einsatz der hydrothermalen Prozesse zur Nährstoffrückgewinnung und für agrarwirtschaftsnahe Kreislaufsysteme sowie hydrothermale Prozesse zur Herstellung flüssiger Energieträger und Chemikalien dar. Zu Bereichen wie der Energiewende, der Zukunft der Entsorgungswirtschaft, der Versorgung mit organischen Materialien und Chemikalien ohne fossile CO2-Emissionen und der nachhaltigen Mobilität können und müssen wir einen Beitrag liefern.

Wesentliches Highlight neben der Vielzahl hervorragender Poster und Vorträge waren auch die vielfältigen Diskussionen in großer wie in kleiner Runde. Es ist immer eine besondere Freude für das DBFZ, dafür den Rahmen bieten zu können.

Vorträge wie Diskussionen verdeutlichten die Chancen aber auch die immer noch bestehenden Herausforderungen, die mit den hydrothermalen Verfahren, aber auch den politischen und gesellschaftlichen Rahmenbedingungen verbunden sind. Wir glauben, es ist unser aller Wunsch, dass mehr gute Ideen zu erfolgreichen Anwendungen werden.

Wir sehen erwartungsvoll dem nächsten HTP-Fachforum 2024 entgegen und würden uns freuen, Sie dann wieder begrüßen zu dürfen.

M. Klemm

Dr. Marco Klemm, DBFZ

Opening Session

Dr. Patrick Biller, Universität Hohenheim

From laboratory to large-scale hydrothermal liquefaction Current challenges and opportunities

Dr. Patrick Biller
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Dr. Stephan Schleissing, Ludwig-Maximilians-Universität München

Ethische Bewertung von Energie aus Biomasse

Dr. Stephan Schleissing
Ludwig-Maximilians-Universität München

Session I:
HTL I

Katarzyna Swiatek, Universität Hohenheim

Production of hydroxymethylfurfural (HMF) from biomass in on-farm biorefinery

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The production of bio-based platform chemicals has recently been the subject of wide research interest. Biomass can be used to synthesized various platform chemicals like levulinic acid, furfural, or 5-hydroxymethylfurfural (HMF). The HMF is a versatile intermediate that offers a wide range of applications, e.g. bio-polymer production. The industrial-scale production of HMF has not yet been realized, even though the synthesis of HMF from fructose is highly efficient. Agricultural raw materials, which contains cellulose, sucrose or inulin, are low-priced starting materials for the manufacture of hexoses.

Agricultural residues that can be directly transformed into HMF are chicory roots. The forced chicory roots are non-edible biomass which is an important advantage in a new generation of biorefineries. Furthermore, inulin is composed of fructose molecules which is the most promising material for synthesizing HMF. In order to extract sugars from the roots, a counter-current continuous extractor was designed. The extract thus obtained contains 3-5% sugars, which is sufficient for further HMF synthesis. HMF synthesis is carried out under hydrothermal conditions at a temperature of about 200 °C and a pressure of 24 bar. In order to determine the possibility of using agricultural biomass for the synthesis of HMF, comparison of HMF synthesis from fructose with chicory roots was done. Research were conducted on the continuous units with TRL 6. The study shows that the biomass has the potential for the production of HMF as part of an environmentally friendly process in a biorefinery. Nevertheless, further research in this direction is needed, especially in the techno-economic field.

In the course of bioeconomy, HMF production from biomass could be conducted in decentralized biorefineries that work with agricultural residues. However, HMF-production is only a part of the biorefinery concept developed. In a biorefinery, also furfural from hemicellulose and the solid fraction can be produced. In addition, the solved organic compounds can be used to generate heat for the process by a biogas production combined with a power plant. Therefore, a stream coupling between the biorefinery and the biogas plant is currently being developed with the help of the AspenPlus®. A holistic approach to the on-farm biorefinery concept in coupling with a biogas plant is crucial for the efficient large-scale production of platform chemicals.

Christian Klüpfel, Deutsches Biomasseforschungszentrum

Hydrothermal liquefaction of waste biomass: a holistic approach for various input materials

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The treatment of wet biomass at near critical conditions (647 K, 22 MPa), more commonly referred to as hydrothermal liquefaction, is a technique for energetic and material wise value creation. The main product of said process is the biocrude, an energy dense fuel precursor which can be used for aviation and shipping. However, depending on the input material, biocrude yields can be as low as 10 ma. % and related challenges can go beyond maximum biocrude yield. Often, most of the carbon is found in the aqueous or solid phase, which are considered unwanted byproducts. Furthermore, concentrations of various elements in the biomass, like phosphorus,
potassium or nitrogen, require the recovery of said nutrients.

This study aims to highlight individual pathways for diverse waste biomass, i.e. sewage sludge, fatty wastes from biodiesel production and digestate. These biomasses were analysed for their biochemical composition and subjected to hydrothermal liquefaction at various processing conditions. Elemental and molecular analyses of the product phases were performed to assess energy recovery and the mobility of nutrients. The processed input materials necessitate and highlight different exploitation schemes: From high biocrude yield to enhanced energy recovery by aqueous phase treatment via wet oxidation followed by anaerobic digestion and nutrient recovery via the solid phase. These will be reviewed in this presentation.

Maximilian Wörner, Karlsruher Institut für Technologie (KIT)

Direkte hydrothermale Verflüssigung (HTL) von Schwarzlauge

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Schwarzlauge ist ein Nebenprodukt der Papierindustrie, genauer dem Kraft-Prozess. Es handelt sich um eine alkalische Lösung, in der Lignin sowie Hemicellulose zusammen mit den Aufschlusschemikalien gelöst sind. Lignin ist ein natürliches Makromolekül bestehend aus sehr vielen verzweigten aromatischen Strukturen. Mithilfe der hydrothermalen Verflüssigung unter hohem Druck (200 – 300 bar) und Temperaturen (300 – 400 °C) ist es möglich, diese Struktur aufzubrechen und das Lignin zu depolymerisieren. Dabei entsteht ein Biocrude, was anschließend zu Kraftstoff für Luft- und Schifffahrt aufbereitet werden kann. Im Rahmen des EU Projektes „Black Liquor 2 Fuels" (BL2F) soll die Schwarzlauge direkt in dem Verflüssigungsprozess verwendet und das Lignin nicht zuvor extrahiert werden. Somit können energiereiche Prozessschritte, wie z.B. mehrstufige Verdampfungsschritte, eingespart und der Vorteil der HTL, nasse Biomasse einzusetzen, ausgenutzt werden

Um die Abbaureaktionen zu verstehen wurden daher Batch Experimente mit Schwarzlauge in Mikroautoklaven durchgeführt. Dabei wurden die Auswirkungen verschiedener Parameter wie Temperatur, Haltezeit oder Salzkonzentration auf den Prozess untersucht. Alle Produktphasen (Gas, Flüssigphase, Feststoff) wurden mittels verschiedener Analyseverfahren (ICP, EA, GC-MS, GC-FID, TC/TOC, …) untersucht und die einzelnen Experimente miteinander verglichen. Außerdem wurde die organische Flüssigphase extrahiert und ebenfalls analysiert. Dabei wurde zum einen die Ausbeuten verschiedener aromatischer Monomere wie Catechol oder Syringol bestimmt und zum anderen das durchschnittliche Molekulargewicht des Biocrudes mithilfe einer GPC Analyse ermittelt. Das Molekulargewicht dient als Indikator der Depolymerisierungsreaktion. Um die während des Prozesses stattfindende Depolymerisierung des Lignins unter dem Einfluss der Salze besser zu verstehen, wird auf Basis der experimentellen Daten ein reaktionskinetisches Modell entwickelt. Zusätzlich soll dieses Modell durch kontinuierliche Experimente validiert werden. Ein Schwerpunkt liegt dabei darauf die Bildung und den Abbau von Oligomeren zu beschreiben, die vermutlich als Zwischenprodukt der Depolymerisierung entstehen. Letztendlich zeigt die Arbeit, dass es möglich ist, Schwarzlauge direkt für die HTL zu benutzen.

Juliano Souza dos Passos, University Aarhus

Chemical recycling of synthetic polymers via hydrothermal liquefaction

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Session II:
Nährstoffe, HTP und Biogas

Timo Zerback, Deutsches Biomasseforschungszentrum

Hydrothermal pretreatment of biogenic residues within a biorefinery concept for the production of renewable methane

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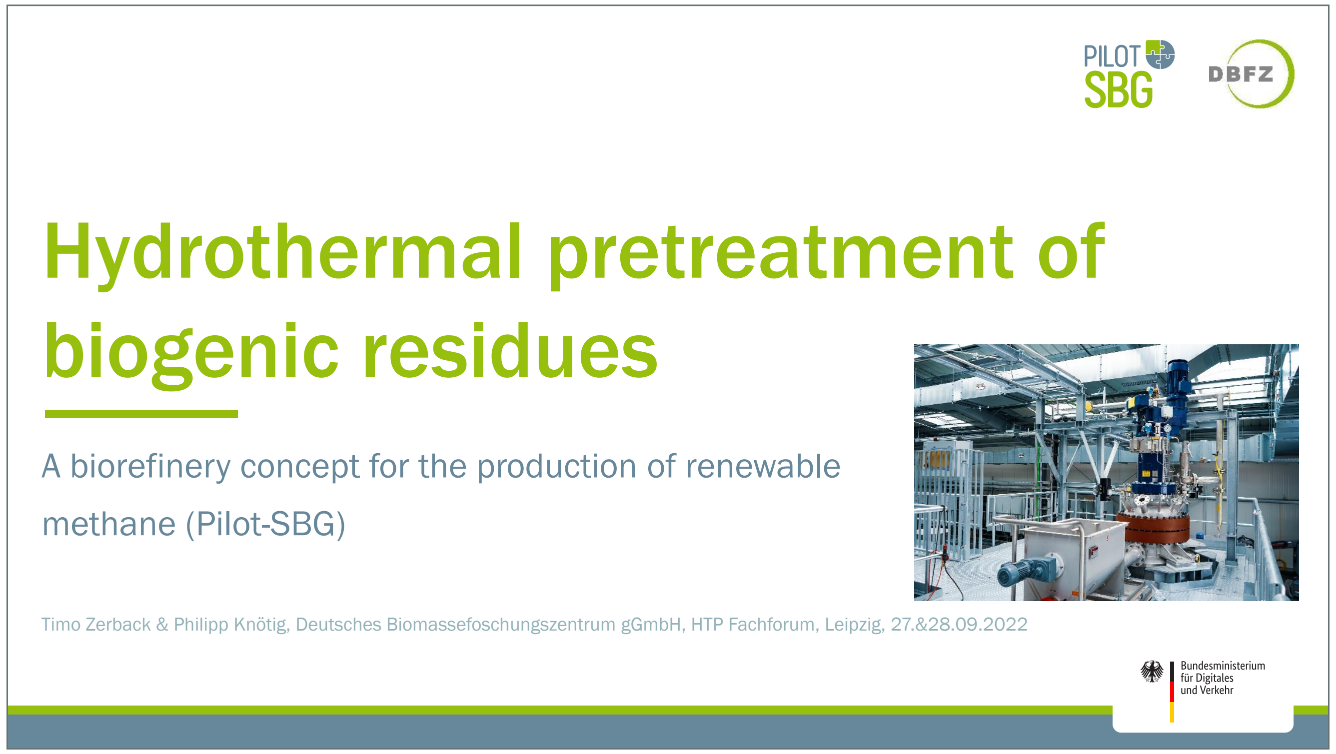
Die steigende Nachfrage nach erneuerbaren Energiequellen und bedarfsorientierter Strombereitstellung macht die anaerobe Vergärung (AD) zu einer der vielversprechendsten Technologien. Neben Energiepflanzen gewinnt die Nutzung urbaner und landwirtschaftlicher Rest- und Abfallstoffe (z.B. Bioabfälle, tierische Exkremente, Getreidestroh) aufgrund ihres mitunter noch ungenutzten, technischen Potenzials von 21-50 PJ zunehmend an Bedeutung. Weiterhin gilt Biomethan, wenn es verkehrlich genutzt wird und aus Rest- und Abfallstoffen nach RED II Anhang IX Teil A hergestellt wurde, als fortschrittlicher Biokraftstoff.

Im Rahmen eines durch das BMDV geförderten Forschungsprojektes (Pilot SBG) wurde eine Pilotanlage zur Produktion von Biogas aus biogenen Reststoffen entwickelt (1,8-2,5 m^3 (i. N.) d-1 erneuerbares Methan aus 22-62 kg d-1 Reststoffen). Teil dieser Prozesskette ist ein 730 L großer Mehrzweck-Reaktor für den hydrothermalen Aufschluss, aber auch andere Verfahren wie die hydrothermale Carbonisierung. Der Einfluss der hydrothermalen Vorbehandlung (HTP) auf die AD von Weizenstroh wurde in Voruntersuchungen sowohl unter diskontinuierlichen als kontinuierlichen Bedingungen untersucht.

Im Rahmen der diskontinuierlichen Versuchsreihe (Hobenheimer Biogasertrags) konnte durch Variation der HTP-Temperaturen (160-180 °C) und Verweilzeiten (15-45 min) in allen Fällen ein signifikanter Anstieg des Biomethanpotenzials (BMP) beobachtet werden. Das höchste BMP (310 mL CH4 g-1 organischer Trockensubstanz (oTS)) (± 14 mL CH4 g-1 oTS) wurde nach einer Vorbehandlung bei 160 °C für 45 min erreicht, was einer Steigerung von 19 % gegenüber unbehandeltem Weizenstroh (261 mL CH4 g-1 oTS) (± 15 mL CH4 g-1 oTS) entspricht. Die Ergebnisse eines multiplen linearen Regressionsmodells zeigten, dass die Solubilisierung von organischem Material von Temperatur und Zeit beeinflusst wird. Darüber hinaus wurde anhand von zwei verschiedenen kinetischen Modellen erster Ordnung eine Erhöhung der AD-Rate während der Hydrolyse durch die Vorbehandlung festgestellt. Die zunehmende Intensität der Vorbehandlungsbedingungen ging jedoch mit einem abnehmenden Trend bei der Umwandlung von Zwischenprodukten in Methan einher.

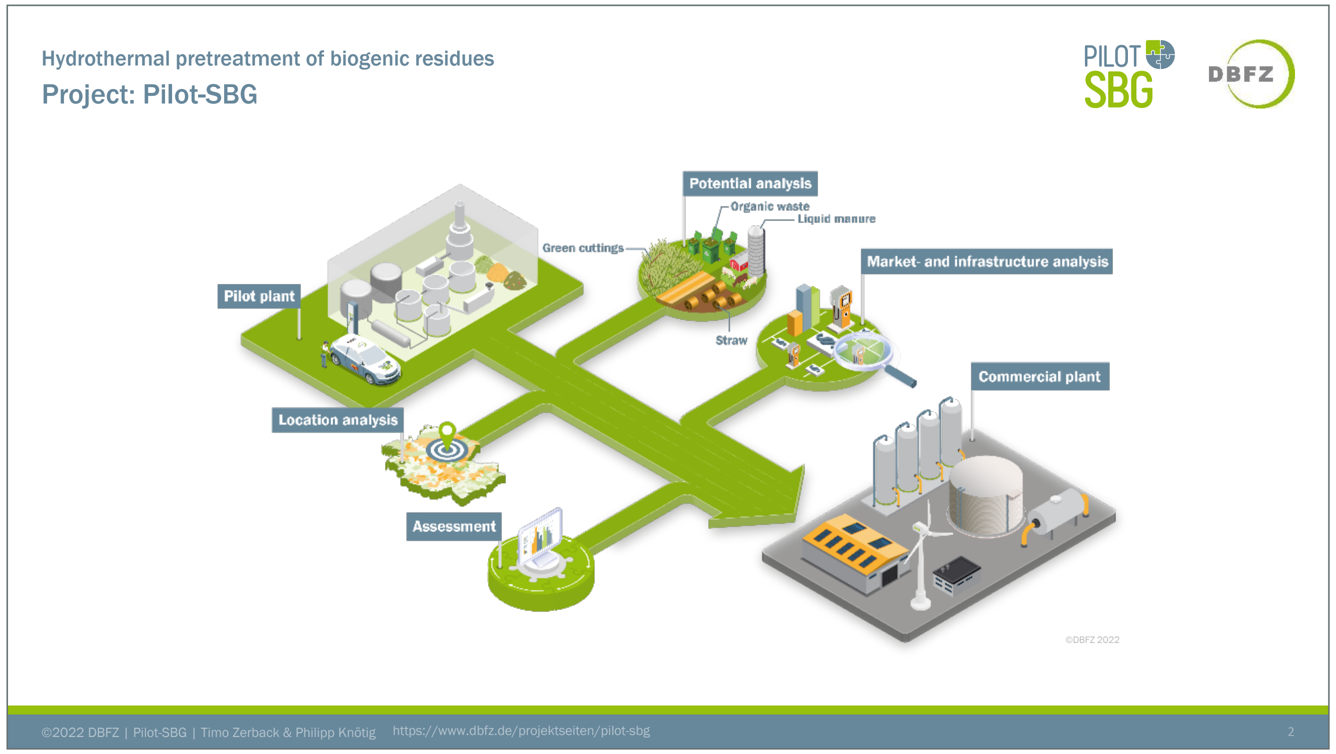
Im Rahmen der kontinuierlichen Versuchsreihe konnten die Effekte der HTP ebenfalls nachgewiesen werden. Durch Variation der anaeroben Prozessparameter (Raumbelastung BR = 3,0 goTS L-1 d-1; Verweilzeit HRT = 18,2 d) konnte unter vergleichsweise milden Aufschlussbedingungen der HTP (160 °C, 15 min) eine signifikante Steigerung der spezifischen Methanproduktion (233 mLCH4 g-1 oTS) (± 17,3 mLCH4 g-1 oTS) um 27 % gegenüber der Referenz, die mit unbehandeltem Weizenstroh (182 mLCH4 g-1 oTS) (± 10,64 mLCH4 g-1 oTS) beschickt wurde, festgestellt werden. Harschere Aufschlussbedingungen (z. B. 180 °C, 45 min) oder längere Verweilzeiten (HRT > 18,2 d) erwiesen sich aufgrund einer merklich instabileren Prozessführung hingegen als ungeeignet.



Hydrothermal pretreatment of biogenic residues

A biorefinery concept for the production of renewable methane (Pilot-SBG)

Timo Zerback & Philipp Knötig, Deutsches Biomassefoschungszentrum gGmbH, HTP Fachforum, Leipzig, 27.&28.09.2022



Hydrothermal pretreatment of biogenic residues

Project: Pilot-SBG

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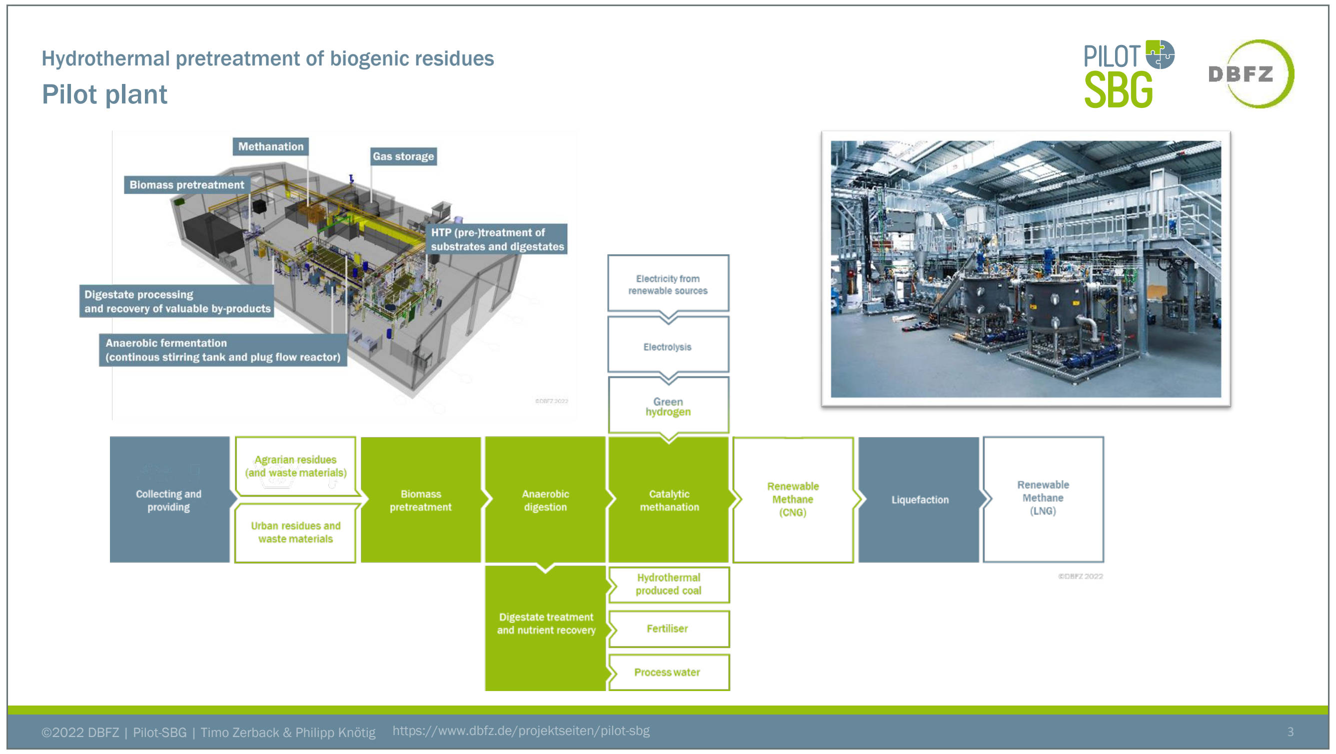

Hydrothermal pretreatment of biogenic residues

Pilot plant

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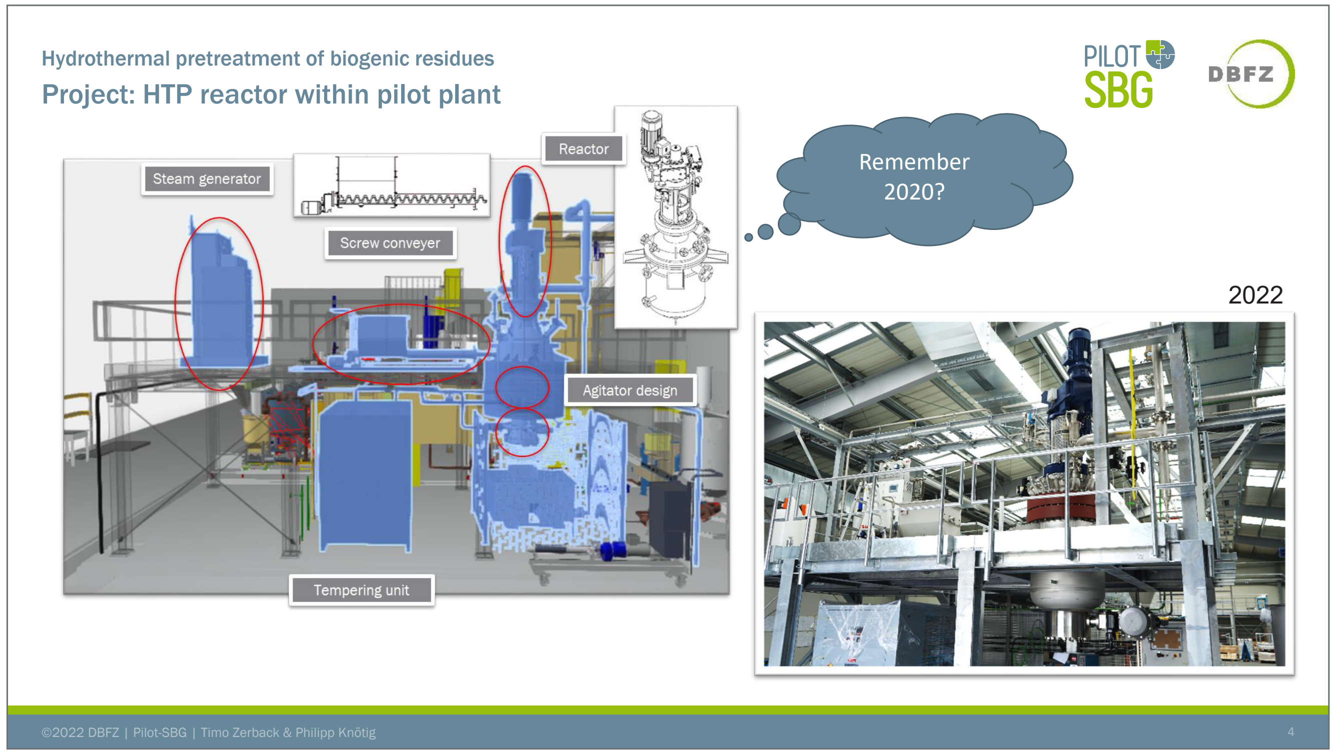

Hydrothermal pretreatment of biogenic residues

Project: HTP reactor within pilot plant

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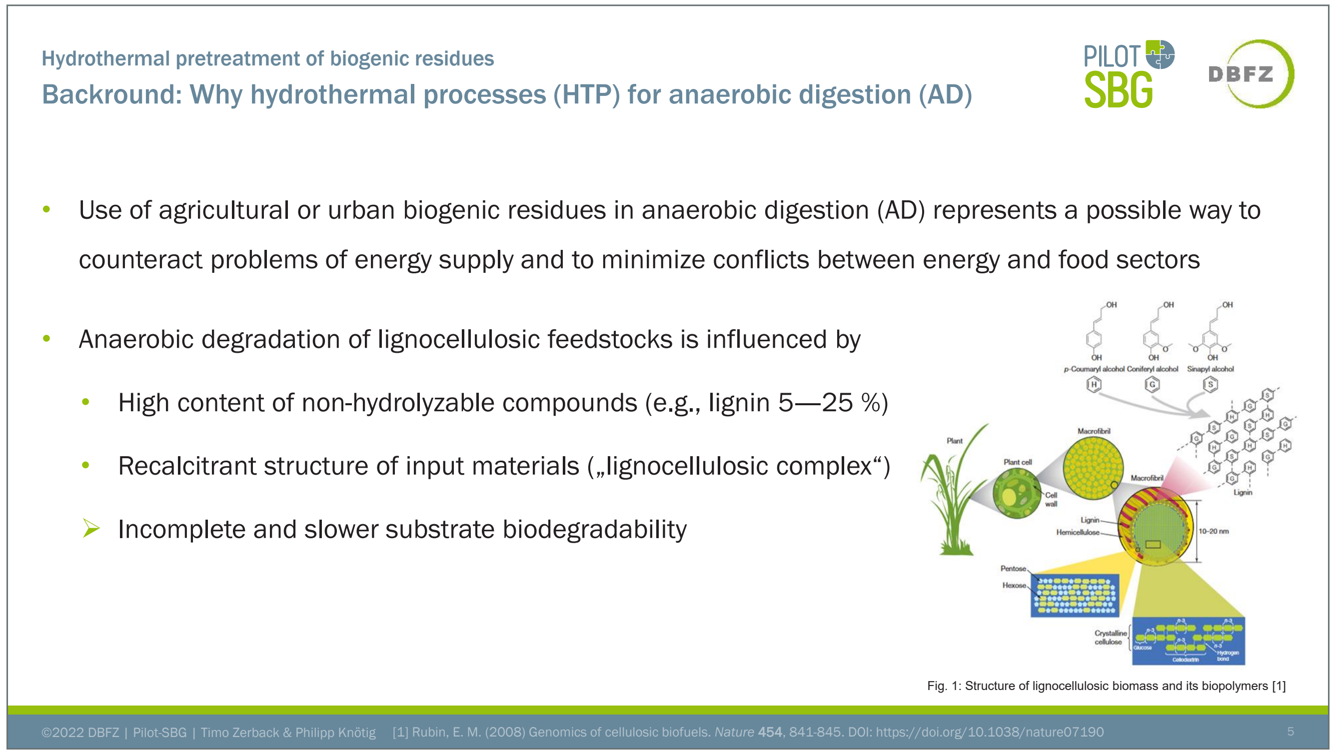

Hydrothermal pretreatment of biogenic residues

Backround: Why hydrothermal processes (HTP) for anaerobic digestion (AD)

- Use of agricultural or urban biogenic residues in anaerobic digestion (AD) represents a possible way to counteract problems of energy supply and to minimize conflicts between energy and food sectors
- Anaerobic degradation of lignocellulosic feedstocks is influenced by
  - High content of non-hydrolyzable compounds (e.g., lignin 5—25 %)
  - Recalcitrant structure of input materials („lignocellulosic complex“)
  - ➢ Incomplete and slower substrate biodegradability

Fig. 1: Structure of lignocellulosic biomass and its biopolymers [1]

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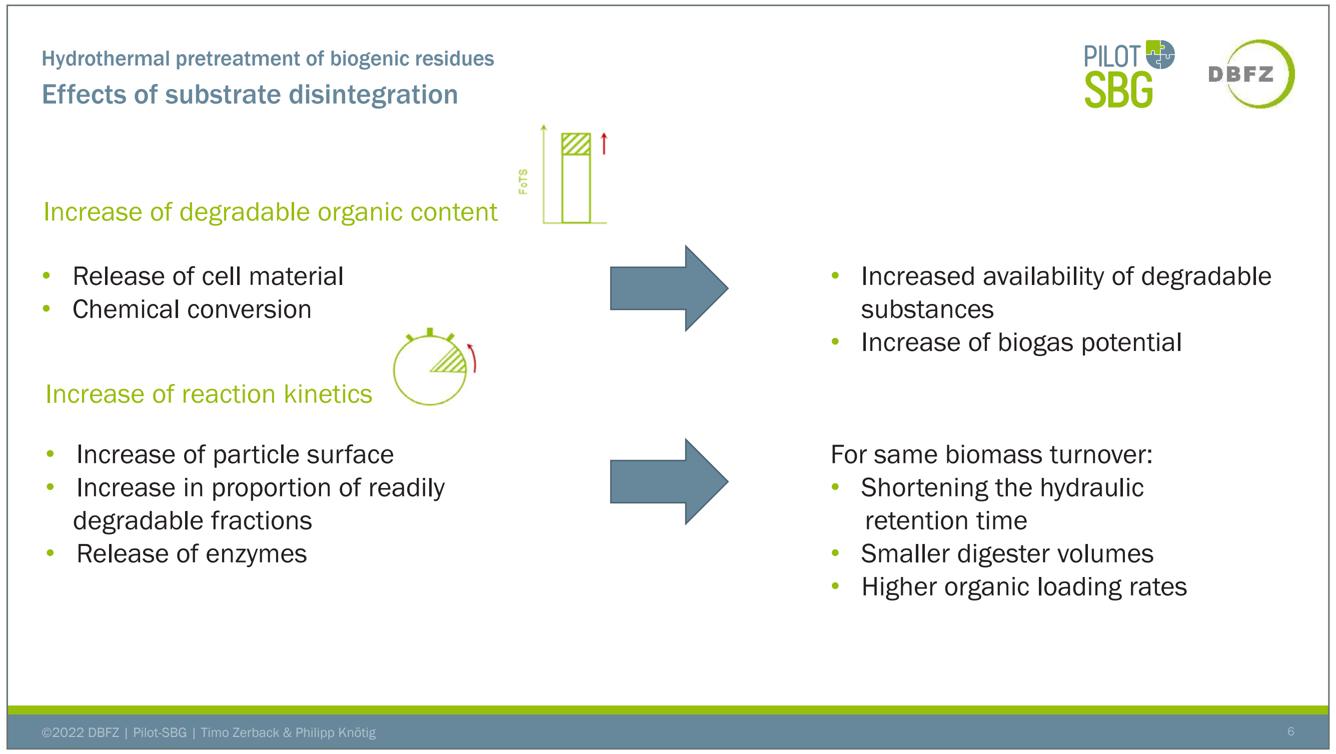

Hydrothermal pretreatment of biogenic residues

Effects of substrate disintegration

Increase of degradable organic content

- Release of cell material
- Chemical conversion

- Increased availability of degradable substances
- Increase of biogas potential

Increase of reaction kinetics

- Increase of particle surface
- Increase in proportion of readily degradable fractions
- Release of enzymes

For same biomass turnover:
- Shortening the hydraulic retention time
- Smaller digester volumes
- Higher organic loading rates

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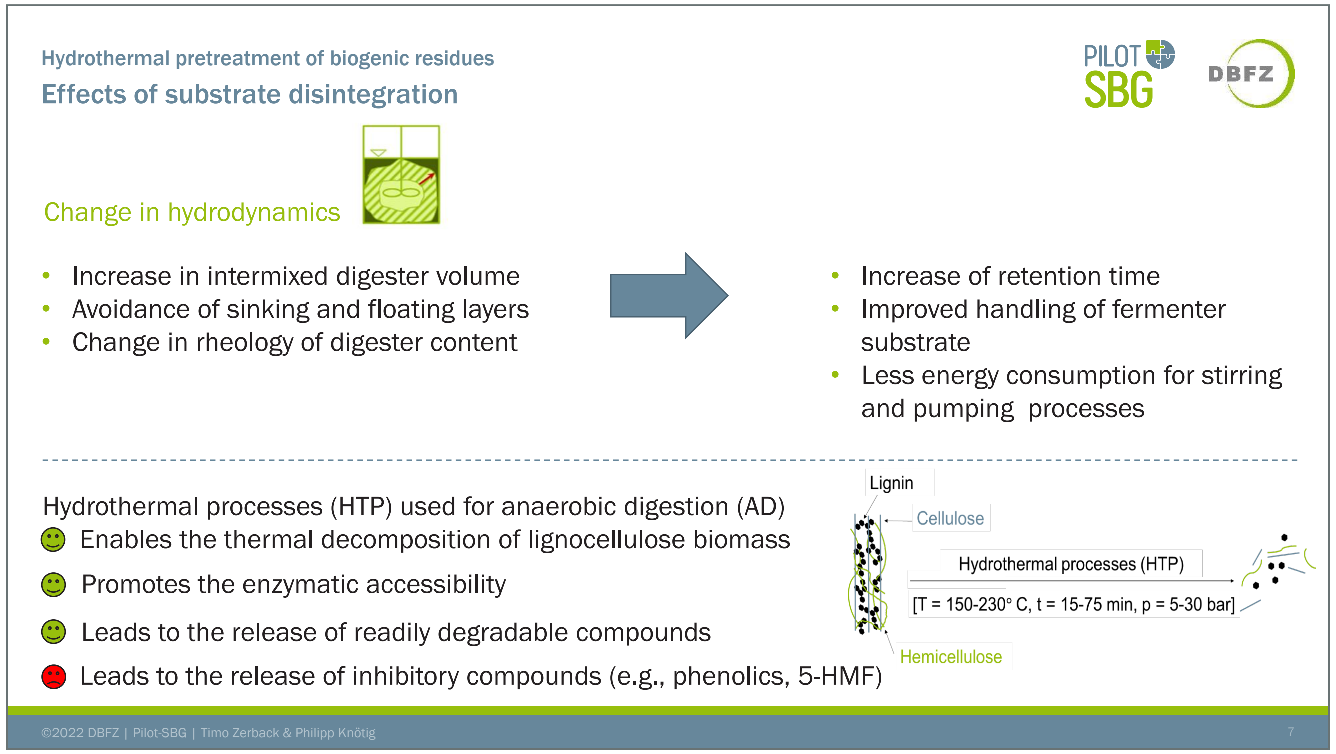


Hydrothermal pretreatment of biogenic residues

Effects of substrate disintegration

Change in hydrodynamics

- Increase in intermixed digester volume
- Avoidance of sinking and floating layers
- Change in rheology of digester content

- Increase of retention time
- Improved handling of fermenter substrate
- Less energy consumption for stirring and pumping processes

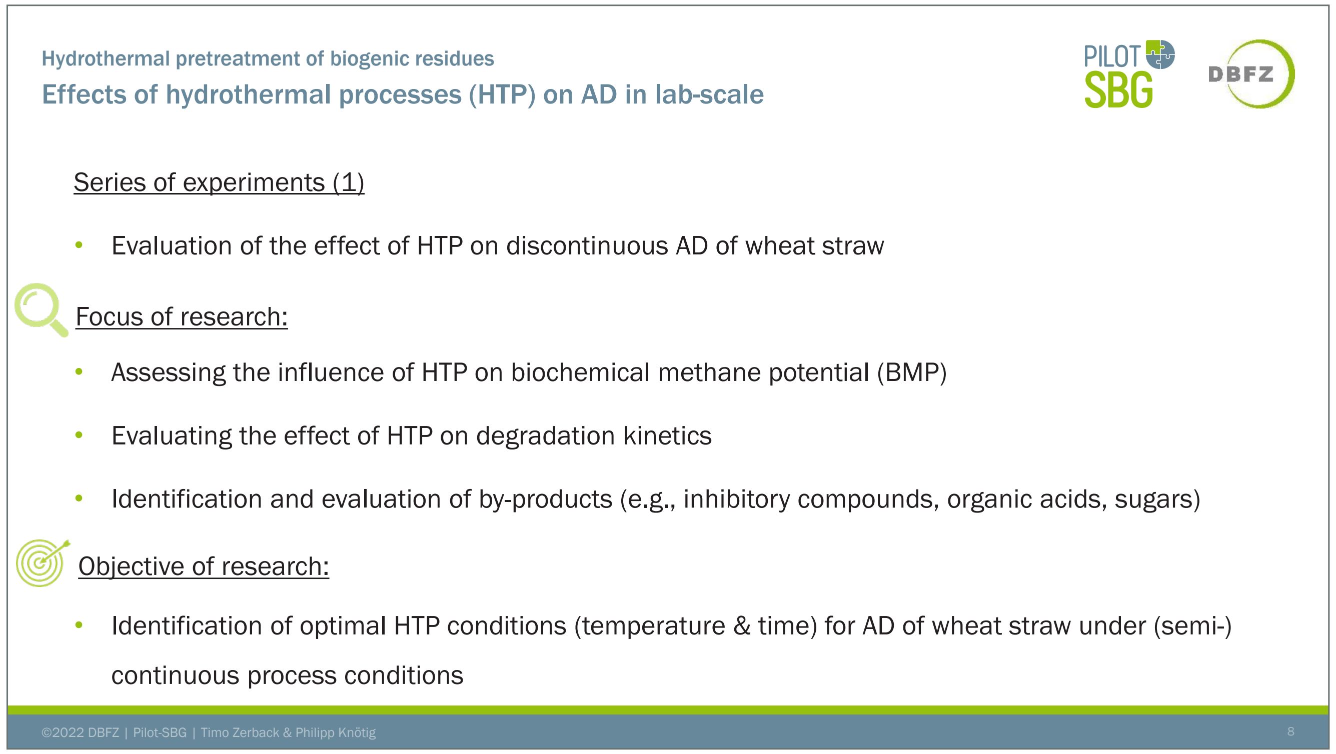
Hydrothermal processes (HTP) used for anaerobic digestion (AD)

☺ Enables the thermal decomposition of lignocellulose biomass

☺ Promotes the enzymatic accessibility

☺ Leads to the release of readily degradable compounds

☹ Leads to the release of inhibitory compounds (e.g., phenolics, 5-HMF)



Hydrothermal pretreatment of biogenic residues

Effects of hydrothermal processes (HTP) on AD in lab-scale

Series of experiments (1)

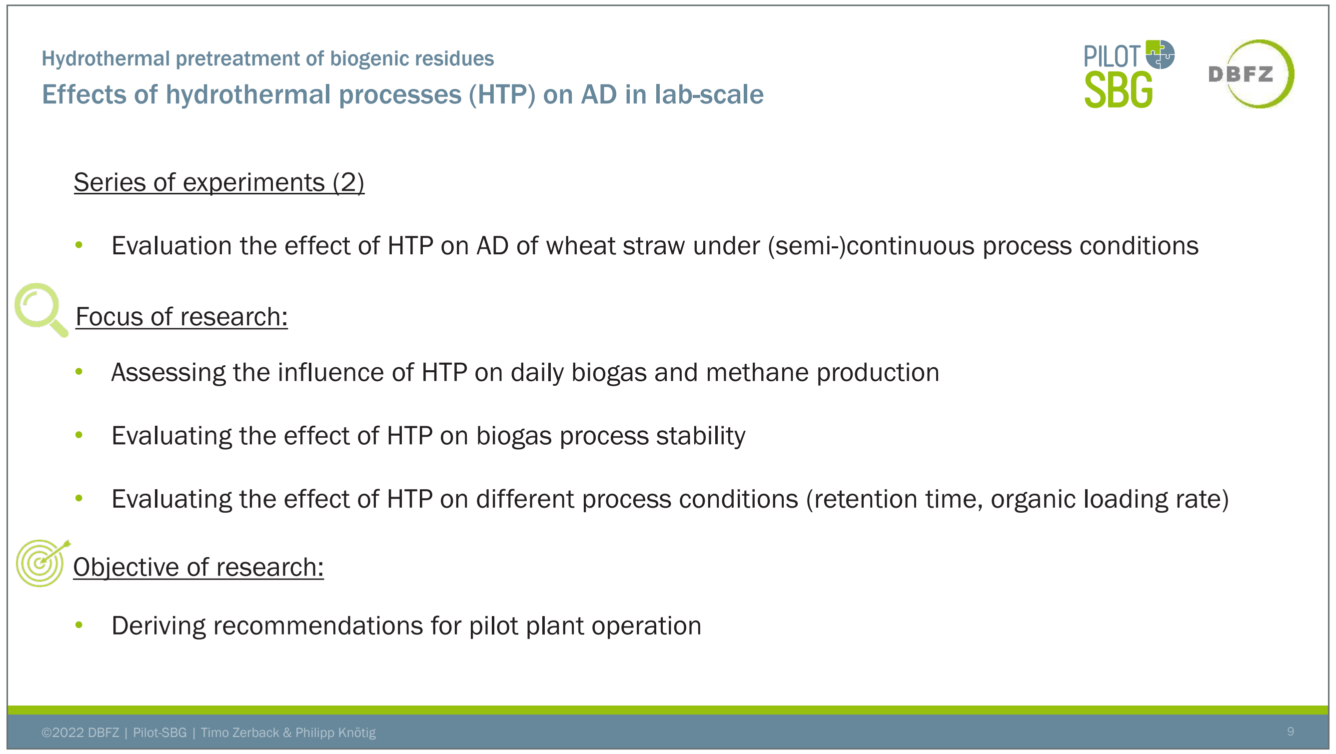
- Evaluation of the effect of HTP on discontinuous AD of wheat straw

Focus of research:

- Assessing the influence of HTP on biochemical methane potential (BMP)
- Evaluating the effect of HTP on degradation kinetics
- Identification and evaluation of by-products (e.g., inhibitory compounds, organic acids, sugars)

Objective of research:

- Identification of optimal HTP conditions (temperature & time) for AD of wheat straw under (semi-) continuous process conditions



Hydrothermal pretreatment of biogenic residues

Effects of hydrothermal processes (HTP) on AD in lab-scale

Series of experiments (2)

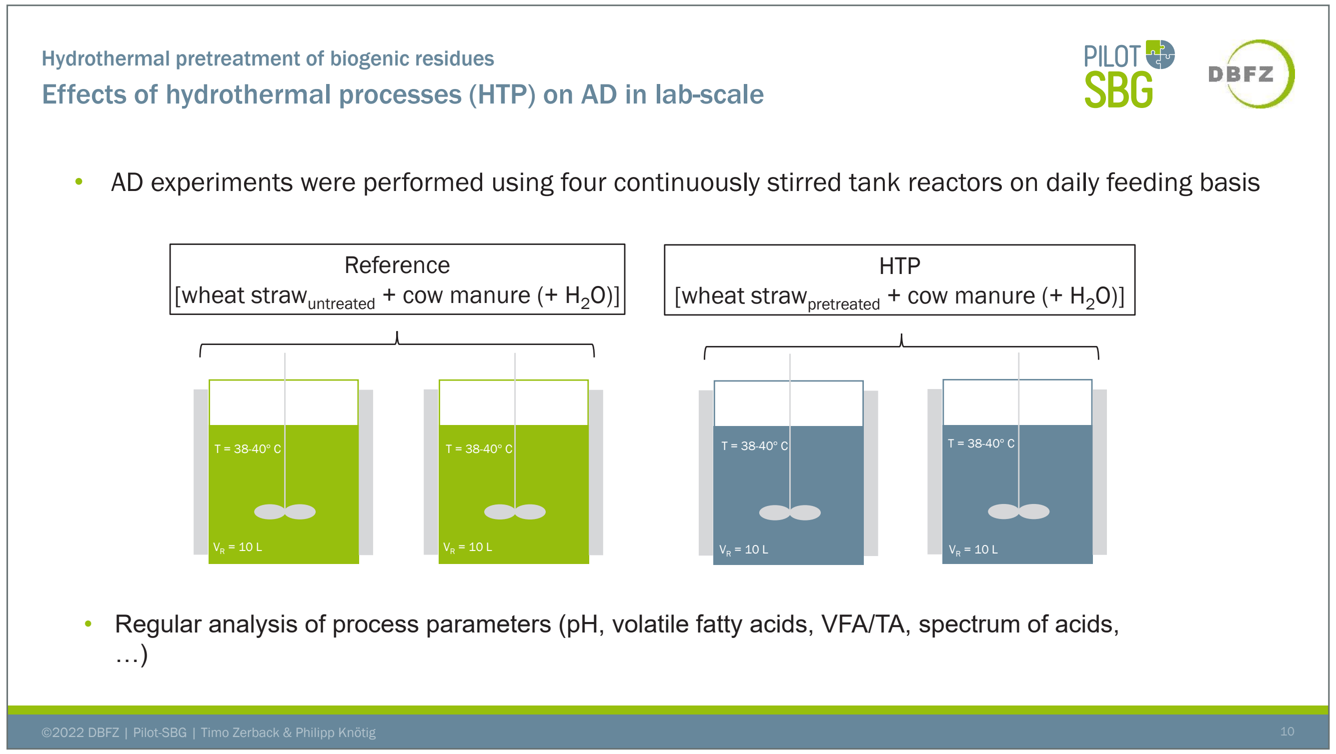
- Evaluation the effect of HTP on AD of wheat straw under (semi-)continuous process conditions

Focus of research:

- Assessing the influence of HTP on daily biogas and methane production
- Evaluating the effect of HTP on biogas process stability
- Evaluating the effect of HTP on different process conditions (retention time, organic loading rate)

Objective of research:

- Deriving recommendations for pilot plant operation



Hydrothermal pretreatment of biogenic residues

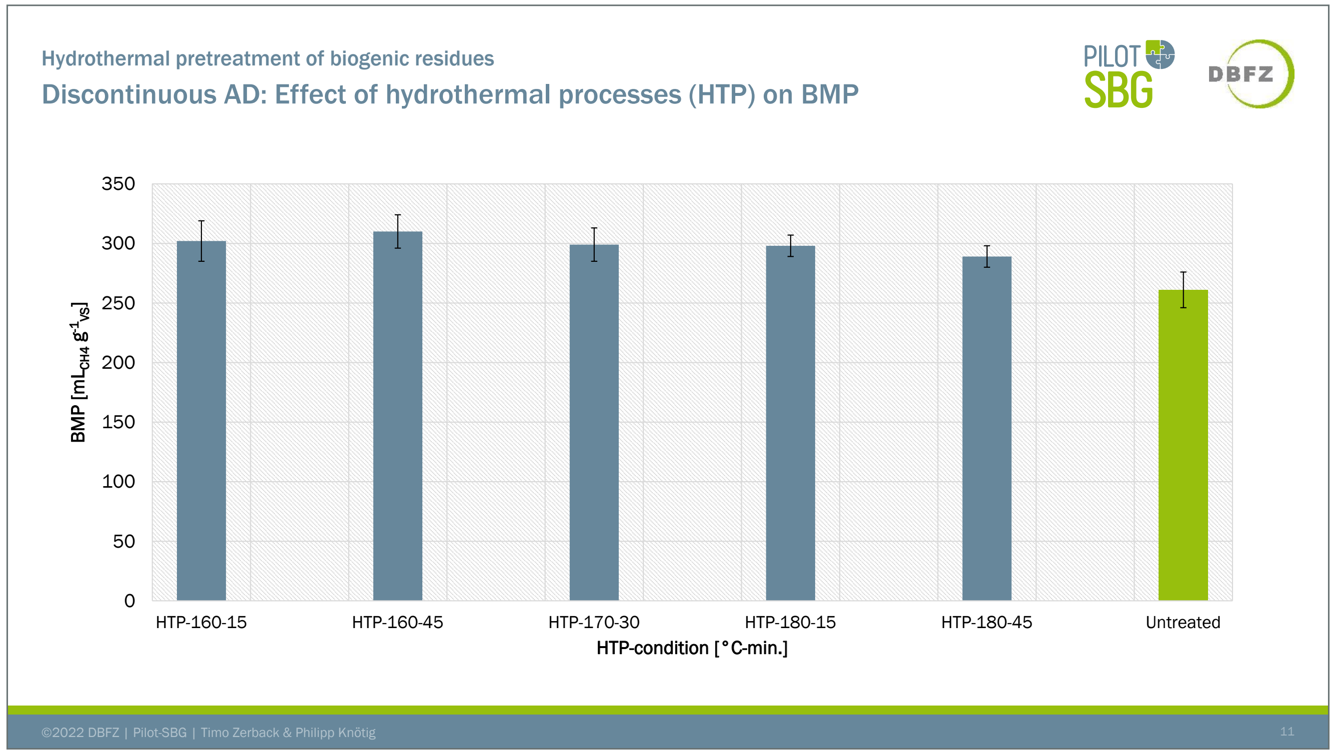
Effects of hydrothermal processes (HTP) on AD in lab-scale

- AD experiments were performed using four continuously stirred tank reactors on daily feeding basis

Reference
[wheat straw$_{untreated}$ + cow manure (+ H_2O)]

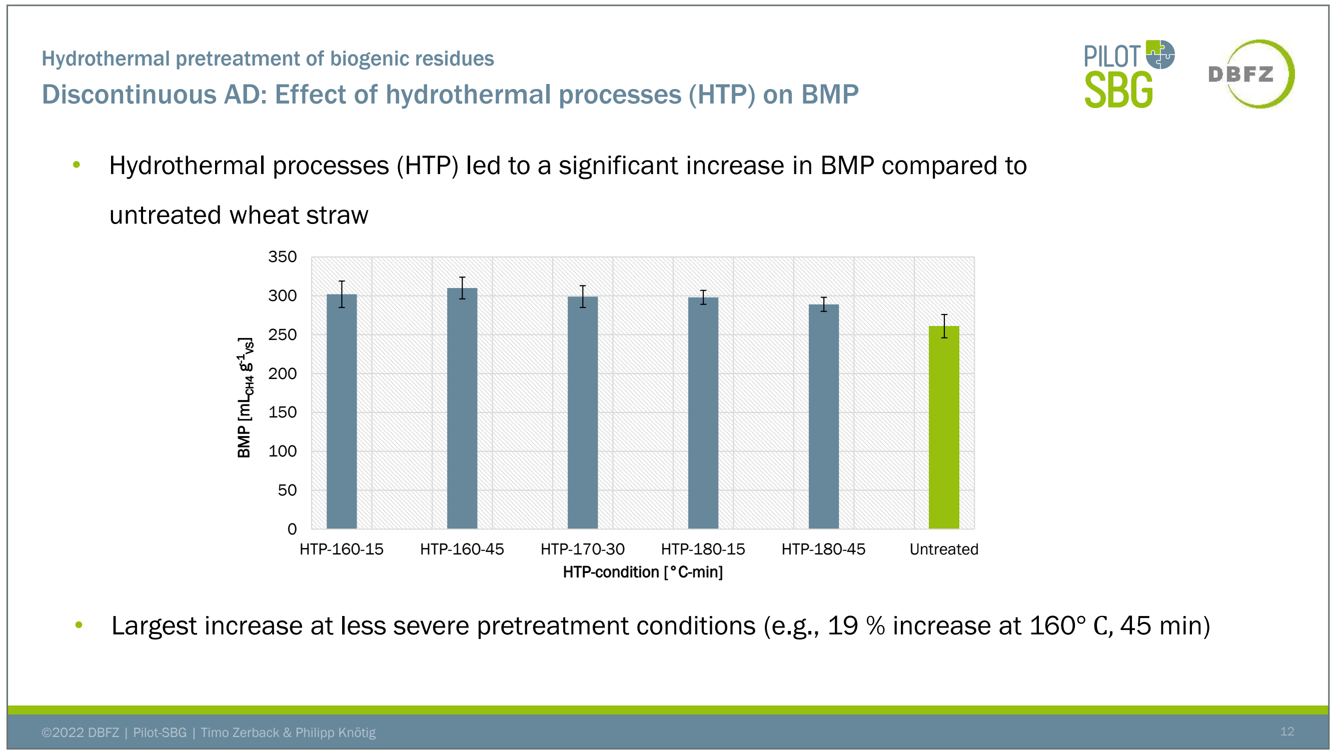
HTP
[wheat straw$_{pretreated}$ + cow manure (+ H_2O)]

- Regular analysis of process parameters (pH, volatile fatty acids, VFA/TA, spectrum of acids, …)



Hydrothermal pretreatment of biogenic residues

Discontinuous AD: Effect of hydrothermal processes (HTP) on BMP

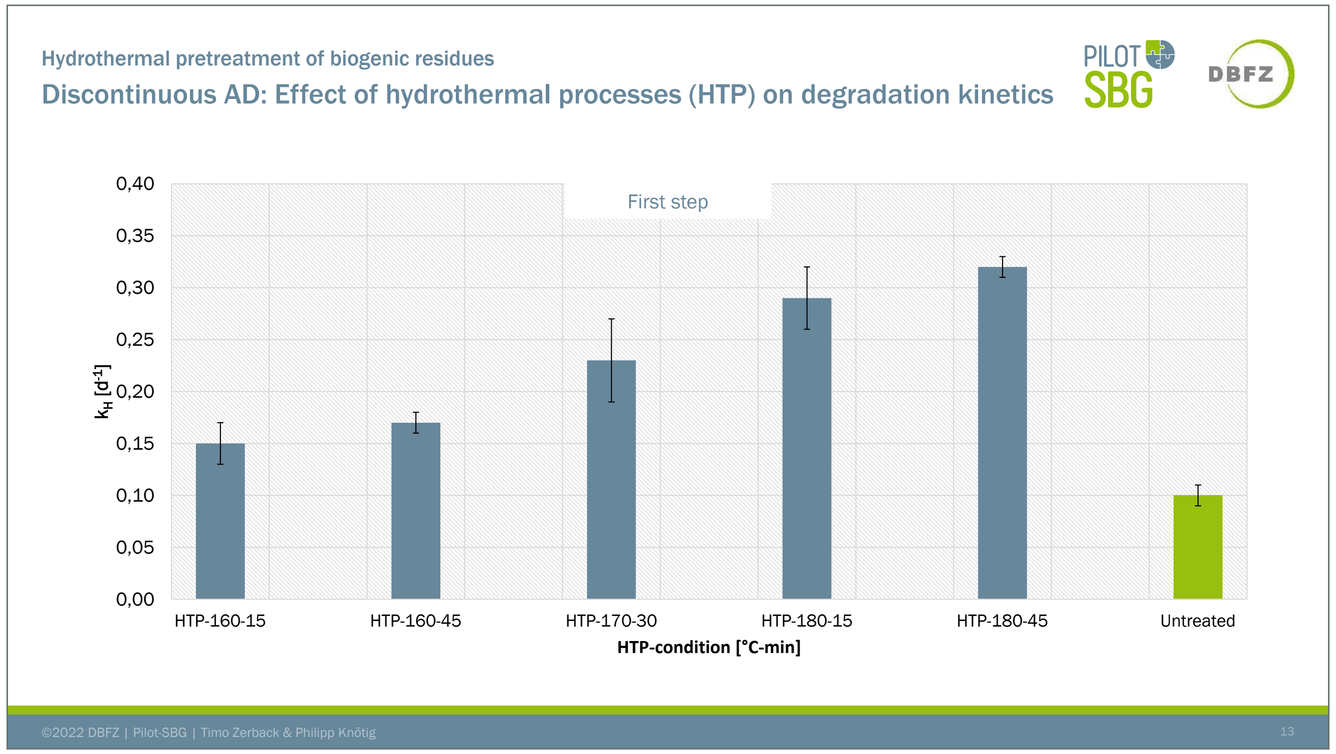


Hydrothermal pretreatment of biogenic residues

Discontinuous AD: Effect of hydrothermal processes (HTP) on BMP

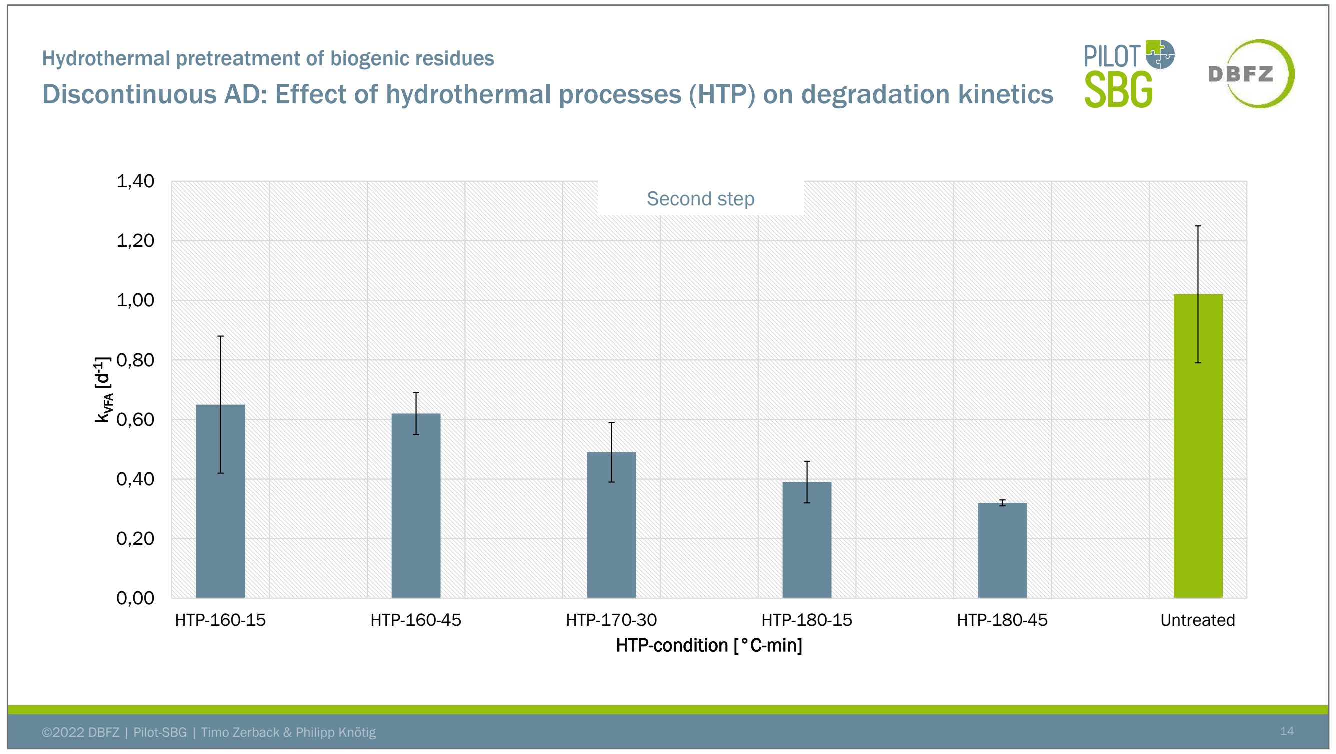
- Hydrothermal processes (HTP) led to a significant increase in BMP compared to untreated wheat straw

- Largest increase at less severe pretreatment conditions (e.g., 19 % increase at 160° C, 45 min)



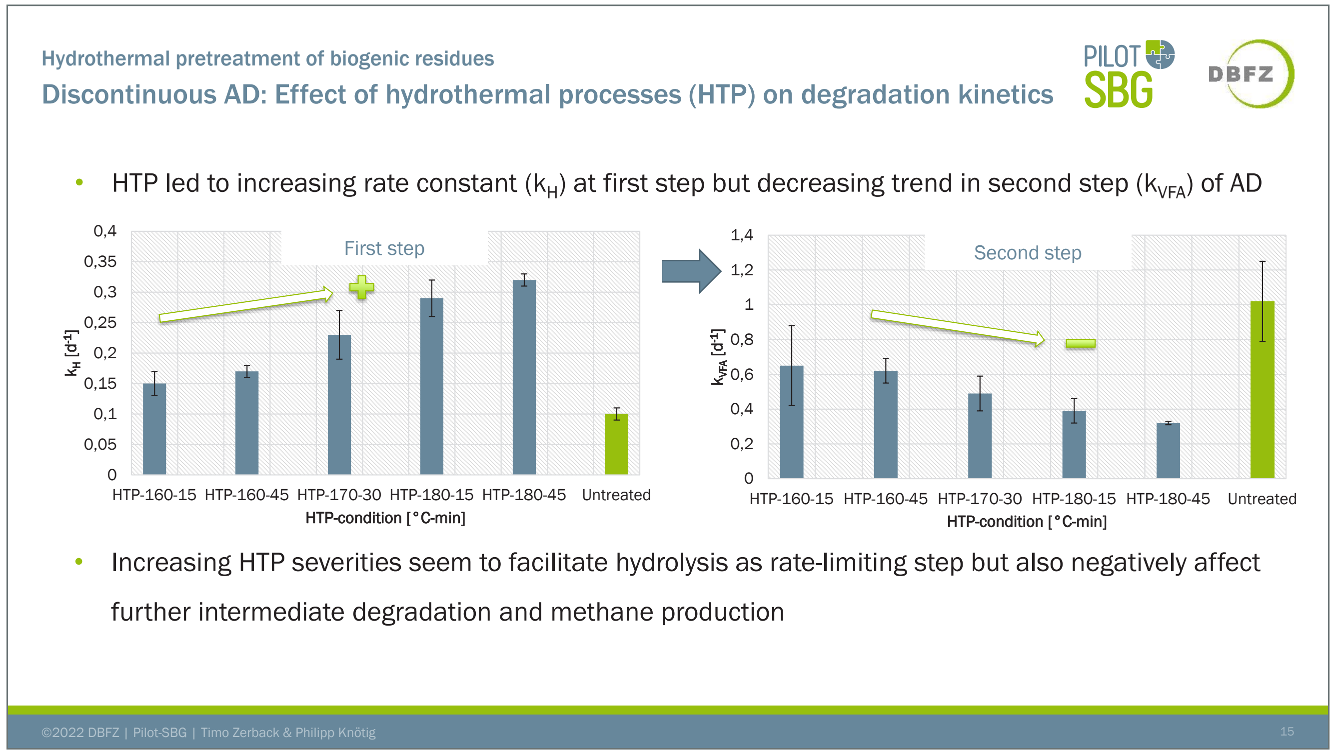
Hydrothermal pretreatment of biogenic residues

Discontinuous AD: Effect of hydrothermal processes (HTP) on degradation kinetics



Hydrothermal pretreatment of biogenic residues

Discontinuous AD: Effect of hydrothermal processes (HTP) on degradation kinetics

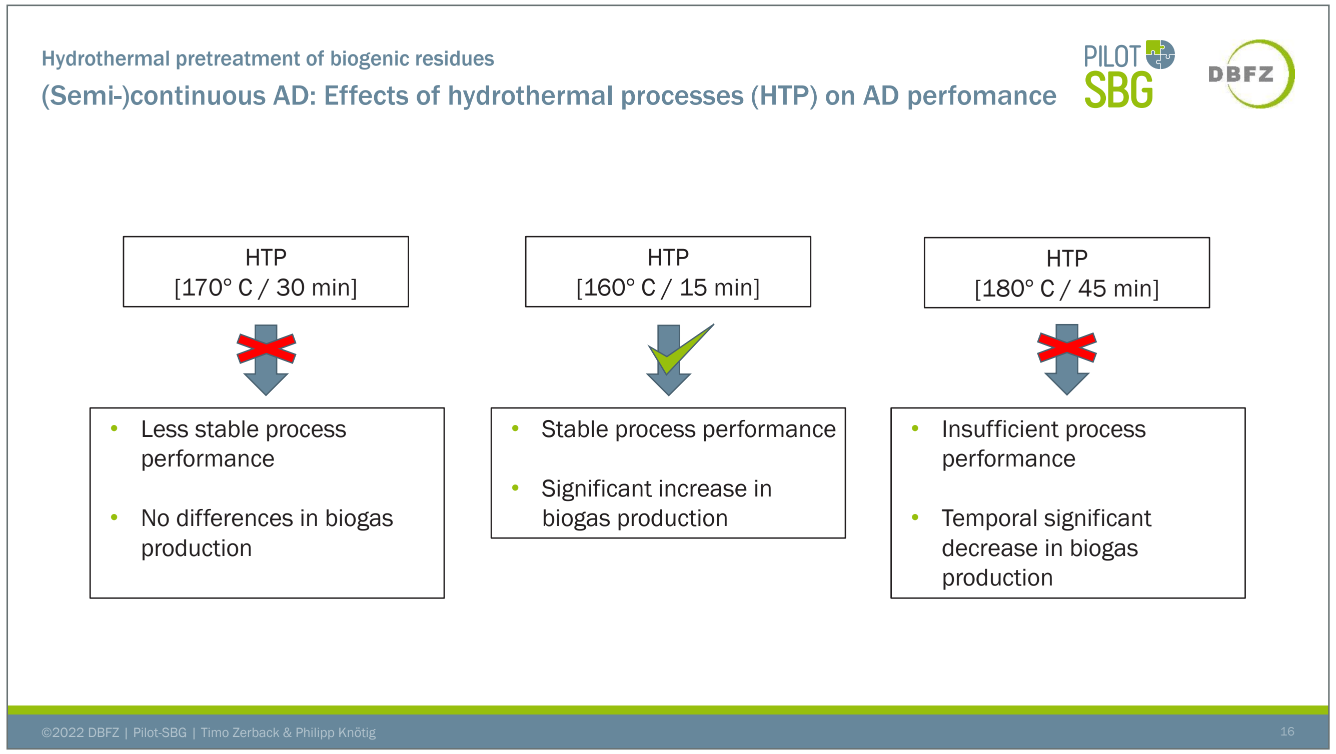


Hydrothermal pretreatment of biogenic residues

Discontinuous AD: Effect of hydrothermal processes (HTP) on degradation kinetics

- HTP led to increasing rate constant (k_H) at first step but decreasing trend in second step (k_{VFA}) of AD

- Increasing HTP severities seem to facilitate hydrolysis as rate-limiting step but also negatively affect further intermediate degradation and methane production



Hydrothermal pretreatment of biogenic residues

(Semi-)continuous AD: Effects of hydrothermal processes (HTP) on AD perfomance

HTP
[170° C / 30 min]

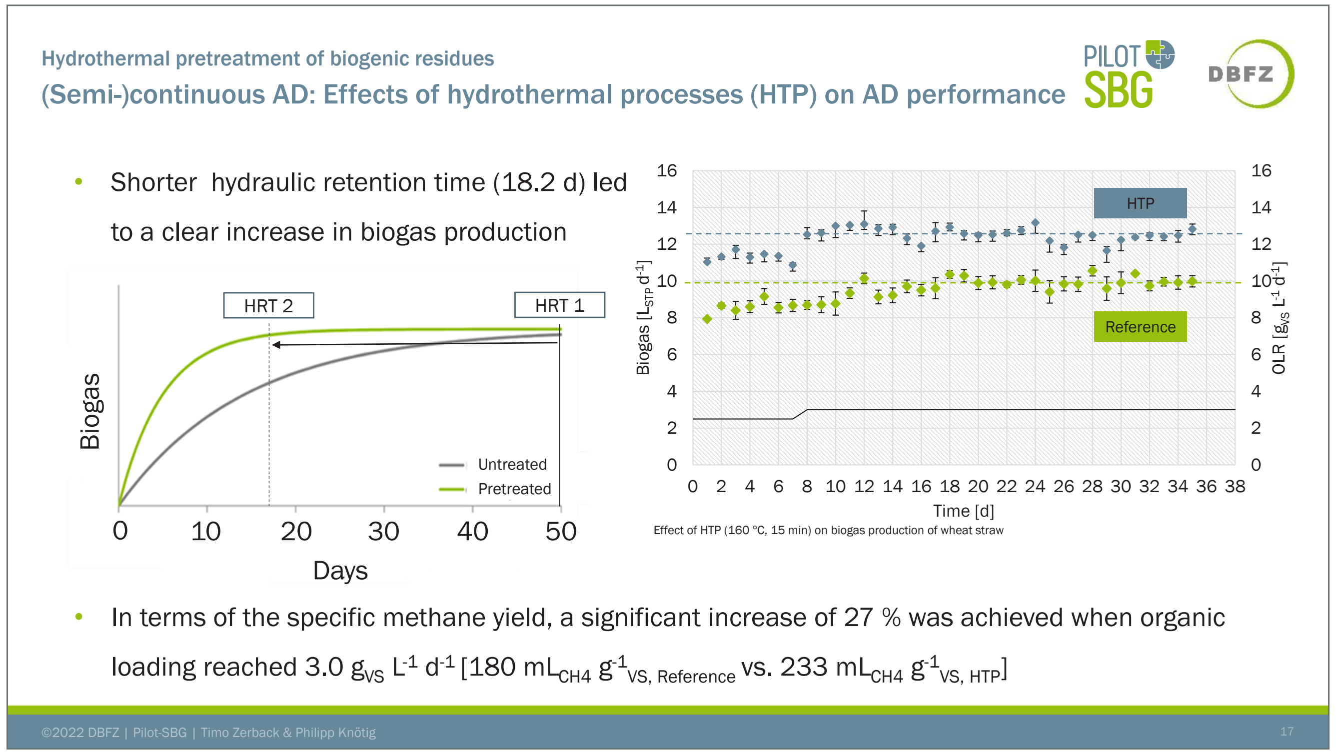
- Less stable process performance
- No differences in biogas production

HTP
[160° C / 15 min]

- Stable process performance
- Significant increase in biogas production

HTP
[180° C / 45 min]

- Insufficient process performance
- Temporal significant decrease in biogas production



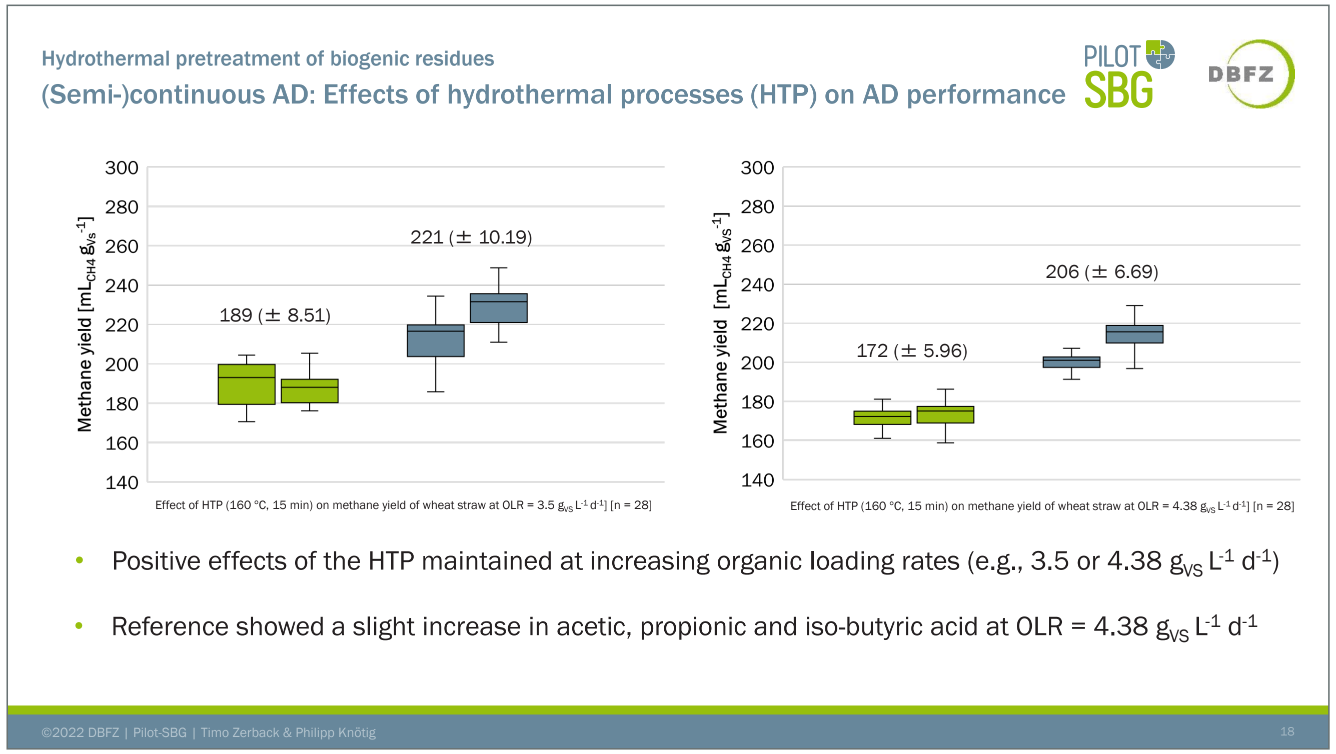
Hydrothermal pretreatment of biogenic residues

(Semi-)continuous AD: Effects of hydrothermal processes (HTP) on AD performance

- Shorter hydraulic retention time (18.2 d) led to a clear increase in biogas production

Effect of HTP (160 °C, 15 min) on biogas production of wheat straw

- In terms of the specific methane yield, a significant increase of 27 % was achieved when organic loading reached 3.0 g_{VS} L^{-1} d^{-1} [180 mL_{CH4} $g^{-1}_{VS,\ Reference}$ vs. 233 mL_{CH4} $g^{-1}_{VS,\ HTP}$]



Hydrothermal pretreatment of biogenic residues

(Semi-)continuous AD: Effects of hydrothermal processes (HTP) on AD performance

Effect of HTP (160 °C, 15 min) on methane yield of wheat straw at OLR = 3.5 g_{VS} L^{-1} d^{-1}] [n = 28]

Effect of HTP (160 °C, 15 min) on methane yield of wheat straw at OLR = 4.38 g_{VS} L^{-1} d^{-1}] [n = 28]

- Positive effects of the HTP maintained at increasing organic loading rates (e.g., 3.5 or 4.38 g_{VS} L^{-1} d^{-1})
- Reference showed a slight increase in acetic, propionic and iso-butyric acid at OLR = 4.38 g_{VS} L^{-1} d^{-1}

Hydrothermal pretreatment of biogenic residues

Conclusion

- BMP results showed a significant increase in specific methane yield at all pretreatment conditions compared to untreated wheat straw
- Increase up to 19% at 160 °C, and 45 min
- Disintegration via HTP facilitates degradation shown by increased kinetics of the rate-limiting step in batch AD
- Severer HTP conditions led to slower degradation in AD
- HTP at mildest conditions has significant benefits at shorter HRTs (18.2 d) in (semi-)continuous AD

Hydrothermal pretreatment of biogenic residues

Thank you for your attention

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Andrés Acosta, Aarhus University / TTZ Bremerhaven

Hydrothermal Carbonisation & Wetland Engineered Treatment Systems for Nutrient Recovery and its Biomass Conversion into High-value Products [Willow-Salix Viminalis]

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Phosphorus [P] is an essential element for industry and food production. The EU is almost entirely dependent on phosphate imports, and its scarcity has encouraged the development of processes to recover P from waste streams.

Despite the rise of hydrothermal routes as resource recovery techniques using nutrient-rich feedstocks (e.g., sewage sludge, manure), few studies have investigated the P recovery potential of engineered wetland systems [EWS] and their biomass conversion by hydrothermal carbonization. EWS are increasingly used worldwide to treat wastewater due to their capacity to remove pollution with less energy requirements and cost than conventional wastewater treatment technologies. Their ability to be incorporated into conventional treatment systems synergistically, provides additional benefits, while high biomass yields can be harvested yearly. The end-use of this biomass is often woodchips used as a soil amendment or simple incineration to produce energy.

The potential of EWS for nutrient recovery and the effects of wastewater on willow growth and its biomass conversation with hydrothermal carbonisation deserves further research attention.

Methods

Our project investigates the factors that influence the extraction (process water) or densification (hydrochar) of phosphorus during the HTC of the willow to explore its potential for nutrient and resource recovery. We compare indigenous willows with three different clones commonly used and harvested from an EW operating system.

Custom-built 20 mL reactors were used for the HTC. We varied the reaction severity at different temperatures (225, 250, 275, and 300 °C) and times (10, 20, 30, and 60 min). Physicochemical properties of hydrochars were characterized using TGA-DSC, CHNS, and FTIR. We systematically determined P- speciation during HTC via combining ICP-OES and chemical P-extractions [HCL-P, H2O-P, NaHCO3-P]. We developed HPLC-ESI-MS2 and GC-MS methods for the quantification of sugars, platform chemicals, and organic acids for the process water analysis (e.g., HMF and levulinic acid).

Results & Conclusion

We observed good densification and P-recovery using indigenous willow without a catalyst for HTC at 250 °C and 60 min (111 % ± 8). P is more likely to be transformed into a more stable P pool [HCl-P] during the HTC. Although EWS biomass has P-content lower than nutrient-rich feedstocks (~1.3 mg . g-1), we estimated that 14 to 91 kg P . ha-1 could be recovered in short coppice rotations. The metal/P molar ratios influenced the P-speciation.

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Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP
Hydrothermale Prozesse

Hydrothermal Processing for Biomass Conversion & Nutrient Recovery using Constructed Wetlands [Willow-*Salix viminalis*]

Andrés Acosta
Supervisors:
Hans Brix ,
Carlos A. Arias,
Patrick Biller

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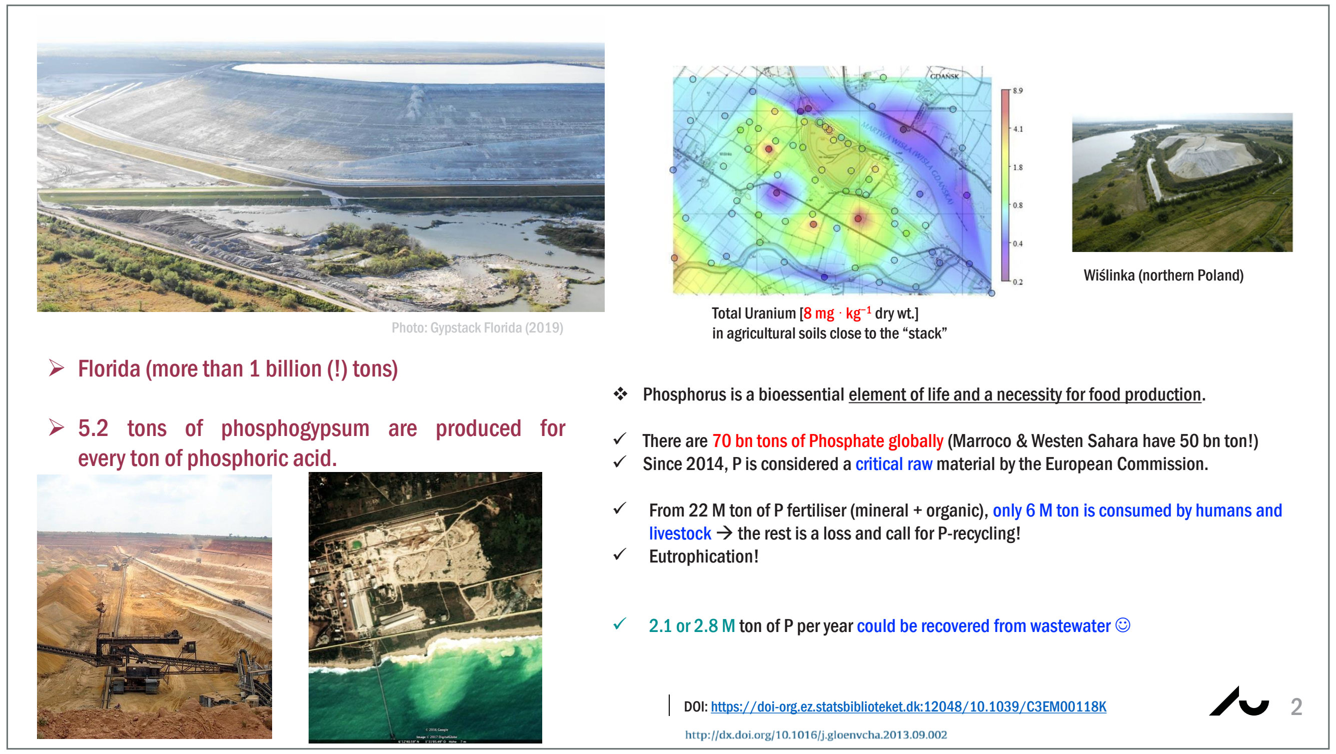

Photo: Gypstack Florida (2019)

Total Uranium [8 mg · kg^{-1} dry wt.]
in agricultural soils close to the "stack"

Wiślinka (northern Poland)

- Florida (more than 1 billion (!) tons)
- 5.2 tons of phosphogypsum are produced for every ton of phosphoric acid.

❖ Phosphorus is a bioessential element of life and a necessity for food production.

✓ There are 70 bn tons of Phosphate globally (Marroco & Westen Sahara have 50 bn ton!)
✓ Since 2014, P is considered a critical raw material by the European Commission.

✓ From 22 M ton of P fertiliser (mineral + organic), only 6 M ton is consumed by humans and livestock → the rest is a loss and call for P-recycling!
✓ Eutrophication!

✓ 2.1 or 2.8 M ton of P per year could be recovered from wastewater ☺

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http://dx.doi.org/10.1016/j.gloenvcha.2013.09.002

2

The material stability and fixed carbon content increased with the reaction severity from 14 to 44 %. HHV levels of the hydrochars ranged from 22 and 28 MJ . kg-1 compared to 19−27 MJ . kg-1 for sub-bituminous coals.

HTC shows potential to convert wetland biomass into valuable products with broad applications (e.g., hydrochar with nutrient content and fixed carbon for soil amendment, fuel, and platform chemicals),

EU-India Water Research Cooperation
RIA – HORIZON 2020

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3

Constructed Wetland [CW]?

An engineered wetland system [EWS] designed to harness natural process for the purpose of improving water quality

Technically and operationally simple, but involving complex interactions between water, soil, plants, micro-organisms, and the atmosphere.

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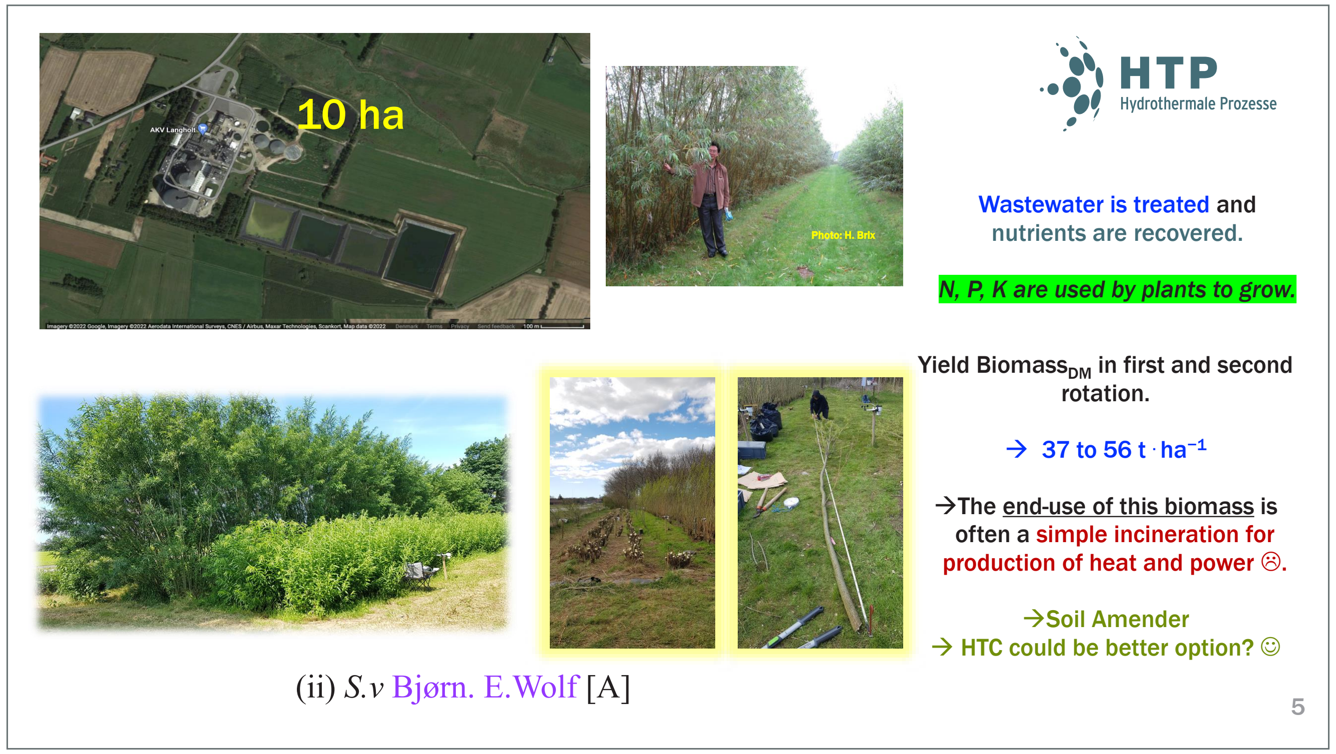
Willow (*Salix viminalis*)
Jan Kops, 1872



HTP Hydrothermale Prozesse

Wastewater is treated and nutrients are recovered.

N, P, K are used by plants to grow.

Yield Biomass$_{DM}$ in first and second rotation.

→ 37 to 56 t · ha^{-1}

→The end-use of this biomass is often a simple incineration for production of heat and power ☹.

→Soil Amender
→ HTC could be better option? ☺

(ii) *S.v* Bjørn. E.Wolf [A]

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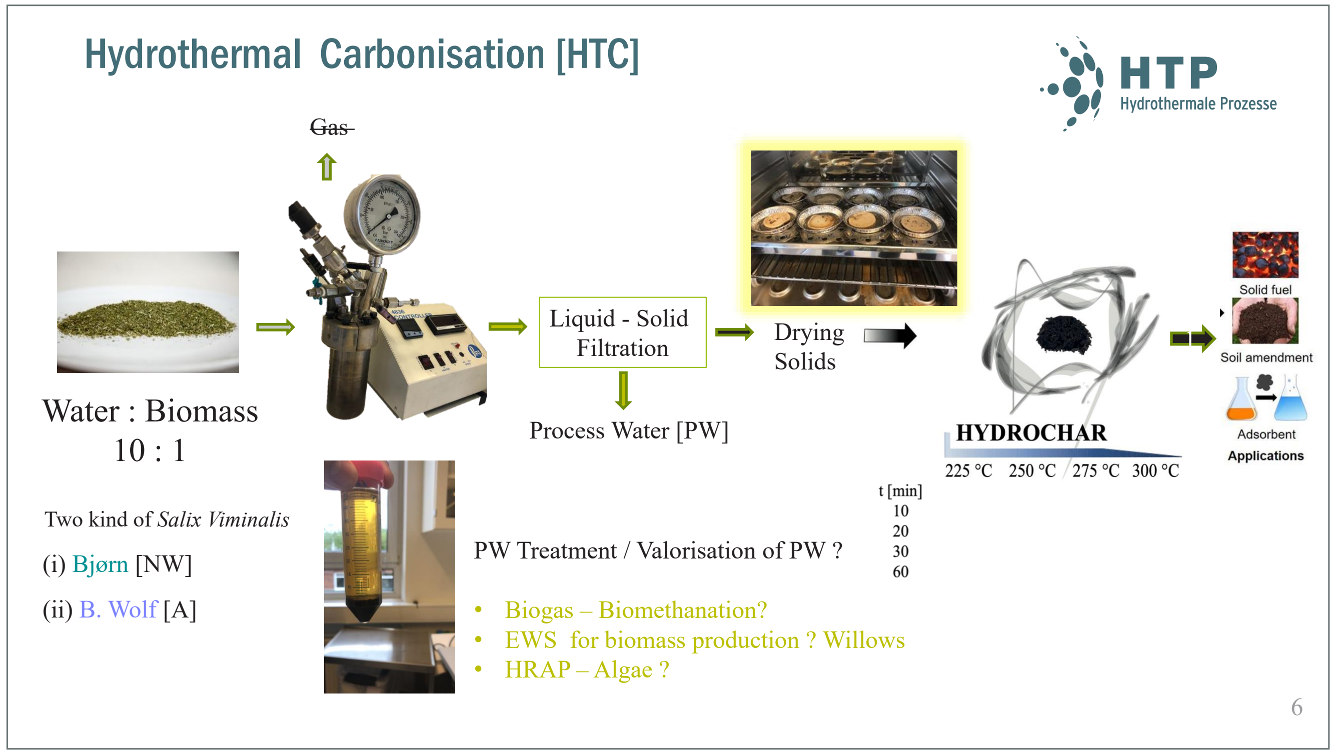

Hydrothermal Carbonisation [HTC]

HTP Hydrothermale Prozesse

Water : Biomass
10 : 1

Two kind of *Salix Viminalis*
(i) Bjørn [NW]
(ii) B. Wolf [A]

PW Treatment / Valorisation of PW ?

- Biogas – Biomethanation?
- EWS for biomass production ? Willows
- HRAP – Algae ?

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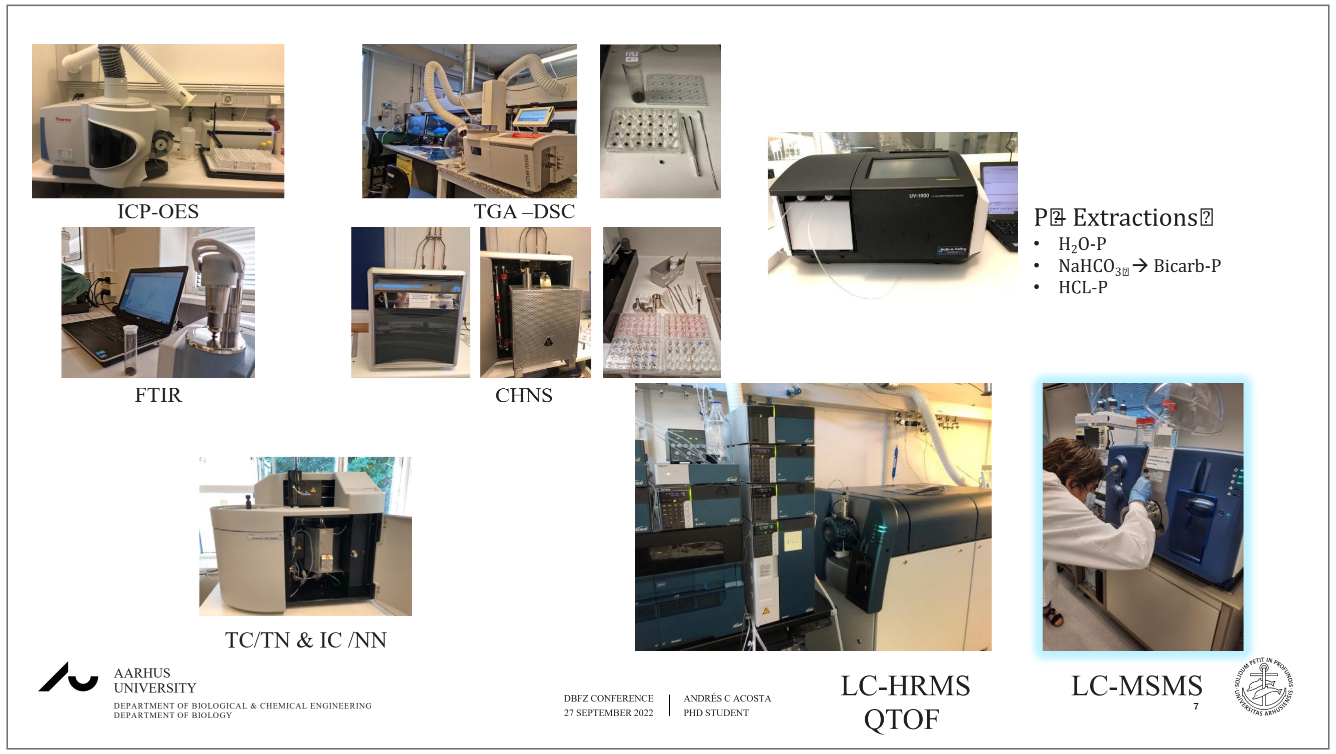

P Extractions

- H_2O-P
- $NaHCO_3$ → Bicarb-P
- HCL-P

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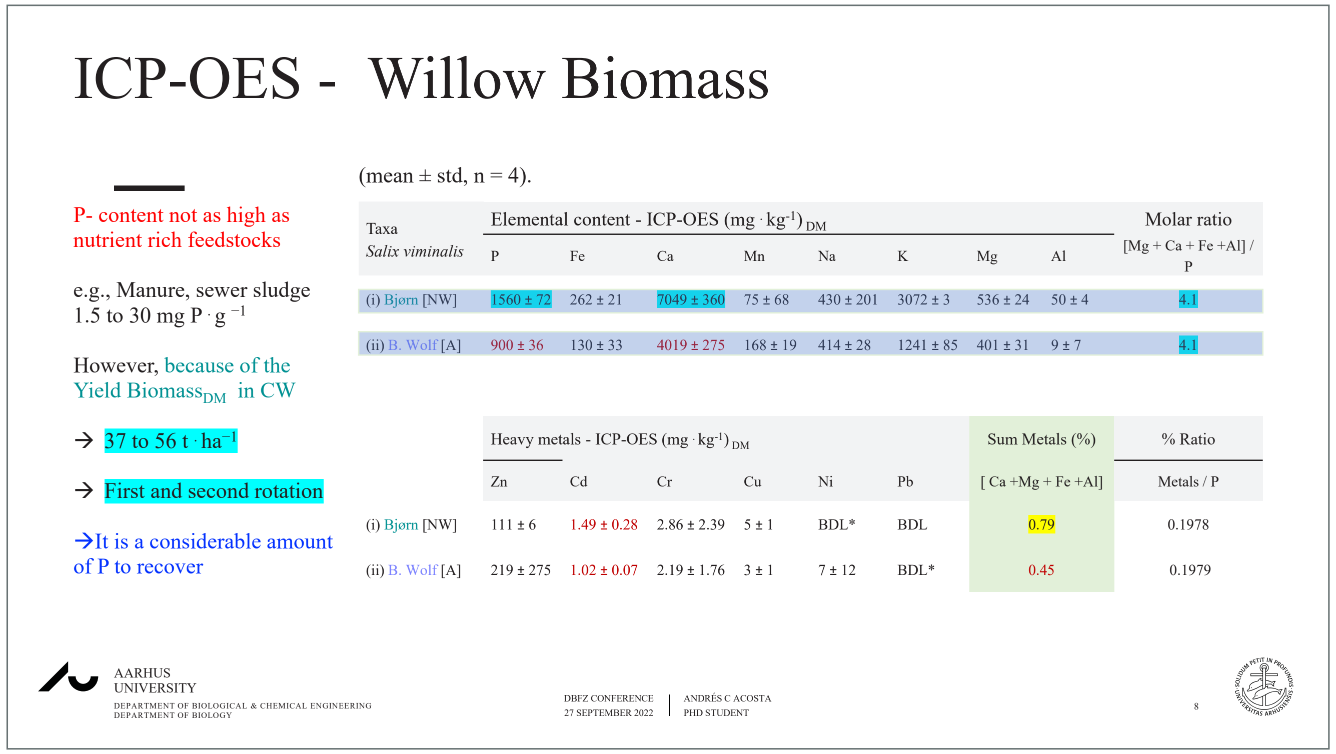

ICP-OES - Willow Biomass

P- content not as high as nutrient rich feedstocks

e.g., Manure, sewer sludge 1.5 to 30 mg P · g $^{-1}$

However, because of the Yield Biomass$_{DM}$ in CW

→ 37 to 56 t · ha^{-1}

→ First and second rotation

→It is a considerable amount of P to recover

(mean ± std, n = 4).

Taxa *Salix viminalis*	Elemental content - ICP-OES (mg · kg^{-1})$_{DM}$								Molar ratio
	P	Fe	Ca	Mn	Na	K	Mg	Al	[Mg + Ca + Fe +Al] / P
(i) Bjørn [NW]	1560 ± 72	262 ± 21	7049 ± 360	75 ± 68	430 ± 201	3072 ± 3	536 ± 24	50 ± 4	4.1
(ii) B. Wolf [A]	900 ± 36	130 ± 33	4019 ± 275	168 ± 19	414 ± 28	1241 ± 85	401 ± 31	9 ± 7	4.1

	Heavy metals - ICP-OES (mg · kg^{-1})$_{DM}$						Sum Metals (%)	% Ratio
	Zn	Cd	Cr	Cu	Ni	Pb	[Ca +Mg + Fe +Al]	Metals / P
(i) Bjørn [NW]	111 ± 6	1.49 ± 0.28	2.86 ± 2.39	5 ± 1	BDL*	BDL	0.79	0.1978
(ii) B. Wolf [A]	219 ± 275	1.02 ± 0.07	2.19 ± 1.76	3 ± 1	7 ± 12	BDL*	0.45	0.1979

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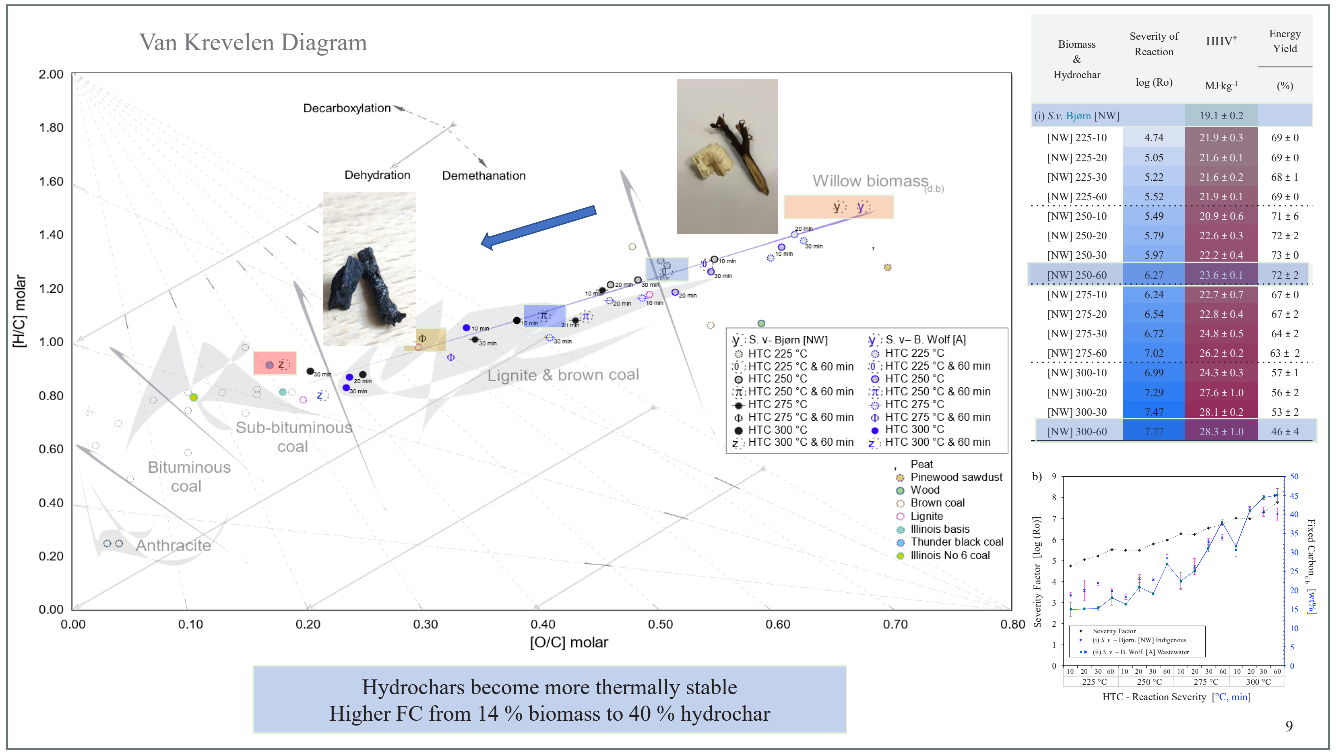

Biomass & Hydrochar	Severity of Reaction log (Ro)	HHV† MJ·kg^{-1}	Energy Yield (%)
(i) *S.v.* Bjørn [NW]		19.1 ± 0.2	
[NW] 225-10	4.74	21.9 ± 0.3	69 ± 0
[NW] 225-20	5.05	21.6 ± 0.1	69 ± 0
[NW] 225-30	5.22	21.6 ± 0.2	68 ± 1
[NW] 225-60	5.52	21.9 ± 0.1	69 ± 0
[NW] 250-10	5.49	20.9 ± 0.6	71 ± 6
[NW] 250-20	5.79	22.6 ± 0.3	72 ± 2
[NW] 250-30	5.97	22.2 ± 0.4	73 ± 0
[NW] 250-60	6.27	23.6 ± 0.1	72 ± 2
[NW] 275-10	6.24	22.7 ± 0.7	67 ± 0
[NW] 275-20	6.54	22.8 ± 0.4	67 ± 2
[NW] 275-30	6.72	24.8 ± 0.5	64 ± 2
[NW] 275-60	7.02	26.2 ± 0.2	63 ± 2
[NW] 300-10	6.99	24.3 ± 0.3	57 ± 1
[NW] 300-20	7.29	27.6 ± 1.0	56 ± 2
[NW] 300-30	7.47	28.1 ± 0.2	53 ± 2
[NW] 300-60	7.77	28.3 ± 1.0	46 ± 4

Hydrochars become more thermally stable
Higher FC from 14 % biomass to 40 % hydrochar

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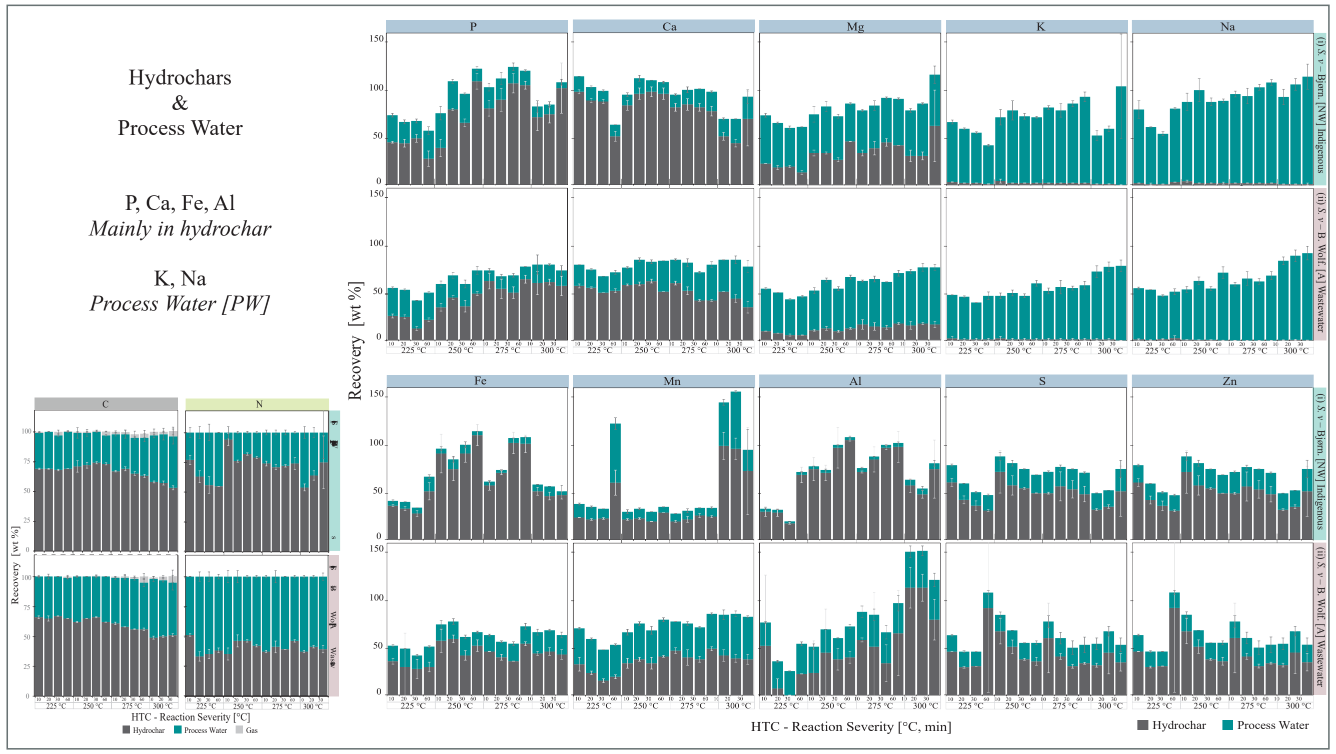
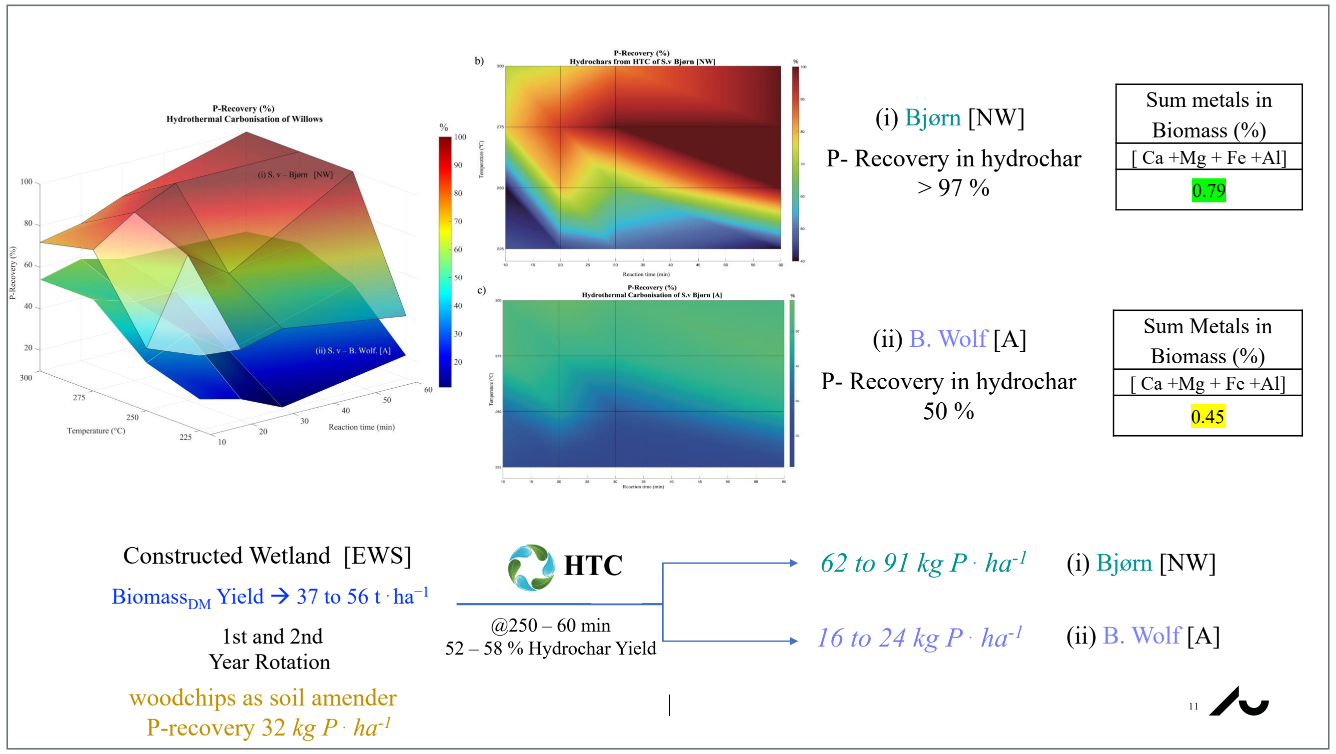


Hydrochars
&
Process Water

P, Ca, Fe, Al
Mainly in hydrochar

K, Na
Process Water [PW]



(i) Bjørn [NW]

P- Recovery in hydrochar > 97 %

Sum metals in Biomass (%)
[Ca +Mg + Fe +Al]
0.79

(ii) B. Wolf [A]

P- Recovery in hydrochar 50 %

Sum Metals in Biomass (%)
[Ca +Mg + Fe +Al]
0.45

Constructed Wetland [EWS]

Biomass$_{DM}$ Yield → 37 to 56 t · ha^{-1}

1st and 2nd Year Rotation

woodchips as soil amender

P-recovery 32 *kg P · ha^{-1}*

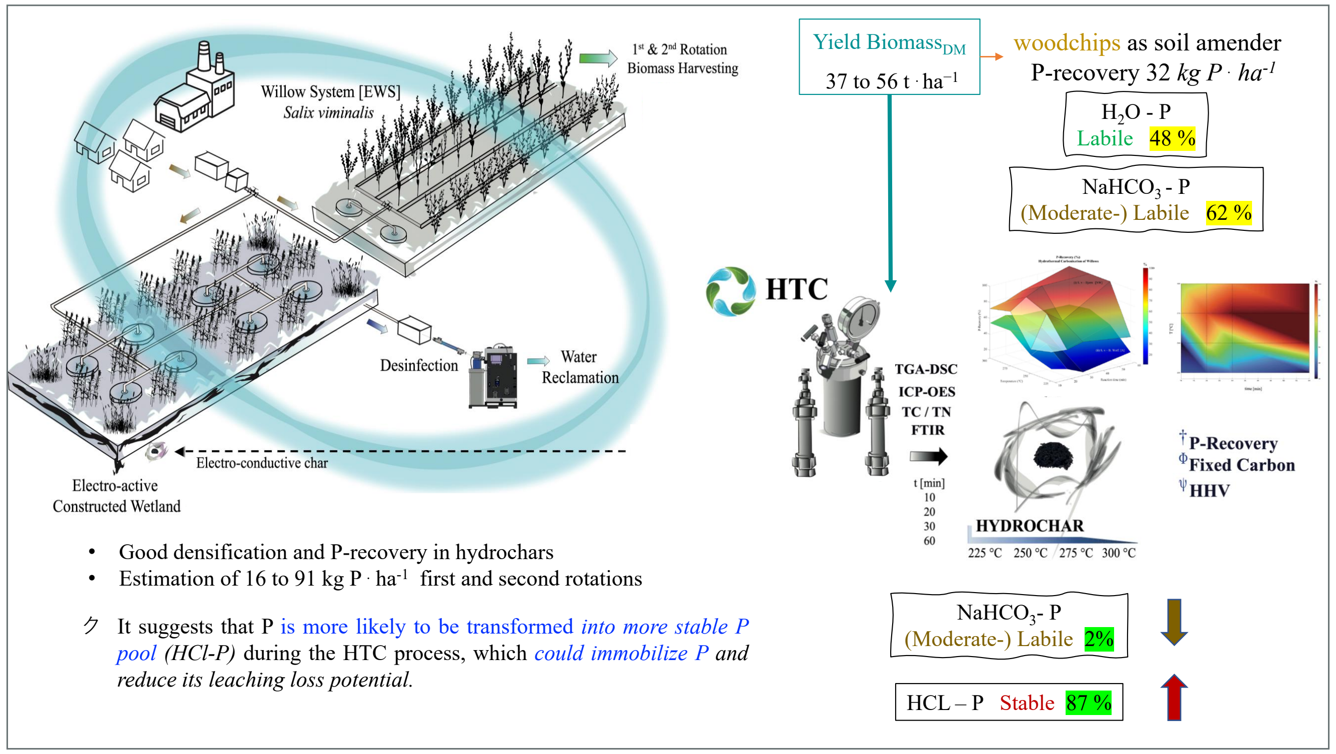
HTC

@250 – 60 min

52 – 58 % Hydrochar Yield

62 to 91 kg P · ha^{-1} (i) Bjørn [NW]

16 to 24 kg P · ha^{-1} (ii) B. Wolf [A]



Yield Biomass$_{DM}$

37 to 56 t · ha^{-1}

woodchips as soil amender

P-recovery 32 *kg P · ha^{-1}*

H_2O - P Labile 48 %

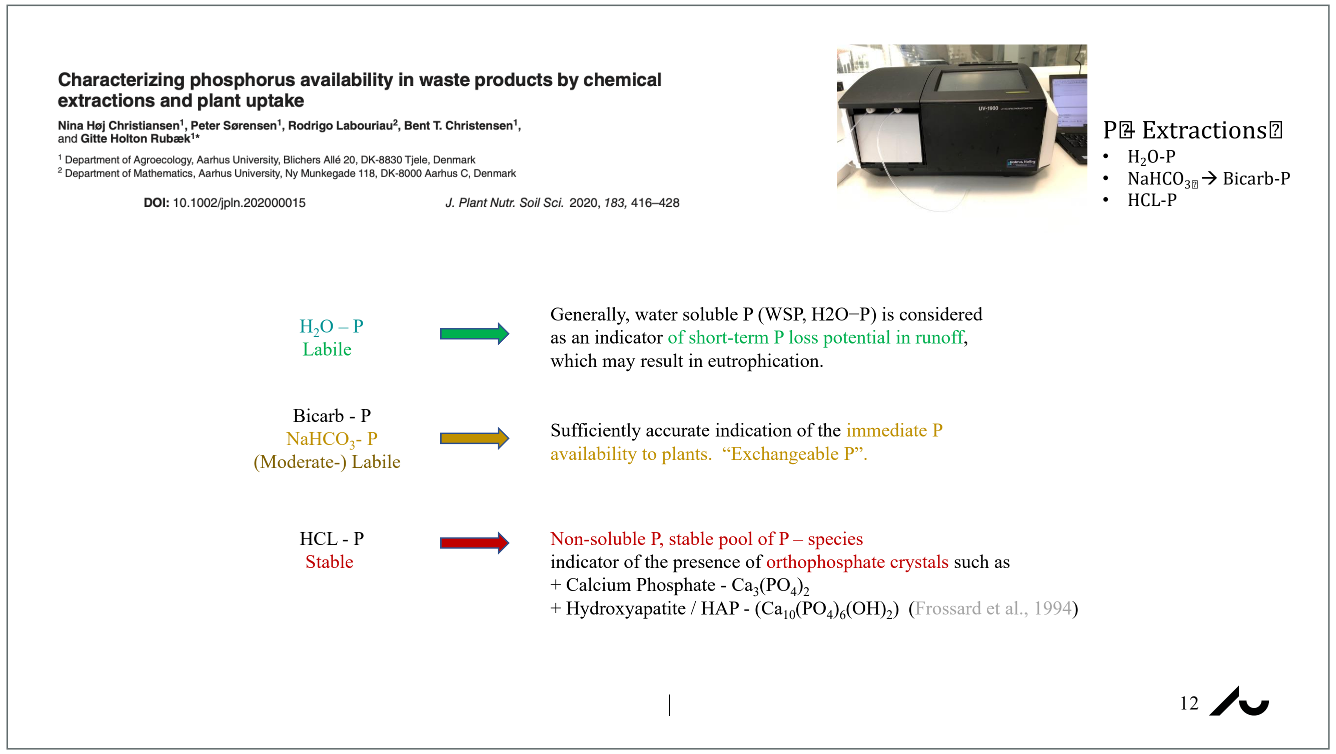
$NaHCO_3$ - P (Moderate-) Labile 62 %

- Good densification and P-recovery in hydrochars
- Estimation of 16 to 91 kg P · ha^{-1} first and second rotations

- It suggests that P is more likely to be transformed *into more stable P pool (HCl-P)* during the HTC process, which *could immobilize P and reduce its leaching loss potential.*

$NaHCO_3$- P (Moderate-) Labile 2%

HCL – P Stable 87 %



Characterizing phosphorus availability in waste products by chemical extractions and plant uptake

Nina Høj Christiansen[1], **Peter Sørensen**[1], **Rodrigo Labouriau**[2], **Bent T. Christensen**[1], and **Gitte Holton Rubæk**[1]*

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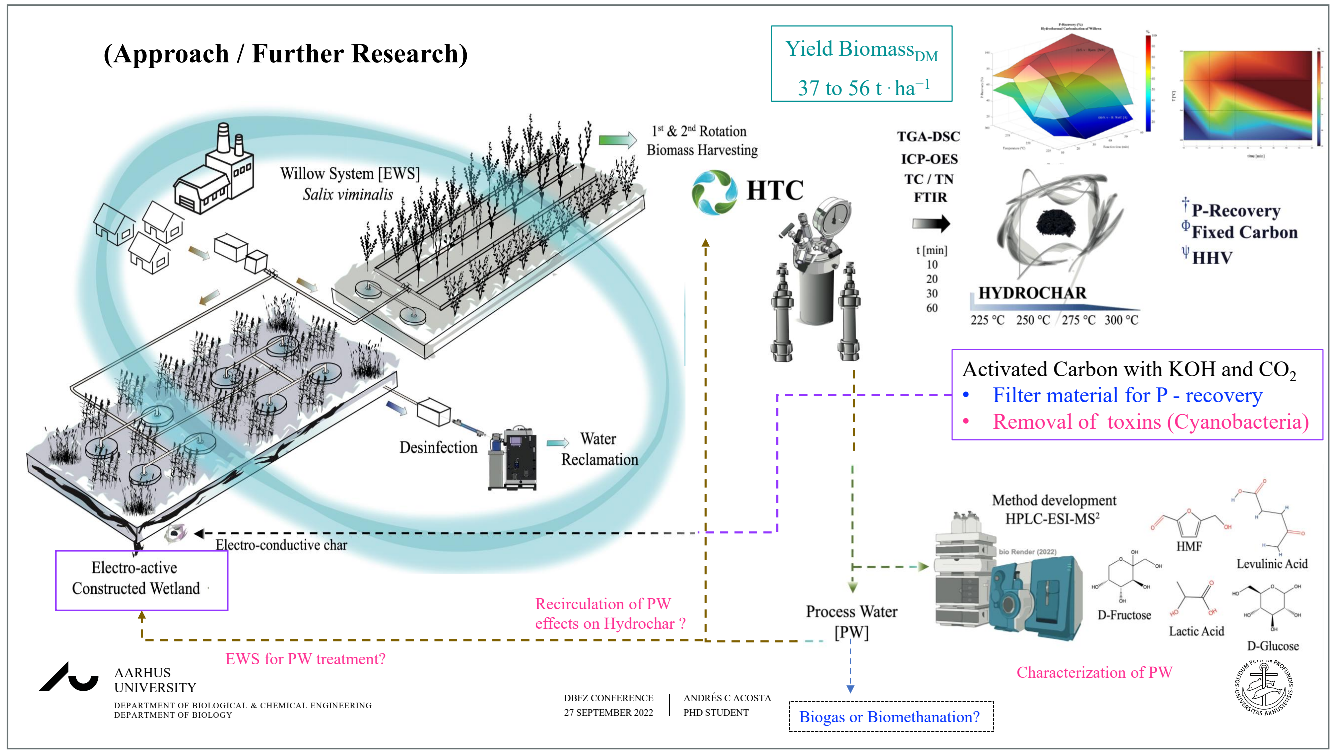
P Extractions

- H_2O-P
- $NaHCO_3$ → Bicarb-P
- HCL-P

H_2O – P Labile	Generally, water soluble P (WSP, H2O−P) is considered as an indicator of short-term P loss potential in runoff, which may result in eutrophication.
Bicarb - P $NaHCO_3$- P (Moderate-) Labile	Sufficiently accurate indication of the immediate P availability to plants. “Exchangeable P”.
HCL - P Stable	Non-soluble P, stable pool of P – species indicator of the presence of orthophosphate crystals such as + Calcium Phosphate - $Ca_3(PO_4)_2$ + Hydroxyapatite / HAP - ($Ca_{10}(PO_4)_6(OH)_2$) (Frossard et al., 1994)



(Approach / Further Research)

Yield Biomass$_{DM}$

37 to 56 t · ha^{-1}

Activated Carbon with KOH and CO_2
- Filter material for P - recovery
- Removal of toxins (Cyanobacteria)

Method development HPLC-ESI-MS²

Electro-active Constructed Wetland

Recirculation of PW effects on Hydrochar ?

EWS for PW treatment?

Process Water [PW]

Characterization of PW

Biogas or Biomethanation?

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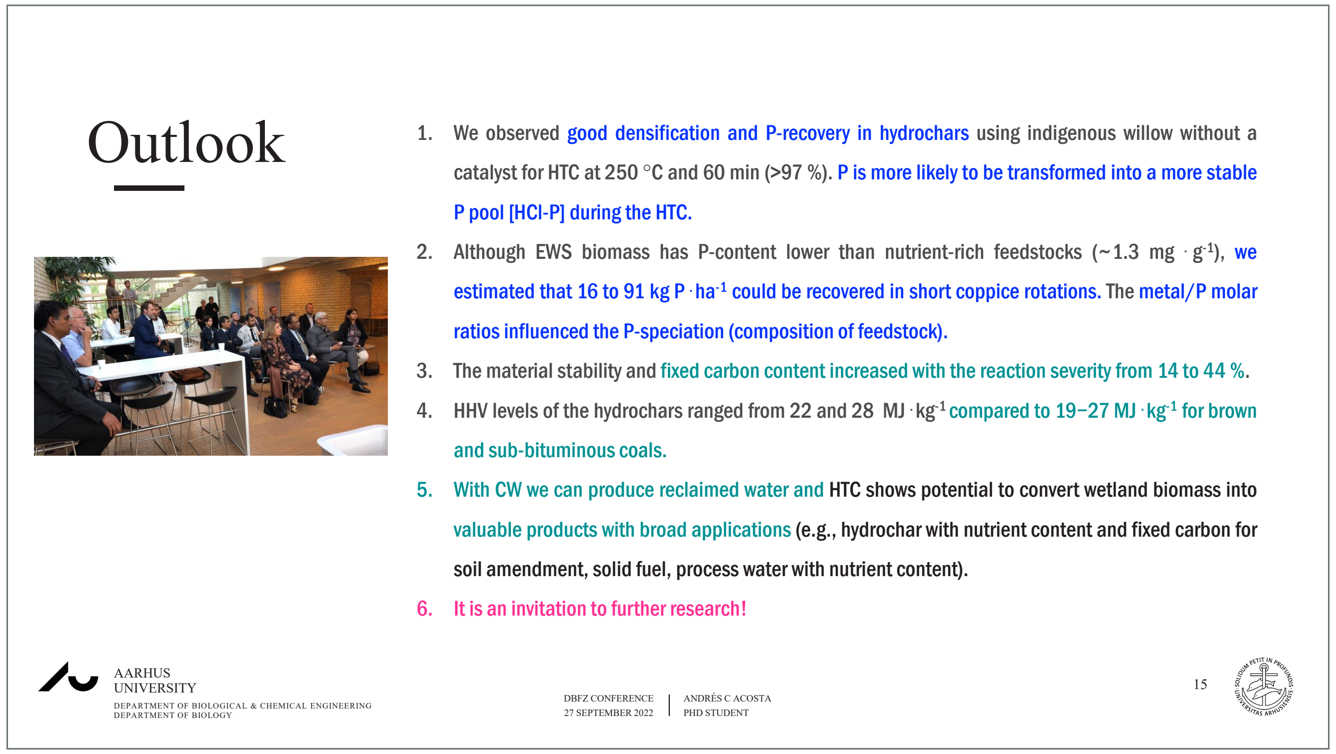

Outlook

1. We observed good densification and P-recovery in hydrochars using indigenous willow without a catalyst for HTC at 250 °C and 60 min (>97 %). P is more likely to be transformed into a more stable P pool [HCl-P] during the HTC.
2. Although EWS biomass has P-content lower than nutrient-rich feedstocks (~1.3 mg · g^{-1}), we estimated that 16 to 91 kg P · ha^{-1} could be recovered in short coppice rotations. The metal/P molar ratios influenced the P-speciation (composition of feedstock).
3. The material stability and fixed carbon content increased with the reaction severity from 14 to 44 %.
4. HHV levels of the hydrochars ranged from 22 and 28 MJ · kg^{-1} compared to 19–27 MJ · kg^{-1} for brown and sub-bituminous coals.
5. With CW we can produce reclaimed water and HTC shows potential to convert wetland biomass into valuable products with broad applications (e.g., hydrochar with nutrient content and fixed carbon for soil amendment, solid fuel, process water with nutrient content).
6. It is an invitation to further research!

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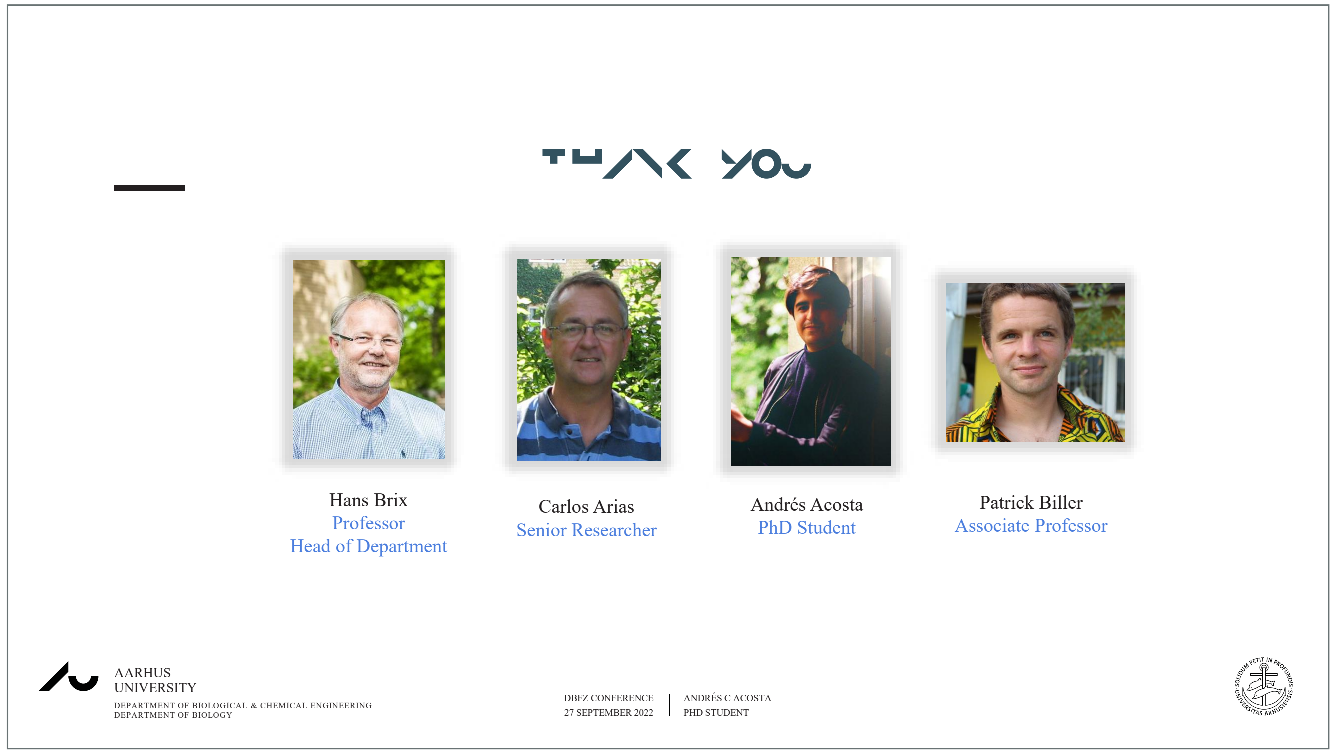

THANK YOU

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7. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

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Daniela Moloeznik Paniagua, Leibniz-Institut für Agrartechnik und Bioökonomie e.V.

Hydroachars produced from Macroalgae from the North Sea as potential fertilizer

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At least 45,000 Mg DM of algal biomass is washed ashore along the German Baltic Sea coast each year and another 60,000 Mg DM on the South of Sweden. These algae are not only rich in nutrients such as nitrogen and phosphorus, but they are also a source of carbon; therefore, there is an untapped potential for carbon sequestration and nutrients recovery. Unfortunately, algae accumulate not only nutrients but also heavy metals and therefore its usage can be very limited.

In this study the macroalgae Fucus vesiculosus, which grows both in the Baltic and in the North Sea, was collected from the North Sea and submitted to hydrothermal carbonization (HTC) process as a potential treatment method to recover nutrients and reduce heavy metals in the chars. The HTC runs took place at different temperatures (160 °C, 190 °C and 220 °C), solid contents (20 wt% DM, 35 wt % DM), and recirculation of process water (true, false) based on a full factorial design of experiments.

The goal of the study is to assess the potential for carbon sequestration through hydrochar at various operating conditions, and to determine the partitioning behaviour of the nutrients N, P, K as well as the fate of heavy metals in the chars. Additionally, the chars were evaluated to assess their compliance with fertilizer regulations, such as the German Fertilizer Ordinance, RAL-Compost, EBC and the IBI certificates.

High solid and carbon yields were obtained at all conditions, ranging from 58-79% and 63-82%, respectively. Analysis of the full factorial design of experiments using a least standard square model showed that, of the three different process parameters, only solid content had a positive significant influence on the carbon yield. Increasing the solid content, increased the carbon yield from 63% (at 220 °C, 20% solid content and recirculation) to 82% (at 220 °C, 35% solid content and no recirculation).

Higher solid content also influenced P and N partitioning, resulting in higher amounts of P and N in the hydrochar. For N, temperature was also a significant factor: higher temperatures decreased the N content in the char. Potassium was mostly transferred into the process water in all HTC conditions.

The different operating parameters did not make significant changes on the fate of the heavy metals. Most of the heavy metals (>90% wt.) that were found in the feedstock remained in the hydrochars. Due to the mass loss during HTC process, these heavy metals concentrations tended to increase and therefore, accumulate in the char. As a result, Cd and Tl surpass the limit values set up by legislation for all produced chars, in contrast to Co, Cu, Hg, Pb which never surpassed them. Potential solutions to lower the Cd and Tl concentrations in the hydrochar for use as fertilizer and estimates for their carbon sequestration potential will be discussed in the presentation.

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Hydrochars from macroalgae from the North Sea as potential fertilizer

Daniela Moloeznik Paniagua
TU Berlin / ATB Potsdam

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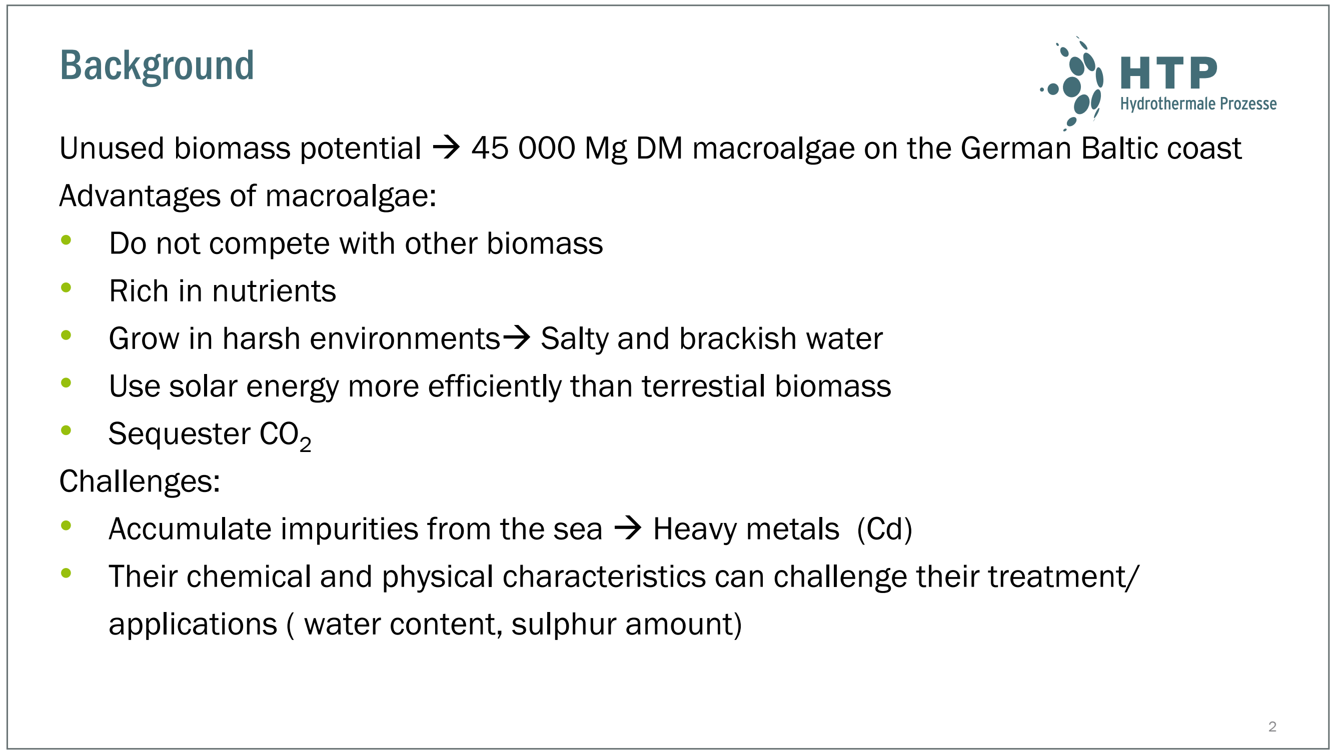


Background

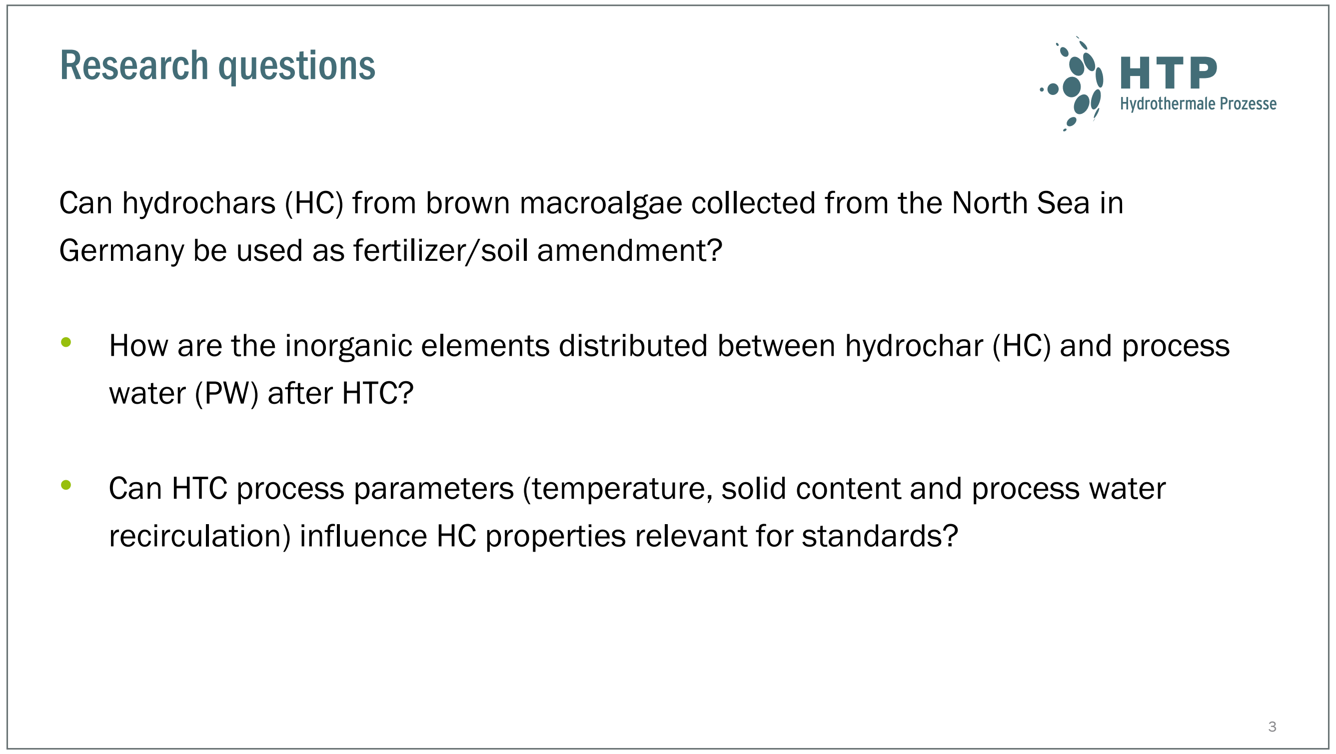
Unused biomass potential → 45 000 Mg DM macroalgae on the German Baltic coast

Advantages of macroalgae:

- Do not compete with other biomass
- Rich in nutrients
- Grow in harsh environments→ Salty and brackish water
- Use solar energy more efficiently than terrestial biomass
- Sequester CO_2

Challenges:

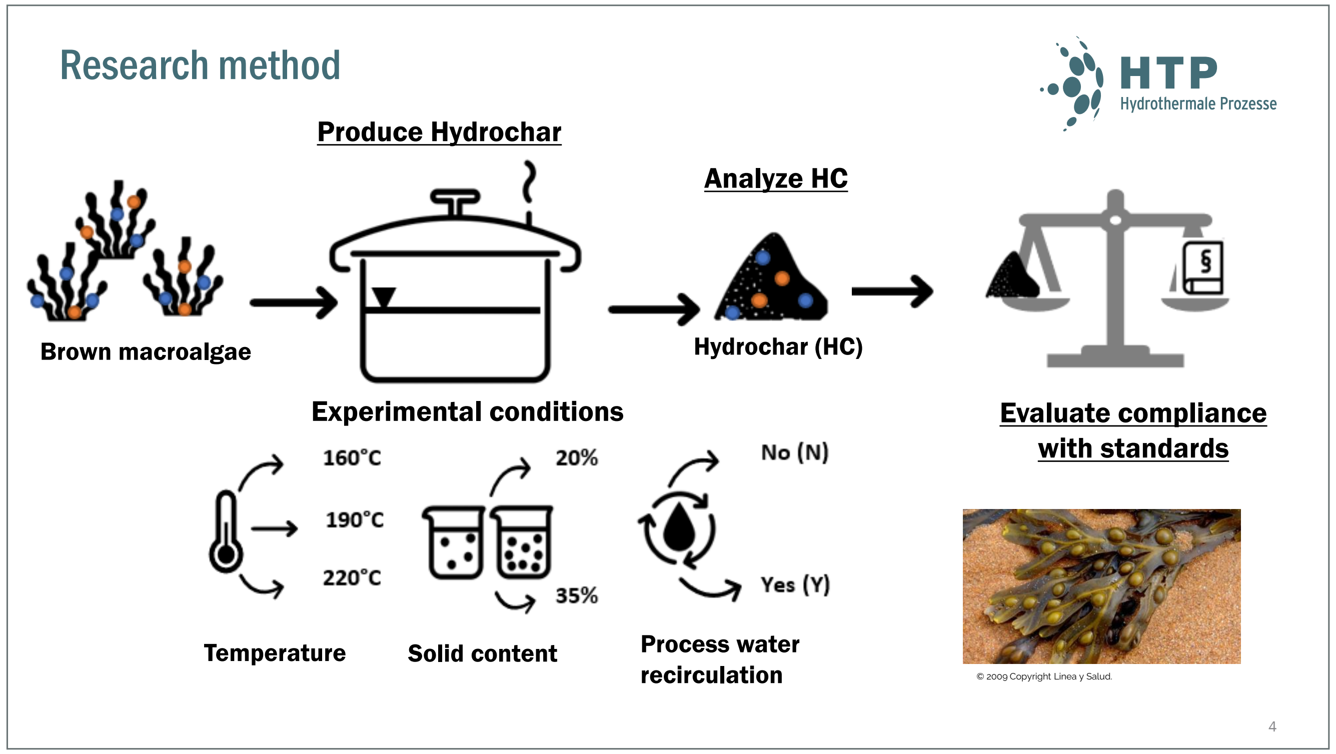
- Accumulate impurities from the sea → Heavy metals (Cd)
- Their chemical and physical characteristics can challenge their treatment/ applications (water content, sulphur amount)



Research questions

Can hydrochars (HC) from brown macroalgae collected from the North Sea in Germany be used as fertilizer/soil amendment?

- How are the inorganic elements distributed between hydrochar (HC) and process water (PW) after HTC?
- Can HTC process parameters (temperature, solid content and process water recirculation) influence HC properties relevant for standards?



Research method

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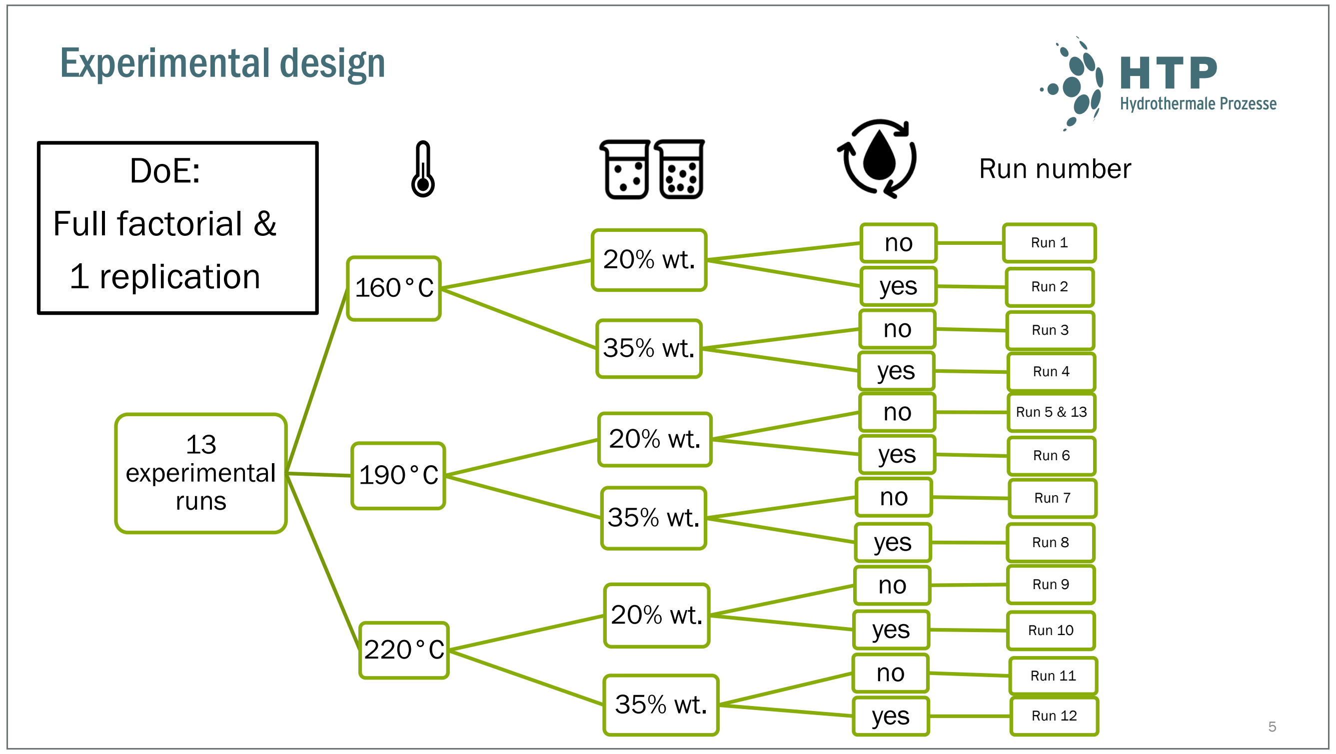
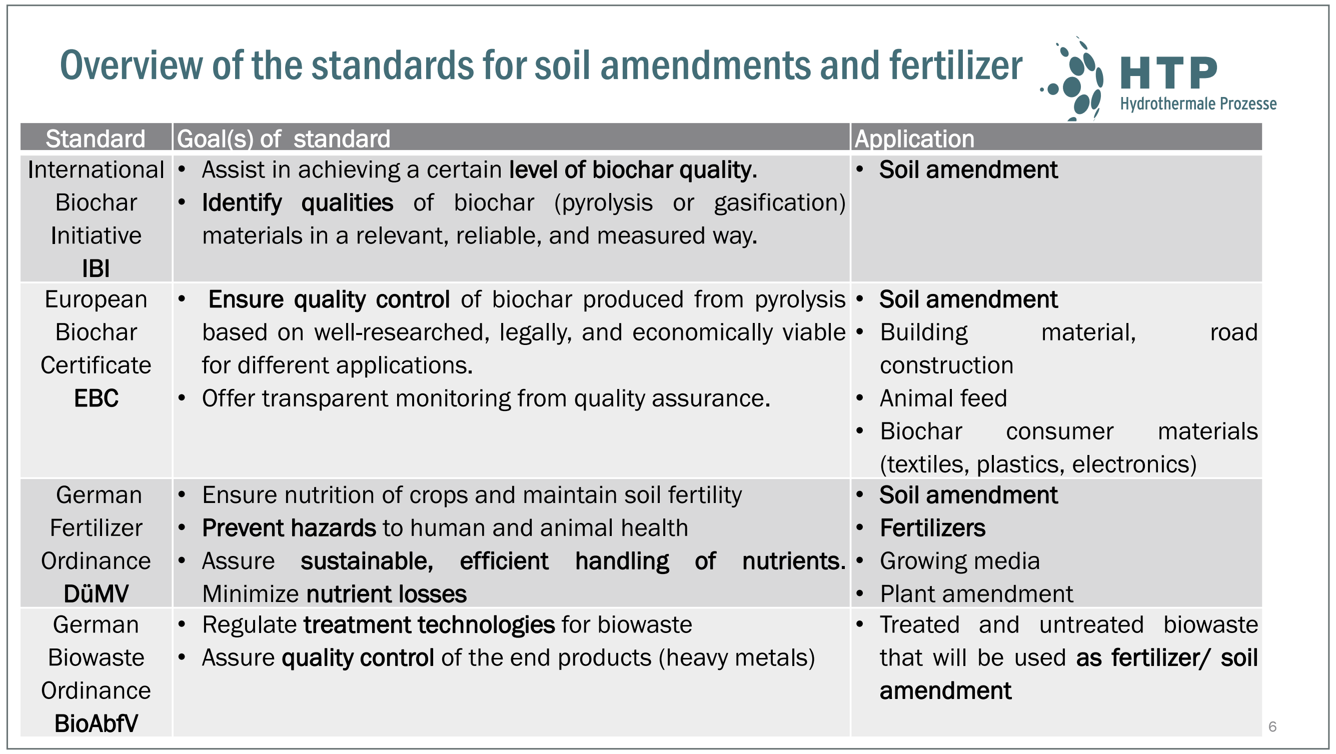


Experimental design



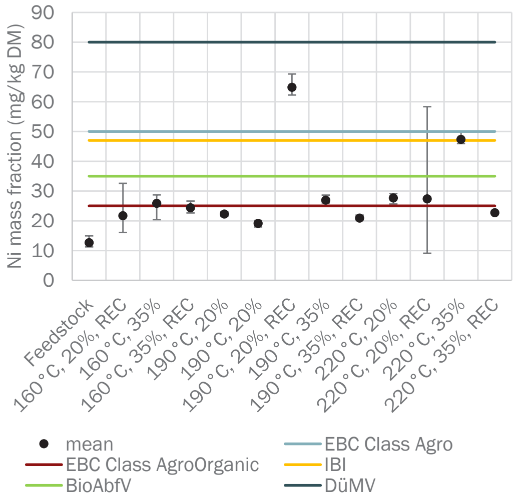
Overview of the standards for soil amendments and fertilizer

Standard	Goal(s) of standard	Application
International Biochar Initiative **IBI**	• Assist in achieving a certain **level of biochar quality.** • **Identify qualities** of biochar (pyrolysis or gasification) materials in a relevant, reliable, and measured way.	• **Soil amendment**
European Biochar Certificate **EBC**	• **Ensure quality control** of biochar produced from pyrolysis based on well-researched, legally, and economically viable for different applications. • Offer transparent monitoring from quality assurance.	• **Soil amendment** • Building material, road construction • Animal feed • Biochar consumer materials (textiles, plastics, electronics)
German Fertilizer Ordinance **DüMV**	• Ensure nutrition of crops and maintain soil fertility • **Prevent hazards** to human and animal health • Assure **sustainable, efficient handling of nutrients.** Minimize **nutrient losses**	• **Soil amendment** • **Fertilizers** • Growing media • Plant amendment
German Biowaste Ordinance **BioAbfV**	• Regulate **treatment technologies** for biowaste • Assure **quality control** of the end products (heavy metals)	• Treated and untreated biowaste that will be used **as fertilizer/ soil amendment**

Comparison of limit values with HC values

Limit values in mg/kg DM	EBC		IBI Biochar lowest	DüMV		BioAbfV
	Class Agro	Class AgroOrganic		Soil amendment	Fertilizer	
As	≤ 13	≤ 13	≤ 13	≤ 40	≤ 40	
Cd	$\leq 1{,}5$	$\leq 0{,}7$	$\leq 1{,}4$	$\leq 1{,}5$	$\leq 1{,}5$	≤ 1
Co			≤ 34			
Cr	≤ 90	≤ 70	≤ 93	≤ 300	≤ 300	≤ 70
Cu	≤ 100	≤ 70	≤ 143	≤ 700	-	≤ 70
Hg	≤ 1	$\leq 0{,}4$	≤ 1	≤ 1	≤ 1	$\leq 0{,}7$
Mo			≤ 5			
Ni	≤ 50	≤ 25	≤ 47	≤ 80	≤ 80	≤ 35
Pb	≤ 150	≤ 45	≤ 121	≤ 150	≤ 150	≤ 100
Se			≤ 2	≤ 5	≤ 5	
Tl				≤ 1	≤ 1	
Zn	≤ 400	< 200	≤ 416	≤ 1000	-	≤ 300
N				≤ 15000	≥ 10000	
P_2O_5				≤ 5000	≥ 3000	
K_2O				≤ 7500	≥ 5000	
S				≤ 3000		

Mass fraction for each element was compared to the standards



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Mass distribution between HC & PW

The distribution of element n in the hydrochar ($X_{n,HC}$) normalized to 100% output

$$X_{n,HC} = \frac{m_{n,HC}}{m_{n,HC}+m_{n,PW}} \cdot 100 \quad \text{where:}$$

$X_{n,HC}$ = mass distribution of element n in the hydrochar in %wt.

$m_{n,HC}$ = mean mass of element n in the hydrochar in mg

$m_{n,PW}$ = mean mass of element n in the process water in mg

A mean $X_{n,HC}$ for each element for the 13 runs was calculated and then assign to a category:

Label	Category	Description
All_HC	$X_{n,HC} \geq 90\%$	Almost all the mass of the n element tends to stay in the HC
Most_HC	$90\% > X_{n,HC} \geq 60\,\%$	Most of the mass of the n element tends to stay in the HC
50_50	$60\% > X_{n,HC} \geq 40\,\%$	The mass of the n element is distributed evenly in both phases, HC, and PW
Most_PW	$40\% > X_{n,HC} \geq 10\,\%$	Most of the mass of the n element tends to stay in the PW
All_PW	$10\% \geq X_{n,HC}$	Almost all the mass of the n element tends to stay in the PW

HC= hydrochar, PW=Process water

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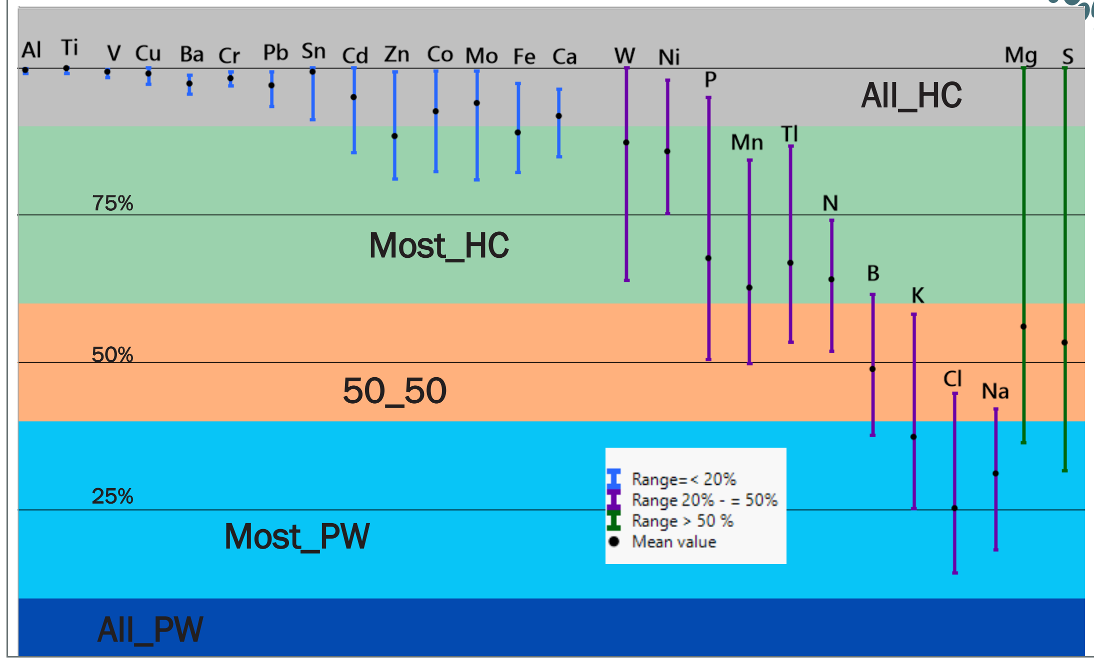
Results. Distribution of inorganic elements between HC & PW



Range for each element: Max – Min

Process conditions can influence the distribution?

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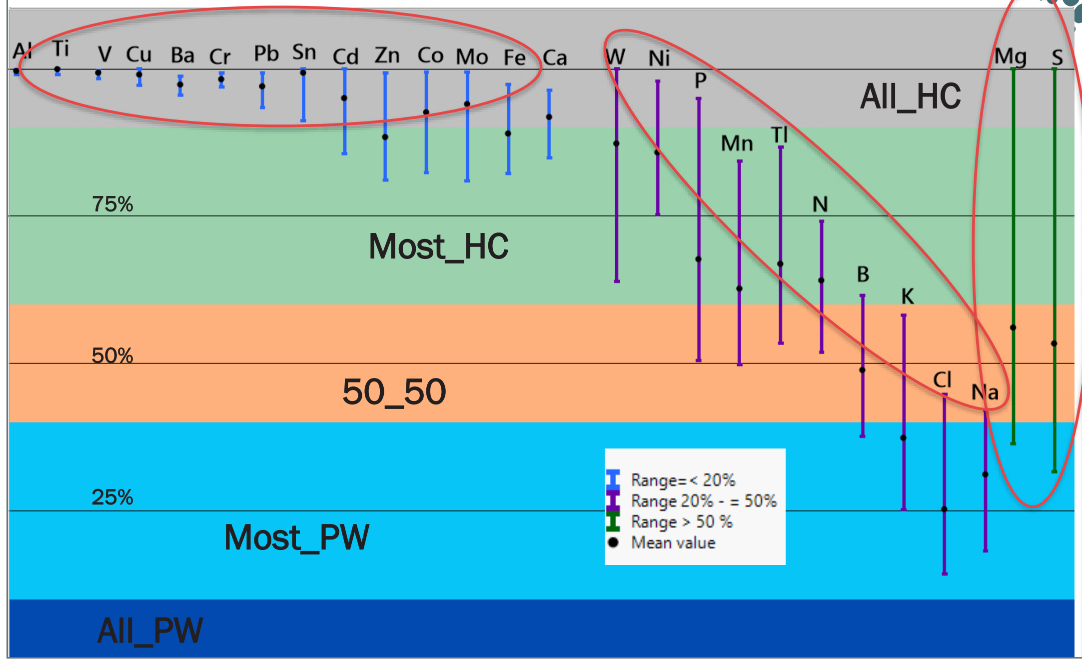
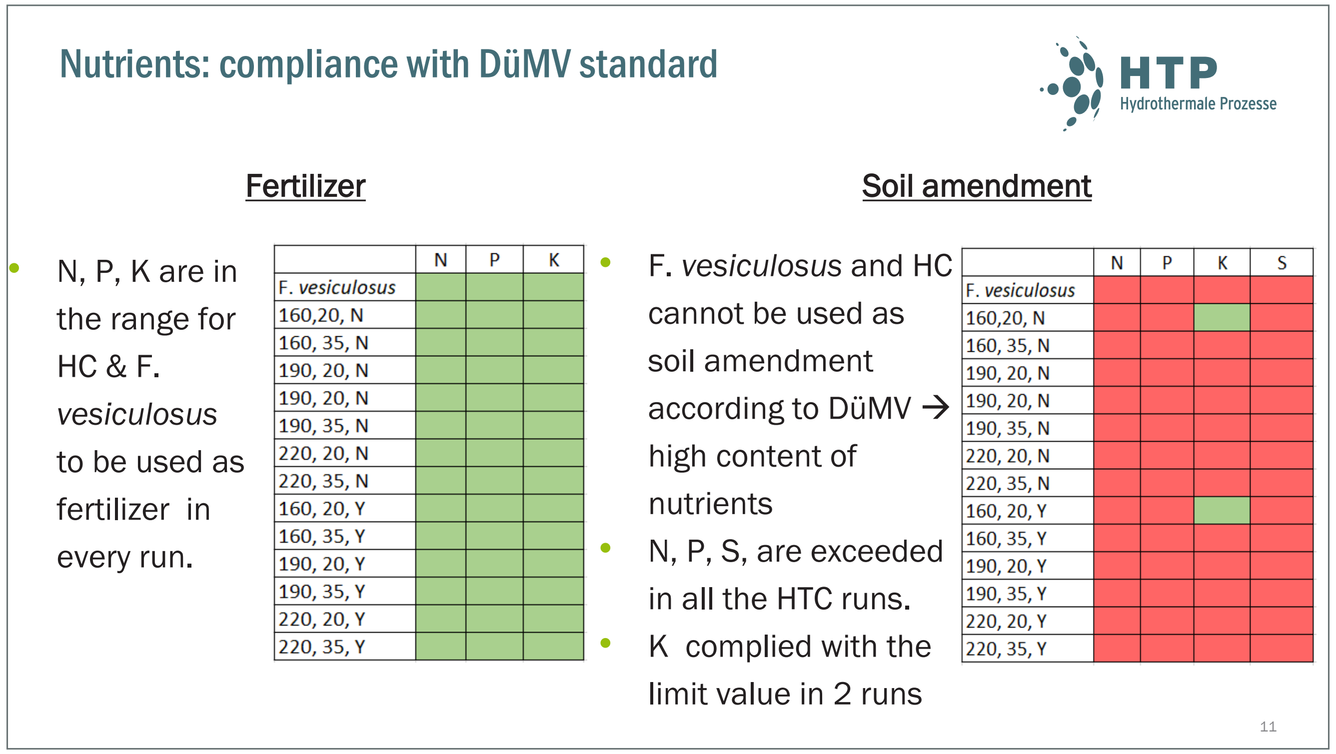
Results. Distribution of inorganic elements between HC & PW



Mg, S showed max. flexibility to change phases

Heavy metals tend to concentrate in the HC. Do not easily move from the HC.

Salts and nutrients have a moderate flexibility to change between different categories.



Nutrients: compliance with DüMV standard

Fertilizer

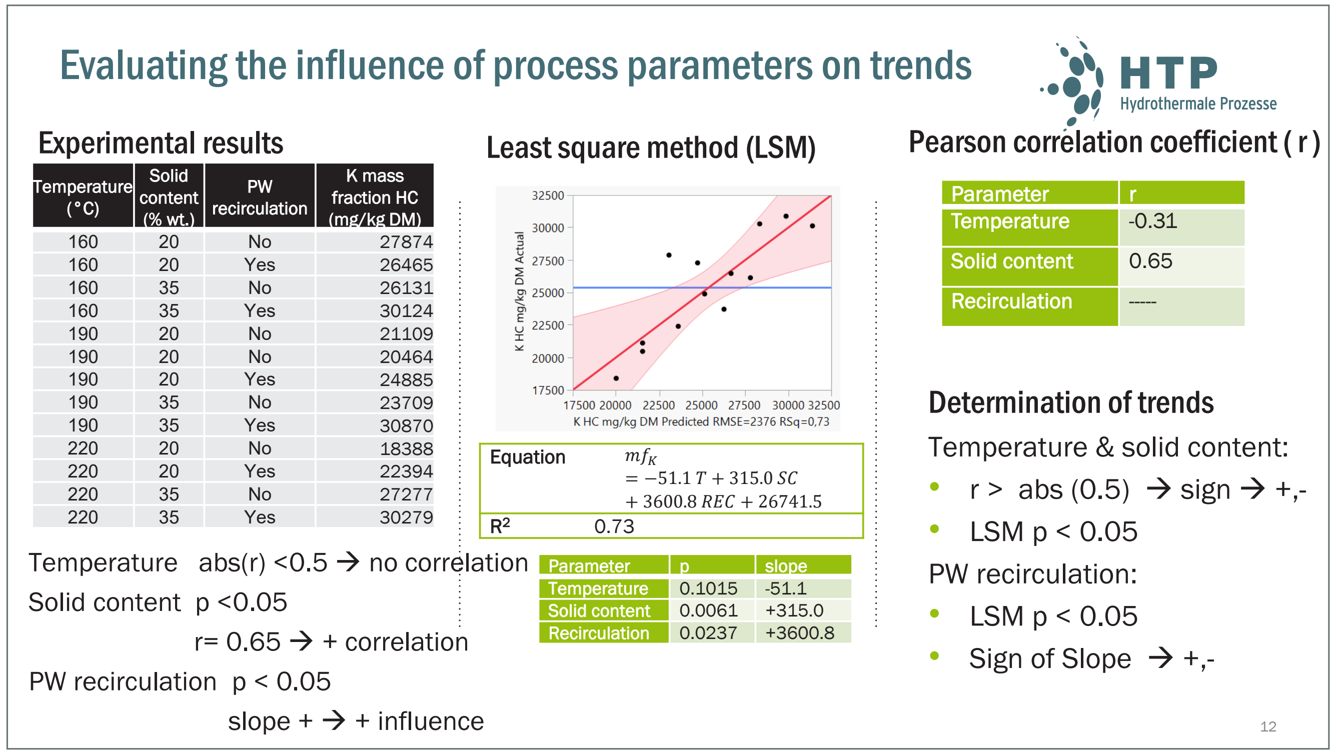
- N, P, K are in the range for HC & F. *vesiculosus* to be used as fertilizer in every run.

	N	P	K
F. *vesiculosus*	🟩	🟩	🟩
160,20, N	🟩	🟩	🟩
160, 35, N	🟩	🟩	🟩
190, 20, N	🟩	🟩	🟩
190, 20, N	🟩	🟩	🟩
190, 35, N	🟩	🟩	🟩
220, 20, N	🟩	🟩	🟩
220, 35, N	🟩	🟩	🟩
160, 20, Y	🟩	🟩	🟩
160, 35, Y	🟩	🟩	🟩
190, 20, Y	🟩	🟩	🟩
190, 35, Y	🟩	🟩	🟩
220, 20, Y	🟩	🟩	🟩
220, 35, Y	🟩	🟩	🟩

Soil amendment

- F. *vesiculosus* and HC cannot be used as soil amendment according to DüMV → high content of nutrients
- N, P, S, are exceeded in all the HTC runs.
- K complied with the limit value in 2 runs

	N	P	K	S
F. *vesiculosus*	🟥	🟥	🟥	🟥
160,20, N	🟥	🟥	🟩	🟥
160, 35, N	🟥	🟥	🟥	🟥
190, 20, N	🟥	🟥	🟥	🟥
190, 20, N	🟥	🟥	🟥	🟥
190, 35, N	🟥	🟥	🟥	🟥
220, 20, N	🟥	🟥	🟥	🟥
220, 35, N	🟥	🟥	🟥	🟥
160, 20, Y	🟥	🟥	🟩	🟥
160, 35, Y	🟥	🟥	🟥	🟥
190, 20, Y	🟥	🟥	🟥	🟥
190, 35, Y	🟥	🟥	🟥	🟥
220, 20, Y	🟥	🟥	🟥	🟥
220, 35, Y	🟥	🟥	🟥	🟥



Evaluating the influence of process parameters on trends

Experimental results

Temperature (°C)	Solid content (% wt.)	PW recirculation	K mass fraction HC (mg/kg DM)
160	20	No	27874
160	20	Yes	26465
160	35	No	26131
160	35	Yes	30124
190	20	No	21109
190	20	No	20464
190	20	Yes	24885
190	35	No	23709
190	35	Yes	30870
220	20	No	18388
220	20	Yes	22394
220	35	No	27277
220	35	Yes	30279

Temperature abs(r) <0.5 → no correlation

Solid content p <0.05

r= 0.65 → + correlation

PW recirculation p < 0.05

slope + → + influence

Least square method (LSM)

Equation	$mf_K = -51.1\,T + 315.0\,SC + 3600.8\,REC + 26741.5$
R^2	0.73

Parameter	p	slope
Temperature	0.1015	-51.1
Solid content	0.0061	+315.0
Recirculation	0.0237	+3600.8

Pearson correlation coefficient (r)

Parameter	r
Temperature	-0.31
Solid content	0.65
Recirculation	-----

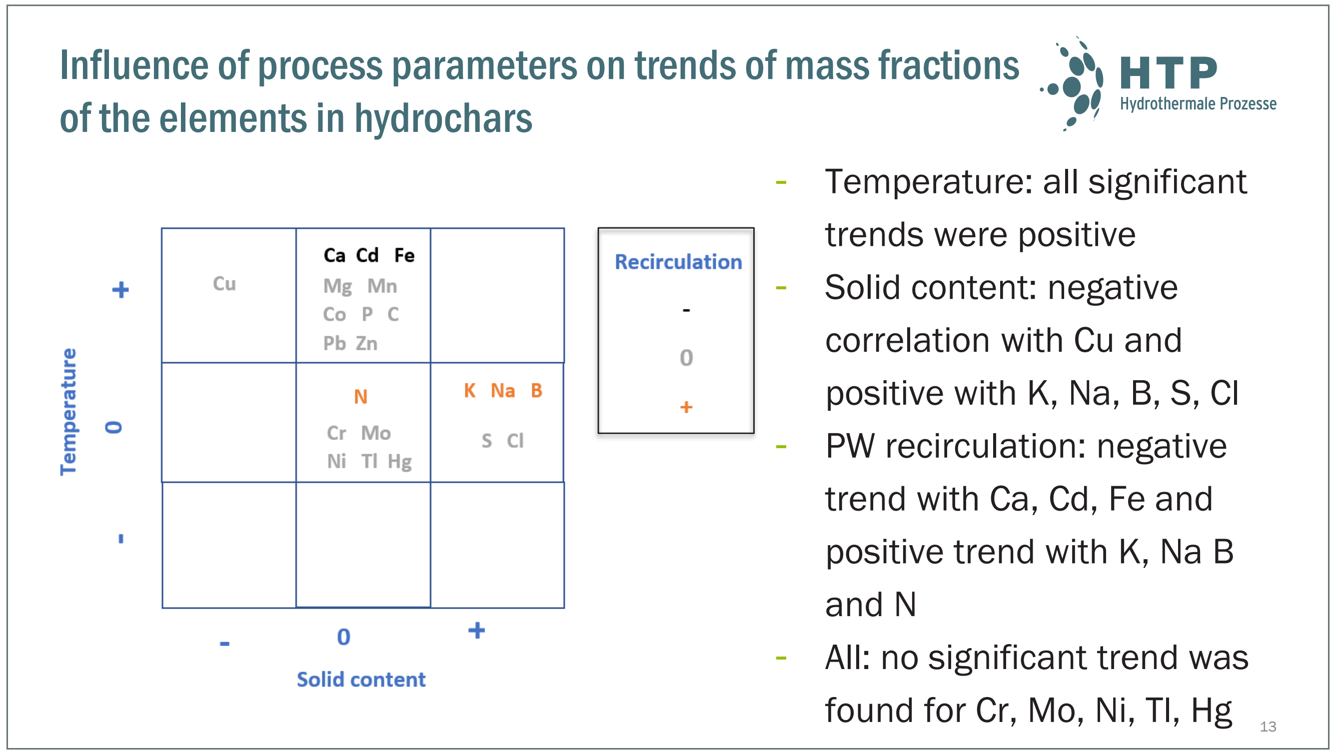
Determination of trends

Temperature & solid content:

- r > abs (0.5) → sign → +,-
- LSM p < 0.05

PW recirculation:

- LSM p < 0.05
- Sign of Slope → +,-



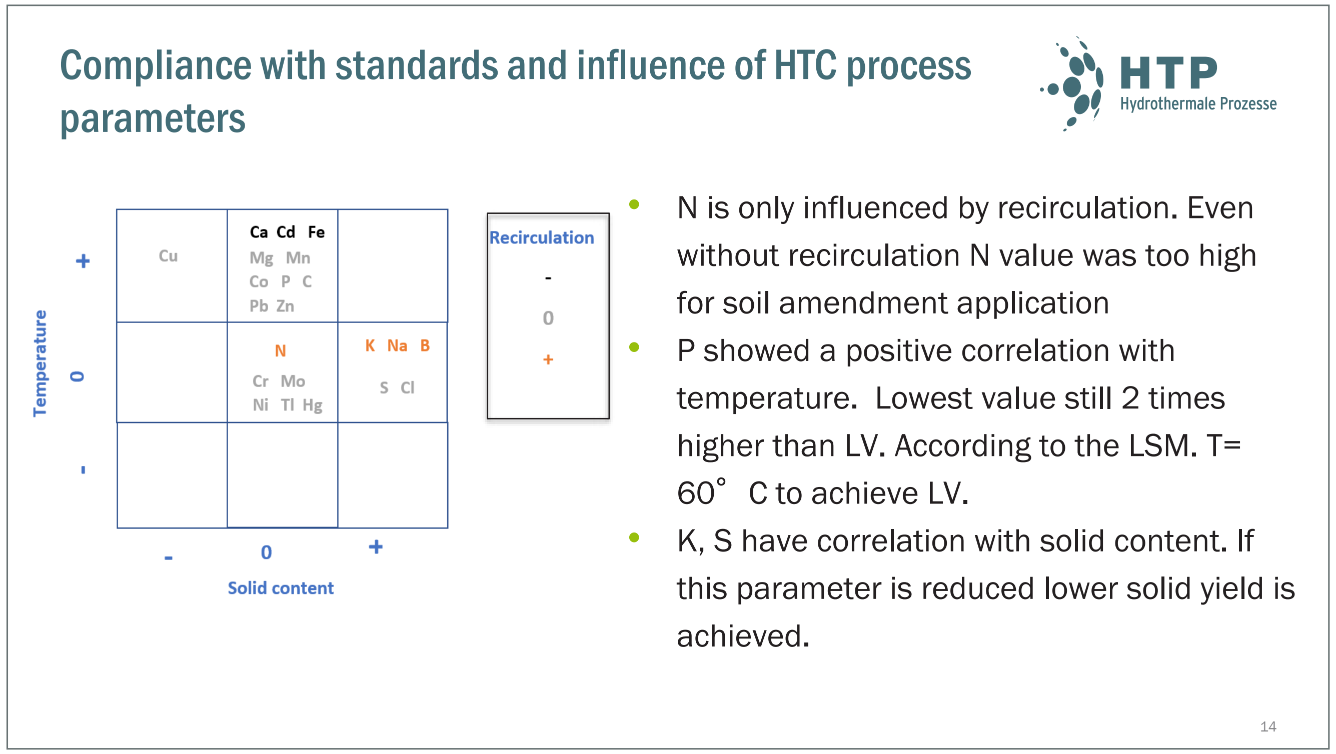
Influence of process parameters on trends of mass fractions of the elements in hydrochars

Temperature	-	0	+
+	Cu	**Ca Cd Fe** Mg Mn Co P C Pb Zn	
0		N Cr Mo Ni Tl Hg	K Na B S Cl
-			

Solid content

Recirculation
-
0
+

- Temperature: all significant trends were positive
- Solid content: negative correlation with Cu and positive with K, Na, B, S, Cl
- PW recirculation: negative trend with Ca, Cd, Fe and positive trend with K, Na B and N
- All: no significant trend was found for Cr, Mo, Ni, Tl, Hg



Compliance with standards and influence of HTC process parameters

Temperature	-	0	+
+	Cu	Ca Cd Fe Mg Mn Co P C Pb Zn	
0		N Cr Mo Ni Tl Hg	K Na B S Cl
-			

Solid content

Recirculation
-
0
+

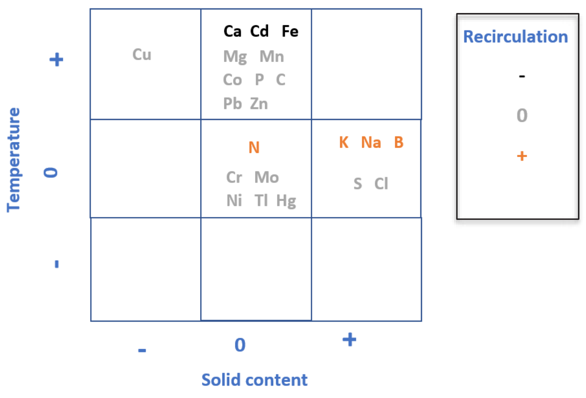
- N is only influenced by recirculation. Even without recirculation N value was too high for soil amendment application
- P showed a positive correlation with temperature. Lowest value still 2 times higher than LV. According to the LSM. T= 60° C to achieve LV.
- K, S have correlation with solid content. If this parameter is reduced lower solid yield is achieved.

Compliance with standards: Heavy metals

- Heavy metals are regulated similarly for SA and F in the DüMV. Except for Cu & Zn.
- HC cannot be used as soil amendments nor fertilizers since Cd and Tl mass fractions surpassed the limit values.
- B, Cr, Mo, Ni sometimes are below LV

	As	Cd	Co	Cr			Cu	Hg	Mo	Ni				Pb	Se	Tl	Zn
	EBC IBI DüMV	All	IBI	BioAbfV EBC AgroOrg	IBI EBC Agro	DüMV	All (Except DüMV Fertilizer)	All	IBI	EBCagrorg	BioAbfV	IBI EBC Agro	DüMV	All	IBI DüMV	DüMV	All (Except DüMV Fertilizer)
F. *vesiculosus*	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩
160,20, N	🟩	🟥	🟩	🟥	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩
160, 35, N	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟥	🟩
190, 20, N	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩
190, 20, N	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩
190, 35, N	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟥	🟩
220, 20, N	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟥	🟩
220, 35, N	🟩	🟥	🟩	🟥	🟥	🟩	🟩	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩	🟥	🟩
160, 20, Y	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩
160, 35, Y	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟥	🟩
190, 20, Y	🟩	🟥	🟩	🟥	🟥	🟩	🟩	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩	🟥	🟩
190, 35, Y	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩
220, 20, Y	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟥	🟩
220, 35, Y	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩

Compliance with standards and influence of HTC process parameters



- Tl did not show any significant trend with any of the three HTC process parameters
- Cd was lowest at low temperature and without recirculation of PW. According to the LSM a temperature of 40° C would be needed to achieve the LV of 1,5 mg/kg DM.
- Post treatments will be needed to treat Cd and Tl in the HC to reach LV or pre-treatments in the F. *vesiculosus*.

Conclusions (1)

Can hydrochars (HC) from brown macroalgae collected from the North Sea in Germany be used as soil amendment?

Heavy metals:

- Standards for chars produced from HTC do not exist yet.
- Most of the heavy metals in the feedstock and HCs complied with the limit values of the standards (IBI, EBC, DüMV and BioAbfV). Exceptions: Cd (for all standards) and Tl (for DüMV). No other standard regulates Tl.
- Cd could not be reduced in the hydrochar because it has a positive correlation with temperature.
- No parameter studied had any influence on Tl.
- If the feedstock contains Tl and Cd above the LV → Post-treatment will be needed to reduce them. HTC did not reduce the values.

Conclusion (2)

Nutrients in soil amendments:

- Only DüMV has maximum values for N,P, K and S as soil amendment. All HC were over these limit values (except for K in 2 runs).
- Further HTC parameters and ranges should be analyzed to find out stronger correlations to achieve nutrients values in the range.

Nutrients in fertilizers:

- According to DüMV: nutrients LV were met by all HC but heavy metals Cd, Tl were not.
- Process parameters for maximal recovery of N,P,K: N and K with recirculation, P at high temperatures, K at high solid content.

7. HTP-Fachforum | 27./28. September 2022
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Thank you for your attention!

www.htp-inno.de

7. HTP-Fachforum
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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Projekt abonoCARE: Bau einer HTC-Technikumsanlage mit integrierter Heißentwässerung

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Die Novellierung der Klärschlammverordnung 2017 schreibt Klärwerken mit einer Auslegungsgröße von über 100.000 Einwohnergleichwerten (EW) eine Phosphorrückgewinnung ab 2029 vor, wenn der entstehende Klärschlamm einen Phosphorgehalt über 20 g je kg Trockenmasse aufweist. Die Phosphorrückgewinnung muss rechtssicher nachgewiesen werden, sodass eine Mitverbrennung von betroffenen Klärschlämmen in Müllverbrennungsanlagen oder Zementwerken als Entsorgungsweg nicht mehr möglich ist. Eine vielversprechende Alternative zu Monoverbrennungsanlagen ist eine dezentrale Anlage, die vor der Verbrennung Phosphor zurückgewinnt, sodass der P-abgereicherte Klärschlamm weiterhin in Bestandsanlagen für die Mitverbrennung eingebracht werden kann.

Ein weiteres Problem bei der derzeitigen Klärschlammentsorgung ist der hohe Wassergehalt. Klärschlamm wird aktuell mittels mechanischer Entwässerungsverfahren auf ca. 20–30 % Trockenmasse entwässert. Der hohe Wassergehalt führt zu hohen Logistik- und Entsorgungskosten. Die hydrothermale Carbonisierung (HTC) erfolgt bei hohen Temperaturen und Drücken, sodass gebundenes Wasser (Zellinnenwasser, Zwischenraumwasser und Oberflächenwasser) nach der Behandlung verfügbar und durch eine anschließende mechanische Entwässerung leichter zu entfernen ist (Kopp, 2001).

Im Projekt abonoCARE wurde eine HTC-Technikumsanlage mit einem Zieldurchsatz an Klärschlamm von 30 kg/d konstruiert, die mit einer gekoppelten Heißentwässerung gleich zwei Probleme der Klärschlammentsorgung adressiert. Zum einen wird Phosphor durch den Einsatz von Säuren während der HTC aus Klärschlamm extrahiert, zum anderen wird der behandelte Klärschlamm in der gekoppelten Heißentwässerung auf höhere Trockensubstanzgehalte von bis zu 50 % entwässert. Eine Kopplung der Heißentwässerung an den Prozess der HTC ermöglicht, dass ein Teil der Wärme und des Drucks direkt für die Entwässerung genutzt werden können. Mit der neuen Technikumsanlage wird systematisch untersucht, welchen Einfluss die HTC-Versuchsparameter auf die Heißentwässerung haben und inwiefern unterschiedliche Hubzeiten dieser Heißentwässerung den Entwässerungsgrad verändern. Außerdem ist ein detaillierter Probenahmeplan für die quasikontinuierlichen Versuche entwickelt worden. Dieser Vortrag stellt konkrete Ergebnisse dieser Versuche vor.

7. HTP-Fachforum | 27./28. September 2022
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

Project abonoCARE: Construction of an HTC pilot plant with integrated hot dewatering

Lisa Röver, Hendrik Etzold, Benjamin Herklotz
DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH

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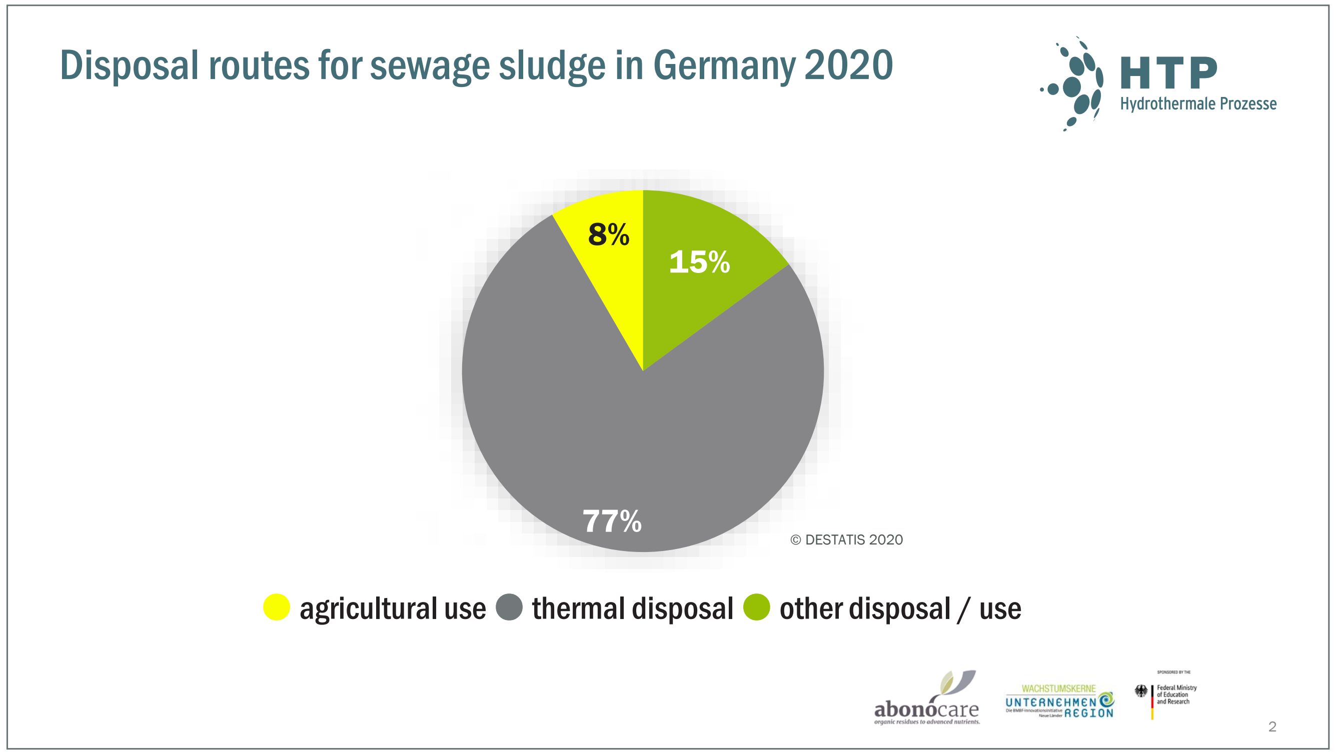


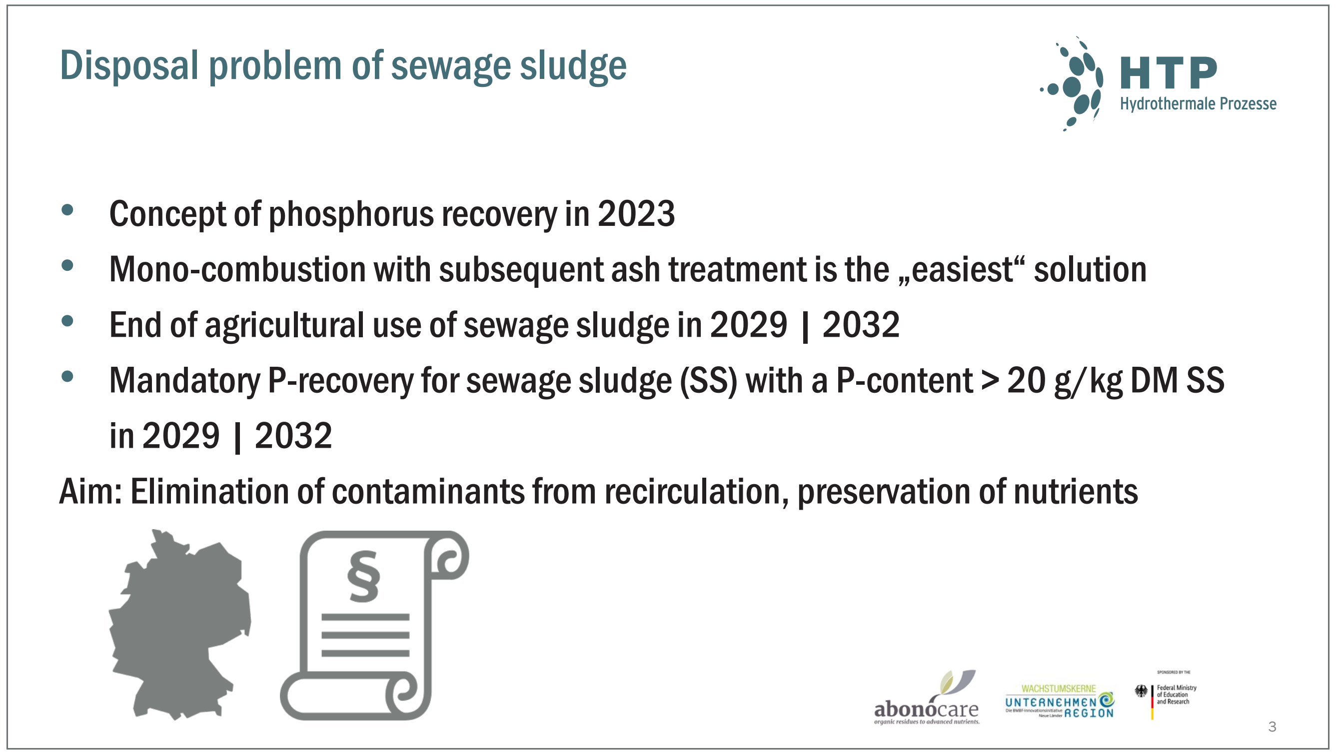
Disposal routes for sewage sludge in Germany 2020

HTP Hydrothermale Prozesse

● agricultural use ● thermal disposal ● other disposal / use

abonocare

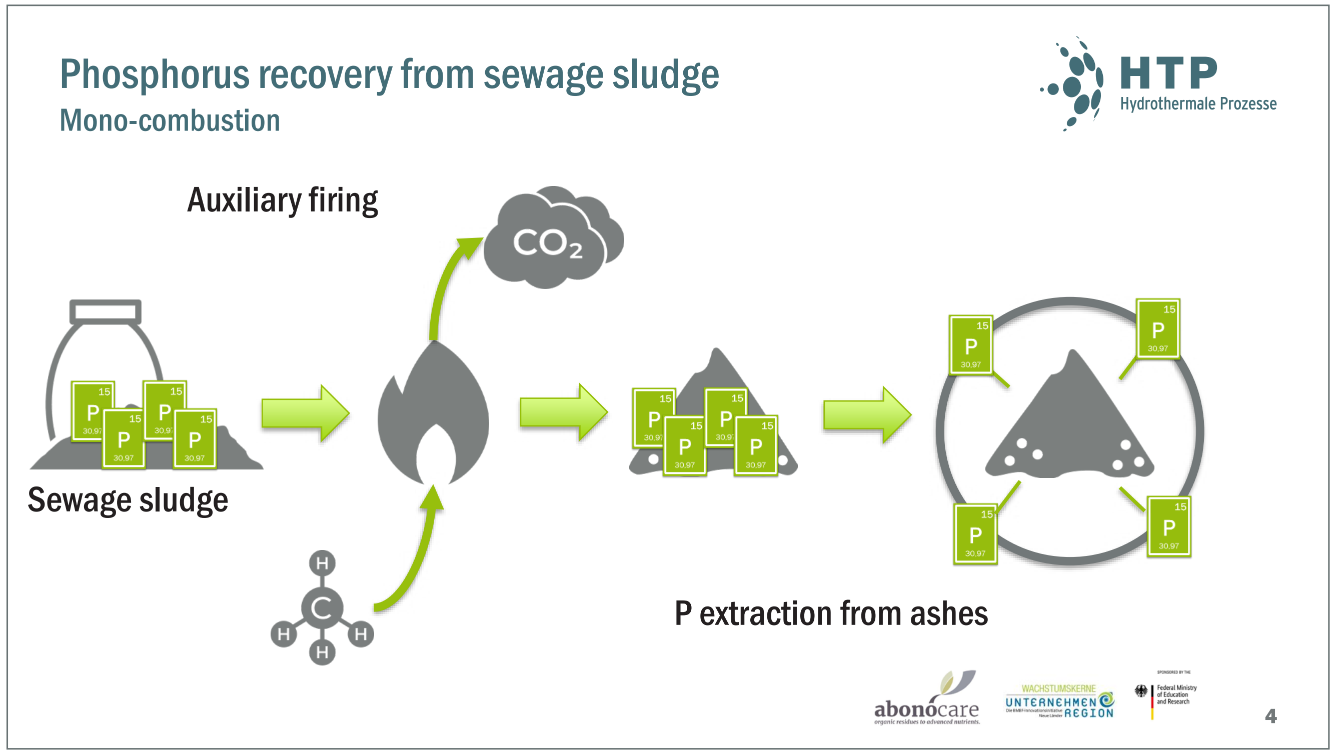
2



Disposal problem of sewage sludge

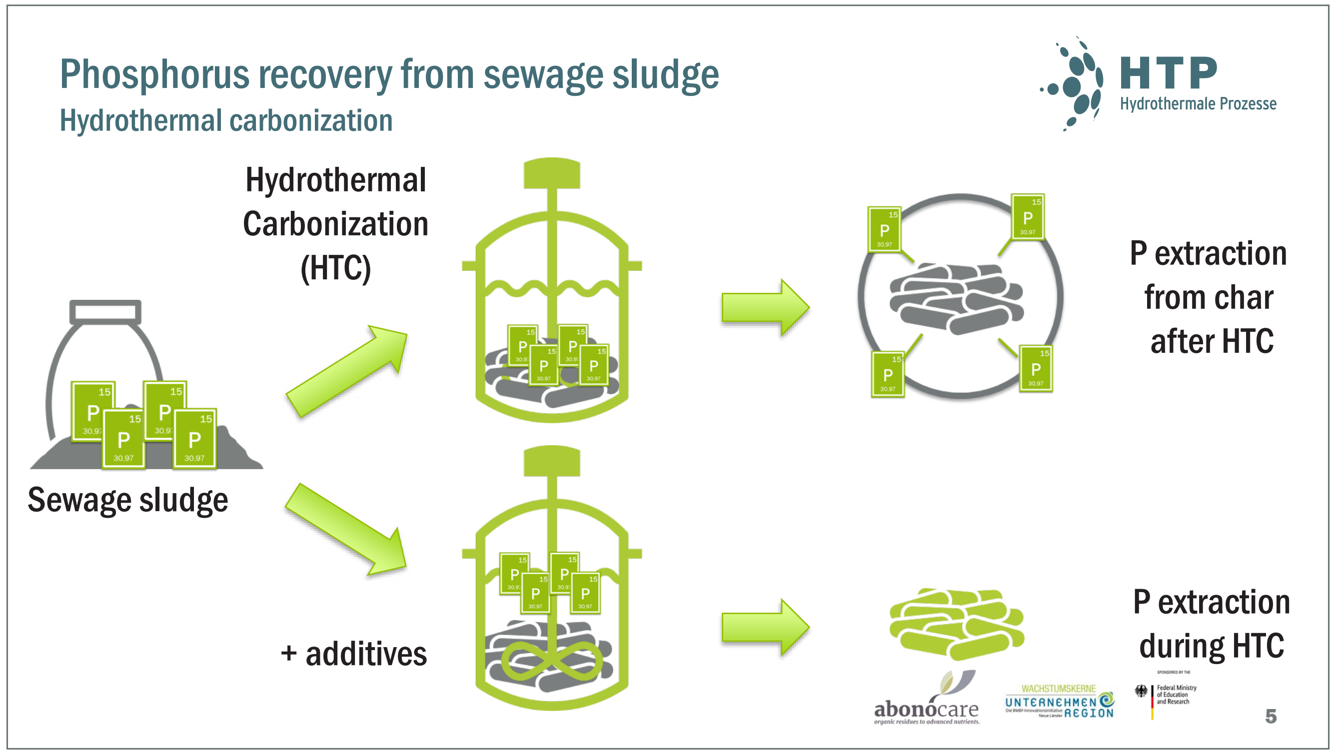
- Concept of phosphorus recovery in 2023
- Mono-combustion with subsequent ash treatment is the „easiest“ solution
- End of agricultural use of sewage sludge in 2029 | 2032
- Mandatory P-recovery for sewage sludge (SS) with a P-content > 20 g/kg DM SS in 2029 | 2032

Aim: Elimination of contaminants from recirculation, preservation of nutrients



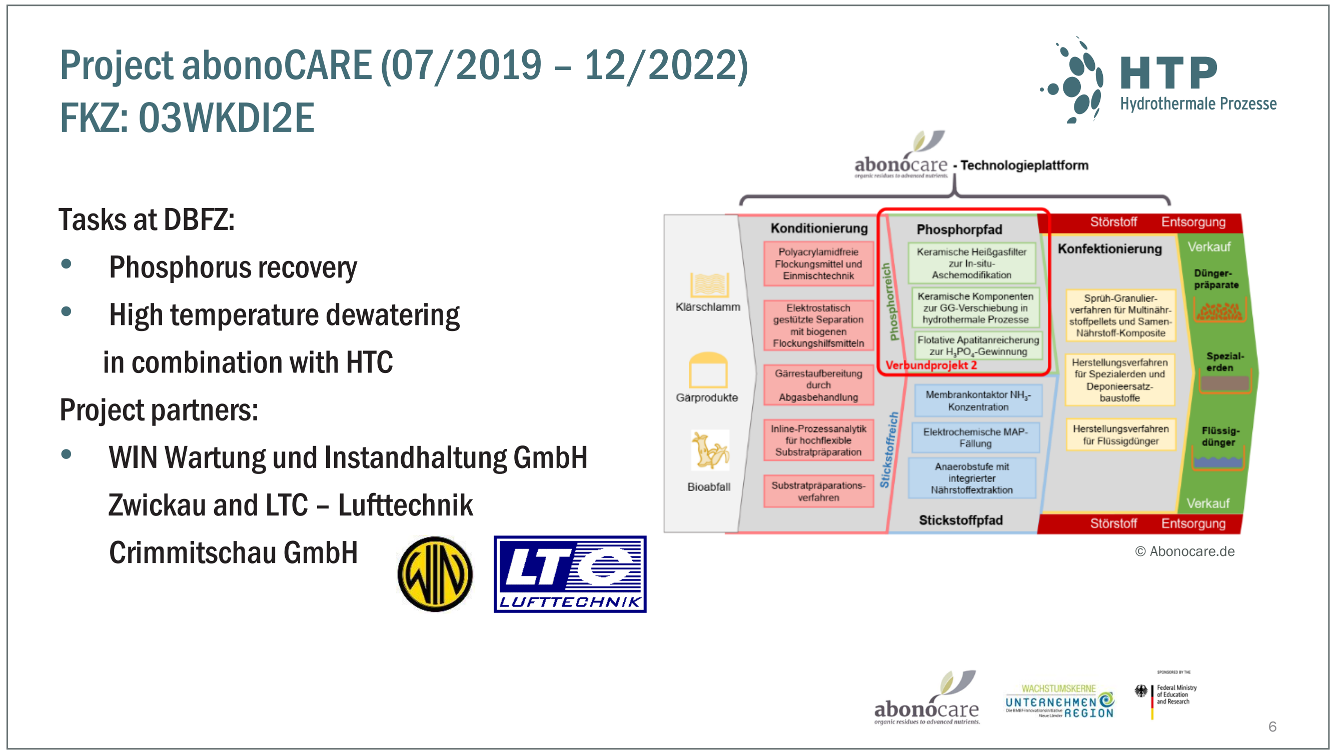
Phosphorus recovery from sewage sludge

Mono-combustion



Phosphorus recovery from sewage sludge

Hydrothermal carbonization



Project abonoCARE (07/2019 – 12/2022)

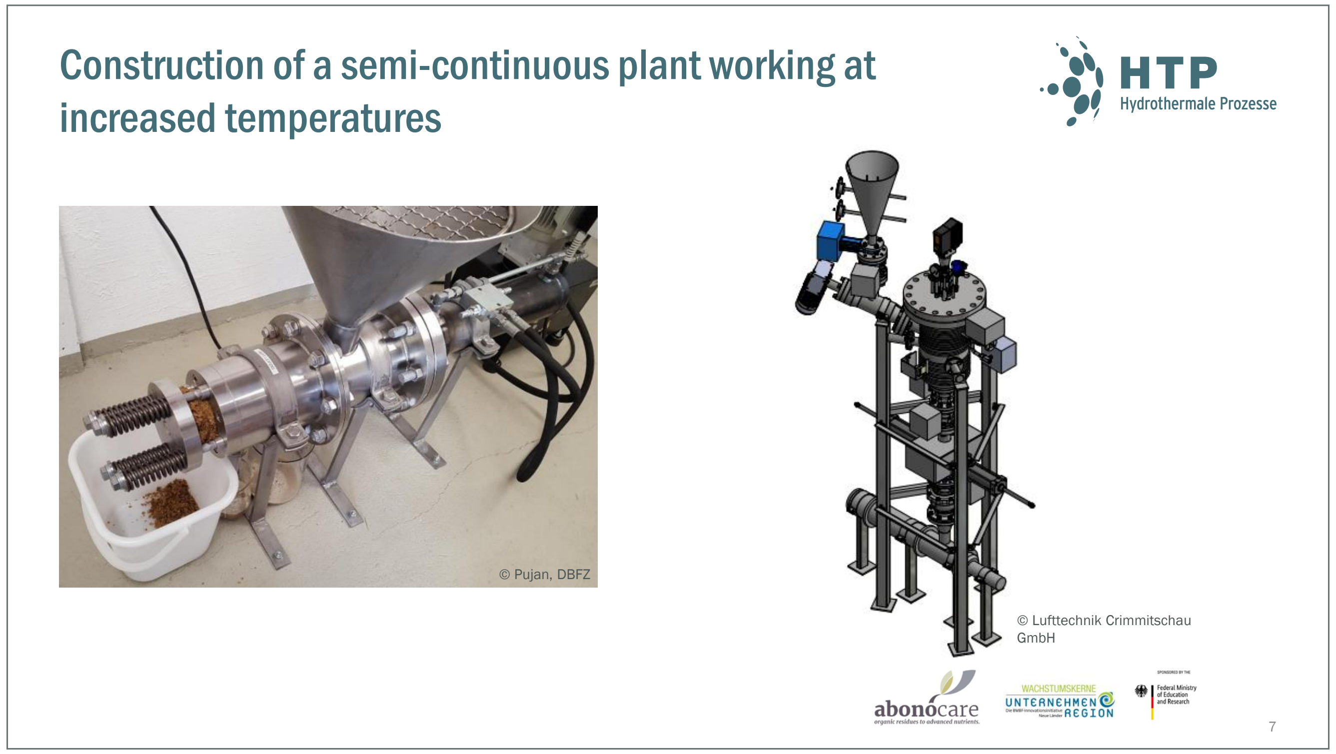
FKZ: 03WKDI2E

Tasks at DBFZ:

- Phosphorus recovery
- High temperature dewatering in combination with HTC

Project partners:

- WIN Wartung und Instandhaltung GmbH Zwickau and LTC – Lufttechnik Crimmitschau GmbH



Construction of a semi-continuous plant working at increased temperatures

© Pujan, DBFZ

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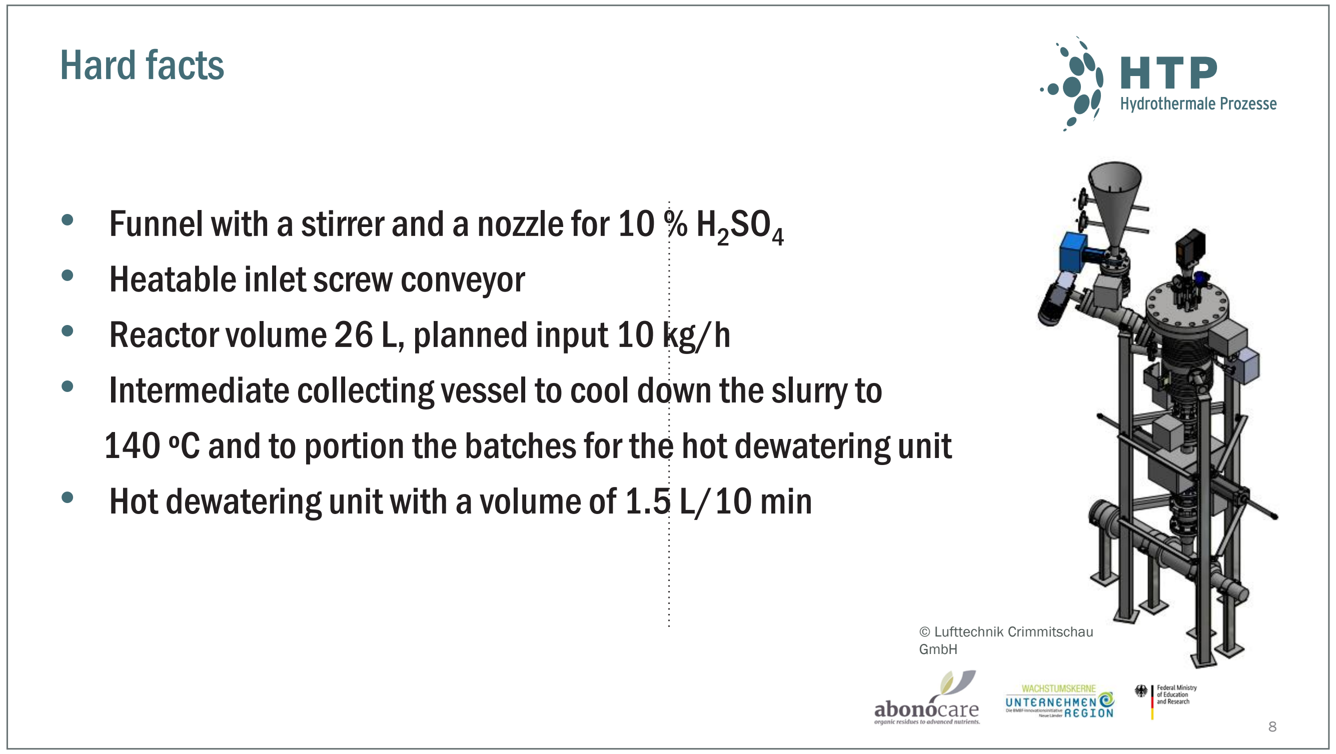

Hard facts

- Funnel with a stirrer and a nozzle for 10 % H_2SO_4
- Heatable inlet screw conveyor
- Reactor volume 26 L, planned input 10 kg/h
- Intermediate collecting vessel to cool down the slurry to 140 °C and to portion the batches for the hot dewatering unit
- Hot dewatering unit with a volume of 1.5 L/10 min

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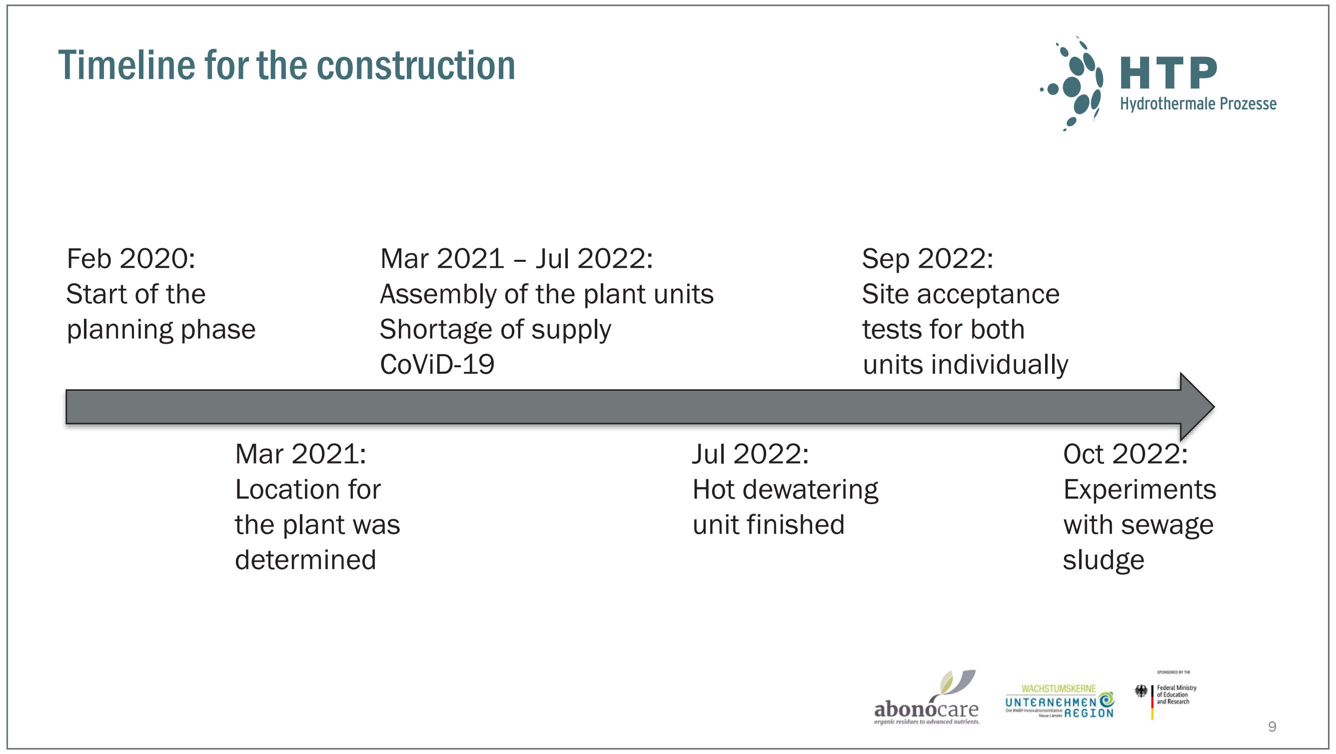


Timeline for the construction

Feb 2020:
Start of the planning phase

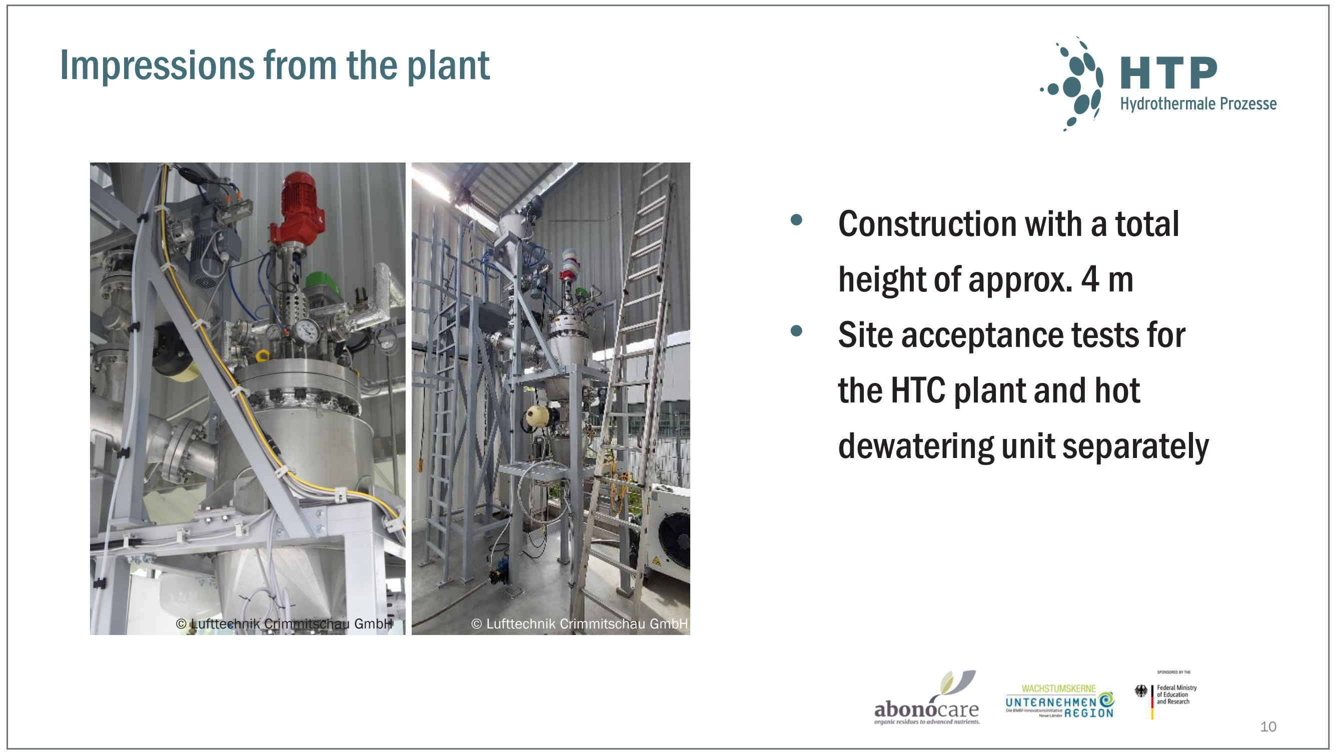
Mar 2021:
Location for the plant was determined

Mar 2021 – Jul 2022:
Assembly of the plant units
Shortage of supply
CoViD-19

Jul 2022:
Hot dewatering unit finished

Sep 2022:
Site acceptance tests for both units individually

Oct 2022:
Experiments with sewage sludge



Impressions from the plant

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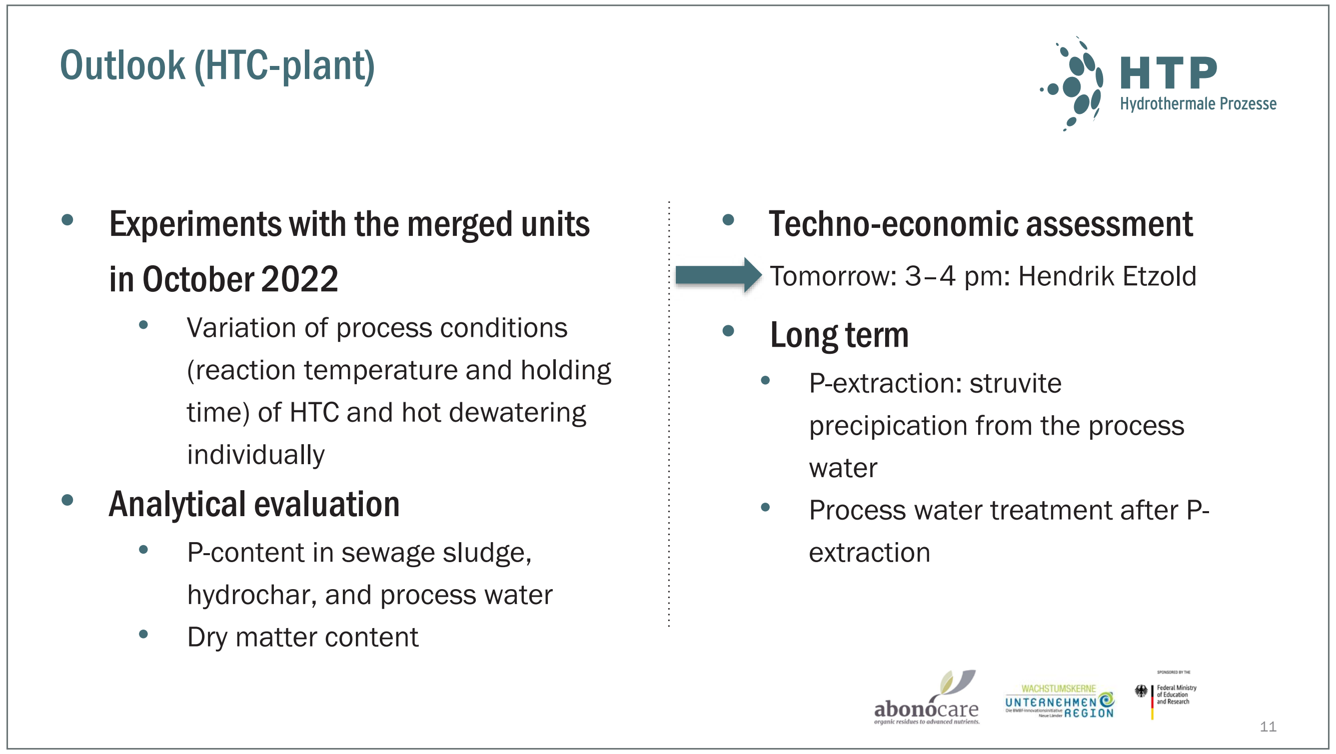
- Construction with a total height of approx. 4 m
- Site acceptance tests for the HTC plant and hot dewatering unit separately



Outlook (HTC-plant)

HTP Hydrothermale Prozesse

- Experiments with the merged units in October 2022
  - Variation of process conditions (reaction temperature and holding time) of HTC and hot dewatering individually
- Analytical evaluation
  - P-content in sewage sludge, hydrochar, and process water
  - Dry matter content

- Techno-economic assessment

→ Tomorrow: 3–4 pm: Hendrik Etzold

- Long term
  - P-extraction: struvite precipication from the process water
  - Process water treatment after P-extraction

Acknowledgements

HTP Hydrothermale Prozesse

Thank you for your attention!

This work was funded by the Federal Ministry of Education and Research under Grant No. 03WKDI2E

abonocare
organic residues to advanced nutrients.

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7. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

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Tommy Ender, Universität Rostock

Prozesswässer aus der hydrothermalen Karbonisierung von Abfällen – Ein Konzept zur Aufbereitung und Nährstoffrückgewinnung

Tommy Ender, Prof. Dr. mont. Michael Nelles, Dipl.-Ing. Stepan Kusche
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Die Hydrothermale Karbonisierung (HTC) ist eine vielversprechende Alternative zur weit verbreiteten thermischen Klärschlammverwertung. Wasser ist bei der HTC nicht nur das umgebende Medium, sondern auch Reaktionspartner und Lösungsmittel. Aus diesem Grund entsteht neben dem Biomassekarbonisat als Hauptprodukt (auch HTC-Kohle genannt) auch eine signifikante Menge an Prozesswasser. Der Prozesswasseranfall variiert unter anderem von der eingesetzten Biomasse. Das Prozesswasser ist heterogen zusammengesetzt und mit CSB-Konzentrationen zwischen 5 und 74 g/l organisch belastet. Das CSB/BSB5-Verhältnis liegt in günstigen Fällen bei 2, in der Regel jedoch bei 3-4, welches eine biologische Abbaubarkeit erschweren kann. Neben den organischen Inhaltsstoffen enthält das Prozesswasser aber auch Nährstoffe, die man zurückgewinnen kann. Dies zu erreichen ist Ziel des laufenden Forschungsprojekts, welches gemeinsam mit der HTCycle AG durchgeführt wird. In gekoppelten Labor- und Technikumsversuchen sollen zunächst kommunale Klärschlämme karbonisiert werden. Nach anschließender Fest-/Flüssigtrennung sollen die Abwässer aus der HTC analysiert und aufbereitet werden. Als Ziel wird die zuverlässige Aufbereitung für die geforderte Indirekteinleiterqualität sowie Rückgewinnung von Nährstoffen aus den HTC-Prozesswässern angestrebt. Die Nährstoffe sollen in ein düngefähiges Rezyklat überführt und für mögliche Pflanzversuchen bereitgestellt werden. Schlussendlich soll ein stabiles und reproduzierbares Konzept zur Aufbereitung und Nährstoffrückgewinnung vorliegen, welches in den technischen Maßstab umgesetzt und angewendet werden kann.

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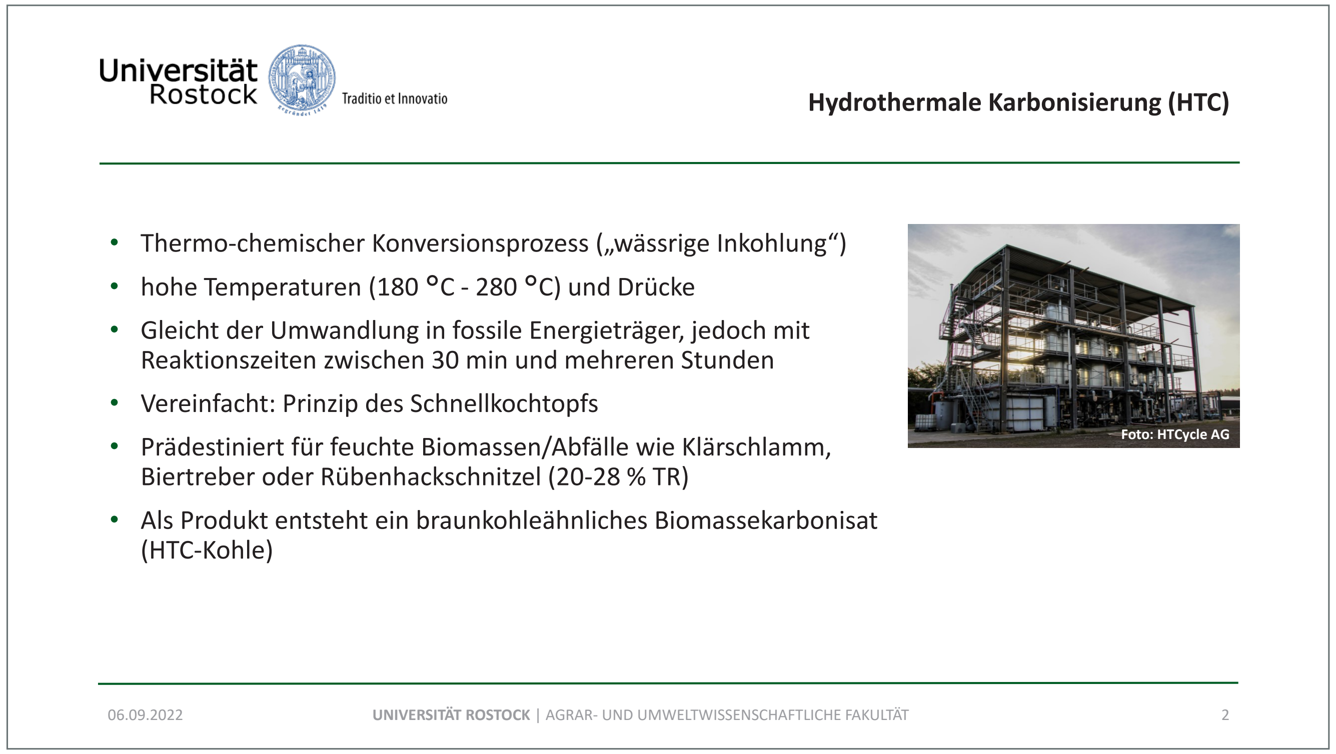
HTP Hydrothermale Prozesse

Prozesswässer aus der hydrothermalen Karbonisierung von Abfällen – Ein Konzept zur Aufbereitung und Nährstoffrückgewinnung

Tommy Ender

Universität Rostock, Professur Abfall- und Stoffstromwirtschaft

06.09.2022 **UNIVERSITÄT ROSTOCK** | AGRAR- UND UMWELTWISSENSCHAFTLICHE FAKULTÄT 1



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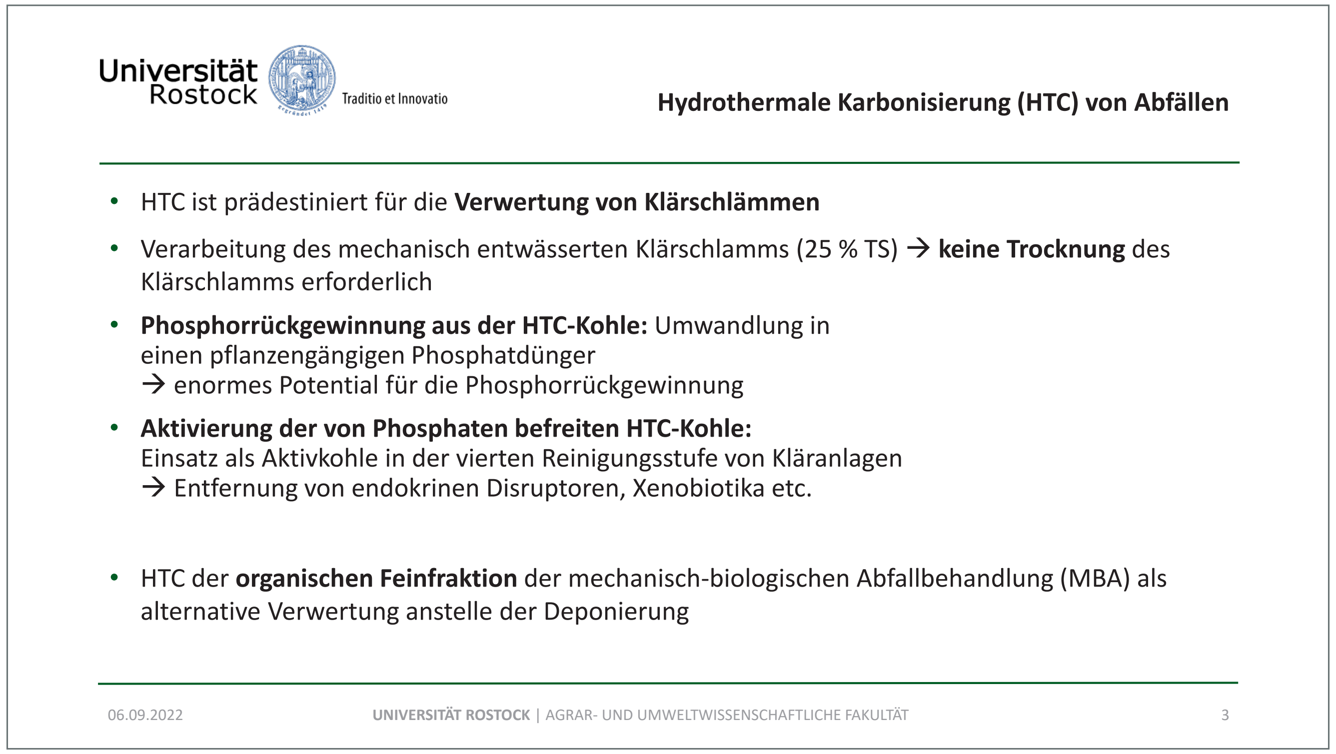
Hydrothermale Karbonisierung (HTC)

- Thermo-chemischer Konversionsprozess („wässrige Inkohlung“)
- hohe Temperaturen (180 °C - 280 °C) und Drücke
- Gleicht der Umwandlung in fossile Energieträger, jedoch mit Reaktionszeiten zwischen 30 min und mehreren Stunden
- Vereinfacht: Prinzip des Schnellkochtopfs
- Prädestiniert für feuchte Biomassen/Abfälle wie Klärschlamm, Biertreber oder Rübenhackschnitzel (20-28 % TR)
- Als Produkt entsteht ein braunkohleähnliches Biomassekarbonisat (HTC-Kohle)

Foto: HTCycle AG

06.09.2022 **UNIVERSITÄT ROSTOCK** | AGRAR- UND UMWELTWISSENSCHAFTLICHE FAKULTÄT 2



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Hydrothermale Karbonisierung (HTC) von Abfällen

- HTC ist prädestiniert für die **Verwertung von Klärschlämmen**
- Verarbeitung des mechanisch entwässerten Klärschlamms (25 % TS) → **keine Trocknung** des Klärschlamms erforderlich
- **Phosphorrückgewinnung aus der HTC-Kohle:** Umwandlung in einen pflanzengängigen Phosphatdünger
  → enormes Potential für die Phosphorrückgewinnung
- **Aktivierung der von Phosphaten befreiten HTC-Kohle:**
  Einsatz als Aktivkohle in der vierten Reinigungsstufe von Kläranlagen
  → Entfernung von endokrinen Disruptoren, Xenobiotika etc.

- HTC der **organischen Feinfraktion** der mechanisch-biologischen Abfallbehandlung (MBA) als alternative Verwertung anstelle der Deponierung

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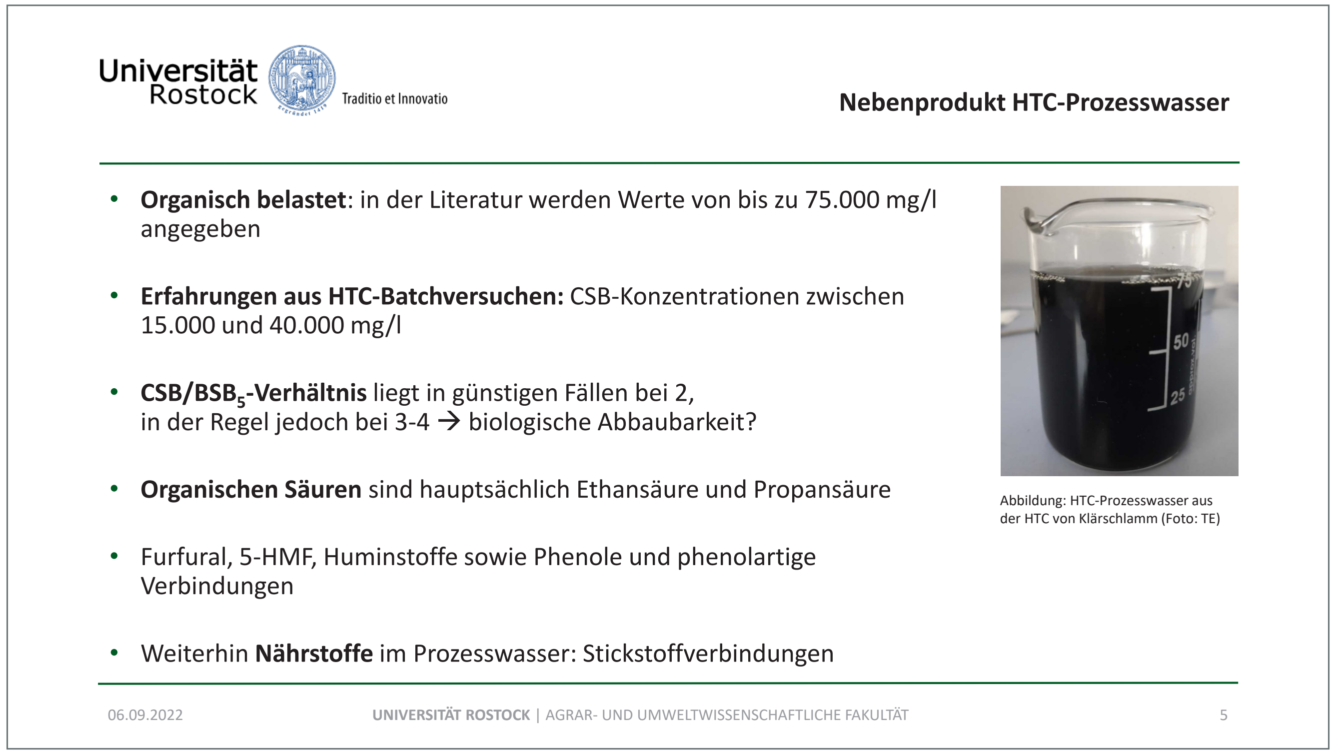
Versuchsanlagen zur HTC im Batchverfahren

Parr 4523 Bench Top Reactor (Foto: TE)

K-335 HTC Technikumsanlage (Foto: TE)

HTC-1 Industrie- und Demonstrationsanlage (Foto: HTCycle AG)



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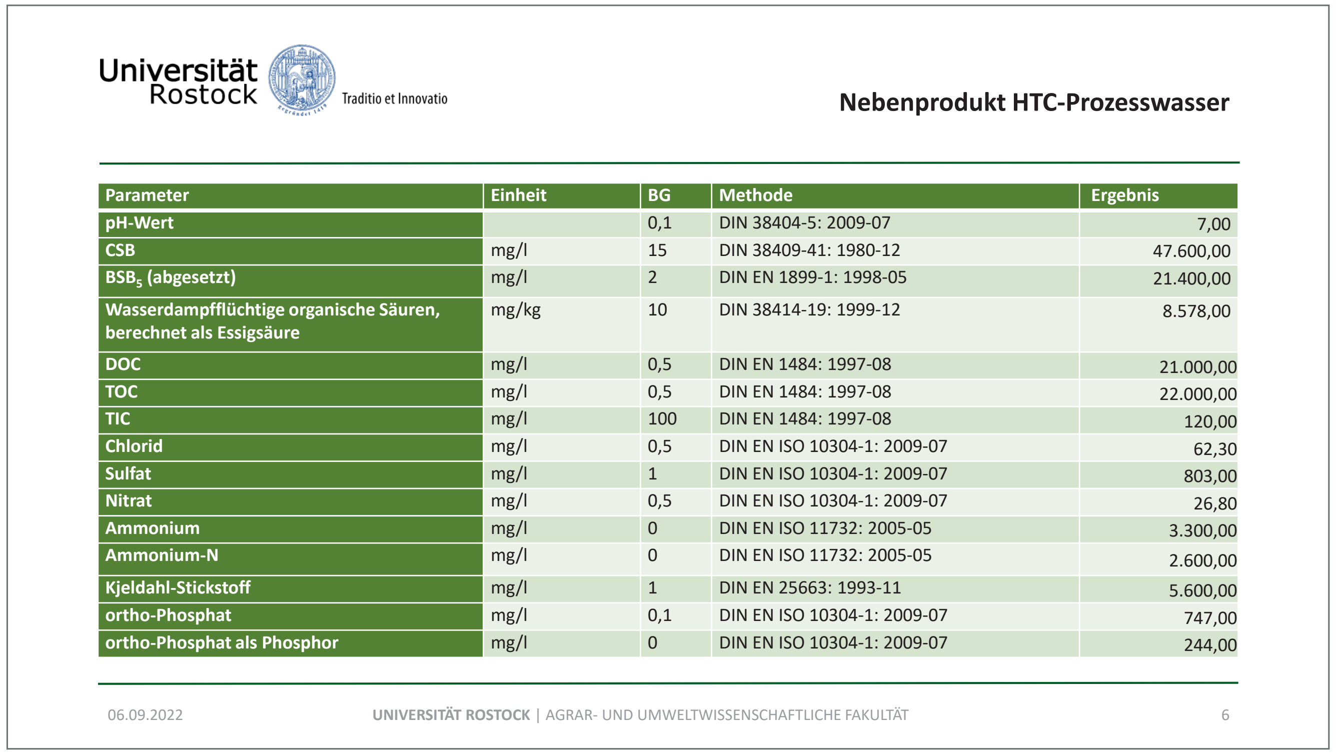
Nebenprodukt HTC-Prozesswasser

- **Organisch belastet**: in der Literatur werden Werte von bis zu 75.000 mg/l angegeben
- **Erfahrungen aus HTC-Batchversuchen:** CSB-Konzentrationen zwischen 15.000 und 40.000 mg/l
- **CSB/BSB$_5$-Verhältnis** liegt in günstigen Fällen bei 2,
  in der Regel jedoch bei 3-4 → biologische Abbaubarkeit?
- **Organischen Säuren** sind hauptsächlich Ethansäure und Propansäure
- Furfural, 5-HMF, Huminstoffe sowie Phenole und phenolartige Verbindungen
- Weiterhin **Nährstoffe** im Prozesswasser: Stickstoffverbindungen

Abbildung: HTC-Prozesswasser aus der HTC von Klärschlamm (Foto: TE)



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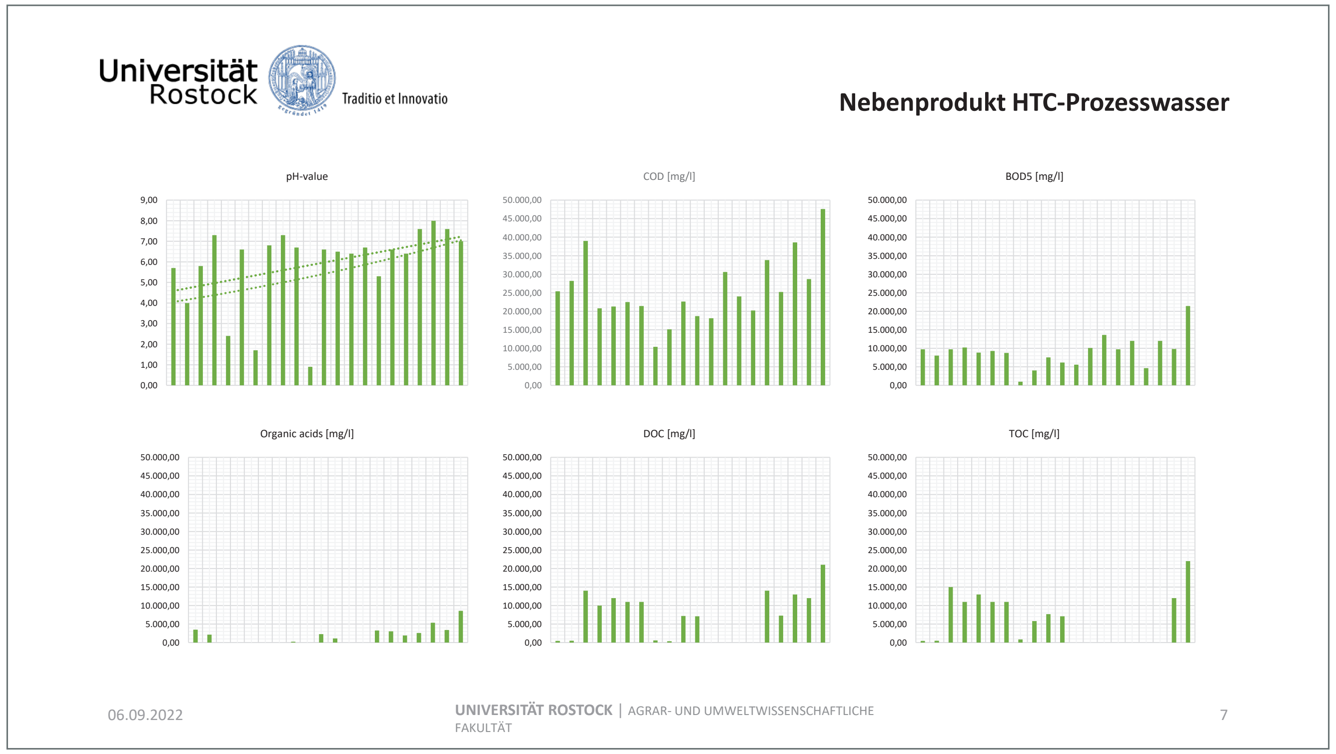
Nebenprodukt HTC-Prozesswasser

Parameter	Einheit	BG	Methode	Ergebnis
pH-Wert		0,1	DIN 38404-5: 2009-07	7,00
CSB	mg/l	15	DIN 38409-41: 1980-12	47.600,00
BSB$_5$ (abgesetzt)	mg/l	2	DIN EN 1899-1: 1998-05	21.400,00
Wasserdampfflüchtige organische Säuren, berechnet als Essigsäure	mg/kg	10	DIN 38414-19: 1999-12	8.578,00
DOC	mg/l	0,5	DIN EN 1484: 1997-08	21.000,00
TOC	mg/l	0,5	DIN EN 1484: 1997-08	22.000,00
TIC	mg/l	100	DIN EN 1484: 1997-08	120,00
Chlorid	mg/l	0,5	DIN EN ISO 10304-1: 2009-07	62,30
Sulfat	mg/l	1	DIN EN ISO 10304-1: 2009-07	803,00
Nitrat	mg/l	0,5	DIN EN ISO 10304-1: 2009-07	26,80
Ammonium	mg/l	0	DIN EN ISO 11732: 2005-05	3.300,00
Ammonium-N	mg/l	0	DIN EN ISO 11732: 2005-05	2.600,00
Kjeldahl-Stickstoff	mg/l	1	DIN EN 25663: 1993-11	5.600,00
ortho-Phosphat	mg/l	0,1	DIN EN ISO 10304-1: 2009-07	747,00
ortho-Phosphat als Phosphor	mg/l	0	DIN EN ISO 10304-1: 2009-07	244,00



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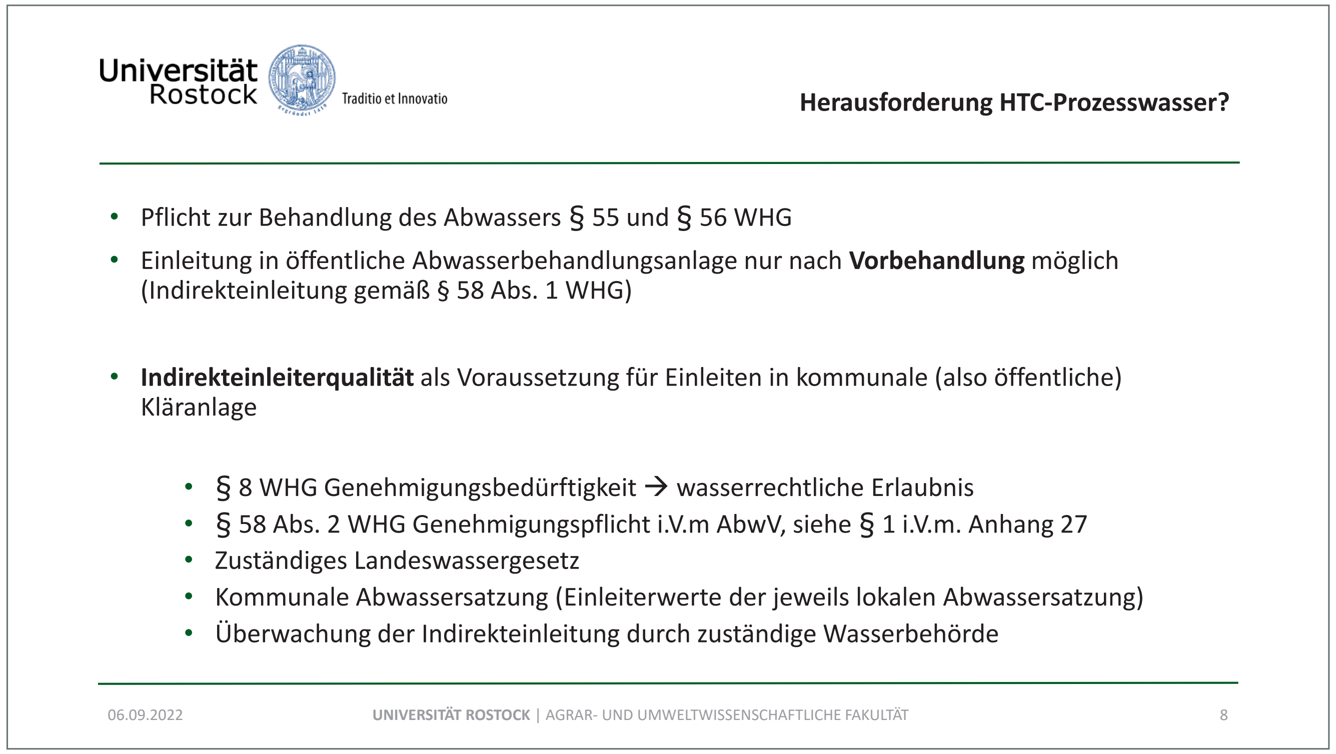
Nebenprodukt HTC-Prozesswasser



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Herausforderung HTC-Prozesswasser?

- Pflicht zur Behandlung des Abwassers § 55 und § 56 WHG
- Einleitung in öffentliche Abwasserbehandlungsanlage nur nach **Vorbehandlung** möglich (Indirekteinleitung gemäß § 58 Abs. 1 WHG)

- **Indirekteinleiterqualität** als Voraussetzung für Einleiten in kommunale (also öffentliche) Kläranlage

    - § 8 WHG Genehmigungsbedürftigkeit → wasserrechtliche Erlaubnis
    - § 58 Abs. 2 WHG Genehmigungspflicht i.V.m AbwV, siehe § 1 i.V.m. Anhang 27
    - Zuständiges Landeswassergesetz
    - Kommunale Abwassersatzung (Einleiterwerte der jeweils lokalen Abwassersatzung)
    - Überwachung der Indirekteinleitung durch zuständige Wasserbehörde

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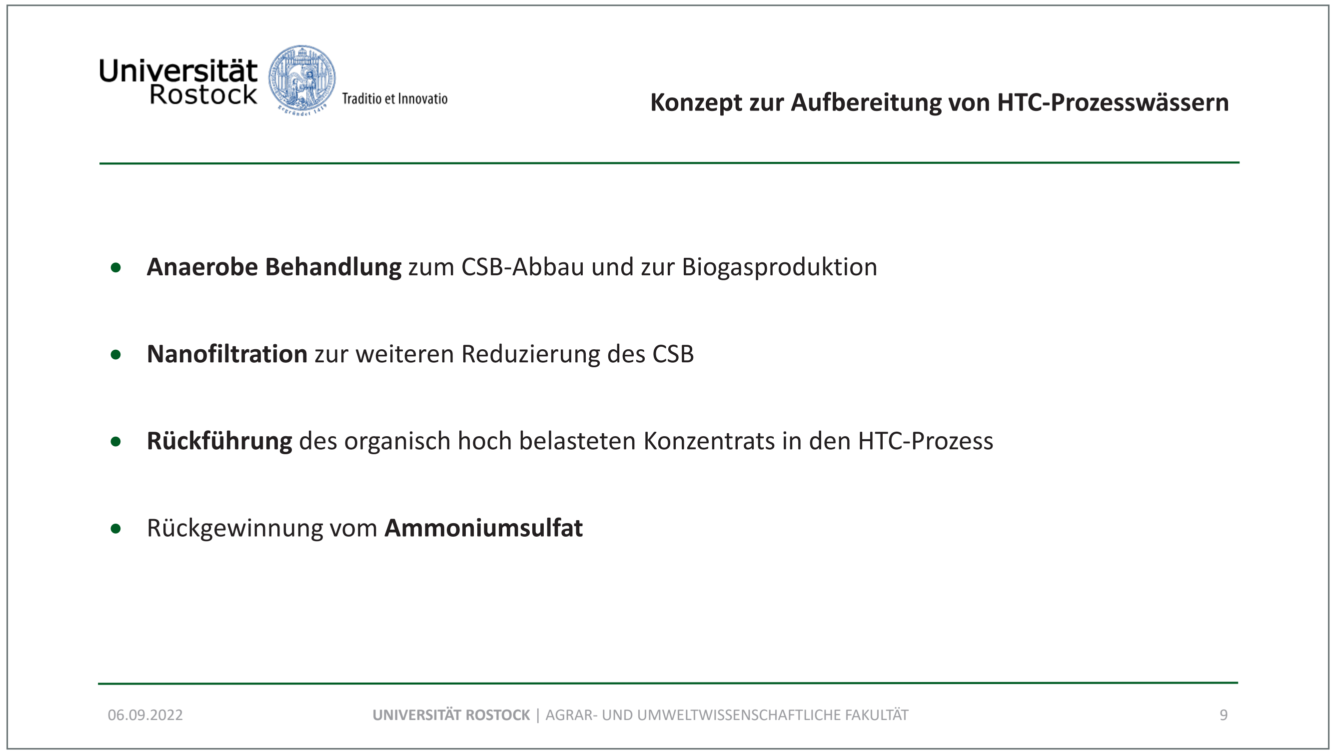

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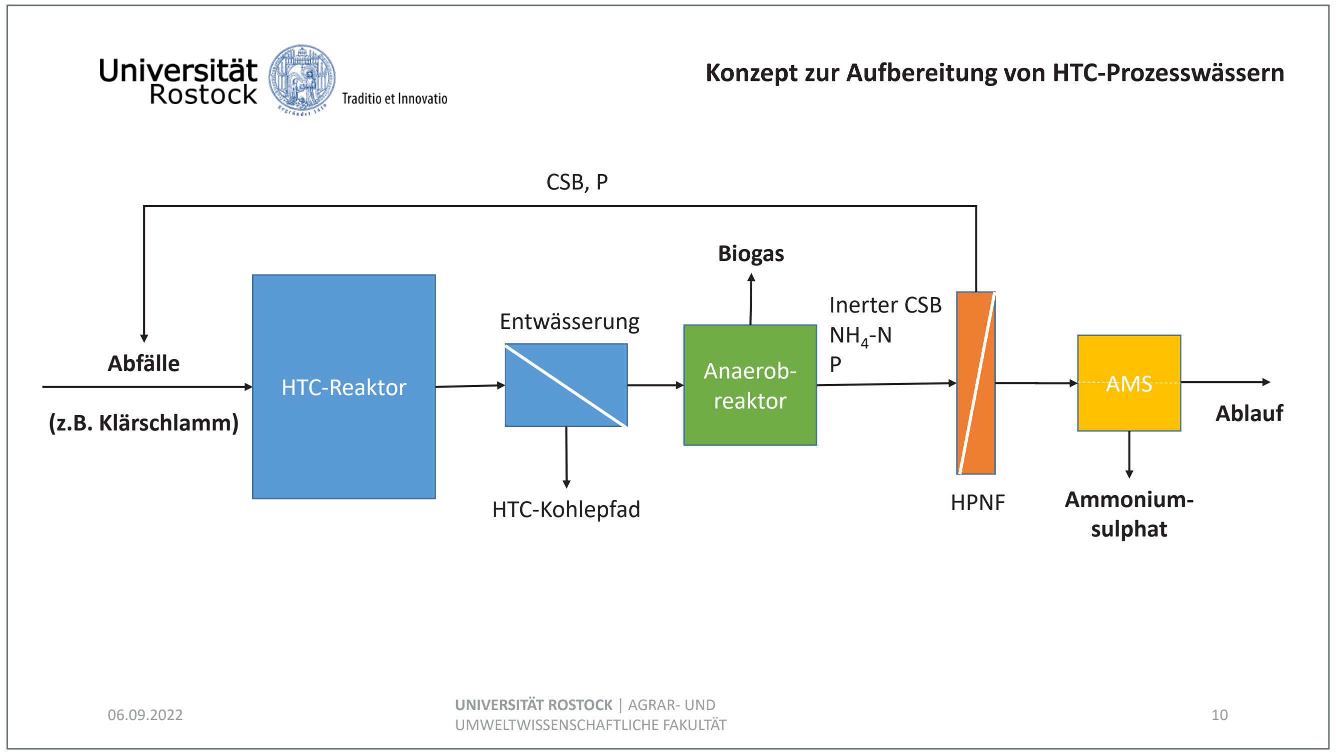
Konzept zur Aufbereitung von HTC-Prozesswässern

- **Anaerobe Behandlung** zum CSB-Abbau und zur Biogasproduktion
- **Nanofiltration** zur weiteren Reduzierung des CSB
- **Rückführung** des organisch hoch belasteten Konzentrats in den HTC-Prozess
- Rückgewinnung vom **Ammoniumsulfat**



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Konzept zur Aufbereitung von HTC-Prozesswässern

CSB, P

Biogas

Abfälle

(z.B. Klärschlamm)

HTC-Reaktor

Entwässerung

HTC-Kohlepfad

Anaerob-reaktor

Inerter CSB
NH_4-N
P

HPNF

AMS

Ablauf

Ammonium-sulphat

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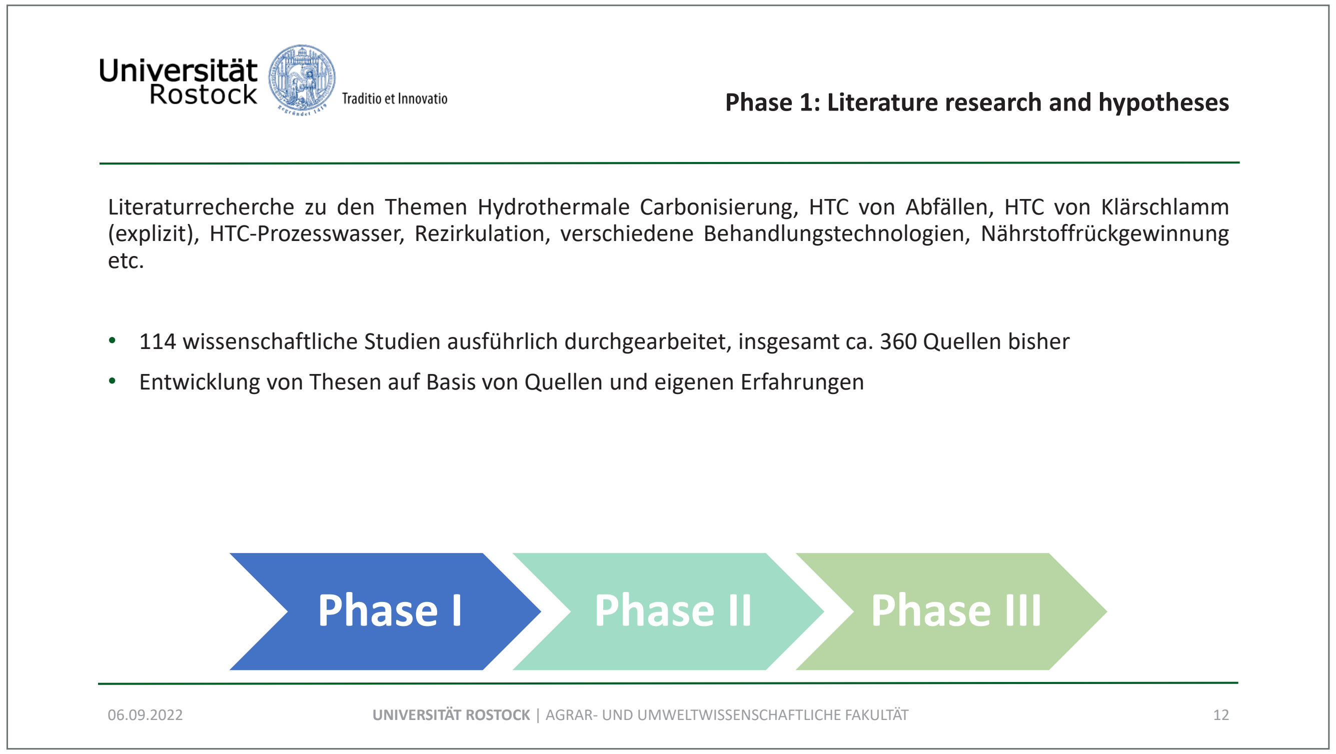
Ziel des Promotionsvorhabens

Das Ziel ist ein **stabiles und zuverlässiges Konzept** für die Aufbereitung

- Umweltschonende Behandlung von HTC-Prozesswasser
- Erreichen und Einhalten der notwendigen Indirekteinleiterqualität
- Rückgewinnung von Stickstoff als Ammoniumsulfat (Vermarktung!)
- Düngemittelversuche mit zurückgewonnenen Nährstoffprodukten
- Umsetzung im industriellen/technischen Maßstab (Upscaling etc.)

HTC-PW ist eine **Herausforderung für alle industriellen HTC-Anlagen**

- Weiterentwicklung der HTC-Technologie
- HTC als alternative Verwertung zur bekannten thermischen Verwertung (z.B. Verbrennung von Klärschlamm)
- HTC von Klärschlamm als Lösung für die Verwertung in ländlichen Gebieten



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Phase 1: Literature research and hypotheses

Literaturrecherche zu den Themen Hydrothermale Carbonisierung, HTC von Abfällen, HTC von Klärschlamm (explizit), HTC-Prozesswasser, Rezirkulation, verschiedene Behandlungstechnologien, Nährstoffrückgewinnung etc.

- 114 wissenschaftliche Studien ausführlich durchgearbeitet, insgesamt ca. 360 Quellen bisher
- Entwicklung von Thesen auf Basis von Quellen und eigenen Erfahrungen

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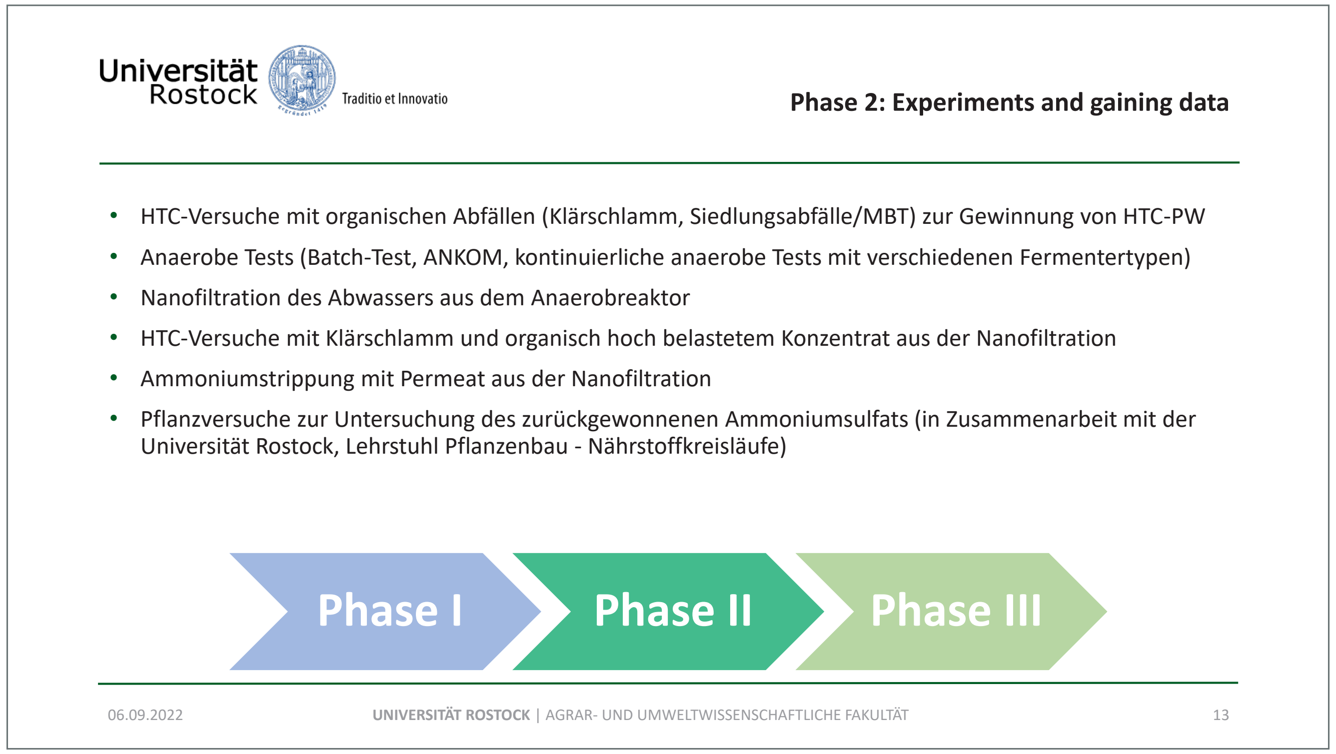

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Phase 2: Experiments and gaining data

- HTC-Versuche mit organischen Abfällen (Klärschlamm, Siedlungsabfälle/MBT) zur Gewinnung von HTC-PW
- Anaerobe Tests (Batch-Test, ANKOM, kontinuierliche anaerobe Tests mit verschiedenen Fermentertypen)
- Nanofiltration des Abwassers aus dem Anaerobreaktor
- HTC-Versuche mit Klärschlamm und organisch hoch belastetem Konzentrat aus der Nanofiltration
- Ammoniumstrippung mit Permeat aus der Nanofiltration
- Pflanzversuche zur Untersuchung des zurückgewonnenen Ammoniumsulfats (in Zusammenarbeit mit der Universität Rostock, Lehrstuhl Pflanzenbau - Nährstoffkreisläufe)

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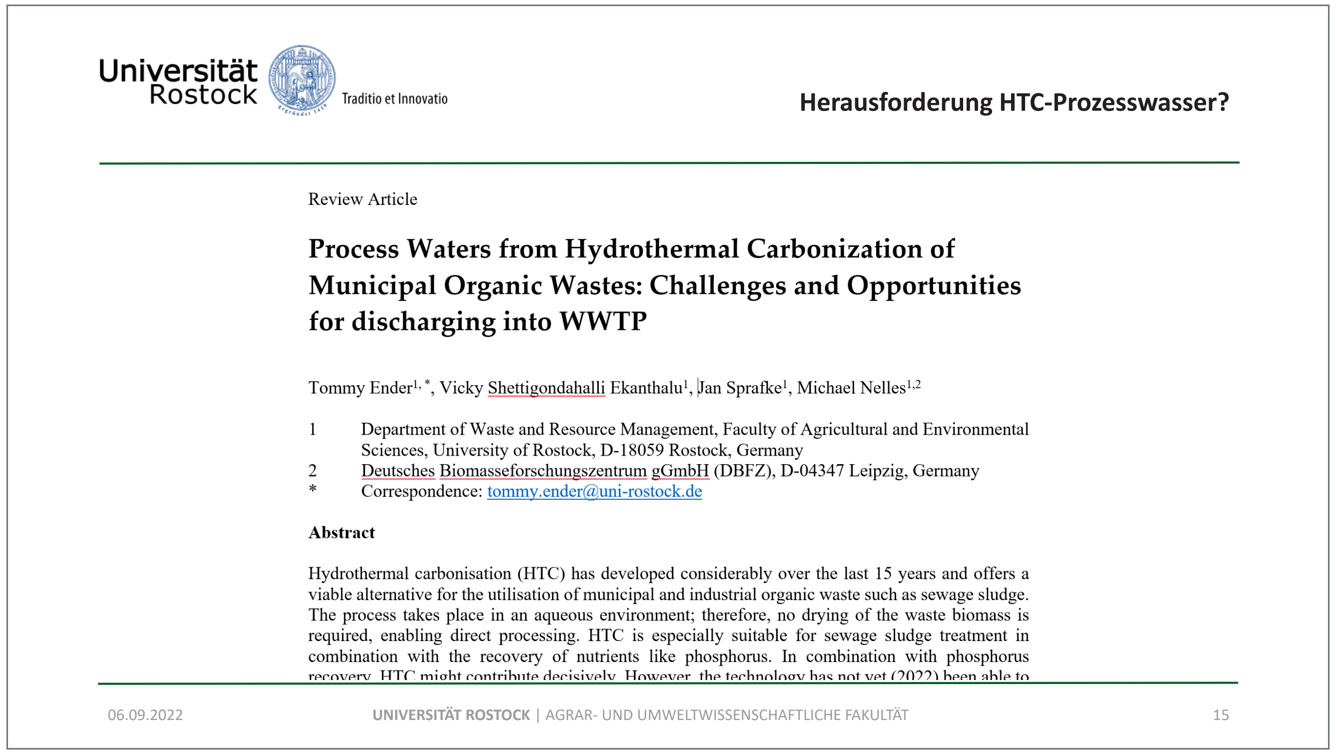
Technikumsanlagen zur Prozesswasserbehandlung

Fotos: TE



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Herausforderung HTC-Prozesswasser?

Review Article

Process Waters from Hydrothermal Carbonization of Municipal Organic Wastes: Challenges and Opportunities for discharging into WWTP

Tommy Ender[1, *], Vicky Shettigondahalli Ekanthalu[1], Jan Sprafke[1], Michael Nelles[1,2]

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2 Deutsches Biomasseforschungszentrum gGmbH (DBFZ), D-04347 Leipzig, Germany
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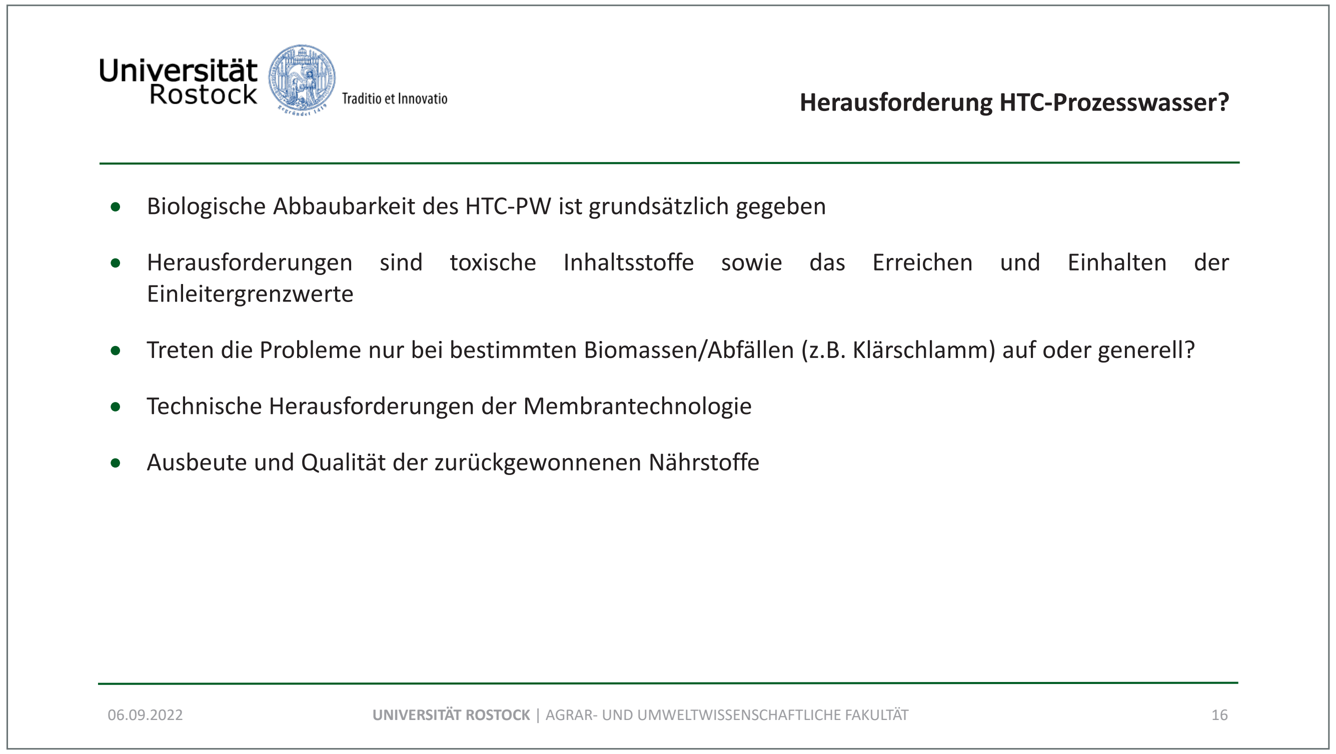
Abstract

Hydrothermal carbonisation (HTC) has developed considerably over the last 15 years and offers a viable alternative for the utilisation of municipal and industrial organic waste such as sewage sludge. The process takes place in an aqueous environment; therefore, no drying of the waste biomass is required, enabling direct processing. HTC is especially suitable for sewage sludge treatment in combination with the recovery of nutrients like phosphorus. In combination with phosphorus recovery, HTC might contribute decisively. However, the technology has not yet (2022) been able to



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Herausforderung HTC-Prozesswasser?

- Biologische Abbaubarkeit des HTC-PW ist grundsätzlich gegeben
- Herausforderungen sind toxische Inhaltsstoffe sowie das Erreichen und Einhalten der Einleitergrenzwerte
- Treten die Probleme nur bei bestimmten Biomassen/Abfällen (z.B. Klärschlamm) auf oder generell?
- Technische Herausforderungen der Membrantechnologie
- Ausbeute und Qualität der zurückgewonnenen Nährstoffe

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Vielen Dank für Ihre Aufmerksamkeit!

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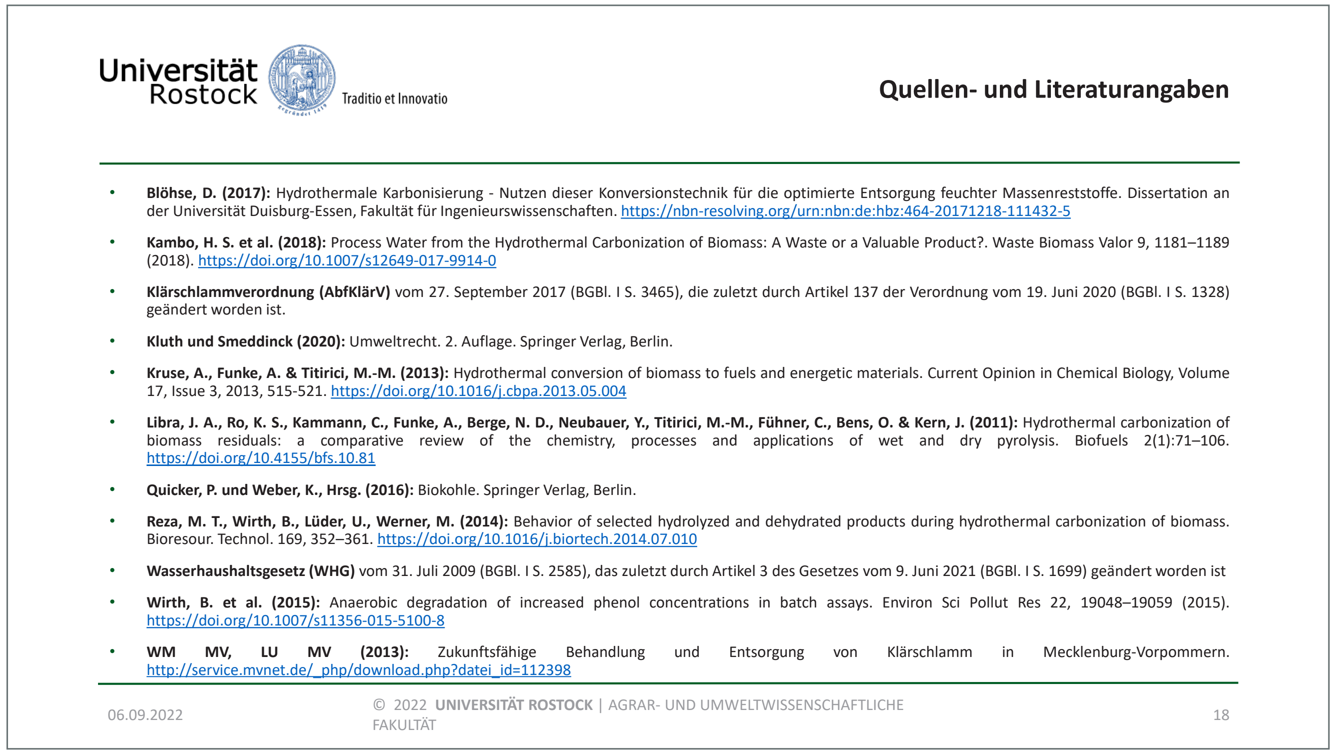
Letzte Bearbeitung am 06.09.2022
Version 1.3



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Session III:
HTL II

Jakob Köchermann, Deutsches Biomasseforschungszentrum

Herstellung von γ-Valerolacton (GVL) aus landwirtschaftlichen Reststoffen mittels eines zweistufigen hydrothermalen Verfahrensansatzes

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Die steigende Weltbevölkerung und die daraus resultierende Verknappung der landwirtschaftlichen Nutzfläche pro Kopf bedeuten, dass landwirtschaftliche Produkte in Zukunft so effektiv wie möglich genutzt werden müssen. Daher muss sich die biomasseverarbeitende Industrie von einem Einproduktzu einem Mehrproduktbetrieb wandeln – der sogenannten Bioraffinerie. In diesem Zusammenhang spielt die Entwicklung biobasierter Produkte wie Chemikalien oder Kraftstoffe aus landwirtschaftlichen Reststoffen, Nebenströmen der Zellstoff- und Papier- oder Forstindustrie eine wichtige Rolle.

Im Rahmen des vom BMBF geförderten Forschungsvorhabens HTKkChem wurden kohlenhydratreiche Reststoffe (wie Stärkereste und Getreidespelzen) als Ausgangsmaterial für die Produktion solch biobasierter Chemikalien verwendet. Das Ziel des Projektes bestand darin, ein zweistufiges hydrothermales Verfahren zur Bereitstellung von γ-Valerolacton (GVL) zu entwickeln. Während in der ersten Stufe die Kohlenhydrate mit Hilfe homogener Katalysatoren zu Lävulinsäure (LA) hydrolysiert und dehydratisiert werden, findet in der zweiten Stufe eine heterogen katalysierte Transferhydrierung von LA zu GVL statt. Der Vorteil dieses Ansatzes besteht darin, dass kein externer Wasserstoff dem Prozess zugeführt werden muss, sondern dieser durch Deprotonierung der als Nebenprodukt gebildeten Ameisensäure bereitgestellt wird.

Im Rahmen des Projektes ist es gelungen eine zweistufige Laboranlage in Betrieb zu nehmen, mit deren Hilfe der am Leibniz-Institut für Katalyse entwickelte Katalysator unter realen Versuchsbedingungen getestet werden konnte. Die Ergebnisse dieser Untersuchungen sollen vorgestellt und kritisch diskutiert werden.

7. HTP-Fachforum | 27./28. September 2022
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

Recovery of γ-Valerolactone (GVL) from agricultural side streams by a two-stage hydrothermal approach

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Federal Ministry of Education and Research

Jakob Köchermann[1], Hanan Atia[2], Udo Armbruster[2], Nilab Feizy[3], Rolf Hommel[3], Marco Klemm[1]

[1] DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH
[2] Leibniz-Institut für Katalyse e. V. (LIKAT)
[3] ifn Forschungs- und Technologiezentrum GmbH (ifnFTZ)

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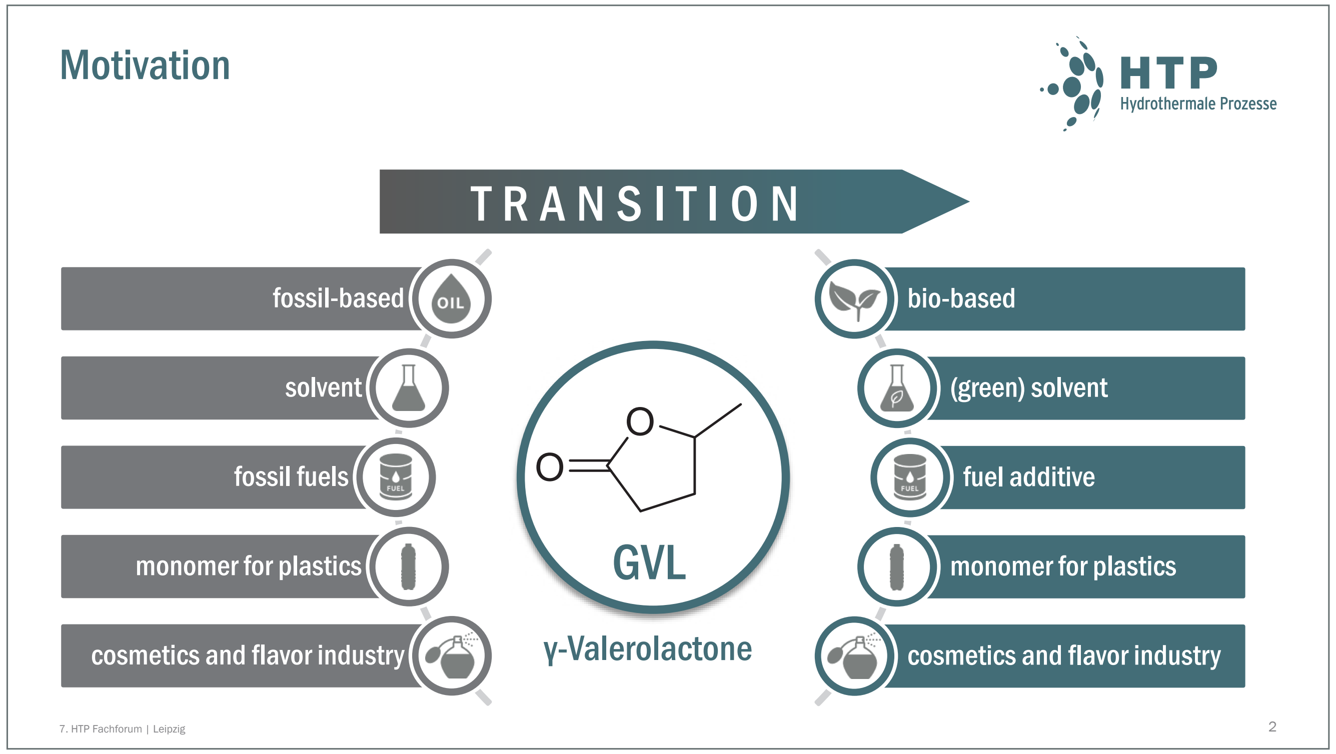


Motivation

HTP Hydrothermale Prozesse

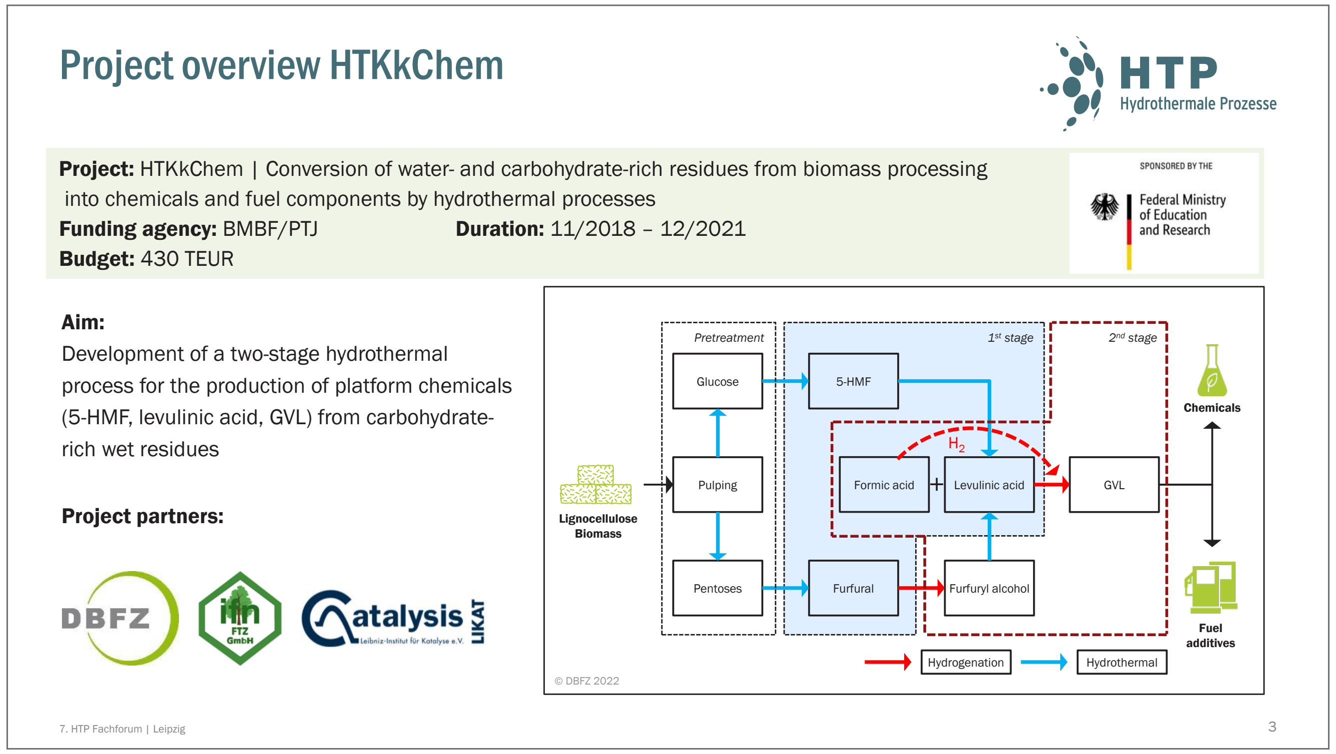
TRANSITION

fossil-based
solvent
fossil fuels
monomer for plastics
cosmetics and flavor industry

bio-based
(green) solvent
fuel additive
monomer for plastics
cosmetics and flavor industry

GVL
γ-Valerolactone

7. HTP Fachforum | Leipzig
2



Project overview HTKkChem

Project: HTKkChem | Conversion of water- and carbohydrate-rich residues from biomass processing into chemicals and fuel components by hydrothermal processes
Funding agency: BMBF/PTJ **Duration:** 11/2018 – 12/2021
Budget: 430 TEUR

Aim:
Development of a two-stage hydrothermal process for the production of platform chemicals (5-HMF, levulinic acid, GVL) from carbohydrate-rich wet residues

Project partners:

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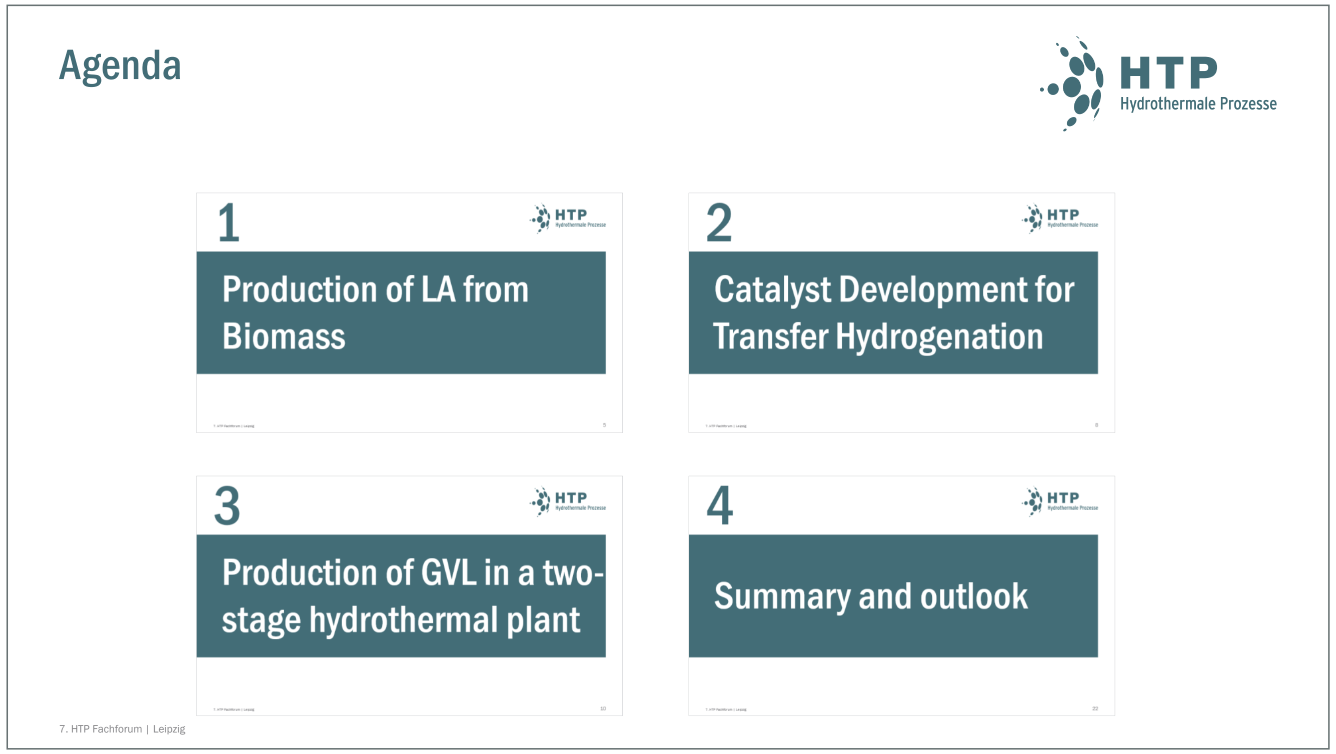


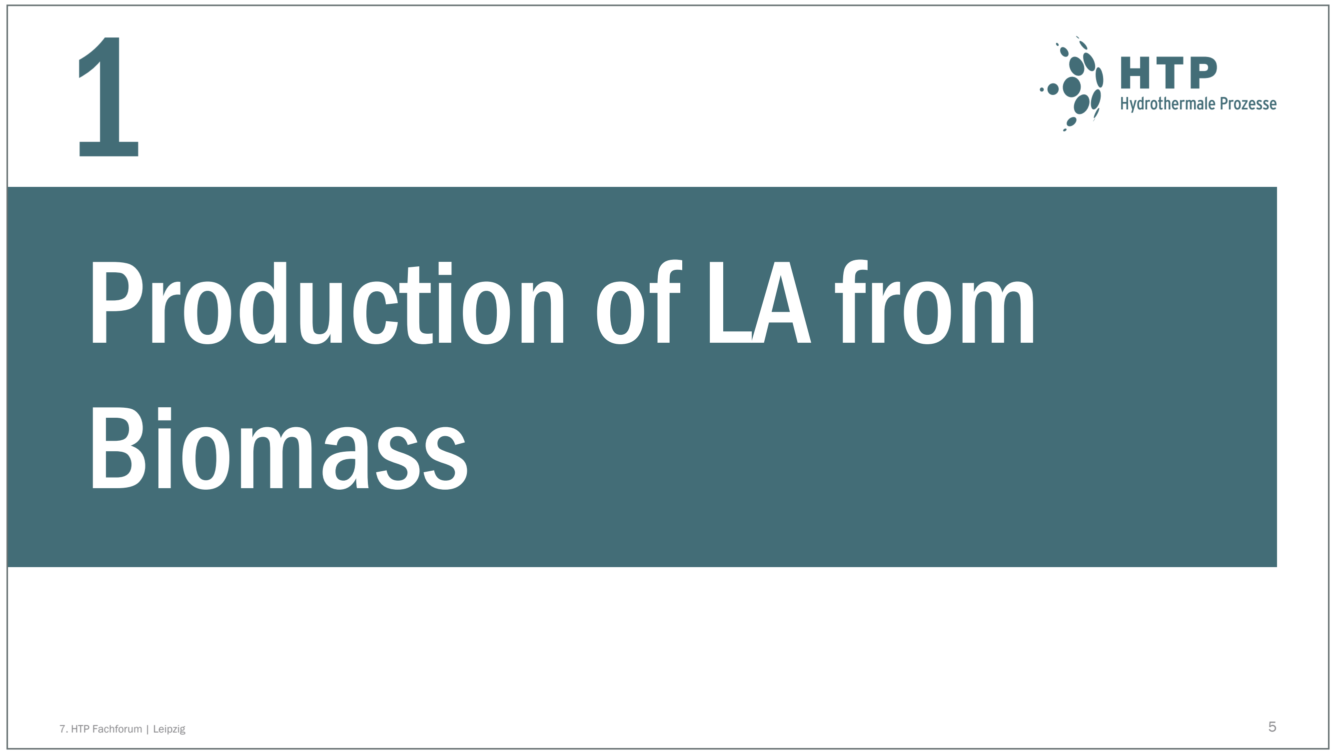
Agenda

1 Production of LA from Biomass

2 Catalyst Development for Transfer Hydrogenation

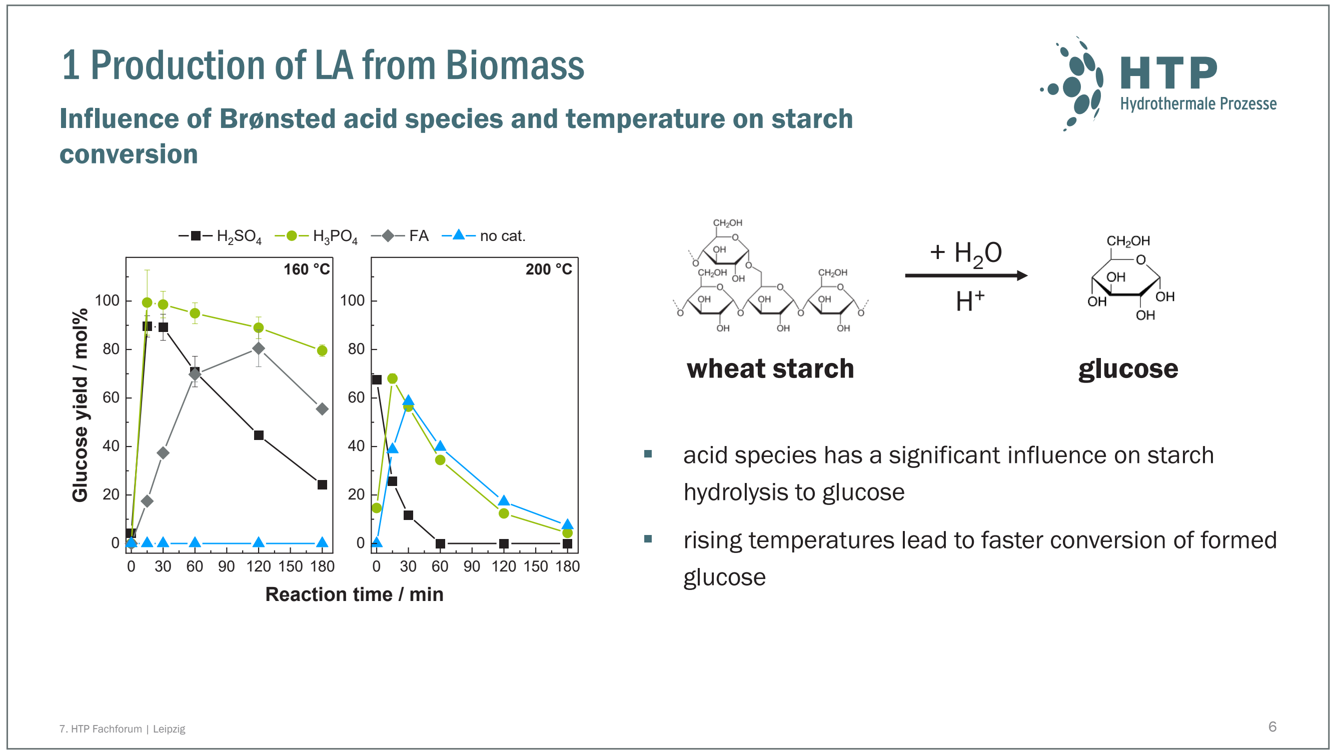
3 Production of GVL in a two-stage hydrothermal plant

4 Summary and outlook



1

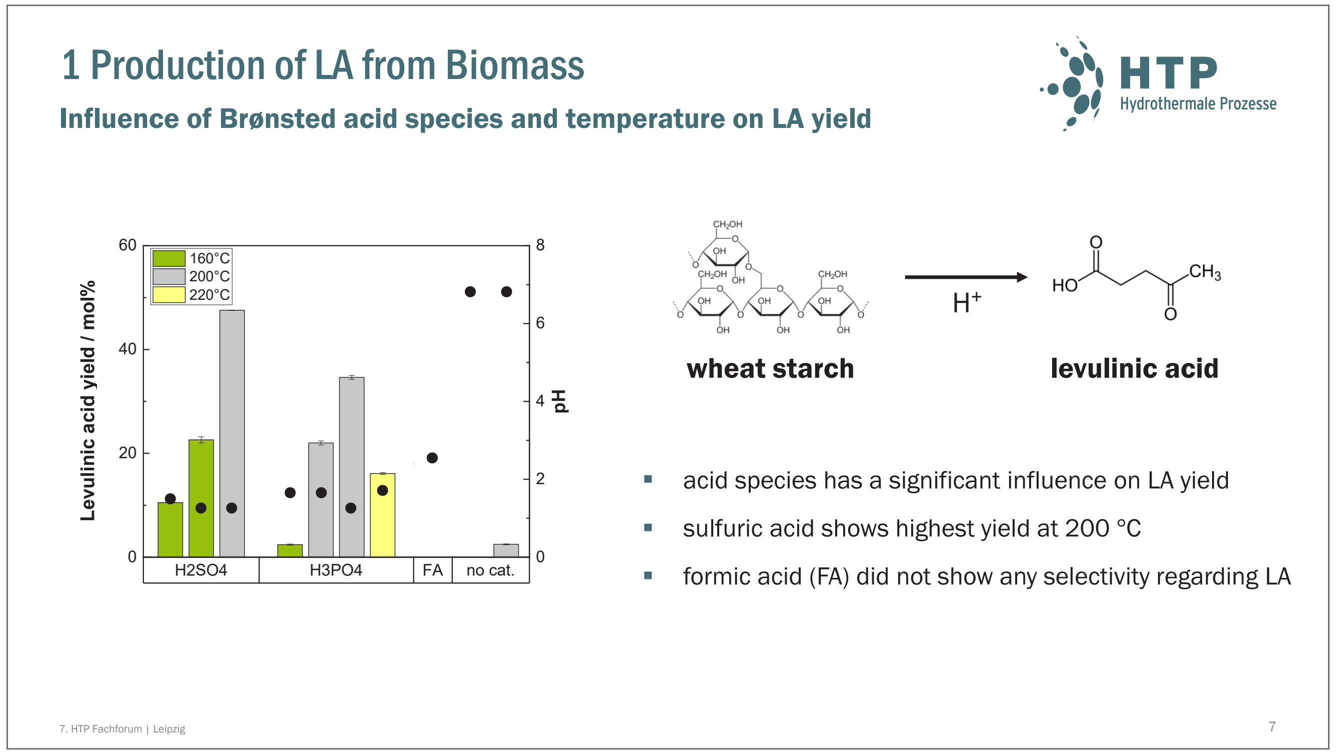
Production of LA from Biomass



1 Production of LA from Biomass

Influence of Brønsted acid species and temperature on starch conversion

- acid species has a significant influence on starch hydrolysis to glucose
- rising temperatures lead to faster conversion of formed glucose



1 Production of LA from Biomass

Influence of Brønsted acid species and temperature on LA yield

HTP Hydrothermale Prozesse

wheat starch

levulinic acid

- acid species has a significant influence on LA yield
- sulfuric acid shows highest yield at 200 °C
- formic acid (FA) did not show any selectivity regarding LA

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2

HTP Hydrothermale Prozesse

Catalyst Development for Transfer Hydrogenation

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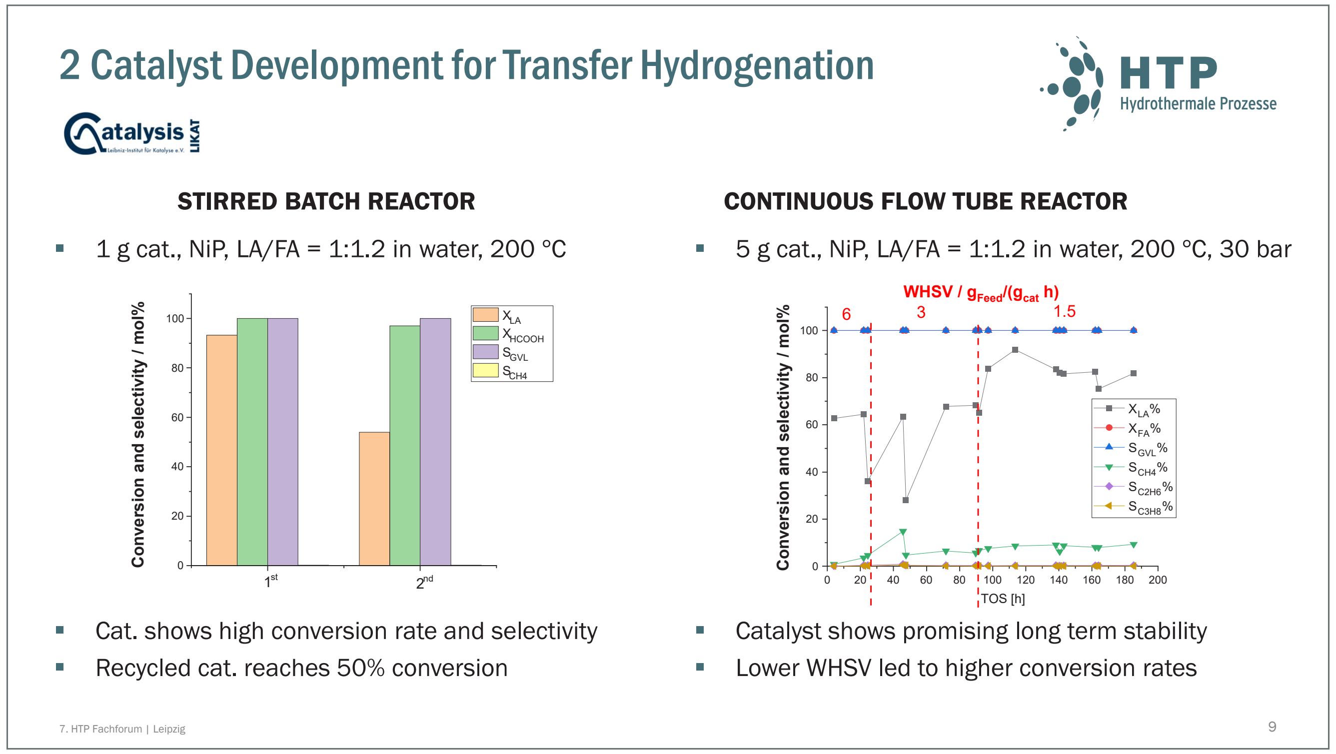

2 Catalyst Development for Transfer Hydrogenation

HTP Hydrothermale Prozesse

Catalysis LIKAT

STIRRED BATCH REACTOR

- 1 g cat., NiP, LA/FA = 1:1.2 in water, 200 °C

- Cat. shows high conversion rate and selectivity
- Recycled cat. reaches 50% conversion

CONTINUOUS FLOW TUBE REACTOR

- 5 g cat., NiP, LA/FA = 1:1.2 in water, 200 °C, 30 bar

- Catalyst shows promising long term stability
- Lower WHSV led to higher conversion rates

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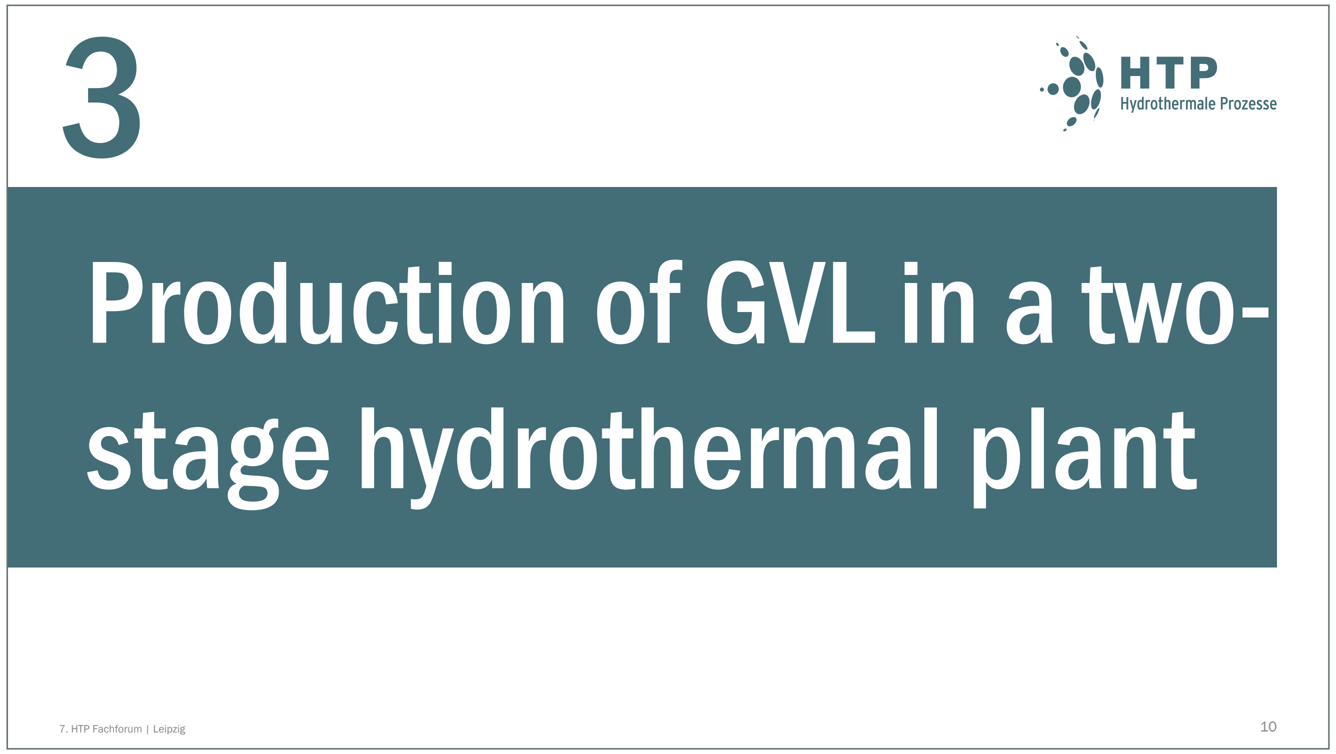

3

HTP Hydrothermale Prozesse

Production of GVL in a two-stage hydrothermal plant

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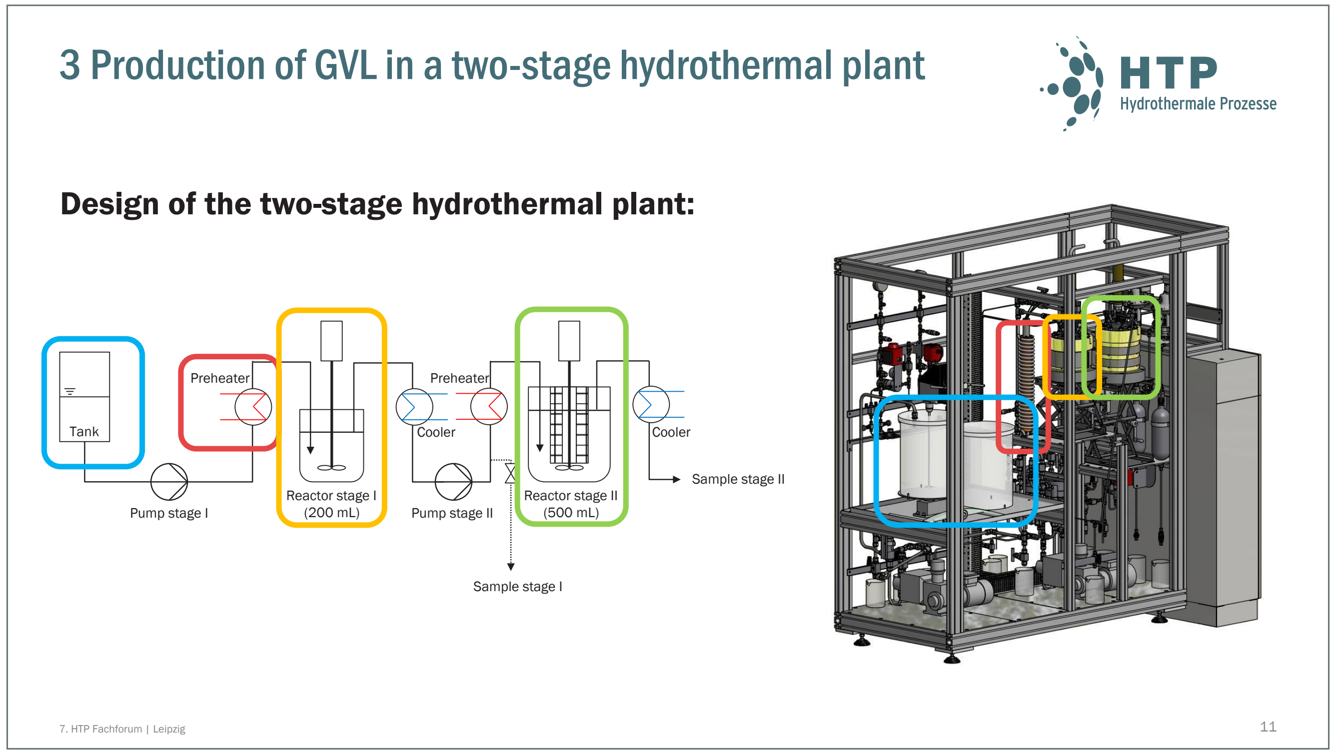
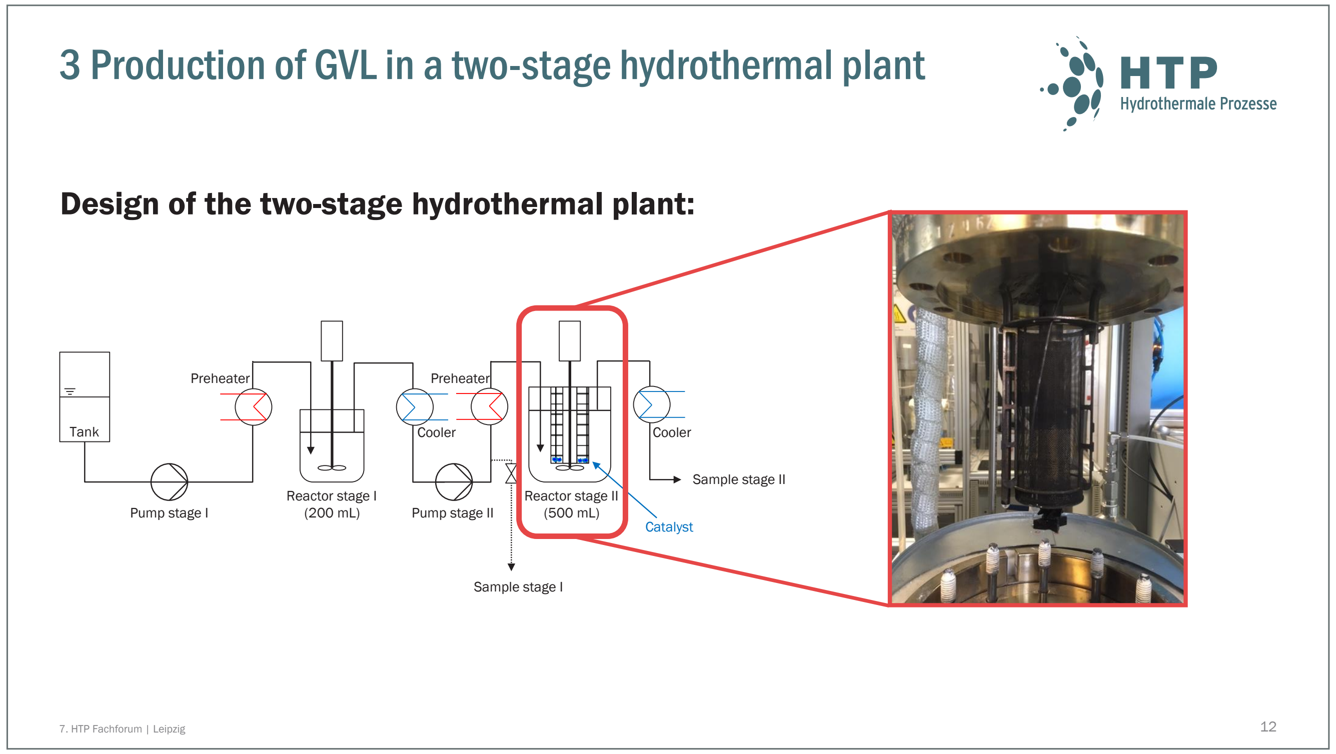


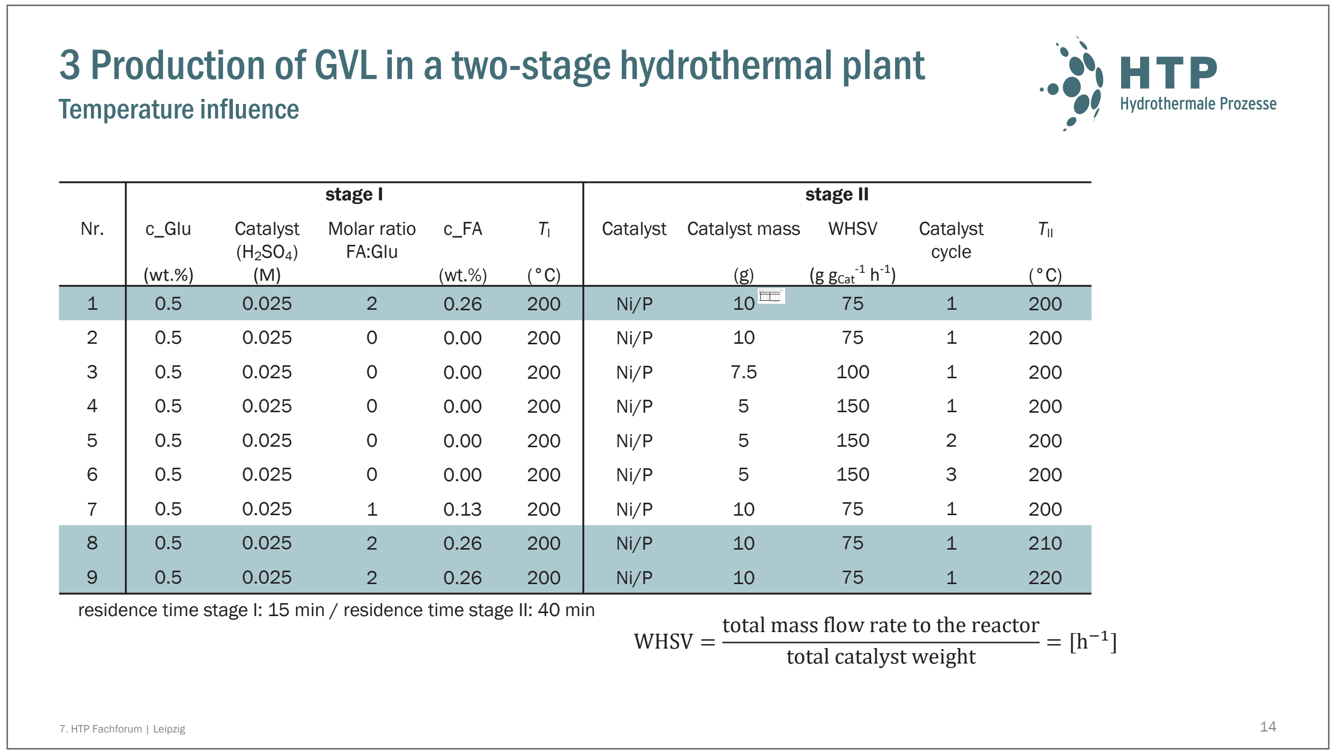
3 Production of GVL in a two-stage hydrothermal plant

Design of the two-stage hydrothermal plant:



3 Production of GVL in a two-stage hydrothermal plant

Design of the two-stage hydrothermal plant:



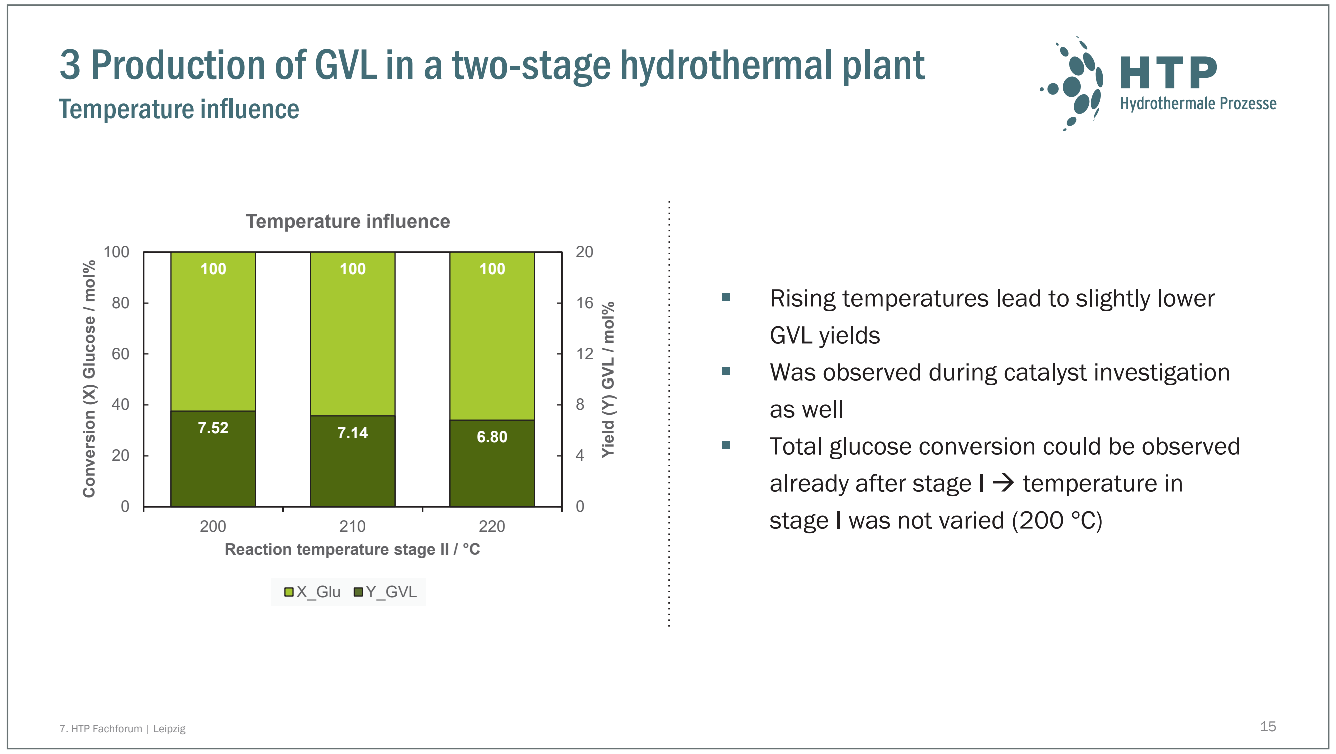
3 Production of GVL in a two-stage hydrothermal plant

Temperature influence

	stage I					stage II				
Nr.	c_Glu (wt.%)	Catalyst (H_2SO_4) (M)	Molar ratio FA:Glu	c_FA (wt.%)	T_I (°C)	Catalyst	Catalyst mass (g)	WHSV (g g_{Cat}^{-1} h^{-1})	Catalyst cycle	T_{II} (°C)
1	0.5	0.025	2	0.26	200	Ni/P	10	75	1	200
2	0.5	0.025	0	0.00	200	Ni/P	10	75	1	200
3	0.5	0.025	0	0.00	200	Ni/P	7.5	100	1	200
4	0.5	0.025	0	0.00	200	Ni/P	5	150	1	200
5	0.5	0.025	0	0.00	200	Ni/P	5	150	2	200
6	0.5	0.025	0	0.00	200	Ni/P	5	150	3	200
7	0.5	0.025	1	0.13	200	Ni/P	10	75	1	200
8	0.5	0.025	2	0.26	200	Ni/P	10	75	1	210
9	0.5	0.025	2	0.26	200	Ni/P	10	75	1	220

residence time stage I: 15 min / residence time stage II: 40 min

$$\text{WHSV} = \frac{\text{total mass flow rate to the reactor}}{\text{total catalyst weight}} = [h^{-1}]$$



3 Production of GVL in a two-stage hydrothermal plant

Temperature influence

- Rising temperatures lead to slightly lower GVL yields
- Was observed during catalyst investigation as well
- Total glucose conversion could be observed already after stage I → temperature in stage I was not varied (200 °C)

3 Production of GVL in a two-stage hydrothermal plant

Catalyst loading

HTP Hydrothermale Prozesse

	stage I					stage II				
Nr.	c_Glu (wt.%)	Catalyst (H_2SO_4) (M)	Molar ratio FA:Glu	c_FA (wt.%)	T_I (°C)	Catalyst	Catalyst mass (g)	WHSV ($g\,g_{Cat}^{-1}\,h^{-1}$)	Catalyst cycle	T_{II} (°C)
1	0.5	0.025	2	0.26	200	Ni/P	10	75	1	200
2	0.5	0.025	0	0.00	200	Ni/P	10	75	1	200
3	0.5	0.025	0	0.00	200	Ni/P	7.5	100	1	200
4	0.5	0.025	0	0.00	200	Ni/P	5	150	1	200
5	0.5	0.025	0	0.00	200	Ni/P	5	150	2	200
6	0.5	0.025	0	0.00	200	Ni/P	5	150	3	200
7	0.5	0.025	1	0.13	200	Ni/P	10	75	1	200
8	0.5	0.025	2	0.26	200	Ni/P	10	75	1	210
9	0.5	0.025	2	0.26	200	Ni/P	10	75	1	220

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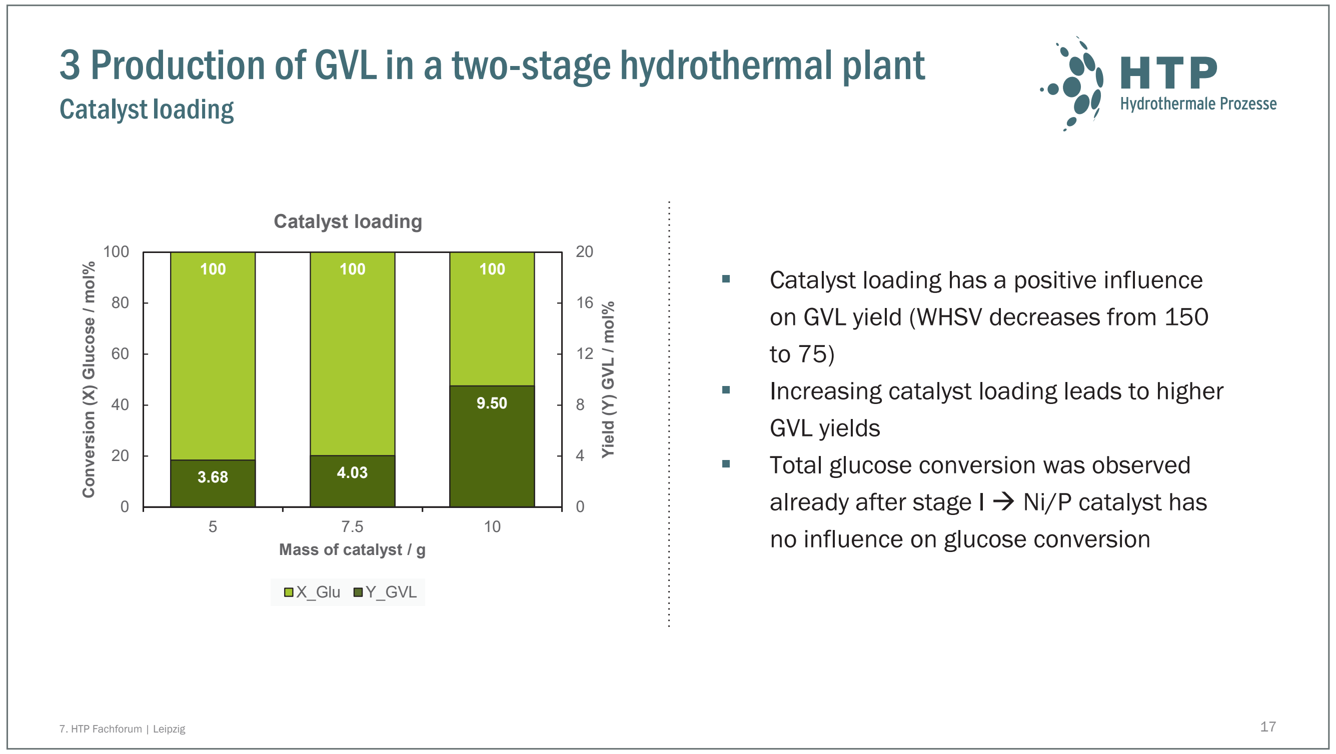
$$\mathrm{WHSV} = \frac{\text{total mass flow rate to the reactor}}{\text{total catalyst weight}} = [h^{-1}]$$



3 Production of GVL in a two-stage hydrothermal plant

Catalyst loading

HTP Hydrothermale Prozesse

- Catalyst loading has a positive influence on GVL yield (WHSV decreases from 150 to 75)
- Increasing catalyst loading leads to higher GVL yields
- Total glucose conversion was observed already after stage I → Ni/P catalyst has no influence on glucose conversion

---

3 Production of GVL in a two-stage hydrothermal plant

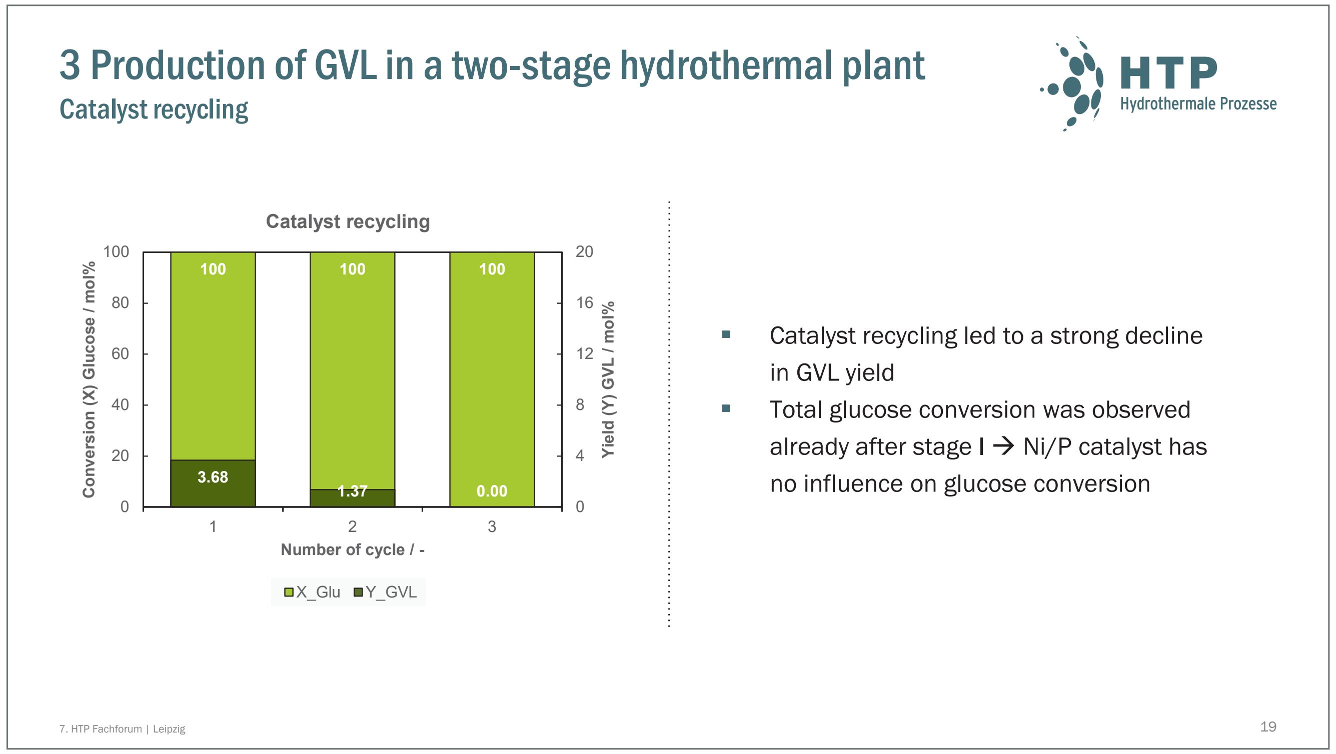
Catalyst recycling

HTP Hydrothermale Prozesse

	stage I					stage II				
Nr.	c_Glu (wt.%)	Catalyst (H_2SO_4) (M)	Molar ratio FA:Glu	c_FA (wt.%)	T_I (°C)	Catalyst	Catalyst mass (g)	WHSV ($g\,g_{Cat}^{-1}\,h^{-1}$)	Catalyst cycle	T_{II} (°C)
1	0.5	0.025	2	0.26	200	Ni/P	10	75	1	200
2	0.5	0.025	0	0.00	200	Ni/P	10	75	1	200
3	0.5	0.025	0	0.00	200	Ni/P	7.5	100	1	200
4	0.5	0.025	0	0.00	200	Ni/P	5	150	1	200
5	0.5	0.025	0	0.00	200	Ni/P	5	150	2	200
6	0.5	0.025	0	0.00	200	Ni/P	5	150	3	200
7	0.5	0.025	1	0.13	200	Ni/P	10	75	1	200
8	0.5	0.025	2	0.26	200	Ni/P	10	75	1	210
9	0.5	0.025	2	0.26	200	Ni/P	10	75	1	220

residence time stage I: 15 min / residence time stage II: 40 min

$$\mathrm{WHSV} = \frac{\text{total mass flow rate to the reactor}}{\text{total catalyst weight}} = [h^{-1}]$$

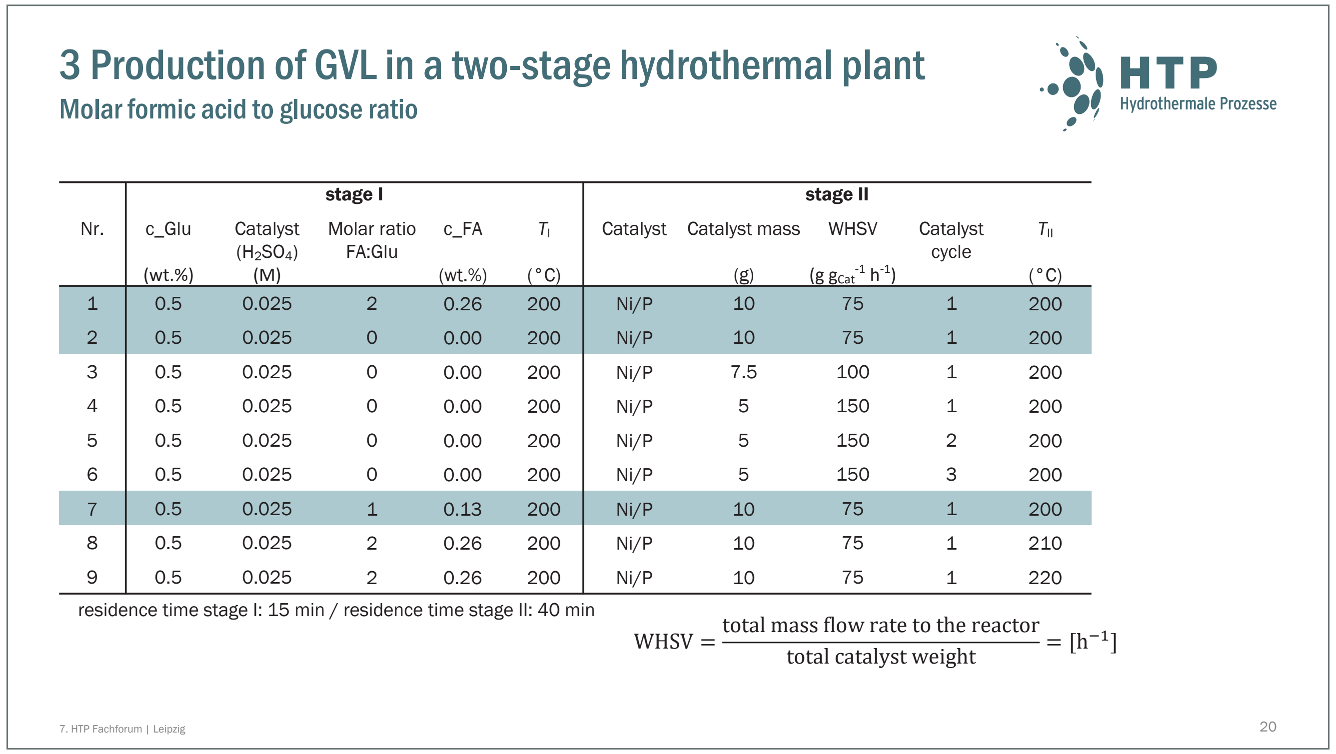


3 Production of GVL in a two-stage hydrothermal plant

Catalyst recycling

HTP Hydrothermale Prozesse

- Catalyst recycling led to a strong decline in GVL yield
- Total glucose conversion was observed already after stage I → Ni/P catalyst has no influence on glucose conversion



3 Production of GVL in a two-stage hydrothermal plant

Molar formic acid to glucose ratio

HTP Hydrothermale Prozesse

	stage I					stage II				
Nr.	c_Glu (wt.%)	Catalyst (H_2SO_4) (M)	Molar ratio FA:Glu	c_FA (wt.%)	T_I (°C)	Catalyst	Catalyst mass (g)	WHSV ($g\ g_{Cat}^{-1}\ h^{-1}$)	Catalyst cycle	T_{II} (°C)
1	0.5	0.025	2	0.26	200	Ni/P	10	75	1	200
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3	0.5	0.025	0	0.00	200	Ni/P	7.5	100	1	200
4	0.5	0.025	0	0.00	200	Ni/P	5	150	1	200
5	0.5	0.025	0	0.00	200	Ni/P	5	150	2	200
6	0.5	0.025	0	0.00	200	Ni/P	5	150	3	200
7	0.5	0.025	1	0.13	200	Ni/P	10	75	1	200
8	0.5	0.025	2	0.26	200	Ni/P	10	75	1	210
9	0.5	0.025	2	0.26	200	Ni/P	10	75	1	220

residence time stage I: 15 min / residence time stage II: 40 min

$$\mathrm{WHSV} = \frac{\text{total mass flow rate to the reactor}}{\text{total catalyst weight}} = [\mathrm{h}^{-1}]$$

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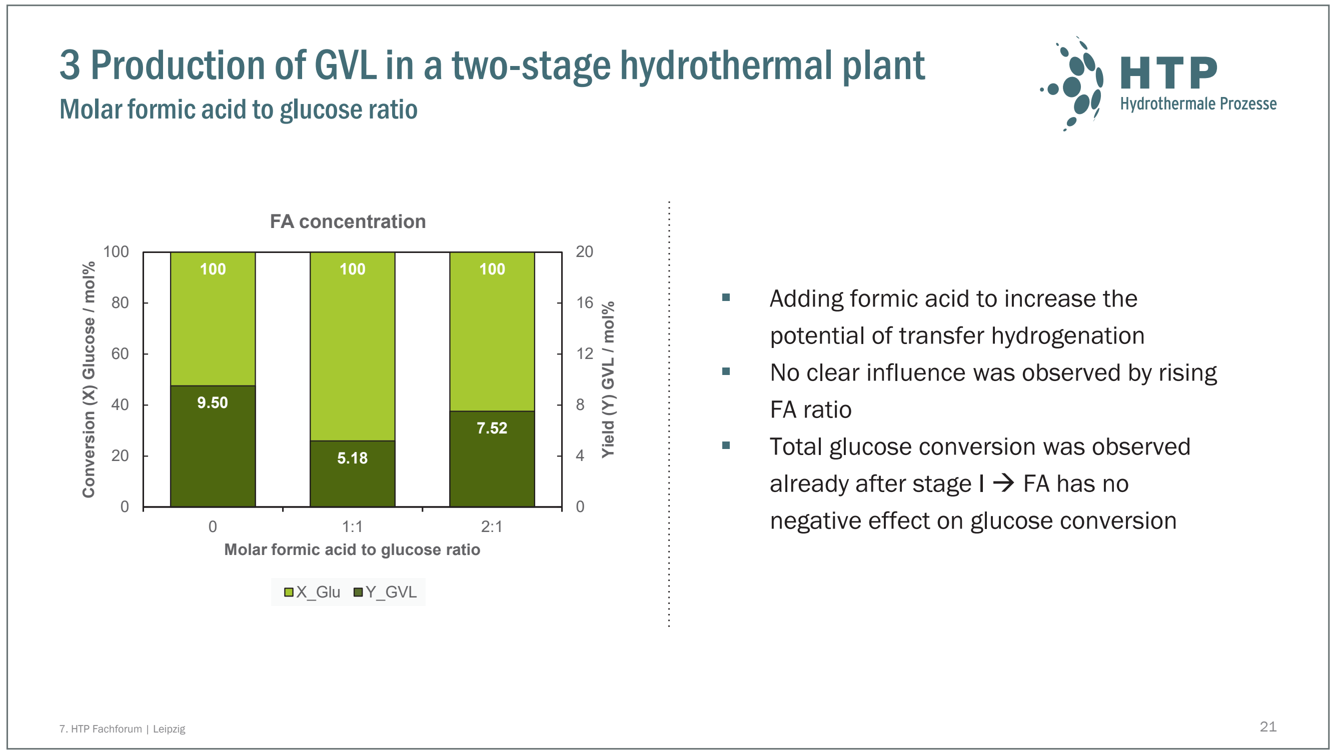

3 Production of GVL in a two-stage hydrothermal plant

Molar formic acid to glucose ratio

HTP Hydrothermale Prozesse

- Adding formic acid to increase the potential of transfer hydrogenation
- No clear influence was observed by rising FA ratio
- Total glucose conversion was observed already after stage I → FA has no negative effect on glucose conversion

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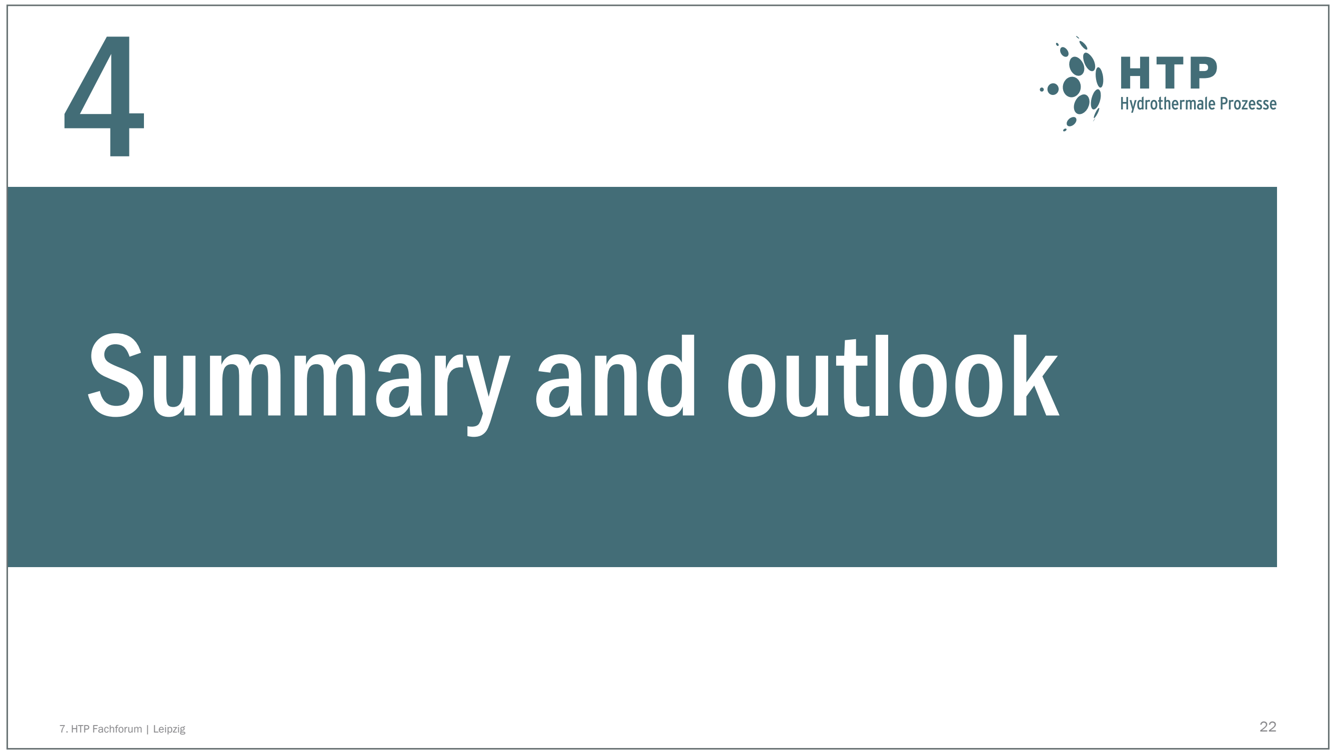

4

HTP Hydrothermale Prozesse

Summary and outlook

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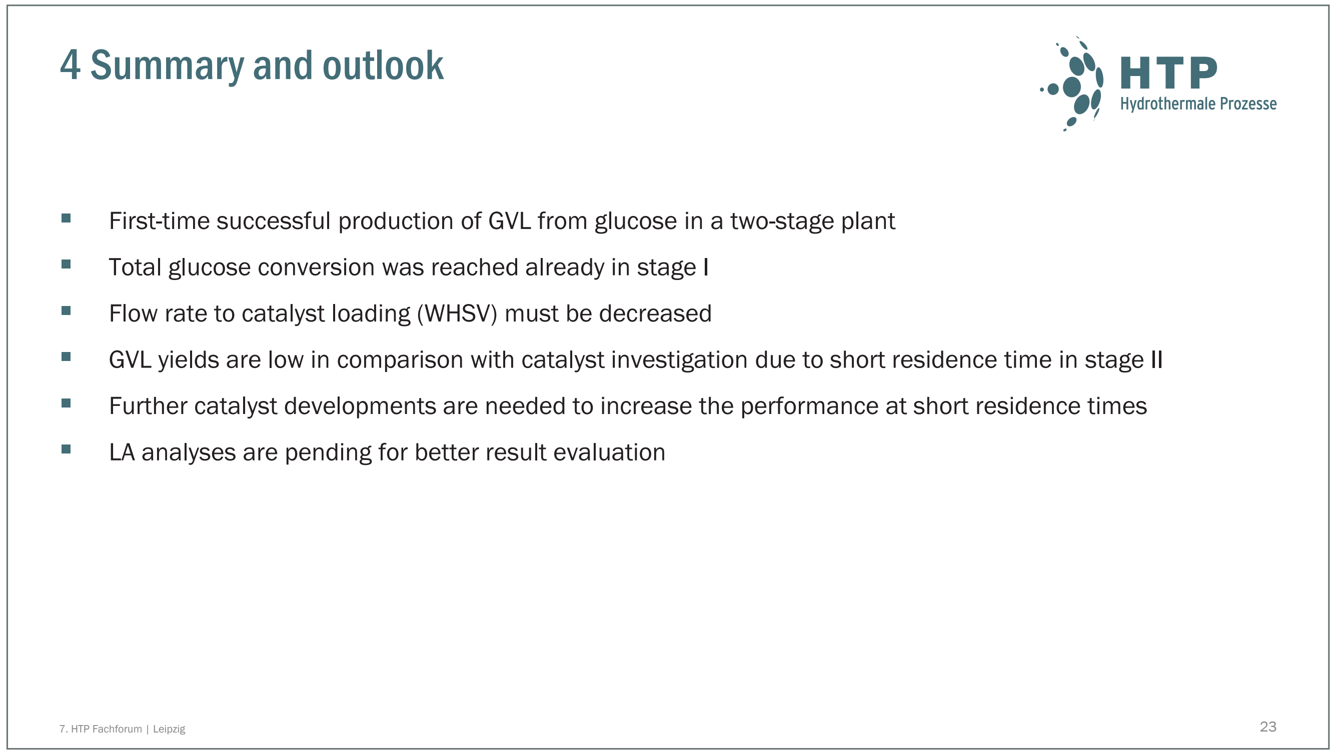

4 Summary and outlook

HTP Hydrothermale Prozesse

- First-time successful production of GVL from glucose in a two-stage plant
- Total glucose conversion was reached already in stage I
- Flow rate to catalyst loading (WHSV) must be decreased
- GVL yields are low in comparison with catalyst investigation due to short residence time in stage II
- Further catalyst developments are needed to increase the performance at short residence times
- LA analyses are pending for better result evaluation

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7. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Thank you for your attention!

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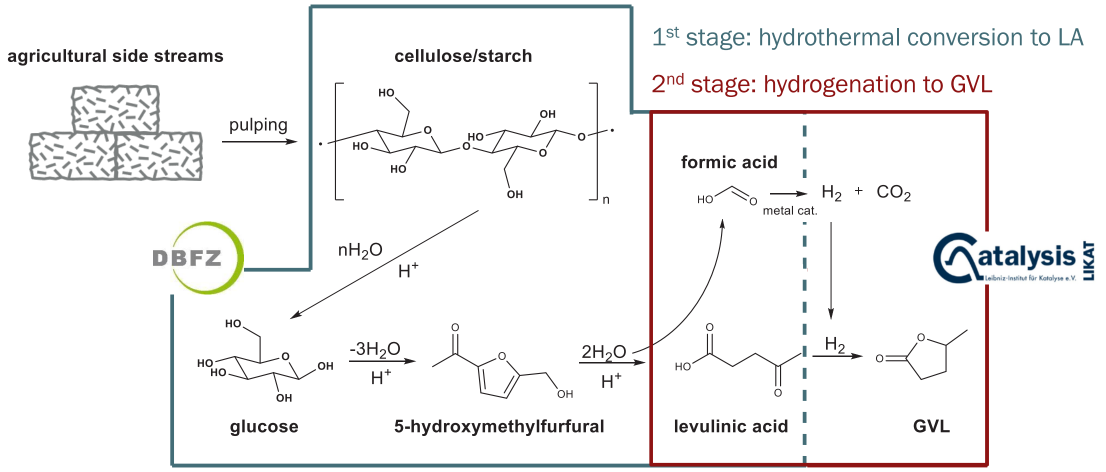
Reaction pathway to GVL



1st stage: hydrothermal conversion to LA

2nd stage: hydrogenation to GVL

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Leonard Moser, Bauhaus Luftfahrt e.V.

System analysis of liquid biofuel production via hydrothermal liquefaction of manure with integrated water electrolysis for hydrogen production

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Scientific innovation and relevance

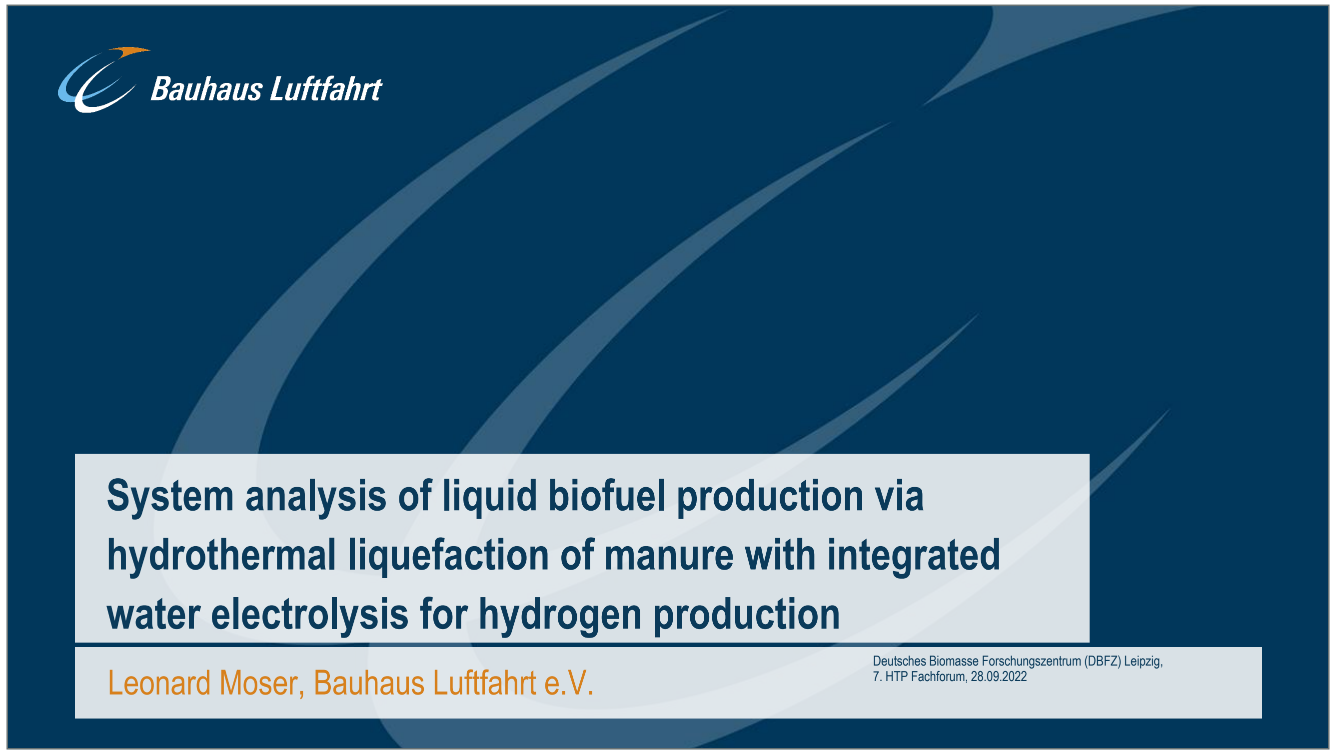
Hydrothermal liquefaction (HTL) is considered one of the most promising liquid fuel production pathways converting wet biomass. From a techno-economic perspective, wet waste streams like sewage sludge, are attractive, due to high disposal treatment cost and in turn negative feedstock cost. In case of manures, current management practices are more complex. Manures are widely used as organic fertilizer, which is associated with a certain value. However, in regions with high livestock density disposal problems occur. Furthermore, a significant amount of greenhouse gas (GHG) emissions is associated with conventional manure management, which can be partly reduced in a HTL scenario. Thus an avoided burden can be assigned for HTL conversion.

Aim and approach

In this work, specific emphasis is put on reducing GHG emissions. Therefore, on the one hand, conventional manure management systems are investigated and compared to manure management including subsequent treatment via HTL. On the other hand, innovative HTL process chains, including water electrolysis for hydrogen production and electrical heating are compared to conventional HTL configurations including steam methane reforming (SMR) and heating with internally produced biogas. Besides this life-cycle assessment (LCA), the implications of an improved manure management system and different HTL process configurations on the minimum fuel selling price (MFSP) are also investigated via a techno-economic analysis (TEA). Subsequently, sensitivity analyses are presented for both LCA and TEA.

Preliminary results

Preliminary results show that the substitution of hydrogen production via natural gas reforming by water electrolysis can reduce GHG emissions of the HTL fuel production pathway substantially. The analysis, however, demonstrates that the GHG emission reduction potential strongly depends on the electricity source. Using an electricity mix of Sweden (13 g CO2 Eq./kWh) e.g., emission reductions of up to 96 % can be achieved compared to conventional jet fuel production. Further improvements can be obtained when process heat generation from natural gas is replaced by electrical heating. Considering the current grid mix of Germany (301 g CO2 Eq./kWh), on the other hand, the HTL concept including water electrolysis performs worse than the HTL concept including steam methane reforming of natural gas. Complementary preliminary TEA results, reveal that hydrogen production via steam methane reforming is usually less expensive than water electrolysis and that heating with internally produced biogas tends to be less expensive than electrical heating. MFSPs lie in the range of 0.42 to 0.64 €/kg upgraded fuel mix. All scenarios show a high sensitivity to feedstock cost, electricity cost represents another major influence within scenarios that include water electrolysis.



System analysis of liquid biofuel production via hydrothermal liquefaction of manure with integrated water electrolysis for hydrogen production

Leonard Moser, Bauhaus Luftfahrt e.V.

Deutsches Biomasse Forschungszentrum (DBFZ) Leipzig,
7. HTP Fachforum, 28.09.2022

- Why do we need HTL?
- What is HTL, what is system analysis?
- Baseline scenario
- Sensitivity analysis
  - Cut-off approach
  - Consequential approach
- Conclusion and outlook

Maria Jose Rivas Arrieta, Aarhus University

Separation and recovery of inorganics during HTL of manure: Towards nutrients circularity

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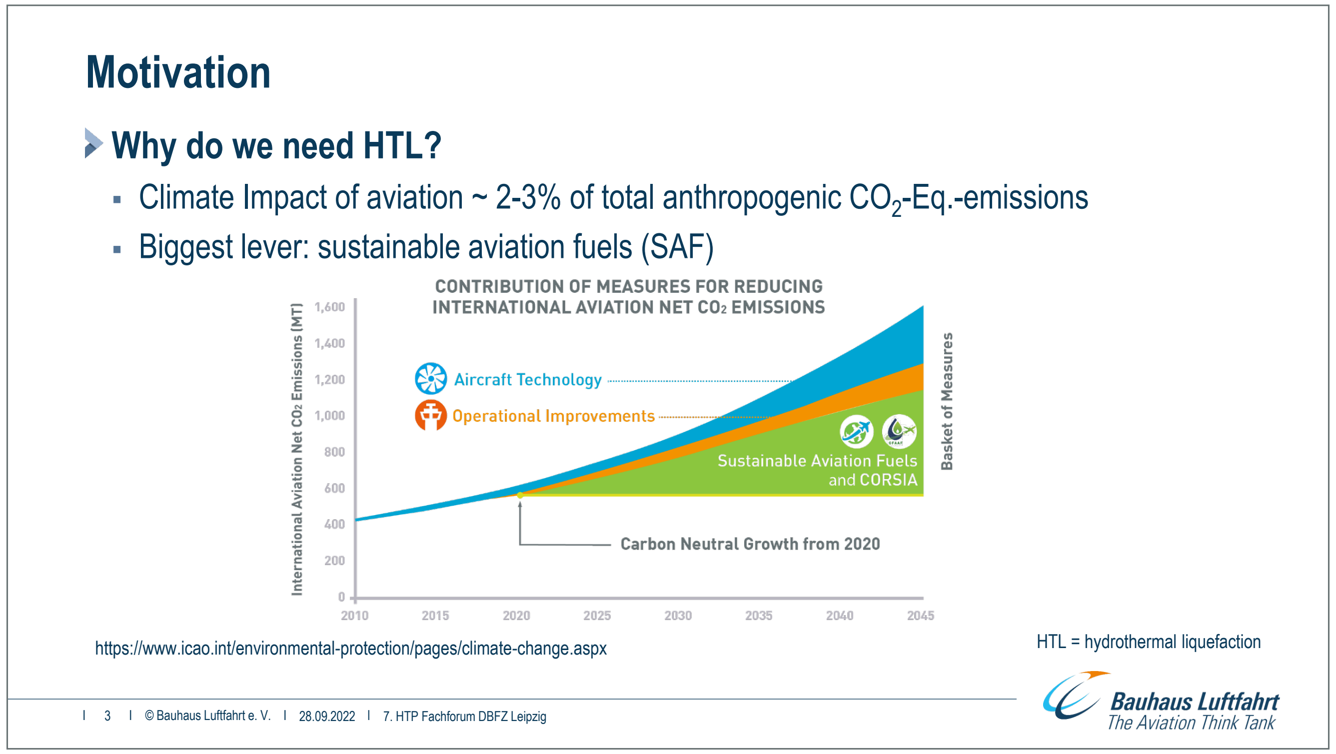

Motivation

- **Why do we need HTL?**
  - Climate Impact of aviation ~ 2-3% of total anthropogenic CO_2-Eq.-emissions
  - Biggest lever: sustainable aviation fuels (SAF)

https://www.icao.int/environmental-protection/pages/climate-change.aspx

HTL = hydrothermal liquefaction

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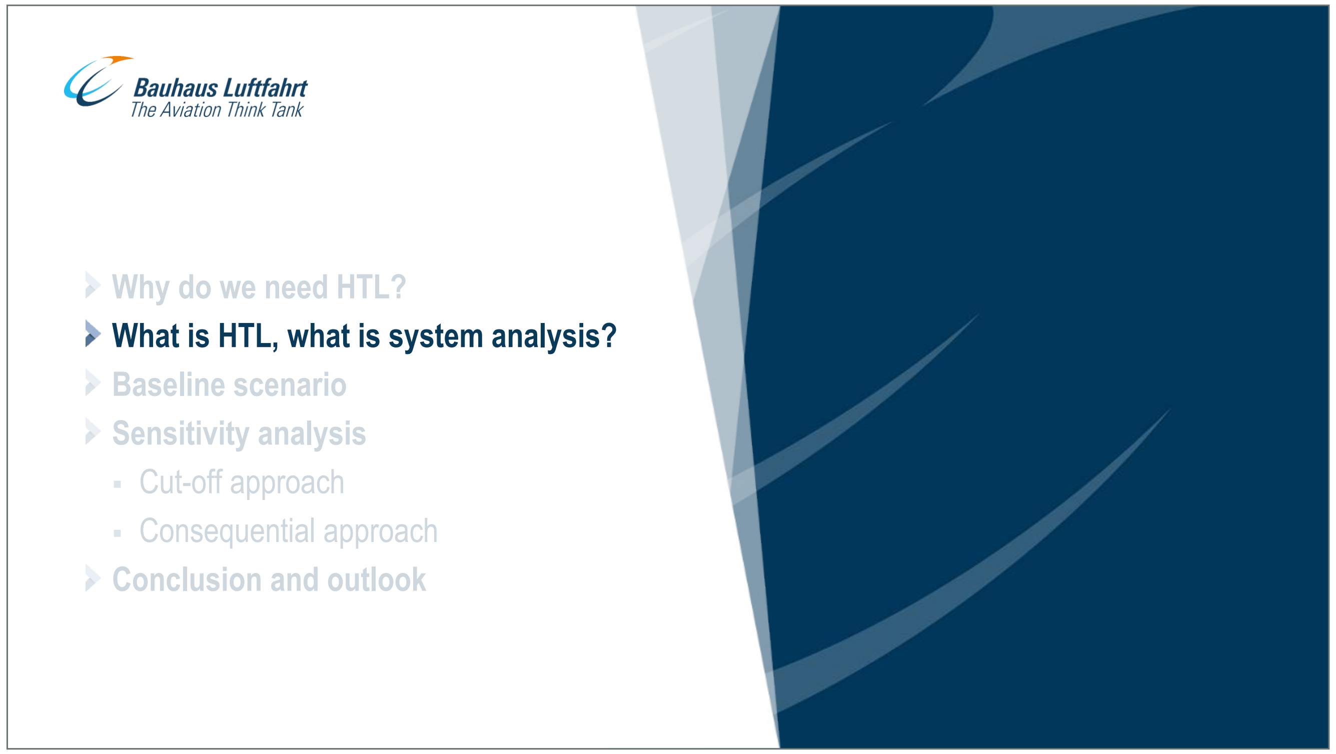

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- Why do we need HTL?
- **What is HTL, what is system analysis?**
- Baseline scenario
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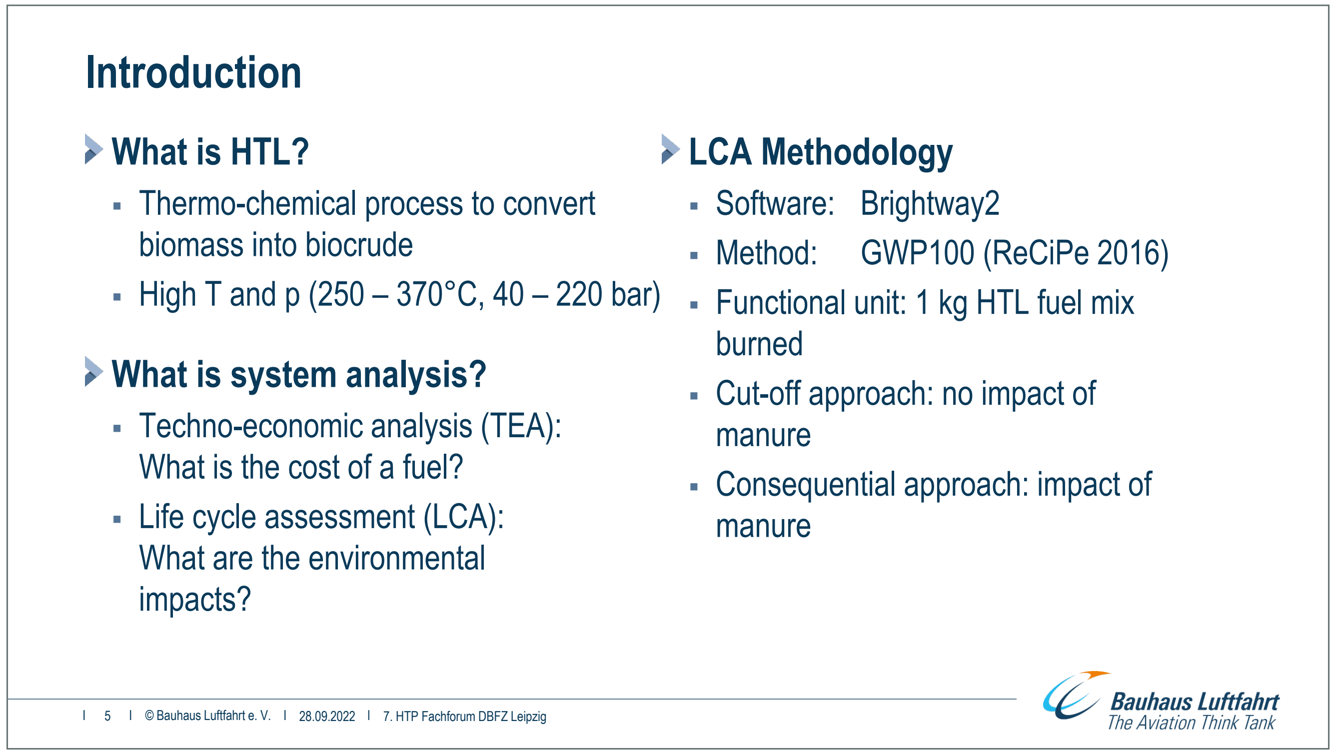

Introduction

- **What is HTL?**
  - Thermo-chemical process to convert biomass into biocrude
  - High T and p (250 – 370°C, 40 – 220 bar)
- **What is system analysis?**
  - Techno-economic analysis (TEA): What is the cost of a fuel?
  - Life cycle assessment (LCA): What are the environmental impacts?
- **LCA Methodology**
  - Software: Brightway2
  - Method: GWP100 (ReCiPe 2016)
  - Functional unit: 1 kg HTL fuel mix burned
  - Cut-off approach: no impact of manure
  - Consequential approach: impact of manure

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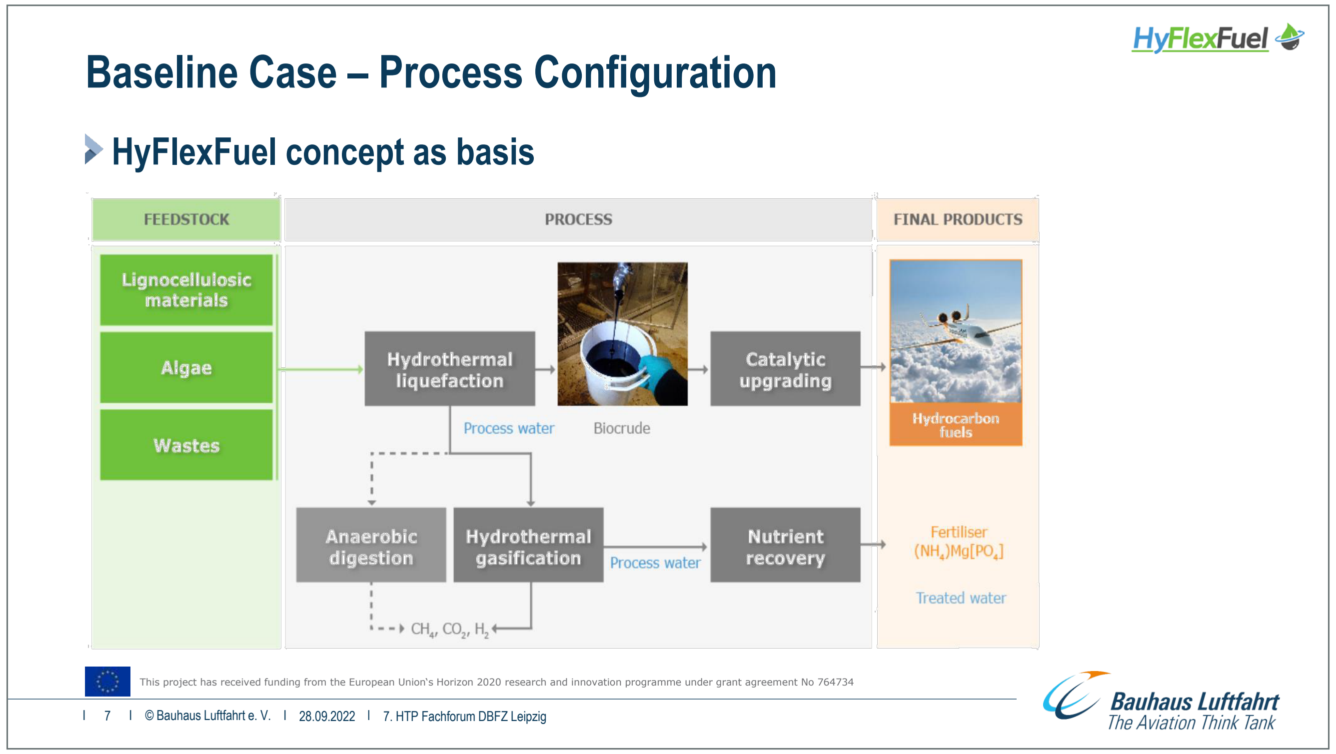

Baseline Case – Process Configuration

- **HyFlexFuel concept as basis**

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 764734

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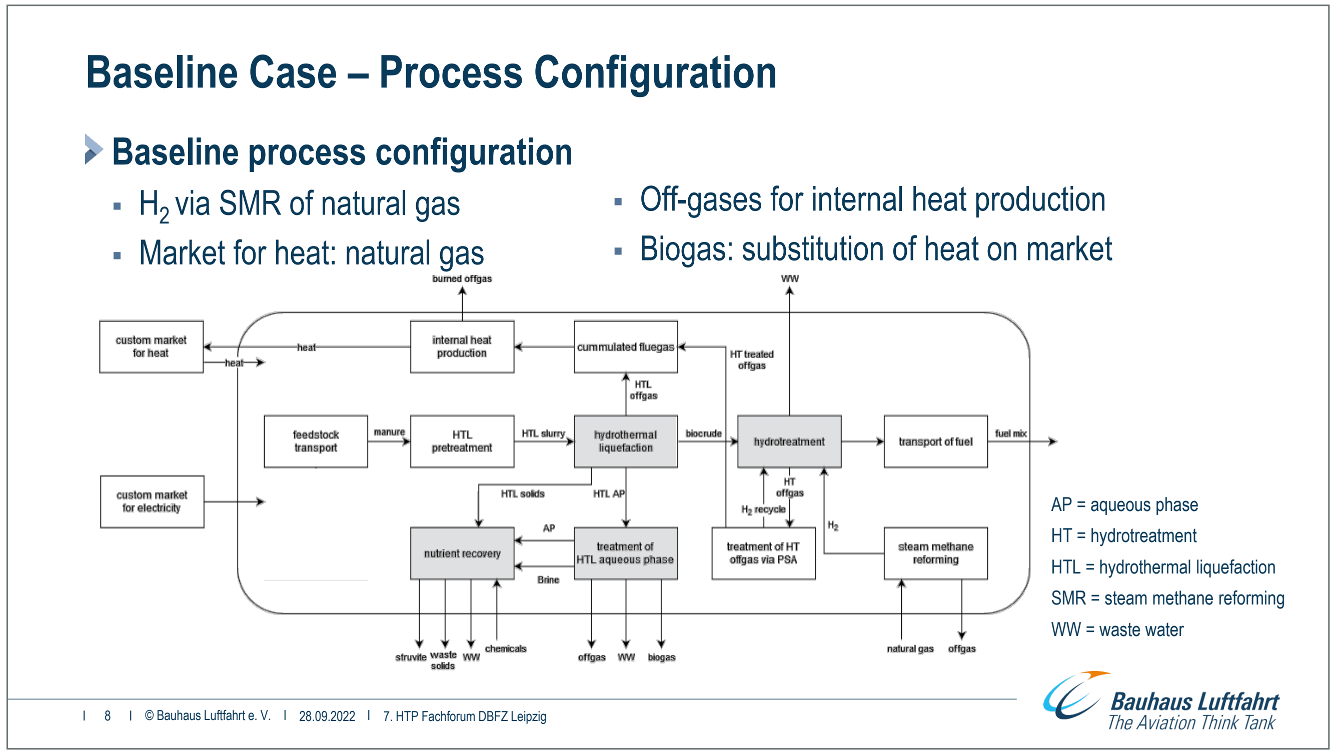

Baseline Case – Process Configuration

- **Baseline process configuration**
  - H_2 via SMR of natural gas
  - Market for heat: natural gas
  - Off-gases for internal heat production
  - Biogas: substitution of heat on market

AP = aqueous phase
HT = hydrotreatment
HTL = hydrothermal liquefaction
SMR = steam methane reforming
WW = waste water

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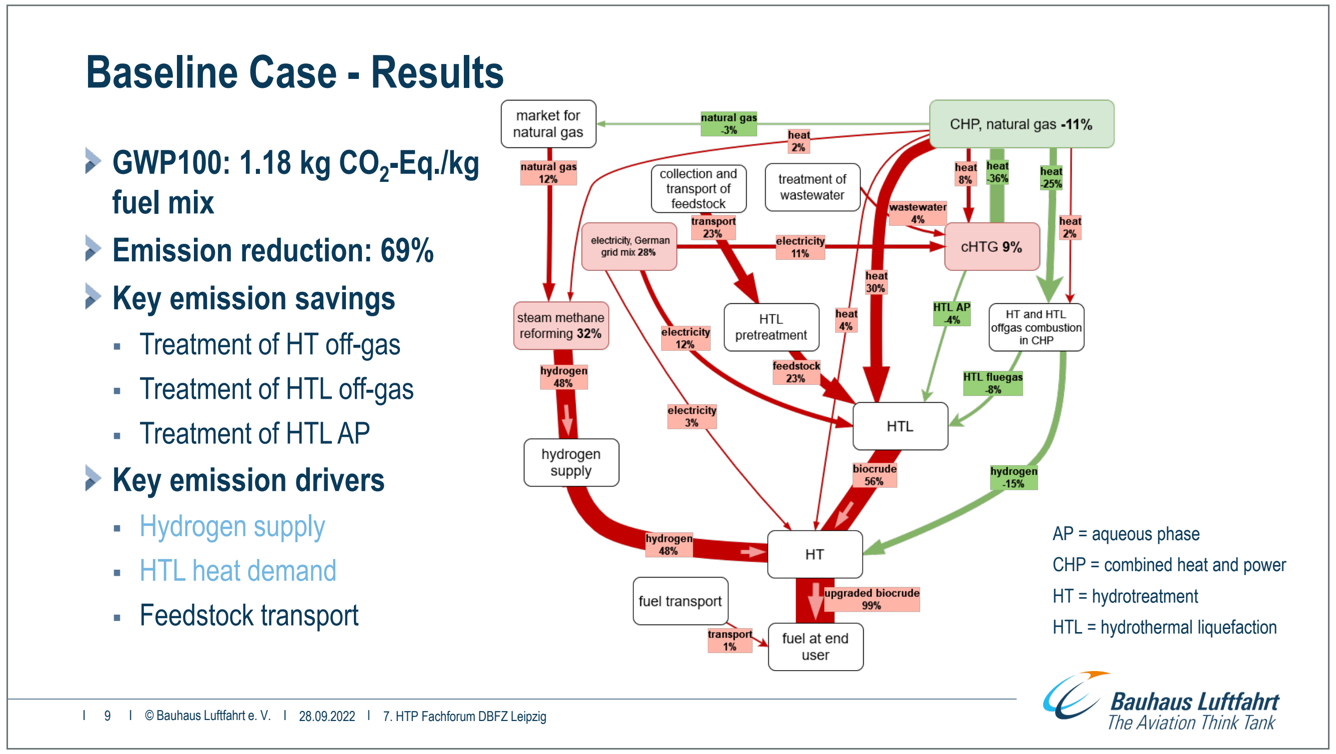

Baseline Case - Results

- **GWP100: 1.18 kg CO_2-Eq./kg fuel mix**
- **Emission reduction: 69%**
- **Key emission savings**
  - Treatment of HT off-gas
  - Treatment of HTL off-gas
  - Treatment of HTL AP
- **Key emission drivers**
  - Hydrogen supply
  - HTL heat demand
  - Feedstock transport

AP = aqueous phase
CHP = combined heat and power
HT = hydrotreatment
HTL = hydrothermal liquefaction

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- Why do we need HTL?
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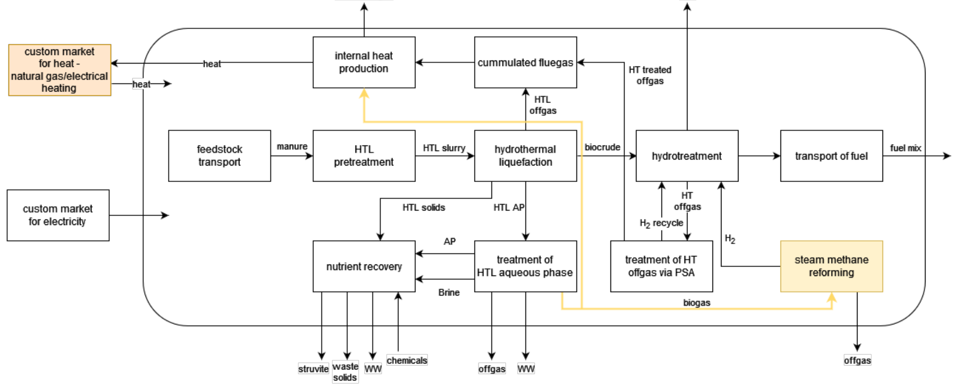
Alternative process configurations: SMR scenarios

- **SMR process configuration**
  - H_2 via SMR of internal biogas
  - Heat supply via internal biogas
- Market for heat: natural gas or electrical heating



AP = aqueous phase
HT = hydrotreatment
HTL = hydrothermal liquefaction
SMR = steam methane reforming
WW = waste water

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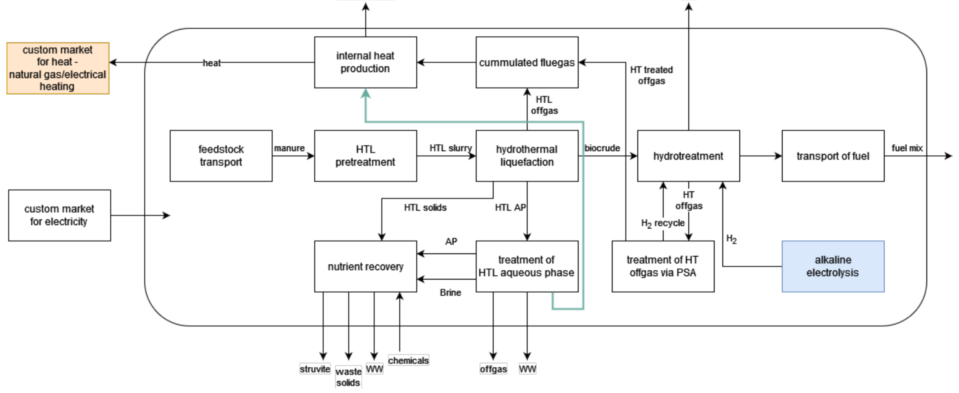
Alternative process configurations: AEL scenarios

- **AEL process configuration**
  - H_2 via AEL of water
  - Heat supply via internal biogas
- Market for heat: natural gas or electrical heating



AEL = alkaline water electrolysis
AP = aqueous phase
HT = hydrotreatment
HTL = hydrothermal liquefaction
WW = waste water

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Sensitivity Analysis – Scenario Overview

- **Variables**
  - Process configurations: **5**
  - Electricity inputs: **5**
  - Manure samples: **2**
- **50 scenarios including BL case**

Ultimate analysis						
Manure	C	H	N	O	S	Ash
1	49.3	6.9	2.9	40.2	0.7	38.6
2	53.1	7.3	5.3	33.7	0.5	17.0

Proximate analysis					
Manure	Lip	Car	Pro	Lig	Ext
1	2.9	46.8	7.4	4.1	0.8
2	8.6	48.4	20.5	5.3	0.8

Process configuration	BL-NG	SMR-BG	SMR-EL	AEL-BG	AEL-EL
Wind	-WI-M1/2	-WI-M1/2	-WI-M1/2	-WI-M1/2	-WI-M1/2
Photovoltaic	-PV-M1/2	-PV-M1/2	-PV-M1/2	-PV-M1/2	-PV-M1/2
German grid mix	-GGM-M1/2	-GGM-M1/2	-GGM-M1/2	-GGM-M1/2	-GGM-M1/2
Natural gas	-NG-M1/2	-NG-M1/2	-NG-M1/2	-NG-M1/2	-NG-M1/2
Hard coal	-HC-M1/2	-HC-M1/2	-HC-M1/2	-HC-M1/2	-HC-M1/2

AEL = alkaline water electrolysis
Lip = lipids
BL = baseline
BG = biogas
Car = carbohydrates
EL = electrical heating
Ext = extractives
GGM = german grid mix
HC = hard coal

Lig = lignin
NG = natural gas
Pro = proteins
PV = photovoltaic
SMR = steam methane reforming
WI = wind

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 764734

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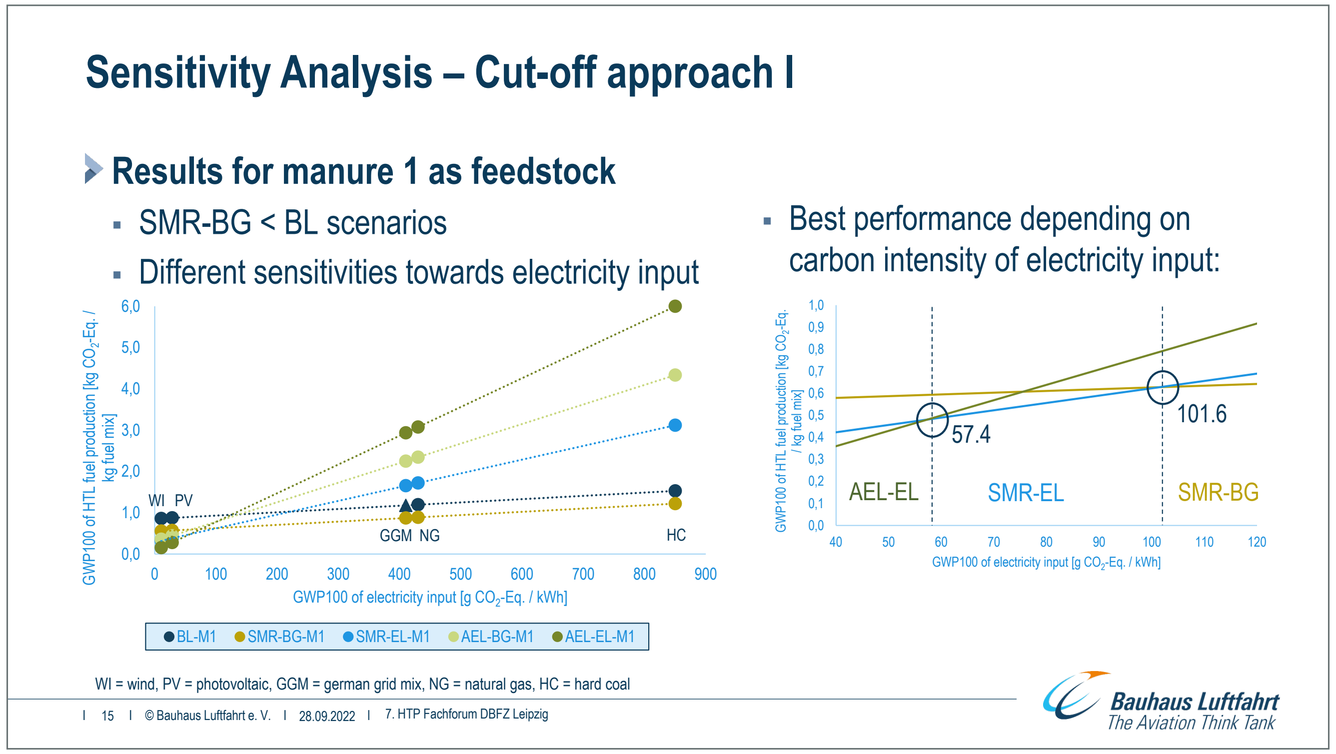
- Why do we need HTL?
- What is HTL, what is system analysis?
- Baseline scenario
- **Sensitivity analysis**
  - Cut-off approach
  - Consequential approach
- Conclusion and outlook



Sensitivity Analysis – Cut-off approach I

- **Results for manure 1 as feedstock**
  - SMR-BG < BL scenarios
  - Different sensitivities towards electricity input
- Best performance depending on carbon intensity of electricity input:

WI = wind, PV = photovoltaic, GGM = german grid mix, NG = natural gas, HC = hard coal

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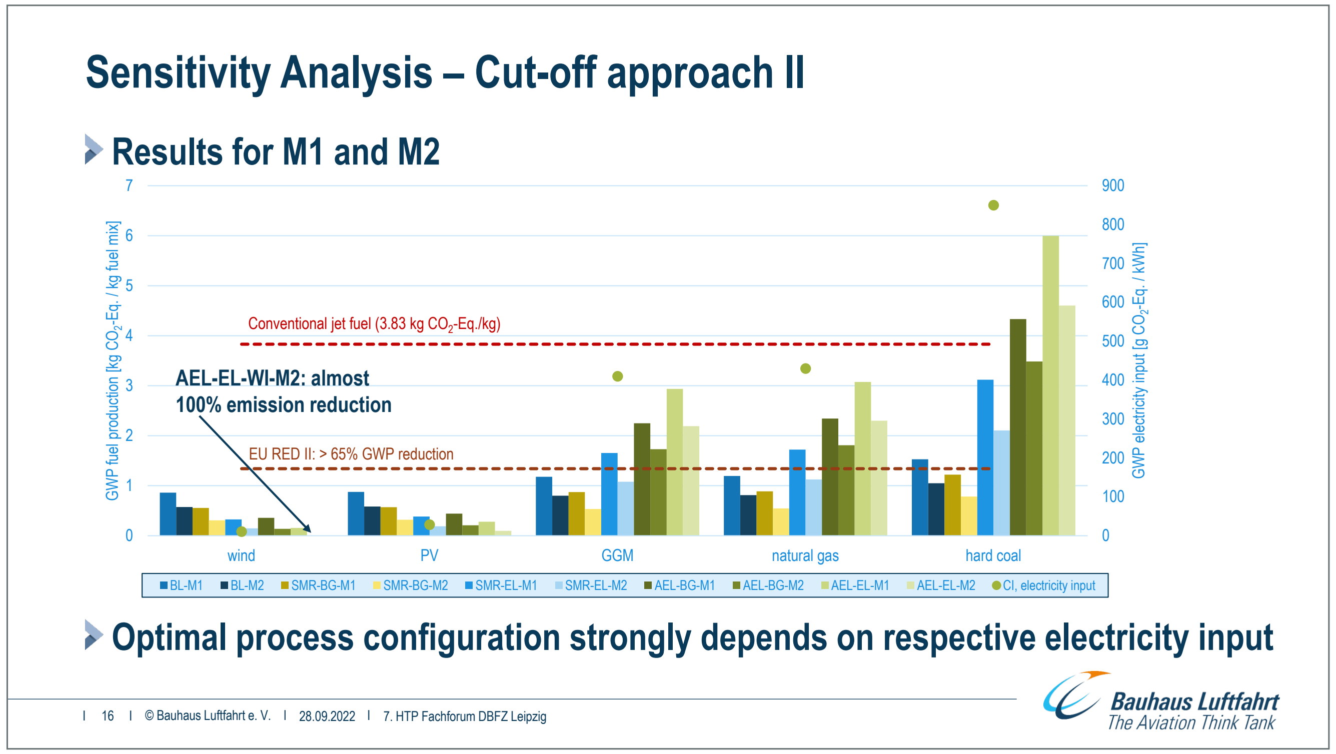

Sensitivity Analysis – Cut-off approach II

- **Results for M1 and M2**

- **Optimal process configuration strongly depends on respective electricity input**

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- Why do we need HTL?
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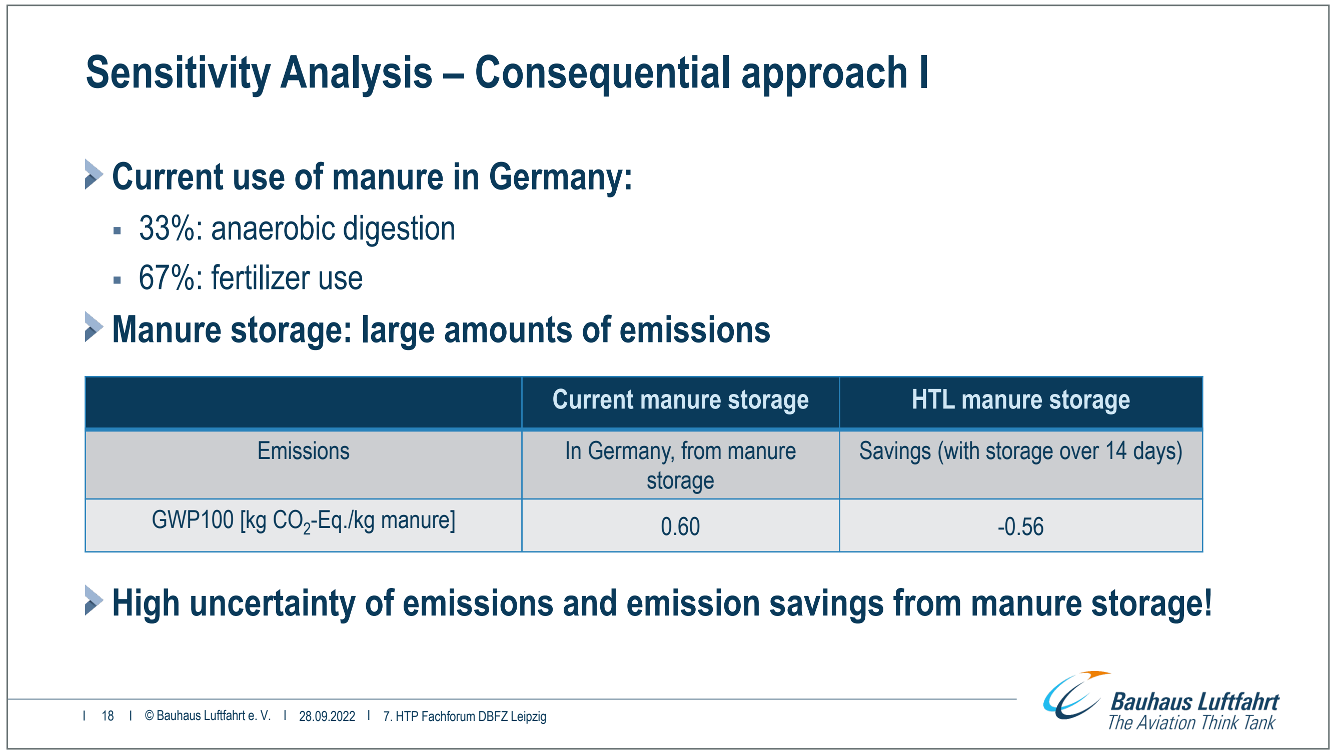

Sensitivity Analysis – Consequential approach I

- **Current use of manure in Germany:**
  - 33%: anaerobic digestion
  - 67%: fertilizer use
- **Manure storage: large amounts of emissions**

	Current manure storage	HTL manure storage
Emissions	In Germany, from manure storage	Savings (with storage over 14 days)
GWP100 [kg CO_2-Eq./kg manure]	0.60	-0.56

- **High uncertainty of emissions and emission savings from manure storage!**

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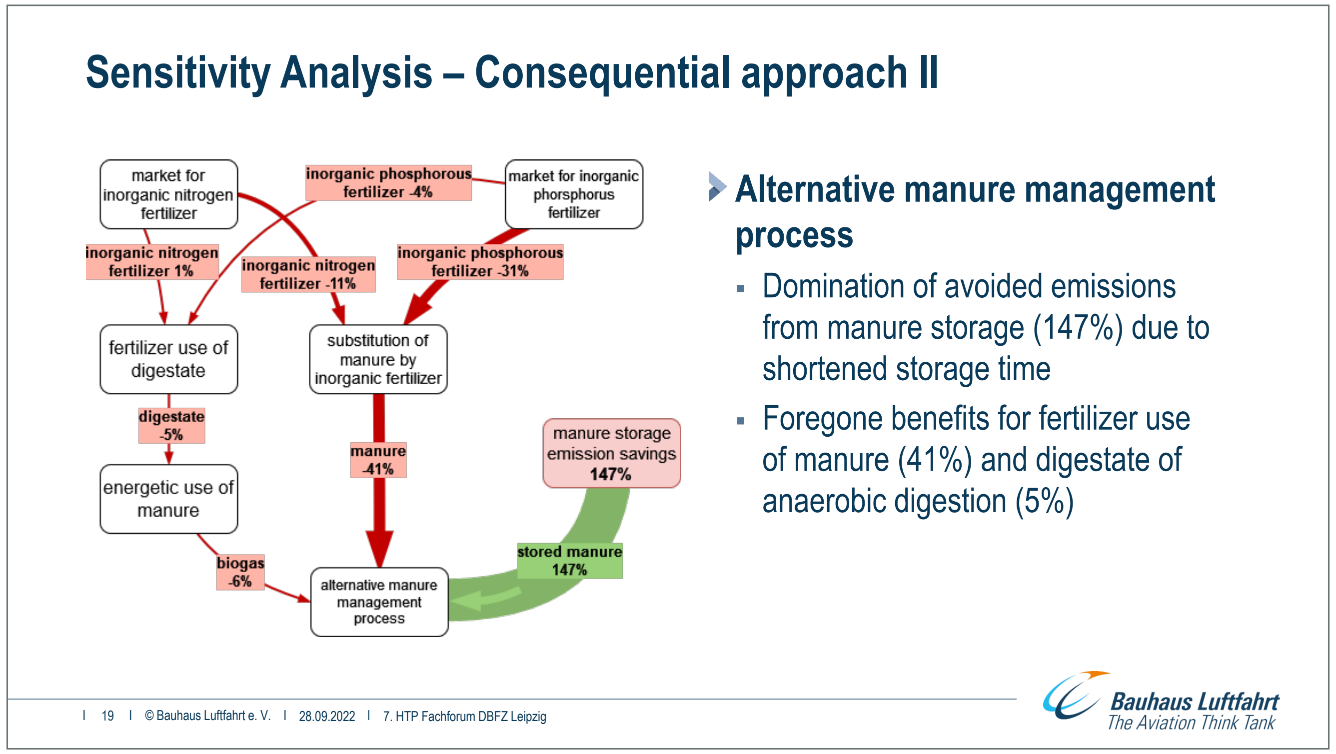

Sensitivity Analysis – Consequential approach II

- **Alternative manure management process**
    - Domination of avoided emissions from manure storage (147%) due to shortened storage time
    - Foregone benefits for fertilizer use of manure (41%) and digestate of anaerobic digestion (5%)

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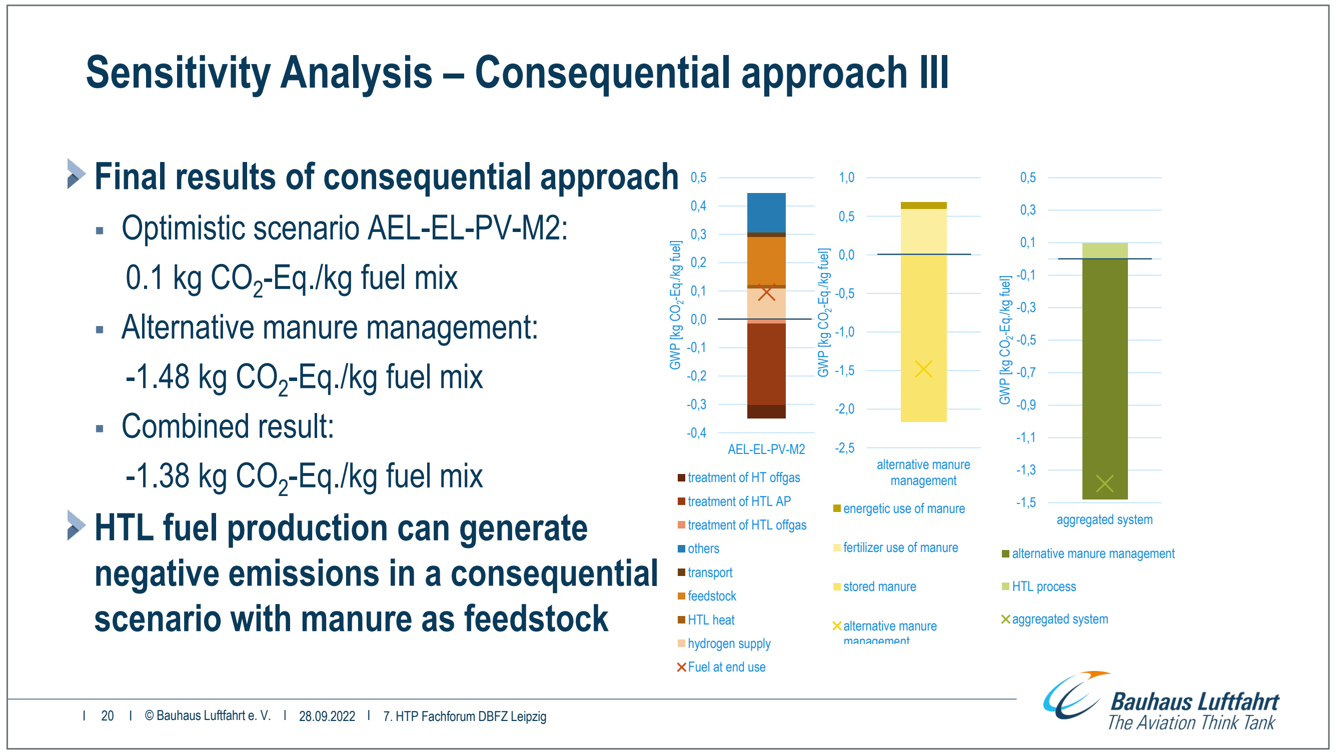

Sensitivity Analysis – Consequential approach III

- **Final results of consequential approach**
    - Optimistic scenario AEL-EL-PV-M2: 0.1 kg CO_2-Eq./kg fuel mix
    - Alternative manure management: -1.48 kg CO_2-Eq./kg fuel mix
    - Combined result: -1.38 kg CO_2-Eq./kg fuel mix
- **HTL fuel production can generate negative emissions in a consequential scenario with manure as feedstock**

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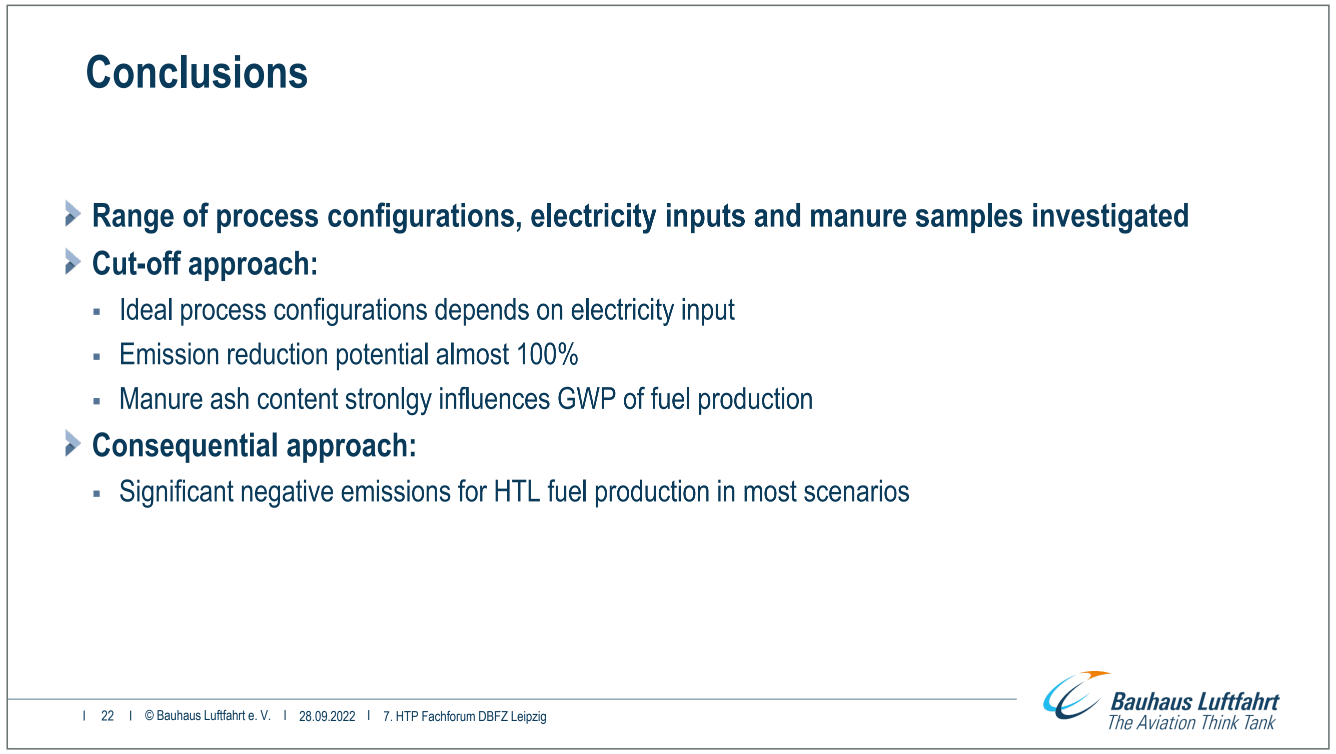
- Why do we need HTL?
- What is HTL, what is system analysis?
- Baseline scenario
- Sensitivity analysis
    - Cut-off approach
    - Consequential approach
- **Conclusion and outlook**



Conclusions

- **Range of process configurations, electricity inputs and manure samples investigated**
- **Cut-off approach:**
    - Ideal process configurations depends on electricity input
    - Emission reduction potential almost 100%
    - Manure ash content stronlgy influences GWP of fuel production
- **Consequential approach:**
    - Significant negative emissions for HTL fuel production in most scenarios

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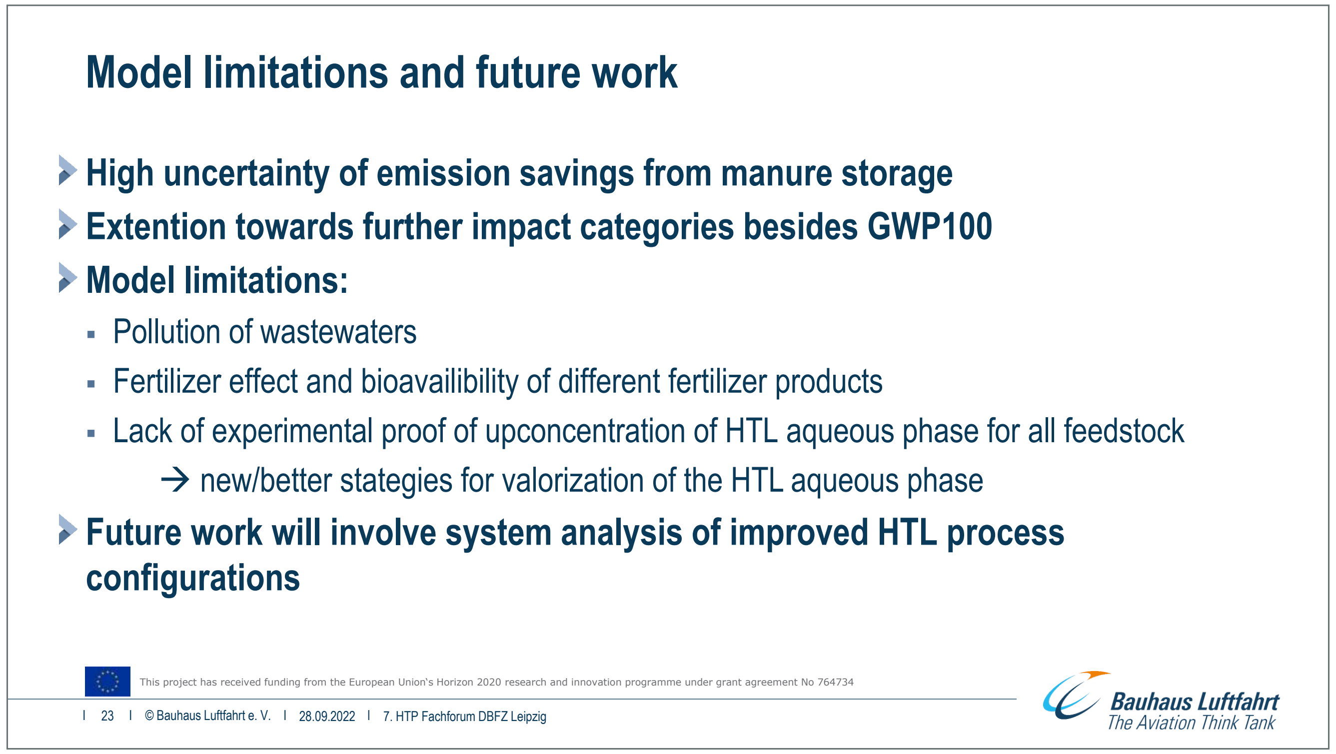

Model limitations and future work

- **High uncertainty of emission savings from manure storage**
- **Extention towards further impact categories besides GWP100**
- **Model limitations:**
  - Pollution of wastewaters
  - Fertilizer effect and bioavailibility of different fertilizer products
  - Lack of experimental proof of upconcentration of HTL aqueous phase for all feedstock

    → new/better stategies for valorization of the HTL aqueous phase
- **Future work will involve system analysis of improved HTL process configurations**

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 764734

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Thank you for your attention!

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G N O S I S

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and Climate Action

on the basis of a decision
by the German Bundestag

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HyFlexFuel
www.hyflexfuel.eu

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Session IV:
Fester Kohlenstoff

Jens Pfersich, Universität Hohenheim

Diskussion der Kohlebildung während der Hydrothermalen Behandlung von Holz

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Einleitung: Während der letzten Jahre hat die Verarbeitung nasser Biomasse mittels Hydrothermaler Carbonisierung (HTC) weiter an Bedeutung gewonnen. Trotz aller Forschung auf diesem Gebiet sind die Einflüsse der Reaktionen, insbesondere im Hinblick auf die Biomasse und das Reaktionsmedium, bislang nicht vollständig geklärt. Zwei parallel ablaufende Reaktionswege werden für die Kohlebildung angenommen, zum einen die fest-fest Konversion zur Bildung von primary char (Pyrokohle), zum Anderen die Bildung von secondary char (Hydrokohle) aus den Abbauprodukten der Biomasse.1 Hierbei wird die Pyrokohle als Keimpunkt für das Wachstum der Hydrokohle betrachtet, welche sich um diese bildet.2

Ziel: Diskussion und visuelle Darstellung der Kohlebildung während der HTC einer lignocellulosehaltigen Biomasse mit steigender Konversionszeit.

Methode: Die HTC von Holzkugeln aus Birkenholz wurde bei 220 °C für Konversionszeiten von 0 min bis 960 min durchgeführt.

Ergebnisse: Zwei verschiedene Arten Kohle werden im selben Biomassepartikel gebildet, eine im Inneren der Biomasse (primary char), die Zweite an der fest-flüssig Grenzfläche der Biomasse (secondary char), wie in Abbildung 1 dargestellt. Die Übergangsschicht zwischen beiden Kohlen verschwindet nach kurzer Konversionszeit. Darüber hinaus wurde am Boden des Reaktors die Abscheidung eines Feststoffs während der HTC festgestellt.

Schlussfolgerung: Ausgehend vom Zentrum der Holzkugel wird primary char durch eine Art Torrefizierung gebildet, während sich gleichzeitig auf der Oberfläche secondary char, ein Produkt verschiedener Reaktionen in der Flüssigphase, bildet. Ferner löst sich entweder die äußere Hülle der Holzkugeln ab oder es fallen Produkte aus der Flüssigphase aus, welche einen Feststoff am Boden des Reaktors bilden. Dieser Feststoff könnte vergleichbar mit der secondary char an der Oberfläche der Holzkugel sein, wobei weitere Reaktionen eine Erhöhung des Kohlenstoff- und Sauerstoffgehalts mit sich bringen sowie die Oberflächenstruktur verändern. Zudem weist die kontinuierliche Zunahme der Masse mit zunehmender Konversionszeit ebenfalls auf Hydrokohle, z.B. durch Dehydrierung von 5-Hydroxymethylfurfural, hin. Schlussendlich sahen die Feststoffe am Boden durchgängig ähnlich aus, da eine Seite immer glänzend, während die andere Seite hingegen matt wirkte.

Olayinka Ahmed Ibitowa, Carl von Ossietzky Universität Oldenburg

Highly porous carbon-based electrodes with enhanced properties for application in sodium-ion batteries

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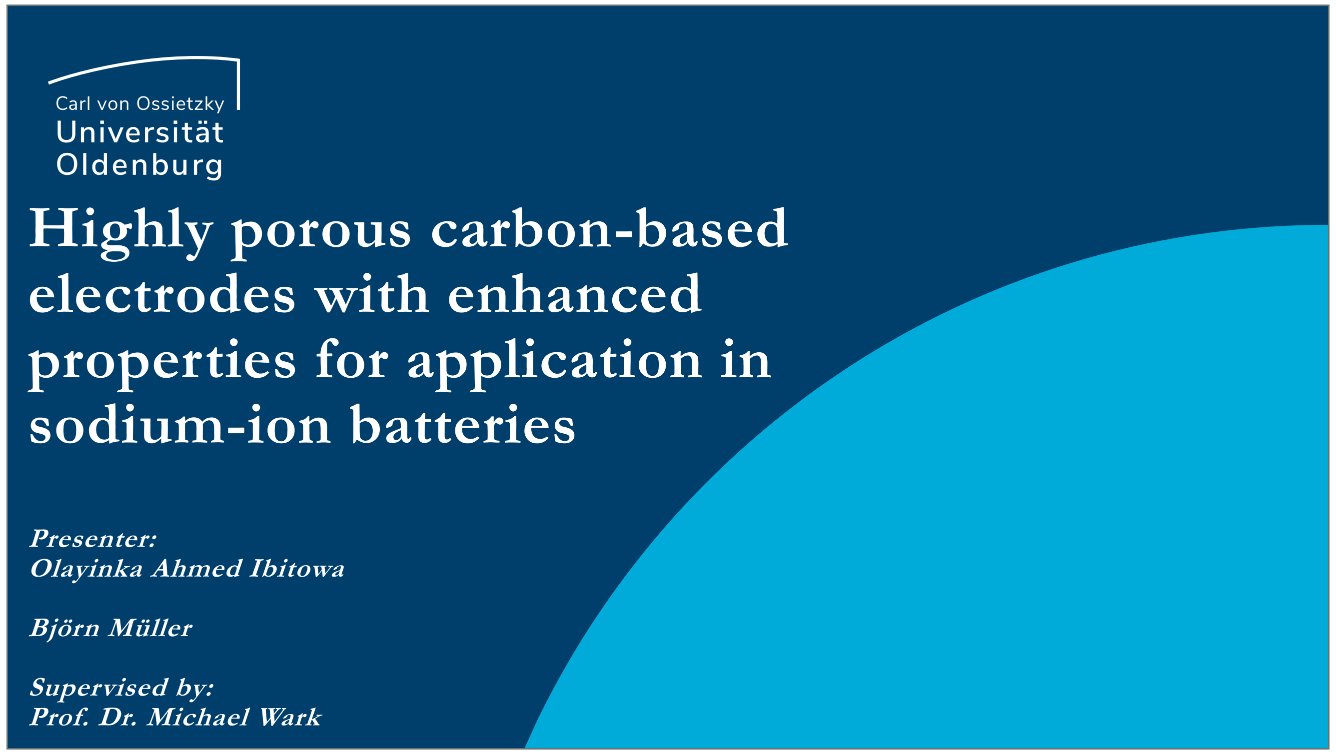
This study reports the production of a highly porous carbon materials for application as carbon-electrodes in sodium-ion batteries. Plant biomass such as sawdust was treated using hydrothermal carbonisation (HTC) at processing temperatures of 200 and 220 °C for 2 and 4 h, and in some cases steam at 750 °C for 1 h to produce a highly porous carbon material. Further treatment via activation at 650 °C for 1 h was used to improve the morphology of the HTC-carbon while no further enhancement was needed for steam produced carbon. The morphology of the activated carbon produced via both methods was analysed using the Brunauer-Emmet-Teller (BET) and the results showed that carbon materials produced directly with steam have a high specific surface area (SSA) of 824 m2g-1 as compared to the 660 m2g-1 obtained from the subsequently steam-activated HTC-carbon. Analysis from the BET results showed that steam produced carbon contains a total pore volume (PV) of 0.91 cm3g-1 out of which 0.8 cm3g-1 were mesopores and 0.1 cm3g-1 were micropores while HTC-carbon contains a PV of 0.28 cm3g-1 only from micropores. Further analysis via mercury intrusion was able to quantify that carbon produced with the use of steam contains macropores of 6.40 cm3g-1 while no larger pores beyond micropores were found in HTC-carbon.

The treatment of plant biomass via steam was further tested on pulverised cassava peels and the technology confirmed that it was possible to produce a porous carbon as compared to the usual HTC. While this technology has proven to be successful in the production of a porous carbon, it is usually accompanied by low a yield of 18 % as to the 53 % obtained when treated with HTC. However, it was possible to further increase the yield from 18 to 83 % when a pyrolytic pre-treatment without any gas is applied prior to the treatment with steam.

Carbon produced via both carbonisation technologies were applied as carbon-electrode for application as anode materials in sodium-ion batteries and their capacitances were compared to a reference carbon-electrode produced using the industrial carbon black (Super_P). The morphological influence such as the pore distributions, specific surface area, carbon and ash content of the carbon-electrodes on the capacitance of the battery were investigated. After 10 cycles, the capacitance produced via steam showed a better capacitance ranging from 128 to 330 mAhg-1 as compared to the very low capacitance obtained from HTC carbon-electrode ranging from 1 to 4 mAhg-1 and the 100 to 120mAhg-1 obtained from Super_P. The results obtained in the electrochemical testing of the carbon materials showed that the capacitance of a battery is of reliance on a high SSA and a large amount of pores contained in the carbon material used for the electrode preparation. Due to the excellent properties shown by steam, this carbonisation method could be the pathway for the production of a carbon-electrode for applications in sodium-ion batteries.



Carl von Ossietzky
Universität
Oldenburg

Highly porous carbon-based electrodes with enhanced properties for application in sodium-ion batteries

Presenter:
Olayinka Ahmed Ibitowa

Björn Müller

Supervised by:
Prof. Dr. Michael Wark

Carl von Ossietzky
Universität
Oldenburg

Major research:
Development of a waste-free Technology for processing biowastes into High valuable Chemicals and carbon materials

UNIVERSITY OF OLDENBURG

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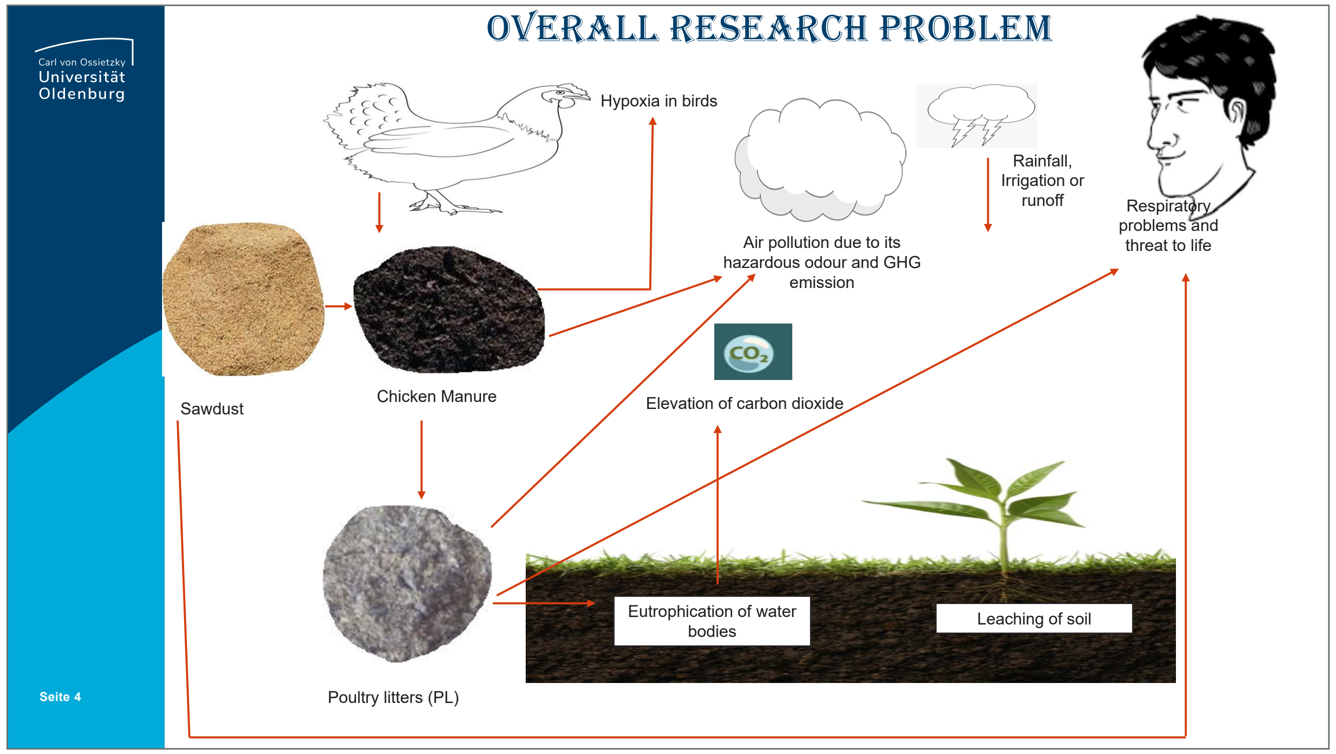


OVERALL RESEARCH PROBLEM

Hypoxia in birds

Rainfall, Irrigation or runoff

Respiratory problems and threat to life

Air pollution due to its hazardous odour and GHG emission

Sawdust

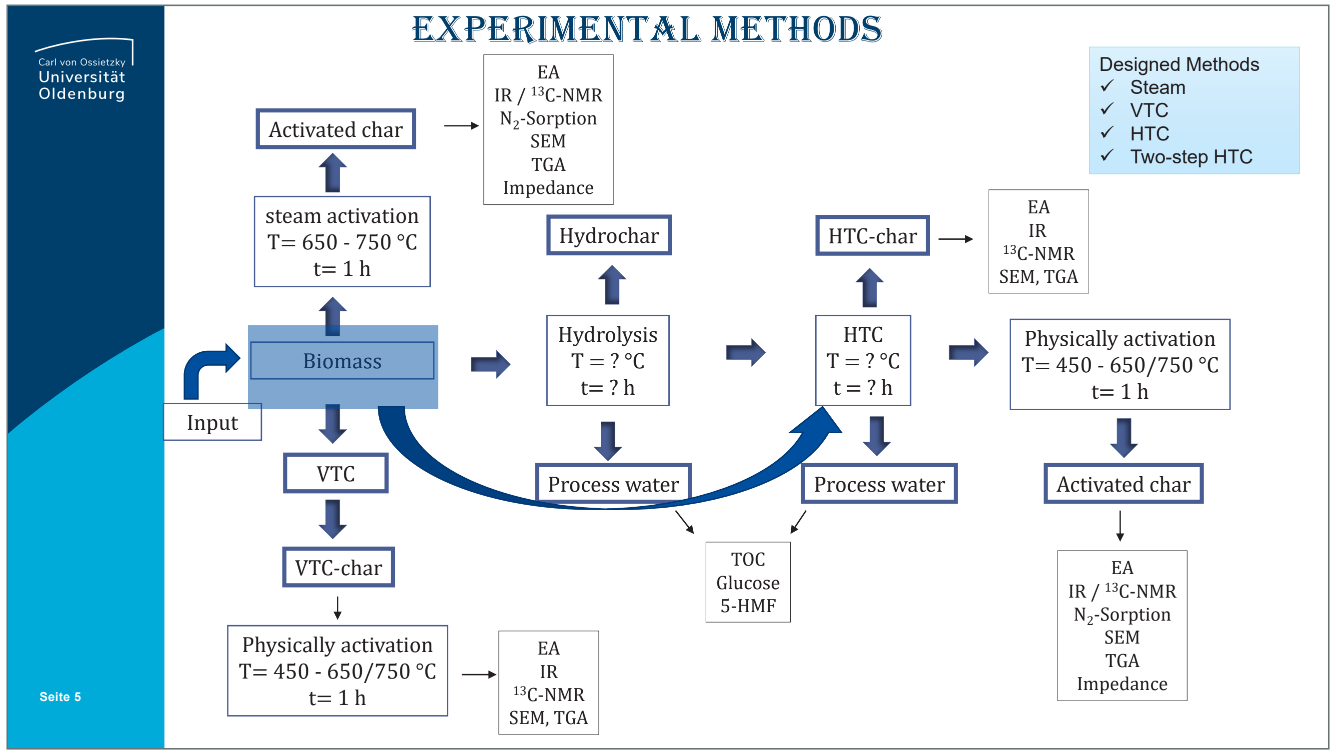
Chicken Manure

Elevation of carbon dioxide

Eutrophication of water bodies

Leaching of soil

Poultry litters (PL)



EXPERIMENTAL METHODS

Designed Methods
✓ Steam
✓ VTC
✓ HTC
✓ Two-step HTC

Input

Biomass

steam activation
T= 650 - 750 °C
t= 1 h

Activated char

EA
IR / ^{13}C-NMR
N_2-Sorption
SEM
TGA
Impedance

VTC

VTC-char

Physically activation
T= 450 - 650/750 °C
t= 1 h

EA
IR
^{13}C-NMR
SEM, TGA

Hydrolysis
T = ? °C
t= ? h

Hydrochar

Process water

TOC
Glucose
5-HMF

HTC
T = ? °C
t = ? h

HTC-char

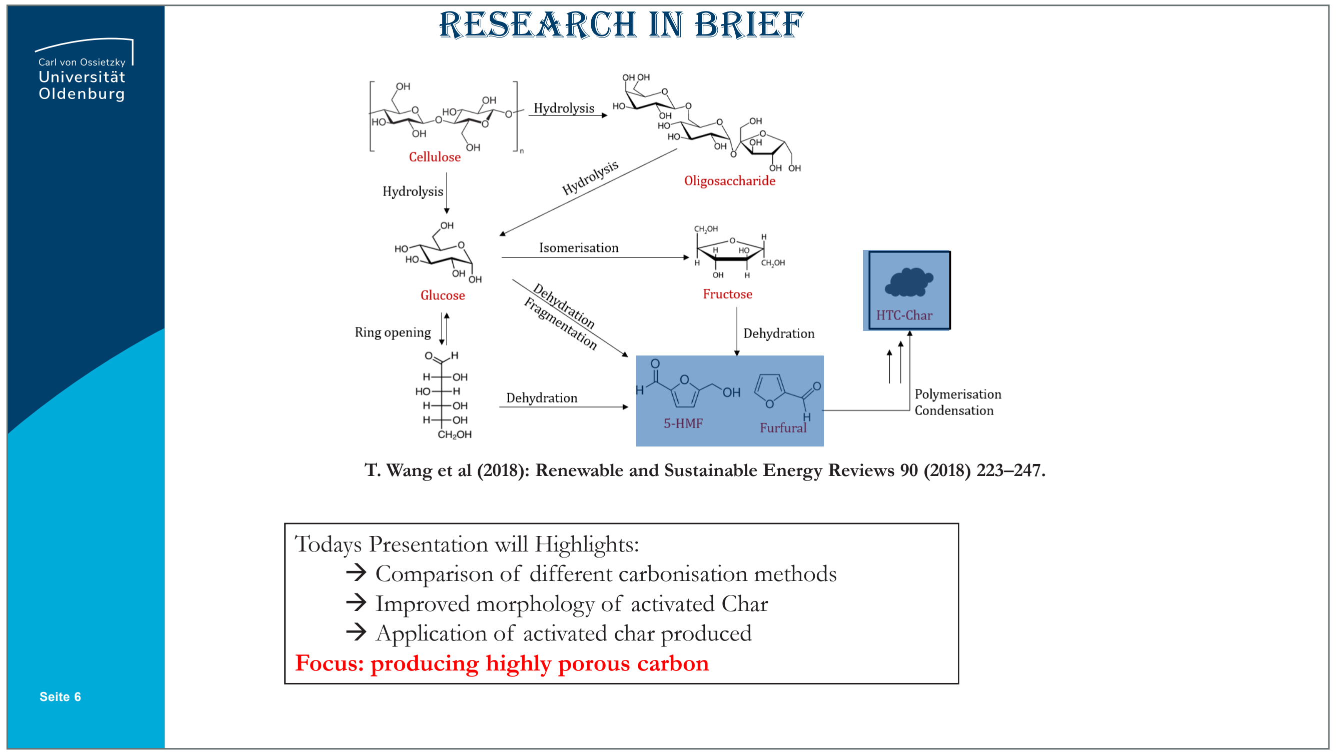
EA
IR
^{13}C-NMR
SEM, TGA

Process water

Physically activation
T= 450 - 650/750 °C
t= 1 h

Activated char

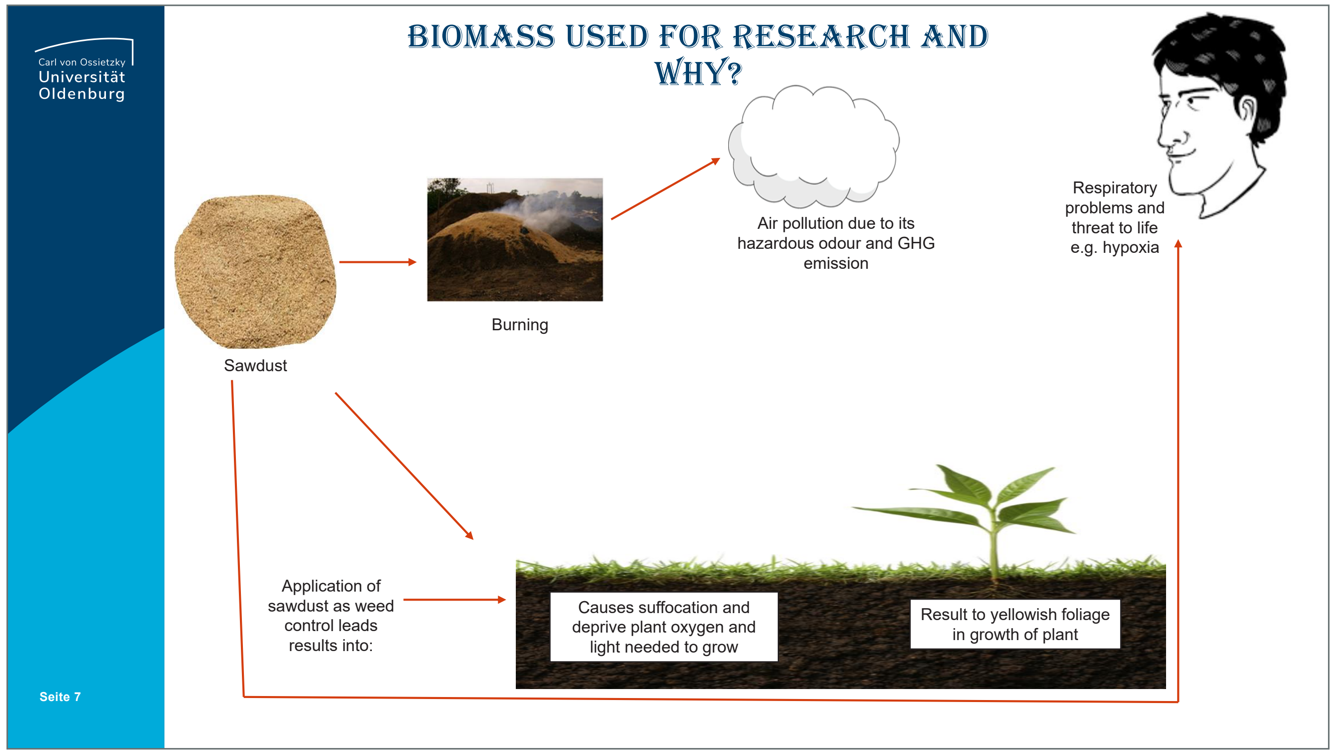
EA
IR / ^{13}C-NMR
N_2-Sorption
SEM
TGA
Impedance



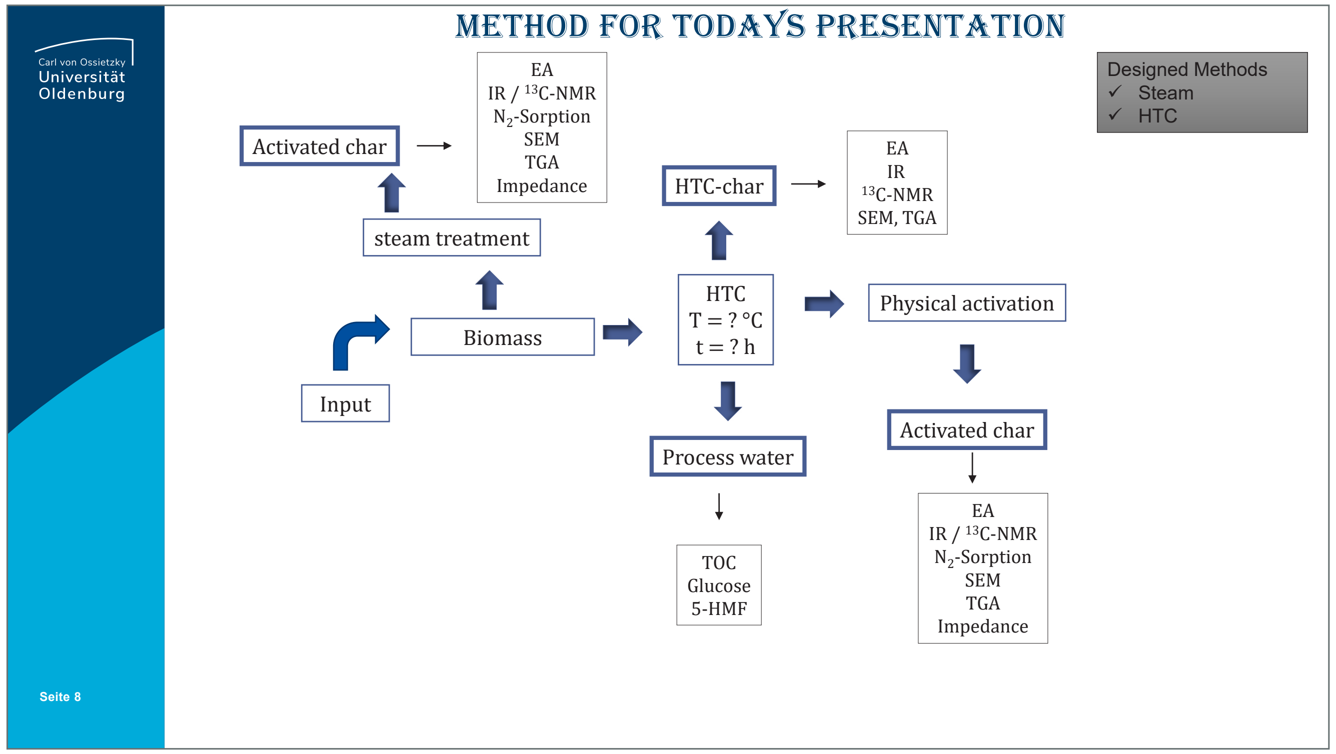
RESEARCH IN BRIEF

T. Wang et al (2018): Renewable and Sustainable Energy Reviews 90 (2018) 223–247.

Todays Presentation will Highlights:
→ Comparison of different carbonisation methods
→ Improved morphology of activated Char
→ Application of activated char produced
Focus: producing highly porous carbon

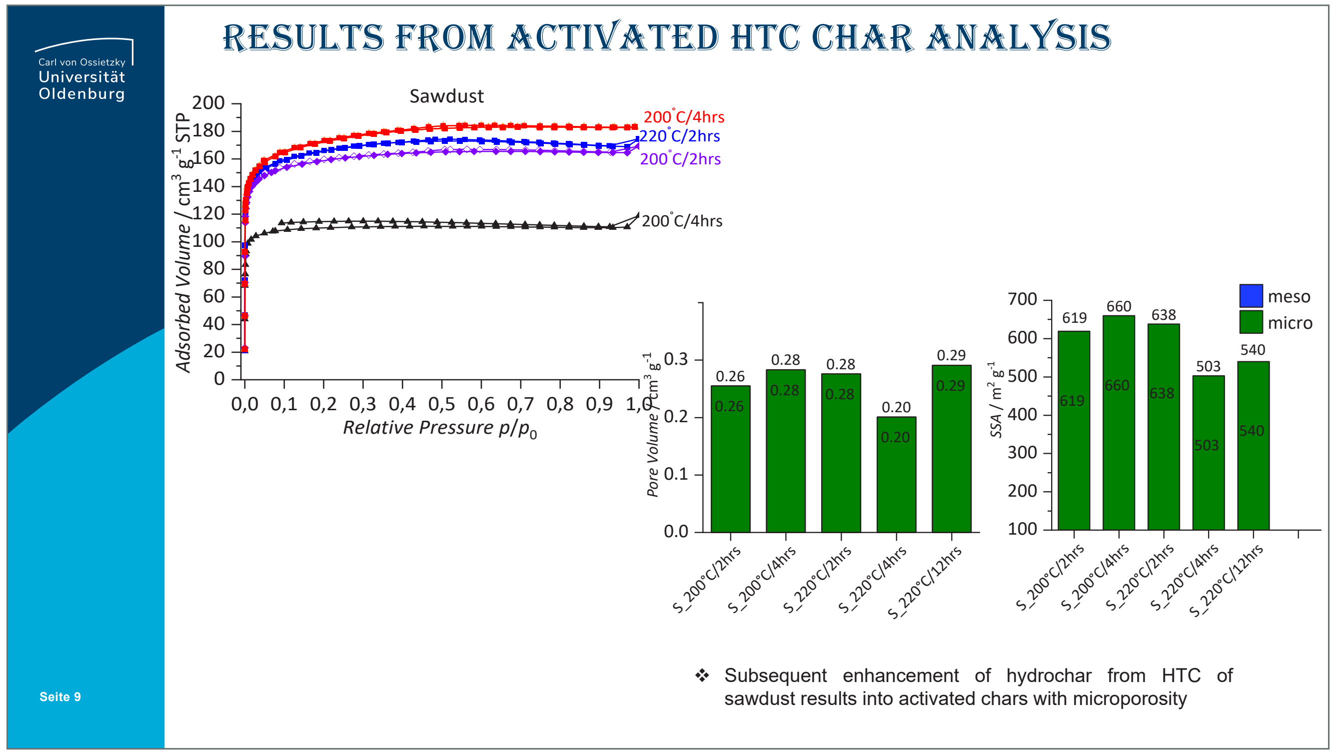


BIOMASS USED FOR RESEARCH AND WHY?



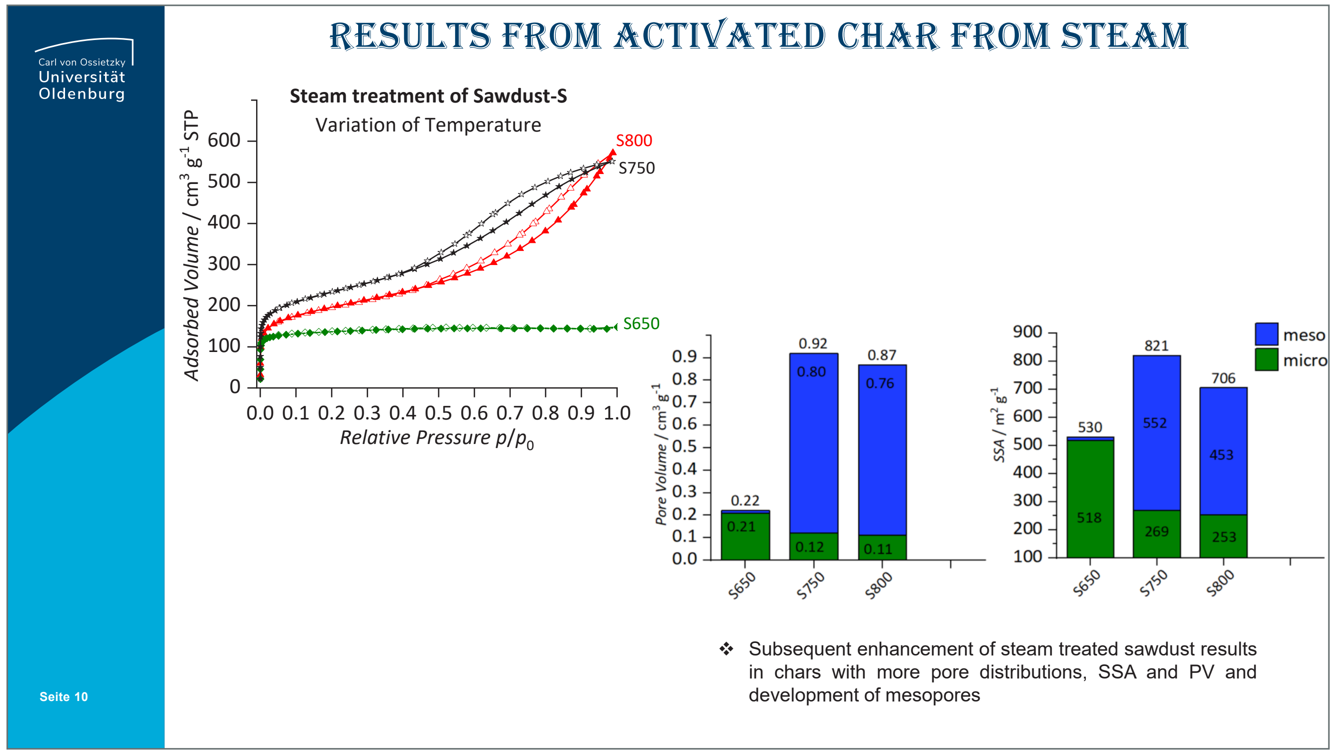
METHOD FOR TODAYS PRESENTATION

Designed Methods
- ✓ Steam
- ✓ HTC



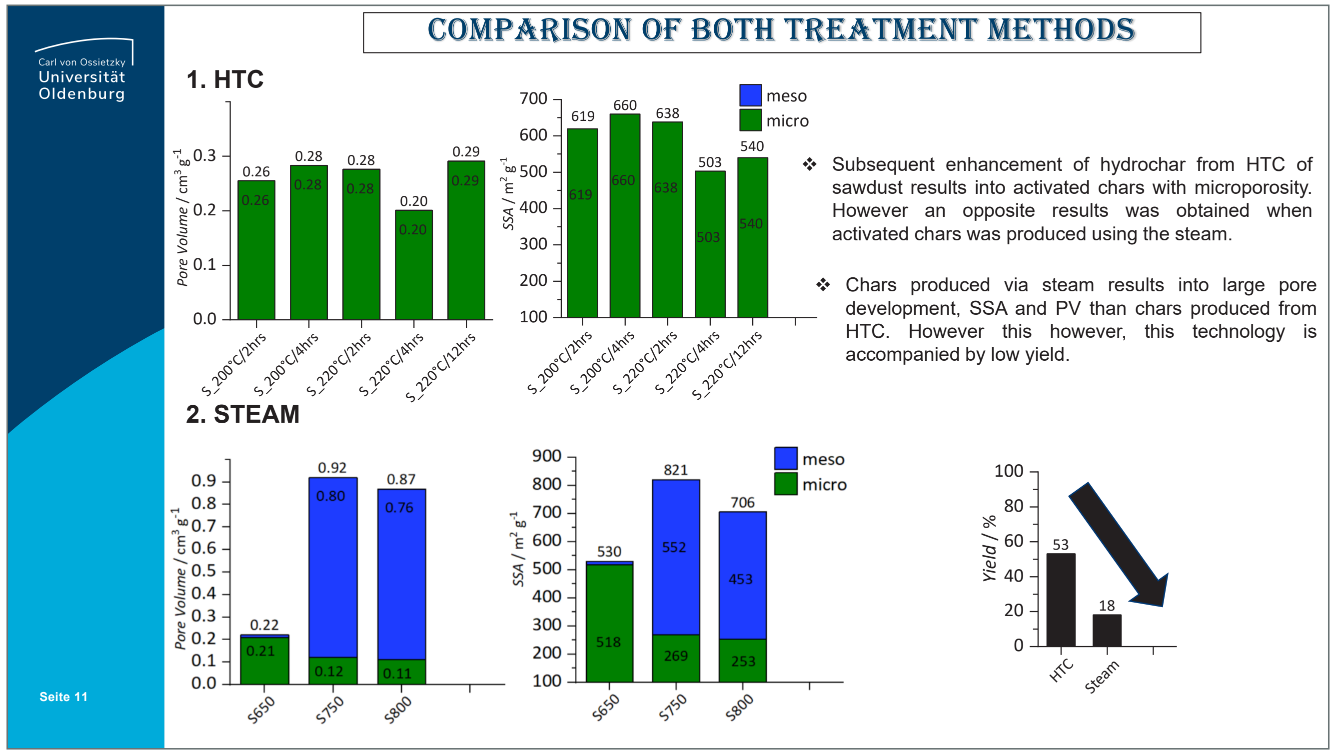
RESULTS FROM ACTIVATED HTC CHAR ANALYSIS

- ❖ Subsequent enhancement of hydrochar from HTC of sawdust results into activated chars with microporosity



RESULTS FROM ACTIVATED CHAR FROM STEAM

- ❖ Subsequent enhancement of steam treated sawdust results in chars with more pore distributions, SSA and PV and development of mesopores

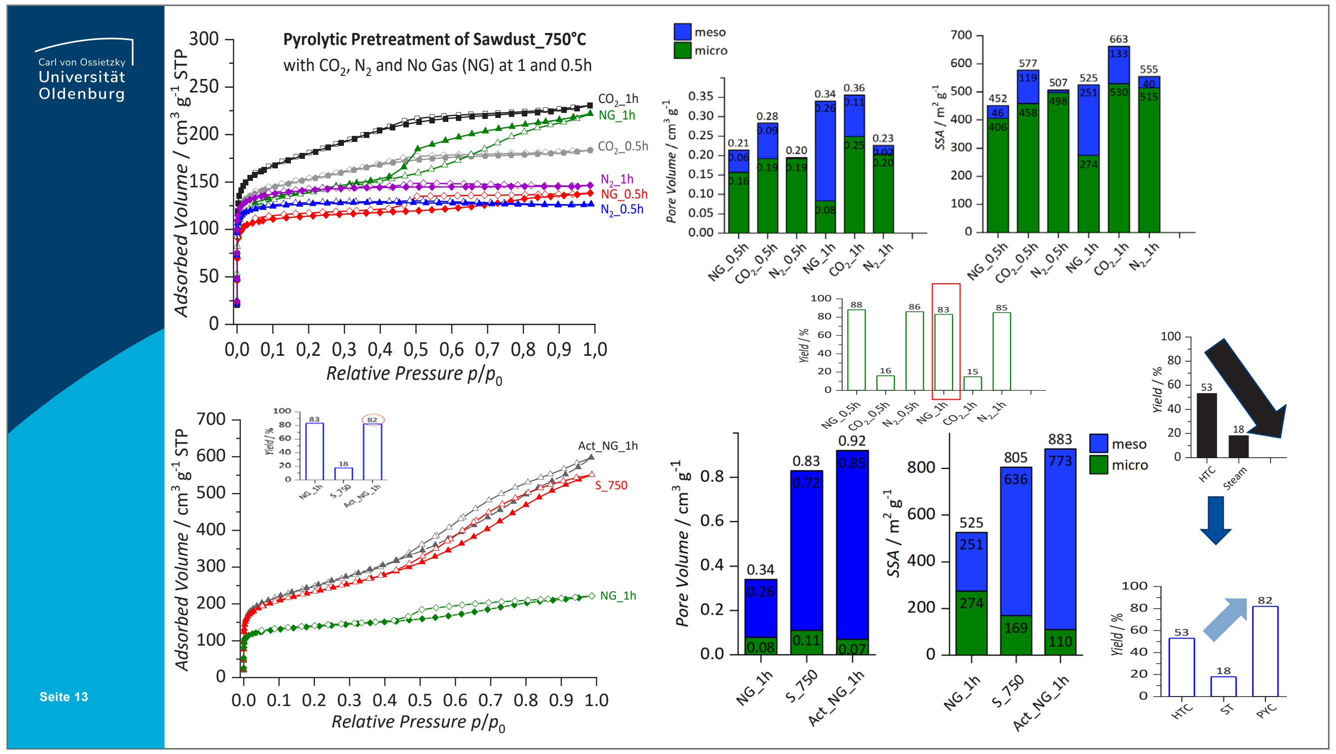


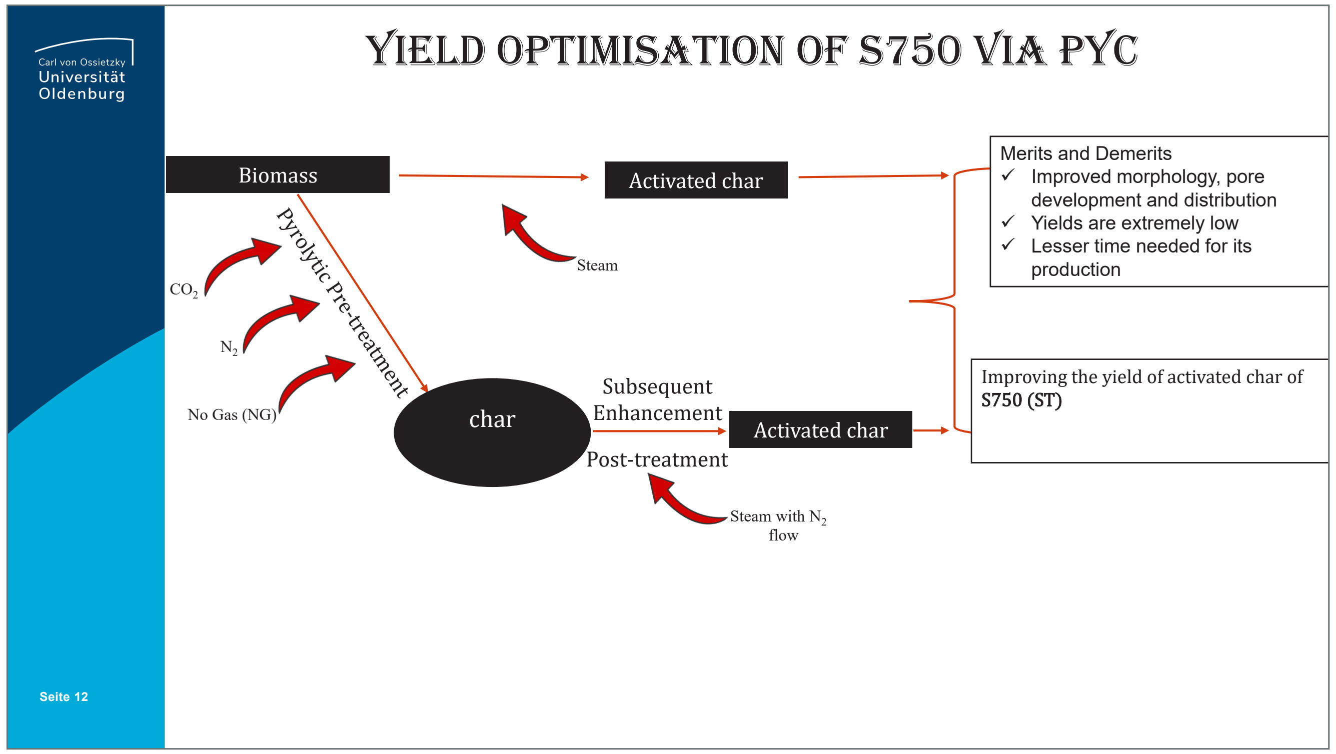
COMPARISON OF BOTH TREATMENT METHODS

1. HTC

- ❖ Subsequent enhancement of hydrochar from HTC of sawdust results into activated chars with microporosity. However an opposite results was obtained when activated chars was produced using the steam.
- ❖ Chars produced via steam results into large pore development, SSA and PV than chars produced from HTC. However this however, this technology is accompanied by low yield.

2. STEAM





YIELD OPTIMISATION OF S750 VIA PYC

Biomass

Activated char

Steam

Pyrolytic Pre-treatment

CO_2

N_2

No Gas (NG)

char

Subsequent Enhancement

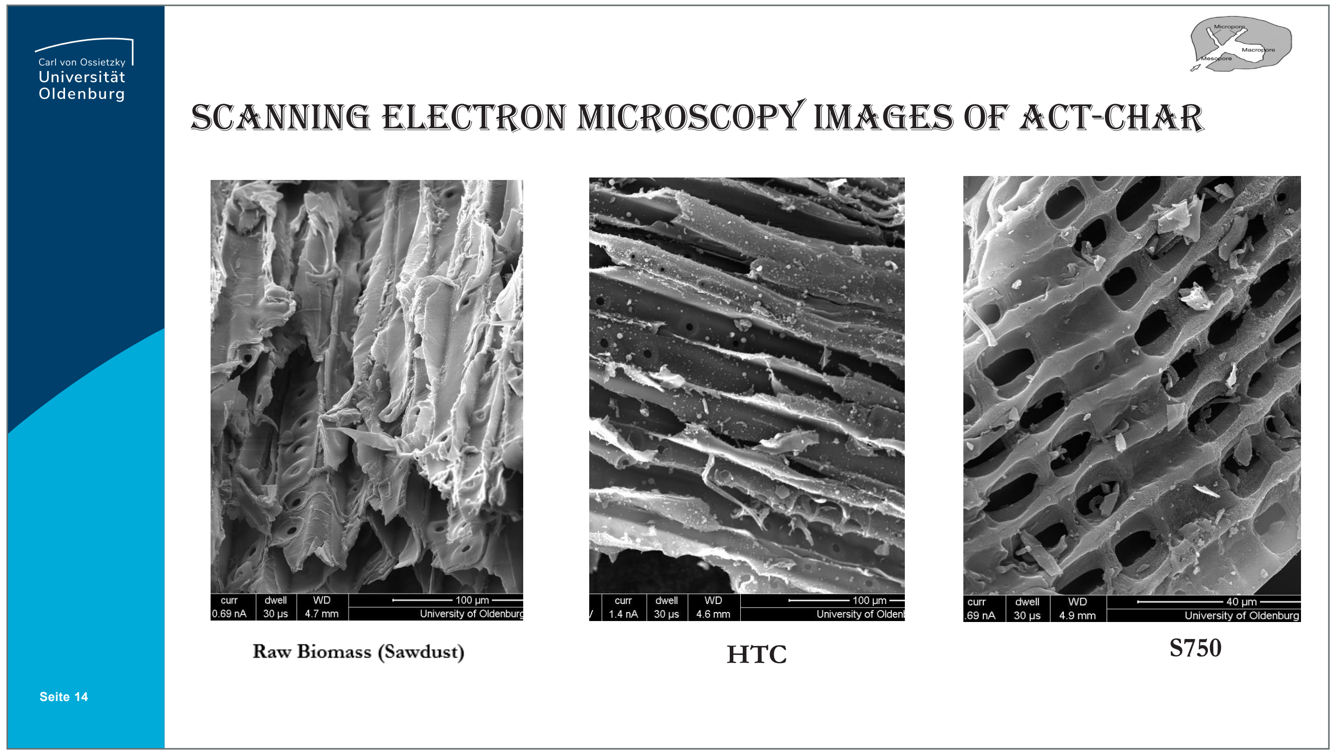
Post-treatment

Activated char

Steam with N_2 flow

Merits and Demerits
- ✓ Improved morphology, pore development and distribution
- ✓ Yields are extremely low
- ✓ Lesser time needed for its production

Improving the yield of activated char of S750 (ST)

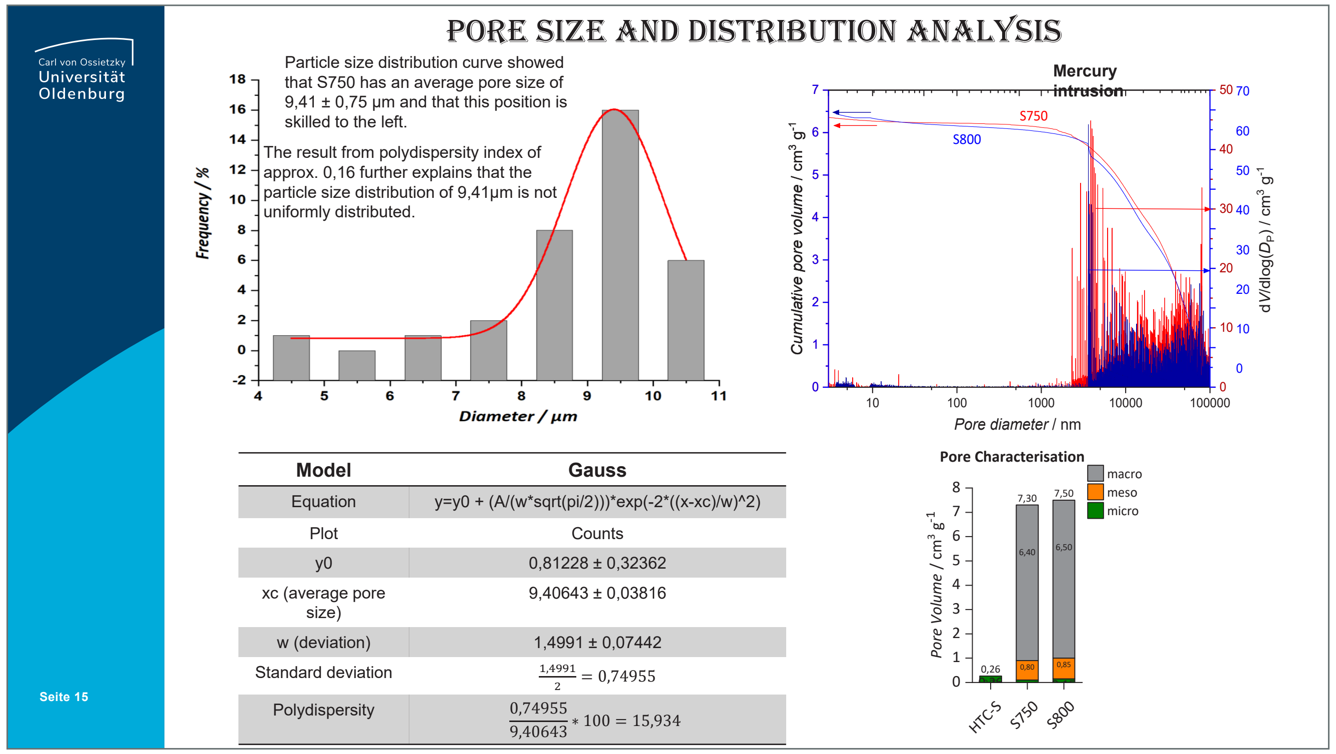


SCANNING ELECTRON MICROSCOPY IMAGES OF ACT-CHAR

Raw Biomass (Sawdust)

HTC

S750

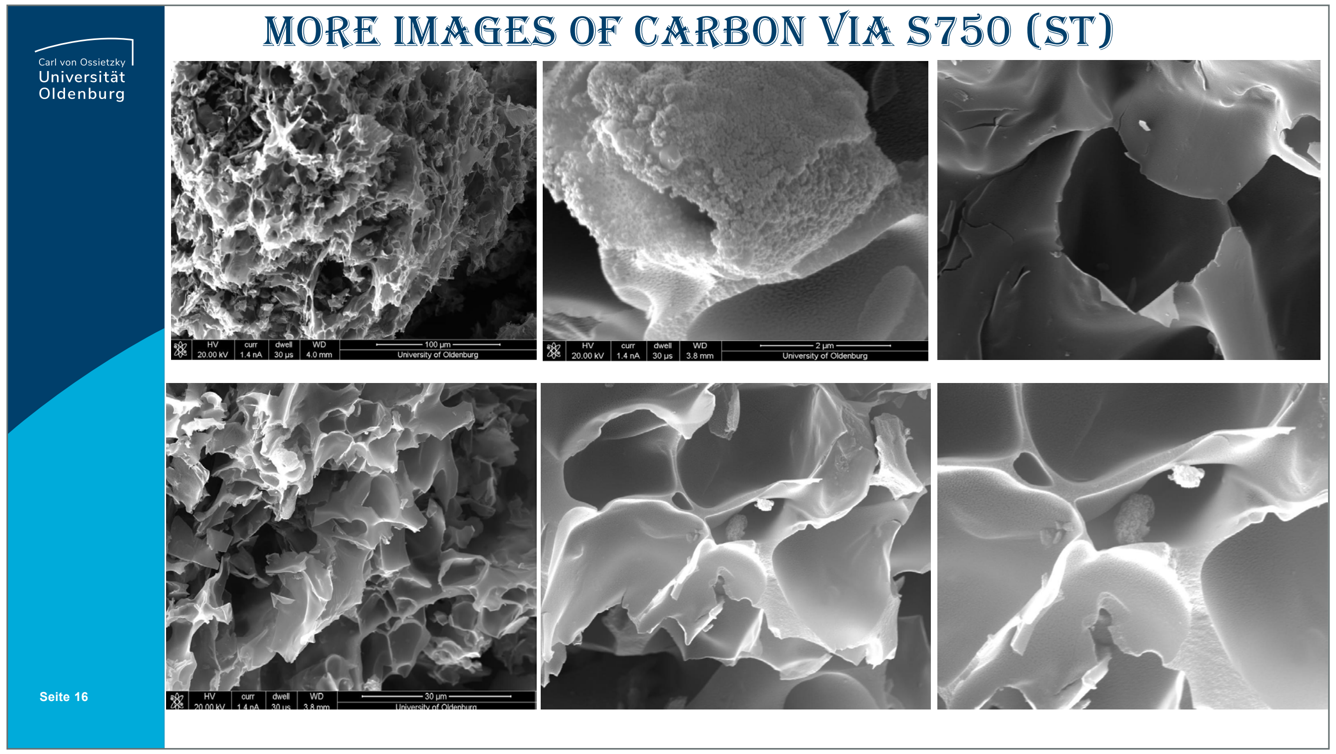


PORE SIZE AND DISTRIBUTION ANALYSIS

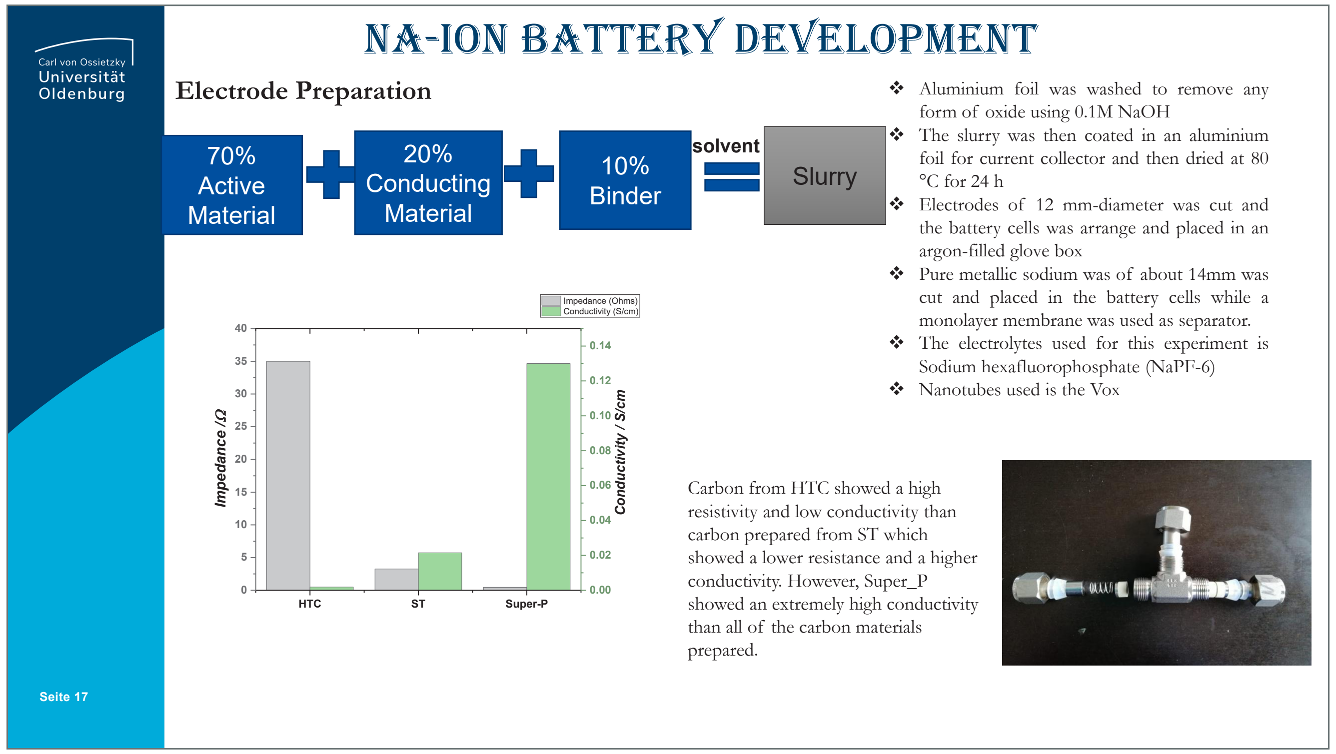
Particle size distribution curve showed that S750 has an average pore size of 9,41 ± 0,75 µm and that this position is skilled to the left.

The result from polydispersity index of approx. 0,16 further explains that the particle size distribution of 9,41µm is not uniformly distributed.

Model	Gauss
Equation	y=y0 + (A/(w*sqrt(pi/2)))*exp(-2*((x-xc)/w)^2)
Plot	Counts
y0	0,81228 ± 0,32362
xc (average pore size)	9,40643 ± 0,03816
w (deviation)	1,4991 ± 0,07442
Standard deviation	$\frac{1,4991}{2} = 0,74955$
Polydispersity	$\frac{0,74955}{9,40643} * 100 = 15,934$



MORE IMAGES OF CARBON VIA S750 (ST)



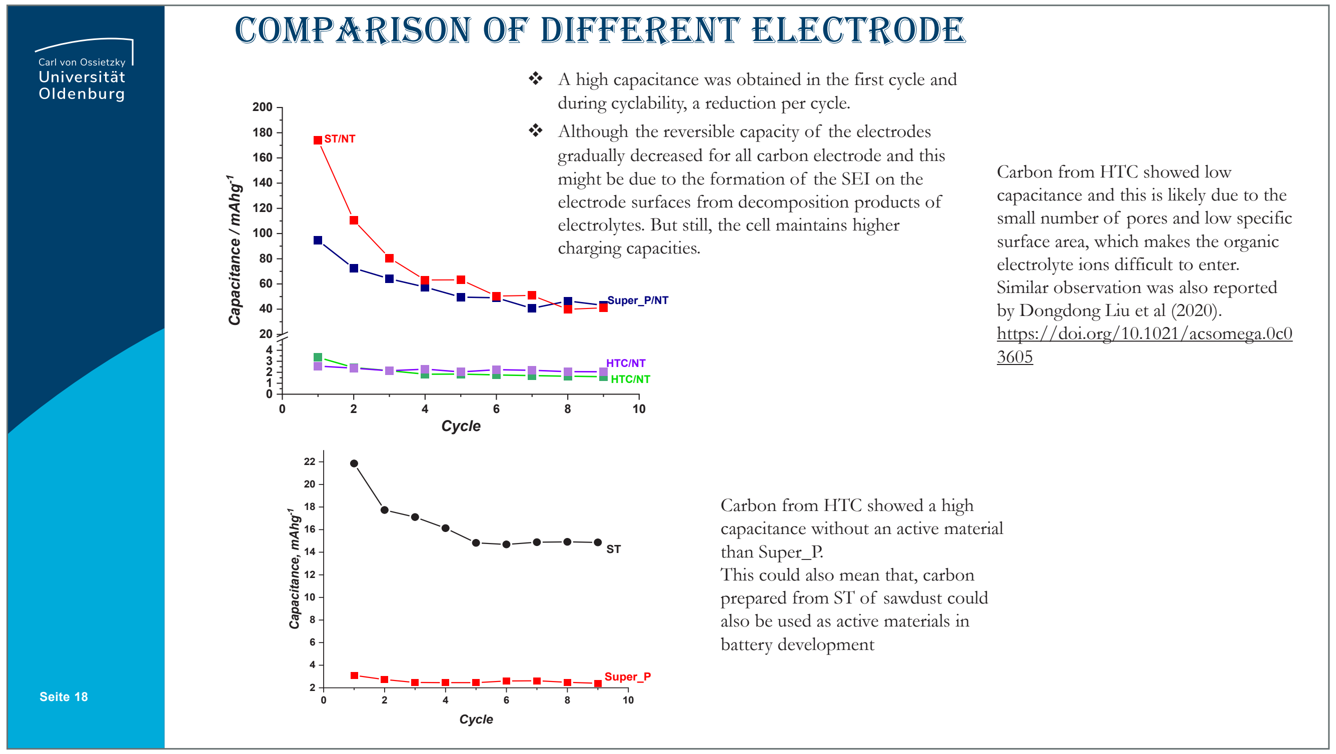
NA-ION BATTERY DEVELOPMENT

Electrode Preparation

70% Active Material + 20% Conducting Material + 10% Binder + solvent = Slurry

- ❖ Aluminium foil was washed to remove any form of oxide using 0.1M NaOH
- ❖ The slurry was then coated in an aluminium foil for current collector and then dried at 80 °C for 24 h
- ❖ Electrodes of 12 mm-diameter was cut and the battery cells was arrange and placed in an argon-filled glove box
- ❖ Pure metallic sodium was of about 14mm was cut and placed in the battery cells while a monolayer membrane was used as separator.
- ❖ The electrolytes used for this experiment is Sodium hexafluorophosphate (NaPF-6)
- ❖ Nanotubes used is the Vox

Carbon from HTC showed a high resistivity and low conductivity than carbon prepared from ST which showed a lower resistance and a higher conductivity. However, Super_P showed an extremely high conductivity than all of the carbon materials prepared.

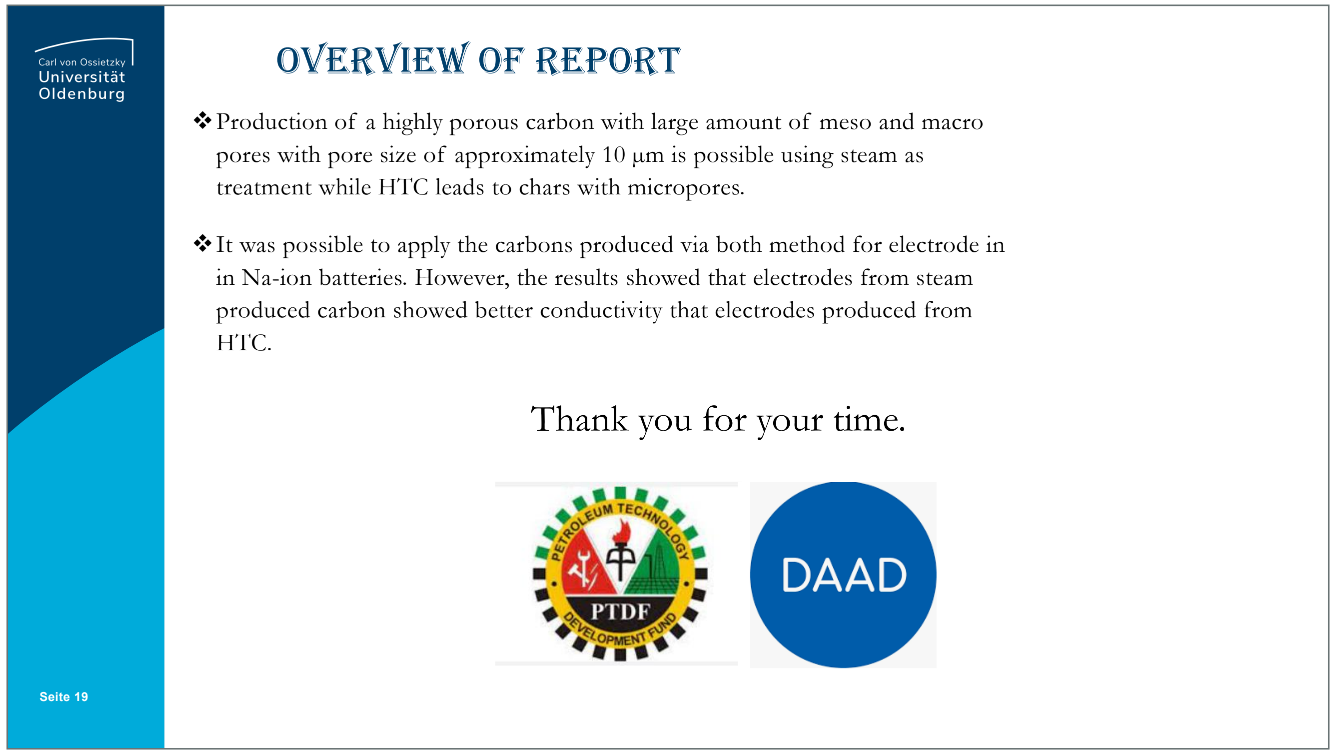


COMPARISON OF DIFFERENT ELECTRODE

- ❖ A high capacitance was obtained in the first cycle and during cyclability, a reduction per cycle.
- ❖ Although the reversible capacity of the electrodes gradually decreased for all carbon electrode and this might be due to the formation of the SEI on the electrode surfaces from decomposition products of electrolytes. But still, the cell maintains higher charging capacities.

Carbon from HTC showed low capacitance and this is likely due to the small number of pores and low specific surface area, which makes the organic electrolyte ions difficult to enter. Similar observation was also reported by Dongdong Liu et al (2020). https://doi.org/10.1021/acsomega.0c03605

Carbon from HTC showed a high capacitance without an active material than Super_P.
This could also mean that, carbon prepared from ST of sawdust could also be used as active materials in battery development



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OVERVIEW OF REPORT

- ❖ Production of a highly porous carbon with large amount of meso and macro pores with pore size of approximately 10 µm is possible using steam as treatment while HTC leads to chars with micropores.
- ❖ It was possible to apply the carbons produced via both method for electrode in in Na-ion batteries. However, the results showed that electrodes from steam produced carbon showed better conductivity that electrodes produced from HTC.

Thank you for your time.

Seite 19

Dr. Muhammad-Jamal Alhnidi, Universität Hohenheim

Carbonization, Activation, and Nitrogen incorporation… all in one Thermal Step

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Chau Huyen Dang, Leibniz-Institut für Agrartechnik und Bioökonomie e.V. (ATB)

Feasibility of using hydrochar from coffee processing by-products as a fossil fuel substitute for drying coffee beans to improve the sustainability of coffee production

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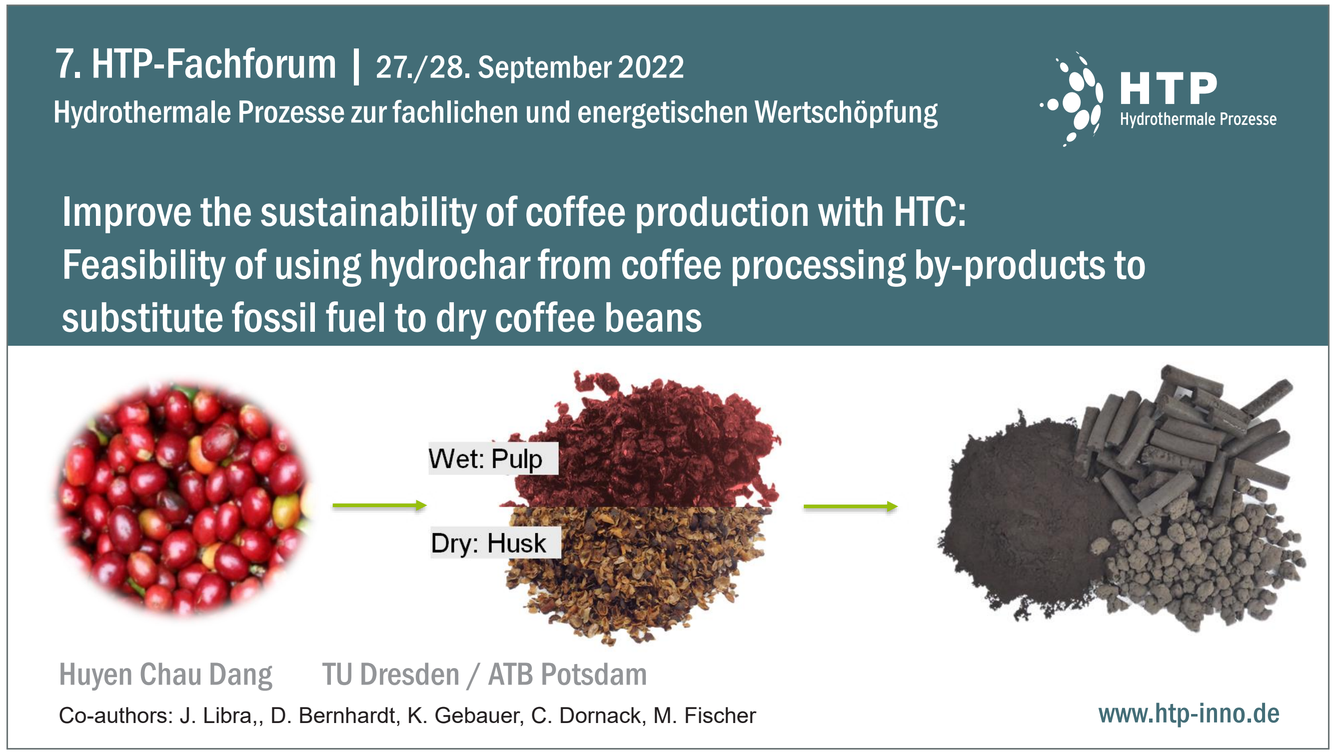
Worldwide production of Arabica and Robusta green coffee beans reached 10 million tons in 2019. This left behind at least the same amount of coffee by-products (e.g. husk, outer skin, parchment and silver skin) from the processing step that needs to be recycled or properly disposed of. Especially for wet-processed coffee beans, solutions are required that exploit the potential of the wet by-products as a renewable energy source for drying or roasting coffee beans and that can ensure adequate treatment of the wastewater.

In this study, the ability of the hydrothermal carbonization process (HTC) to improve the properties of coffee by-products for fuel application was investigated. The goal was to determine the optimal process settings to obtain hydrochar that combines high energetic properties with an efficient combustion performance.

Experiments were carried out based on a definitive screening design with six process variables to determine the influence of HTC conditions on the hydrochar properties. The process parameters varied included: temperatures (160 – 240 °C), holding times (1 – 5 h), pH values (7 – 13), solid content (15 – 25 w%-db), agitation (0 – 200 rpm) and by-product mixture (0 – 100 w%-db). The fuel properties of the hydrochars were analyzed to assess the feasibility of their use as a fossil fuel substitute for drying or roasting coffee beans. The change in the energetic properties of the hydrochars with process settings will be presented. The hydrochars were evaluated according to the fuel quality criteria (incl: ash melting behavior, volatile matter, chlorine, and elements). The over-all assessment of substituting hydrochar from coffee by-products for fossil coal was done based on the calculation of slagging risk value as well as the potential formation of corrosive compounds released during combustion. The feasibility of making this substitution in the combustion system of our partner wet-processing company in Vietnam was evaluated and potential reductions in greenhouse gas emissions were estimated.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Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

Improve the sustainability of coffee production with HTC:
Feasibility of using hydrochar from coffee processing by-products to substitute fossil fuel to dry coffee beans

Huyen Chau Dang TU Dresden / ATB Potsdam
Co-authors: J. Libra,, D. Bernhardt, K. Gebauer, C. Dornack, M. Fischer
www.htp-inno.de


Background

HTP Hydrothermale Prozesse

Case study: Wet-coffee processing in Vietnam
Project funding: BMEL – PhD programme
Project duration: 01.09.2019 – 31.09.2023

Fig 1. Discussion with local farmer in Dak Lak 2019.

Fig 2. Coffee berries harvest, season 2020/21, Vietnam.

Germany
ATB Leibniz-Institut für Agrartechnik und Bioökonomie
Technische Universität Dresden
Bayerischer BauernVerband
Agrokraft
MR
Artec Biotechnologie GmbH

Vietnam
Vanlang University
GreenMessage Water & Environmental
Coffee Phuocan

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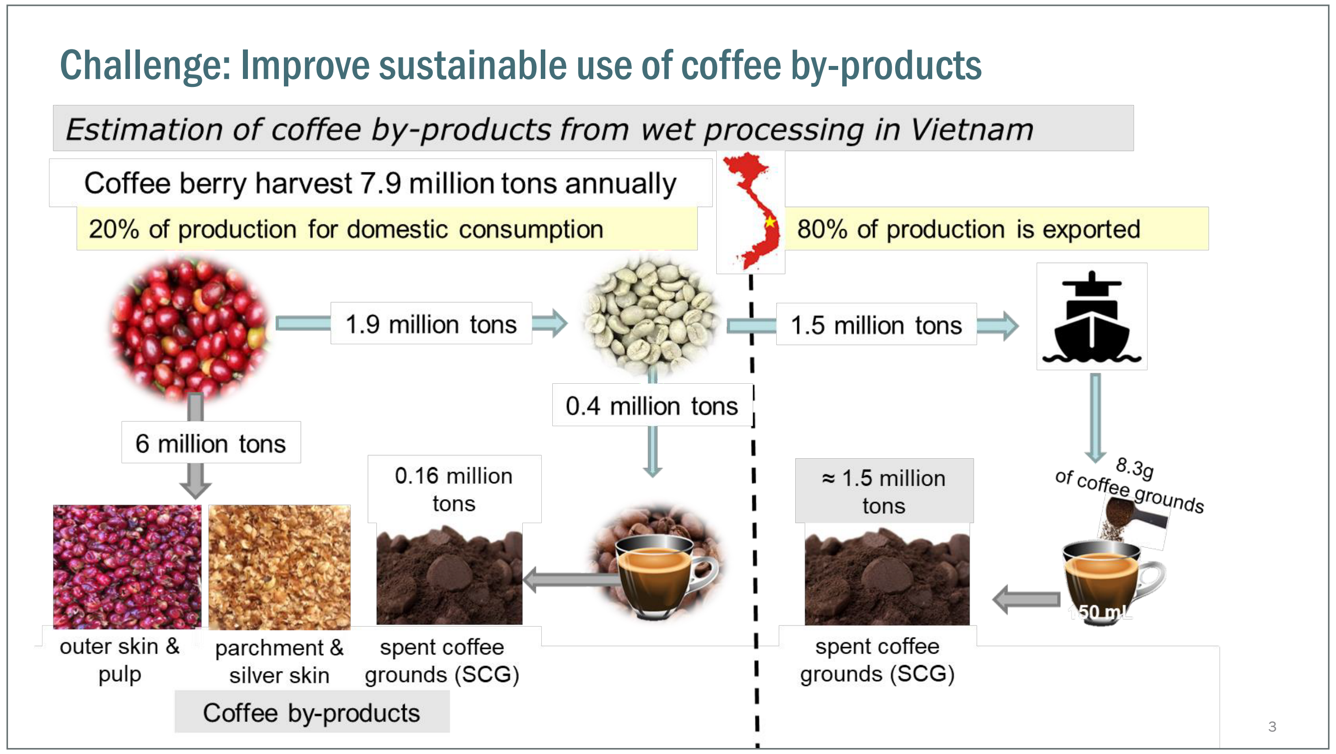


Challenge: Improve sustainable use of coffee by-products

Estimation of coffee by-products from wet processing in Vietnam

Coffee berry harvest 7.9 million tons annually

20% of production for domestic consumption

80% of production is exported

1.9 million tons

0.4 million tons

6 million tons

0.16 million tons

1.5 million tons

≈ 1.5 million tons

8.3g of coffee grounds

50 ml

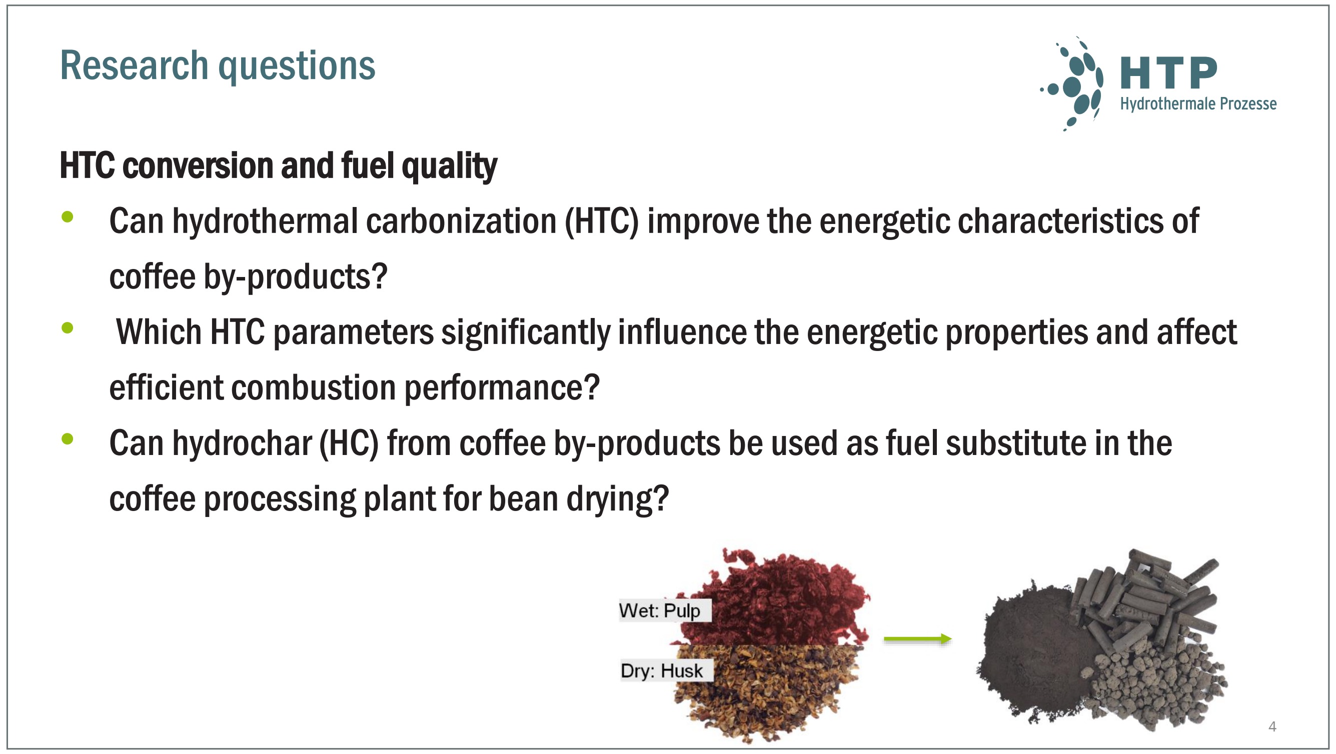
outer skin & pulp

parchment & silver skin

spent coffee grounds (SCG)

spent coffee grounds (SCG)

Coffee by-products

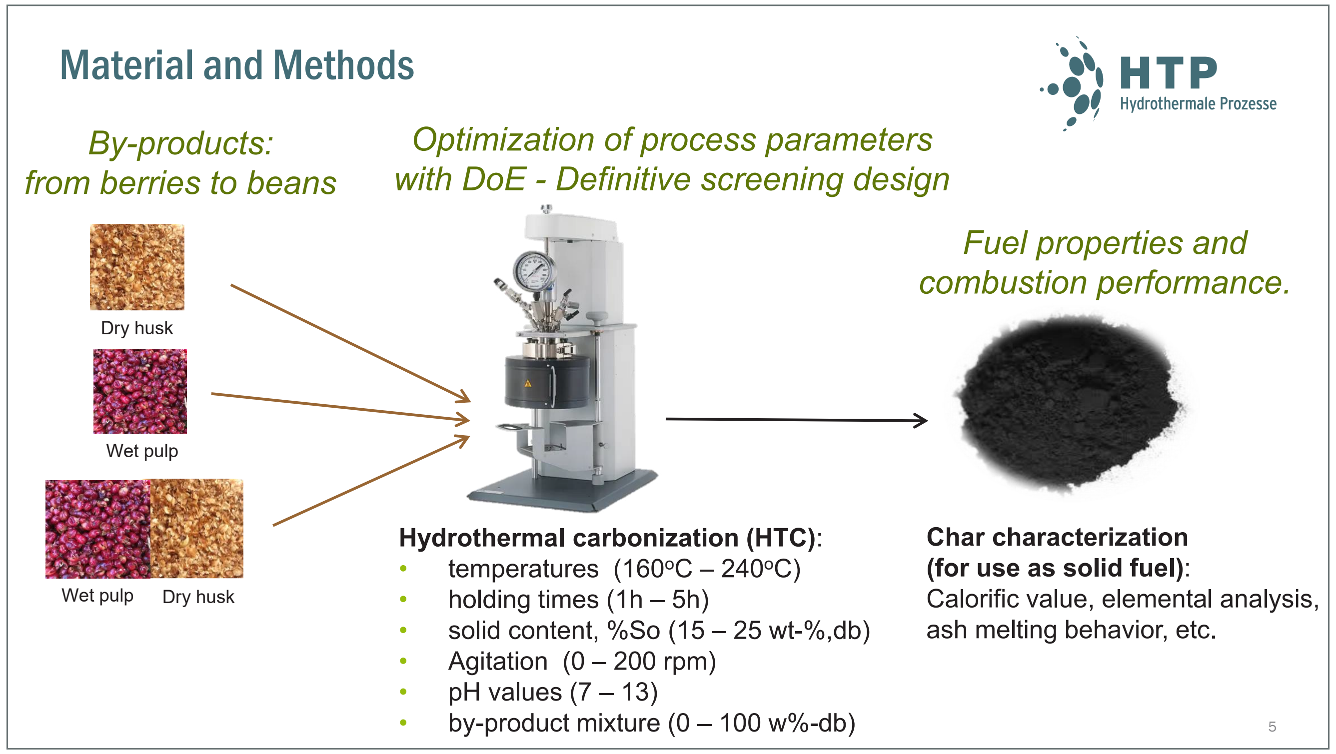


Research questions

HTP Hydrothermale Prozesse

HTC conversion and fuel quality

- Can hydrothermal carbonization (HTC) improve the energetic characteristics of coffee by-products?
- Which HTC parameters significantly influence the energetic properties and affect efficient combustion performance?
- Can hydrochar (HC) from coffee by-products be used as fuel substitute in the coffee processing plant for bean drying?



Material and Methods

HTP Hydrothermale Prozesse

By-products: from berries to beans

Optimization of process parameters with DoE - Definitive screening design

Fuel properties and combustion performance.

Hydrothermal carbonization (HTC):
- temperatures (160°C – 240°C)
- holding times (1h – 5h)
- solid content, %So (15 – 25 wt-%,db)
- Agitation (0 – 200 rpm)
- pH values (7 – 13)
- by-product mixture (0 – 100 w%-db)

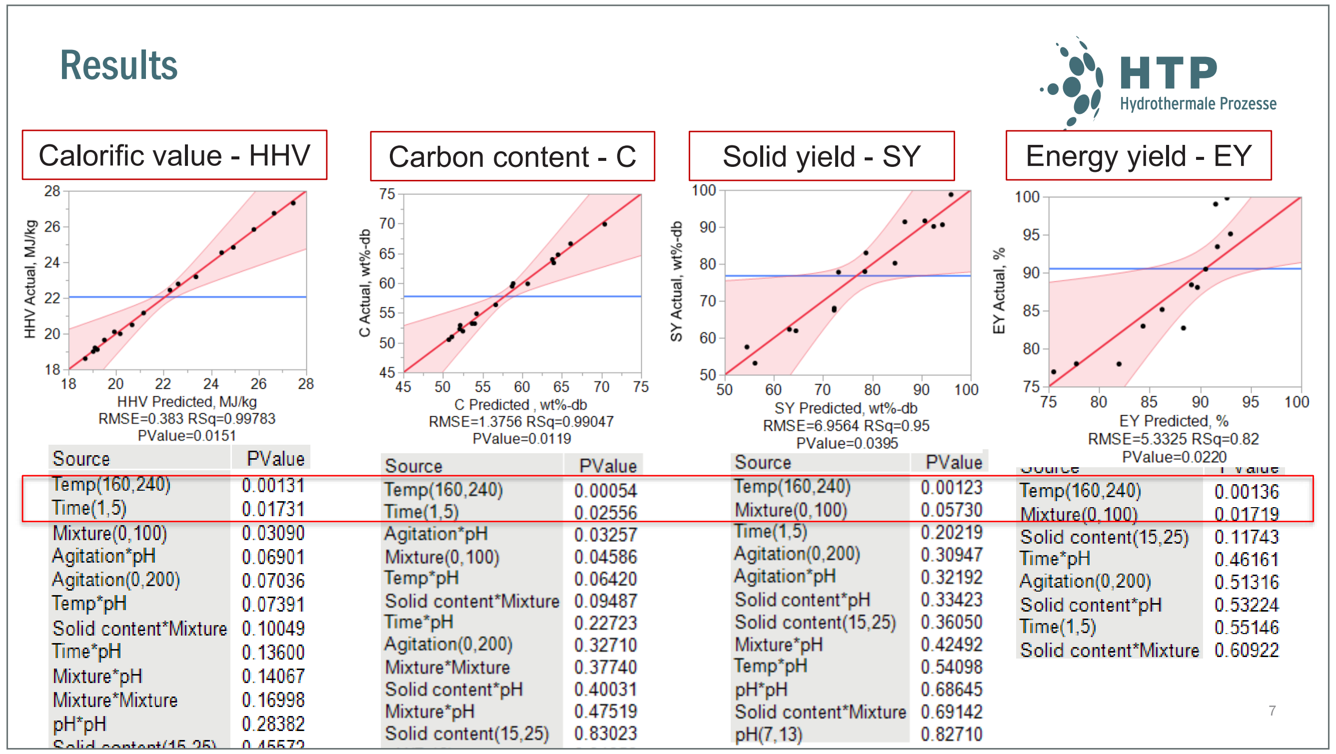
Char characterization (for use as solid fuel):
Calorific value, elemental analysis, ash melting behavior, etc.

Methodology

HTP Hydrothermale Prozesse

DoE - Definitive Screening Design
6 parameters varied, 17 HTC runs

Runs	T,°C	t, h	A, rmp	S_o, wt%-db	Mix, wt%-db		pH
1	200	1	0	15	0% dry	100% wet	7
2	160	1	200	15	100% dry	0% wet	13
3	160	1	200	25	50% dry	50% wet	7
4	200	5	200	25	100% dry	0% wet	13
5	240	1	100	25	100% dry	0% wet	7
6	160	5	0	25	100% dry	0% wet	10
7	240	3	200	25	0% dry	100% wet	13
8	240	1	0	20	100% dry	0% wet	13
9	160	5	100	15	0% dry	100% wet	13
10	240	5	0	15	50% dry	50% wet	13
11	160	1	0	25	0% dry	100% wet	13
12	160	5	200	20	0% dry	100% wet	7
13	200	3	100	20	50% dry	50% wet	10
14	240	5	200	15	100% dry	0% wet	7
15	160	3	0	15	100% dry	0% wet	7
16	240	1	200	15	0% dry	100% wet	10
17	240	5	0	25	0% dry	100% wet	7



Results

Calorific value - HHV

Carbon content - C

Solid yield - SY

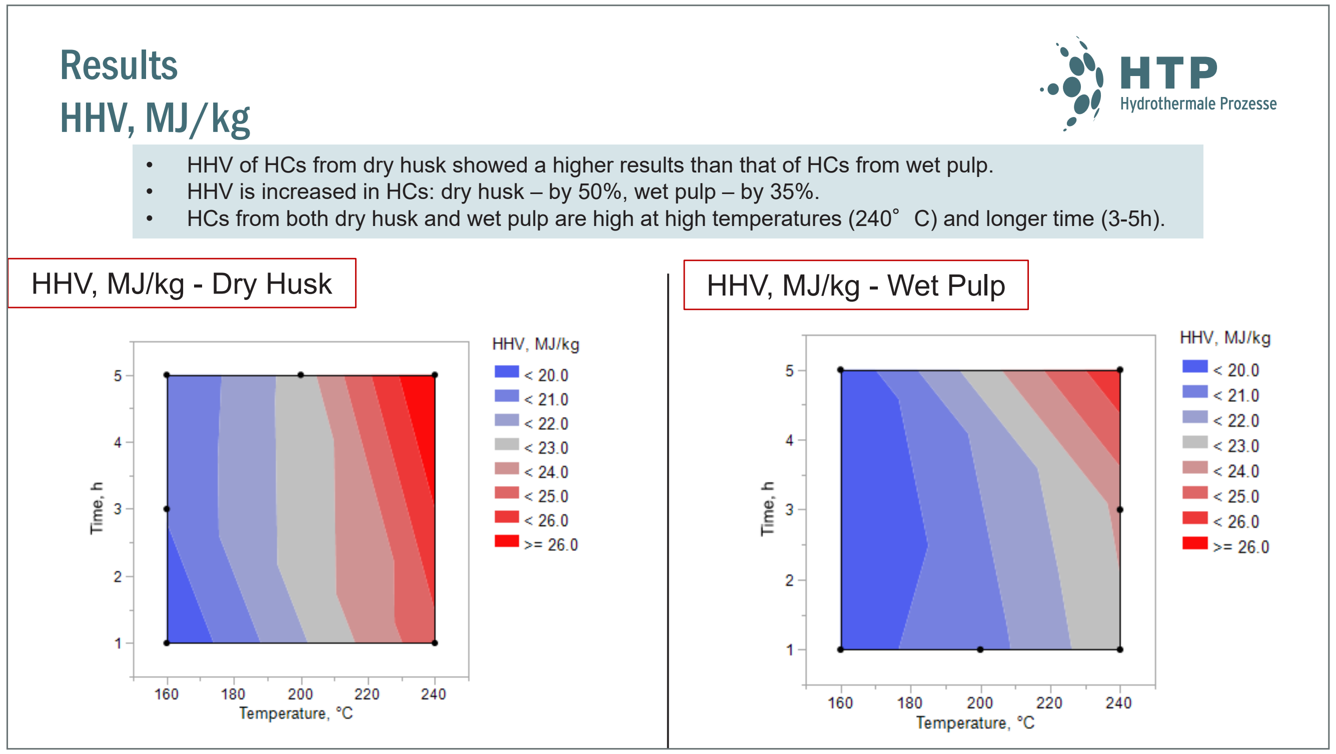
Energy yield - EY

Source	PValue
Temp(160,240)	0.00131
Time(1,5)	0.01731
Mixture(0,100)	0.03090
Agitation*pH	0.06901
Agitation(0,200)	0.07036
Temp*pH	0.07391
Solid content*Mixture	0.10049
Time*pH	0.13600
Mixture*pH	0.14067
Mixture*Mixture	0.16998
pH*pH	0.28382
Solid content(15,25)	0.45572

Source	PValue
Temp(160,240)	0.00054
Time(1,5)	0.02556
Agitation*pH	0.03257
Mixture(0,100)	0.04586
Temp*pH	0.06420
Solid content*Mixture	0.09487
Time*pH	0.22723
Agitation(0,200)	0.32710
Mixture*Mixture	0.37740
Solid content*pH	0.40031
Mixture*pH	0.47519
Solid content(15,25)	0.83023

Source	PValue
Temp(160,240)	0.00123
Mixture(0,100)	0.05730
Time(1,5)	0.20219
Agitation(0,200)	0.30947
Agitation*pH	0.32192
Solid content*pH	0.33423
Solid content(15,25)	0.36050
Mixture*pH	0.42492
Temp*pH	0.54098
pH*pH	0.68645
Solid content*Mixture	0.69142
pH(7,13)	0.82710

Source	PValue
Temp(160,240)	0.00136
Mixture(0,100)	0.01719
Solid content(15,25)	0.11743
Time*pH	0.46161
Agitation(0,200)	0.51316
Solid content*pH	0.53224
Time(1,5)	0.55146
Solid content*Mixture	0.60922

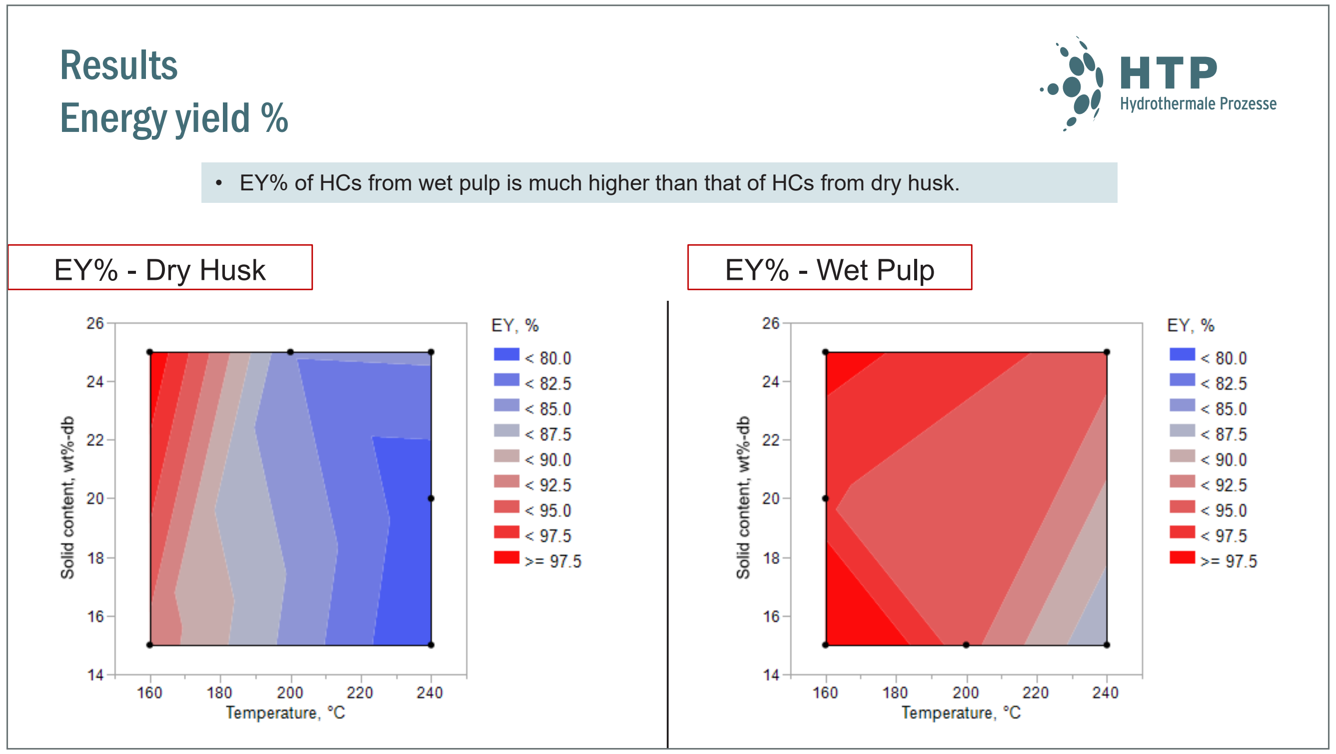


Results
HHV, MJ/kg

- HHV of HCs from dry husk showed a higher results than that of HCs from wet pulp.
- HHV is increased in HCs: dry husk – by 50%, wet pulp – by 35%.
- HCs from both dry husk and wet pulp are high at high temperatures (240° C) and longer time (3-5h).

HHV, MJ/kg - Dry Husk

HHV, MJ/kg - Wet Pulp

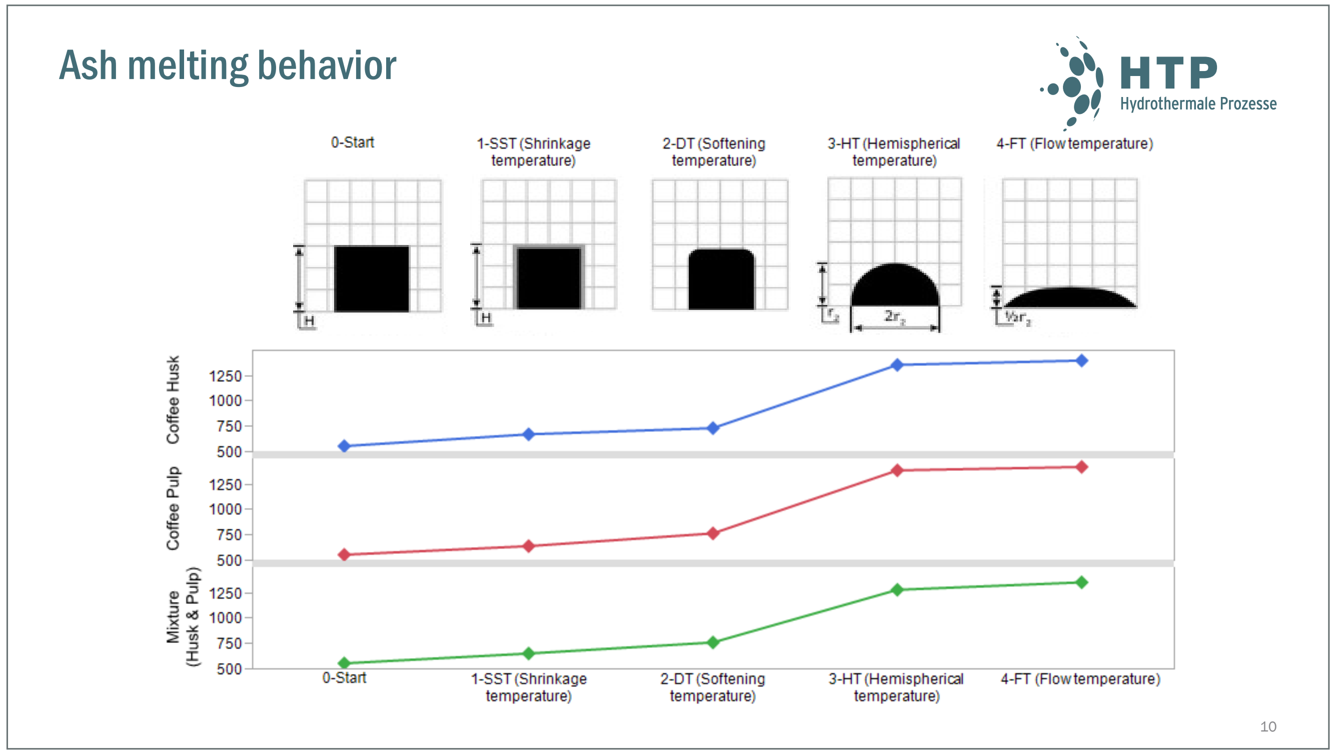


Results
Energy yield %

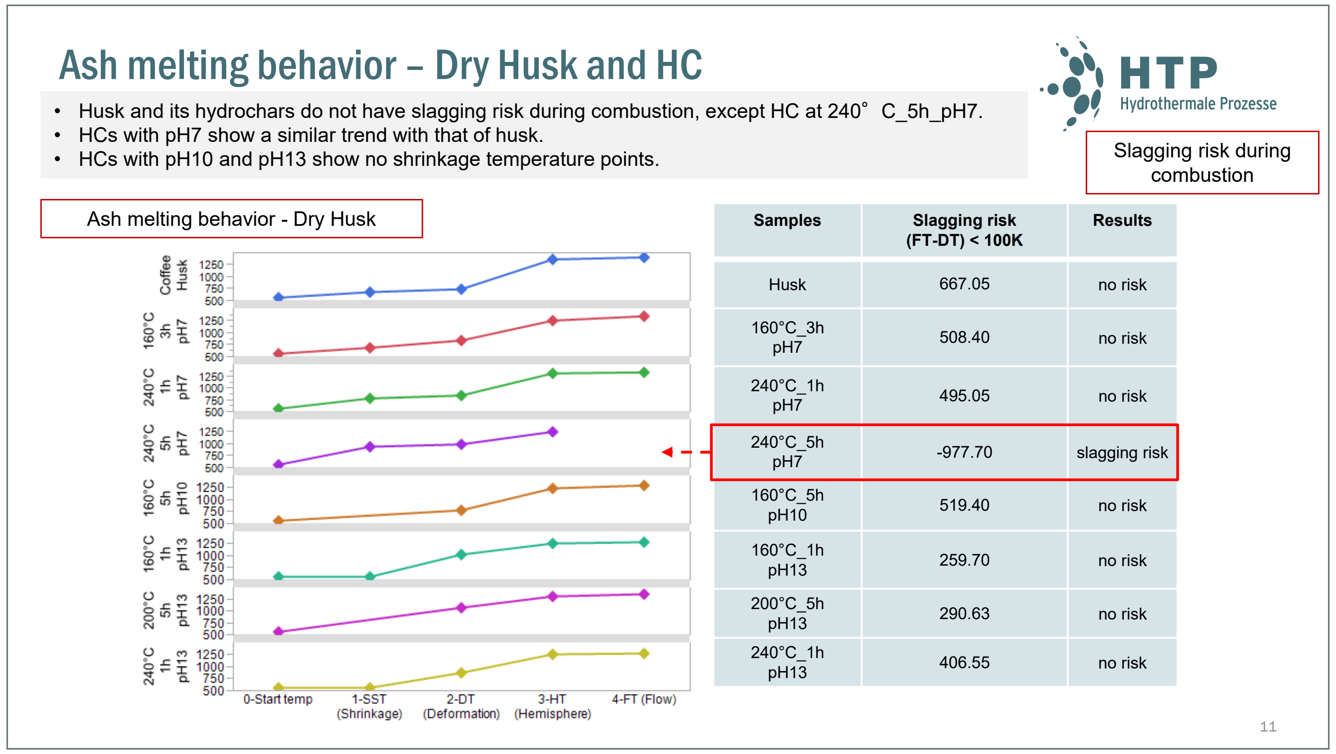
- EY% of HCs from wet pulp is much higher than that of HCs from dry husk.

EY% - Dry Husk

EY% - Wet Pulp



Ash melting behavior



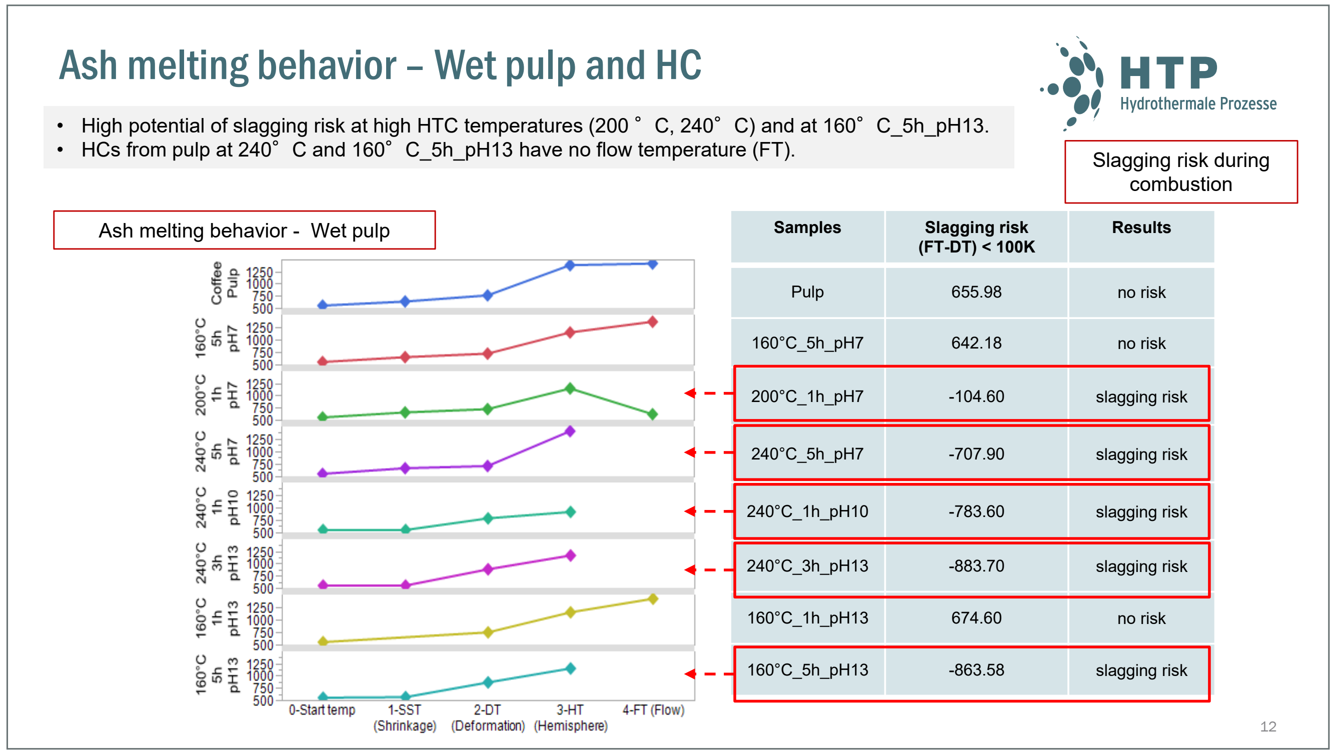
Ash melting behavior – Dry Husk and HC

- Husk and its hydrochars do not have slagging risk during combustion, except HC at 240˚ C_5h_pH7.
- HCs with pH7 show a similar trend with that of husk.
- HCs with pH10 and pH13 show no shrinkage temperature points.

Slagging risk during combustion

Ash melting behavior - Dry Husk

Samples	Slagging risk (FT-DT) < 100K	Results
Husk	667.05	no risk
160°C_3h pH7	508.40	no risk
240°C_1h pH7	495.05	no risk
240°C_5h pH7	-977.70	slagging risk
160°C_5h pH10	519.40	no risk
160°C_1h pH13	259.70	no risk
200°C_5h pH13	290.63	no risk
240°C_1h pH13	406.55	no risk



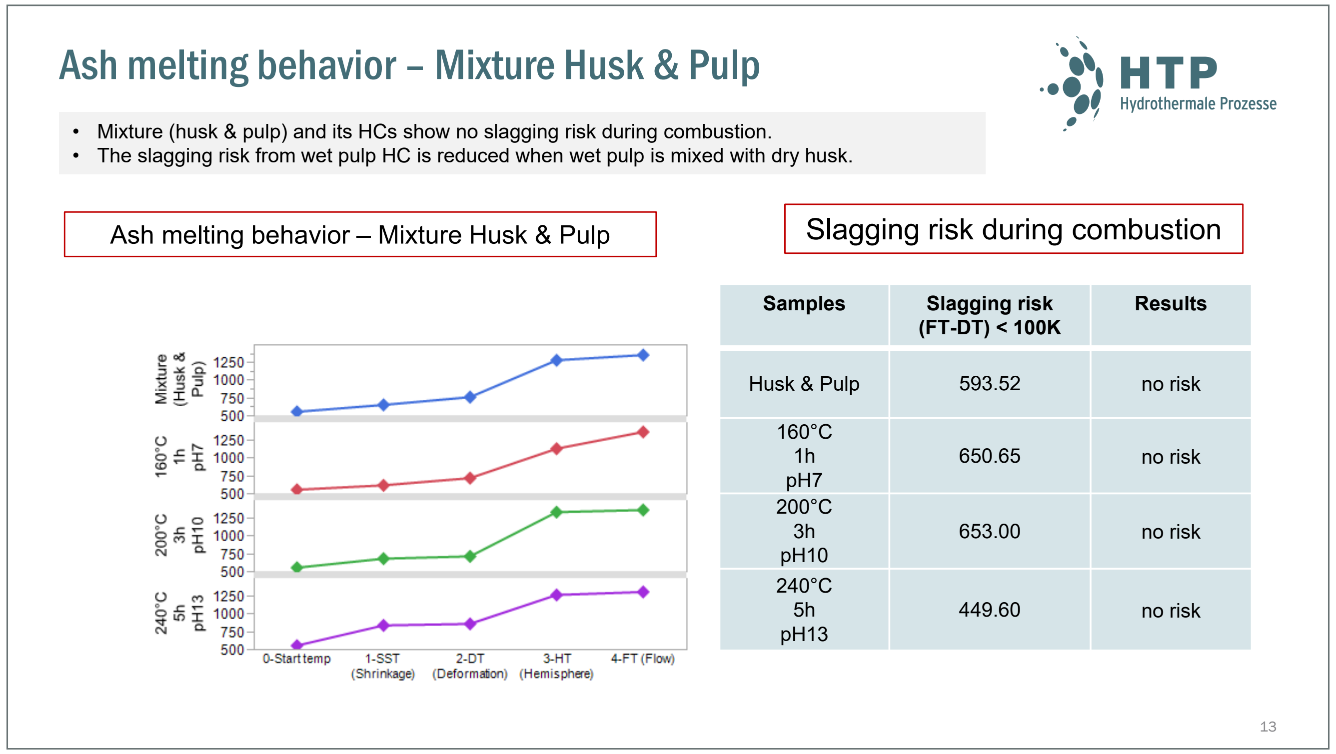
Ash melting behavior – Wet pulp and HC

- High potential of slagging risk at high HTC temperatures (200 ˚ C, 240˚ C) and at 160˚ C_5h_pH13.
- HCs from pulp at 240˚ C and 160˚ C_5h_pH13 have no flow temperature (FT).

Slagging risk during combustion

Ash melting behavior - Wet pulp

Samples	Slagging risk (FT-DT) < 100K	Results
Pulp	655.98	no risk
160°C_5h_pH7	642.18	no risk
200°C_1h_pH7	-104.60	slagging risk
240°C_5h_pH7	-707.90	slagging risk
240°C_1h_pH10	-783.60	slagging risk
240°C_3h_pH13	-883.70	slagging risk
160°C_1h_pH13	674.60	no risk
160°C_5h_pH13	-863.58	slagging risk



Ash melting behavior – Mixture Husk & Pulp

- Mixture (husk & pulp) and its HCs show no slagging risk during combustion.
- The slagging risk from wet pulp HC is reduced when wet pulp is mixed with dry husk.

Ash melting behavior – Mixture Husk & Pulp

Slagging risk during combustion

Samples	Slagging risk (FT-DT) < 100K	Results
Husk & Pulp	593.52	no risk
160°C 1h pH7	650.65	no risk
200°C 3h pH10	653.00	no risk
240°C 5h pH13	449.60	no risk

Conclusions

Energetic properties of HCs

- HHV is increased in HCs: by 50% for dry husk and mixture (husk & pulp), and 35% for wet pulp.
- Energy yield of 99% achieved in HCs converted from wet pulp (240˚ C_3h), dry husk (160˚ C_5h) and mixture (160˚ C_1h).

Slagging risk

- Dry husk and its HCs showed less risk of slagging during combustion.
- A high potential of slagging risk occurs mostly with wet pulp and its HCs (at 200˚ C and 240˚ C).
- Mixture (husk and pulp) is a promissing solution to reduce the slagging risk when using HCs from wet pulp.

Fossil fuel substitution

- It is possible to substitute fossil fuel by using HCs from coffee by-products for drying beans.
- HC from mixture of both by-products at 240˚ C_5h showed a high HHV (27 MJ/kg), EY (78%) with no slagging risk can be a good HC for using as solid fuel in drying phase.

Further evaluation

- Ash compositions will be checked, then fouling and corrosion during combustion will be estimated.
- Combustion tests using HCs in drying furnace needs to be carried out.

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HTP Hydrothermale Prozesse

Thank you for your attention!

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7. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

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Kevin Bohlke, Deutsches Biomasseforschungszentrum

HTCGas: Vergasung von HTC-Kohle

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Die Schließung des Kohlenstoffkreislaufes ist elementarer Bestandteil einer CO2-neutralen Zukunft. Durch die Weiterentwicklung und Integration bekannter Verfahrensabläufe der hydothermalen Carbonisierung (HTC), Pelletierung und Vergasung soll im HTCGas-Projekt ein weiterer Beitrag dazu gewonnen werden. Ziel ist es, durch die Prozessführung die HTC Brennstoffeigenschaften so zu beeinflussen, dass günstige Ausgangsbedingungen für die Vergasung geschaffen werden. Das bezieht sich zum einen auf den verringerten Wassergehalt der Biomasse, zum anderen können unterschiedliche Elemente wie bspw. Kalium und Natrium, die die Asche hinsichtlich Menge und Eigenschaften beeinflussen, aus dem Produkt entfernt werden. Zusätzlich wird durch die HTC der Anteil flüchtiger Bestandteile verringert, wodurch der Teeranteil im Produktgas reduziert wird. Dadurch kann mit der HTC die stoffliche Nutzung von Rest- und Abfallstoffen adressiert werden und eine anschließende Vergasung stellt eine weiterführende Nutzung des Produktes dar. Somit lassen sich die beiden Technologien zur Basis eines umfassenden Bioraffineriekonzept kombinieren.

Neue Erkenntnisse werden zum Verhalten von HTC-Kohle im Vergasungsprozess in Bezug auf die Durchführbarkeit und Produktqualität erwartet. Als Einsatzstoffe sollen Holz und Stroh verwendet werden. Die Versuchsreihe soll Aufschluss über die Nutzbarkeit der Kombination von HTC und Vergasung geben.

Im HTC-Prozess wird der Einsatzstoff nach vorher definierten Versuchsparametern karbonisiert. Mithilfe der HTC sollen Stoffe, die zu Störungen im Vergasungsprozess führen, vorab ins Prozesswasser überführt werden (u. a. Alkaliverbindungen), um so die Vergasung zu optimieren. Die gewonnene HTC-Kohle sowie die unbehandelten Biomassen werden pelletiert. Abschließend erfolgt die Vergasung unter vorher definierten Parametern in einem Festbettvergaser. Zur Versuchsbewertung dienen Massenbilanzen, die Produktgasqualität, sowie die Aschestruktur. Zusätzlich sollen Teerproben zur Teeranalytik gewonnen werden.

Aus den Ergebnissen eröffnet sich ein breites Spektrum an neuen Potentialen für hydrothermale und Vergasungsprozesse. So ist eine Anwendung für HTP-Produkte mit einer Entsorgungsproblematik wie Gärreste und Klärschlammkohlen denkbar. Hier liegt der Fokus auf einer stofflichen Nutzung während der HTC (Nährstoffrückgewinnung) und eine weiterführende Wertschöpfung aus den Reststoffen der HTC durch die Vergasung. Die Vergasung eröffnet den Zugang zu erweiterten Anwendungen für HTC-Kohle wie Verstromung im kleinen Leistungsbereich, Synthesen und Wasserstoffbereitstellung.

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Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTCGas: Gasification of HTC char

Lisa Röver, Kevin Bohlke
DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH

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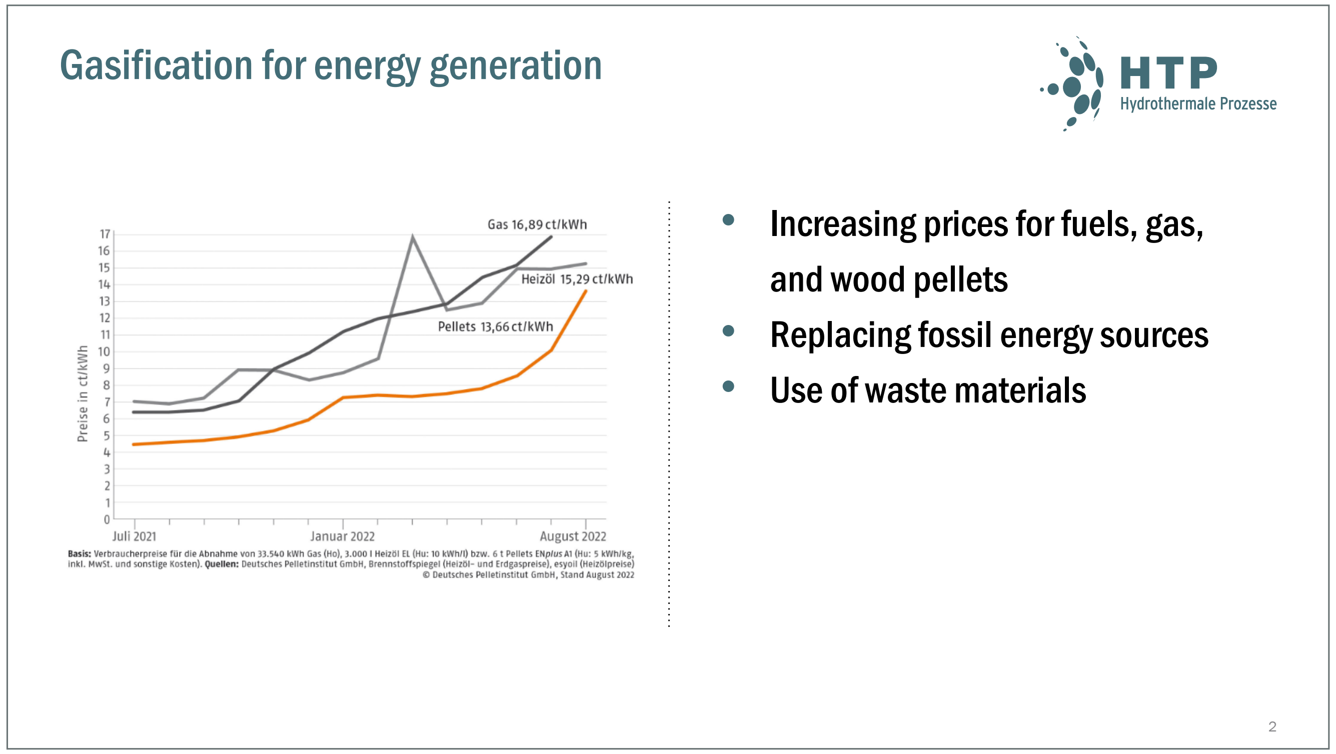

Gasification for energy generation

Basis: Verbraucherpreise für die Abnahme von 33.540 kWh Gas (Ho), 3.000 l Heizöl EL (Hu: 10 kWh/l) bzw. 6 t Pellets EN*plus* A1 (Hu: 5 kWh/kg, inkl. MwSt. und sonstige Kosten). **Quellen:** Deutsches Pelletinstitut GmbH, Brennstoffspiegel (Heizöl- und Erdgaspreise), esyoil (Heizölpreise)
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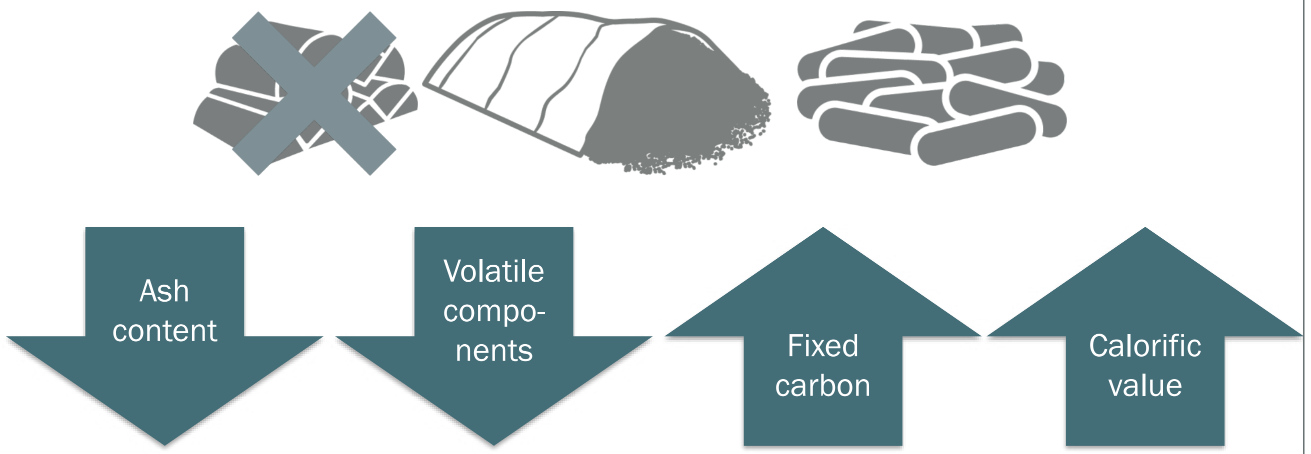
- Increasing prices for fuels, gas, and wood pellets
- Replacing fossil energy sources
- Use of waste materials

Hydrothermal carbonization as a pretreatment for the input materials – Requirements



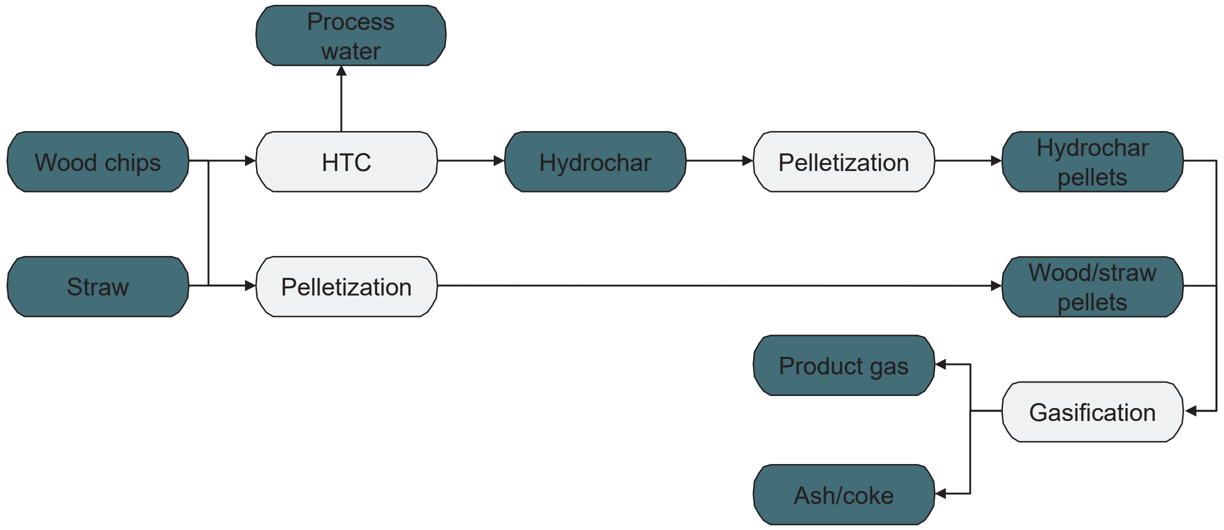
Ash content

Volatile components

Fixed carbon

Calorific value

Preliminary experiments



Process water

Wood chips

HTC

Hydrochar

Pelletization

Hydrochar pellets

Straw

Pelletization

Wood/straw pellets

Product gas

Gasification

Ash/coke

Pellets for the gasification process

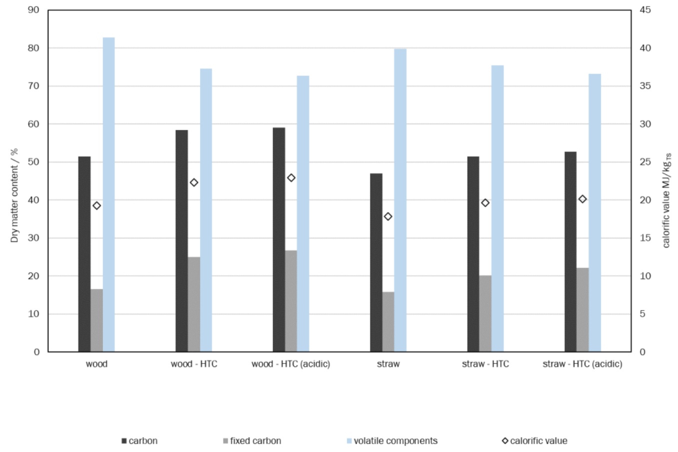
© Bohlke, DBFZ

Examined pellets: wood, straw, 2 x HTC wood, 2 x HTC straw

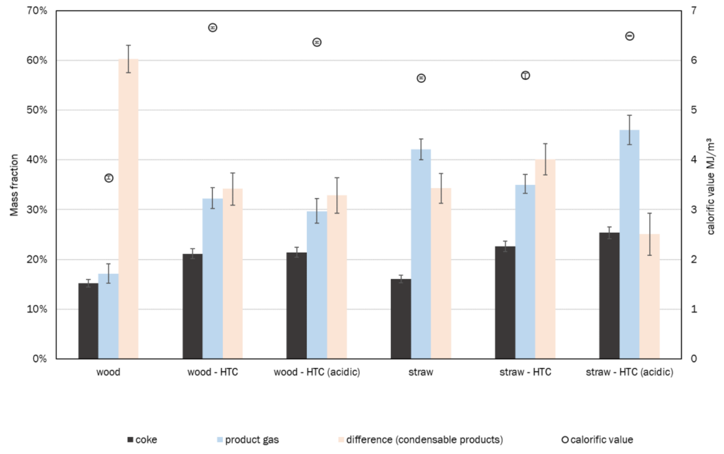
© Bohlke, DBFZ

Comparison HTC wood (left) and HTC straw (right)

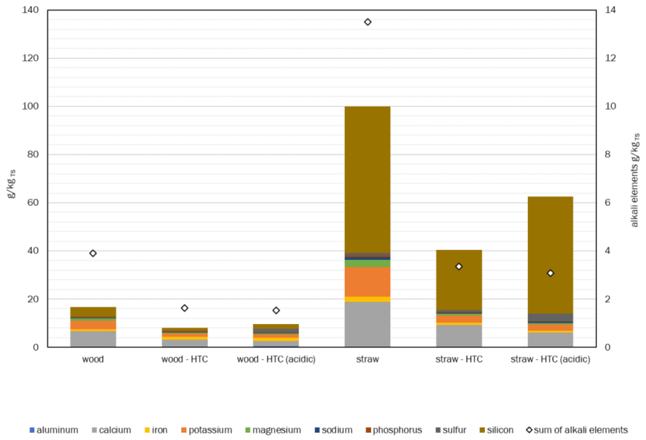
Pellet analysis



Gasification results



Gasification ash content and composition



Outlook

- **Upcoming experiments with „real“ biogenic residues from agricultural or urban sources**
  - Process parameter variation in HTC and gasification
  - Techno-economical assessment

7. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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Session V:
Anwendungen I

Gabriel Gerner, ZHAW

HTC Innovationscampus Rheinmühle - Pilotanlage zur Biomasseverwertung

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Dr. Tammo Rebling, umwelttechnik & ingenieure GmbH

Energetische und stoffliche Optimierung der Bioabfallvergärung durch Einbindung der Hydrothermalen Carbonisierung

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umwelttechnik & ingenieure GmbH
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30163 Hannover

Session VI:
Anwendungen II

Dr. Fritz Keller & Nina Stahl, Act4Carbon/klima.bond

Umsetzung von Kohlenstoffsequestrierung in der Praxis: Modellprojekt Tübingen, act4carbon, klima.bond, 4C-Chem und Jaden X - let‘s do it!

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Themengebiet - Optimierung und Weiterentwicklung hydrothermaler Prozesse und Anlagen am Beispiel der Kommune Tübingen: Kaskadische HTC / Universität Hohenheim und das „Tübinger Modell“

Wir wollen gerne in Tübingen den kompletten End-to-End Prozess zur Erreichung von Negativemissionen darstellen. Beginnen wollen wir mit der markt-reifen Pyrolyse und der Nutzung der kommunalen Häckselmasse. Dieser Kreislauf wird bereits in anderen Kommunen gestartet, allerdings endet die wirtschaftliche Nutzung bei der Pflanzenkohle/Wärmegewinnung und der Zertifikatehandel ist noch außen vor. Wir wollen den Zertifikatehandel ebenfalls kommunal darstellen, was mit Hilfe der existierenden Zertifizierungsstelle CBI und der Marktplattform Carbonfuture möglich ist. Während der Planungs- und Bauphase der Pyrolyseanlage wird direkt in unmittelbarer Umgebung Tübingens mit der Universität Hohenheim und einem Biogasbauern ein Forschungsprojekt zur Verwertung von Gärresten laufen. In dieser Forschungsanlage wird zusätzlich Bioabfall des Landkreises Tübingen getestet werden und mit Unterstützung der Studenten werden die Stoffkreisläufe Tübingens auf ihre Nutzung in der HTC dargestellt. Verlaufen diese Arbeiten positiv kann im nächsten Schritt der komplette kaskadische Aufbau mittels einer Demoanlage HTC vor der (sich bis dahin im Betrieb befindenden) Pyrolyseanlage dargestellt werden.
Problemstellungen: Vertragliche Bindungen der Biomasseverwertungen und Klärschlämme

Torben Bauer, Lulea University of Technology

Optimal integration of hydrothermal carbonisation into sewage sludge treatment systems

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Sewage sludge is an organic waste stream with high water content, which makes it a potential feed for hydrothermal carbonisation (HTC). HTC treatment of sewage sludge could dewater, stabilize and hygienize the sludge and prepare it for storage and transport or further treatment such as incineration or resource recovery. Despite the benefits of HTC, full-scale treatment systems involving HTC are rarely found. Researchers tend to focus on improving singular characteristics of HTC or its products and not on the implementation of HTC into existing treatment systems and interaction with the existing infrastructure, e.g., effects and mass and energy flows.
This study aims to understand key issues of the implementation of HTC into existing sludge treat-ment systems and to explore how HTC affects existing infrastructure. By that, the most suitable scenarios for implementing HTC are identified.

The results cover:
- A complete material flow analysis (MFA) for the HTC process including substances, energy, support materials, side products. The MFA is based on data from demo scale applications of HTC in combination with data from literature and own lab scale experiments.
- A universal LCA module which can be utilized in different LCA scenarios. The module includes detailed data of the distribution of heavy metals and organic matter (including their biodegradability) into the three output streams of HTC (hydrochar, process water, gas). Additionally, the module includes information on consumption and production of energy, support materials and side products.
- An analysis of the effects of HTC and its products on existing treatment systems and the environment using several impact categories. This helps to understand which scenarios are most suitable for the implementation of HTC.

The results are combined with results from a study on non-technical hinders for the implementation of new techniques in sewage sludge management, enabling a more holistic perspective on the implementation of HTC into existing systems.

OPTIMAL INTEGRATION OF HYDROTHERMAL CARBONISATION INTO SEWAGE SLUDGE TREATMENT SYSTEMS

2022-09-28

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[2]Technical University of Denmark, Circularity & Environmental Impact

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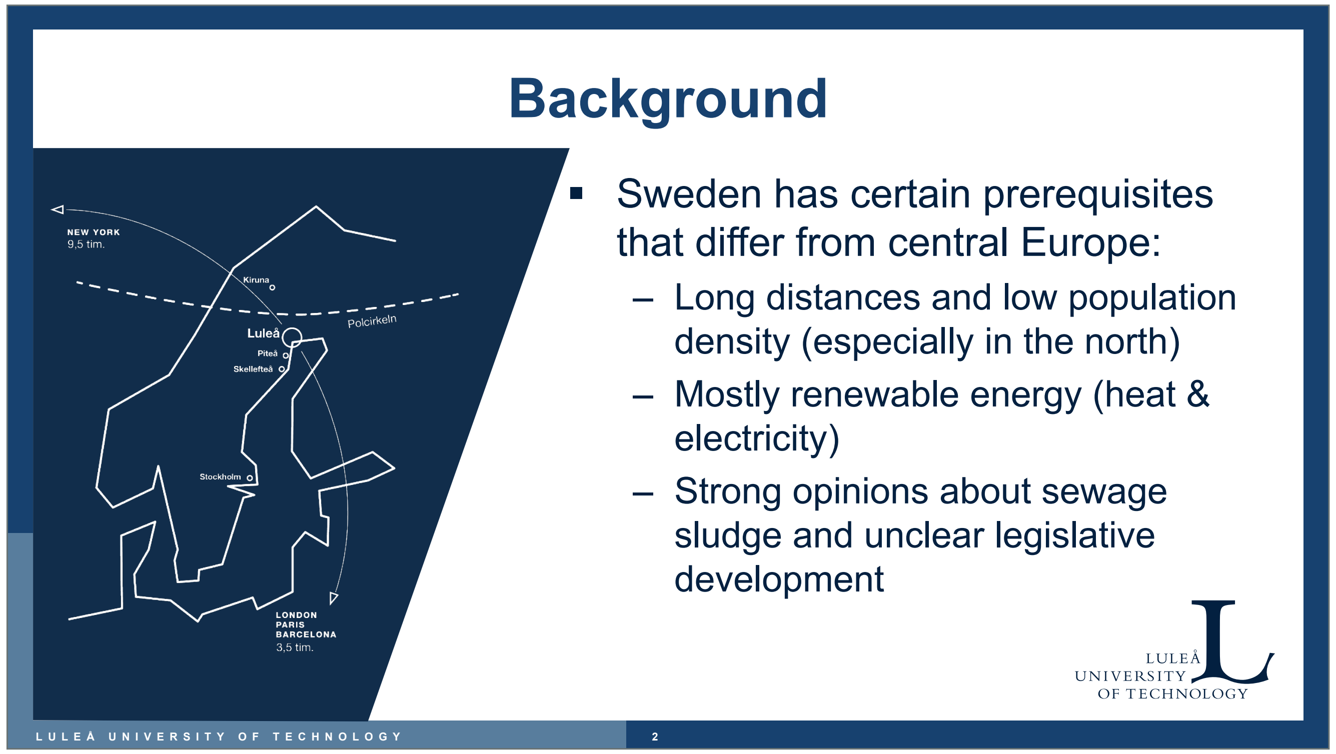

Background

- Sweden has certain prerequisites that differ from central Europe:
  - Long distances and low population density (especially in the north)
  - Mostly renewable energy (heat & electricity)
  - Strong opinions about sewage sludge and unclear legislative development

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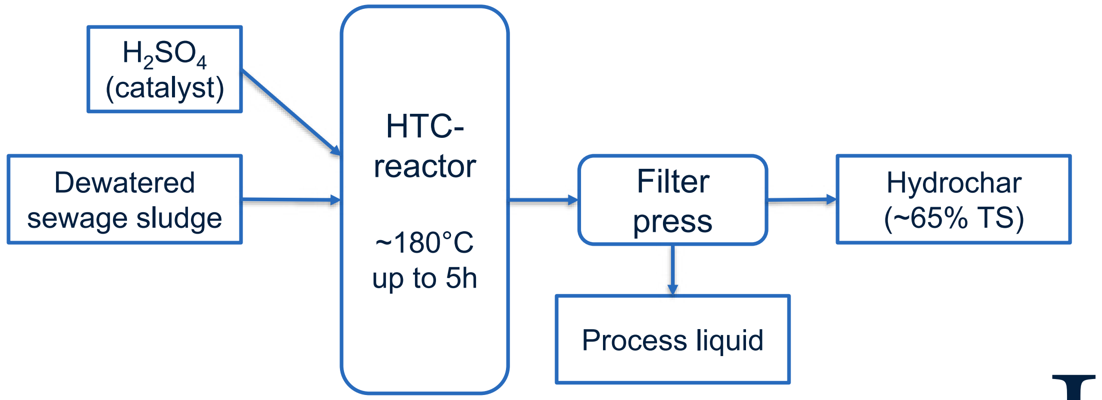
What does it mean?

- Unclear how sludge can be used in the future
  - Coverage of landfills and mines will phase out
  - Agricultural usage and soil production might phase out
- Transportation of sludge/sludge derived products will get crucial
- Hydrochar can only be incinerated in waste incinerators
  - Sludge mono incinerators do not exist.
  - No allowance for biomass incinerators at the moment

HTC Terra Nova® Ultra

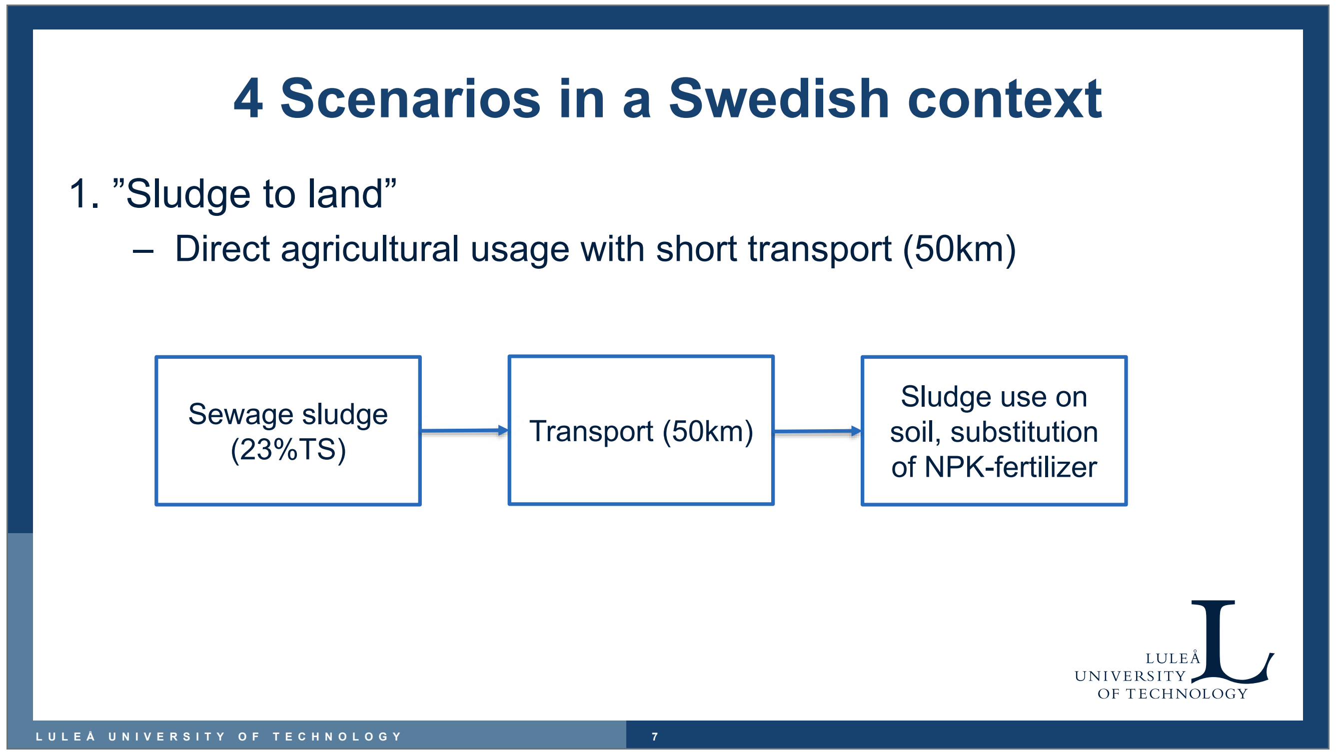


Objectives

- How can HTC be a part in Swedish sewage sludge management?
- What are key issues in the implementation of HTC into existing infrastructure?

Method: Lifecycle Assessment

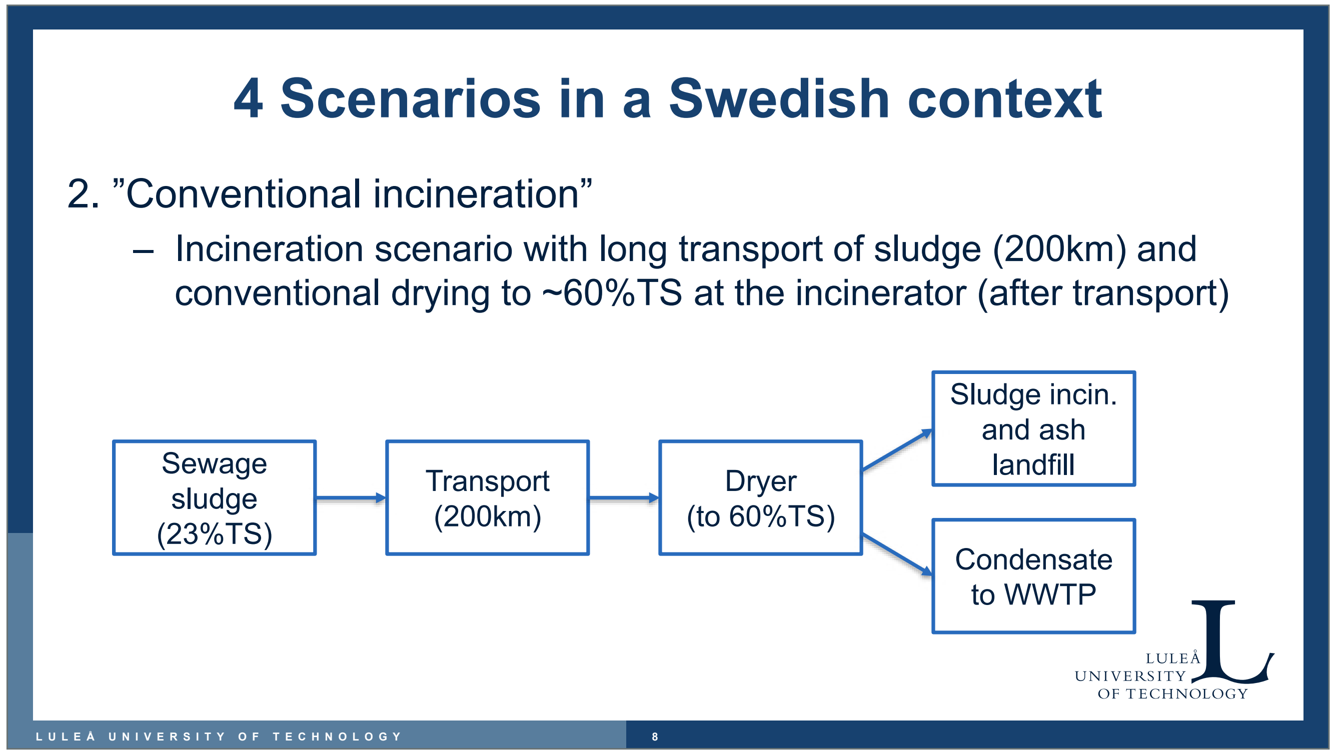
- LCA modelling in EASETECH (DTU)
- Functional unit: treatment of 1000kg digested and dewatered sewage sludge with ~23% TS
- Marginal electricity: 2019 electricity mix in Sweden (0.04kg CO_2-eq/kWh)
- Marginal heat: 2019 district heating mix in Sweden (0.005kg CO_2-eq/MJ)
- HTC process based on pilot data of TerraNova® Ultra process
- Other processes from EASETECH database and literature



4 Scenarios in a Swedish context

1. ”Sludge to land”
   - Direct agricultural usage with short transport (50km)

Sewage sludge (23%TS) → Transport (50km) → Sludge use on soil, substitution of NPK-fertilizer

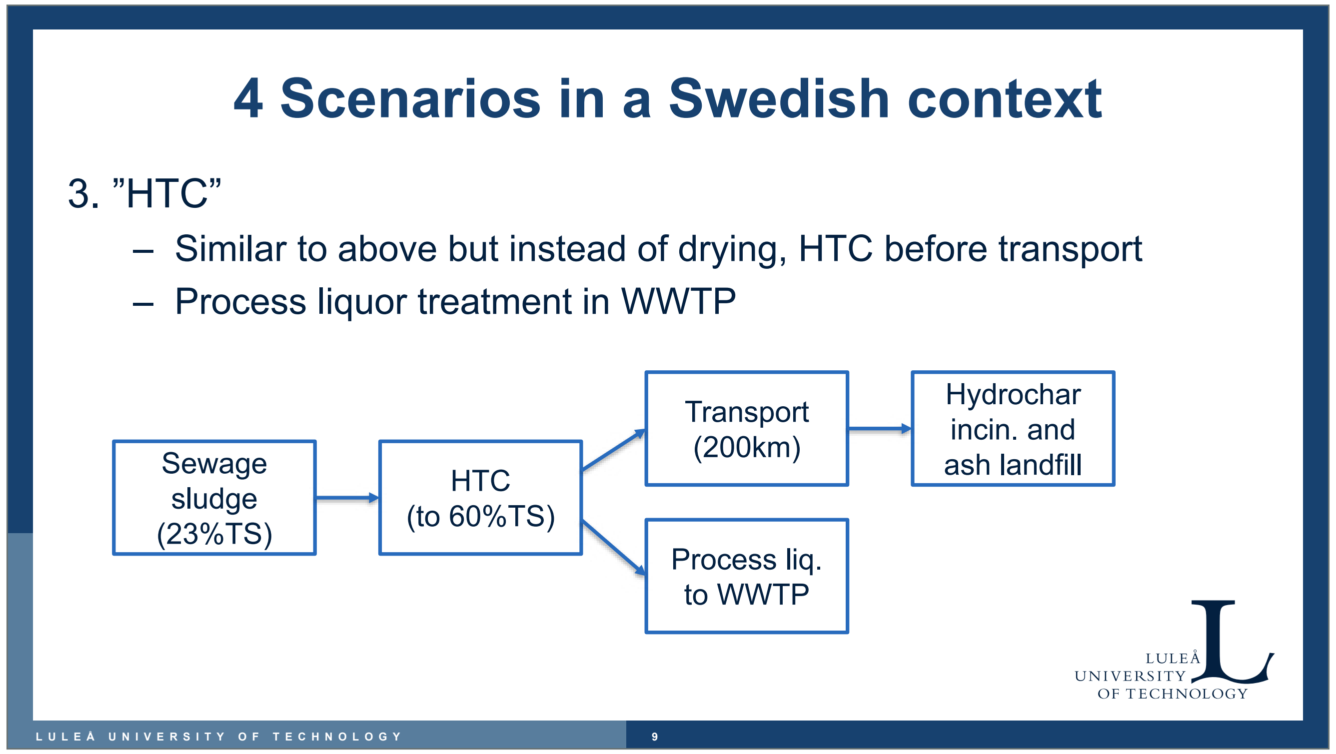


4 Scenarios in a Swedish context

2. ”Conventional incineration”
   - Incineration scenario with long transport of sludge (200km) and conventional drying to ~60%TS at the incinerator (after transport)

Sewage sludge (23%TS) → Transport (200km) → Dryer (to 60%TS) → Sludge incin. and ash landfill

Dryer (to 60%TS) → Condensate to WWTP

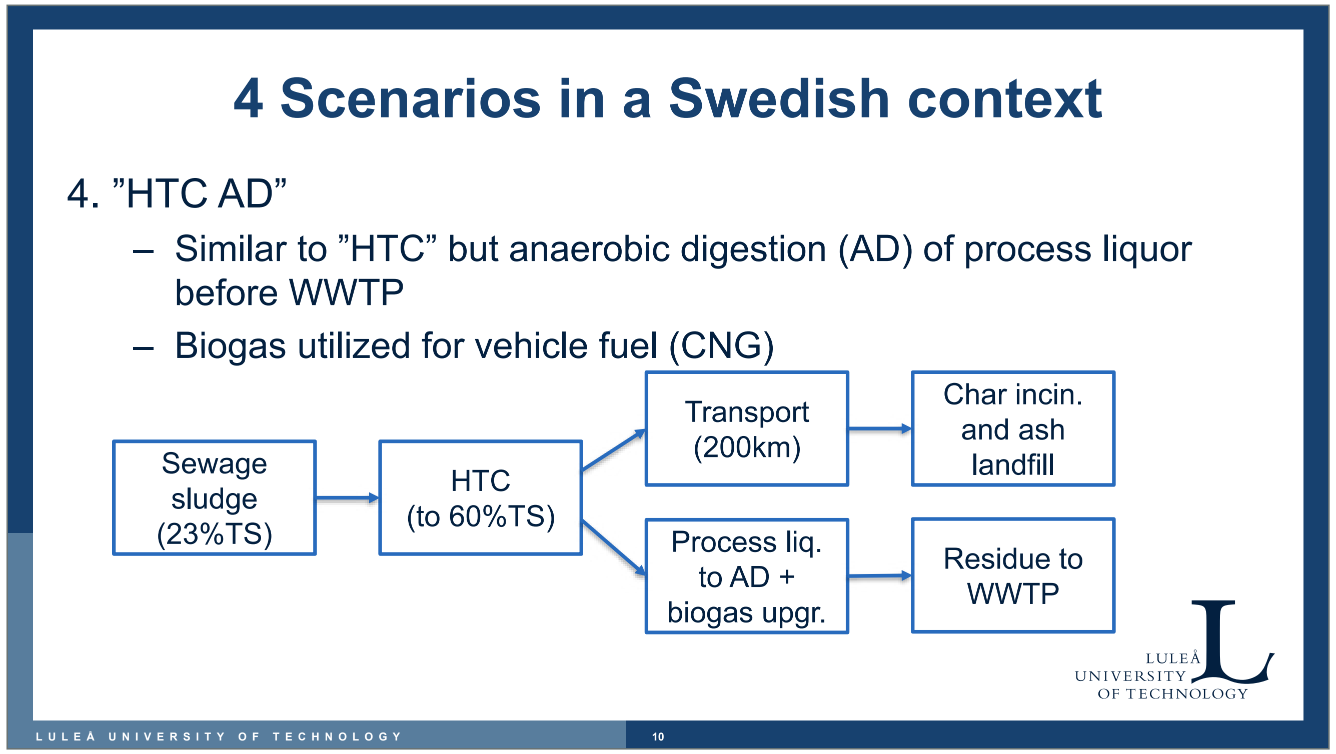


4 Scenarios in a Swedish context

3. ”HTC”
   - Similar to above but instead of drying, HTC before transport
   - Process liquor treatment in WWTP

Sewage sludge (23%TS) → HTC (to 60%TS) → Transport (200km) → Hydrochar incin. and ash landfill

HTC (to 60%TS) → Process liq. to WWTP



4 Scenarios in a Swedish context

4. ”HTC AD”
   - Similar to ”HTC” but anaerobic digestion (AD) of process liquor before WWTP
   - Biogas utilized for vehicle fuel (CNG)

Sewage sludge (23%TS) → HTC (to 60%TS) → Transport (200km) → Char incin. and ash landfill

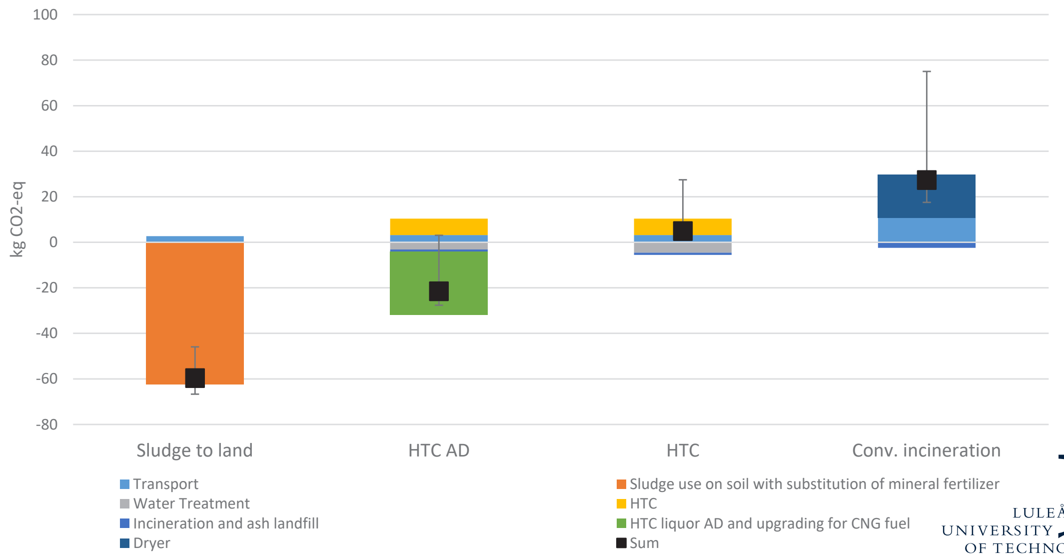
HTC (to 60%TS) → Process liq. to AD + biogas upgr. → Residue to WWTP

Scenario comparison

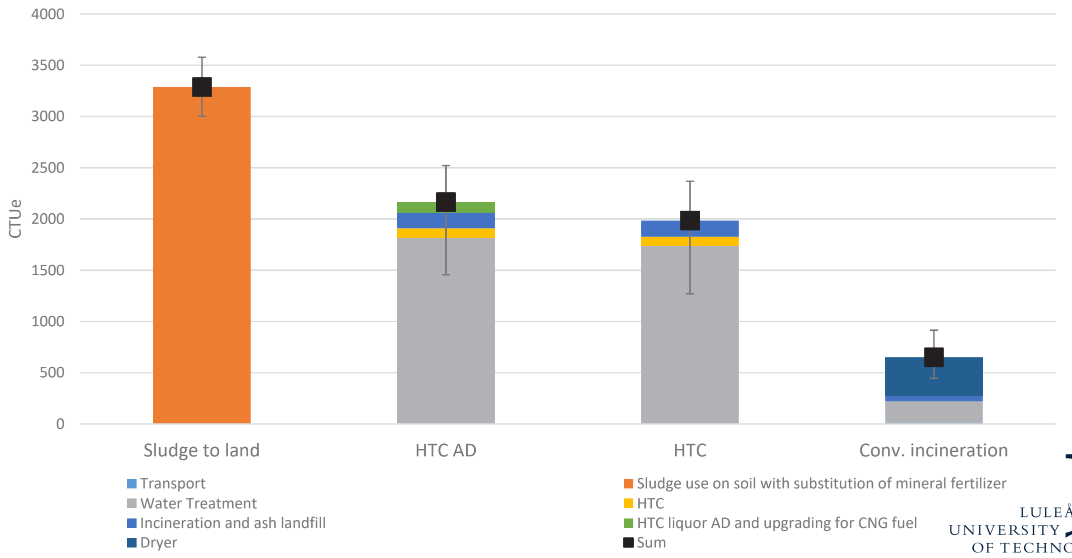
	Sludge to land	Conv. inciner.	HTC	HTC AD
Fate of pollutants:				
- Organic	Soil	Destruction, (condensate)	Destruction, process liquid	Destruction, process liquid
- Inorganic	Soil	Ash landfill, (condensate)	Ash landfill, process liquid	Ash landfill, process liquid
Utilization of sludge:				
- Energy	-	Heat/electricity	Heat/electricity	Heat/el./CNG
- Resources	NPK in soil	-	-	-

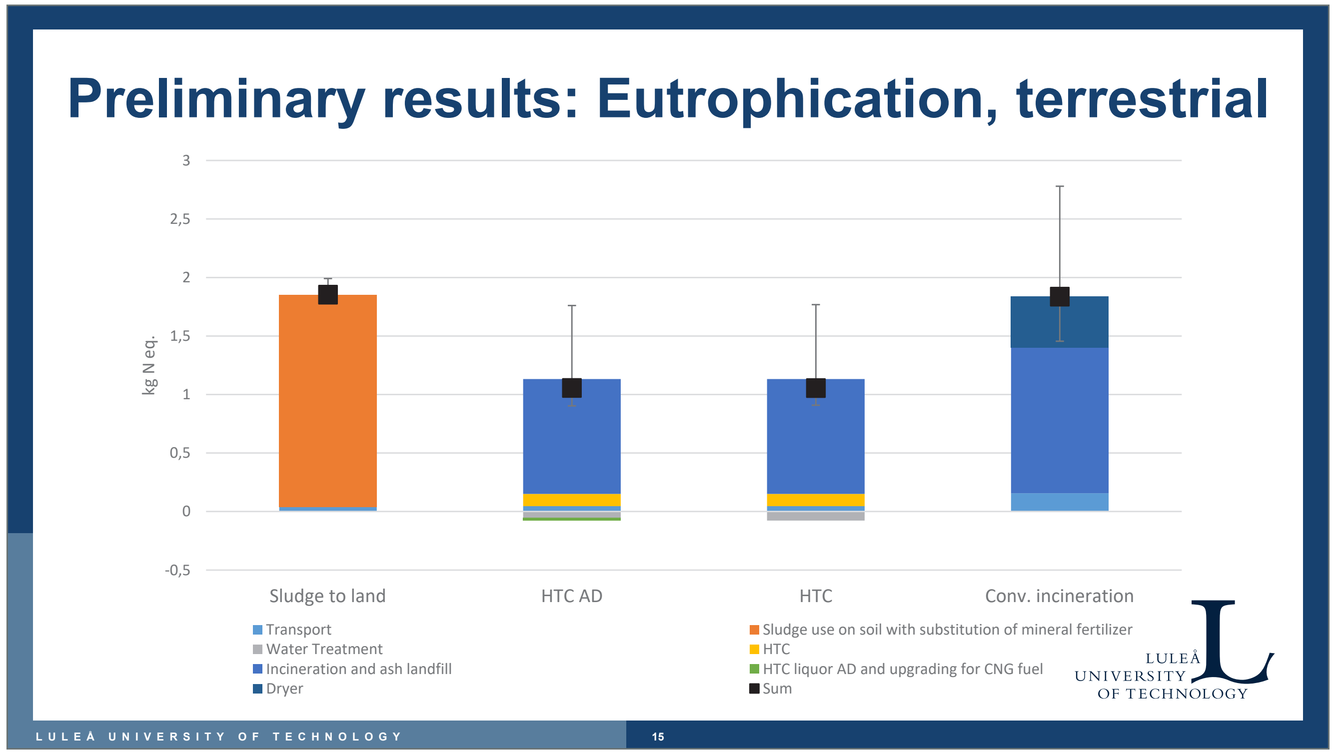
Preliminary Results & Discussion

Preliminary results: GHG potential

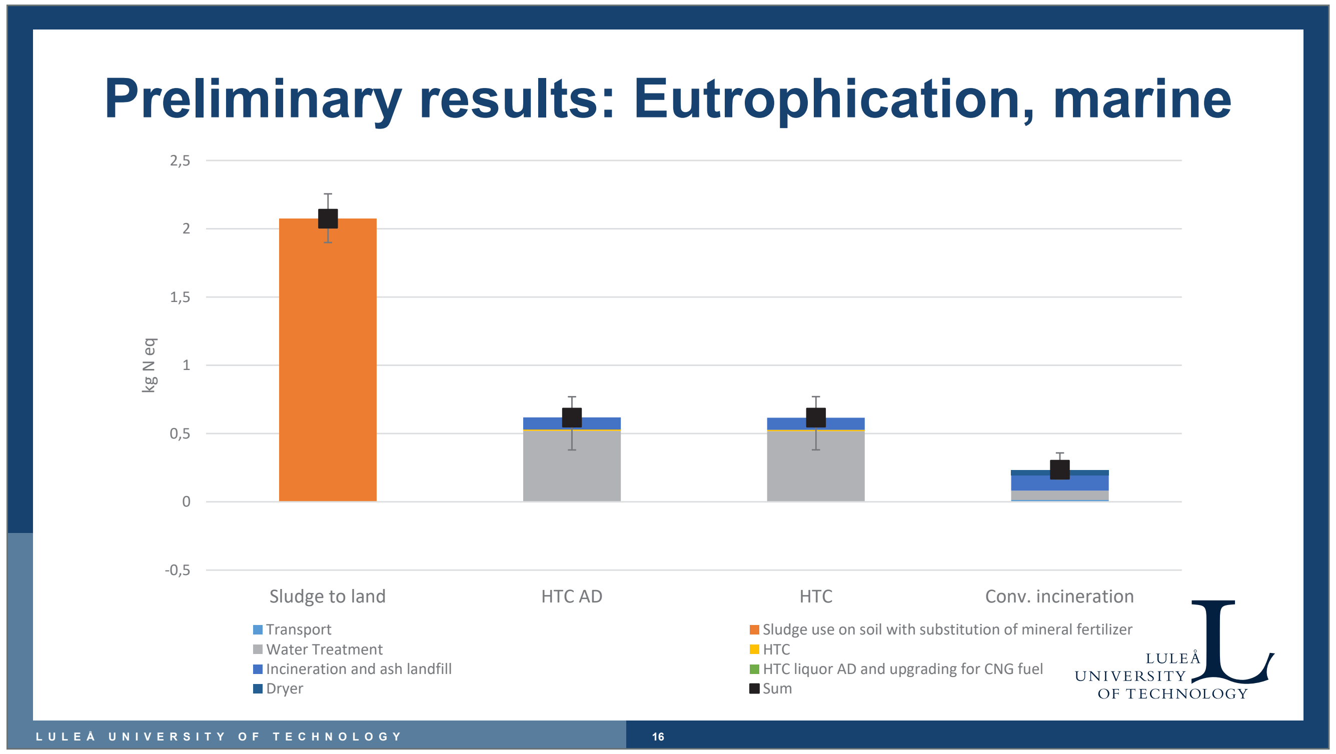


Preliminary results: Ecotoxicity, freshwater





Preliminary results: Eutrophication, terrestrial



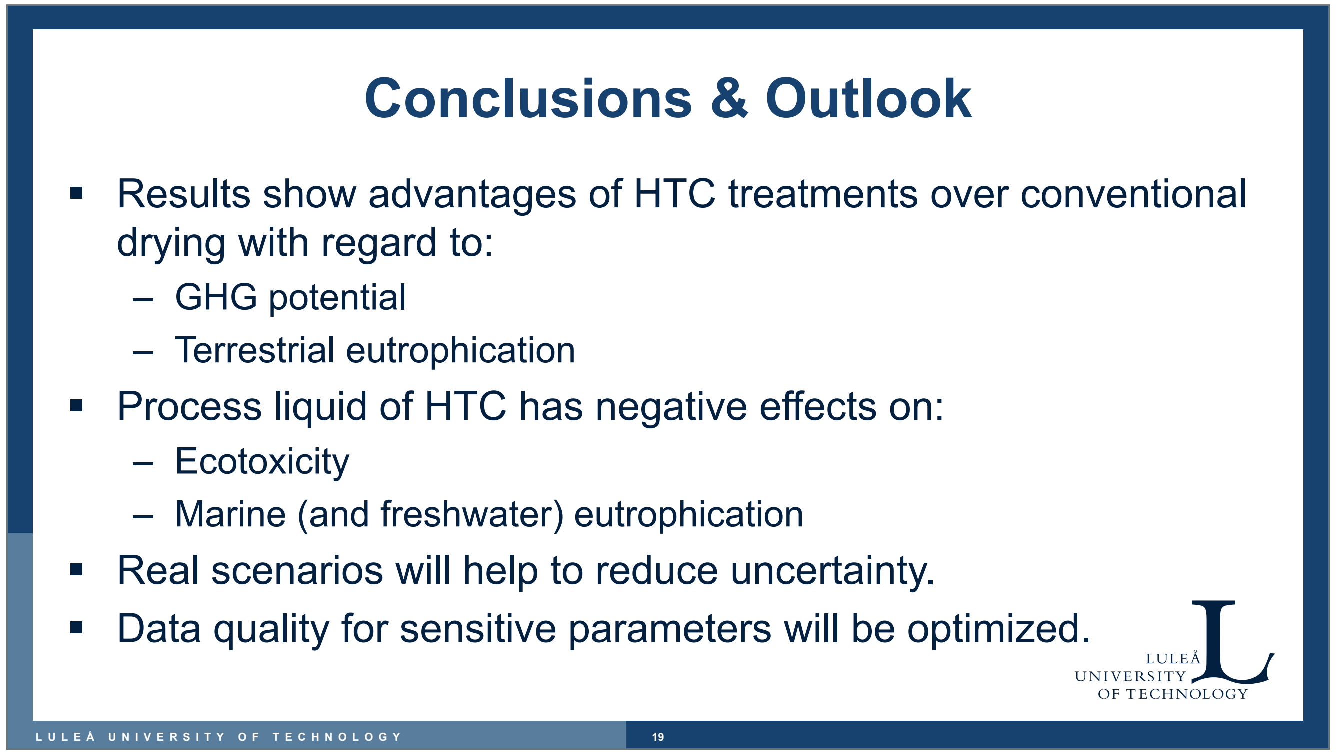
Preliminary results: Eutrophication, marine

Discussion: Sensitivity & Uncertainty

- High uncertainty in data quality due to archetype scenarios
- More than 10 parameters with high uncertainty were analysed for their sensitivity (more to come)
- Most sensitive parameters:
  - TS/water content of ingoing sludge
  - Dewaterability of hydrochar
  - Energy consumption of dryer

Discussion: Scenario optimization

- Change to real scenarios with:
  - existing infrastructure
  - real transport distances
  - local energy sources
- Implementation of a mono-incineration scenario with P-recovery
  - In different treatment combinations
  - Short and long transport distances
- Implementation of a hydrochar on land scenario
  - Possibility for carbon sequestration and NPK-recycling
  - Currently questionable due to legislation



Conclusions & Outlook

- Results show advantages of HTC treatments over conventional drying with regard to:
  - GHG potential
  - Terrestrial eutrophication
- Process liquid of HTC has negative effects on:
  - Ecotoxicity
  - Marine (and freshwater) eutrophication
- Real scenarios will help to reduce uncertainty.
- Data quality for sensitive parameters will be optimized.

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Thank you for your attention.

Questions? Contact me:
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Hendrik Etzold, Deutsches Biomasseforschungszentrum

HTC im Rahmen des Phosphorrecyclings bei Klärschlamm - eine techno-ökonomische Betrachtung

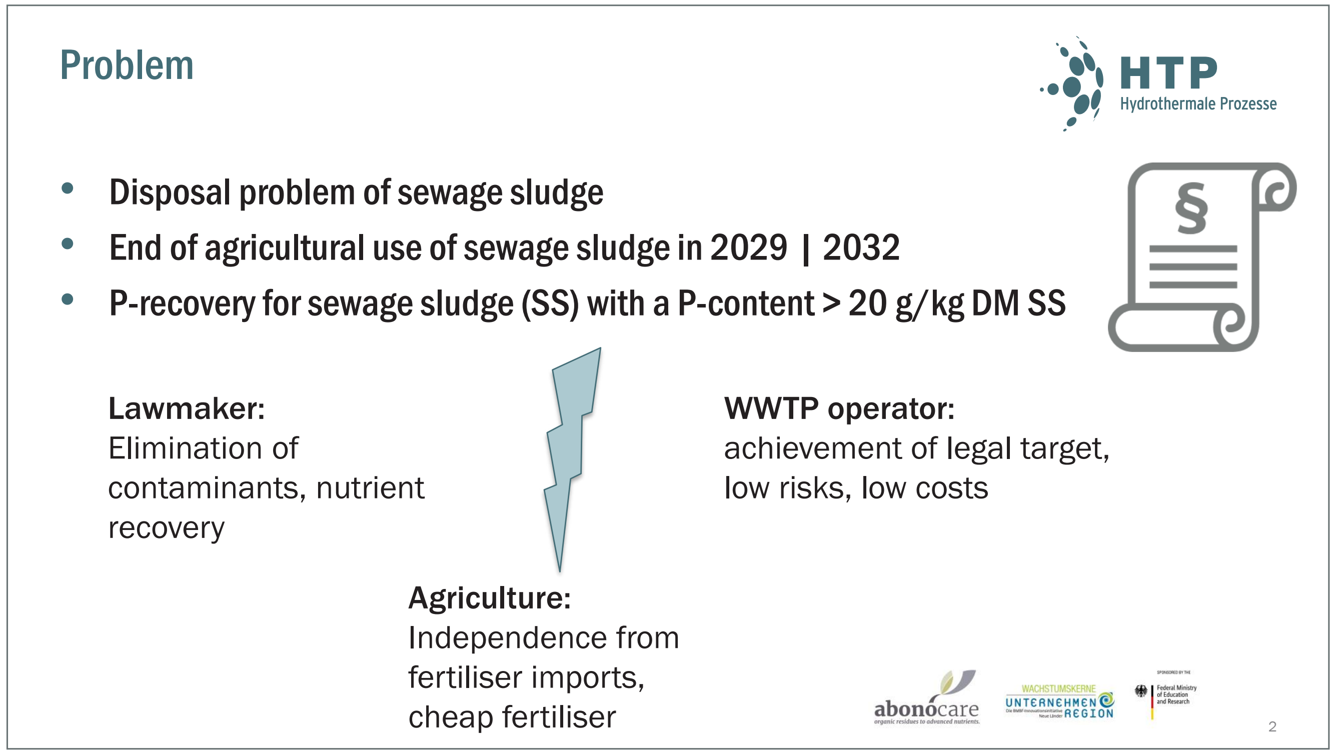
Hendrik Etzold, Benjamin Herklotz
Deutsches Biomasseforschungszentrum
Torgauer Straße 116
04347 Leipzig

7. HTP-Fachforum | 27./28. September 2022
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTC in the context of phosphorus recycling from sewage sludge – Techno-economic view

Hendrik Etzold, Lisa Röver, Benjamin Herklotz
DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH

www.htp-inno.de



Problem

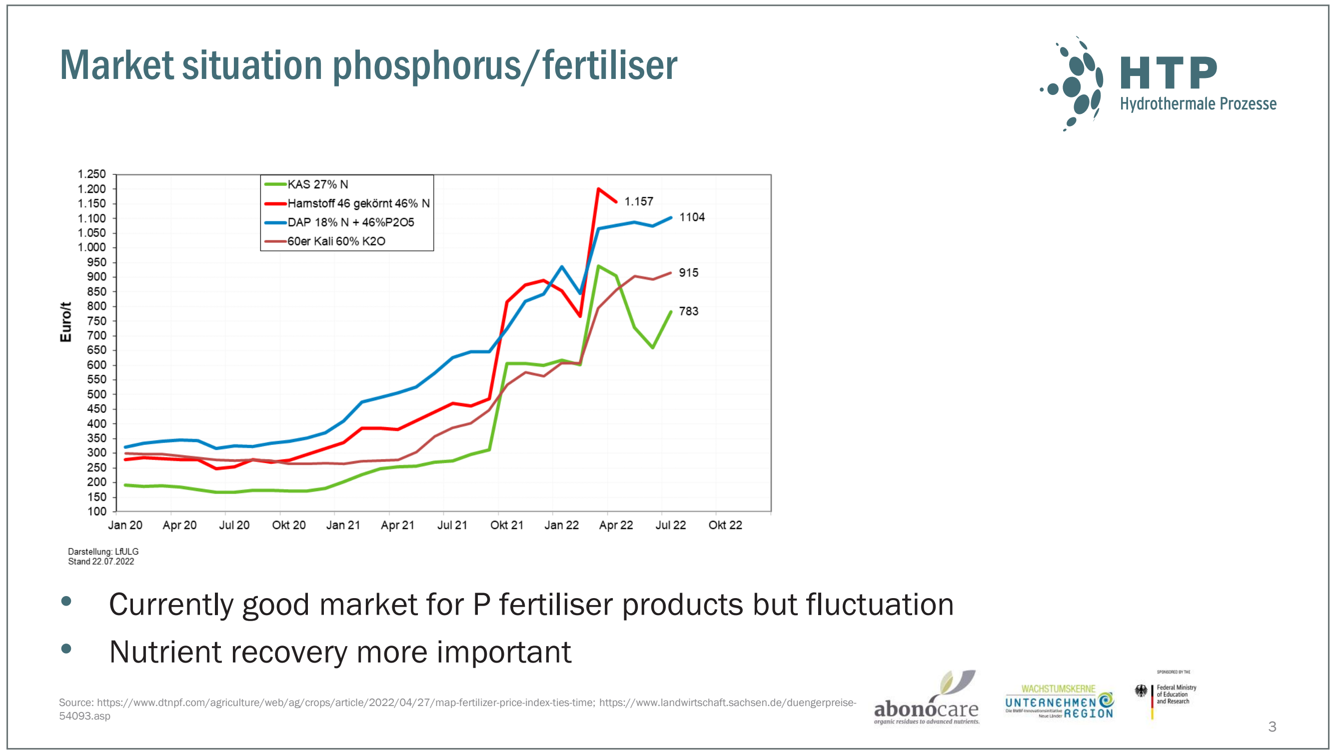
- Disposal problem of sewage sludge
- End of agricultural use of sewage sludge in 2029 | 2032
- P-recovery for sewage sludge (SS) with a P-content > 20 g/kg DM SS

Lawmaker:
Elimination of contaminants, nutrient recovery

WWTP operator:
achievement of legal target, low risks, low costs

Agriculture:
Independence from fertiliser imports, cheap fertiliser

2

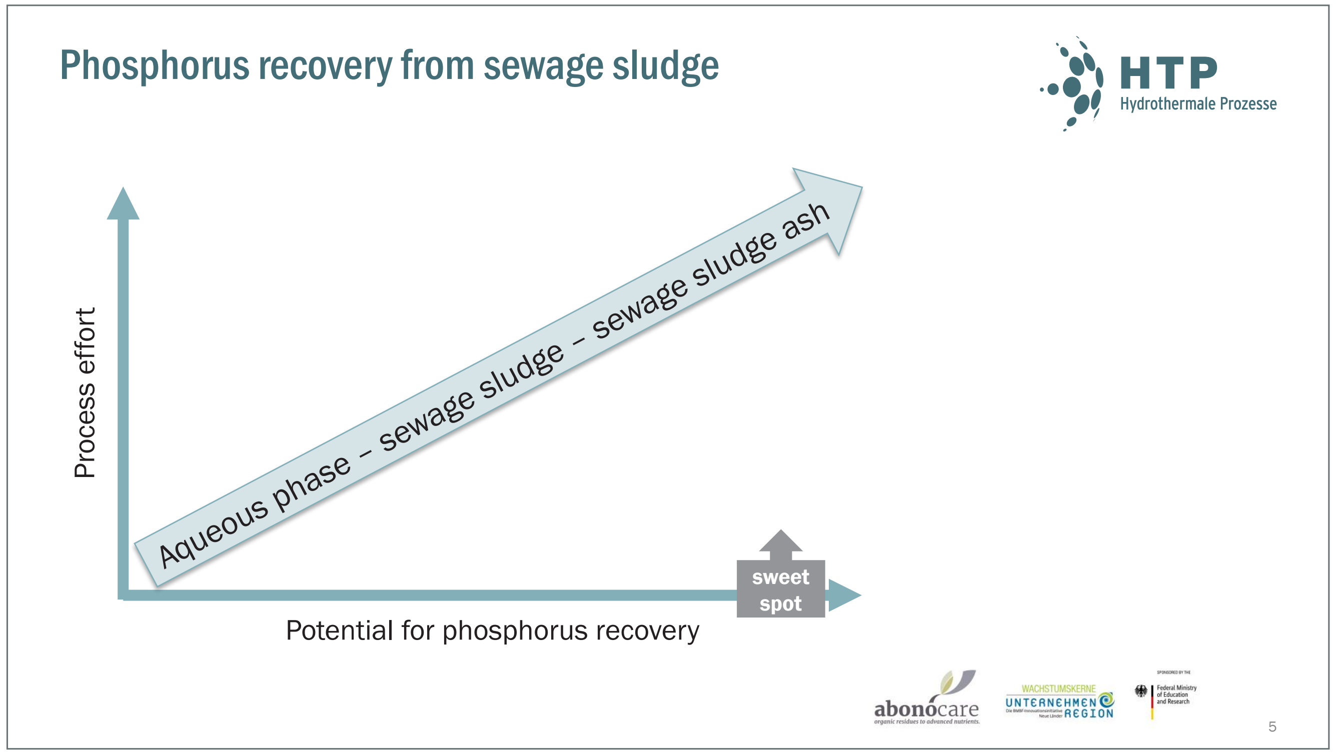


Market situation phosphorus/fertiliser

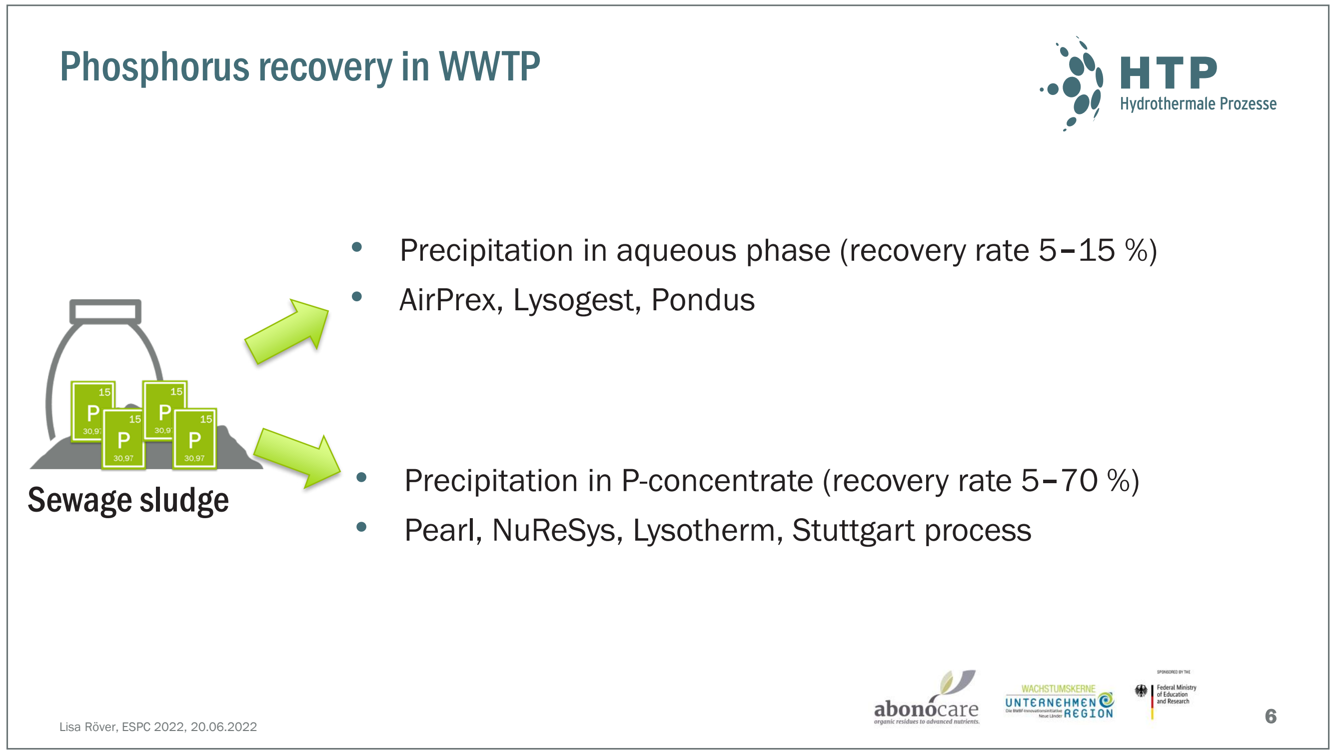
Darstellung: LfULG
Stand 22.07.2022

- Currently good market for P fertiliser products but fluctuation
- Nutrient recovery more important

Source: https://www.dtnpf.com/agriculture/web/ag/crops/article/2022/04/27/map-fertilizer-price-index-ties-time; https://www.landwirtschaft.sachsen.de/duengerpreise-54093.asp



Phosphorus recovery from sewage sludge

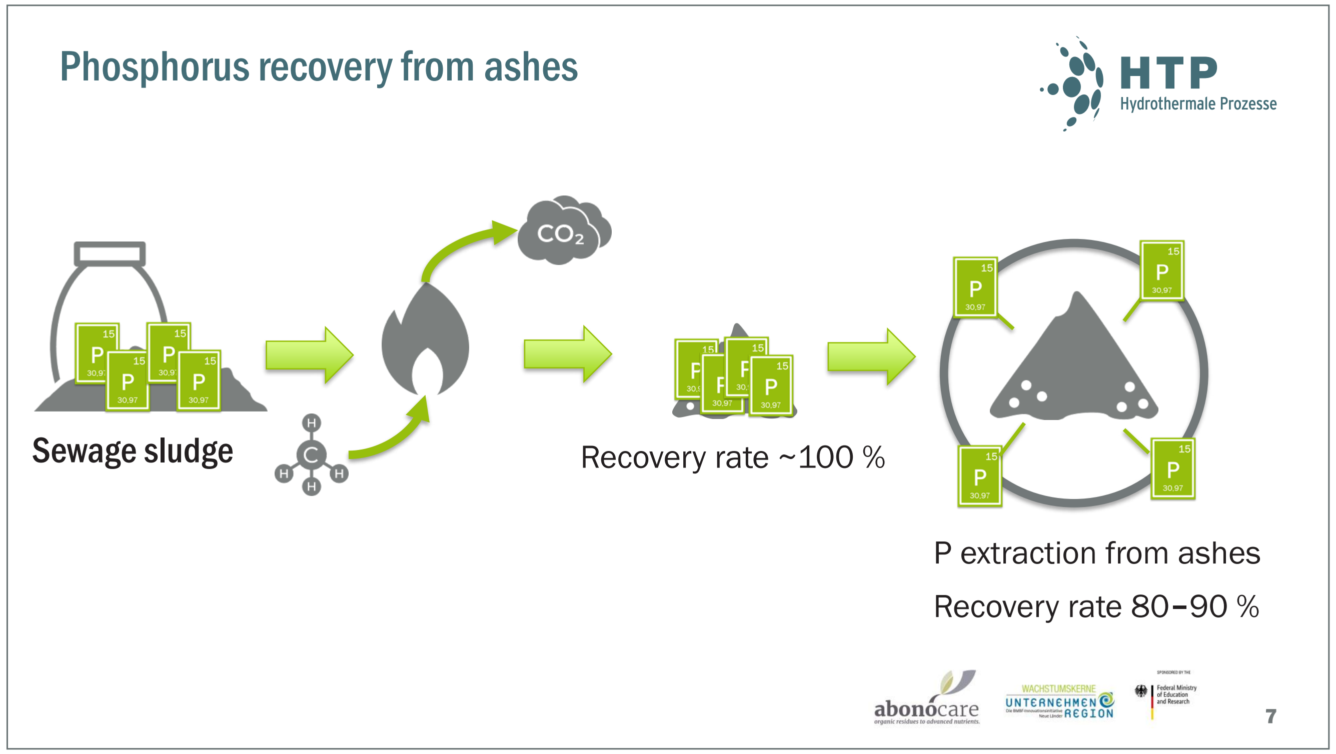


Phosphorus recovery in WWTP

- Precipitation in aqueous phase (recovery rate 5–15 %)
- AirPrex, Lysogest, Pondus

- Precipitation in P-concentrate (recovery rate 5–70 %)
- Pearl, NuReSys, Lysotherm, Stuttgart process

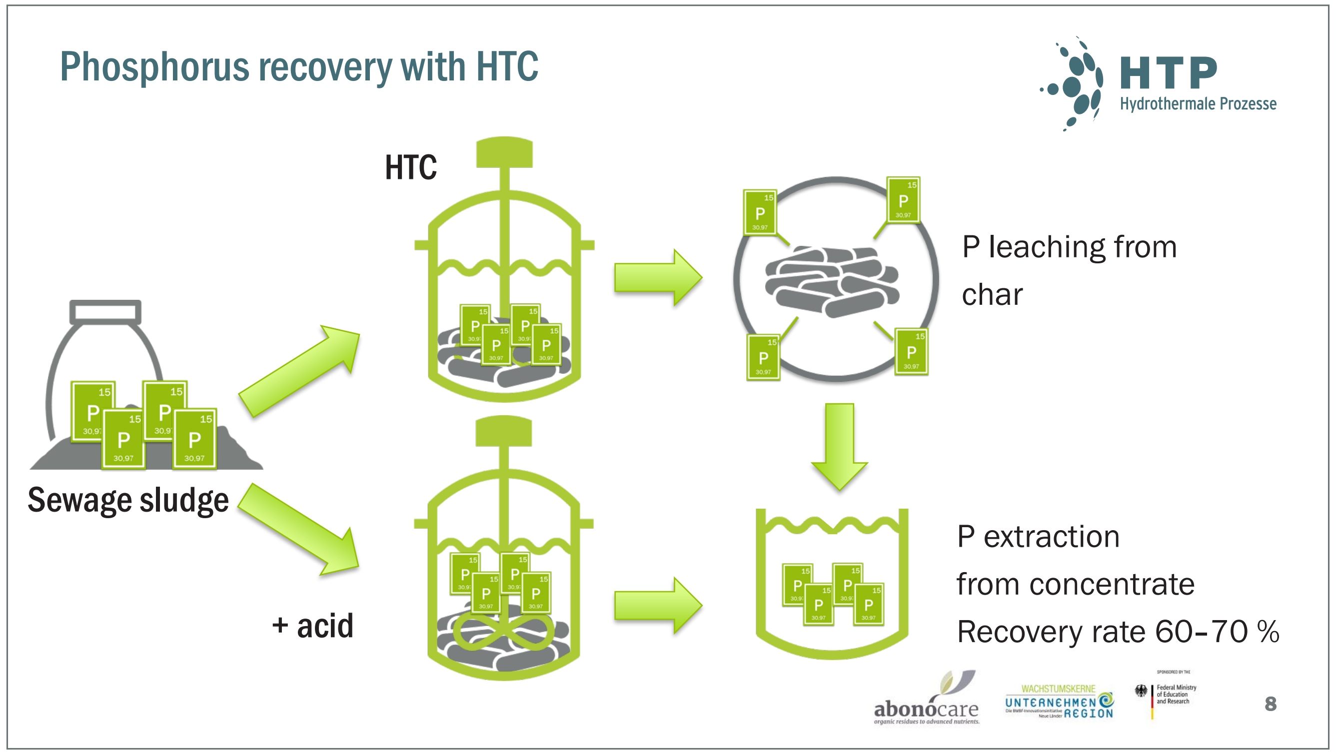
Lisa Röver, ESPC 2022, 20.06.2022



Phosphorus recovery from ashes

P extraction from ashes

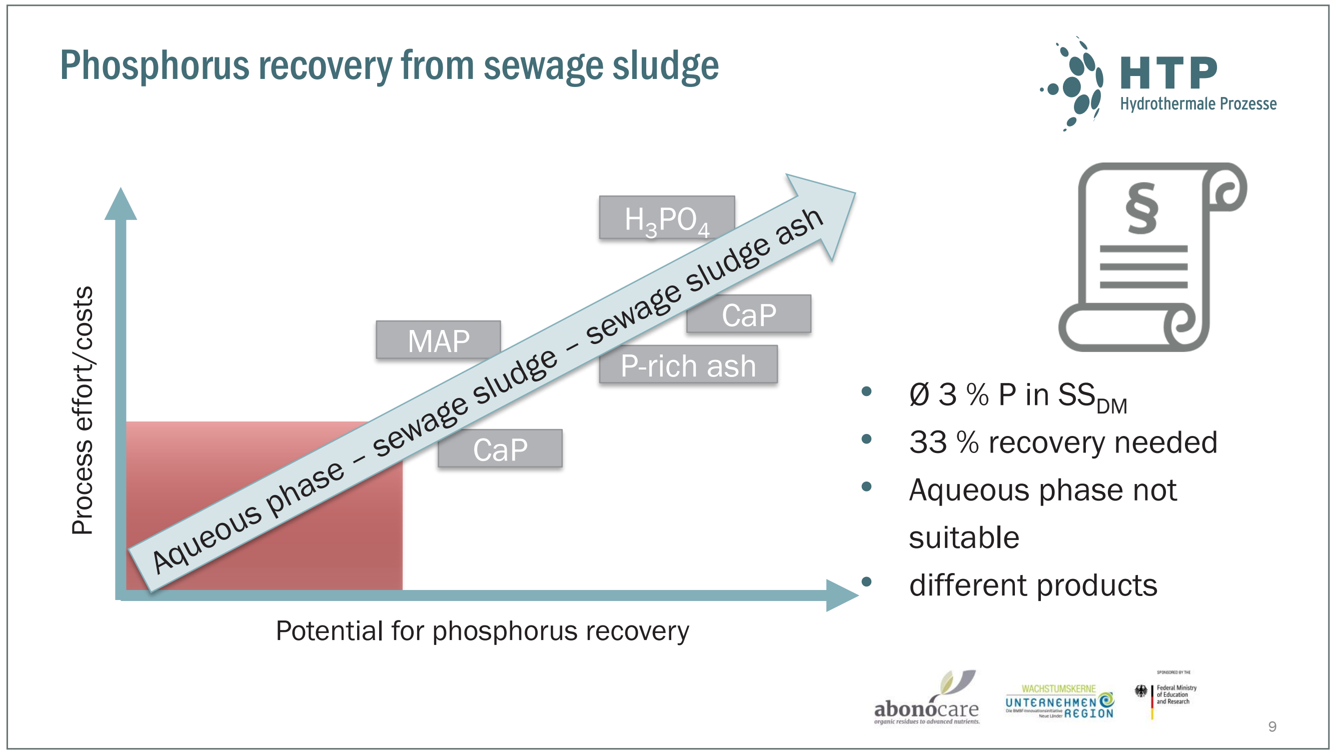
Recovery rate 80–90 %



Phosphorus recovery with HTC

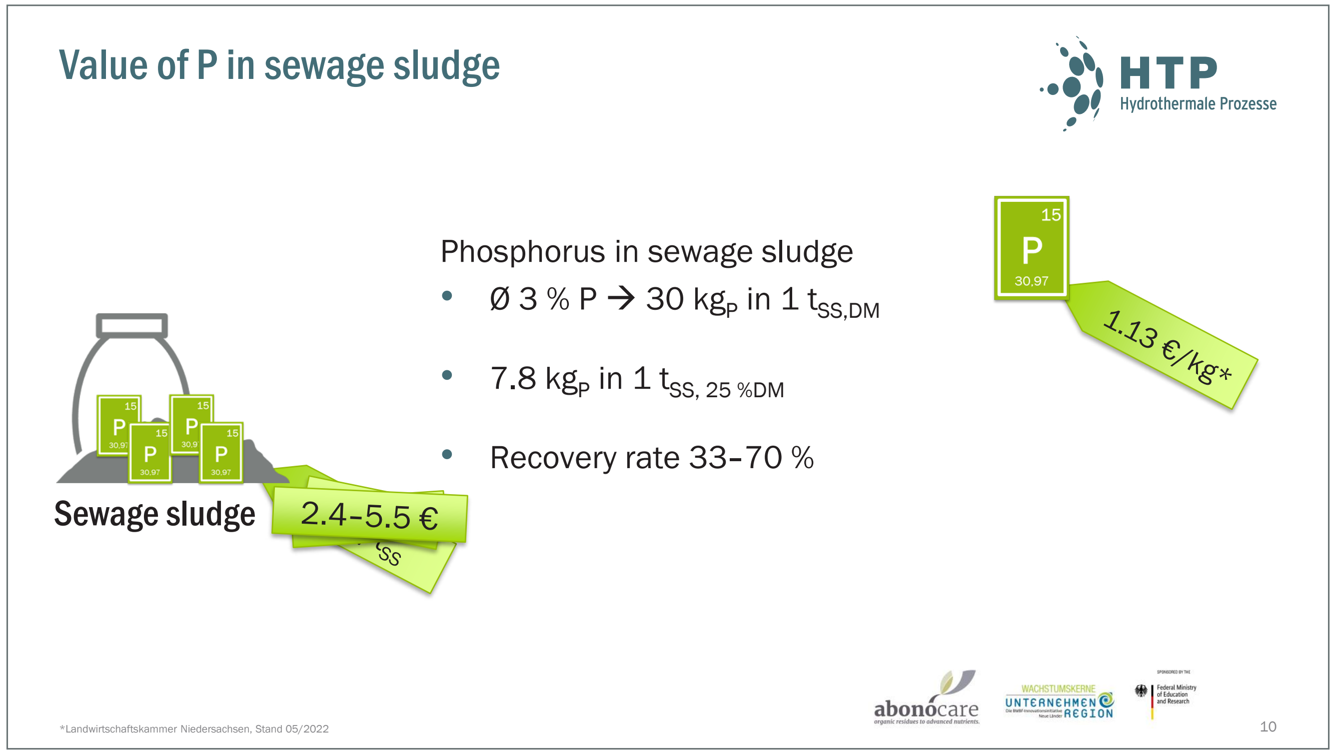
P leaching from char

P extraction from concentrate
Recovery rate 60–70 %



Phosphorus recovery from sewage sludge

- Ø 3 % P in SS_{DM}
- 33 % recovery needed
- Aqueous phase not suitable
- different products

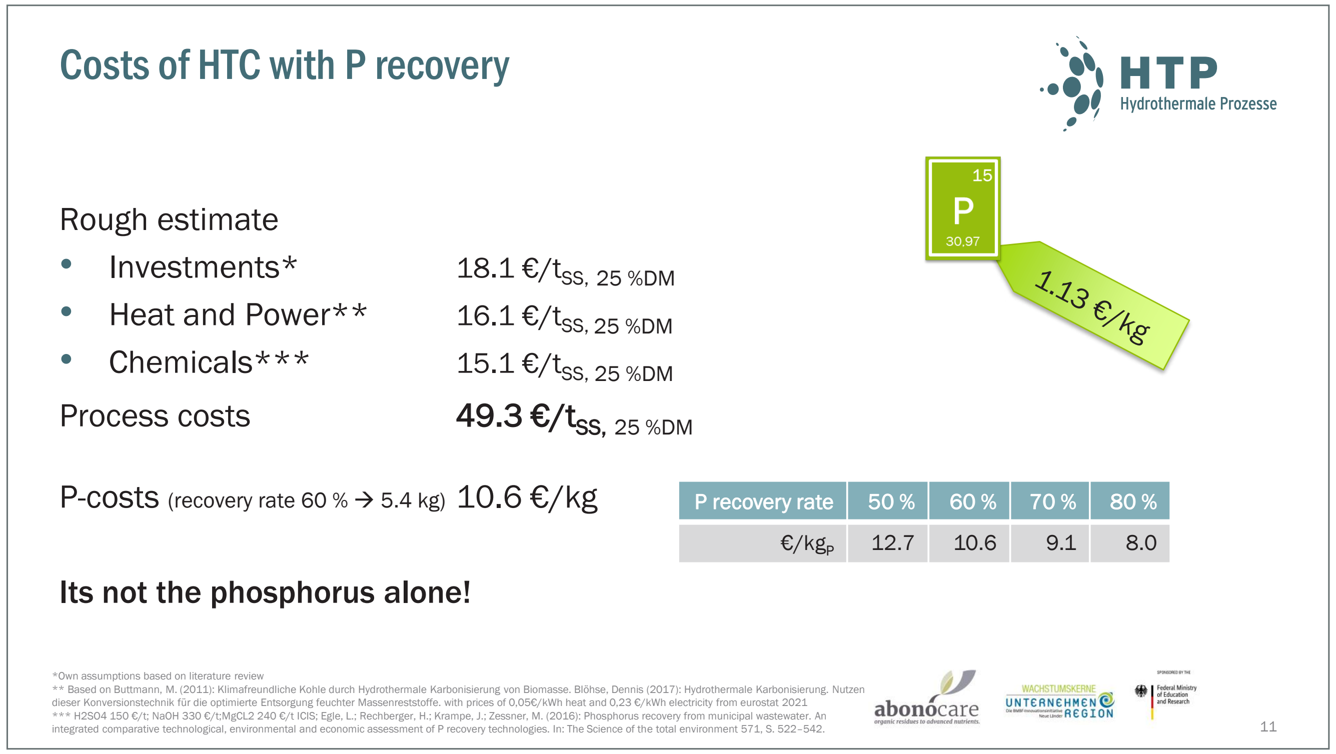


Value of P in sewage sludge

Phosphorus in sewage sludge

- Ø 3 % P → 30 kg_P in 1 $t_{SS,DM}$
- 7.8 kg_P in 1 $t_{SS,\ 25\ \%DM}$
- Recovery rate 33–70 %

*Landwirtschaftskammer Niedersachsen, Stand 05/2022



Costs of HTC with P recovery

Rough estimate

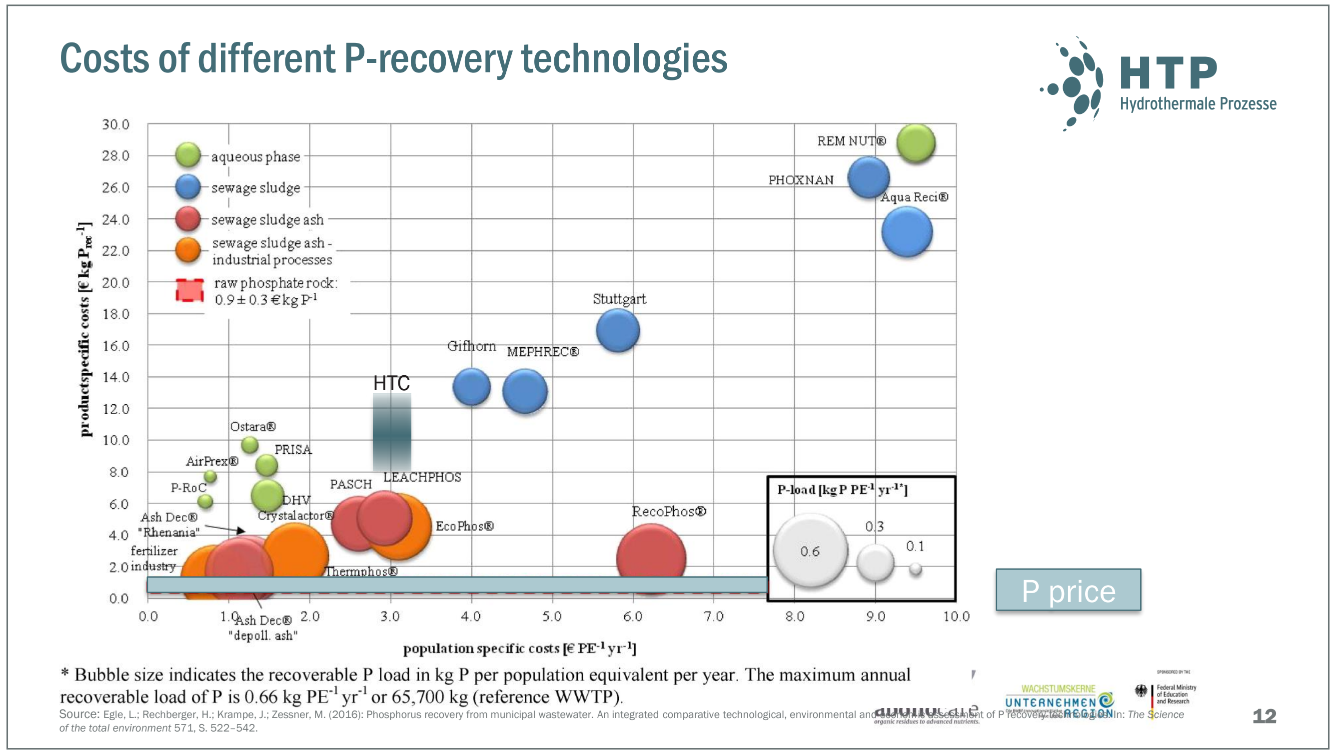
• Investments*	18.1 €/$t_{SS,\ 25\ \%DM}$
• Heat and Power**	16.1 €/$t_{SS,\ 25\ \%DM}$
• Chemicals***	15.1 €/$t_{SS,\ 25\ \%DM}$
Process costs	**49.3 €/$t_{SS,\ 25\ \%DM}$**

P-costs (recovery rate 60 % → 5.4 kg) 10.6 €/kg

P recovery rate	50 %	60 %	70 %	80 %
€/kg_P	12.7	10.6	9.1	8.0

Its not the phosphorus alone!

*Own assumptions based on literature review
** Based on Buttmann, M. (2011): Klimafreundliche Kohle durch Hydrothermale Karbonisierung von Biomasse. Blöhse, Dennis (2017): Hydrothermale Karbonisierung. Nutzen dieser Konversionstechnik für die optimierte Entsorgung feuchter Massenreststoffe. with prices of 0,05€/kWh heat and 0,23 €/kWh electricity from eurostat 2021
*** H2SO4 150 €/t; NaOH 330 €/t;MgCL2 240 €/t ICIS; Egle, L.; Rechberger, H.; Krampe, J.; Zessner, M. (2016): Phosphorus recovery from municipal wastewater. An integrated comparative technological, environmental and economic assessment of P recovery technologies. In: The Science of the total environment 571, S. 522–542.



Costs of different P-recovery technologies

* Bubble size indicates the recoverable P load in kg P per population equivalent per year. The maximum annual recoverable load of P is 0.66 kg PE^{-1} yr^{-1} or 65,700 kg (reference WWTP).

Source: Egle, L.; Rechberger, H.; Krampe, J.; Zessner, M. (2016): Phosphorus recovery from municipal wastewater. An integrated comparative technological, environmental and economic assessment of P recovery technologies. In: *The Science of the total environment* 571, S. 522–542.

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Monetarise the benefits of HTC

Main product is hydrochar

- Aim → added value from energetic use (waste status)
- Energy production from hydrochar greater than energy demand HTC
- Assumption: coverage of own energy requirements

P-costs (recovery rate 60 % → 5.4 kg) 7.1 €/kg

Recovery rate	50 %	60 %	70 %	80 %
€/kg	8.6	7.1	6.1	5.4

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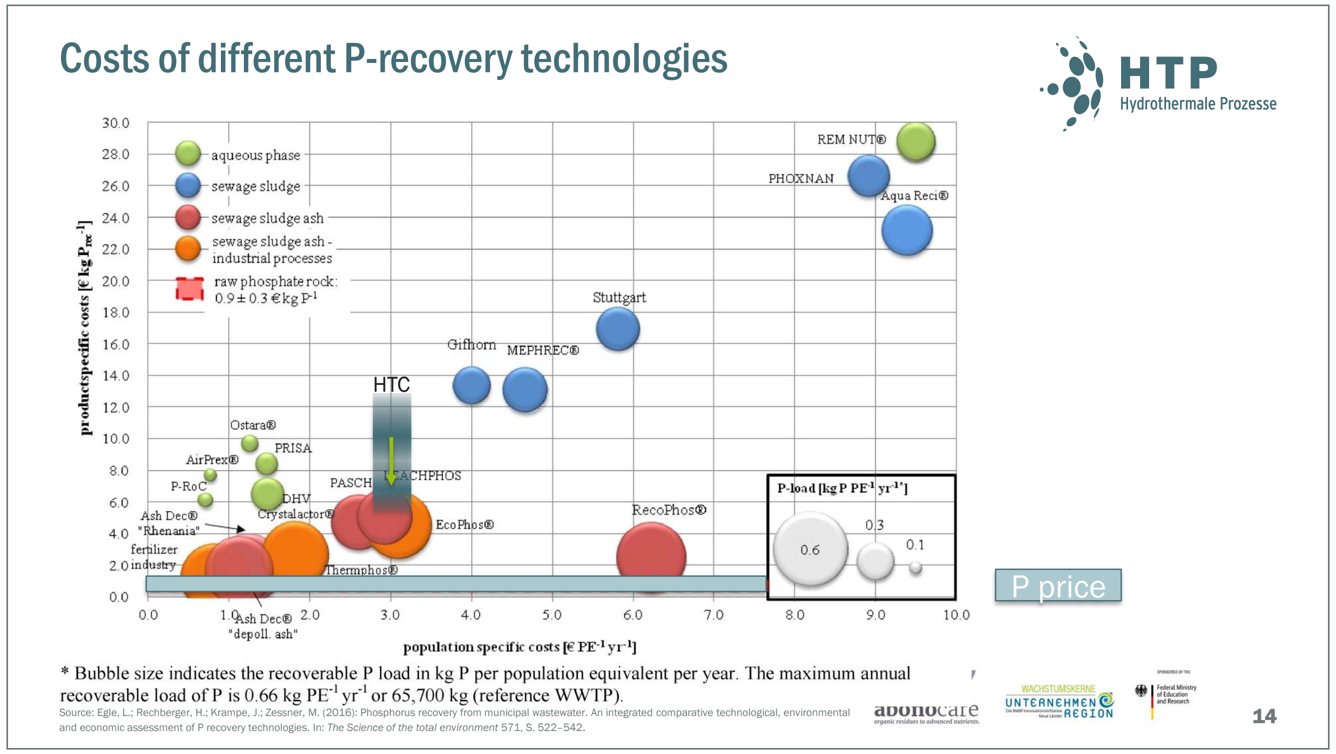

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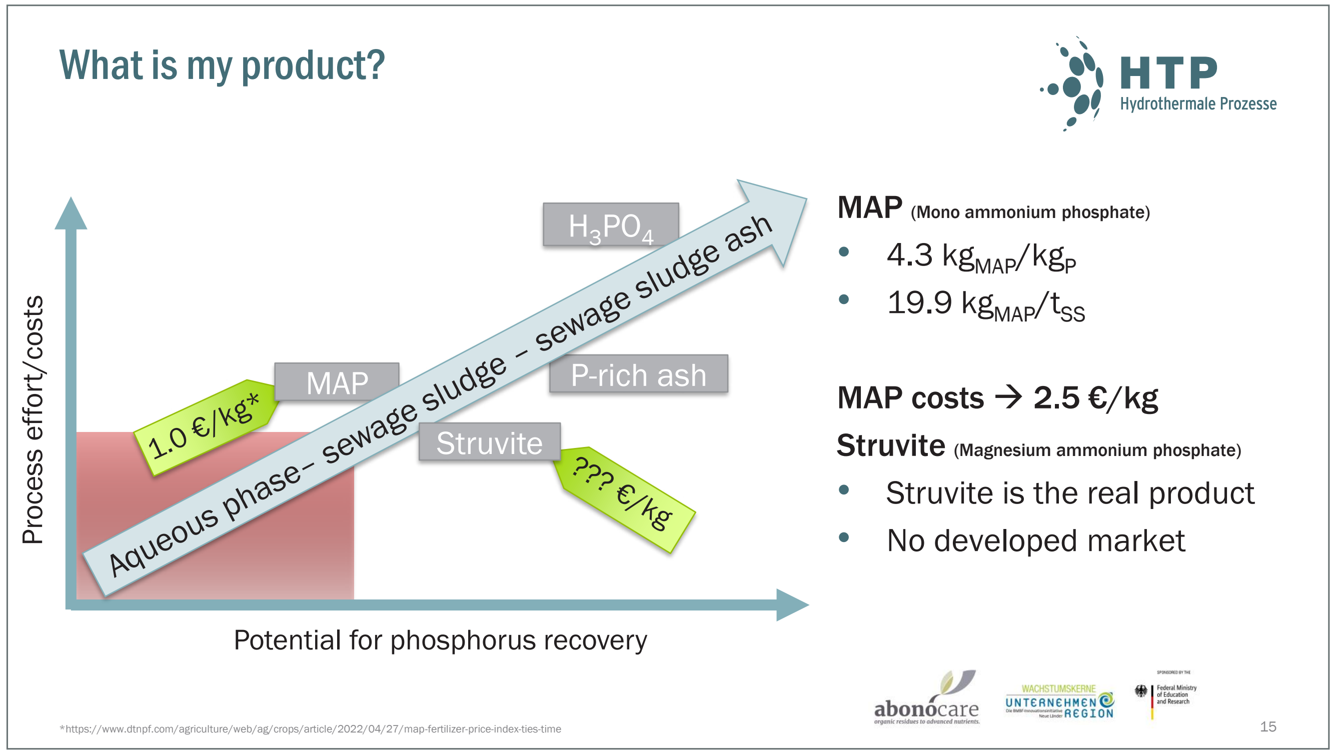

What is my product?

MAP (Mono ammonium phosphate)

- 4.3 kg_{MAP}/kg_P
- 19.9 kg_{MAP}/t_{SS}

MAP costs → 2.5 €/kg

Struvite (Magnesium ammonium phosphate)

- Struvite is the real product
- No developed market

*https://www.dtnpf.com/agriculture/web/ag/crops/article/2022/04/27/map-fertilizer-price-index-ties-time

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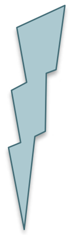
Other benefits to monetarise

- **More efficient dewatering**
  - High temperature dewatering as linking process → Project abonoCARE
  - Lower polymer demand for dewatering in WWTP
- **Avoidance of unwanted struvite precipitation in WWTP**

*Source https://www.nova-umwelt.de/media/map-ablagerungen/map-ablagerungen-02.jpg

Problem solved?

Lawmaker:
Elimination of
contaminants,
nutrient recovery ✓



WWTP operator:
achievement of legal target, ✓
low risks, ?
low costs ?

Agriculture:
Independence from
fertiliser imports, ✓
cheap fertiliser ?

Conclusions

- **Over-fulfilment of regulations should be the aim for HTC**
- **Optimum of energy demand, chemical use and P recovery rate crucial**
- **HTC for P recovery more expensive than P recovery from ash**
- **Revenues from hydrochar usage and WWTP integration required**
- **Comparison of P recovery technologies is difficult (system boundaries, educts, products)**

Lisa Röver, ESPC 2022, 20.06.2022

Project abonoCARE (07/2019 – 12/2022)
FKZ: 03WKDI2E

Tasks at DBFZ:

- Phosphorus recovery
- High temperature dewatering in combination with hydrothermal carbonisation

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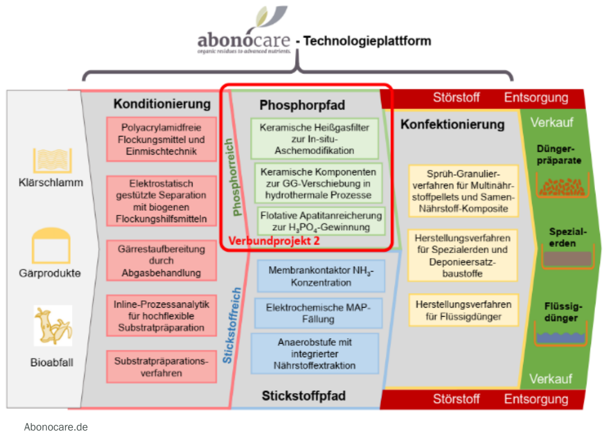

Abonocare.de

7. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP
Hydrothermale Prozesse

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Poster Speed Presentation

Fiaz Ahmad, Estonian University of Life Sciences

Conversion of Chlorella Vulgaris and liquid fraction of anaerobic digestate into biocrude by hydrothermal co-liquefaction

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Vicky Shettigondahalli Ekanthalu, Universität Rostock

Pre- and post-acid treatment effects during hydrothermal carbonization of sewage sludge on Phosphorus-transformation characteristics and the properties of hydrochar

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The recovery of phosphorus (P) from alternative P-rich residues is essential to meet the global demand for food. In spite of the fact that sewage sludge is a potential source of phosphorus, its direct application to agricultural lands is controversial due to the presence of heavy metals and organic pollutants. In addition, most available technologies for P recovery and sludge management are expensive because they often require mandatory dewatering of sewage sludge. The hydrothermal carbonization (HTC) process has gained considerable attention in this regard as a promising process for treating sewage sludge without the need for dewatering, and it can simultaneously recover P.

This study aimed to examine and compare the effects of acid addition (H2SO4) during and after HTC of sewage sludge on P leaching and hydrochar characteristics. Results of the study indicated that even with the same amount of H2SO4, P leaching from solid to liquid phase was significantly higher when acid was used after the HTC process instead of acid utilization during the HTC process. In contrary to using acids during the HTC process, utilization of acids after HTC has led to the reduction in the acid-buffering capacity of sewage sludge and an increase in solubility of phosphate precipitating metal ions which had a greater influence on the mobilization of P from solid to liquid phase. On the other hand, using H2SO4 in different process conditions did not have a great impact on the proximate analysis results or calorific value of the hydrochar produced.

Julia Lüttmann, Carl von Ossietzky Universität Oldenburg

Hydrochar of bioplastics – Porosity investigation and process water treatment by Chlorella vulgaris

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Due to the increasing amounts of wastes, especially plastic waste, there is a need for an effective and ecological utilisation. Conversion of moist biomass, like manure or degradable bioplastics, via Hydrothermal Carbonisation (HTC) into hydrochar is one promising route to fulfil the demanding requirements of the Paris Agreement. The obtained hydrochar is structurally and energetically like fossil brown coal exhibiting only small surface areas of about 10 m2/g. Thus, a following activation step is necessary to reach the high surface areas required for adsorption processes. Biomass derived activated carbons are promising alternatives to petroleum-based products like adsorbents, electrode material or catalyst carrier.

HTC (220 °C, 3-4 h) with lignin, cellulose, spruce wood, and a bioplastic based on corn starch (MS) were carried out. For example, activation of hydrochar made from bioplastic based on corn starch at 650 °C for 1 h results under different atmospheres (steam, N2, CO2) in moderate surface areas of 419-434 m2/g. An increased activation temperature to 750 °C enhances the surface area up to 30 %. Also, an improved contact between char and gas phase using an “activation cage” augments the surface area by 79 %. Thus, at 750 °C under steam high surface areas of about 900 m2/g are obtained; the absence of steam (only N2 or CO2) however, the activation leads to only 490 m2/g.Next to the hydrochar a significant amount of process water also forms. The obtained process waters contain high amounts of organic substances which result in a total carbon (TC) up to 35 g/L (cellulose) and caused by formation of organic acids a low pH of 2.6 (MS). Thus, in an industrial application a process water treatment is mandatory and often a costly procedure. We tested the HTC process water as a potential growth medium for microalgae like Chlorella vulgaris. The highest TC degradation is shown by the process water from spruce wood (65 %). During their growth Chlorella vulgaris produces useful fatty acids, primarily C16 and C18, which could be applied in food and biodiesel production. The easy and ecological degradation of some main substances in the HTC water, i.e. formic acid, levulinic acid and 5-HMF (5 Hydroxymethylfurfural) by Chlorella vulgaris was systematically carried out. Some other chemicals, e.g., benzoic acid as aromatic compound, were tested for comparison. The results point out that the degradation by Chlorella vulgaris is depending on the complexity of the substance. The highest TC degradation rate within 14 days was observed for formic acid (92 %). Aromatic carbon systems like benzoic acid are not degraded. Thus, process water from lignin is less degraded (49 %) due to its high content of aromatic compounds, mostly derivates of coniferyl alcohol. The fatty acid content depends on the used carboxylic acid; the highest fatty acid content being reached with levulinic acid (5.6 %).

Veranstalter

DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH

Unser Auftrag

Das DBFZ wurde 2008 durch das ehemalige Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz (BMELV) mit dem Ziel gegründet, eine zentrale Forschungseinrichtung für alle relevanten Forschungsfelder der Bioenergie einzurichten und die Ergebnisse der sehr vielschichtigen deutschen Forschungslandschaft in diesem Sektor zu vernetzen. Der wissenschaftliche Auftrag des DBFZ ist es, die effiziente Integration von Biomasse als eine wertvolle Ressource für eine nachhaltige Energiebereitstellung wissenschaftlich im Rahmen angewandter Forschung umfassend zu unterstützen. Dieser Auftrag umfasst technische, ökologische, ökonomische, soziale sowie energiewirtschaftliche Aspekte entlang der gesamten Prozesskette (von der Produktion, über die Bereitstellung, bis zur Nutzung). Die Entwicklung neuer Prozesse, Verfahren und Konzepte wird durch das DBFZ in enger Zusammenarbeit mit industriellen Partnern begleitet und unterstützt. Gleichzeitig erfolgt eine enge Vernetzung mit der öffentlichen deutschen Forschung im Agrar-, Forst- und Umweltbereich, wie auch mit den europäischen und internationalen Institutionen. Gestützt auf diesen breiten Forschungshintergrund erarbeitet das DBFZ darüber hinaus wissenschaftlich fundierte Entscheidungshilfen für die Politik erarbeiten.

Kommende Veranstaltungen

09. FEBRUAR 2023

Präsenz-Veranstaltung

14. Fachgespräch „Partikelabscheider in häuslichen Feuerungen“

22.-23. MÄRZ 2023

Präsenz-Veranstaltung

VI. International Conference on Monitoring and Control of Anaerobic Digestion Processes

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