Deutsches Biomasseforschungszentrum
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DBFZ

# HTP EXPERT FORUM

## 8th Expert Forum on Hydrothermal Processes

TAGUNGSREADER 33


#HTP2024

www.htp-inno.de

LEIPZIG | NOVEMBER 12/13, 2024

HTP
Hydrothermale Prozesse

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# HTP EXPERT FORUM

## 8th Expert Forum on Hydrothermal Processes

## TAGUNGSREADER, No. 33

November 12/13, 2024, Leipzig

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# Welcome note from Dr. Benjamin Herklotz, DBFZ

**Dear Participants of the 8th Expert Forum on Hydrothermal Processes,**

I would like to take this opportunity to thank you for your active participation in the 8th edition of our international expert forum dedicated to hydrothermal processes.

Hydrothermal technologies are crucial parts of modern biorefinery concepts that are needed for a sustainable bio-based economy. They are still focus of intense research. Even more as new fields of hydrothermal applications like hydrothermal humification (HTH) and catalytic hydrothermal synthesis (HTS) emerge besides established hydrothermal carbonisation (HTC), hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG). Witnessing advances in all these technologies from edition to edition emphasizes the importance of this event and intense exchange.

However, the curveball session at the end of the first day of the event illustrated the major challenges yet to be resolved for hydrothermal technologies to step into practice at larger scale. In the past, focussing on hydrothermal technologies as a stand-alone technology have not proven to be economically feasible. Today, hydrothermal technologies should be understood as an integral part of modern biorefinery concepts pre-treating biomass, upgrading intermediates or post-treating residual streams.

One of these major challenges was intensely discussed on the second day of the event. The necessary treatment of aqueous side streams of hydrothermal processes focusses on technologies like anaerobic digestion, wet oxidation, freeze drying and much more. The best option may turn out to be a combination of those technologies to overcome drawbacks of individual approaches.

I hope you enjoyed your time at DBFZ and in Leipzig with intense discussions, behind-the-scenes views into our labs and networking with like-minded people from all over Europe. I assure you, I did!

As scientific head of the event, I would like to thank you once again. Not only for your participation, but specifically for your intensive contribution on a professional scientific level, many new impulses and insights into your research topics. With your help, the Expert Forum on Hydrothermal Processes was a success and will be able to be a success in future editions.

With kind regards,

Dr. Benjamin Herklotz
Working Group Leader Hydrothermal Processes





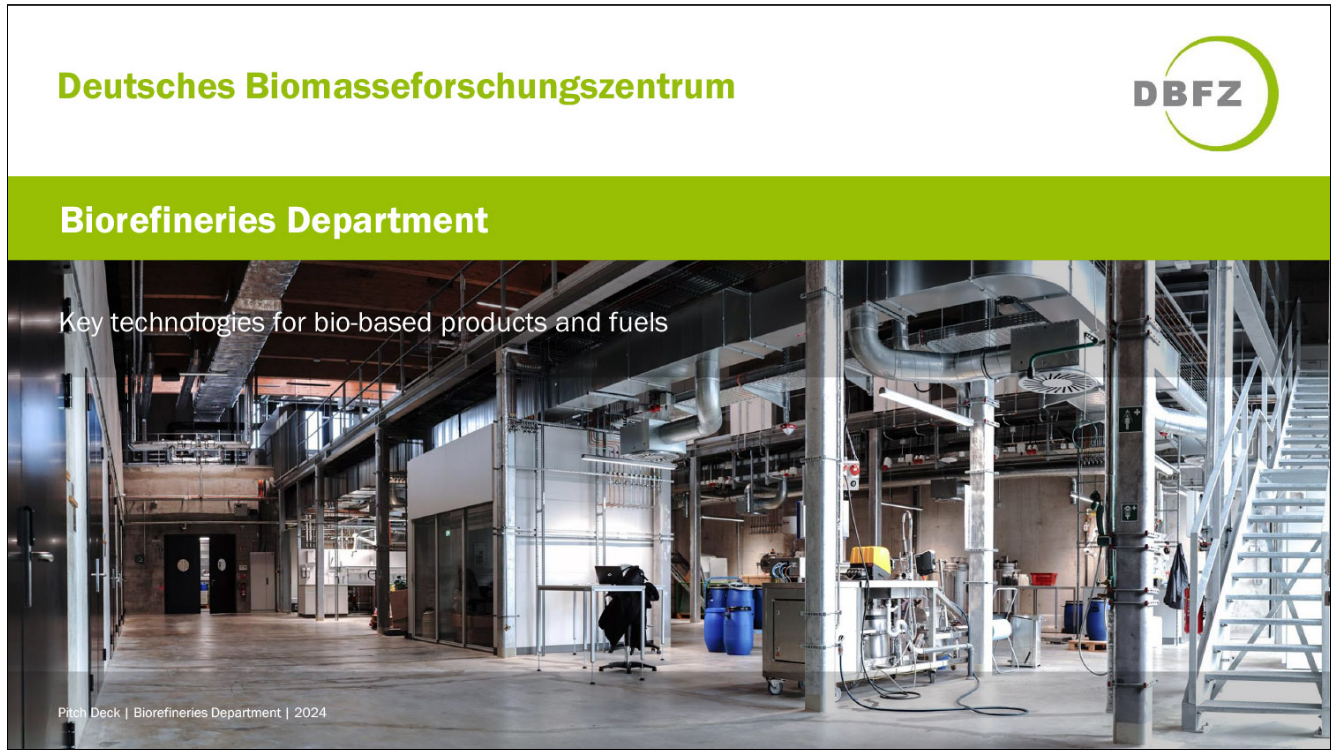
# Impressions







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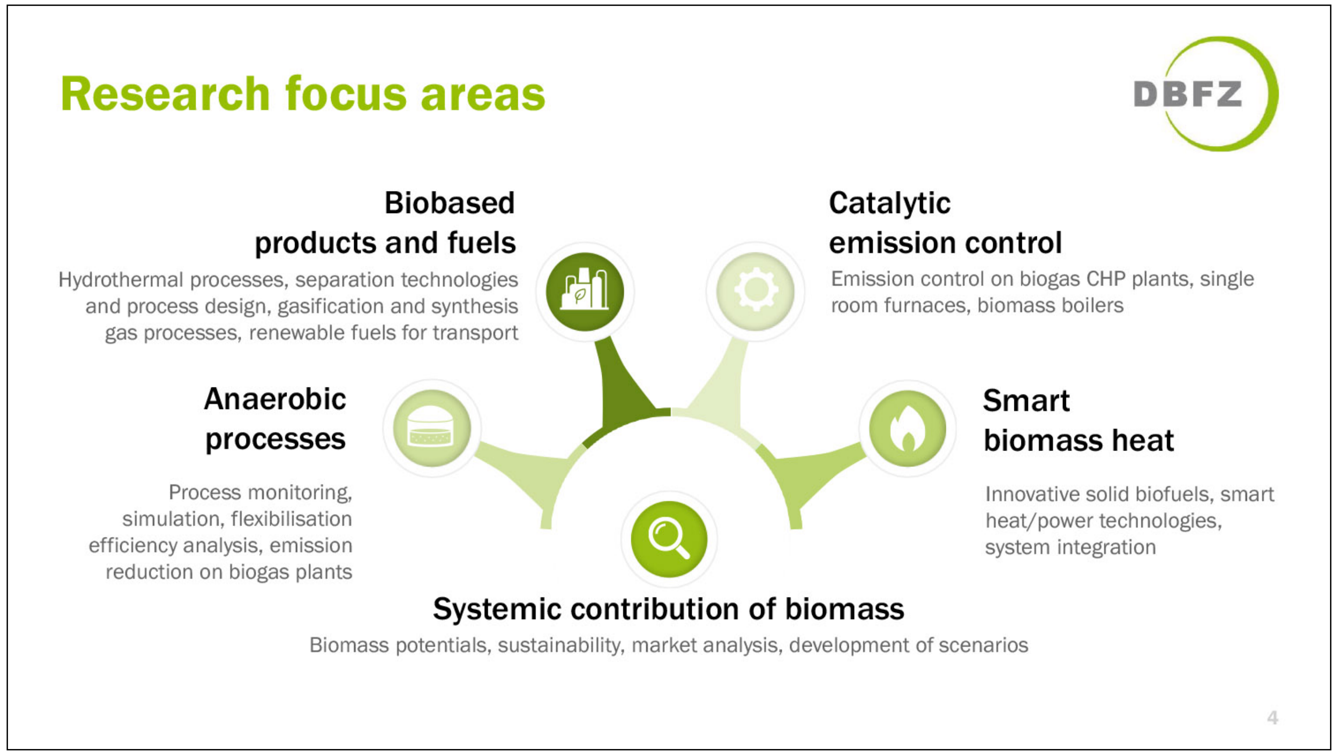
Biorefineries Department
Key technologies for bio-based products and fuels
Pitch Deck | Biorefineries Department | 2024


DBFZ in a nutshell
DBFZ
Applied Research & Development for Biomass
Non-profit company,
Shareholder Federal republic Germany
275 Employees in 2023
About 29 mil. EUR turnover (2023)
Certified ISO 9001
Familie & Beruf etc.






Research focus areas
DBFZ
Biobased products and fuels
Hydrothermal processes, separation technologies and process design, gasification and synthesis gas processes, renewable fuels for transport
Catalytic emission control
Emission control on biogas CHP plants, single room furnaces, biomass boilers
Anaerobic processes
Process monitoring, simulation, flexibilisation efficiency analysis, emission reduction on biogas plants
Smart biomass heat
Innovative solid biofuels, smart heat/power technologies, system integration
Systemic contribution of biomass
Biomass potentials, sustainability, market analysis, development of scenarios
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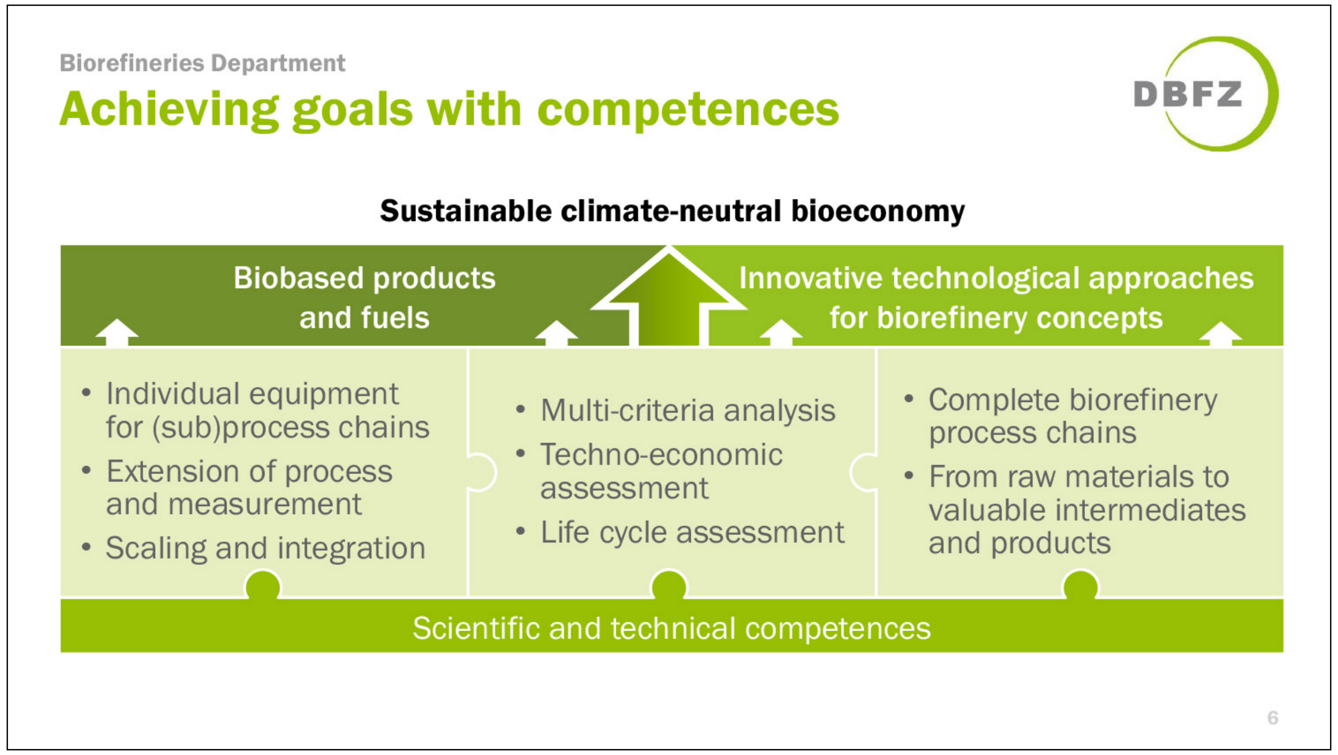
Biobased products and fuels
Biorefineries Department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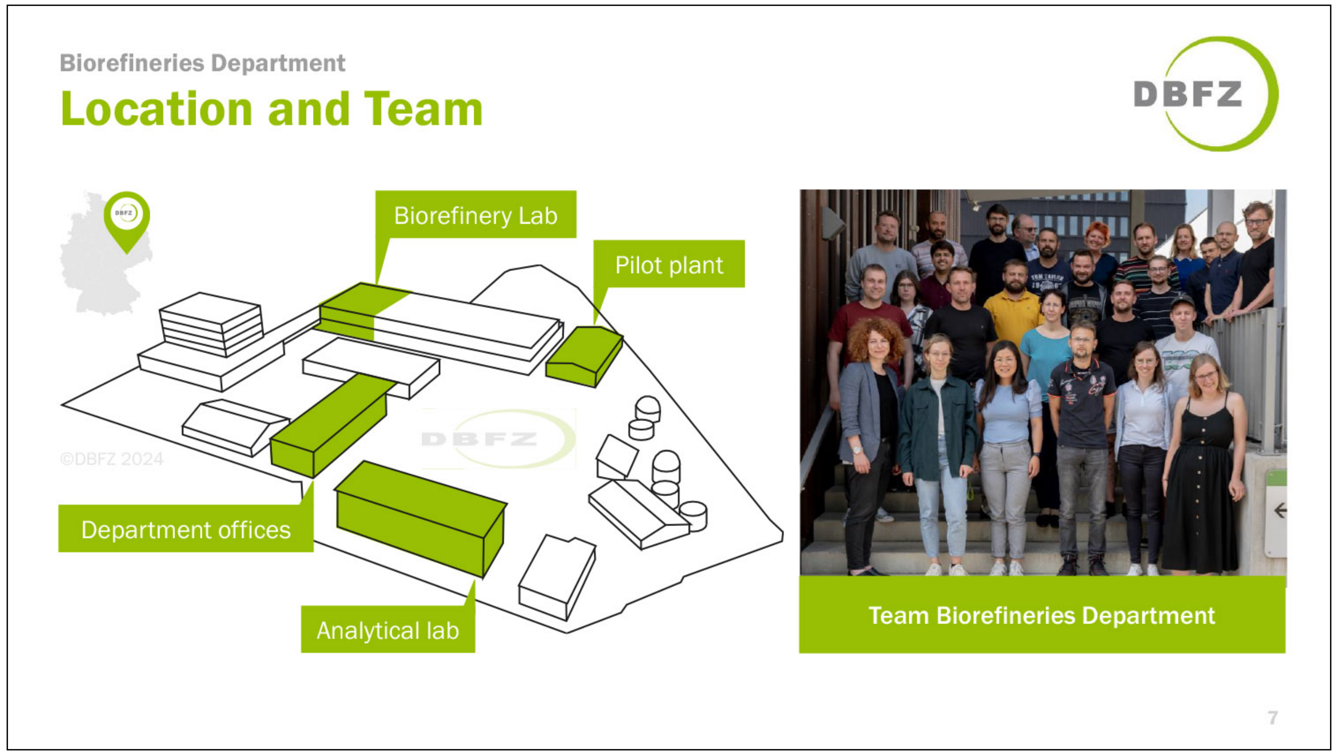
Achieving goals with competences
DBFZ
Sustainable climate-neutral bioeconomy
Biobased products and fuels
Innovative technological approaches for biorefinery concepts
• Individual equipment for (sub)process chains
• Extension of process and measurement
• Scaling and integration
• Multi-criteria analysis
• Techno-economic assessment
• Life cycle assessment
• Complete biorefinery process chains
• From raw materials to valuable intermediates and products
Scientific and technical competences
6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Location and Team
DBFZ
Biorefinery Lab
Pilot plant
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Department offices
Analytical lab
Team Biorefineries Department
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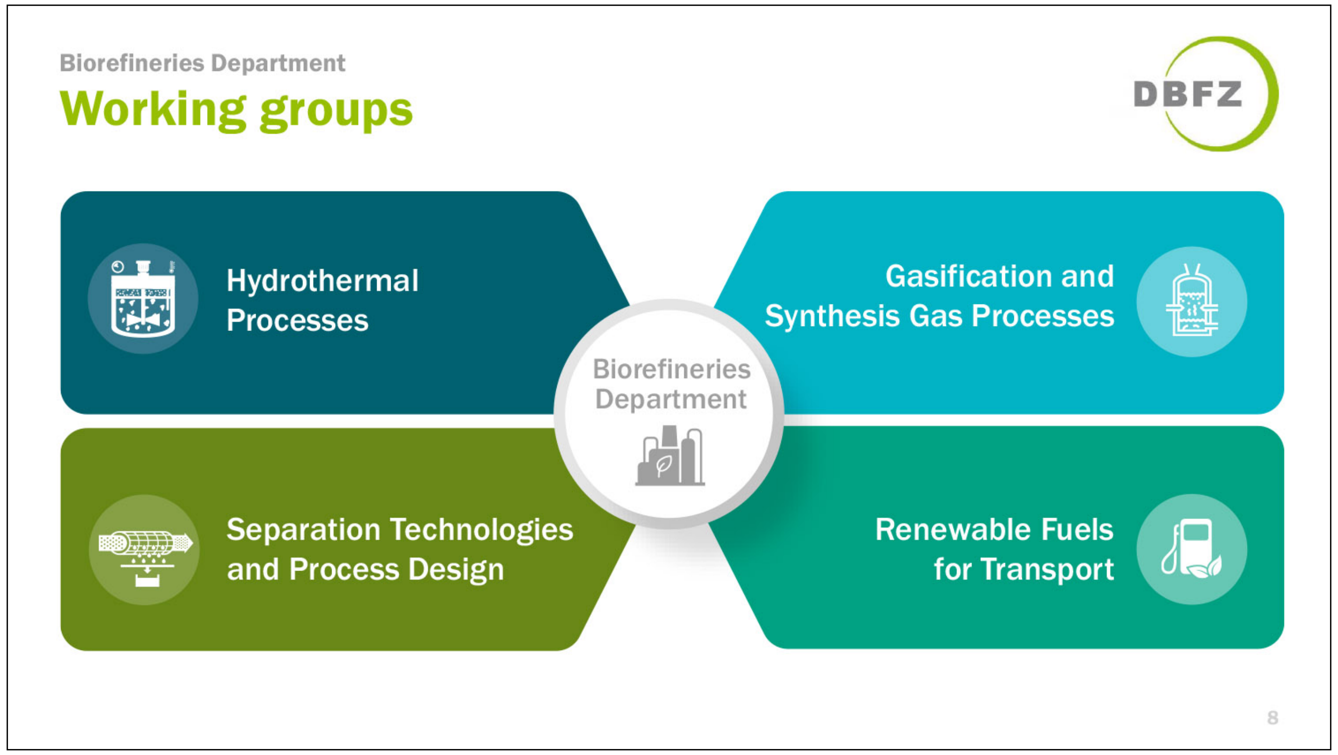
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Working groups
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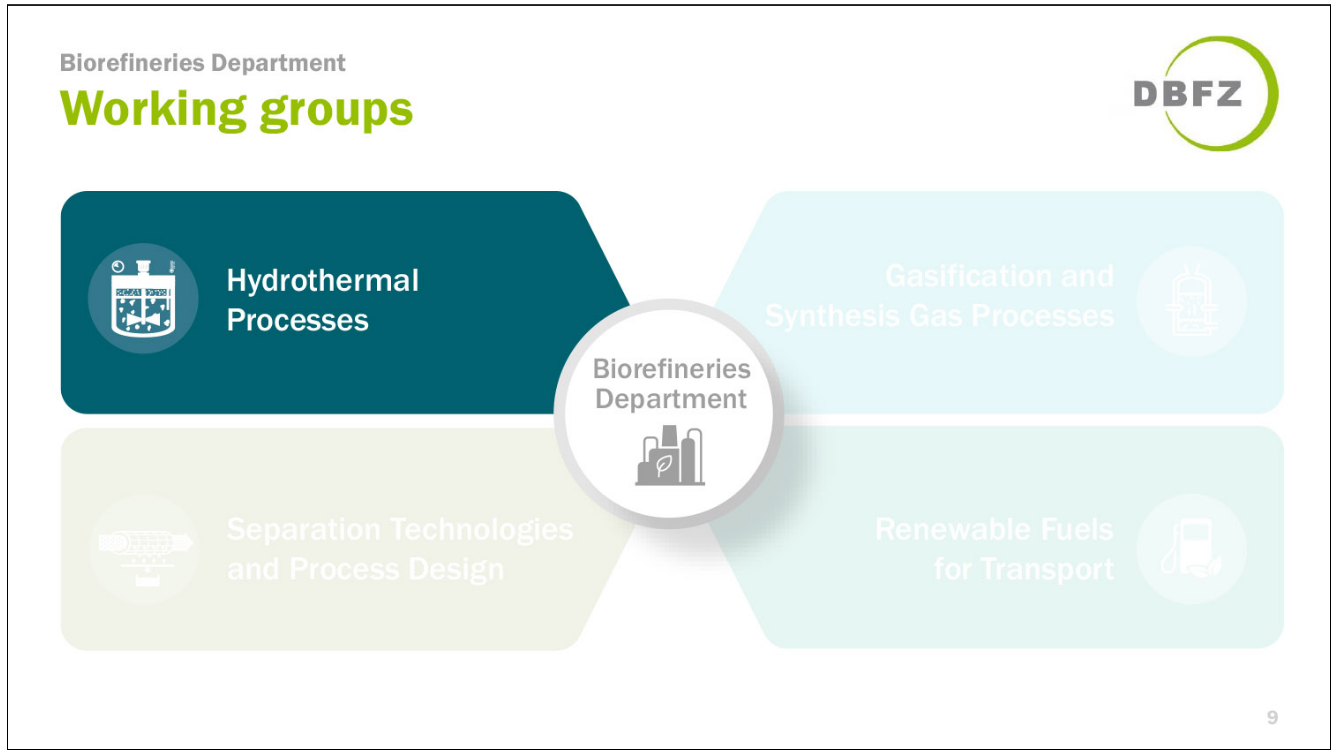
Hydrothermal Processes
Gasification and Synthesis Gas Processes
Biorefineries Department
Separation Technologies and Process Design
Renewable Fuels for Transport
8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Renewable Fuels for Transport
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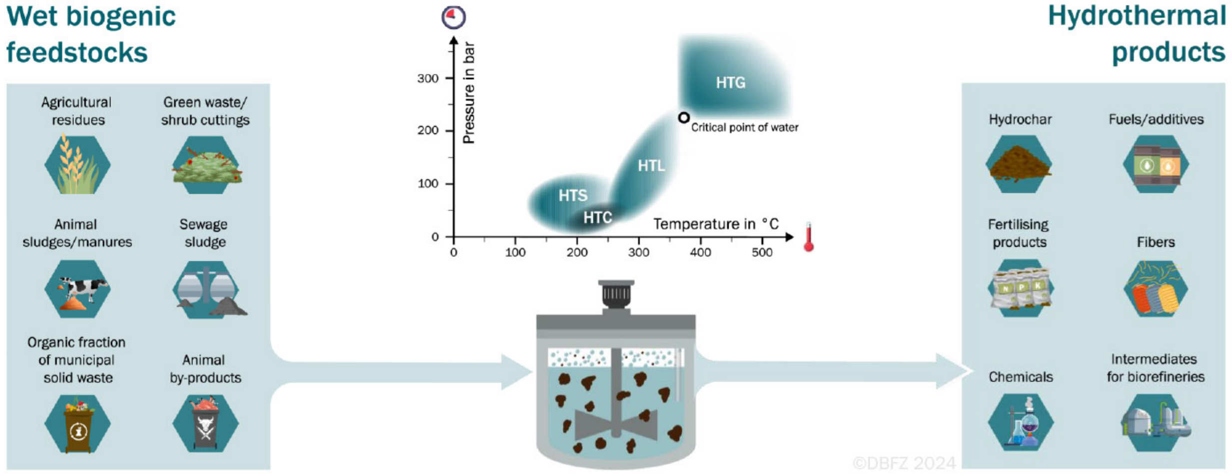
Working group: Hydrothermal Processes

## Overview

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Working group: Hydrothermal Processes

## Focus topics

| | |
|---|---|
| Processes and technologies for hydrothermal biomass conversion: Hydrothermal carbonisation (HTC), hydrothermal liquefaction (HTL) and catalytic hydrothermal synthesis (HTS) | Biomass disintegration and fractionation under mild hydrothermal conditions for downstream processes |

| | | |
|---|---|---|
| Hydrothermal processes as an opportunity to recover nutrients from biogenic residues | Hydrothermally produced chars for use as an energy source, adsorbent or in plant substrates | Production of chemicals and fuel precursors using hydrothermal processes |

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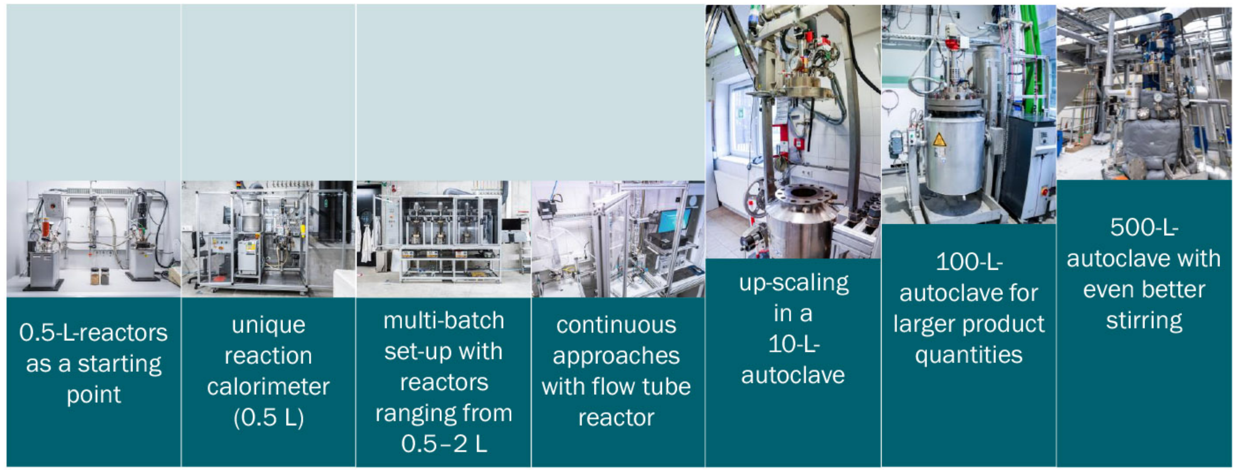
Working group: Hydrothermal Processes

## Equipment

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# KEYNOTE

*Aidan Smith, Aarhus University*

## Developing an oxygen assisted hydrothermal reactor for dewatering sludges

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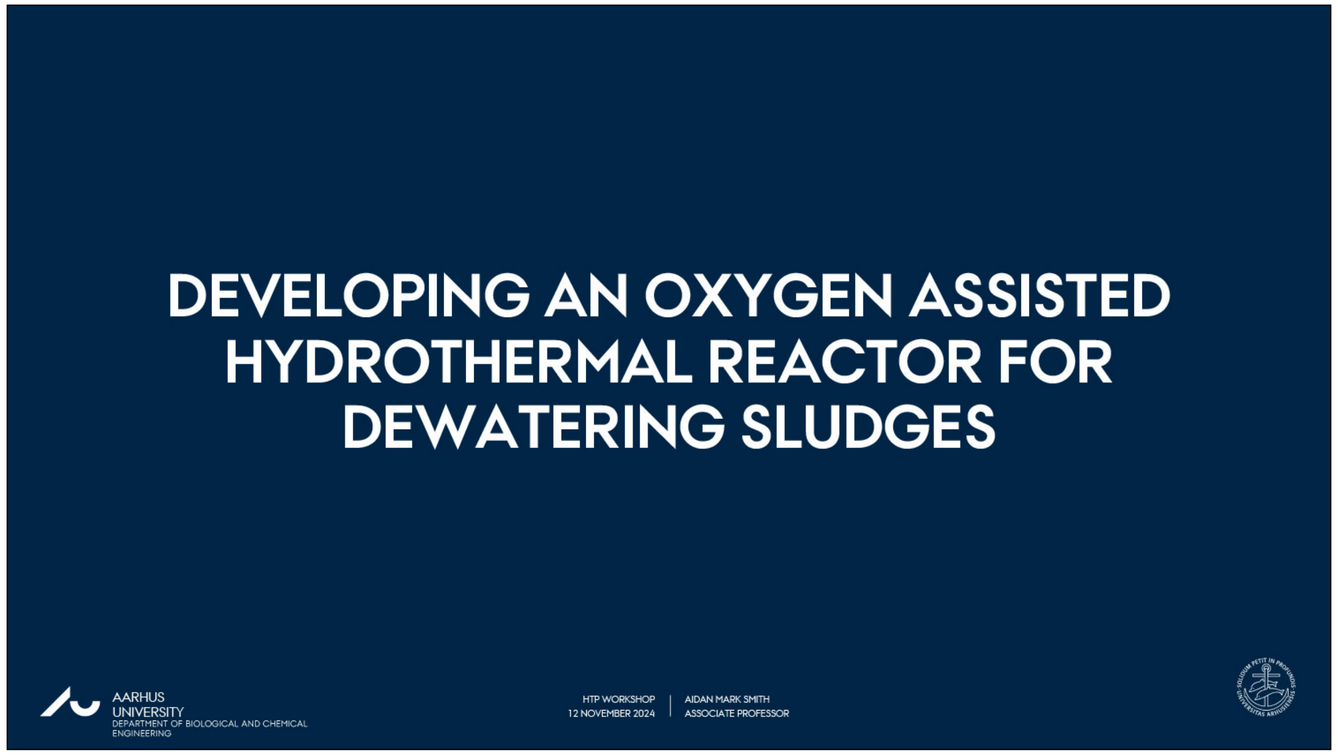
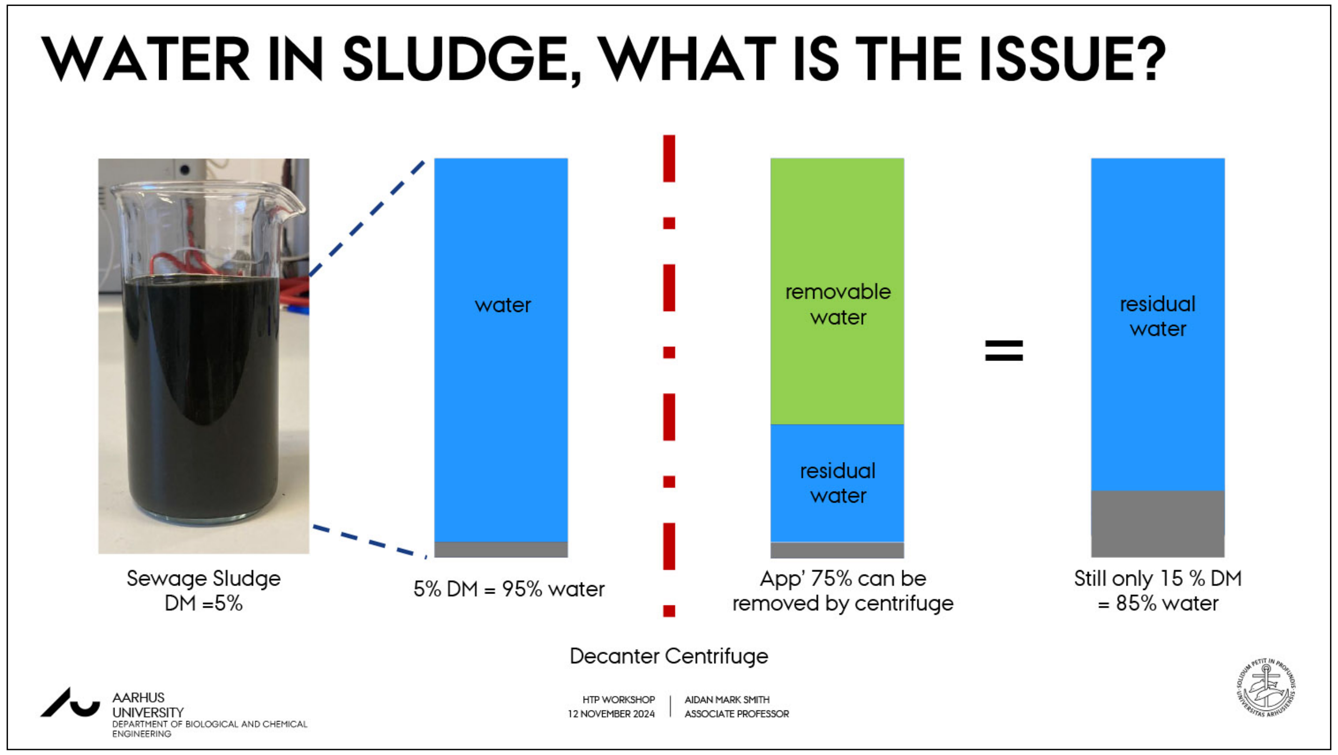
Abstract was not available at the time of editorial deadline.



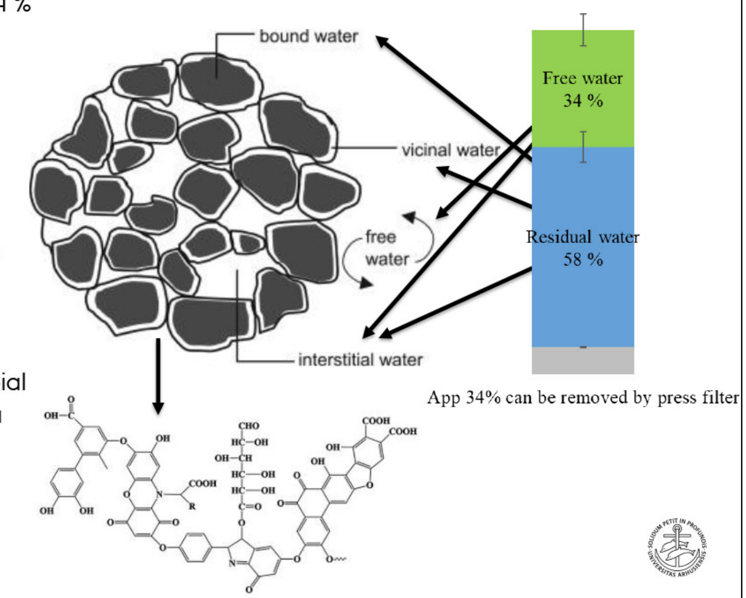




# WATER TYPES IN SLUDGE

- Sludge without centrifuge 93-96 % water, 7-4 % DM.
- Free water: removed by pressing or gravity settling.
- Interstitial water: water trapped between particles in the sludge.
- Vicinal water is hydrogen bonded to oxygen functional groups.
- Chemical bound water.
- Sludges contains humic material and microbial biomass so probably has a high surface area and a preponderance of hydroxyl functional groups.
- How does HTC sort this?

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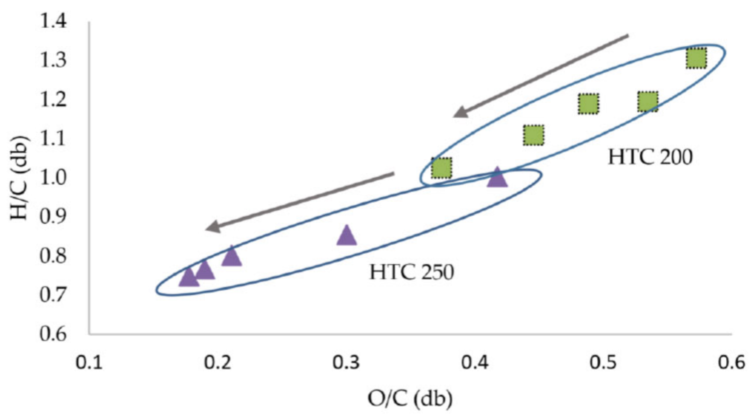
# HTC IS OVERWELMINGLY DEHYDRATION

Severity Factor = Log (time (min)) * e [(temp (°C) -100)/14.75]




Overend and Chornet (1987) Fractionation of lignocellulosics by steam-aqueous pretreatments. Philosophical Transactions of the Royal Society of London Series A, Mathematical and Physical Sciences;321(1561):523-36.

Smith and Ross (2019). The Influence of Residence Time during Hydrothermal Carbonisation of Miscanthus on Bio-Coal Combustion Chemistry. Energies, 12, 523.

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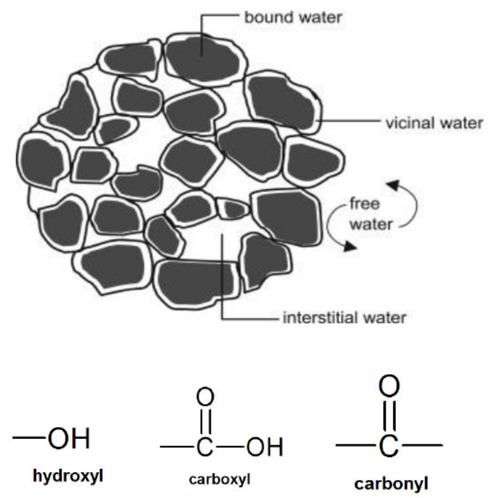
# HTC AND DEWATERING

- HTC will remove surface functional groups
- Vicinal water is hydrogen bonded to functional groups
  - Reduced functional groups = reduced vicinal water?
- Dehydrated sludge releases vicinal into free water
  - Free water easily mechanically recovered
- Functional groups increase polarity
  - Polar attracts water
  - Non-polar repels water
- Dehydrated sludge is hydrophobic – will actively expel water
- Aromatisation reactions should further flocculate material

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# INITIAL HYPOTHESIS

"Surface functionality is a major variable in determining a materials ability to retain water by influencing the materials polarity and by providing bonding sites for the water molecules, leading to a requirement for thermal drying"

"Dehydration of the sludges molecular structure, will reduce the materials polarity and reduce the waters binding sites, reducing vicinal water"

"Dehydration and dewatering via HTC can be done using less energy than conventional thermal drying?"

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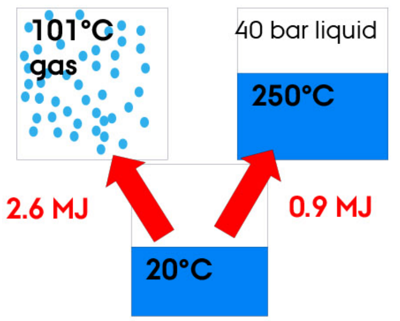
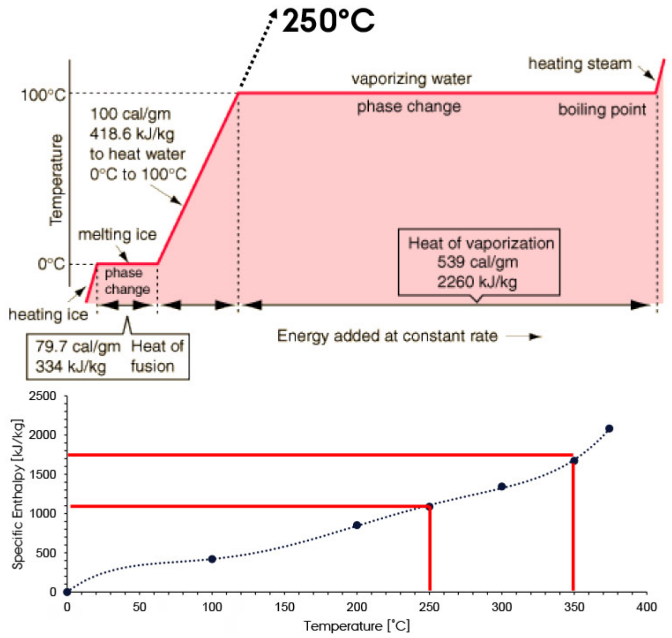
# LATENT HEAT OF VAPORIZATION

**Energy required to heat 1 kg of water**

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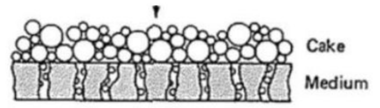
# SO DOES THIS HYPOTHESIS HOLD WATER…. OR NOT…. LITURALLY

Processing – Parr reactor

- Residence time: 5 minutes and 1 hour
  - Shorter resonance times favour better throughput but might reduce repolymerisation / dehydration
- Kozeny-Carman theory can then be used to quantify behaviour using different filters




$$\frac{p_k}{l} = \frac{v_0 \eta (2-\varepsilon)^2}{\varepsilon^3 d_p^2}$$

**Kozeny Carman equation**

*Assumes that the filtrate flows laminar though thin capillary tubes through the filter cake*

$p_k$ is the pressure loss over the filter cake
$l$ is the thickness of the filter cake
$v_0$ is the velocity of the filtrate
$\eta$ viscosity
$\varepsilon$ porosity of filter cake
$d$ particle diameter

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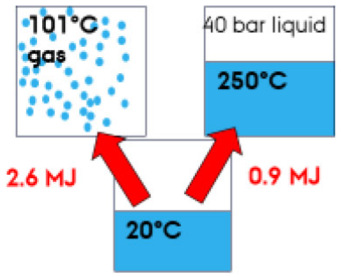
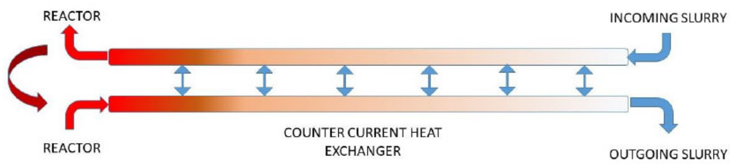
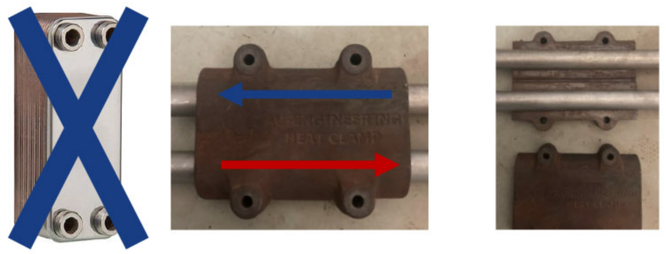
# IMPORTANCE OF HEAT EXCHANGER




- Heat clamp heat exchanger can transfer 85 % heat exchange between pipes
- To thermally dry sediment it requires 2.6 MJ/kg water
- HTC requires 0.9 MJ/kg water
- With heat exchange it can be reduced to 0.2 MJ/kg



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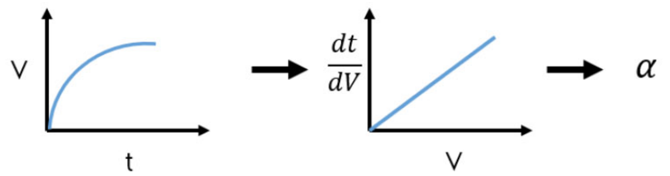
# CALCULATING KOZENY-CARMAN THEORY

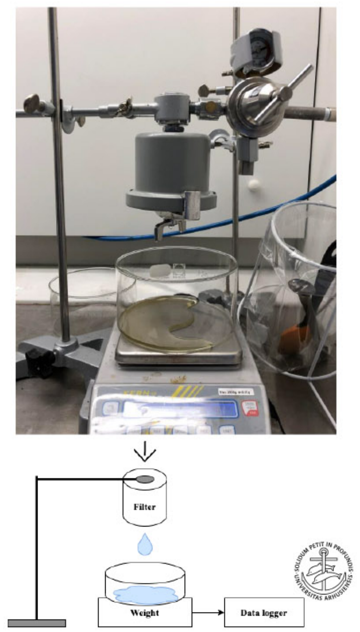



$$\frac{\tau}{V} = \frac{1}{2}\frac{\alpha s \eta}{p_f} V + \frac{\alpha s \eta}{p_f} V_d$$

$\tau$ = time
V= total amount of filtrate per m2
$V_d$= imagined filtrate per m2
s= dry matter content of slurry (kg/m3)
$pf$ =pressure loss over filter cake
$\alpha$=specific cake resistance

$\frac{1}{2}\frac{\alpha s \eta}{p_f}$= slope $\frac{\alpha s \eta V_d}{p_f}$=intercept

$$\frac{\tau}{V} = slope * V + intercept$$

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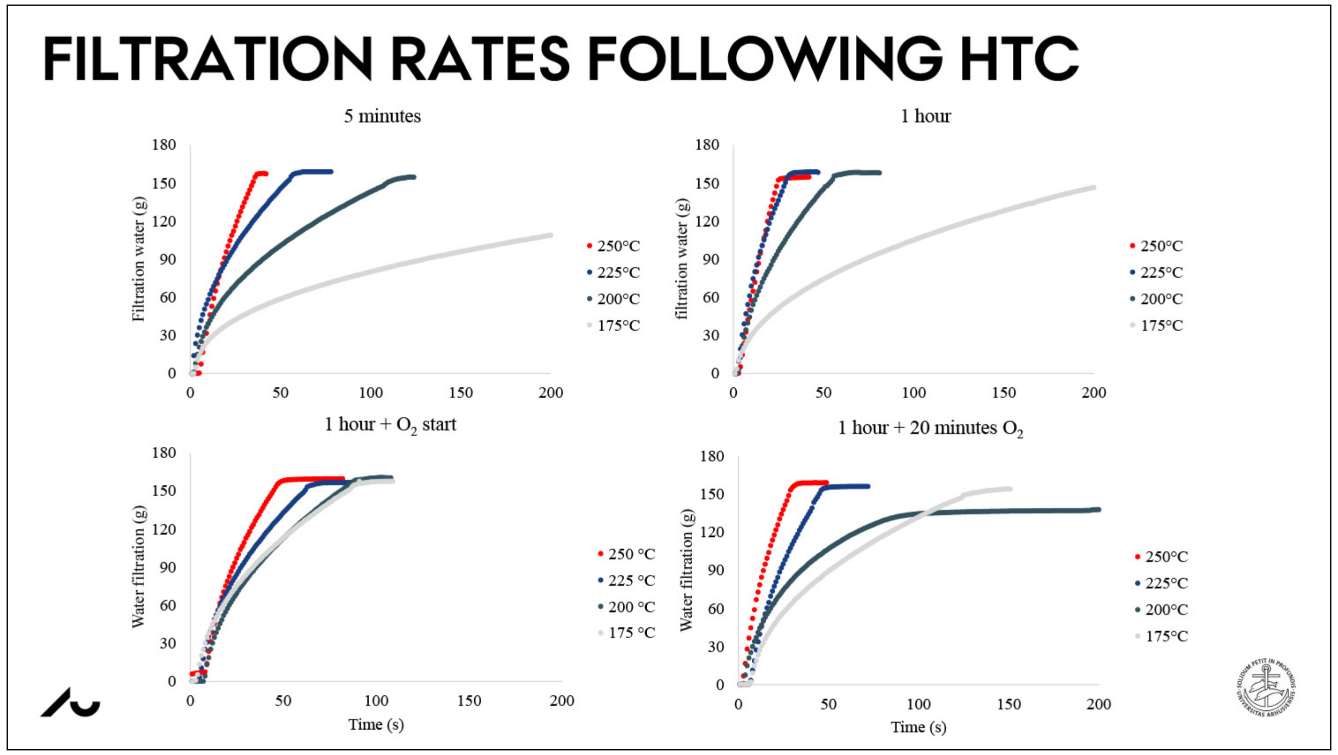
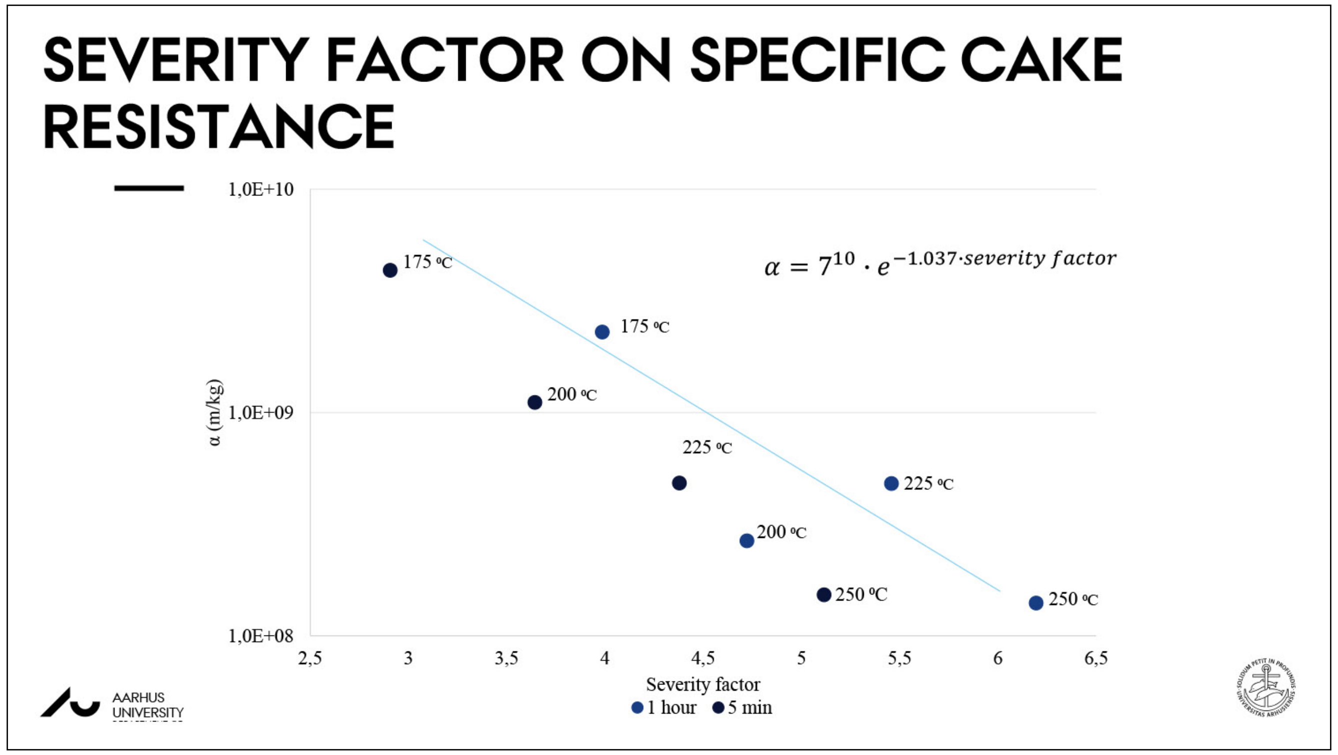

FILTRATION RATES FOLLOWING HTC
5 minutes
1 hour
1 hour + $O_2$ start
1 hour + 20 minutes $O_2$
Filtration water (g)
Water filtration (g)
Time (s)
250°C
225°C
200°C
175°C


SEVERITY FACTOR ON SPECIFIC CAKE RESISTANCE
$\alpha = 7^{10} \cdot e^{-1.037 \cdot severity\ factor}$
α (m/kg)
Severity factor
1 hour
5 min
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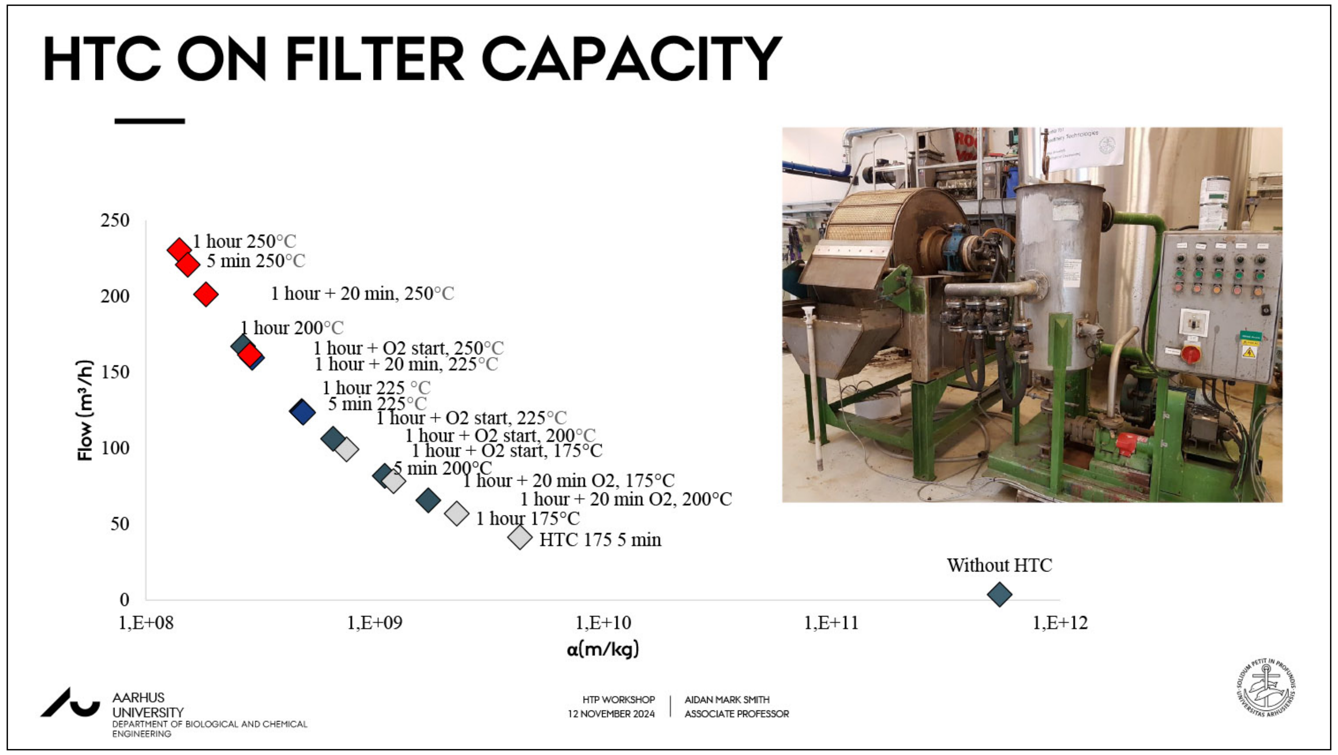
HTC ON FILTER CAPACITY
Flow (m³/h)
α(m/kg)
1 hour 250°C
5 min 250°C
1 hour + 20 min, 250°C
1 hour 200°C
1 hour + O2 start, 250°C
1 hour + 20 min, 225°C
1 hour 225 °C
5 min 225°C
1 hour + O2 start, 225°C
1 hour + O2 start, 200°C
1 hour + O2 start, 175°C
5 min 200°C
1 hour + 20 min O2, 175°C
1 hour + 20 min O2, 200°C
1 hour 175°C
HTC 175 5 min
Without HTC
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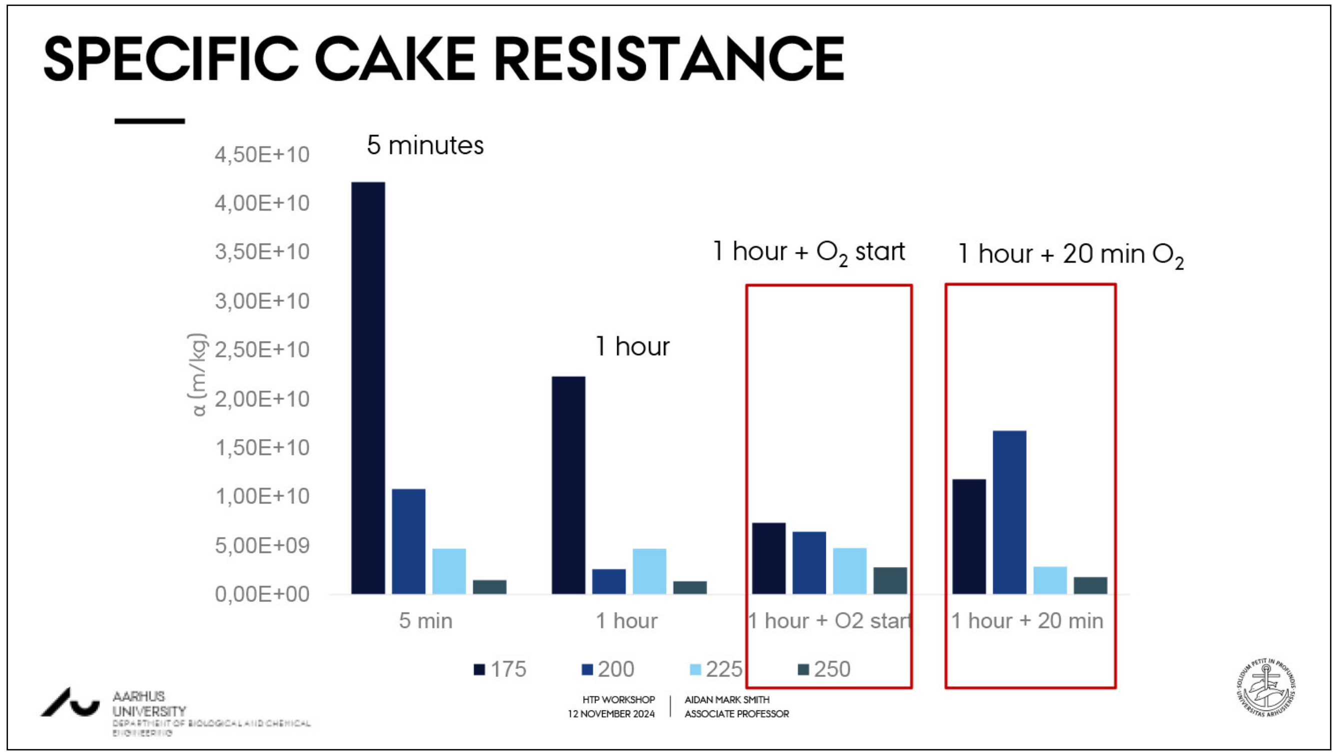
SPECIFIC CAKE RESISTANCE
5 minutes
1 hour
1 hour + $O_2$ start
1 hour + 20 min $O_2$
α (m/kg)
5 min
1 hour
1 hour + O2 start
1 hour + 20 min
175
200
225
250
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# UPSCALING

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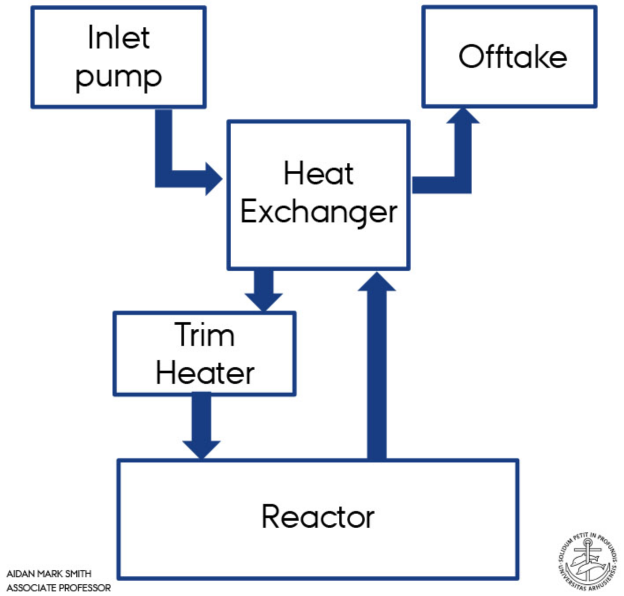
# ENERGY AND CONTINUOUS REACTOR SYSTEMS

- On continuous systems outgoing material heats the incoming material in heat exchanger
- Reaction temperature "topped up" by trim heater
- Slurry maintained at set temperature in reactor for desired resonance time
- Higher water content = lower DM throughput
- Slurries above 15% DM difficult to pump
- HTC = Carbonisation = Exothermic Reaction
  - 0.5 - 1.5 MJ/kg(dm) heat release
  - @15% DM = 0.07-0.23 MJ kg feed

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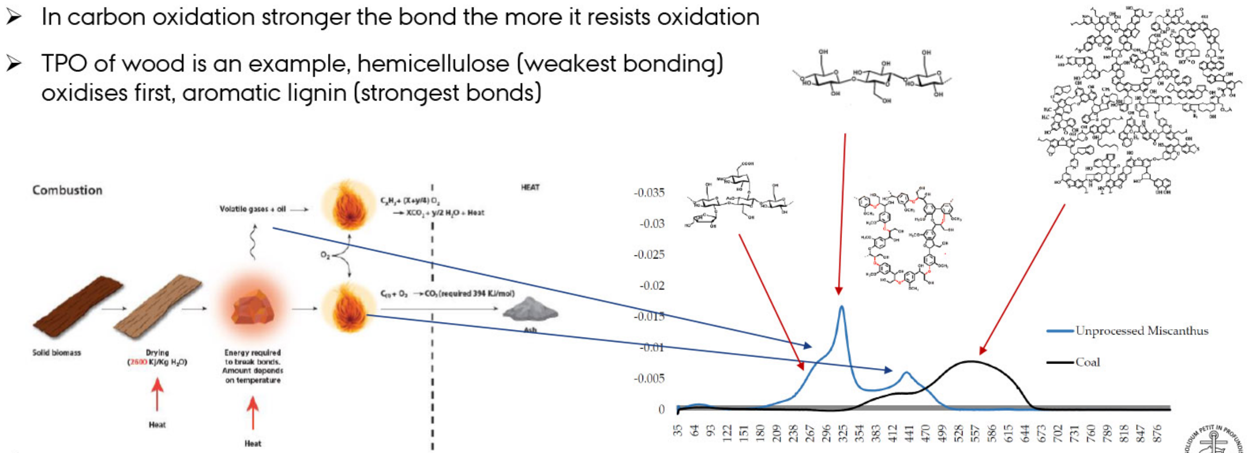
# OXYGEN AND CARBON – COMBUSTION THEORY

- In carbon oxidation stronger the bond the more it resists oxidation
- TPO of wood is an example, hemicellulose (weakest bonding) oxidises first, aromatic lignin (strongest bonds)

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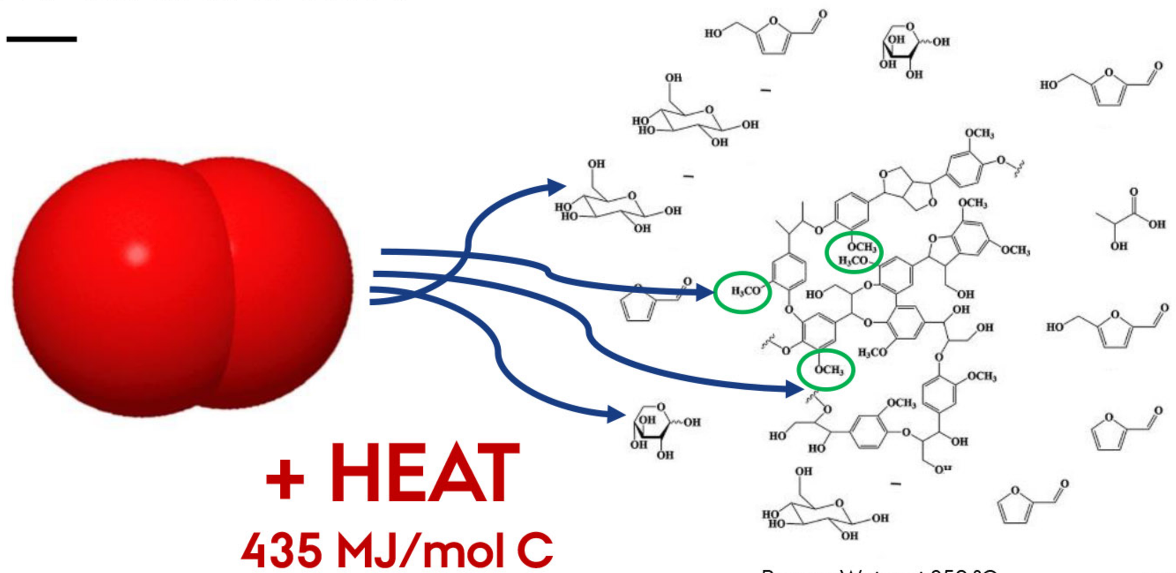
# WET OXIDATION

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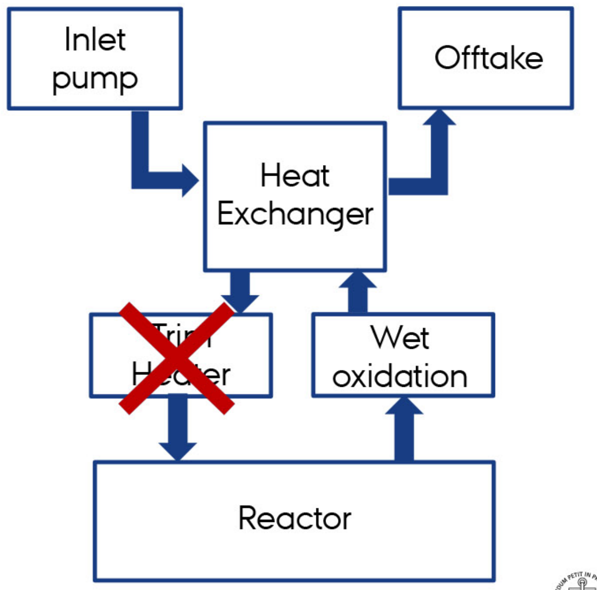
# WET OX IN CONTINUOUS SYSTEM?

- At end of reactor stage char forming reactions come to an end
- Oxidise these VFA we release energy increasing water temperature
- Higher water temperature in heat exchanger will boost heat in slurry heaving heat exchanger
- Could this negate the need for trim heater?
- Exothermic carbonisation reactions in reactor could offset heat losses?
- Will aromatic structures resist oxidation?
- Will oxygen should target VFA in aqueous phase?

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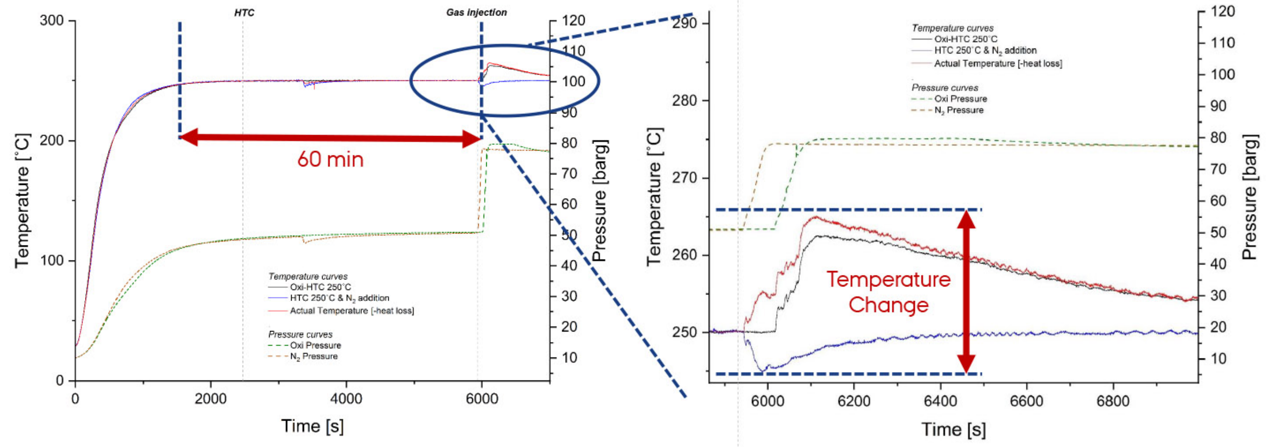
# WET OXIDATION HEAT RELEASE

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# WORKING OUT HEAT RELEASE

- Custom made reactors with very high temperature control (+/- 0.1˚C) and ability to add reactive gas
- Continuous monitoring of internal pressure and temperature
- Reactors repressurized in Ar to avoid water evaporation (latent heat)
- HTC = 175, 200, 225 and 250 ˚C +60 min resonance time
- @ 60 minutes $O_2$ or $N_2$ (reference) added and run for further 20 minutes
- $O_2$ added at 20 % stoichiometry by charging to pre-determined pressure, taking into account, $O_2$ density, media expansion...... etc.
- Differences between $O_2$ or Ar (reference) runs analysed

$$m_{add-O_2} = \frac{m_{biomass}\cdot DM \cdot x_C \cdot 0.2}{M_C}\cdot M_{O_2}$$

$$p_{O_2} = \frac{\frac{m_{add-O_2}}{\rho_{O_2}(T)}}{V_T - HS\cdot\beta}\cdot P_{amb}$$

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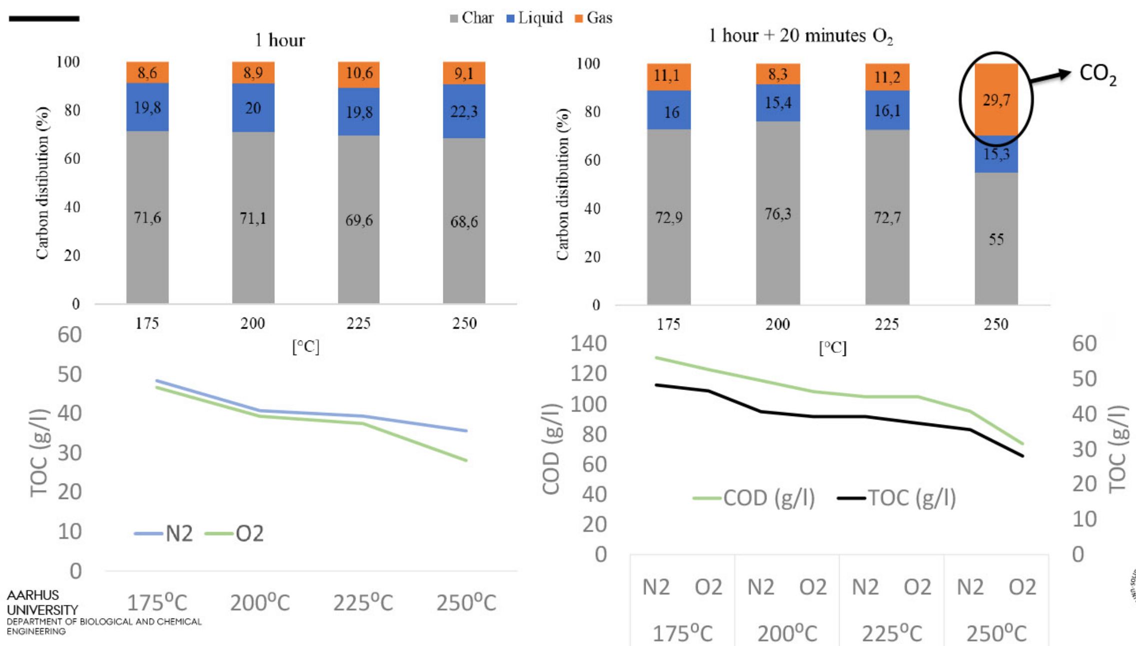
# OXYGEN AND THE CARBON BALANCE

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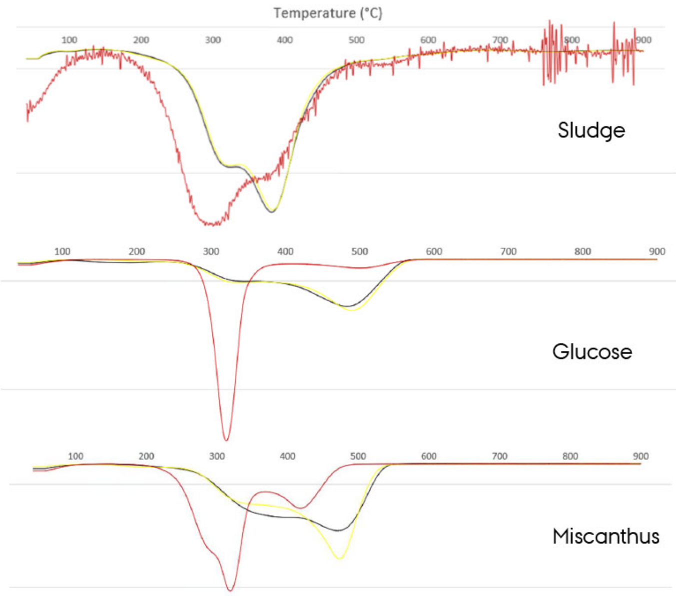
# WHERE IS THE CARBON COMING FROM?

- TGA suggests inorganics in oxi-HTC is oxidised in the process
- TPO analysis of glucose samples shows 10% weight loss between 100-250°C for HTC suggesting removal of light volatiles 🙂
- TPO analysis of sludge samples shows limited difference between samples 😐
- TPO analysis of miscanthus samples suggests reductions in aromatic carbon / reduced oxidation stability 😔

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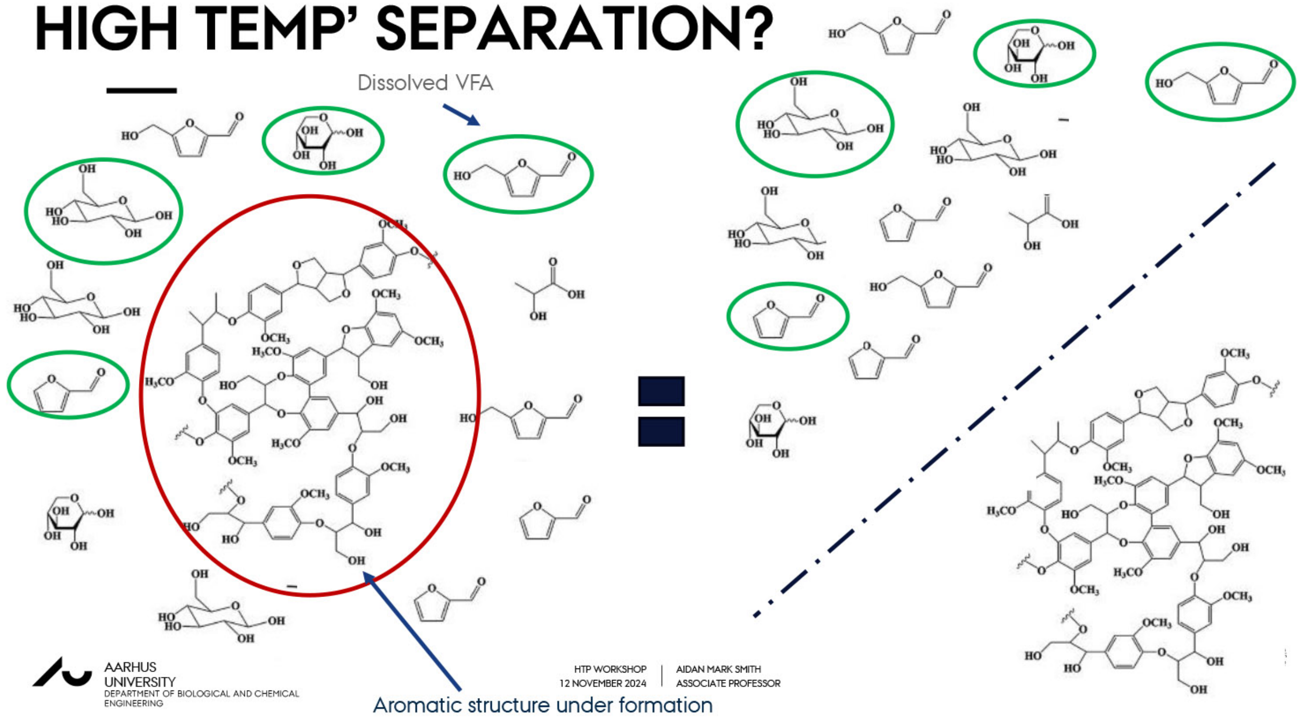
HTP WORKSHOP 12 NOVEMBER 2024 | AIDAN MARK SMITH ASSOCIATE PROFESSOR

# HIGH TEMP' SEPARATION?

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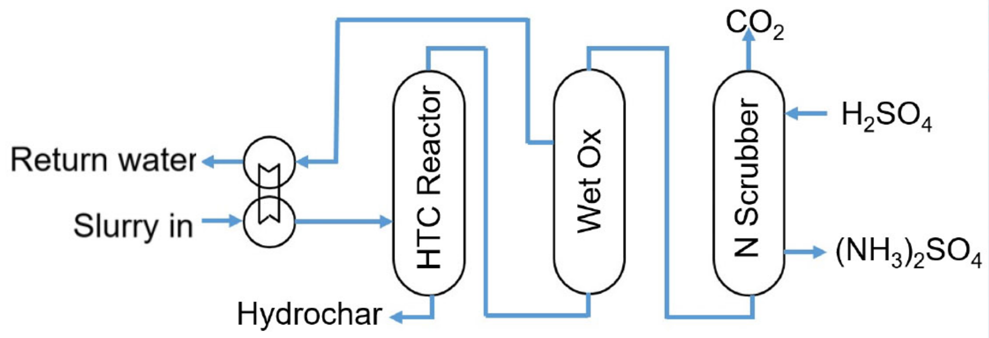
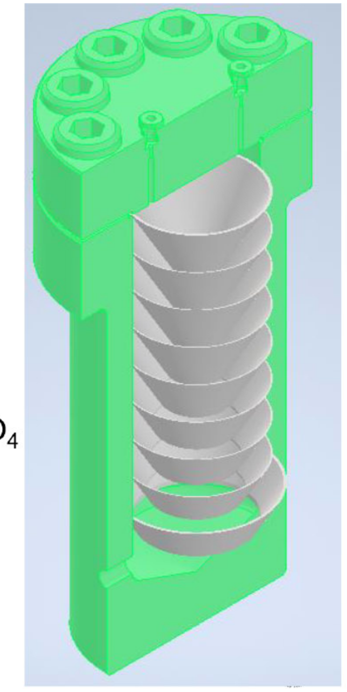
# SEPARATION DESIGN



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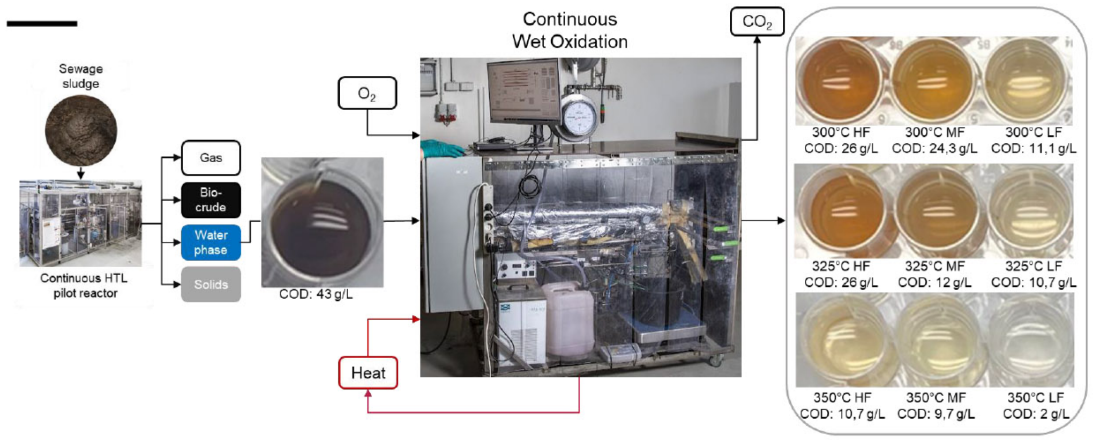
# WETOX OF PROCESS WATER WORKS… BUT THIS IS ON COLD SPERATED WATER…




Carolin Schuck will give excellent presentation on this with HTL process waters at 14:15 today

- Challenges we face here are different (apologies if it appears to contradict her presentation)

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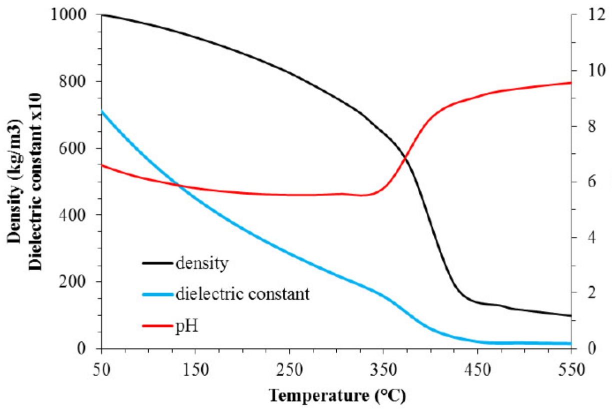
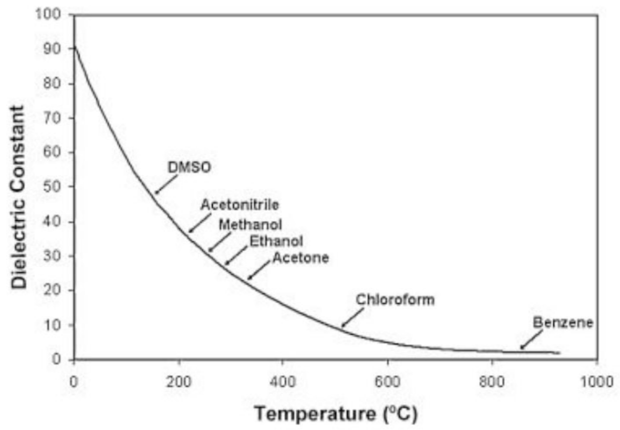
# WATER UNDER PRESSURE

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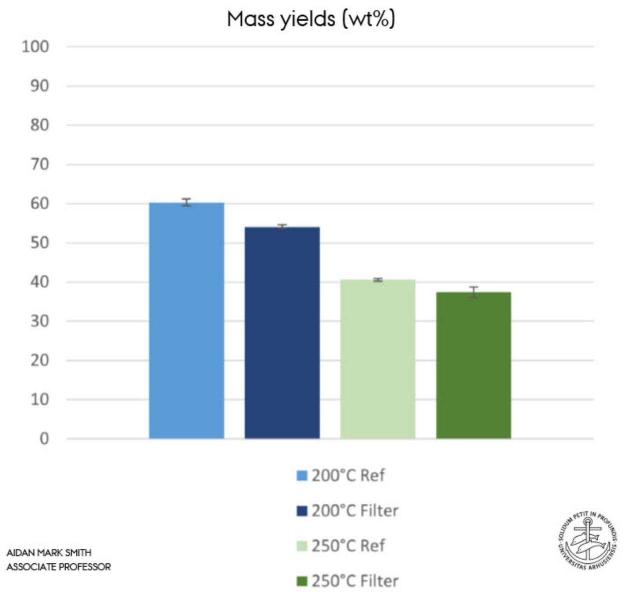
# DOES HOT FILTERING EFFECT HYDROCHAR?

- Short answer yes!!!!
- Mass yields lower… as expected
- Carbon yields lower… as expected
- At 250°C fixed carbon higher… as expected
- At 200°C fixed carbon lower… 🤔
- Carbon contents of hydrochar lower for both 200°C and 250°C 🤔
- This is ongoing work so I can tell you more next time….
- Current hypothesis is cooling / water polarity change is really important in repolymerisation with complex feedstocks

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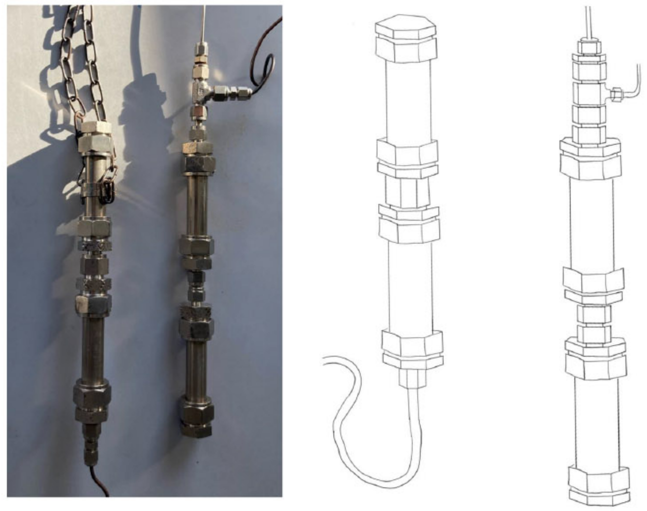
# HIGH TEMPERATURE HYDROCHAR SEPARATION

- By separating process water from char, the char hopefully wont oxidise
- Process water can be more intensely oxidised – perhaps in presence of 'catalysts'
- Hot separation might also remove problematic organic acids, PFAS etc.
- Prevents recondensation of char (could be positive or negative)
  - What are carbon yields?



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# SUMMARY

- Hypothesis that for sludges vicinal water is hydrogen bonded to oxygen functional groups and removing functional groups in HTC appears to explain HTC dewatering behaviour
- Dewaterability is correlated to reaction severity until 250°C+1h
- HTC is an exothermic process and when heat energy is effectively recovered in heat exchangers it should only require minimal energy input
- Oxygen addition immediately before heat exchanger will boost slurry temperature immediately before it passes into the heat exchanger
- Increasing temperature differential in heat exchanger should increase temperature of material entering reactor stage – minimising or removing trim heater input
- At 20% stoichiometry carbon in process water is reduced, with increased carbon in gas
- Increases in char carbon is seen in at 225°C when oxygen is added but char is oxidised when oxygen is added at 250 °C
- High temperature filtration /water separation should give cleaner char
- Cleaner water is possible if water and solids are separated before wet oxidation
- See me soon to see all the pieces joined up!!!

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ANY QUESTONS?
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# SESSION I

## FUNDAMENTAL RESEARCH OF HYDROTHERMAL PROCESSES AND THE PRODUCTION OF CHEMICALS

*Filippo Marchelli, University of Trento*

# Simulating the fluid dynamics of a hydrothermal reactor

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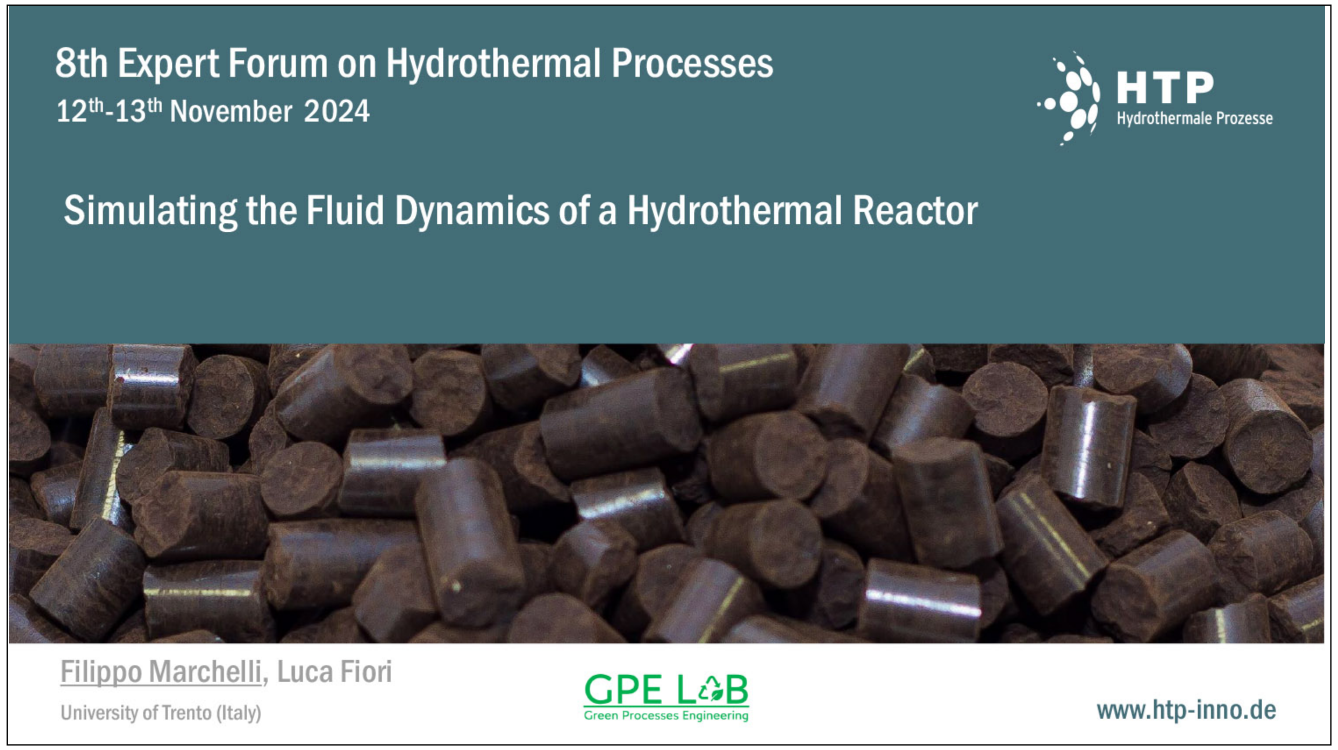
**Keywords:** Modelling, simulation, thermal homogeneity, HTP reactor, hydrothermal processes

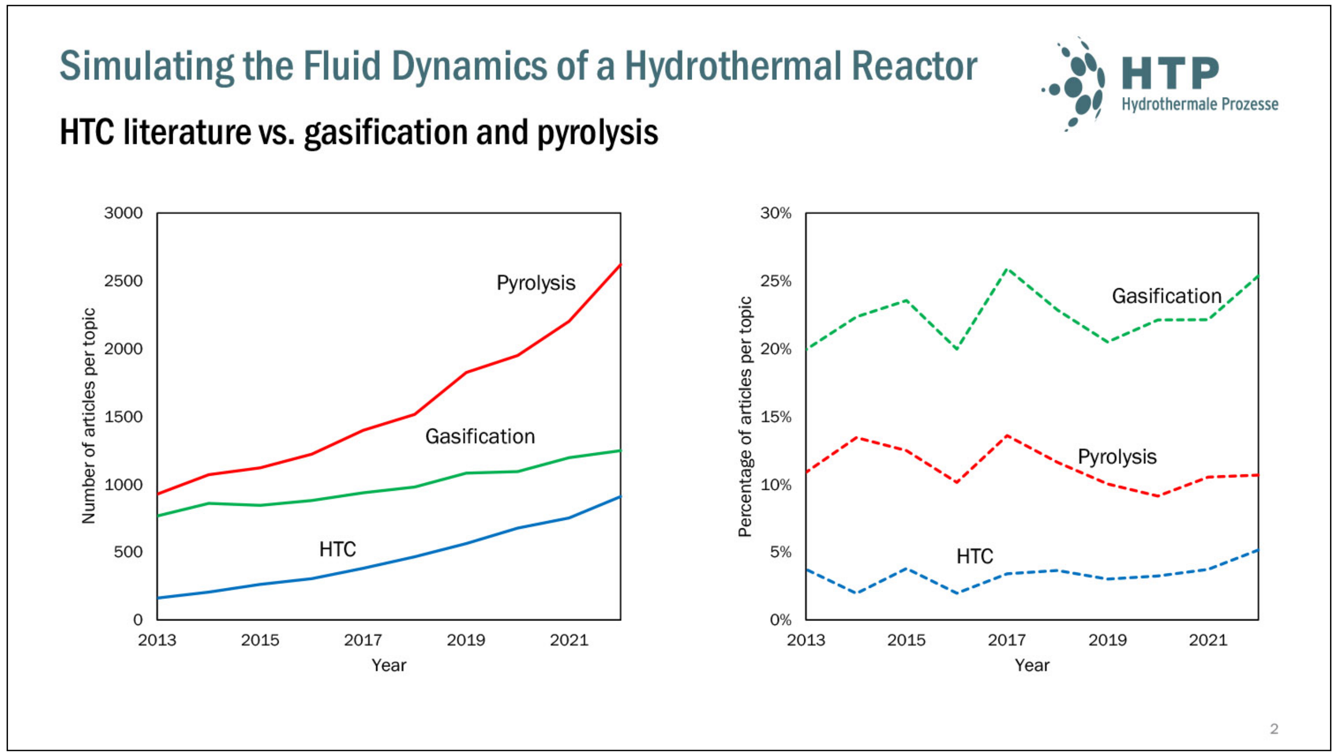
The industrial deployment of hydrothermal processes could be aided by modelling techniques, but the research on this topic has thus far been lacking. The thermo-fluid dynamic phenomena that take place within hydrothermal reactors are indeed complex and reproducing them in simulations is non-trivial. In this work, we show how to correctly take them into account to reproduce the behaviour of a bench-scale hydrothermal reactor, showing how, when dealing with plain water, natural convection is sufficient to guarantee a good thermal homogeneity even without an internal stirring element.

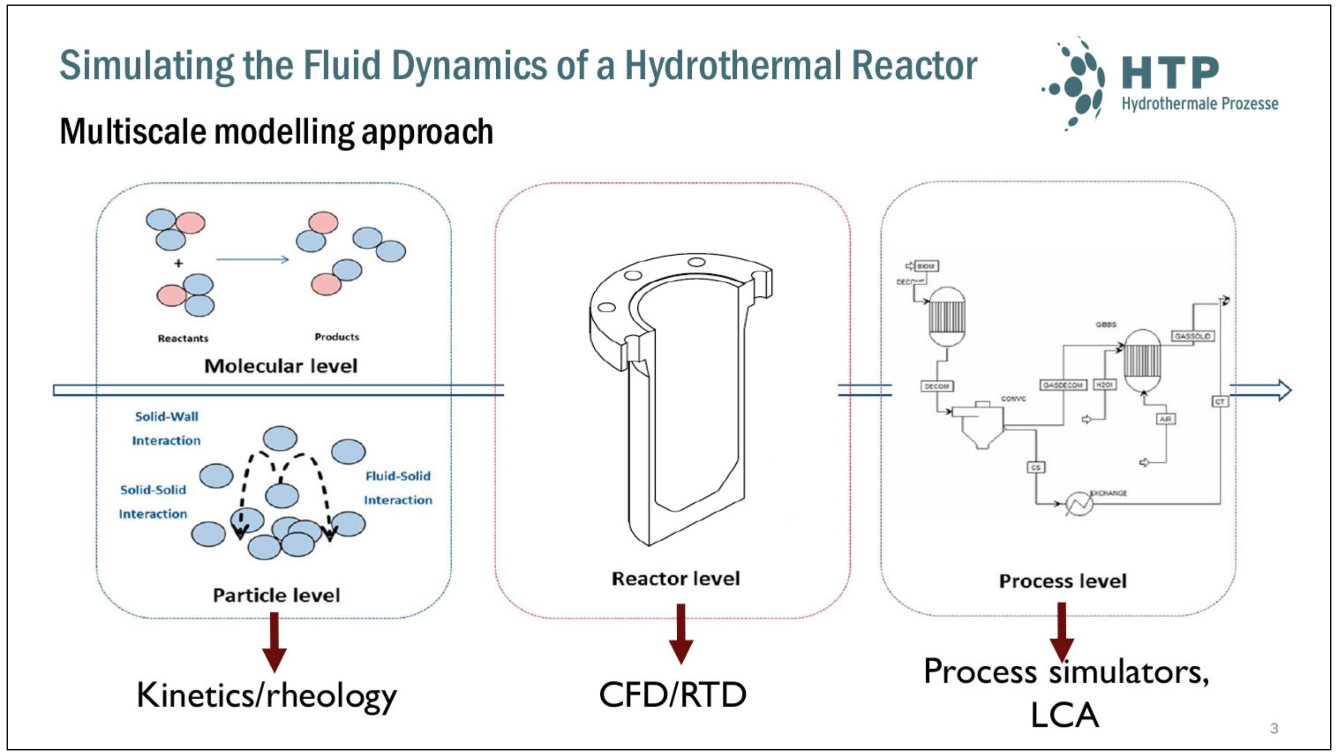
We then proceed to discuss various approaches to correctly model biomass particles, showing how these can complicate the simulative approach and in what cases the internal homogeneity of the reactor may be hindered. Various open questions remain and they will require interdisciplinary efforts.

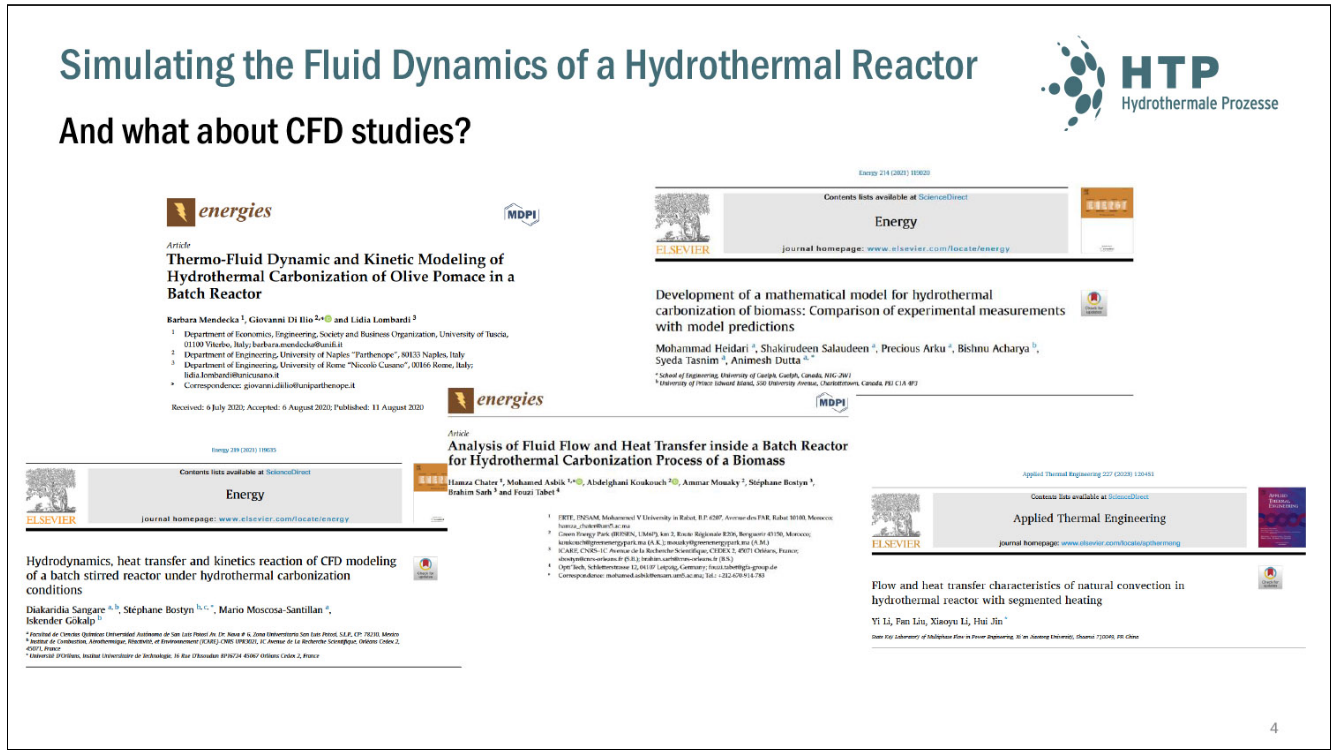






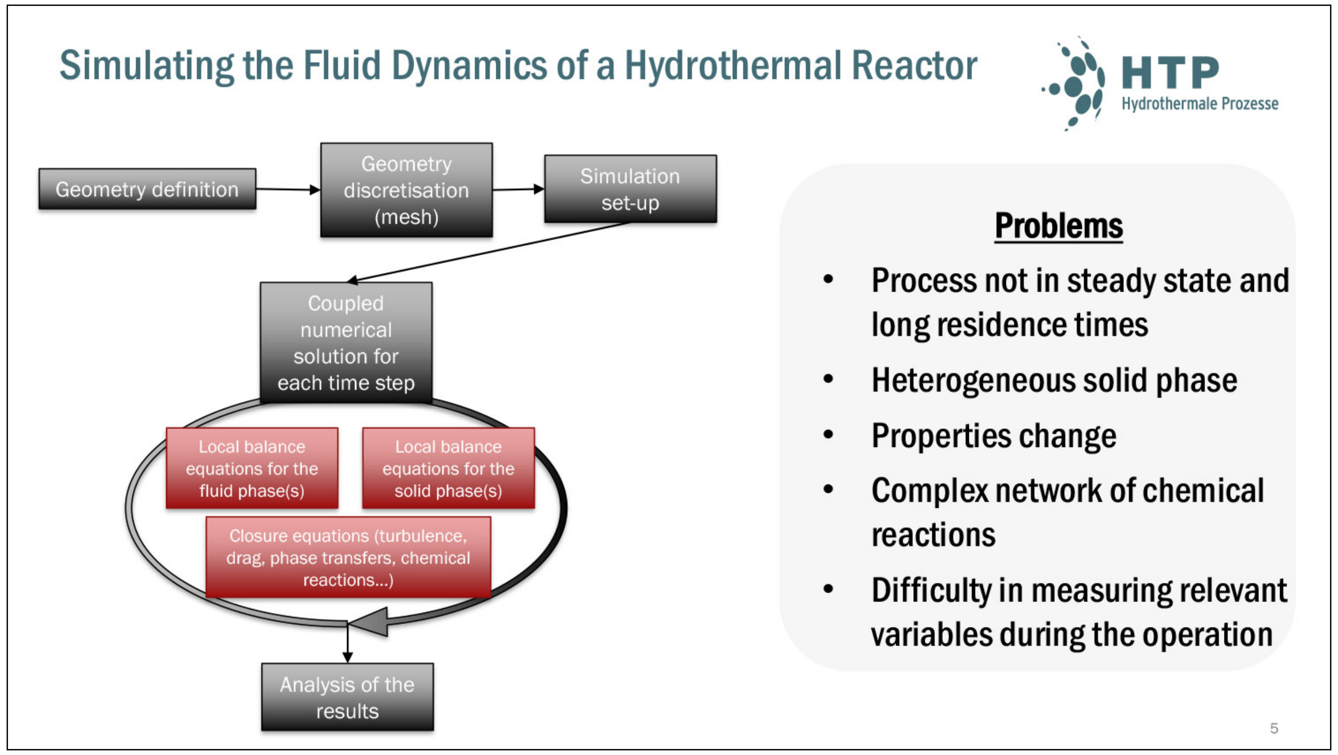




Simulating the Fluid Dynamics of a Hydrothermal Reactor
HTP Hydrothermale Prozesse
Multiscale modelling approach
Reactants
Products
Molecular level
Solid-Wall Interaction
Fluid-Solid Interaction
Solid-Solid Interaction
Particle level
Reactor level
Process level
Kinetics/rheology
CFD/RTD
Process simulators, LCA
3


Simulating the Fluid Dynamics of a Hydrothermal Reactor
HTP Hydrothermale Prozesse
And what about CFD studies?
energies
Thermo-Fluid Dynamic and Kinetic Modeling of Hydrothermal Carbonization of Olive Pomace in a Batch Reactor
Energy
Development of a mathematical model for hydrothermal carbonization of biomass: Comparison of experimental measurements with model predictions
energies
Analysis of Fluid Flow and Heat Transfer inside a Batch Reactor for Hydrothermal Carbonization Process of a Biomass
Energy
Hydrodynamics, heat transfer and kinetics reaction of CFD modeling of a batch stirred reactor under hydrothermal carbonization conditions
Applied Thermal Engineering
Flow and heat transfer characteristics of natural convection in hydrothermal reactor with segmented heating
4






Simulating the Fluid Dynamics of a Hydrothermal Reactor
HTP Hydrothermale Prozesse
Geometry definition
Geometry discretisation (mesh)
Simulation set-up
Coupled numerical solution for each time step
Local balance equations for the fluid phase(s)
Local balance equations for the solid phase(s)
Closure equations (turbulence, drag, phase transfers, chemical reactions...)
Analysis of the results
Problems
• Process not in steady state and long residence times
• Heterogeneous solid phase
• Properties change
• Complex network of chemical reactions
• Difficulty in measuring relevant variables during the operation
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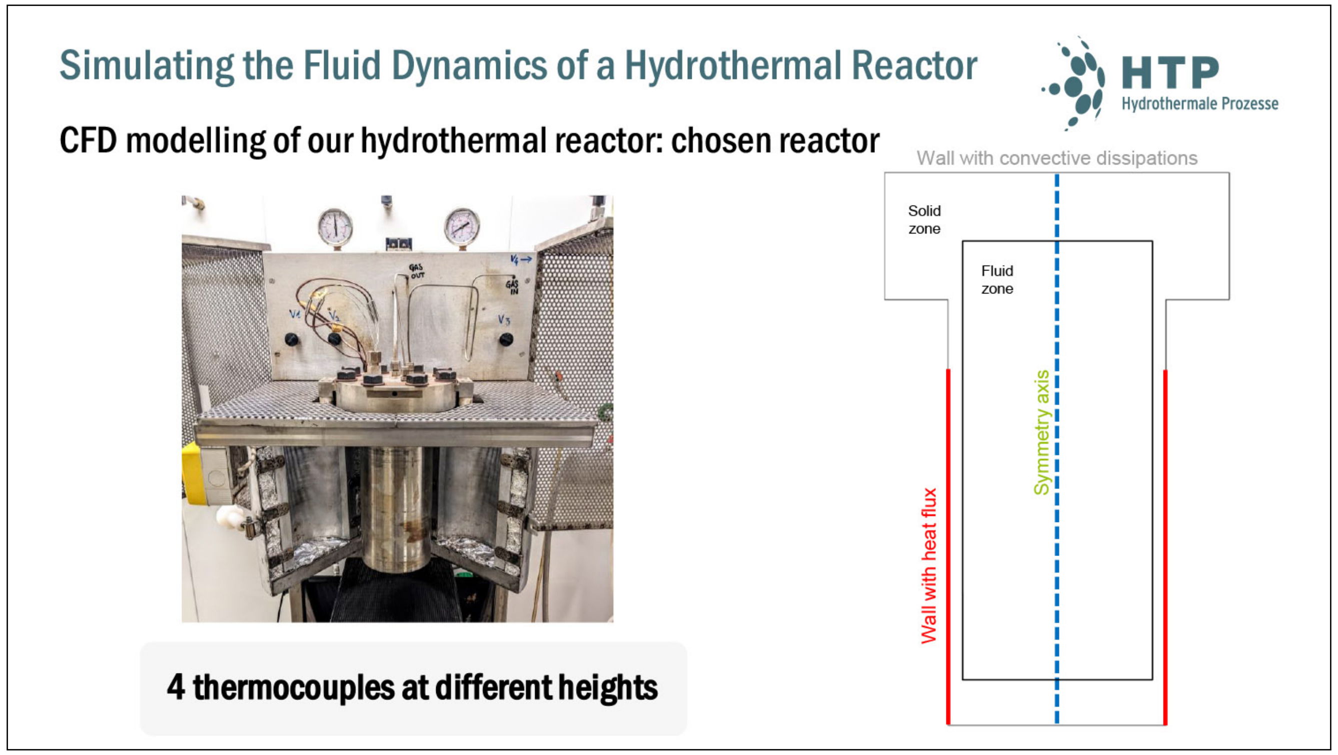
Simulating the Fluid Dynamics of a Hydrothermal Reactor
HTP Hydrothermale Prozesse
CFD modelling of our hydrothermal reactor: chosen reactor
Wall with convective dissipations
Solid zone
Fluid zone
Symmetry axis
Wall with heat flux
4 thermocouples at different heights

## Simulating the Fluid Dynamics of a Hydrothermal Reactor

HTP Hydrothermale Prozesse

First simulations: heating of liquid water up to 180/220/250 °C

- VOF approach for the multiphase (used for immiscible phases)
  - Primary phase: pure water
  - Secondary phase: gas (nitrogen + water)
- K-ω turbulence model
- Lee evaporation model (with $T_{sat} = f(p)$)
- Density and viscosity = f(T)
- Time step: $10^{-3}$ s, 30 min of simulation -> about 1-2 weeks of calculations
- Beginning: everything at 20 °C, water fills 70% of the internal volume

Ansys FLUENT

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## Simulating the Fluid Dynamics of a Hydrothermal Reactor

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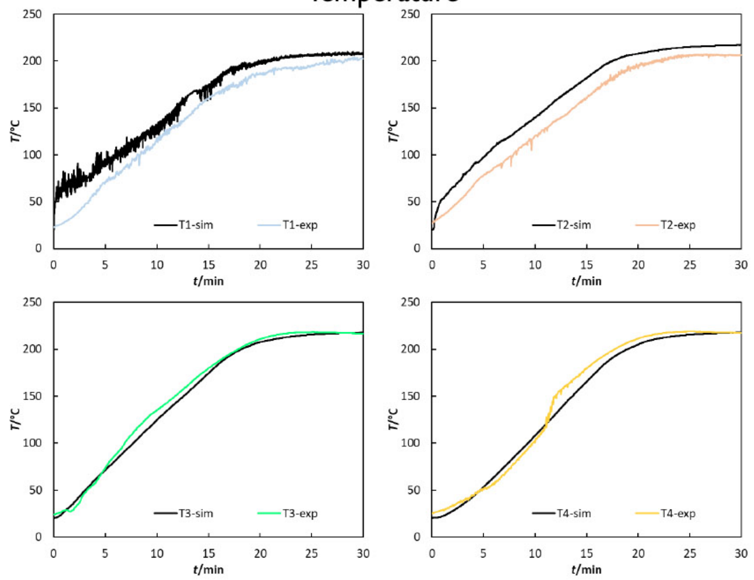
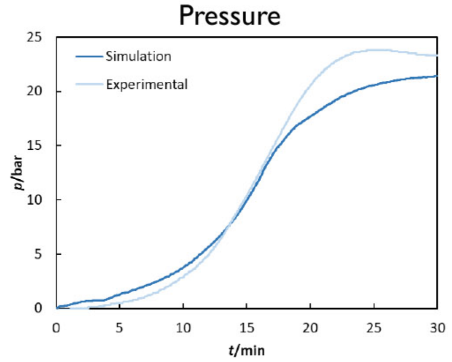
### Validation

Temperature




Pressure

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## Simulating the Fluid Dynamics of a Hydrothermal Reactor

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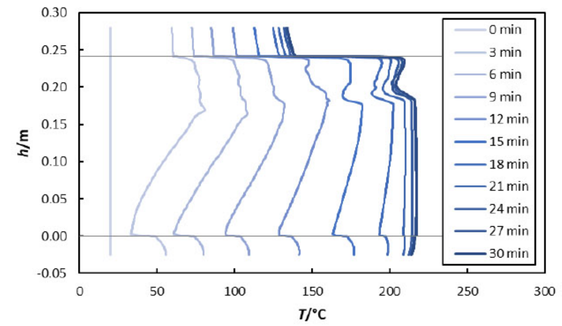
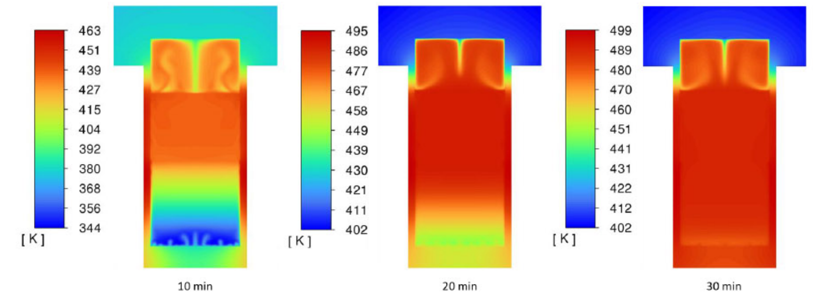
### Thermal profiles

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## Simulating the Fluid Dynamics of a Hydrothermal Reactor

HTP Hydrothermale Prozesse

How can we include biomass?

- As discrete elements
- As another continuum phase
- As a static porous zone
- As a pseudo-single phase with water

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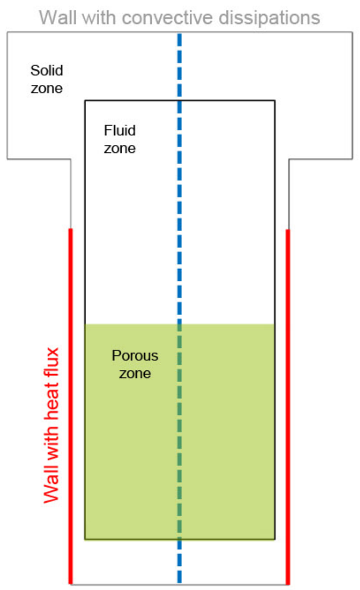
## Simulating the Fluid Dynamics of a Hydrothermal Reactor

HTP Hydrothermale Prozesse

### Biomass as a static porous medium

OK if particles
- Do not move
- Do not change drastically during the process

Pros:
- Very simple: + sink term in momentum equation
- Only two parameters needed: permeability, inertial loss coefficient
- Conservative hypothesis

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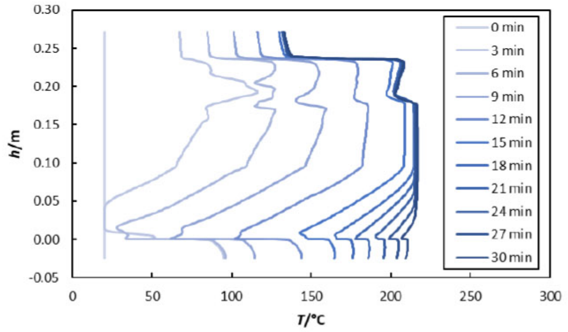
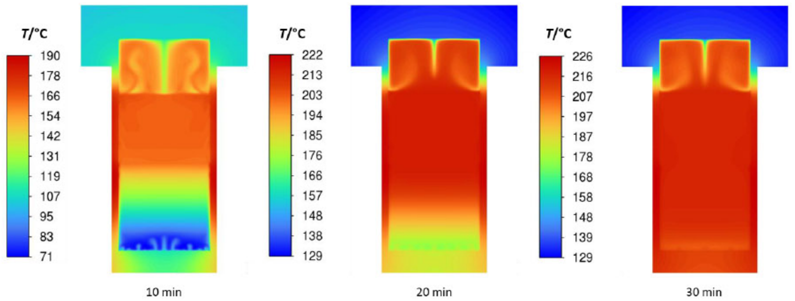
## Simulating the Fluid Dynamics of a Hydrothermal Reactor

HTP Hydrothermale Prozesse

### Thermal profiles

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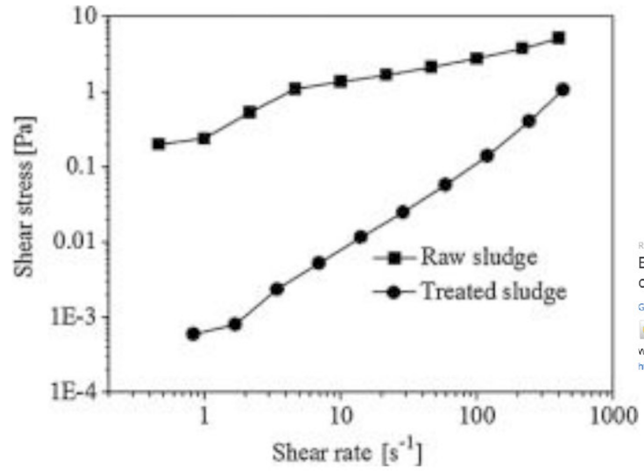
## Simulating the Fluid Dynamics of a Hydrothermal Reactor

HTP Hydrothermale Prozesse

### Pseudo-single phase

- Good for fine particles and sludges
- Effect included through non-ideal viscosity




Effects of thermal hydrolysis temperature on physical characteristics of municipal sludge

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## Simulating the Fluid Dynamics of a Hydrothermal Reactor

HTP Hydrothermale Prozesse

**According to Feng et al.:**

$$\eta = k\dot{\gamma}^{n-1}$$

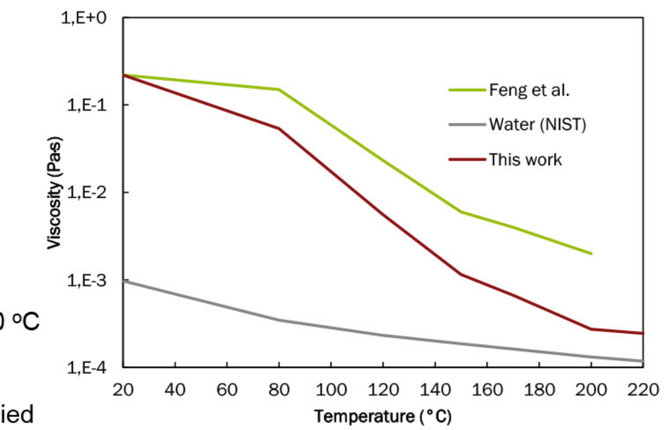
- With $k$ and $n$ depending on the HT temperature.
- But measuring $\eta$ after cooling at ambient $T$.

**Our proposal:**

$$\eta(T) = k(T)\dot{\gamma}^{n(T)-1}\frac{\mu(T)}{\mu_{20°C}}$$

- $k$ and $n$ as per Feng et al.
- $\mu(T)$ and $\mu_{20C}$ the viscosities of water at $T$ and at 20 °C

Pro: Likely a better estimate
Con: Viscosity changes instantaneously as $T$ is applied

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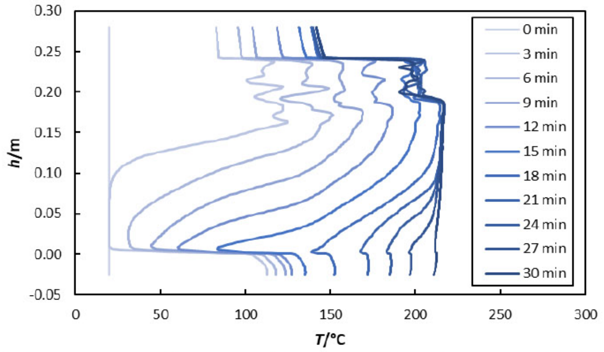
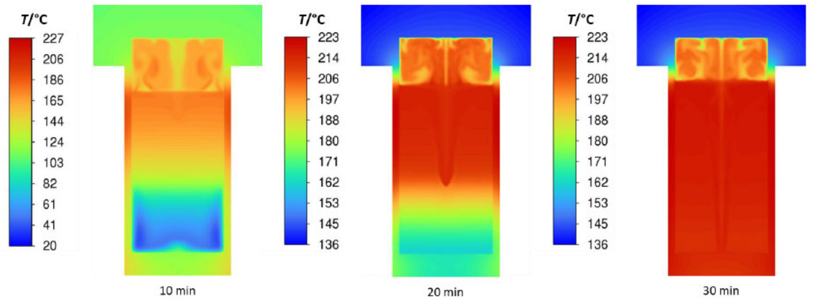
## Simulating the Fluid Dynamics of a Hydrothermal Reactor

HTP Hydrothermale Prozesse

### Thermal profiles

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## Simulating the Fluid Dynamics of a Hydrothermal Reactor

HTP Hydrothermale Prozesse

**Conclusions**

- Procedure flexible and scalable
- Mixing not needed here, but may be elsewhere
- Extra care when thermal gradients are present

**The steps forward**

- More realistic biomass particles
- Chemical reaction and kinetics
- Better modelling of viscosity

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## 8th Expert Forum on Hydrothermal Processes

HTP Hydrothermale Prozesse

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paper on the simulations

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*Behnam Jabbari Kalkhoran, University of Trento*

# HTC of glucose to produce carbon materials for electrochemical applications: Preliminary results

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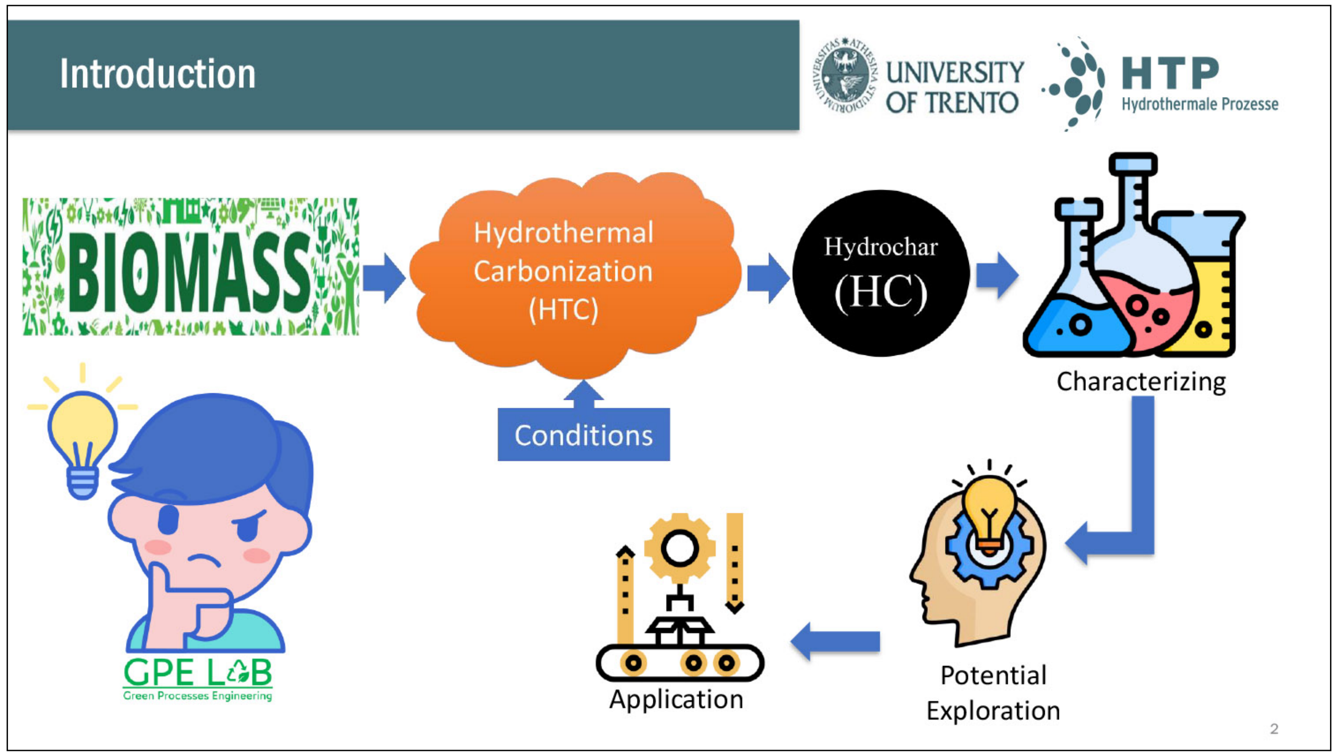
**Keywords:** Glucose, waste biomass, hydrochar, biomass, electrochemistry

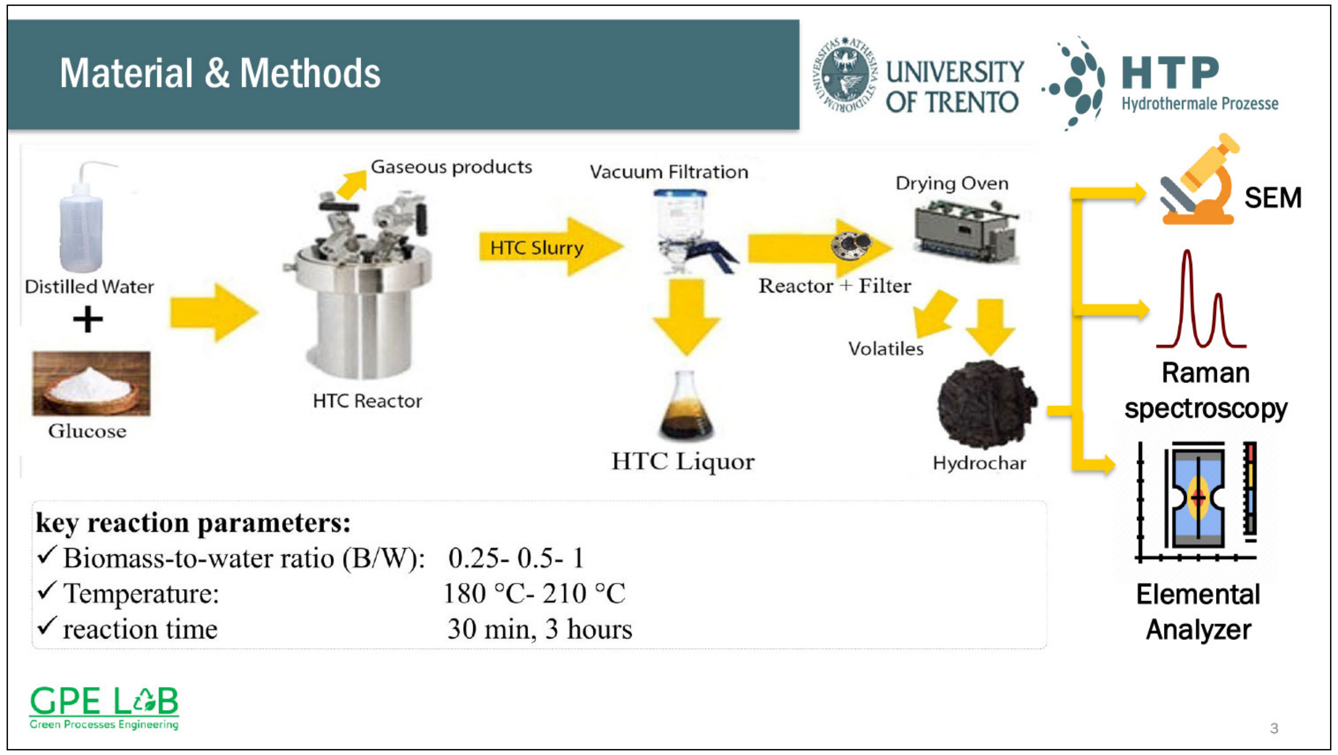
This study investigates the conversion of glucose, representative of waste biomasses rich in carbohydrathes, into valuable carbon materials for electrochemical applications through hydrothermal carbonization (HTC). A controlled and systematic approach was employed to investigate the influence of key reaction parameters on the properties of the final product, hydrochar. HTC experiments were conducted in a 50 mL reactor filled to 70% capacity with an aqueous glucose solution in the presence of gaseous nitrogen atmoshpere. The feedstock-to-water ratio was carefully varied (0.25, 0.5, and 1) to explore the impact of glucose concentration on the HTC process and resulting hydrochar. Reaction temperatures of 180 and 210 °C were chosen to investigate the influence of temperature on the degree of carbonization and the properties of the hydrochar. Additionally, reaction times of 30 minutes and 3 hours were employed to understand the effect of reaction duration on hydrochar yield and characteristics.

Following HTC, the reaction mixture was filtered to separate the liquid phase from the solid residue, the hydrochar. The hydrochar was dried in an oven at 105 °C to ensure complete removal of moisture and obtain the final product. The recovered hydrochar holds great potential for utilization in electrochemical applications owing to its unique properties, such as high surface area and potentially enhanced electrical conductivity. This research contributes significantly to the development of sustainable waste valorization strategies by transforming readily available biomass into valuable functional materials for clean energy technologies. By understanding the relationship between process parameters and hydrochar properties, this study enables the targeted synthesis of hydrochar with properties specifically tailored for high-performance electrochemical applications.






Material & Methods
UNIVERSITY OF TRENTO
HTP Hydrothermale Prozesse
Distilled Water
+
Glucose
Gaseous products
HTC Reactor
HTC Slurry
Vacuum Filtration
HTC Liquor
Reactor + Filter
Drying Oven
Volatiles
Hydrochar
SEM
Raman spectroscopy
Elemental Analyzer
key reaction parameters:
✓ Biomass-to-water ratio (B/W): 0.25- 0.5- 1
✓ Temperature: 180 °C- 210 °C
✓ reaction time 30 min, 3 hours
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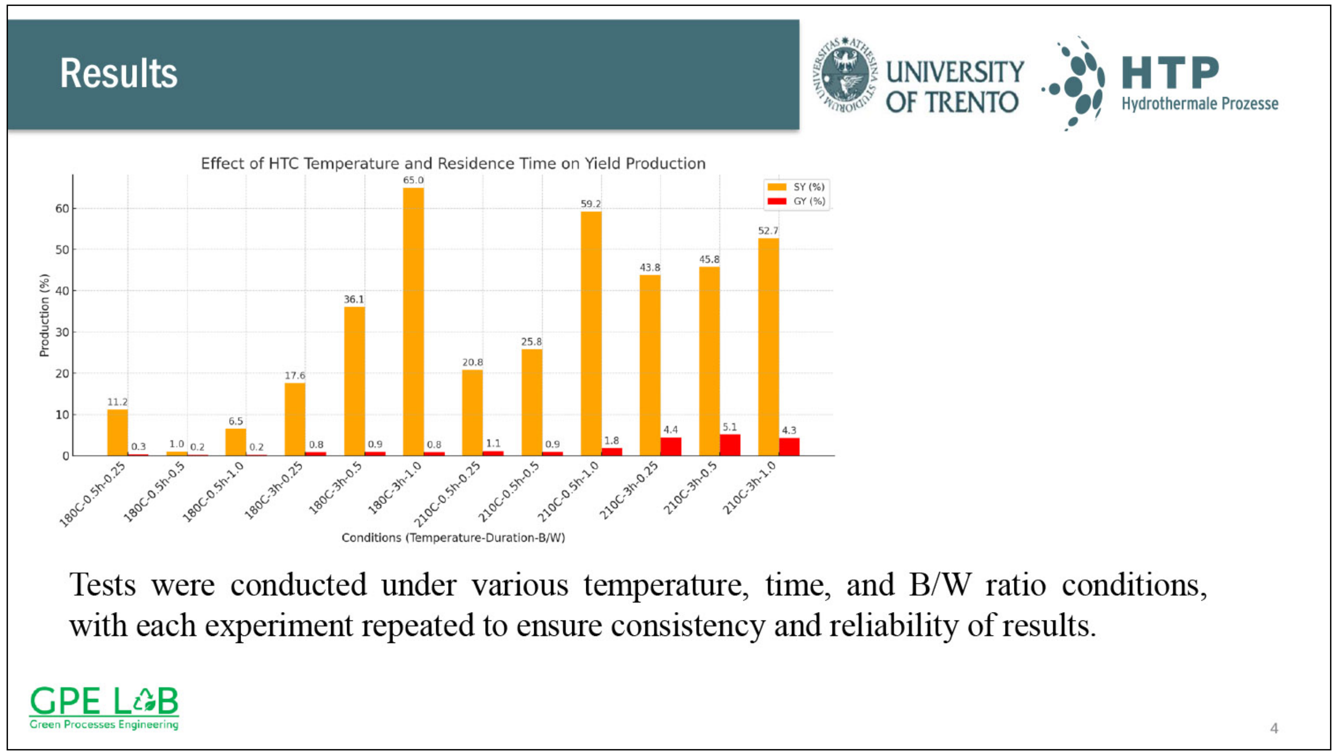
Results
UNIVERSITY OF TRENTO
HTP Hydrothermale Prozesse
Effect of HTC Temperature and Residence Time on Yield Production
Production (%)
Conditions (Temperature-Duration-B/W)
Tests were conducted under various temperature, time, and B/W ratio conditions, with each experiment repeated to ensure consistency and reliability of results.
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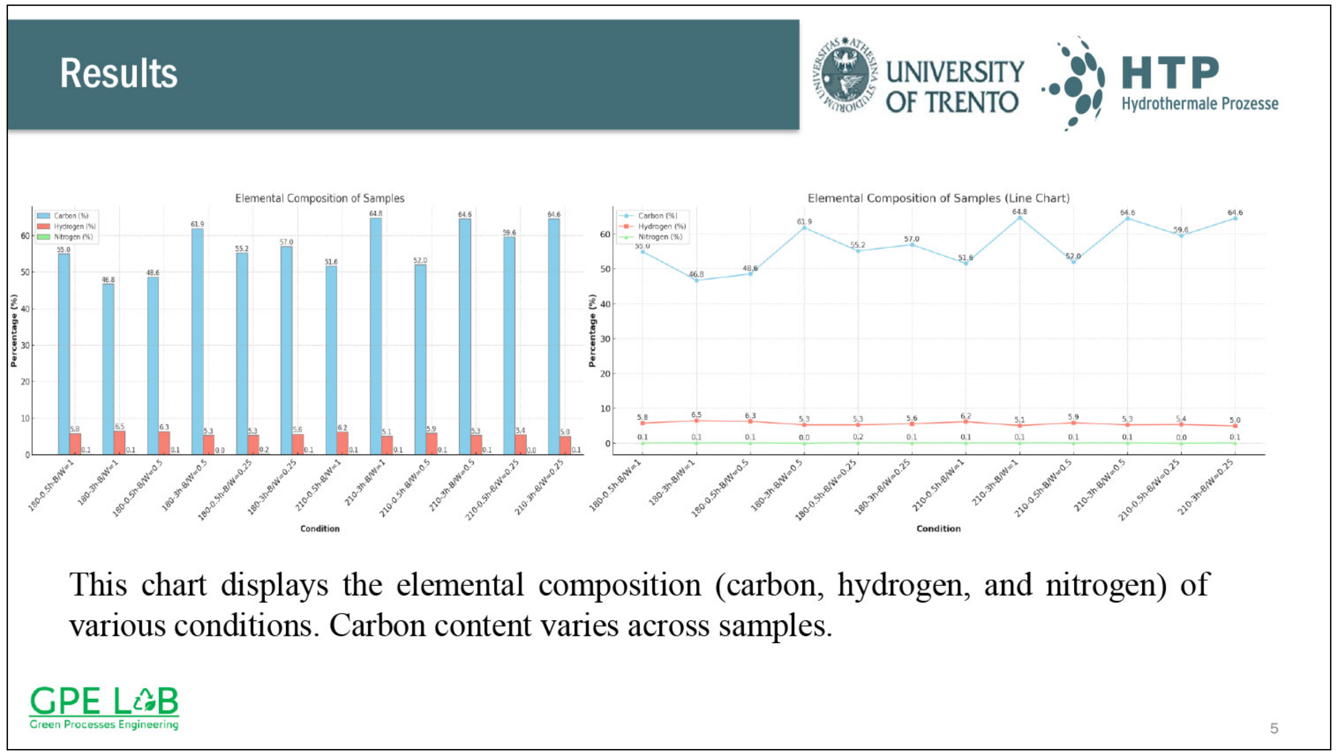
Results
UNIVERSITY OF TRENTO
HTP Hydrothermale Prozesse
Elemental Composition of Samples
Elemental Composition of Samples (Line Chart)
This chart displays the elemental composition (carbon, hydrogen, and nitrogen) of various conditions. Carbon content varies across samples.
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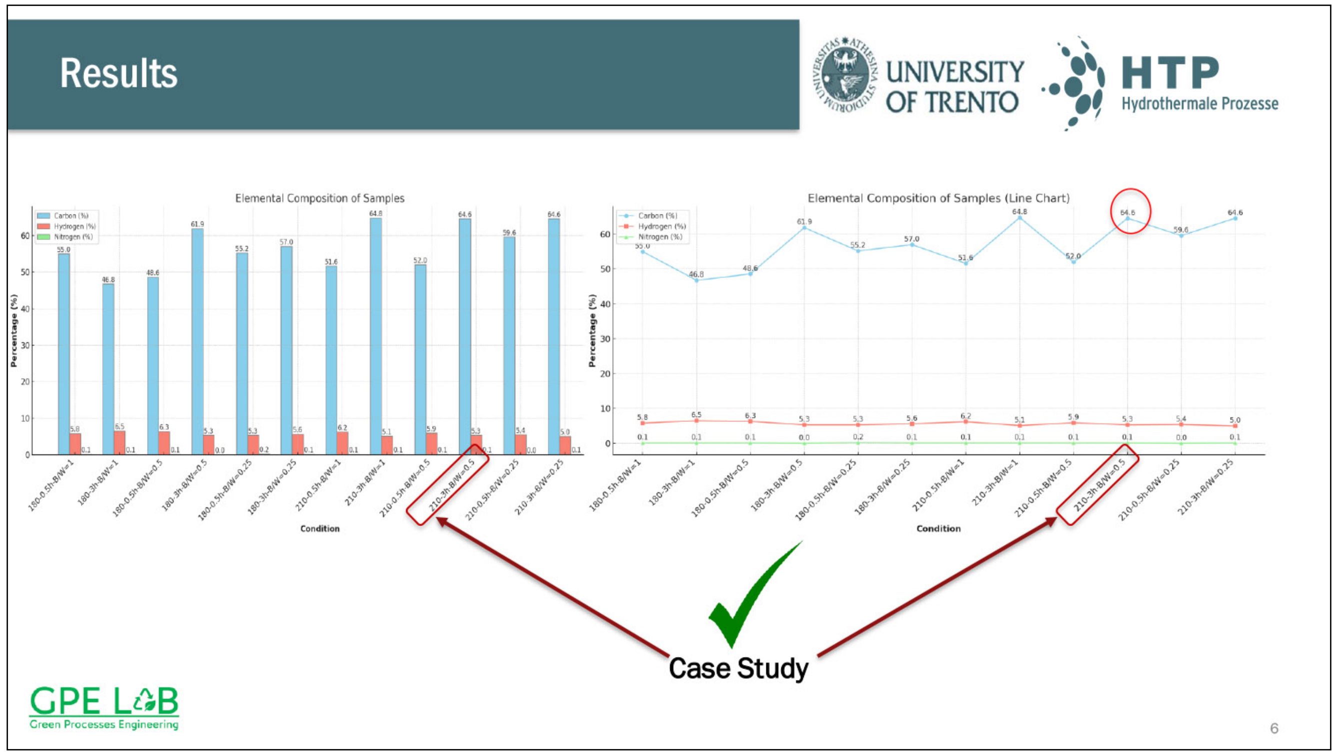
Results
UNIVERSITY OF TRENTO
HTP Hydrothermale Prozesse
Elemental Composition of Samples
Elemental Composition of Samples (Line Chart)
Case Study
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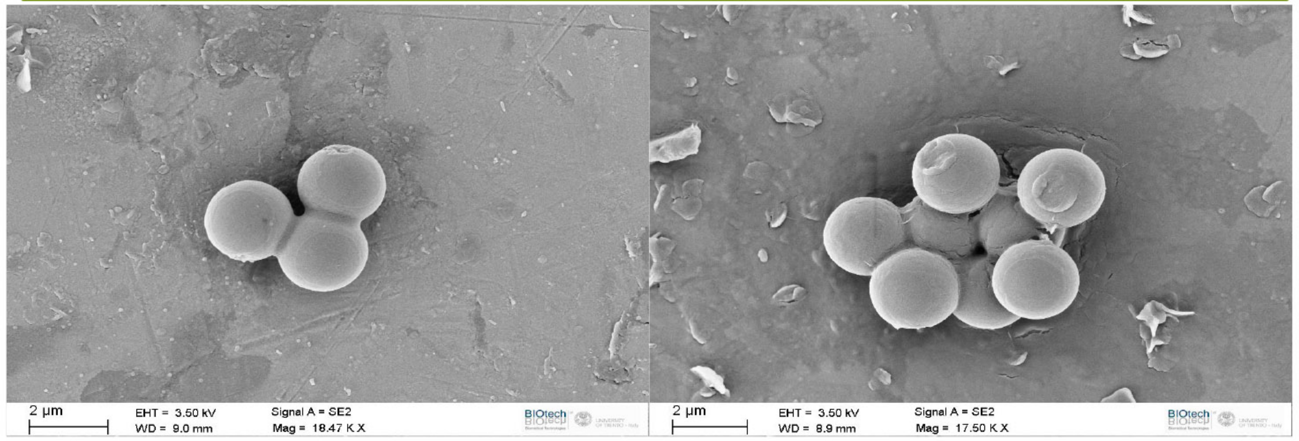
6

## Results

UNIVERSITY OF TRENTO HTP Hydrothermale Prozesse

### SEM Preliminary Results for Characterization 210 °C -3h-0.5




SEM images show well-formed, uniform carbon spheres with smooth surfaces, indicating HTC's effectiveness for electrochemical material synthesis.

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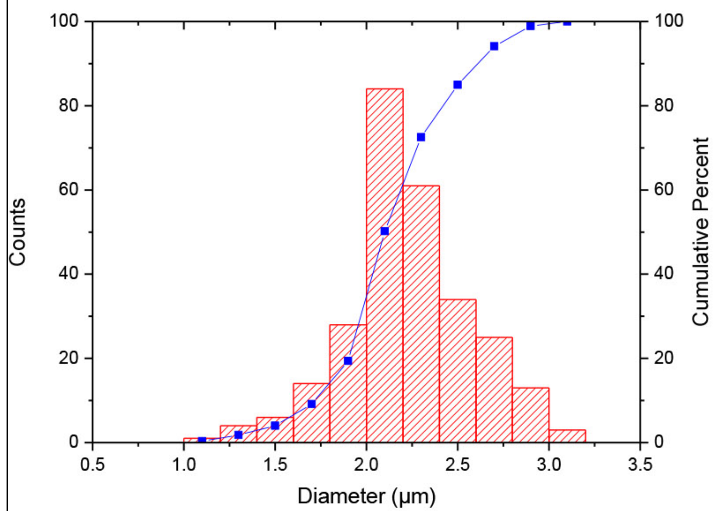
## Results

UNIVERSITY OF TRENTO HTP Hydrothermale Prozesse




- ✓**Particle Size Range**: Most particles are around 2.0 μm, with sizes ranging from 1.0 to 3.5 μm.
- ✓**Uniform Distribution**: Approximately 80% of particles are below 2.5 μm, ensuring consistent electrochemical performance.

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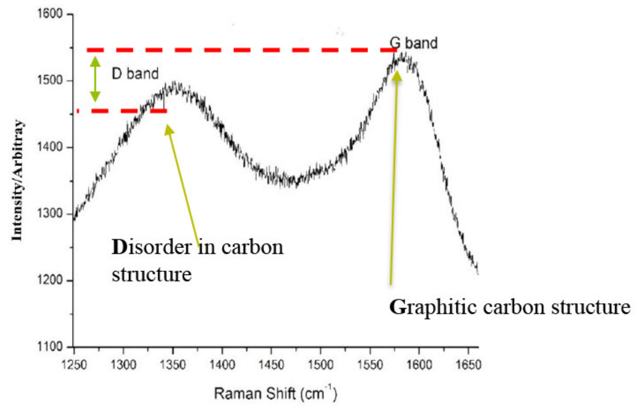
## Results

UNIVERSITY OF TRENTO HTP Hydrothermale Prozesse

### Preliminary Raman spectroscopy Results 210 °C -3h-0.5




- ✓ **Clear D and G Bands**: Presence of both disordered and graphitic structures in HC
- ✓ **G/D Ratio < 2**: Indicates amorphous, defect-rich structure with minimal graphitic ordering.

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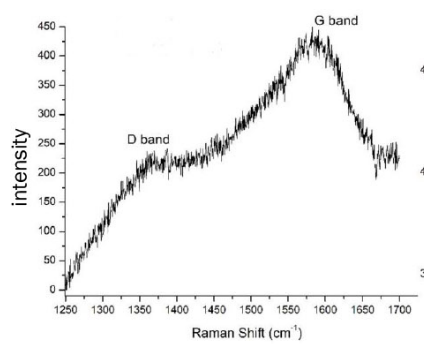
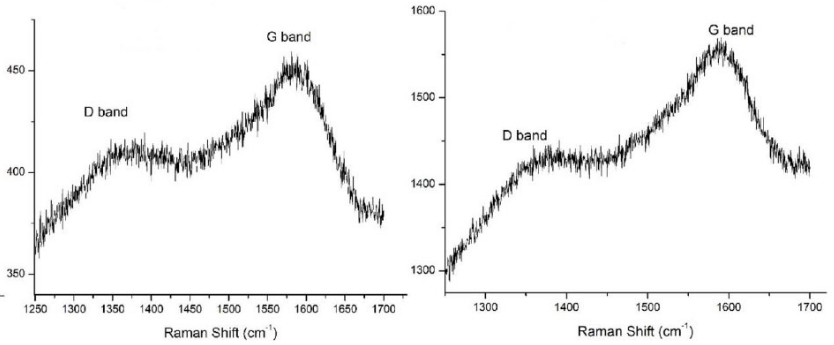
## Results

UNIVERSITY OF TRENTO HTP Hydrothermale Prozesse

### Preliminary Raman spectroscopy Results other Samples




180-3h-B/W=0.5
G/D = 1.87




210-3h-B/W=0.25
G/D = 1.1

180-3h-B/W=1
G/D = 1.09

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10

## Discussion

- Higher temperatures and longer durations in HTC increase SY yield, with optimal results at 210° C and 3 hours. These findings align with existing literature, indicating that optimized parameters may enhance hydrochar production efficiency.
- Additionally, SEM images reveal that the carbon microspheres were well-formed, uniform in size, and display a smooth surface texture. The carbon microspheres maintained a consistent spherical shape, with no significant evidence of aggregation or deformation with uniform distribution.
- The existence of clear G and D bands in Raman spectroscopy indicates amorphous and disordered or graphitic structure which could be suitable for different electrochemical applications .

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## 8th Expert Forum on Hydrothermal Processes

Speaker:
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Email: B.jabbarikalkhoran@unitn.it
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*Andrés Acosta, Deutsches Biomasseforschungszentrum*

# Catalytic hydrothermal synthesis [HTS] of platform chemicals: Paving the way for an integrated biorefinery approach

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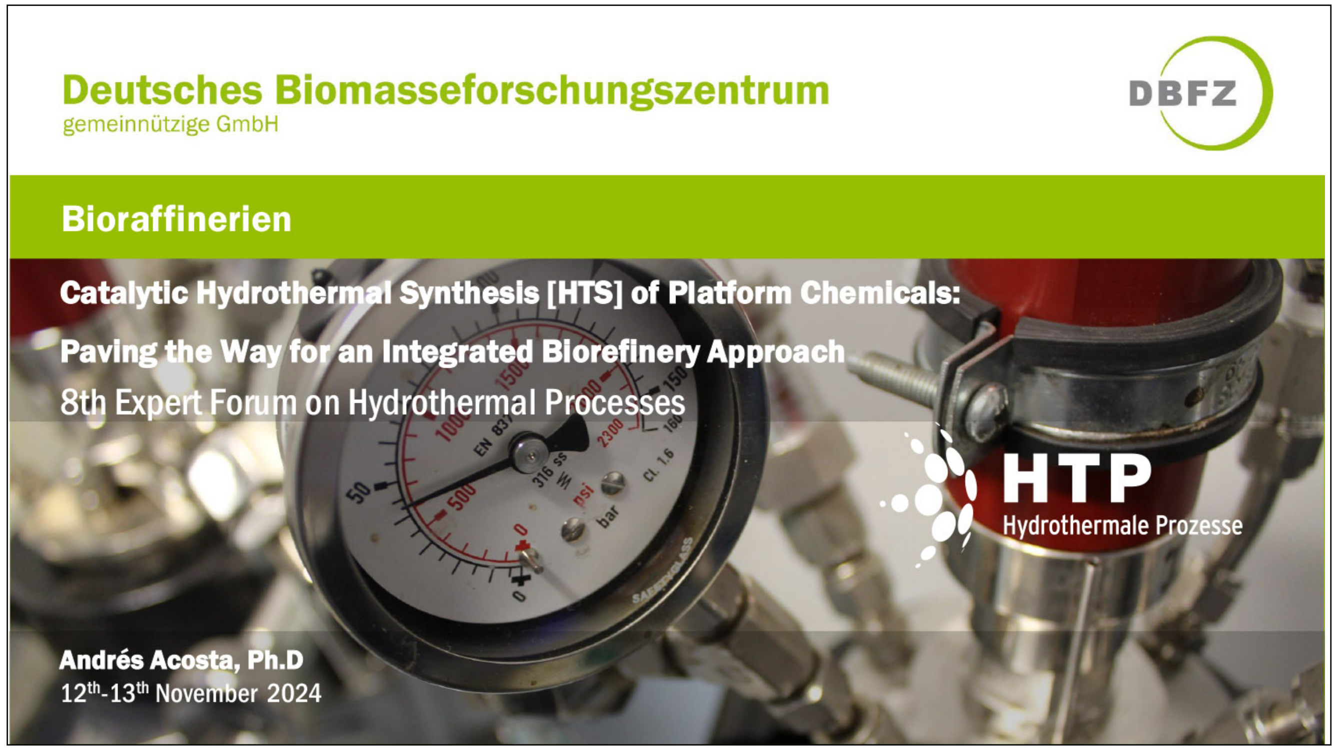
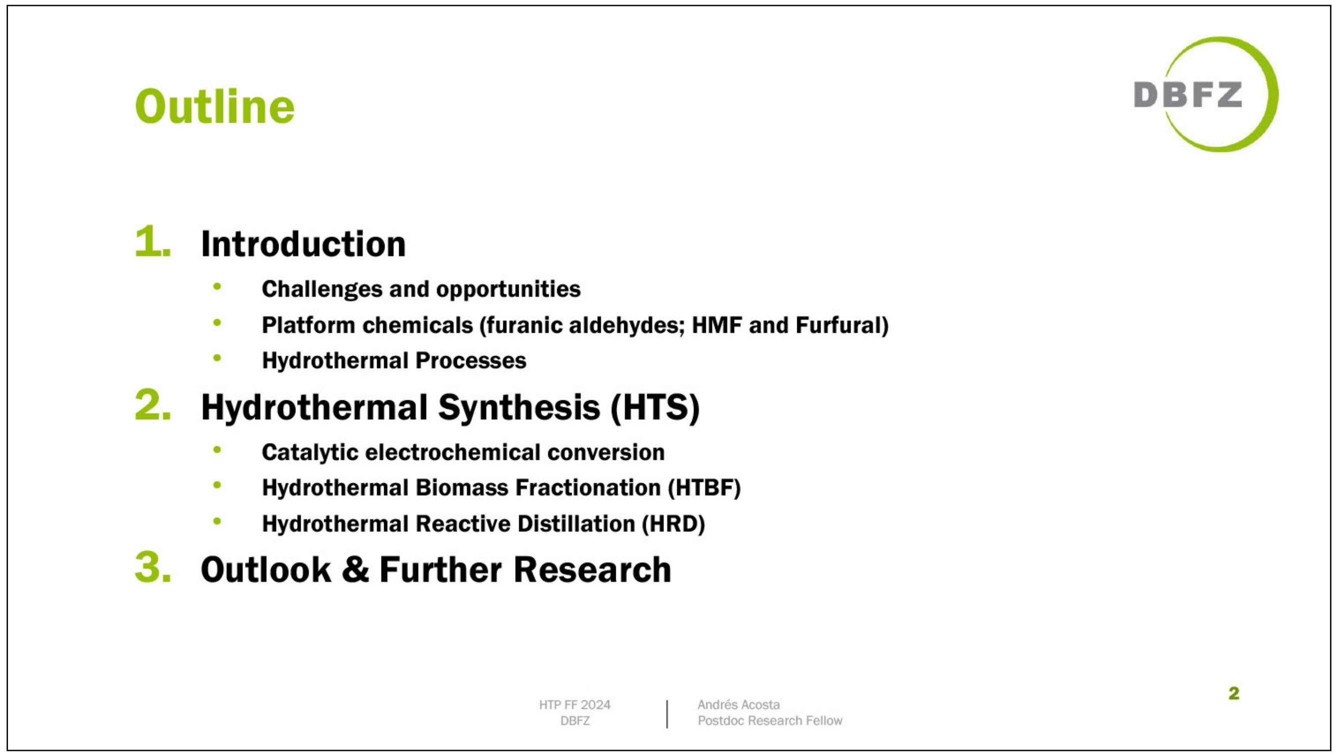
**Keywords:** Platform chemicals, Catalytic hydrothermal synthesis, biomass fractionation, Hydrolysate, Furfural, 5-hydroxymethrylfurfural

Platform chemicals such as furans, especially furfural and 5-(hydroxymethyl)furfural (HMF), offer transformative potential. Sourced from renewable lignocellulosic biomass, they act as precursors for a diverse range of materials including biofuels, resins, and plastics. Positioned at the vanguard of bioeconomy, they hold promise for a more sustainable future. Hydrothermal conversion, among various biomass conversion technologies, stands out due to its adaptability to different feedstocks. It offers the advantage of utilizing water as the reaction medium and using hot water under pressure as a reaction medium, which improves the efficiency of acid catalysts. However, the challenge remains in optimizing the production and purification of furans, underscoring the importance of our research.

Our study investigates the catalytic hydrothermal synthesis (HTS) of furfural and HMF and its potential integration with cutting-edge processes, such as biomass fractionation using two-phase aqueous systems, as well as the electrochemical conversion of value-added derivatives 2,5-furandicarboxylic acid (FDCA) and 2,5-dimethylfuran (DMF). Our project also explores the innovative integration of HTS with hydrothermal reactive distillation (HRD) and hydrothermal carbonization (HTC) for the simultaneous synthesis of platform chemicals and hydrochars. This dual-production capability emerges as a ground-break finding for the scientific community, paving the way for an integrated biorefinery approach.



## Challenges and opportunities

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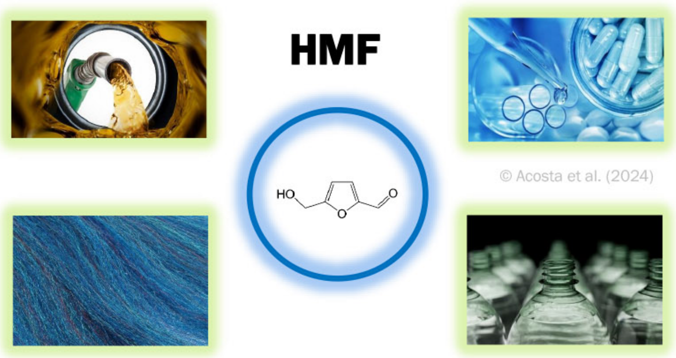
- ✓ The chemical industry and energy production primarily rely on carbon from fossil resources [1].
- ✓ In the long term, the conversion of biomass in biorefineries will become a major source of carbon for chemicals.




5-(Hydroxymethyl)furfural
"Sleeping Giant"

[1] (Zhu et al., 2020)
https://doi.org/10.1016/B978-0-444-64307-0.00003-2

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## HTS in Conventional Hydrothermal Processes

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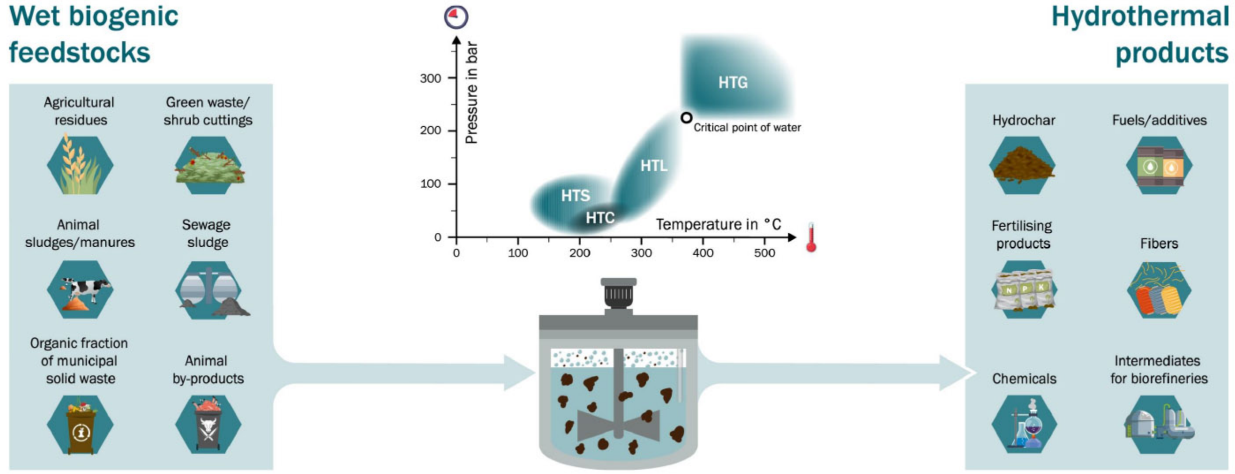


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## Why Sleeping?

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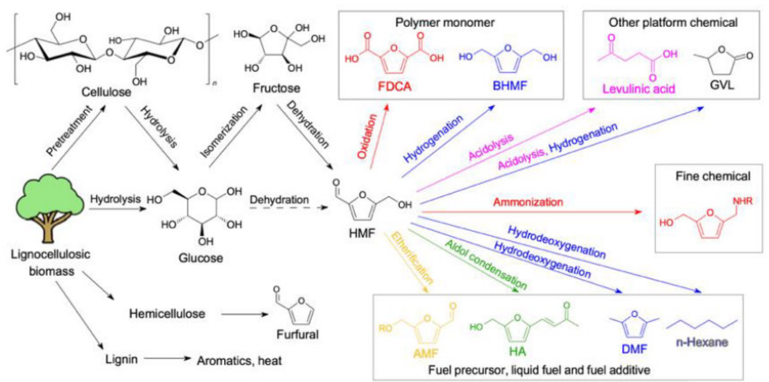


https://doi.org/10.1021/acssuschemeng.1c08429
*ACS Sustainable Chem. Eng.* 2022, 10, 2830−2843

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## Van Krevelen Diagram

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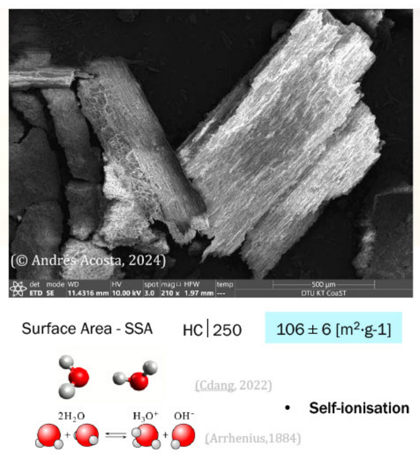


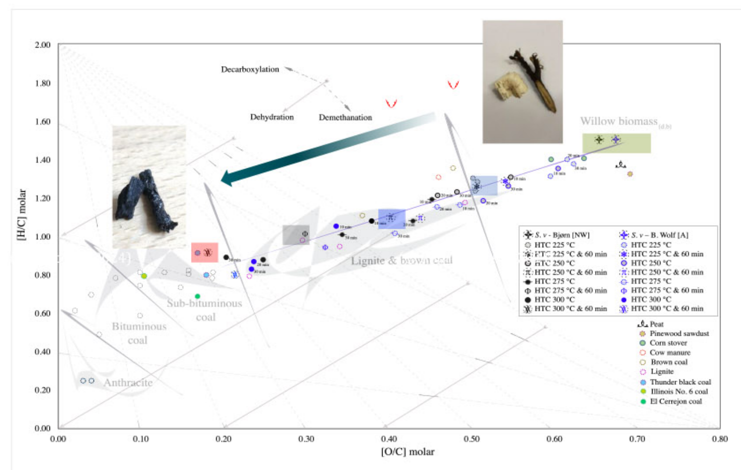


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https://doi.org/10.1016/j.jclepro.2024.140962

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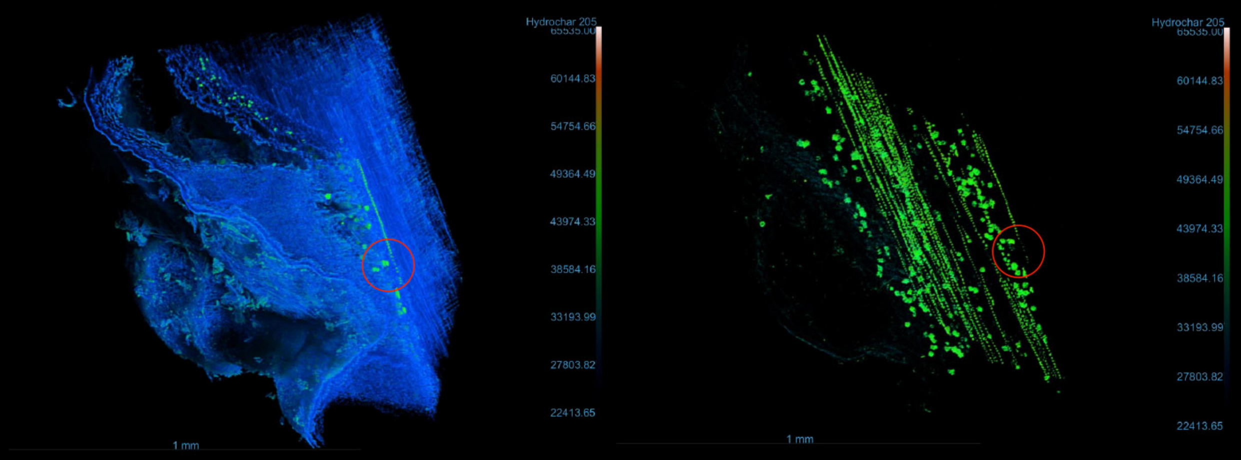
## Hydrochar | X-Ray µ-Computed Tomography

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https://doi.org/10.1016/j.cej.2024.151916

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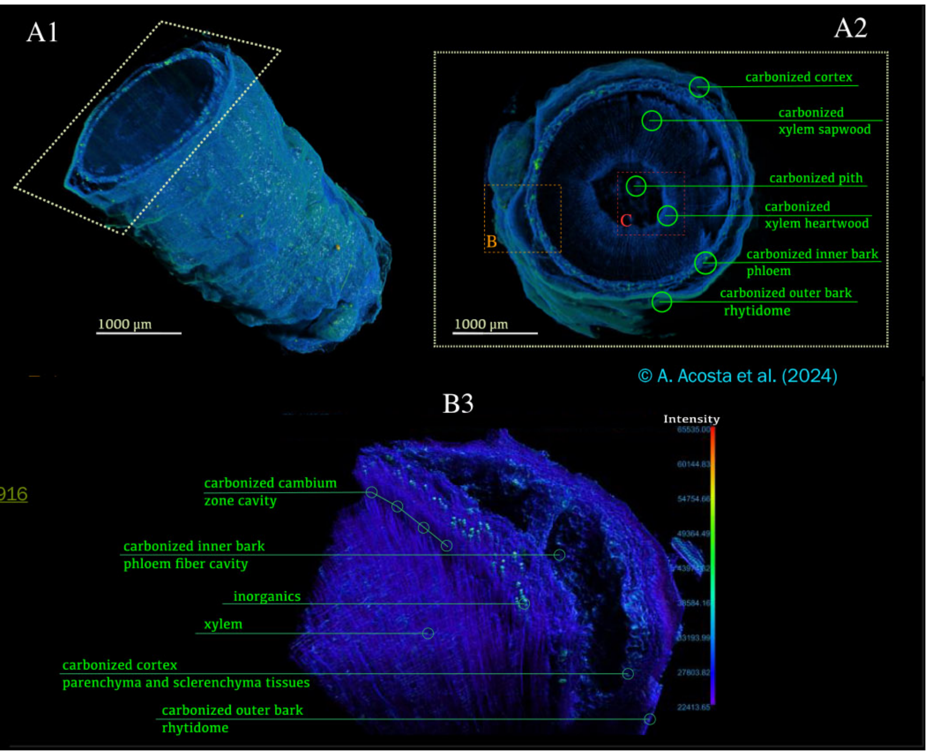
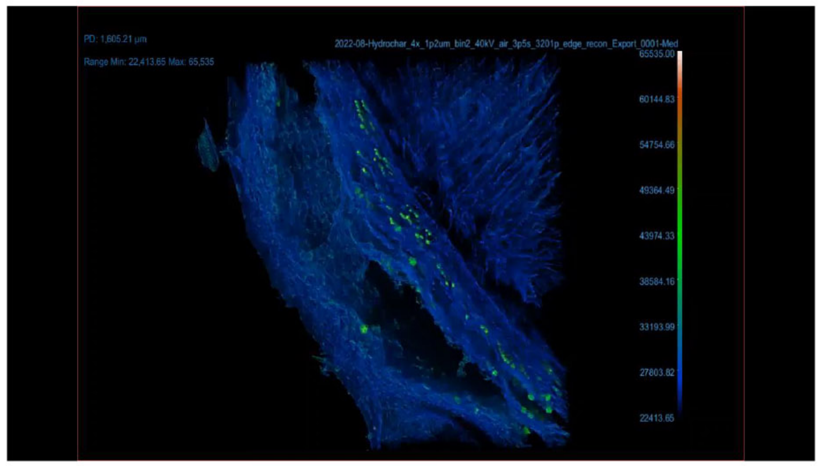



## Hydrochar | X-Ray µ-Computed Tomography



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https://doi.org/10.1016/j.cej.2024.151916

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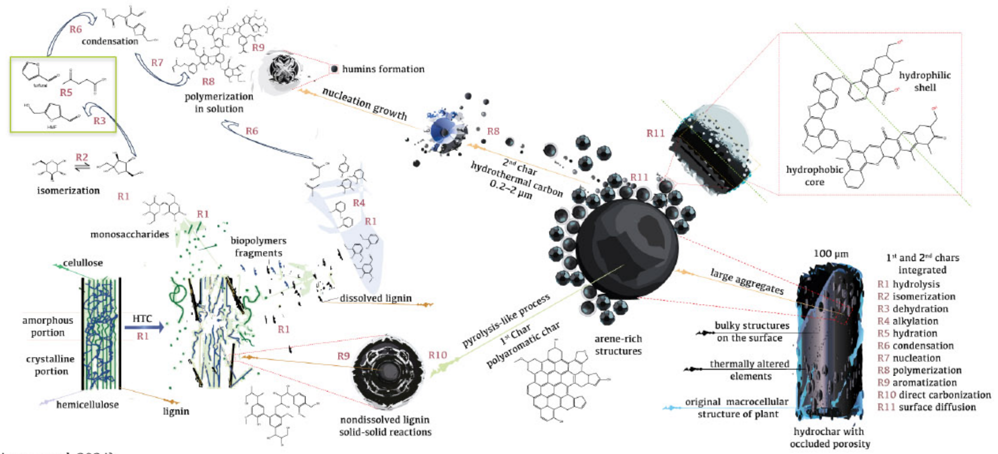
## HMF & FF in Hydrochar Synthesis

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https://doi.org/10.1016/j.cej.2024.151916

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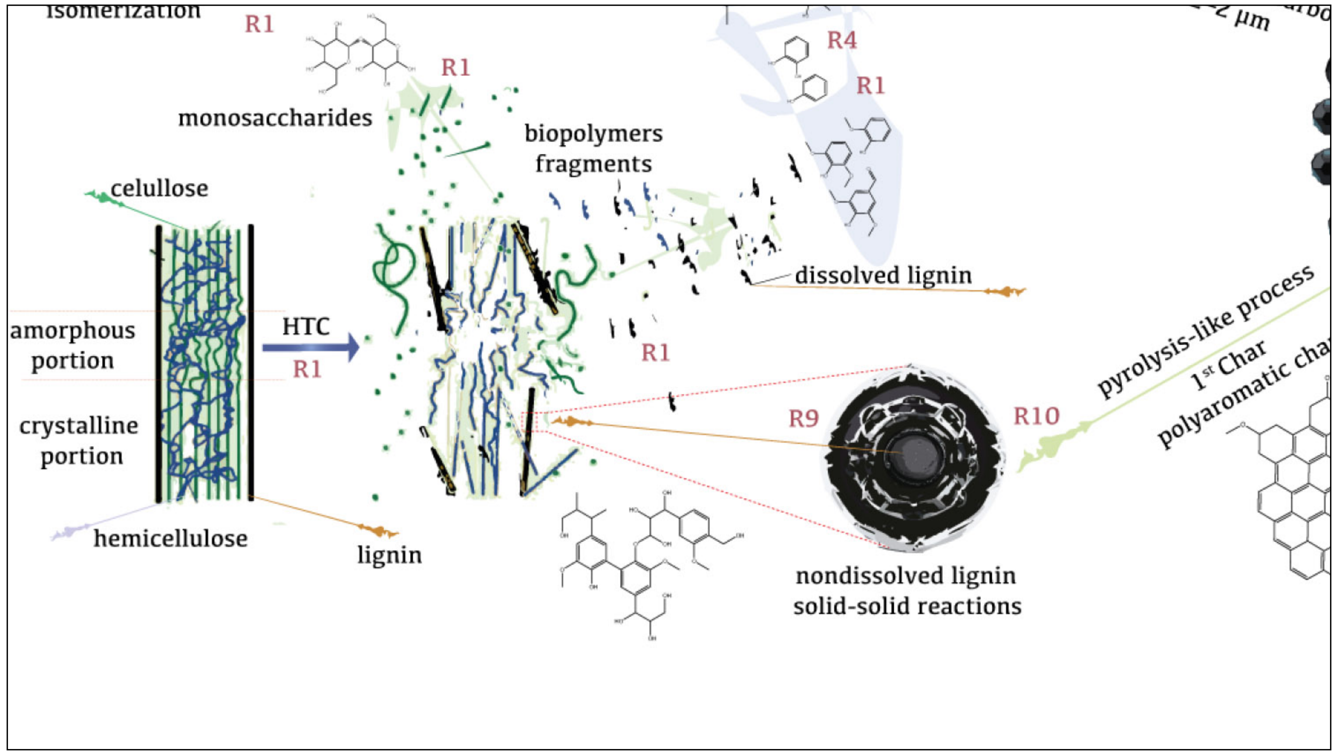


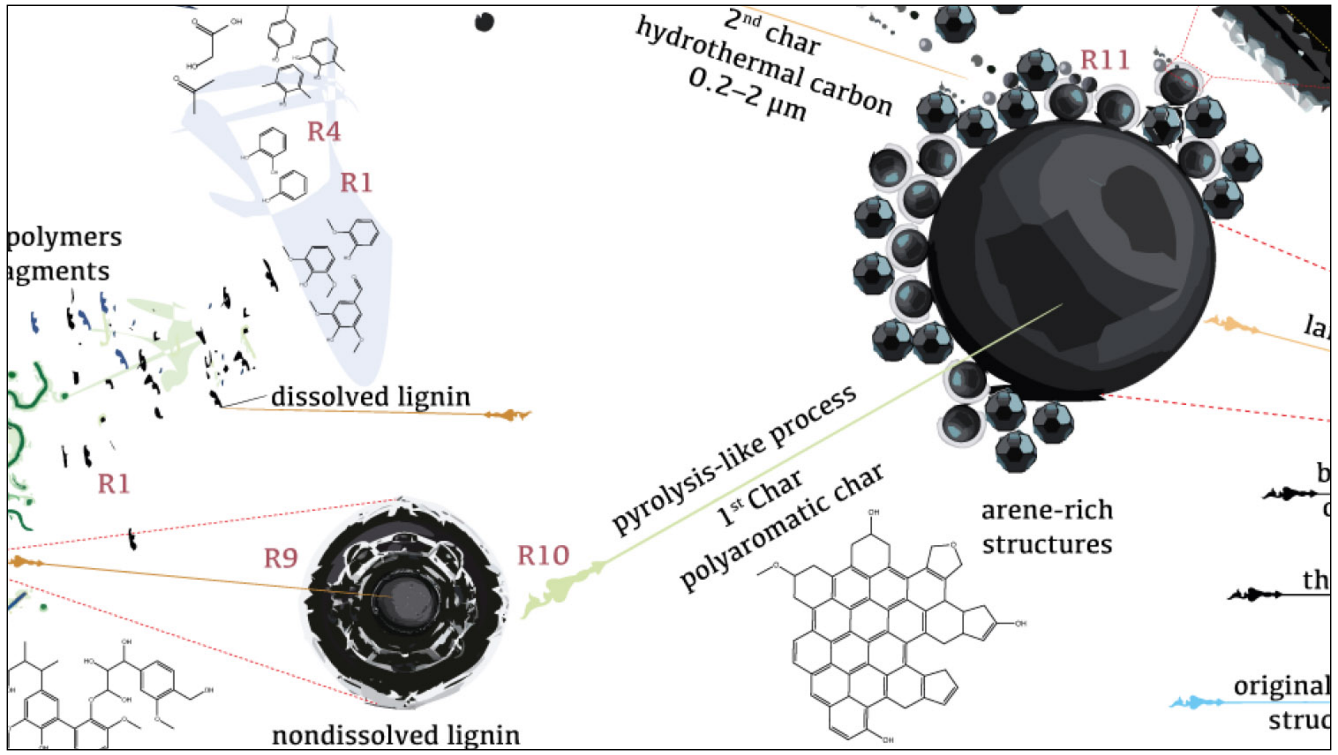




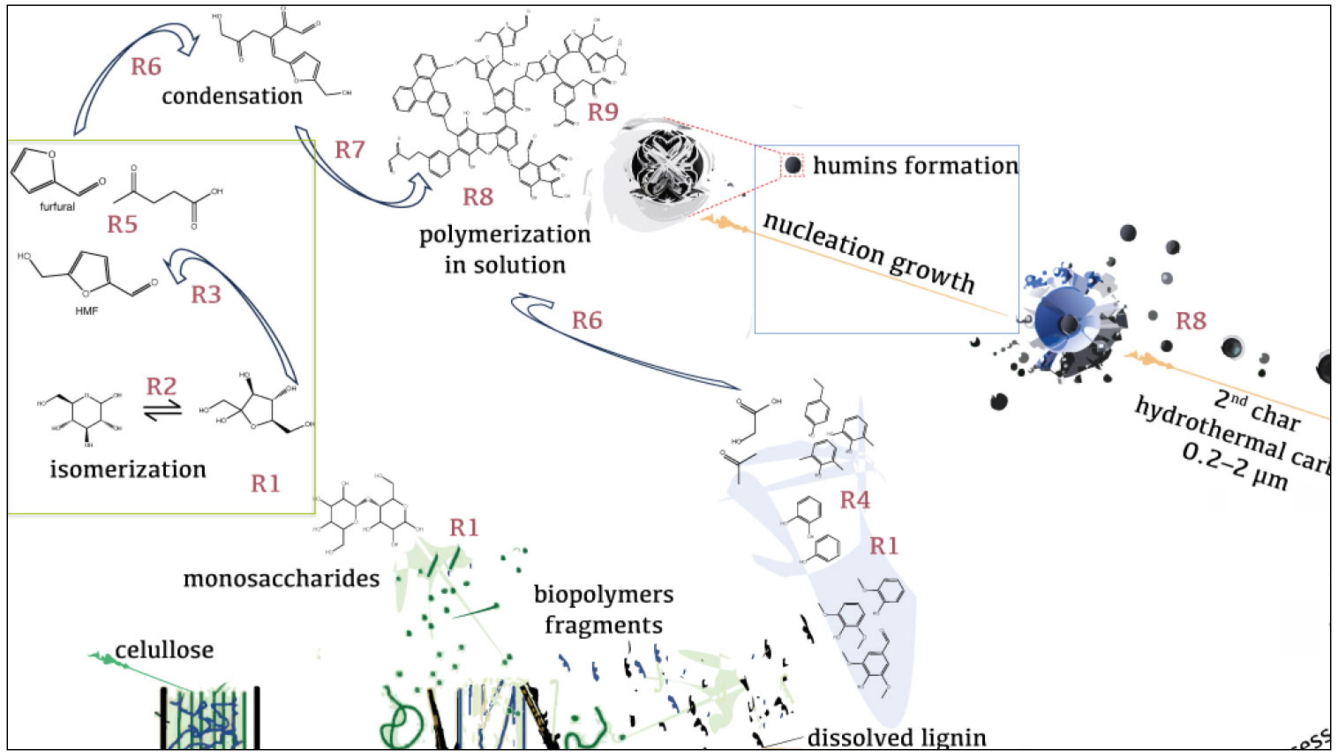


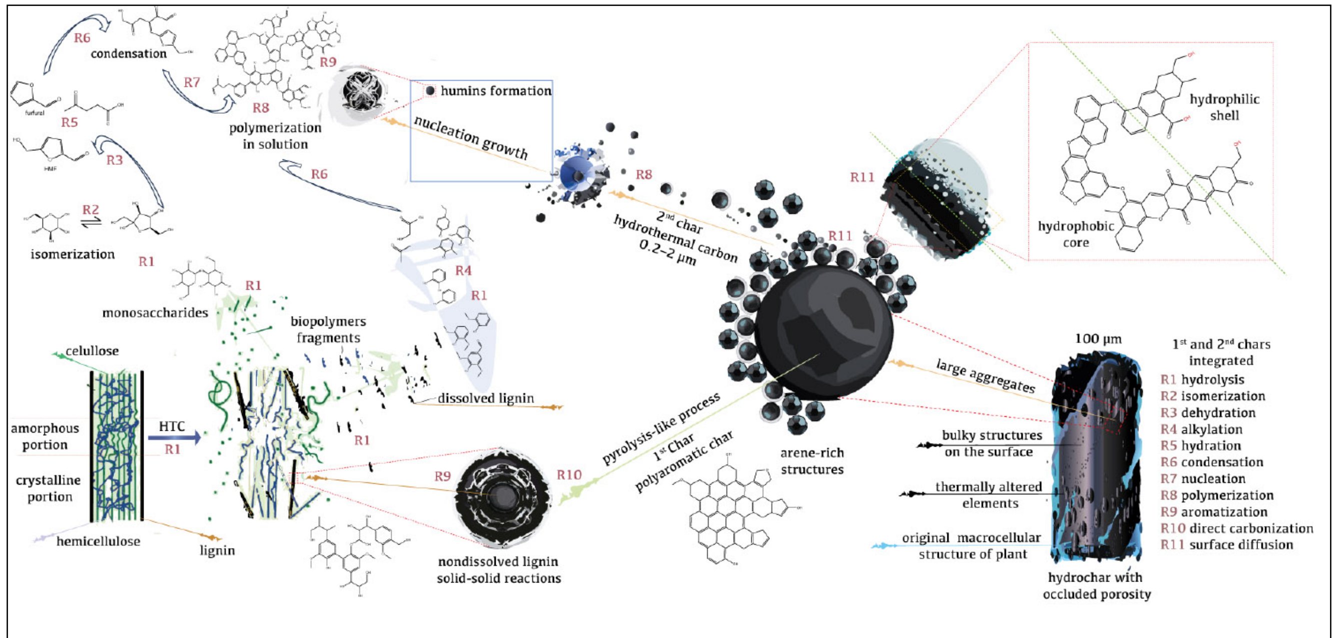


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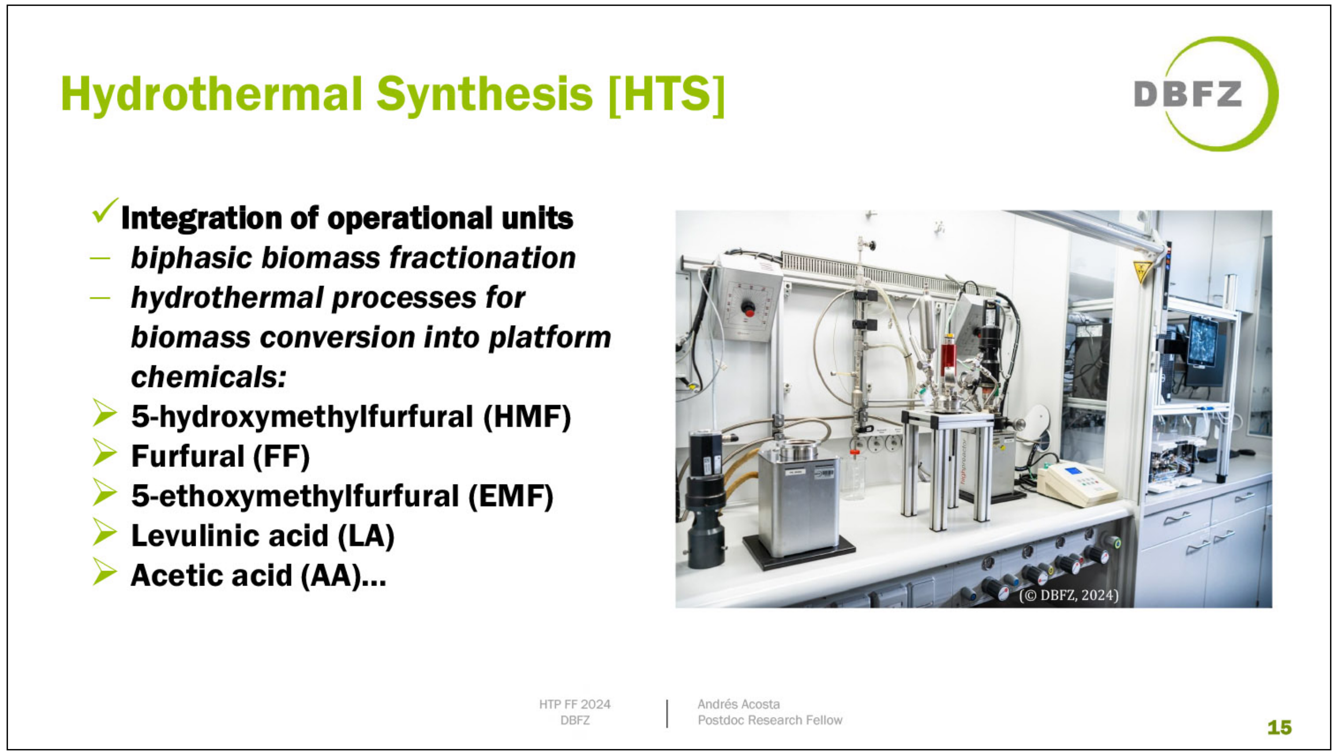
https://doi.org/10.1016/j.cej.2024.151916


Hydrothermal Synthesis [HTS]
DBFZ
Integration of operational units
biphasic biomass fractionation
hydrothermal processes for biomass conversion into platform chemicals:
5-hydroxymethylfurfural (HMF)
Furfural (FF)
5-ethoxymethylfurfural (EMF)
Levulinic acid (LA)
Acetic acid (AA)...
(© DBFZ, 2024)
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Postdoc Research Fellow
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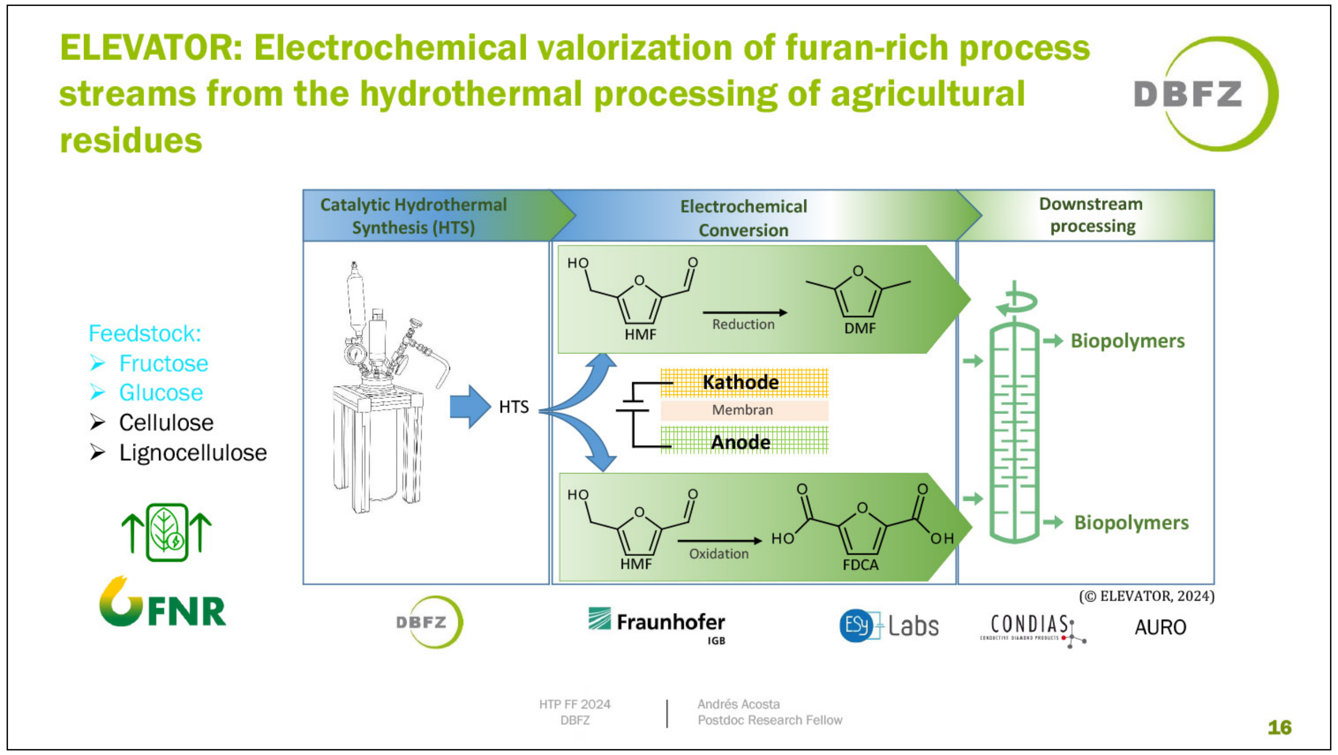
ELEVATOR: Electrochemical valorization of furan-rich process streams from the hydrothermal processing of agricultural residues
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Catalytic Hydrothermal Synthesis (HTS)
Electrochemical Conversion
Downstream processing
Feedstock:
Fructose
Glucose
Cellulose
Lignocellulose
HTS
HMF
Reduction
DMF
Kathode
Membran
Anode
HMF
Oxidation
FDCA
Biopolymers
Biopolymers
FNR
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DBFZ
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IGB
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CONDIAS
AURO
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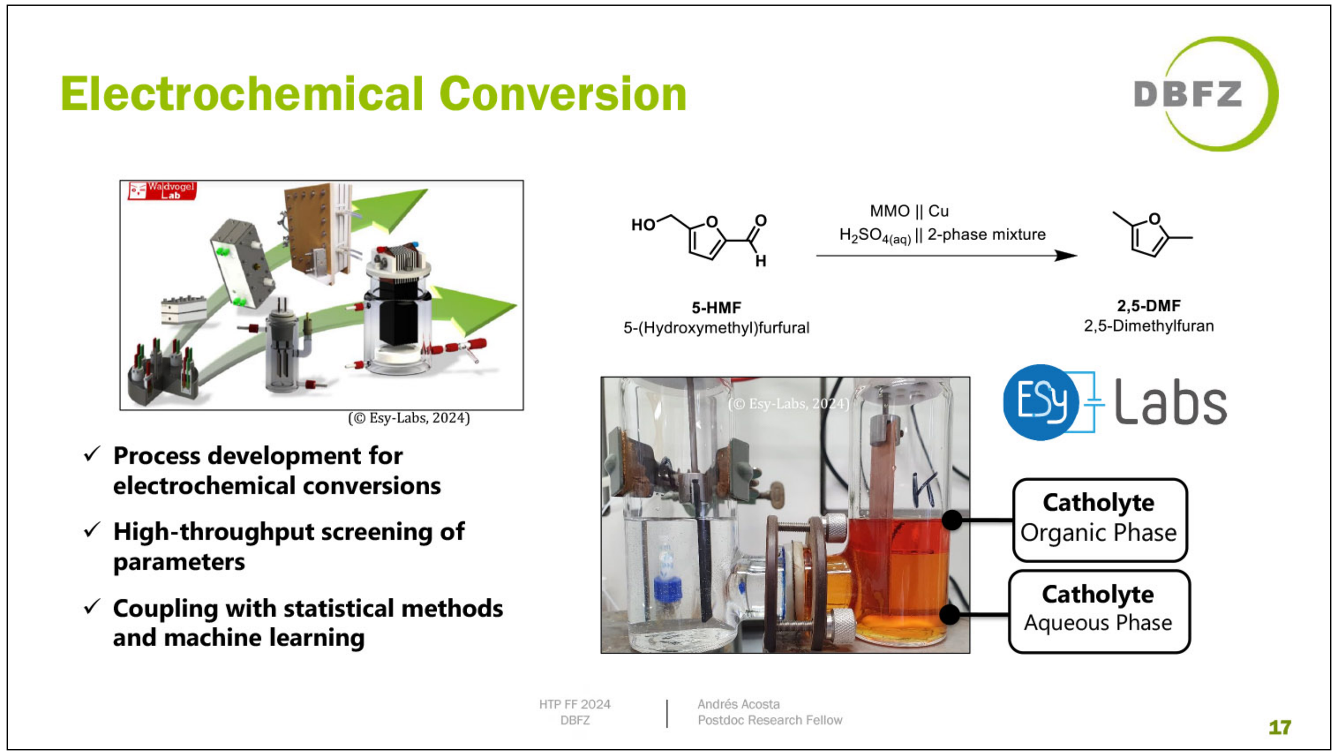
Electrochemical Conversion
DBFZ
(© Esy-Labs, 2024)
Process development for electrochemical conversions
High-throughput screening of parameters
Coupling with statistical methods and machine learning
MMO || Cu
H2SO4(aq) || 2-phase mixture
5-HMF
5-(Hydroxymethyl)furfural
2,5-DMF
2,5-Dimethylfuran
Labs
Catholyte
Organic Phase
Catholyte
Aqueous Phase
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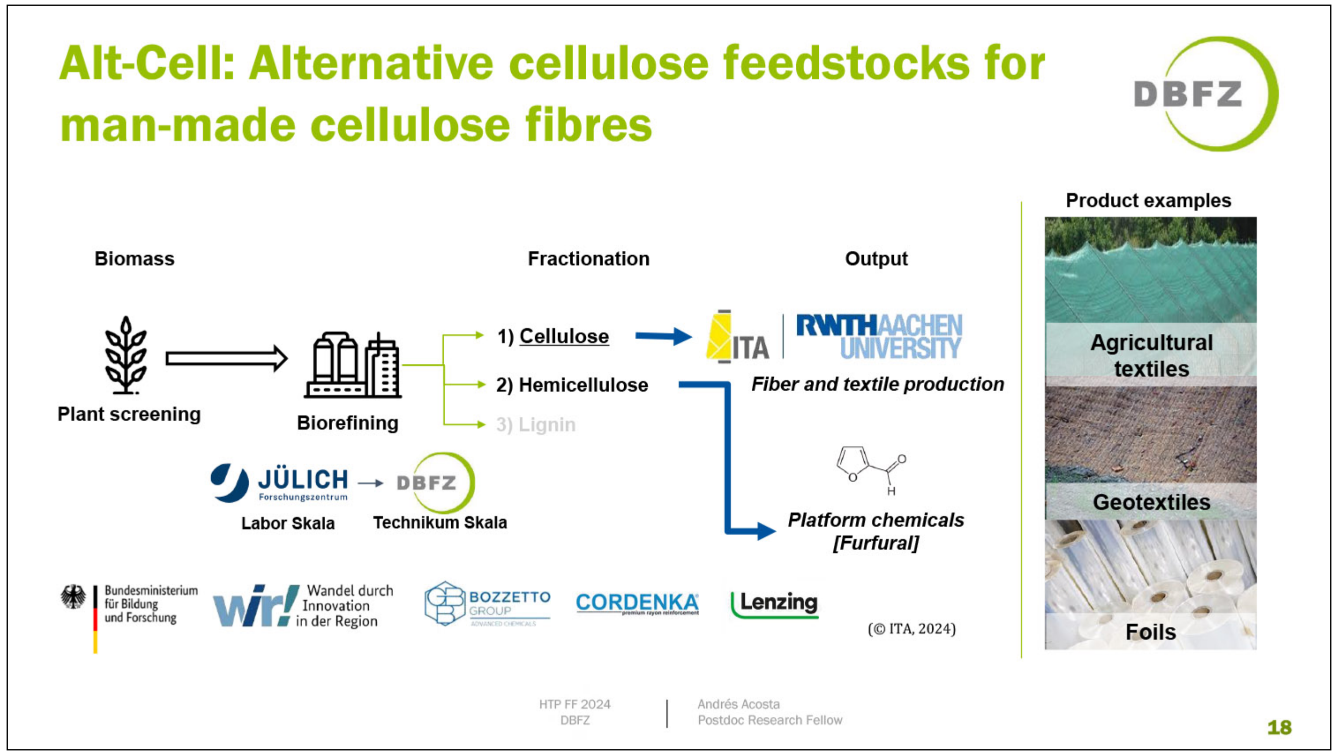
Alt-Cell: Alternative cellulose feedstocks for man-made cellulose fibres
DBFZ
Biomass
Fractionation
Output
Product examples
Plant screening
Biorefining
1) Cellulose
2) Hemicellulose
3) Lignin
ITA
RWTH AACHEN UNIVERSITY
Fiber and textile production
Platform chemicals [Furfural]
JÜLICH
Forschungszentrum
DBFZ
Labor Skala
Technikum Skala
Agricultural textiles
Geotextiles
Foils
Bundesministerium für Bildung und Forschung
Wandel durch Innovation in der Region
BOZZETTO GROUP
CORDENKA
Lenzing
(© ITA, 2024)
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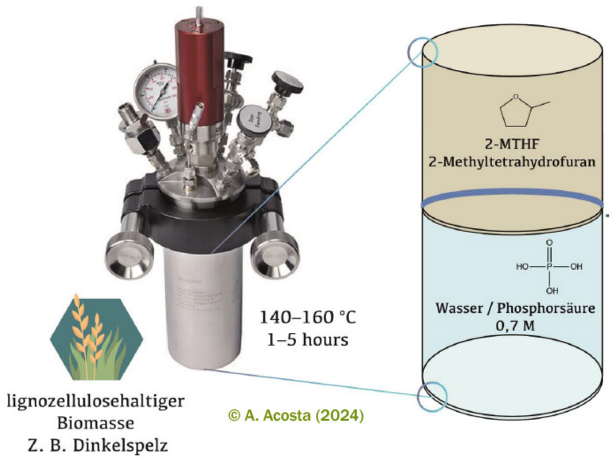
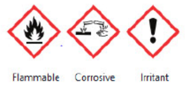
## Hydrothermal biomass fractionation (HTBF)




**Hydrothermal Biomass Fractionation (HTBF)** for the separation of biomass into its biopolymeric components

- Andrés Acosta
- Benjamin Hertklotz
- Alexander Feist
- Christian Klüpfel

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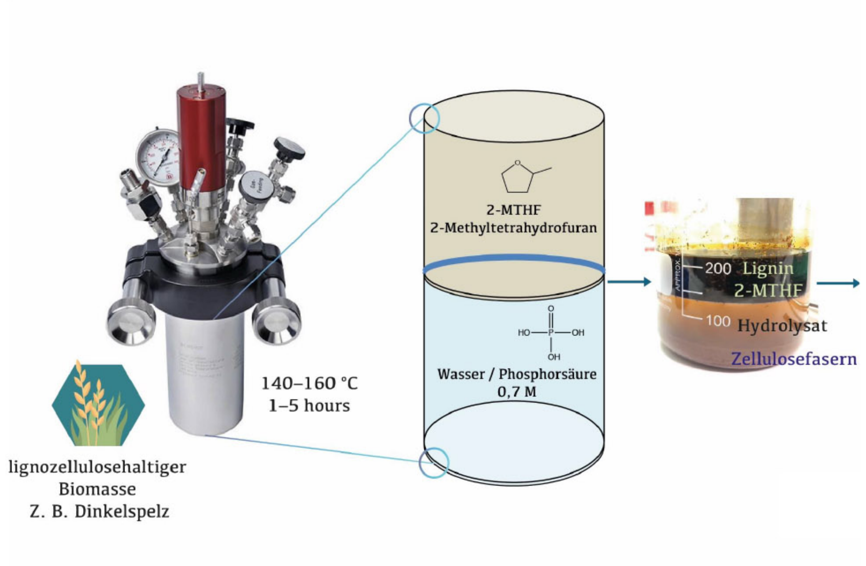
## From residues to valuable materials

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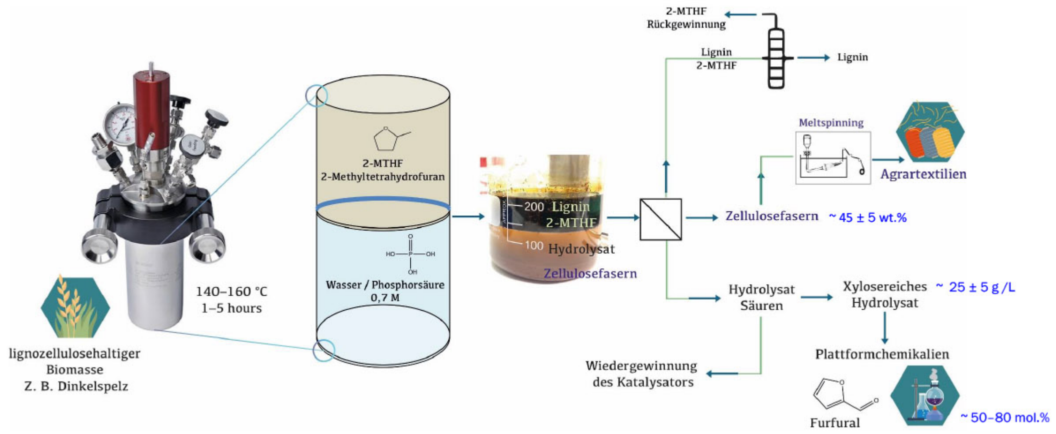
## From residues to valuable materials

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## Upscaling



**0.5 L and 2 L reactors**

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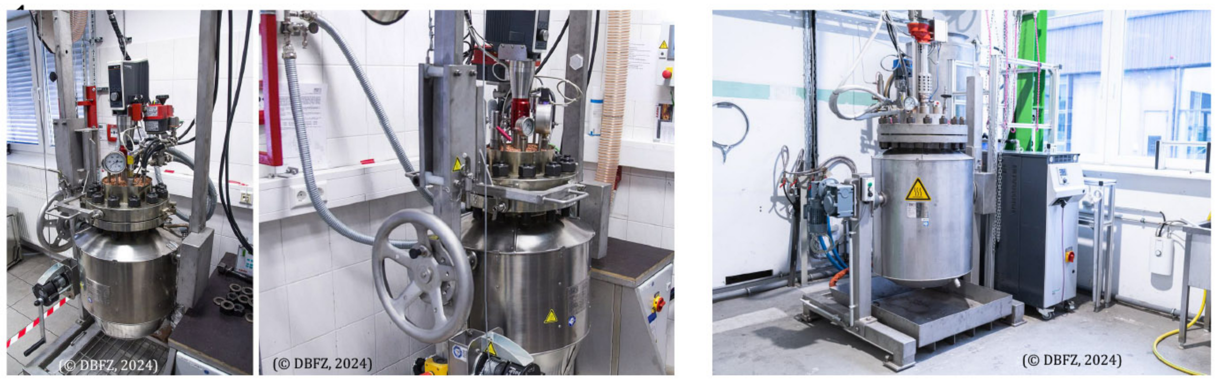
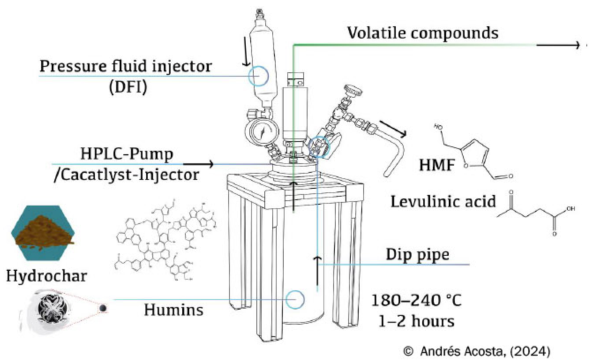
## Upscaling




**10 L and 100 L reactors**



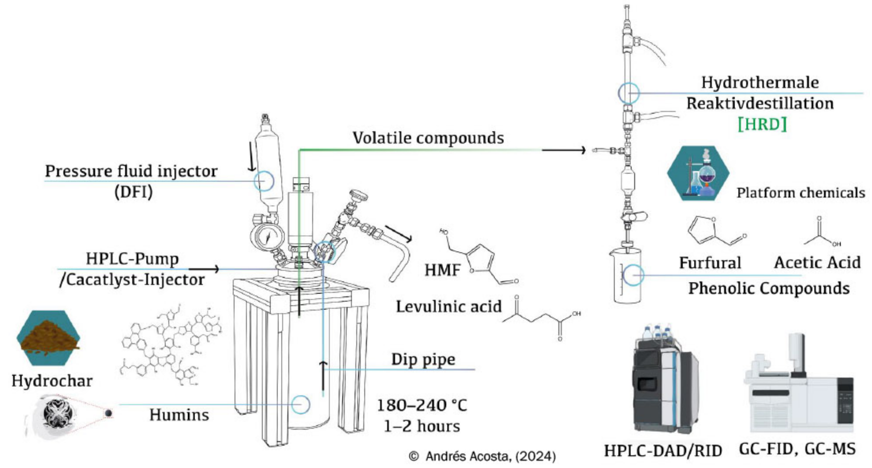
## Hydrothermal Synthesis (HTS) and Hydrothermal Reactive Destillation (HRD)








## Hydrothermal Synthesis (HTS) and Hydrothermal Reactive Destillation (HRD)

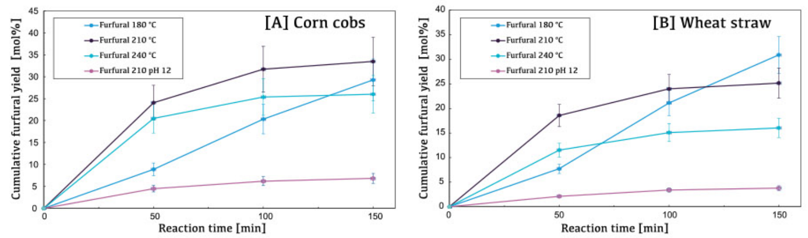



Jakob Köchermann

Fraunhofer CBP



## Simultaneous hydrothermal synthesis of furfural and hydrochar


Fraunhofer CBP

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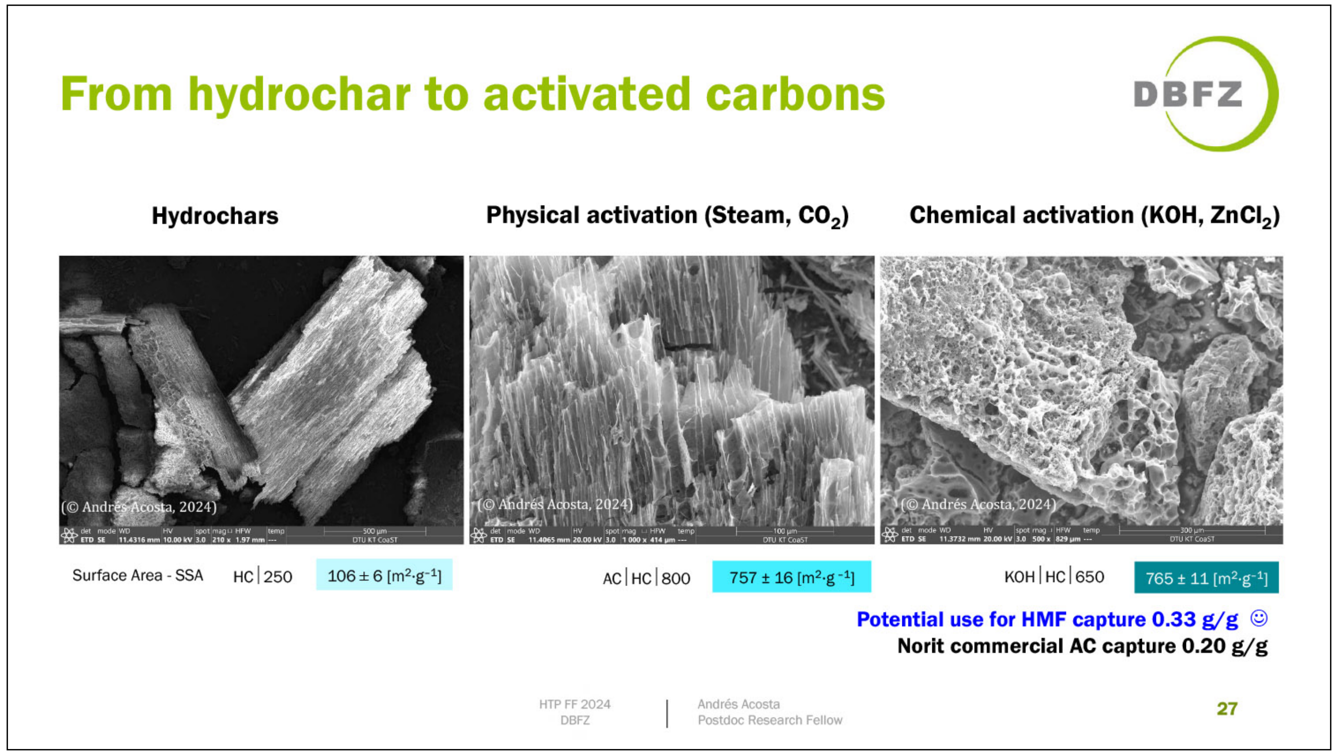
From hydrochar to activated carbons
DBFZ
Hydrochars
Physical activation (Steam, $CO_2$)
Chemical activation (KOH, $ZnCl_2$)
(© Andrés Acosta, 2024)
(© Andrés Acosta, 2024)
(© Andrés Acosta, 2024)
Surface Area - SSA
HC|250
106 ± 6 [$m^2 \cdot g^{-1}$]
AC|HC|800
757 ± 16 [$m^2 \cdot g^{-1}$]
KOH|HC|650
765 ± 11 [$m^2 \cdot g^{-1}$]
Potential use for HMF capture 0.33 g/g ☺
Norit commercial AC capture 0.20 g/g
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Postdoc Research Fellow
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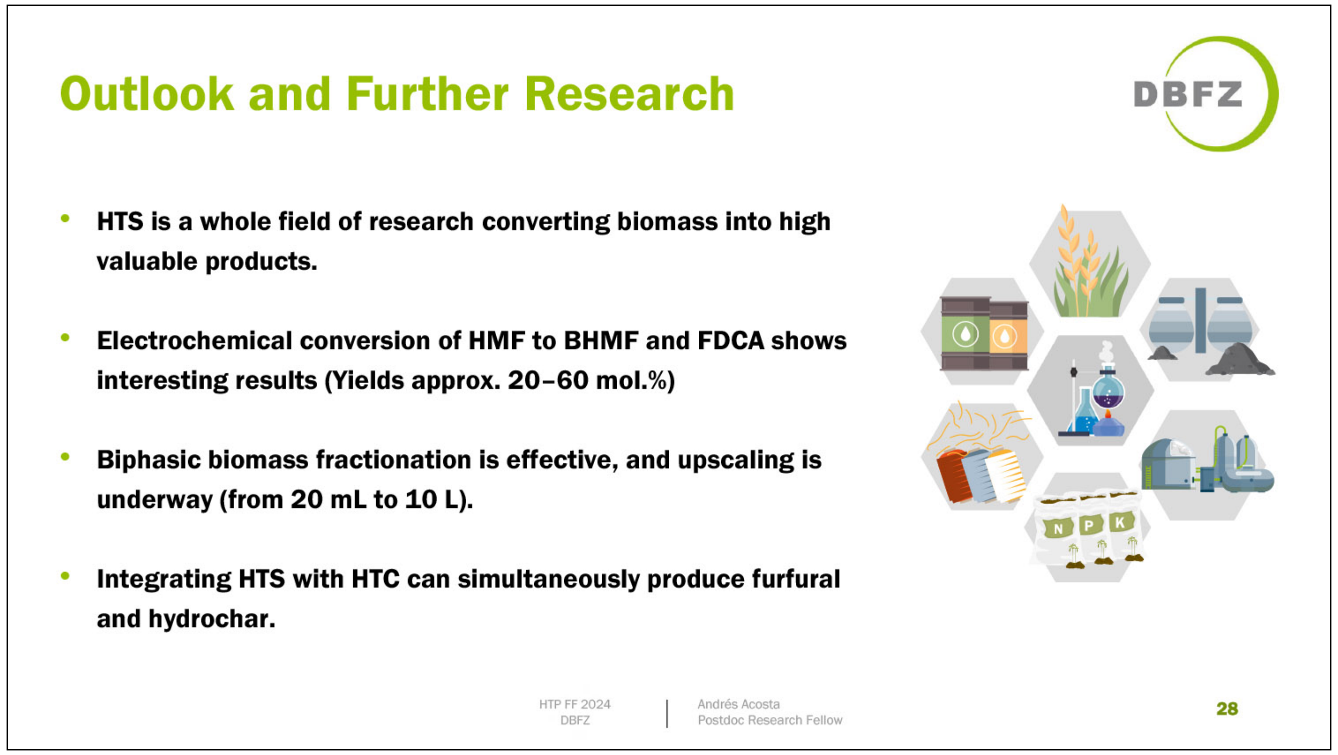
Outlook and Further Research
DBFZ
• HTS is a whole field of research converting biomass into high valuable products.
• Electrochemical conversion of HMF to BHMF and FDCA shows interesting results (Yields approx. 20–60 mol.%)
• Biphasic biomass fractionation is effective, and upscaling is underway (from 20 mL to 10 L).
• Integrating HTS with HTC can simultaneously produce furfural and hydrochar.
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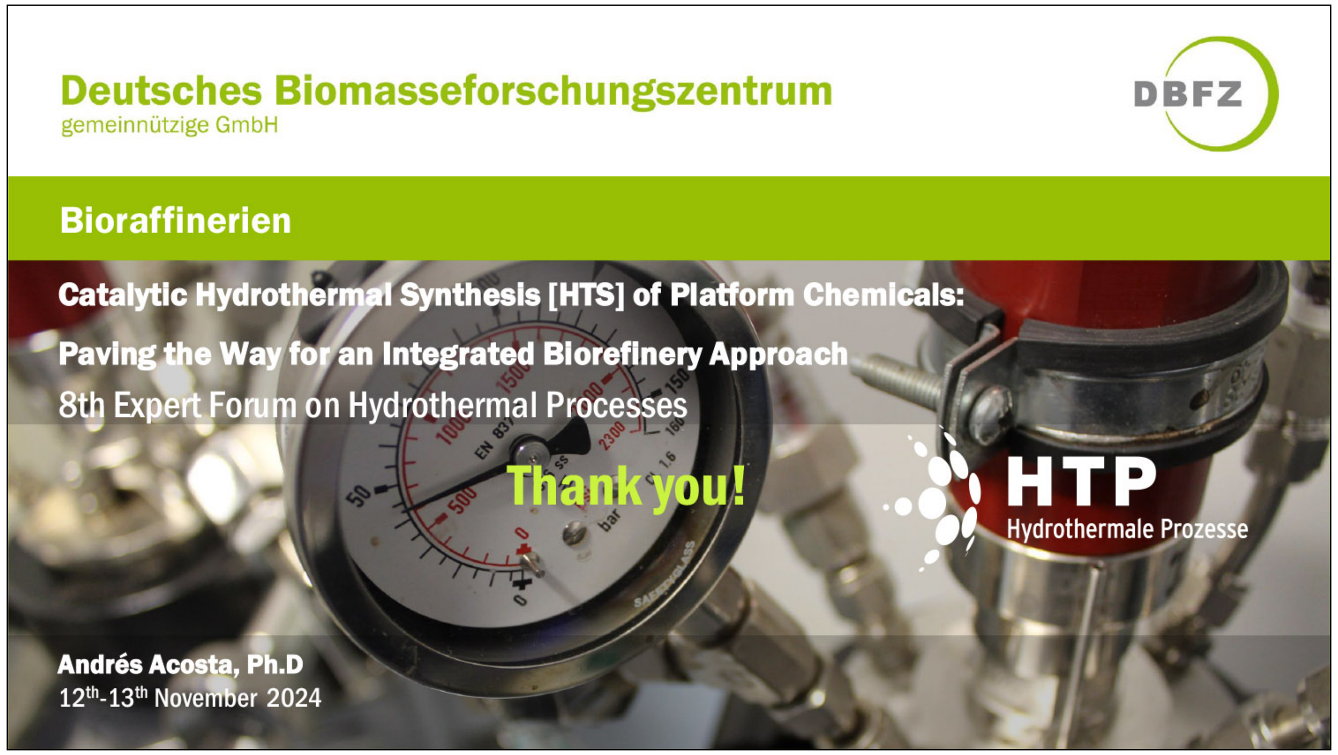
Deutsches Biomasseforschungszentrum
gemeinnützige GmbH
DBFZ
Bioraffinerien
Catalytic Hydrothermal Synthesis [HTS] of Platform Chemicals:
Paving the Way for an Integrated Biorefinery Approach
8th Expert Forum on Hydrothermal Processes
Thank you!
HTP
Hydrothermale Prozesse
Andrés Acosta, Ph.D
12th-13th November 2024


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gemeinnützige GmbH
DBFZ
HTP
Hydrothermale Prozesse
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*Svitlana Filonenko, Max Planck Institute of Colloids and Interfaces*

## Peculiarities of synthesis and properties of artificial humic substances

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**Keywords:** hydrothermal humification, artificial humic substances, methanization, plant micronutrients, carbon sequestration

Carbon in the form of organic matter is a prerequisite for soil health, which is defined by beneficial mechanical and physicochemical characteristics required for soil to function as a base for a thriving ecosystem. Naturally formed organic matter, resulting from the decomposition and recombination of plant and animal litter in soil or composting, is referred to as humic matter. Increasing the carbon content in soil can be achieved artificially by applying sources of inorganic carbon, such as pyrochar, hydrochar, or biochar. The advantage of the latter is the ability to engineer its production and control the amount of added carbon.

Artificial humic substances represent a technology that combines the benefits of natural composting—specifically, the production of organic matter—with the engineering possibilities of biomass processing while preserving carbon during the process. These substances are designed for agricultural applications, with an emphasis on soil restoration and crop yield improvement, linked to the positive effects of humus in soil.

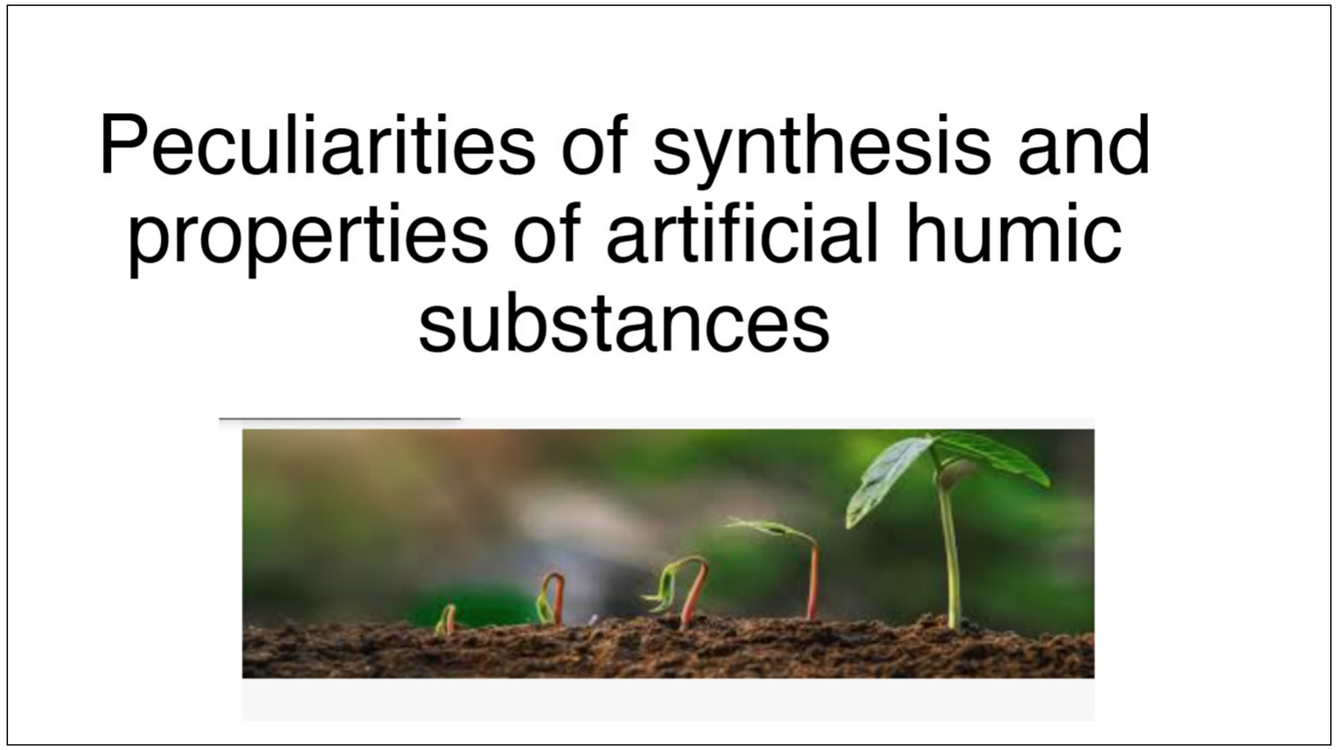
The process of preparing artificial humic substances can be chemically adjusted by adding a base, which modifies the resulting products both qualitatively and quantitatively in solid and liquid phases. The main product is an irregular polymer rich in acidic groups, exhibiting spectroscopic characteristics similar to those of naturally occurring humic matter. In contrast to hydrothermal carbonization under neutral or acidic conditions—where aromatic compounds predominate—this modified hydrothermal synthesis, known as hydrothermal humification, primarily yields sugars and organic acids as low-molecular-weight compounds in the liquid phase. This composition is beneficial for methanization, resulting in a 40% increase in methane yield compared to digestate or hydrothermal carbonization products. Additionally, the initial pH of the process influences phosphate crystallization, providing a mechanism for phosphate management in biogas production and agriculture.

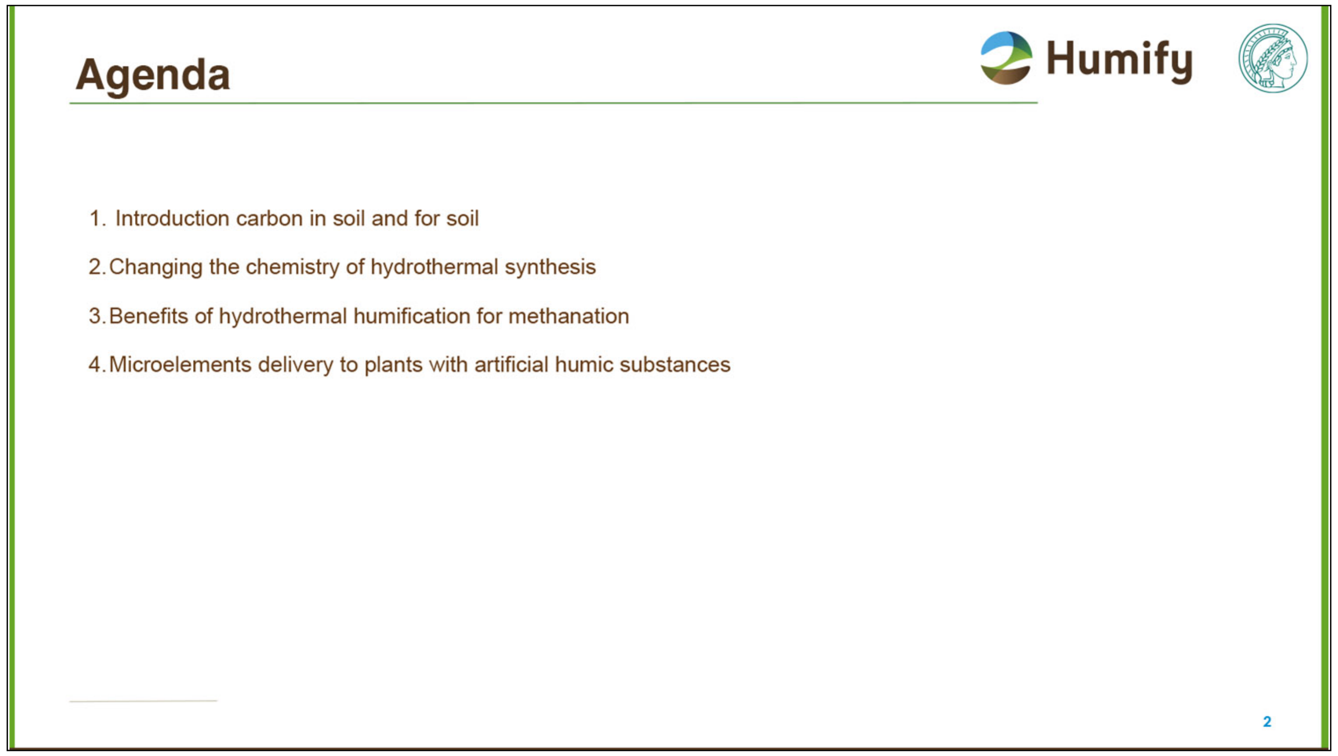
The use of metal salts during hydrothermal humification enables the incorporation of these metals into artificial humic substances, enhancing their bioavailability. In particular, manganese-containing artificial humic substances improve manganese availability for cucumbers, while iron uptake in plants increases in the presence of artificial humic substances. These findings support the broad role of humic substances in soil mineral availability for plants.

Our research demonstrated the broad potential to modify hydrothermal synthesis products through the addition of a base, allowing for their tailored adaptation to practical agricultural applications.







## Natural humic substances in soil

Humify

**Humic substances are vital part of soil organic matter that participates in defining the structure and viability of soil**

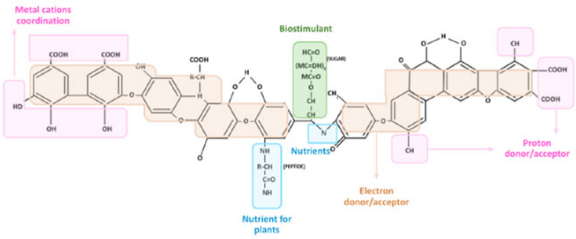
- Humic substances help to increase water retention and prolong drying time
- Humic substances bind mineral elements of soil and participate in structuring the pore system of the soils
- Helps to maintain soil stability and integrity agains erosion
- Humic substance participate in formation of viable for soil microbiome aggregates

3

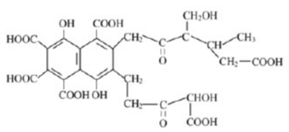
## Chemistry of humic substances for plants

Humify

Terra preta soil




Humic Acid (Stevenson 1982)



Fulvic Acid (Buffalo 1977)

**Plant health and crop yields are directly influenced by the humus content in soil**

- promote healthy plant growth by improving disease resistance and root development in plants
- form complexes with trace minerals in a form that can be more easily absorbed by plants, due to chelating ability
- produces anti-oxidants that combat free radicals and reduce negative influence on plants
- Contains sugars that are especially important for flowering and bud generation, organically enhance flavor, color and aroma of fruits

4





## Solutions for carbon application in soil

Humify

Compost is well known and easy to perform method of artificial humification
Depending on the type of biomass it takes from month to ears to compost it completely
Composting is sensitive to conditions: aerobic or anaerobic
Composting results in up to 60 % of carbon to be lost as carbon dioxide

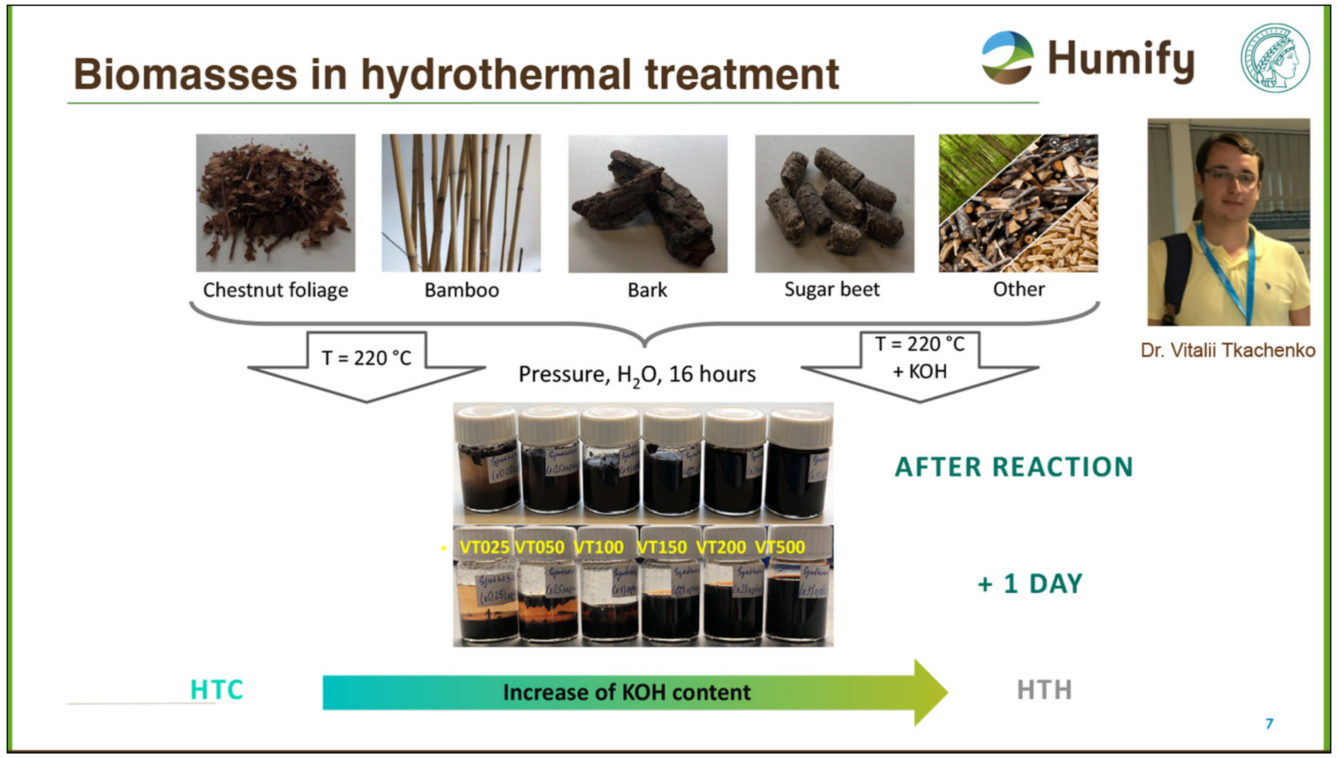
Biochar as a famous and the most often used soil amendment
Depending on the production method considerable losses of carbon take place
Positive effects in soil depend on the soil type and conditions and can be overtaking by the negative influences on soil or plants (high pH, inhibition of germination)

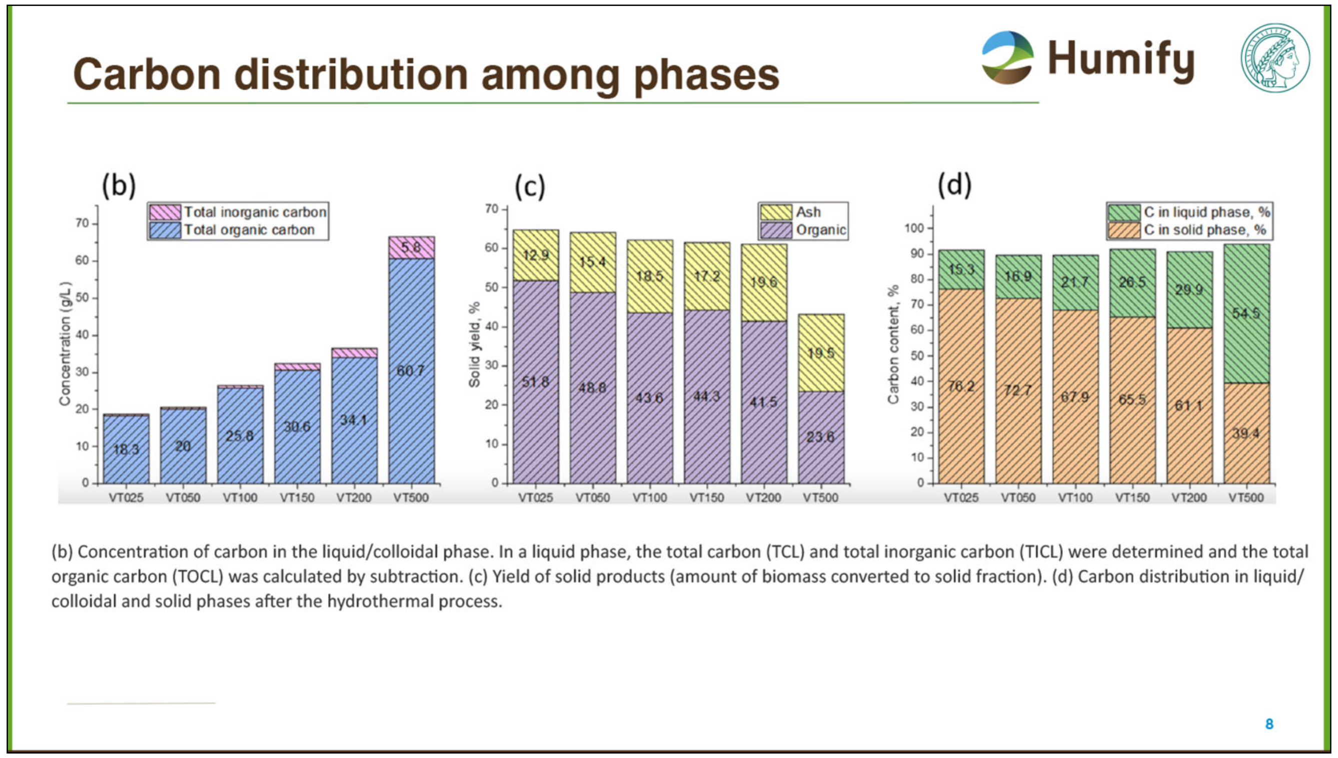
5

## Hydro-/aerogels artificial humic substances

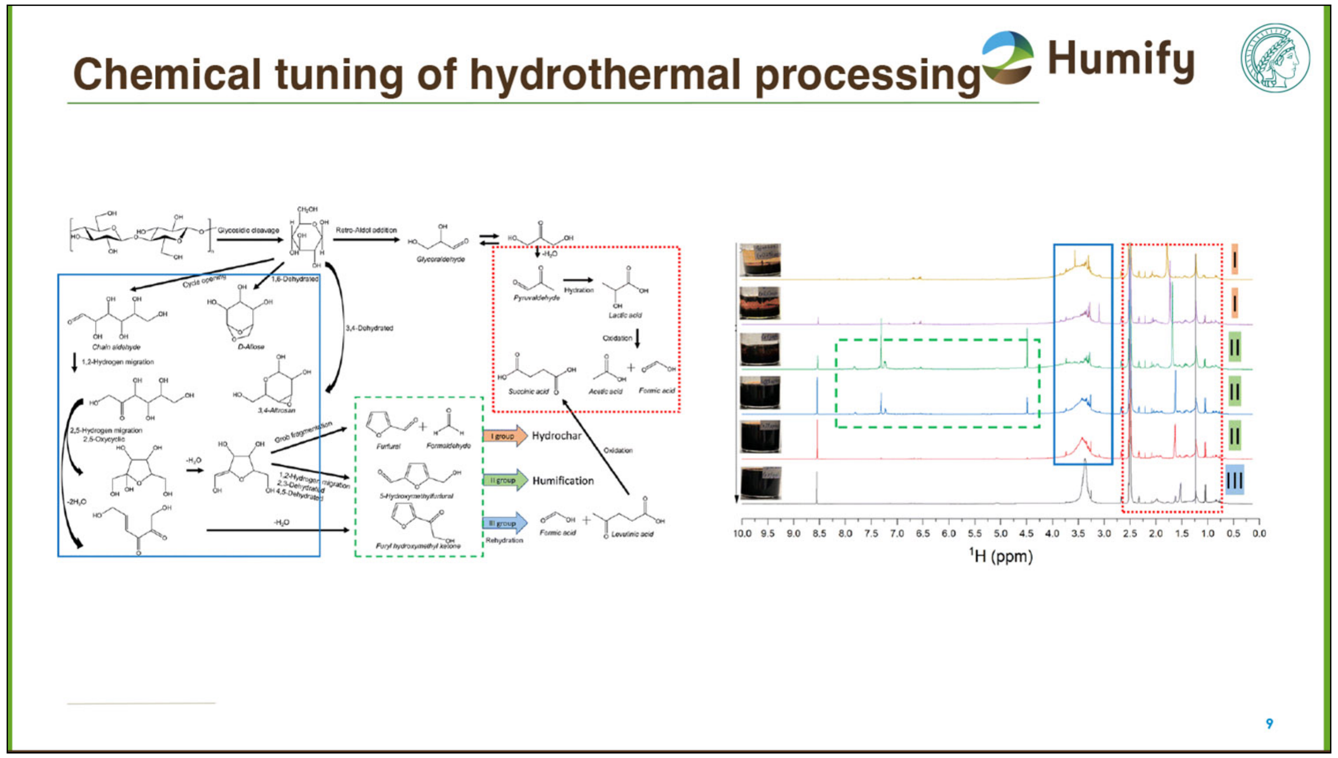
Humify

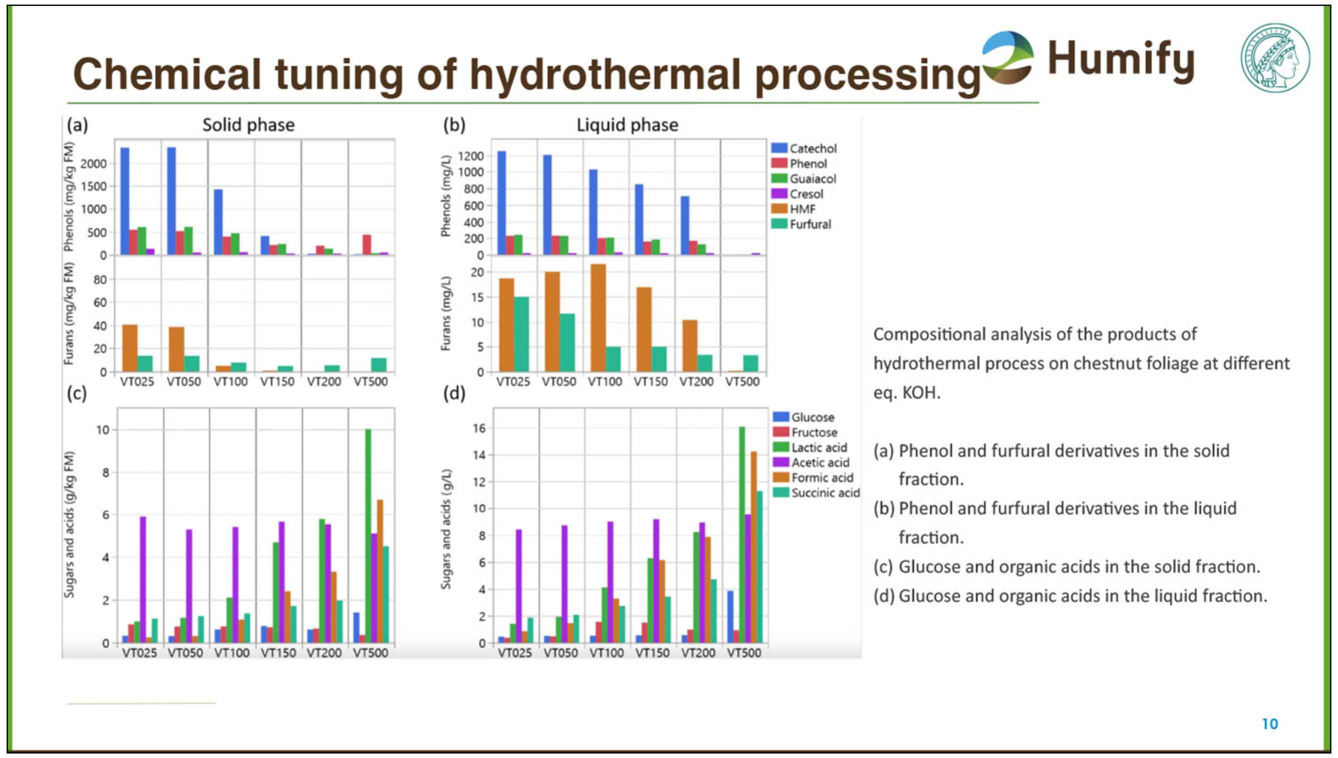
6



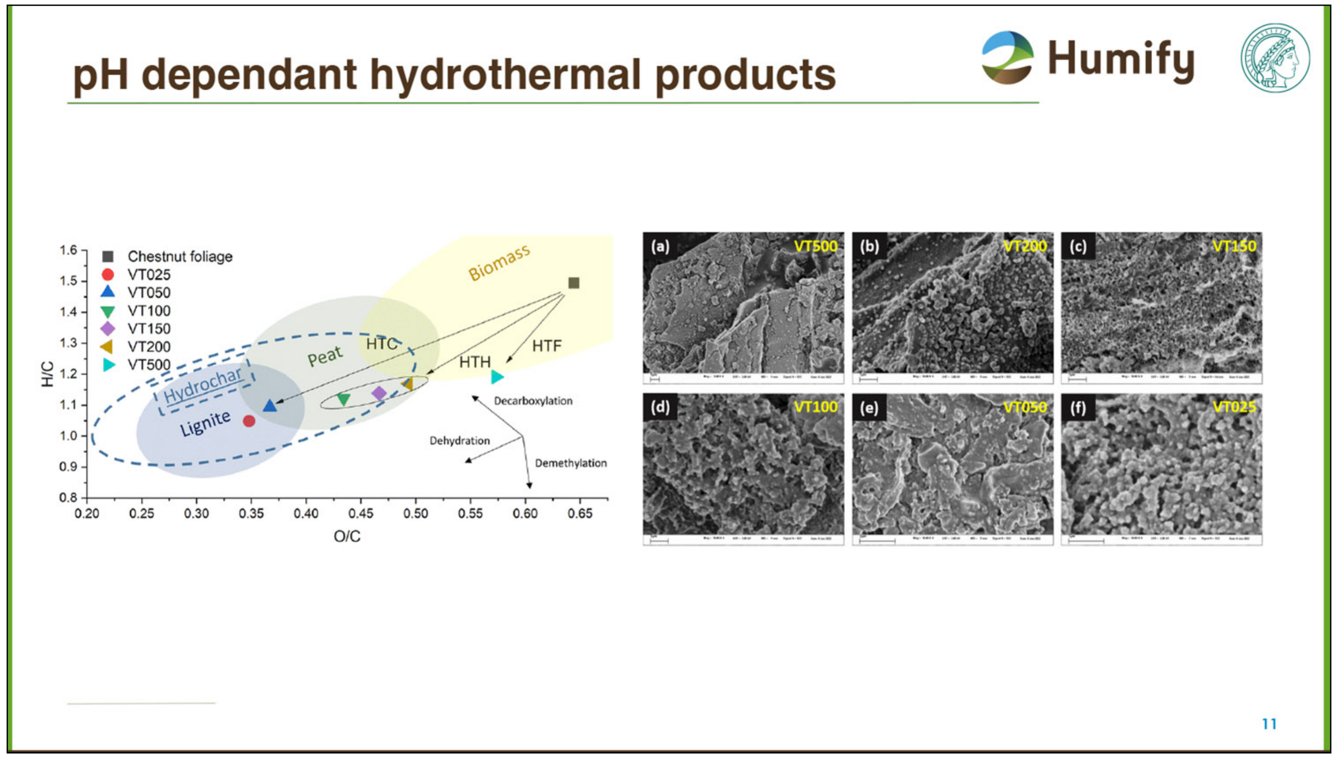





8th Expert Forum on Hydrothermal Processes


pH dependant hydrothermal products
Humify
Chestnut foliage
VT025
VT050
VT100
VT150
VT200
VT500
Biomass
HTC
HTF
HTH
Peat
Hydrochar
Lignite
Decarboxylation
Dehydration
Demethylation
H/C
O/C
(a) VT500
(b) VT200
(c) VT150
(d) VT100
(e) VT050
(f) VT025
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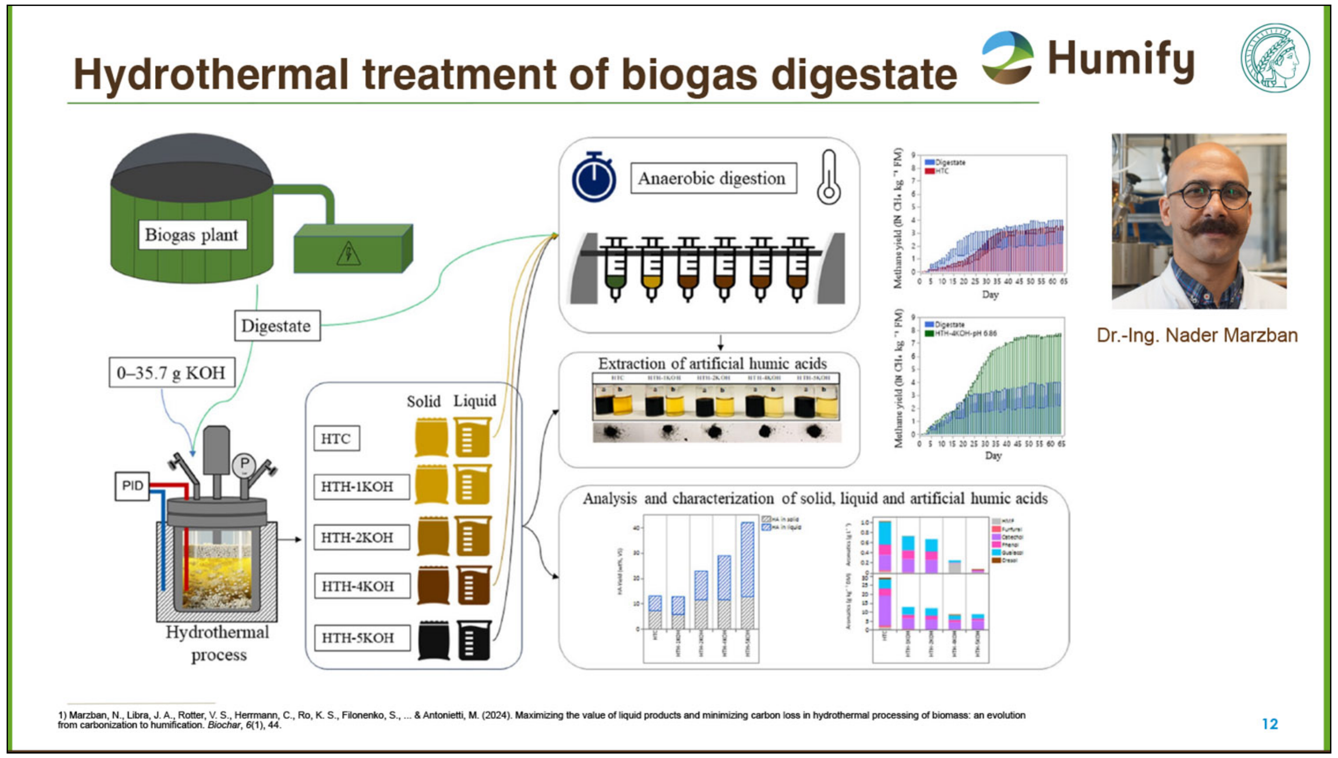
Hydrothermal treatment of biogas digestate
Humify
Biogas plant
Digestate
0–35.7 g KOH
PID
Hydrothermal process
Solid Liquid
HTC
HTH-1KOH
HTH-2KOH
HTH-4KOH
HTH-5KOH
Anaerobic digestion
Extraction of artificial humic acids
Analysis and characterization of solid, liquid and artificial humic acids
Day
Dr.-Ing. Nader Marzban
1) Marzban, N., Libra, J. A., Rotter, V. S., Herrmann, C., Ro, K. S., Filonenko, S., ... & Antonietti, M. (2024). Maximizing the value of liquid products and minimizing carbon loss in hydrothermal processing of biomass: an evolution from carbonization to humification. Biochar, 6(1), 44.
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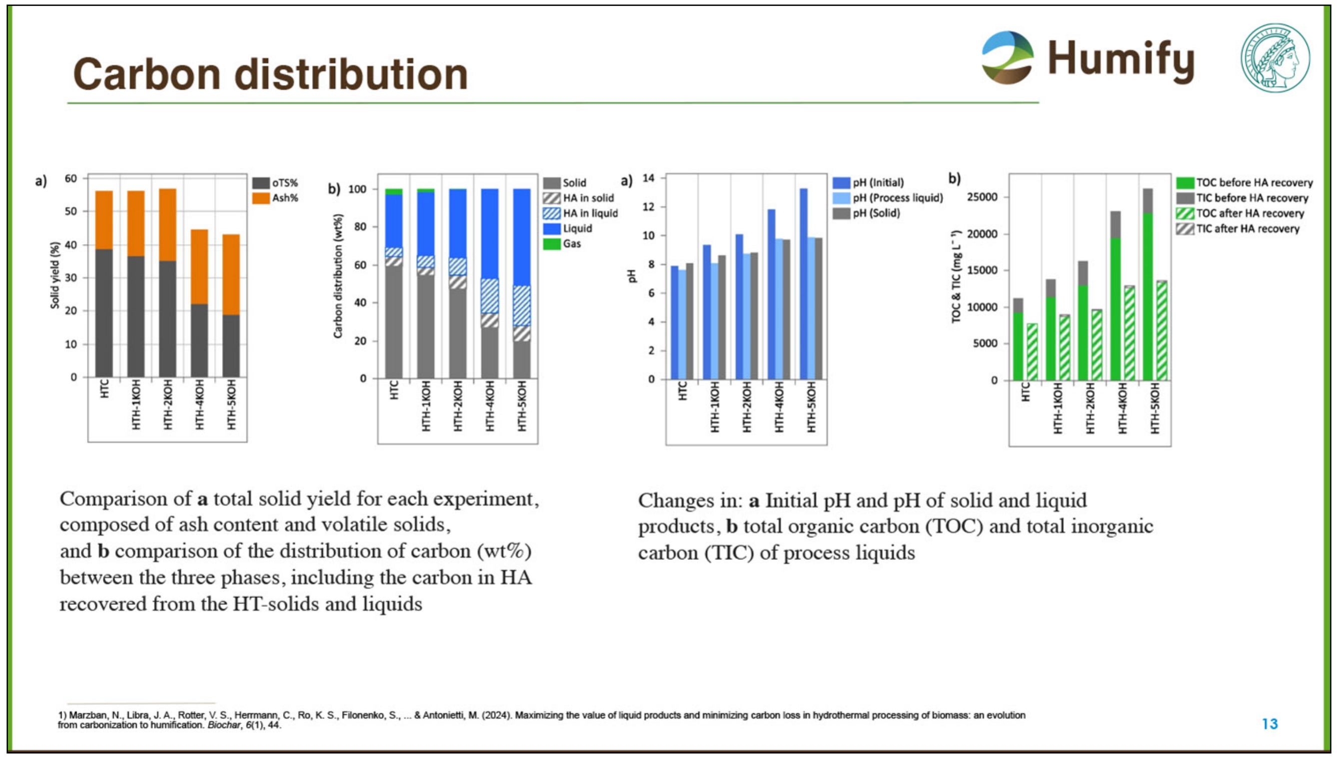
Carbon distribution
Humify
a) b) a) b)
HTC
HTH-1KOH
HTH-2KOH
HTH-4KOH
HTH-5KOH
Comparison of a total solid yield for each experiment, composed of ash content and volatile solids, and b comparison of the distribution of carbon (wt%) between the three phases, including the carbon in HA recovered from the HT-solids and liquids
Changes in: a Initial pH and pH of solid and liquid products, b total organic carbon (TOC) and total inorganic carbon (TIC) of process liquids
1) Marzban, N., Libra, J. A., Rotter, V. S., Herrmann, C., Ro, K. S., Filonenko, S., ... & Antonietti, M. (2024). Maximizing the value of liquid products and minimizing carbon loss in hydrothermal processing of biomass: an evolution from carbonization to humification. Biochar, 6(1), 44.
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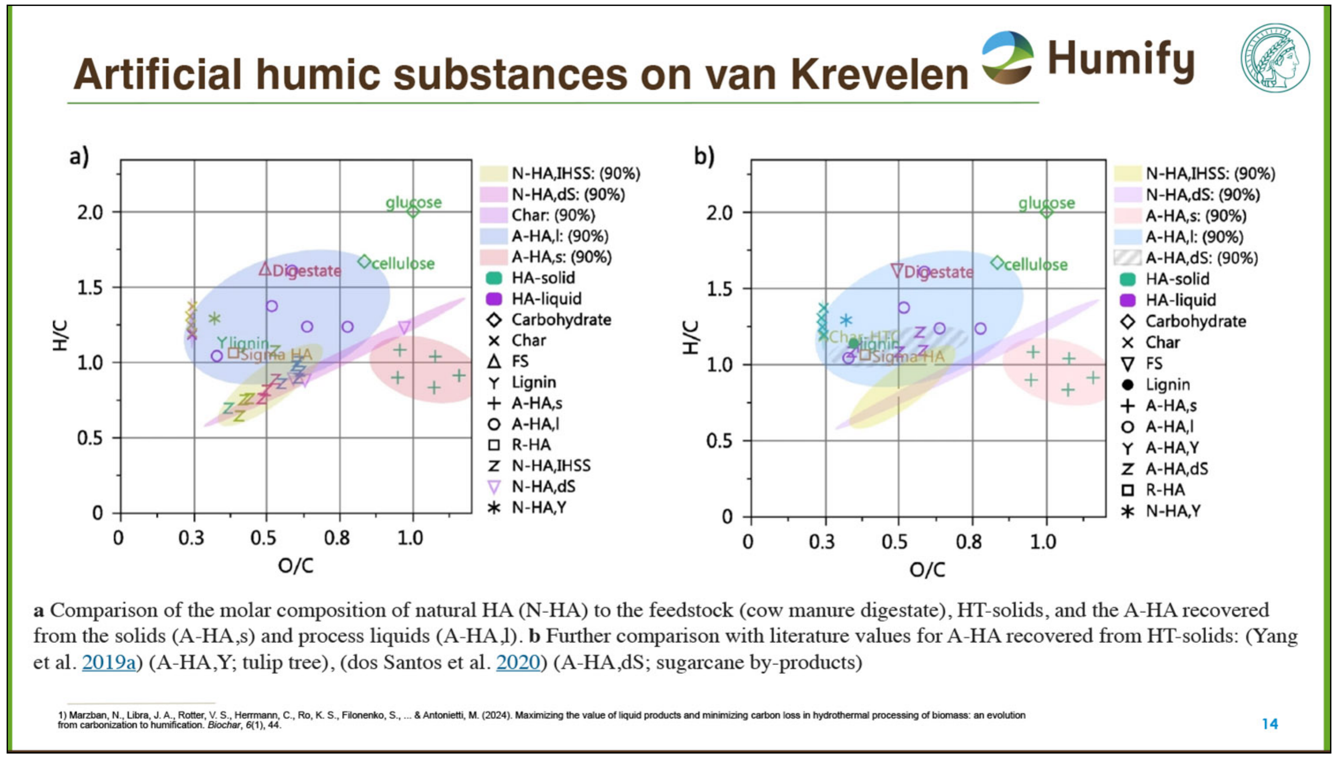
Artificial humic substances on van Krevelen
Humify
a)
b)
H/C
O/C
glucose
cellulose
Digestate
Lignin
Sigma HA
N-HA,IHSS: (90%)
N-HA,dS: (90%)
Char: (90%)
A-HA,l: (90%)
A-HA,s: (90%)
A-HA,dS: (90%)
HA-solid
HA-liquid
Carbohydrate
Char
FS
Lignin
A-HA,s
A-HA,l
A-HA,Y
A-HA,dS
R-HA
N-HA,IHSS
N-HA,dS
N-HA,Y
a Comparison of the molar composition of natural HA (N-HA) to the feedstock (cow manure digestate), HT-solids, and the A-HA recovered from the solids (A-HA,s) and process liquids (A-HA,l). b Further comparison with literature values for A-HA recovered from HT-solids: (Yang et al. 2019a) (A-HA,Y; tulip tree), (dos Santos et al. 2020) (A-HA,dS; sugarcane by-products)
1) Marzban, N., Libra, J. A., Rotter, V. S., Herrmann, C., Ro, K. S., Filonenko, S., ... & Antonietti, M. (2024). Maximizing the value of liquid products and minimizing carbon loss in hydrothermal processing of biomass: an evolution from carbonization to humification. Biochar, 6(1), 44.
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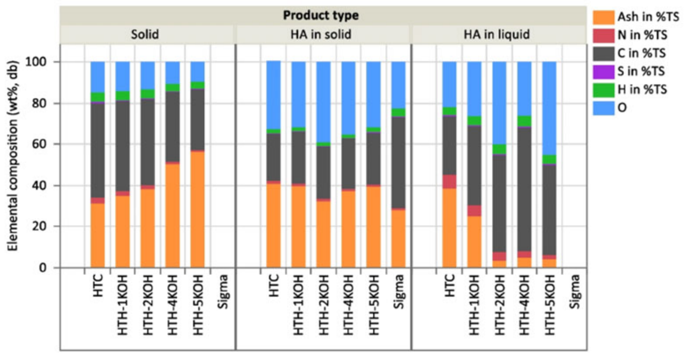
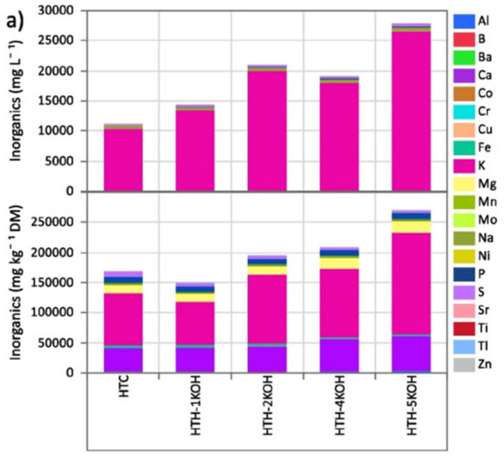
## Elements distribution




Elemental composition of solids (wt%, db) from HTC and HTH runs and the humic acids recovered from the solids and process liquid compared to the digestate and humic acid from Sigma Aldrich Chemicals. (db: dry basis)




**a** Content of ICP-OES elements found in HT-solid and process liquids

1) Marzban, N., Libra, J. A., Rotter, V. S., Herrmann, C., Ro, K. S., Filonenko, S., ... & Antonietti, M. (2024). Maximizing the value of liquid products and minimizing carbon loss in hydrothermal processing of biomass: an evolution from carbonization to humification. *Biochar*, 6(1), 44.

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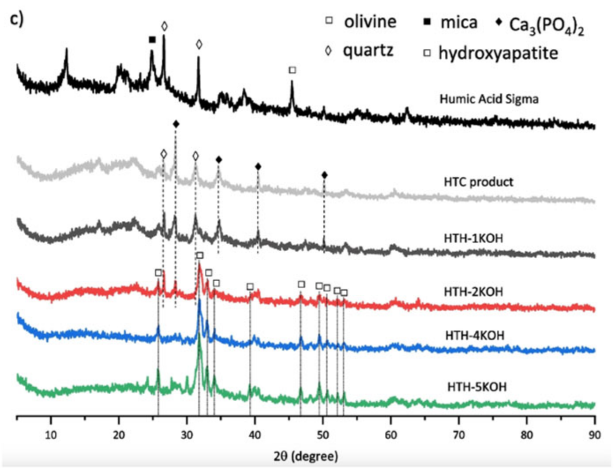
## Phosphates in hydrothermal treatment




XRD patterns of the commercial and A-HAs; increase of the pH during the hydrothermal treatment results in crystallization of calcium phosphates as neutral salt (lower pH) or basic salt (higher pH), and appearance of the quartz at lower pH

1) Marzban, N., Libra, J. A., Rotter, V. S., Herrmann, C., Ro, K. S., Filonenko, S., ... & Antonietti, M. (2024). Maximizing the value of liquid products and minimizing carbon loss in hydrothermal processing of biomass: an evolution from carbonization to humification. *Biochar*, 6(1), 44.

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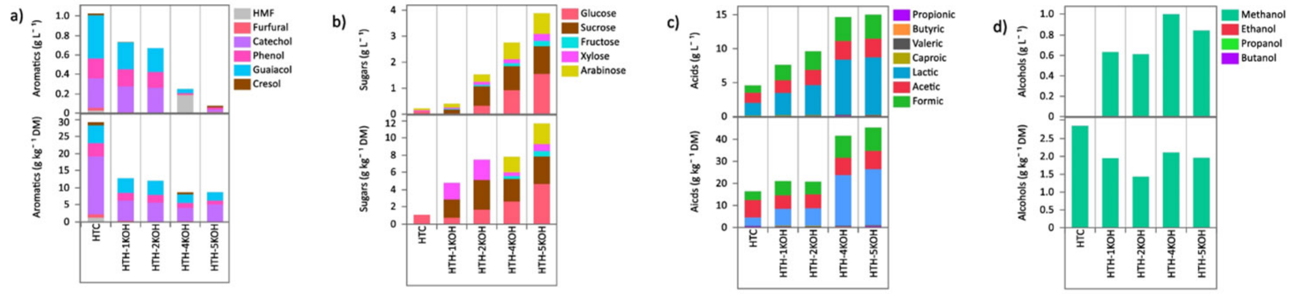
## Compositional changes




Change in the concentration of **a** aromatics, **b** sugars, **c** acids, and **d** alcohols in the liquid (g L-1) and solid ( g L-1 DM) products with increasing initial KOH content

1) Marzban, N., Libra, J. A., Rotter, V. S., Herrmann, C., Ro, K. S., Filonenko, S., ... & Antonietti, M. (2024). Maximizing the value of liquid products and minimizing carbon loss in hydrothermal processing of biomass: an evolution from carbonization to humification. *Biochar*, 6(1), 44.

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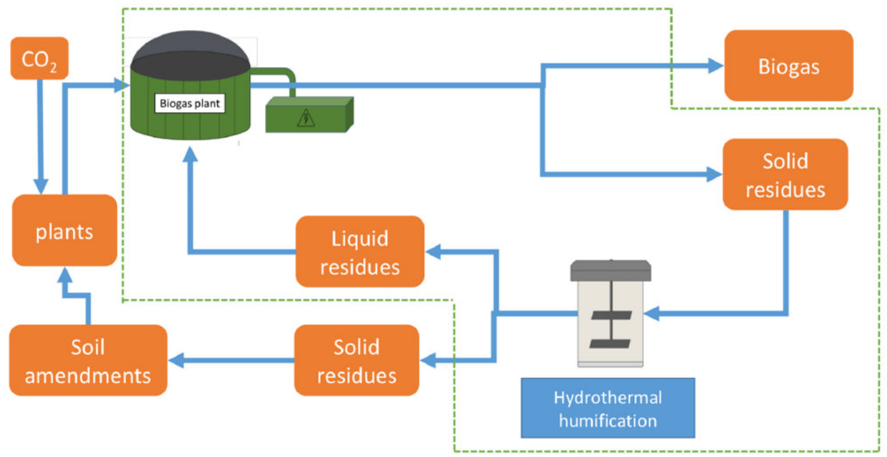
## Carbon cycle in biogas production




1) Marzban, N., Libra, J. A., Rotter, V. S., Herrmann, C., Ro, K. S., Filonenko, S., ... & Antonietti, M. (2024). Maximizing the value of liquid products and minimizing carbon loss in hydrothermal processing of biomass: an evolution from carbonization to humification. *Biochar*, 6(1), 44.

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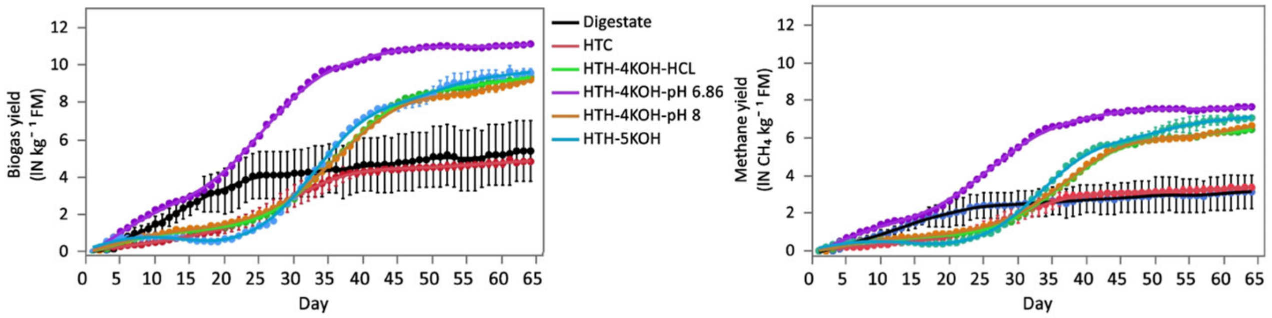
## Maximising biogas production




Biogas and methane yield (lN kg$^{-1}$FM) of HTC and HTH process liquids. The pH of HTH-4KOH process liquid was adjust using HCl (labeled HTH-4KOH-HCl) the same as HTH-5KOH. In addition, the pH of HTH-4KOH was adjusted using cation exchange resins (HTH-4KO-pH 8, and HTH-4KO-pH 6.86)

1) Marzban, N., Libra, J. A., Rotter, V. S., Herrmann, C., Ro, K. S., Filonenko, S., ... & Antonietti, M. (2024). Maximizing the value of liquid products and minimizing carbon loss in hydrothermal processing of biomass: an evolution from carbonization to humification. *Biochar*, *6*(1), 44.

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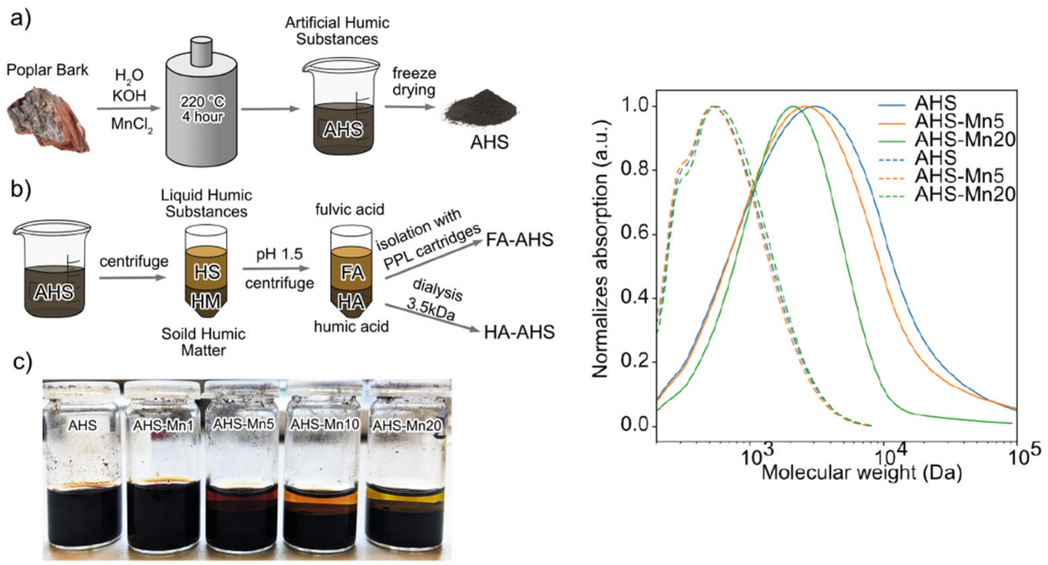
## Humic substances for Mn delivery to plants




Dr. Alexander Volikov

1) Volikov, A., Schneider, H., Tarakina, N. V., Marzban, N., Antonietti, M., & Filonenko, S. (2024). Artificial humic substances as sustainable carriers for manganese: Development of a novel bio-based microfertilizer. *Biofuel Research Journal*, *11*(1), 2013-2024.

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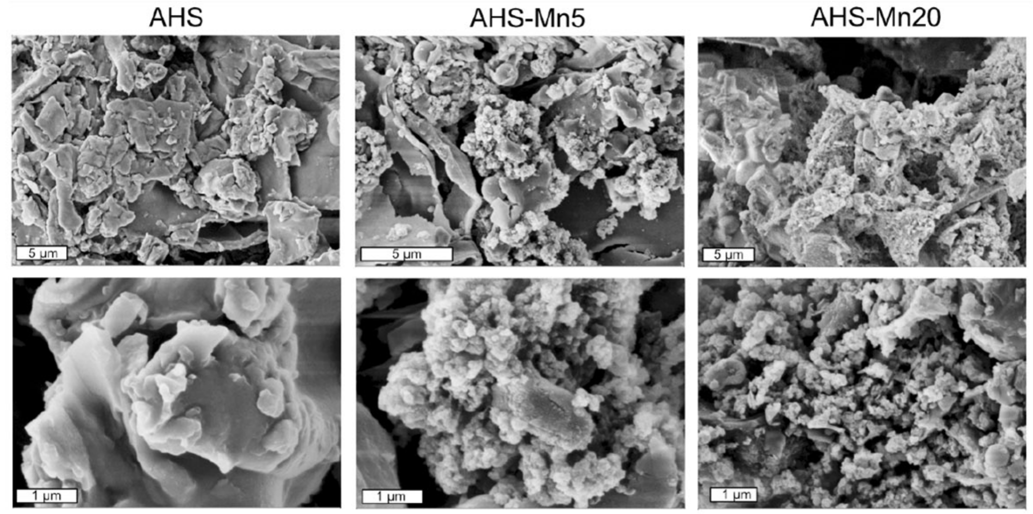
## SEM humic substances with Mn




1) Volikov, A., Schneider, H., Tarakina, N. V., Marzban, N., Antonietti, M., & Filonenko, S. (2024). Artificial humic substances as sustainable carriers for manganese: Development of a novel bio-based microfertilizer. *Biofuel Research Journal*, *11*(1), 2013-2024.

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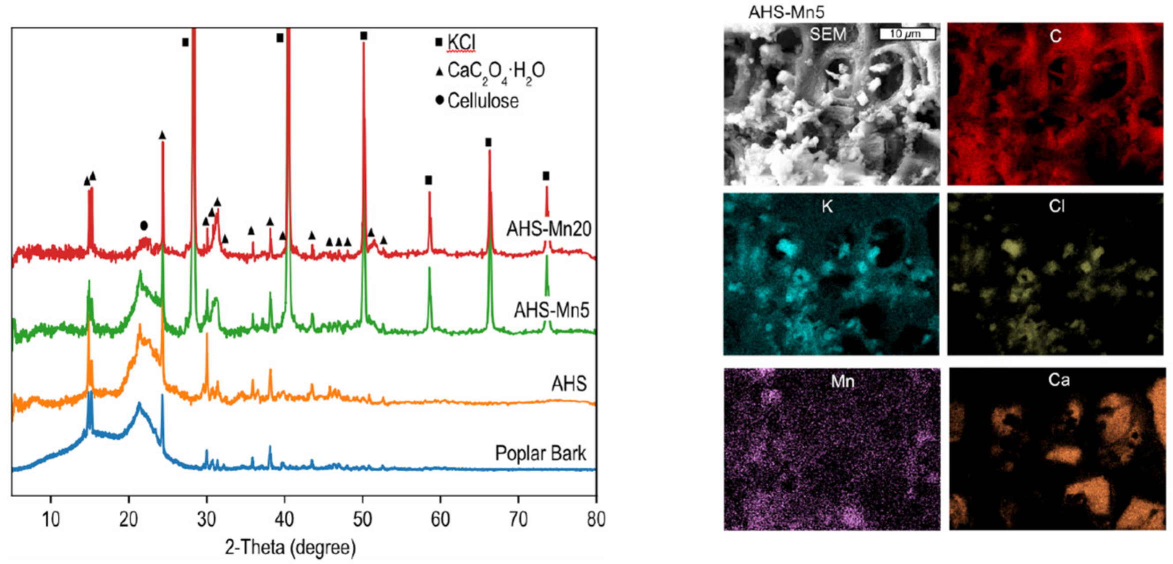
## Crystal phase formation




1) Volikov, A., Schneider, H., Tarakina, N. V., Marzban, N., Antonietti, M., & Filonenko, S. (2024). Artificial humic substances as sustainable carriers for manganese: Development of a novel bio-based microfertilizer. *Biofuel Research Journal*, *11*(1), 2013-2024.

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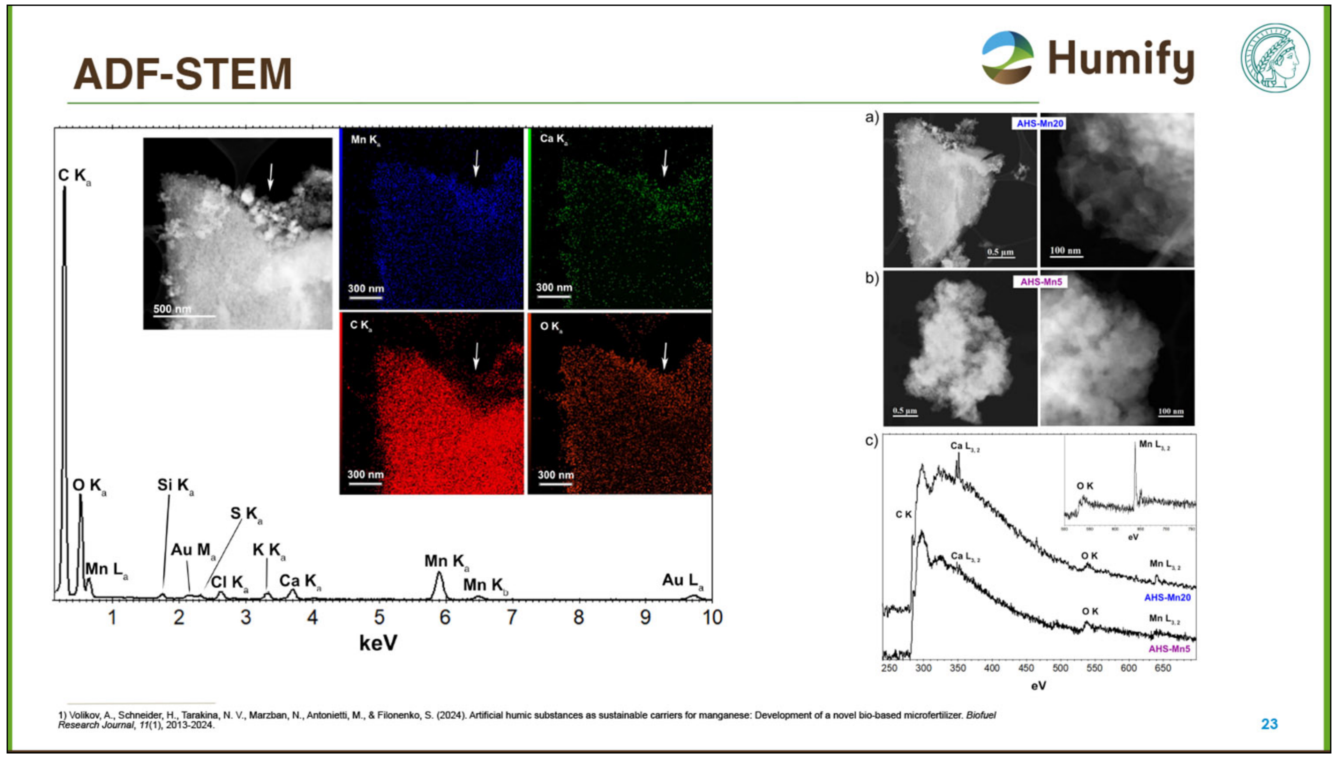
ADF-STEM
Humify
C K
O K
Si K
S K
Au M
K K
Cl K
Ca K
Mn L
Mn K
Mn K
Au L
1 2 3 4 5 6 7 8 9 10
keV
500 nm
300 nm
a)
b)
c)
AHS-Mn20
AHS-Mn5
eV
1) Volikov, A., Schneider, H., Tarakina, N. V., Marzban, N., Antonietti, M., & Filonenko, S. (2024). Artificial humic substances as sustainable carriers for manganese: Development of a novel bio-based microfertilizer. Biofuel Research Journal, 11(1), 2013-2024.
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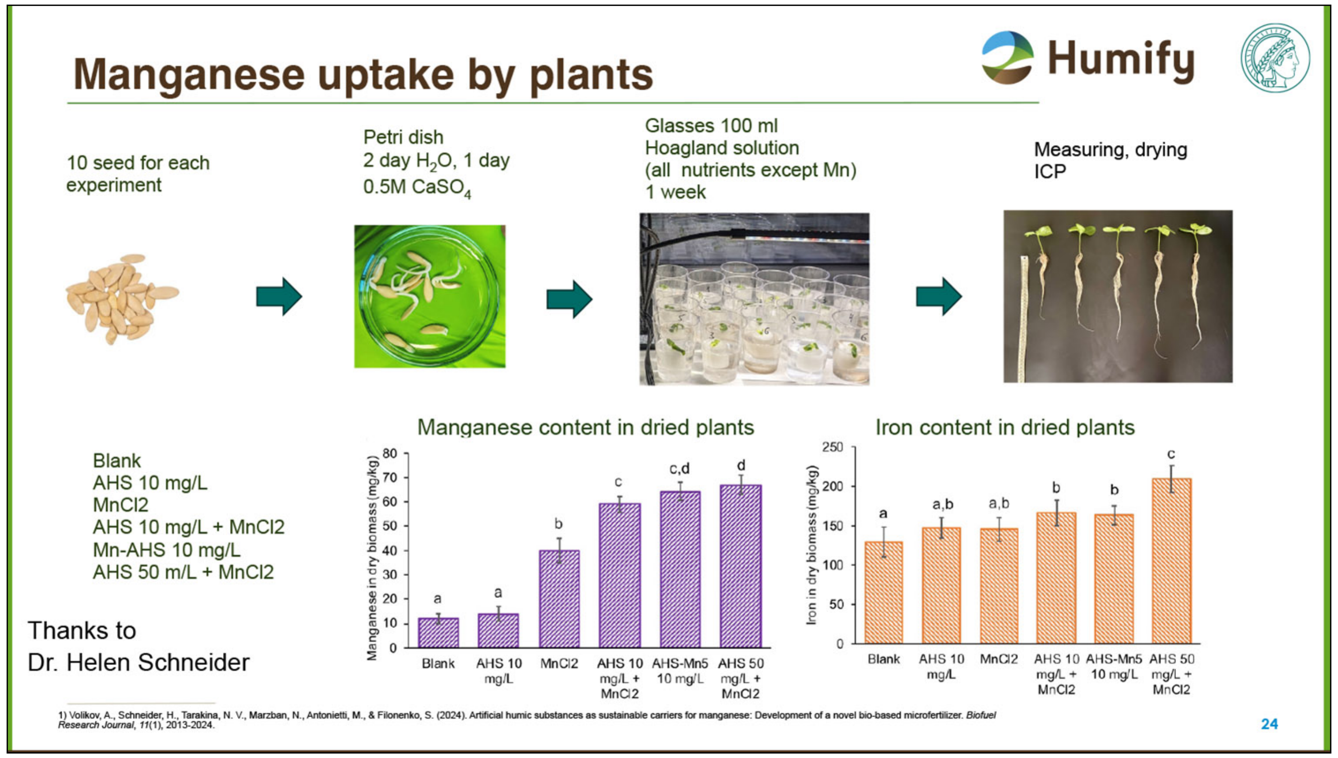
Manganese uptake by plants
Humify
10 seed for each experiment
Petri dish
2 day H2O, 1 day
0.5M CaSO4
Glasses 100 ml
Hoagland solution
(all nutrients except Mn)
1 week
Measuring, drying
ICP
Manganese content in dried plants
Iron content in dried plants
Blank
AHS 10 mg/L
MnCl2
AHS 10 mg/L + MnCl2
Mn-AHS 10 mg/L
AHS 50 m/L + MnCl2
Thanks to
Dr. Helen Schneider
Manganese in dry biomass (mg/kg)
Iron in dry biomass (mg/kg)
1) Volikov, A., Schneider, H., Tarakina, N. V., Marzban, N., Antonietti, M., & Filonenko, S. (2024). Artificial humic substances as sustainable carriers for manganese: Development of a novel bio-based microfertilizer. Biofuel Research Journal, 11(1), 2013-2024.
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Tina Seemann
Antje Volkel
Marlies Gräwert
Jessica Brandt
ATB
Dr. habil. Judy Libra
Dr.-Ing. Nader Marzban
Prof. Thomas Hofmann
Thank you!

*Luca Fiori, University of Trento*

## Recovery of energy and platform chemicals from bioplastics through hydrothermal processes

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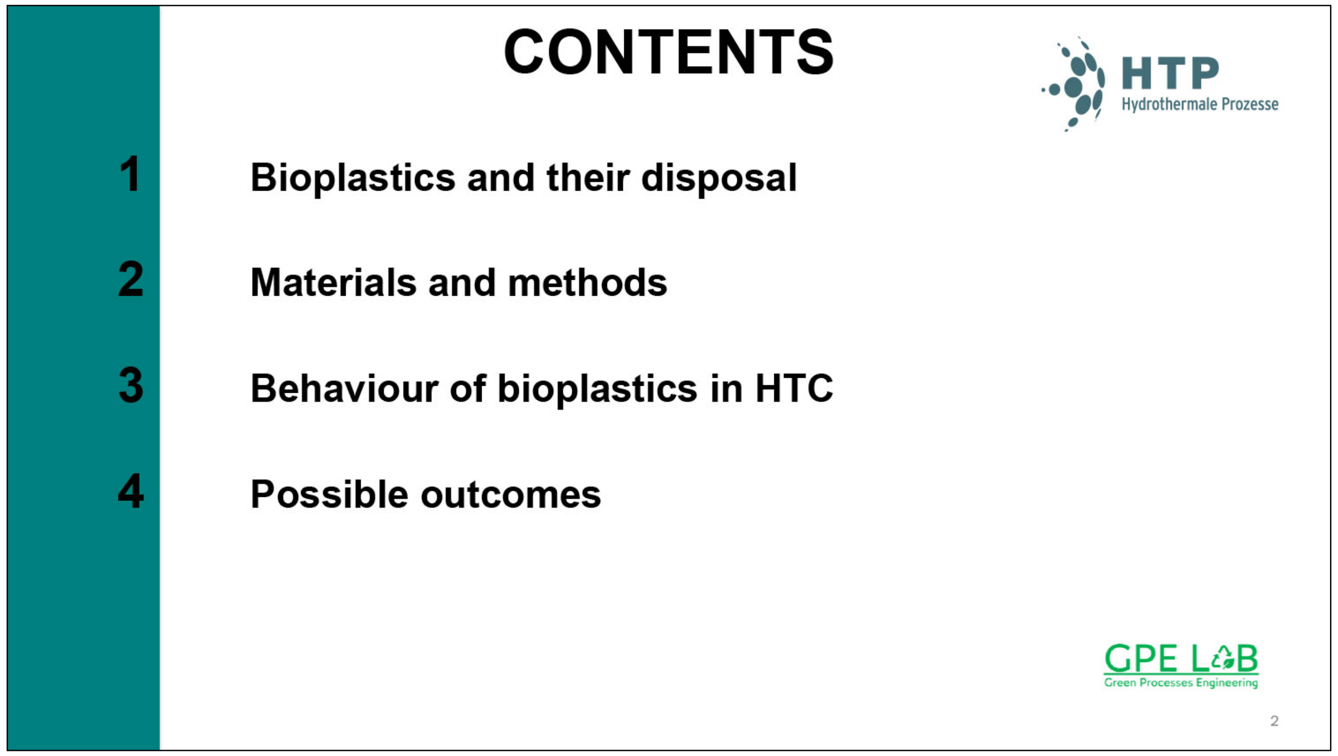
**Keywords:** Bioplastics, hydrolysis, anaerobic digestion, hydrothermal process

The production of biodegradable plastics (or bioplastics) is growing exponentially, but how to best dispose of them remains dubious, since they degrade at much lower rates compared to the other types of organic waste they are collected with. To overcome this problem, we have subjected various types of bioplastics to hydrothermal carbonization under various operating temperatures. The experiments showed that all types of bioplastics are affected by the process, getting disintegrated and hydrolysing partially or totally.

If the hydrothermally treated bioplastics are fed to anaerobic digestion, much higher biogas production yields and rates are observed: a hydrothermal pretreatment could thus make bioplastics suitable for plants that treat organic wastes. Nonetheless, various analytical techniques revealed that the liquid product obtained from the process may contain various chemicals of industrial interest, such as lactic acid, succinic acid, levulinic acid, 5-HMF, etc. Especially if a residual bioplastic is available as a pure stream, a material valorisation may hence also be an interesting route.





# CONTENTS

HTP Hydrothermale Prozesse



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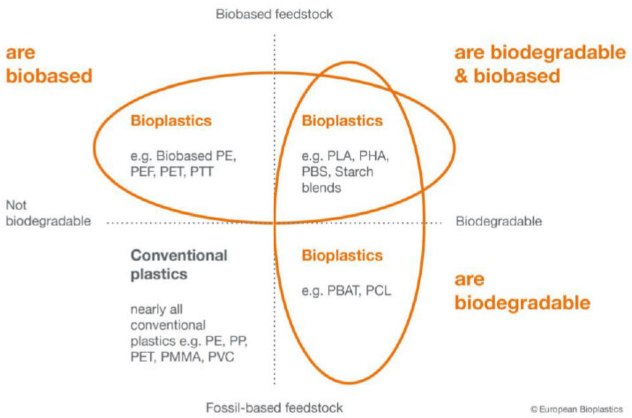
## Bioplastics

HTP Hydrothermale Prozesse

Polymeric materials with mechanical properties similar to traditional plastics that also are:

- either bio-based
- or biodegradable
- or both bio-based AND biodegradable (most common meaning)




https://www.european-bioplastics.org/bioplastics/materials/

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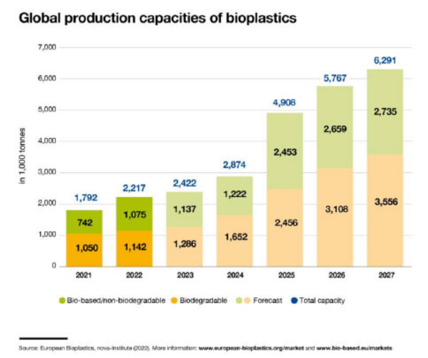
## Bioplastics

HTP Hydrothermale Prozesse

Polymeric materials with mechanical properties similar to traditional plastics that also are:

- either bio-based
- or biodegradable
- or both bio-based AND biodegradable (most common meaning)




Bioplastic production will triple in the next three years.

https://www.european-bioplastics.org/bioplastics/materials/

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## Problems in bioplastics disposal

HTP Hydrothermale Prozesse

**Bioplastics disposal**

Disposed of with the organic fraction of municipal solid waste (OFMSW).

BAT OFMSW treatment plants: anaerobic digestion (AD) and composting.

Bioplastics are problematic for these plants, often get discarded.

Long residence time

**EN 13432**
A material is biodegradable if in composting conditions it degrades by 90% over **6 months**

**BAT OFMSW plants**
**15-30 days** of anaerobic digestion
+
**20-30 days** of composting

Short residence time

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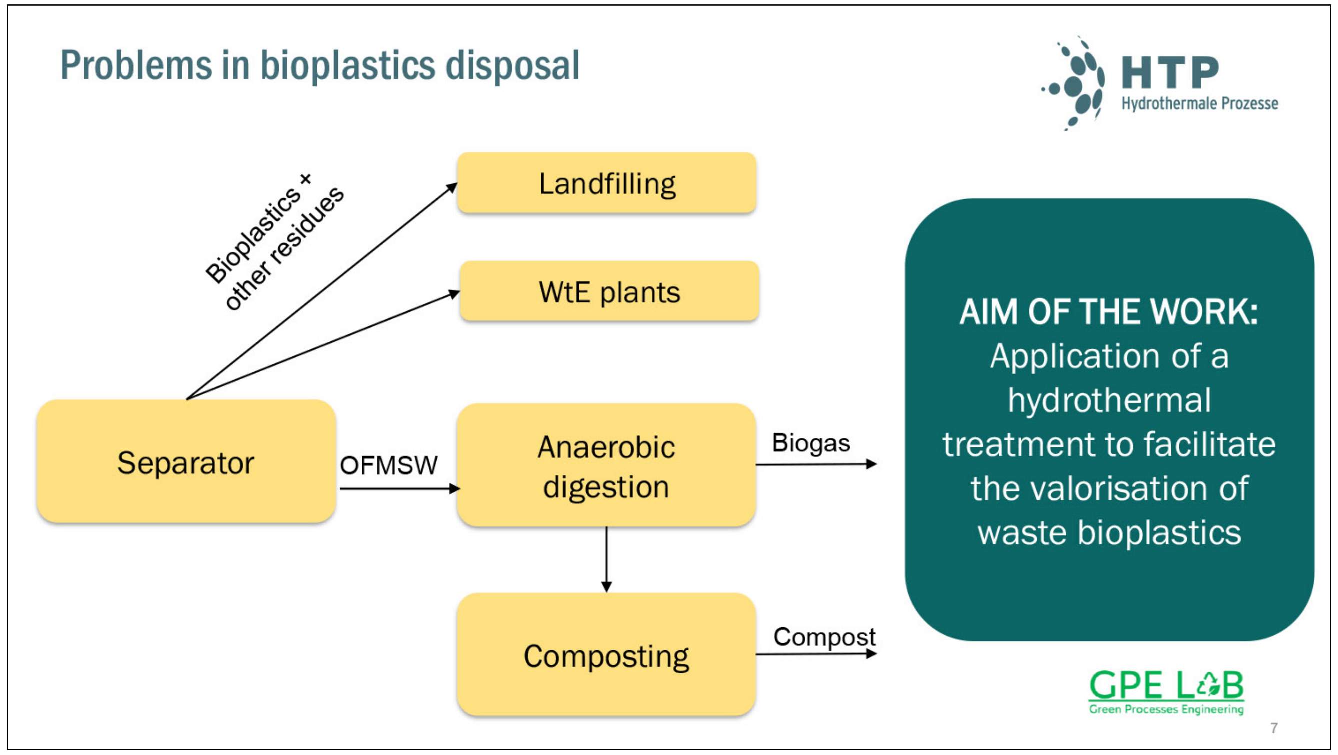


## CONTENTS

1 Bioplastics and their disposal

2 **Materials and methods**

3 Behaviour of bioplastics in HTC

4 Possible outcomes

8





## Hydrothermal treatment

- **Hydrothermal treatments** (HT) performed in liquid water at moderate temperatures.
- **Liquid water** behaves as a catalyst and facilitates some reactions.
- Applied to **break down** waste biomasses and facilitate subsequent processing steps.
- As a **pre-treatment before anaerobic digestion** increases the biogas yield.
- Literature on HT of bioplastics is scarce.

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## Hydrothermal treatment

**Bioplastics tested in GPE Lab:**

- Cellulose acetates
- Polylactic acid (PLA)
- Polybutylene succinate (PBS)
- Galalith (from casein)
- Blends of starch (shopping bags etc)

**What have we observed?**

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# CONTENTS

HTP Hydrothermale Prozesse



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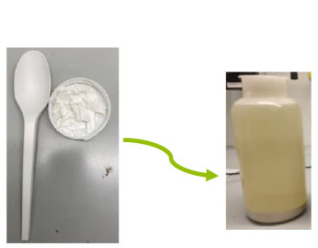
## Hydrothermal treatment

HTP Hydrothermale Prozesse

**The behaviour in HT strongly depends on the material. Three possible outcomes:**

**Materials that dissolve completely and remain in the liquid phase**



PLA, PBS

**Materials that dissolve partially, with some brown solid remaining**

Starch blends, galalith

**Materials that dissolve completely, but then recondense and form char**

Cellulose acetates

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## Hydrothermal treatment

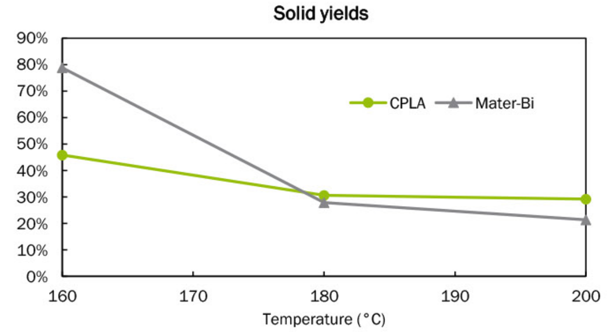
HTP Hydrothermale Prozesse

**Materials that dissolve completely and remain in the liquid phase**

PLA
(most produced bioplastic)

Mater-Bi (PLA+PBS)

T = 160-200 °C
t = 1 h
BP/$H_2O$ = 0.1




- At 180+ °C, both materials dissolve in the liquid, only inorganics (20%) remain in the solid

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## Hydrothermal treatment

HTP Hydrothermale Prozesse

**Materials that dissolve completely and remain in the liquid phase**

PLA
(most produced bioplastic)

Mater-Bi (PLA+PBS)

T = 160-200 °C
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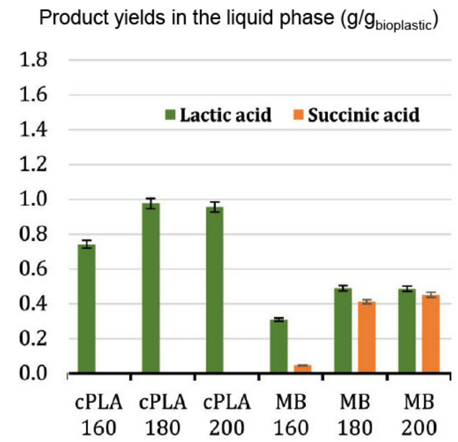


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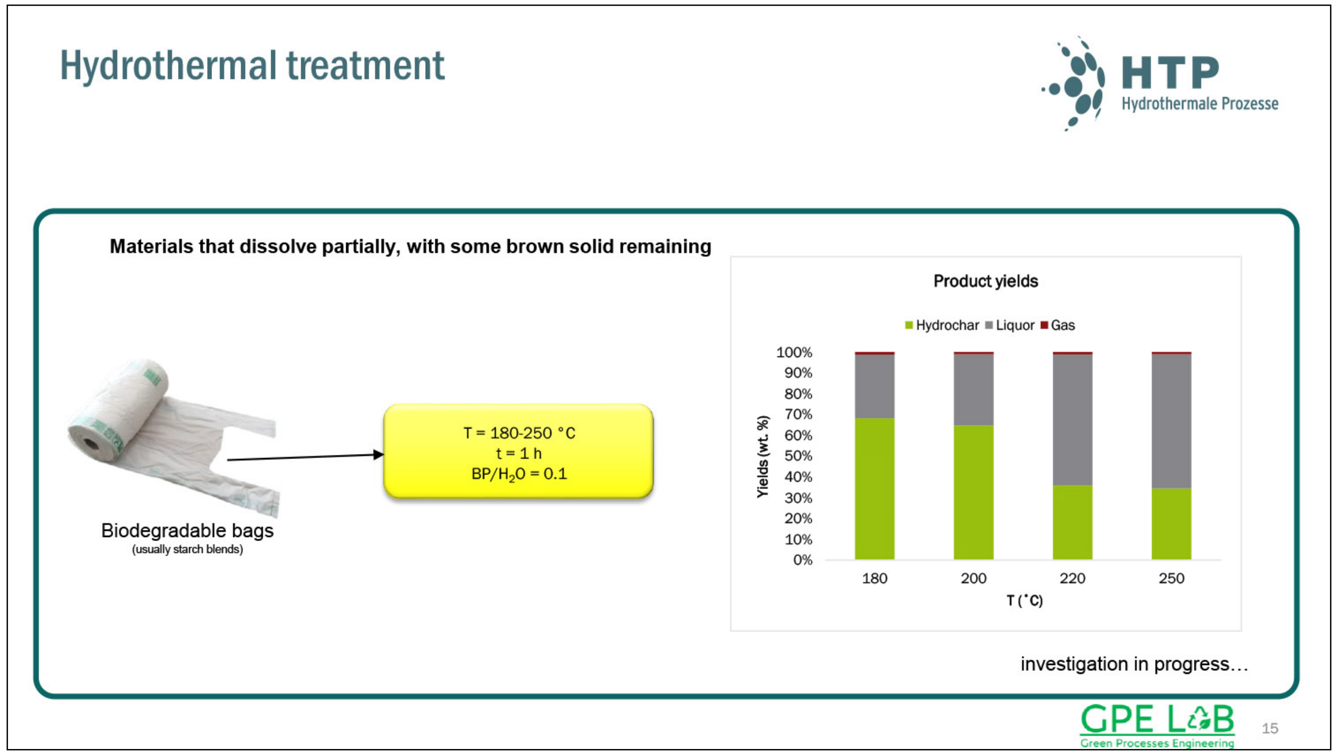
Hydrothermal treatment
HTP
Hydrothermale Prozesse
Materials that dissolve partially, with some brown solid remaining
Biodegradable bags
(usually starch blends)
T = 180-250 °C
t = 1 h
BP/H$_2$O = 0.1
Product yields
Hydrochar Liquor Gas
Yields (wt. %)
T (°C)
investigation in progress…
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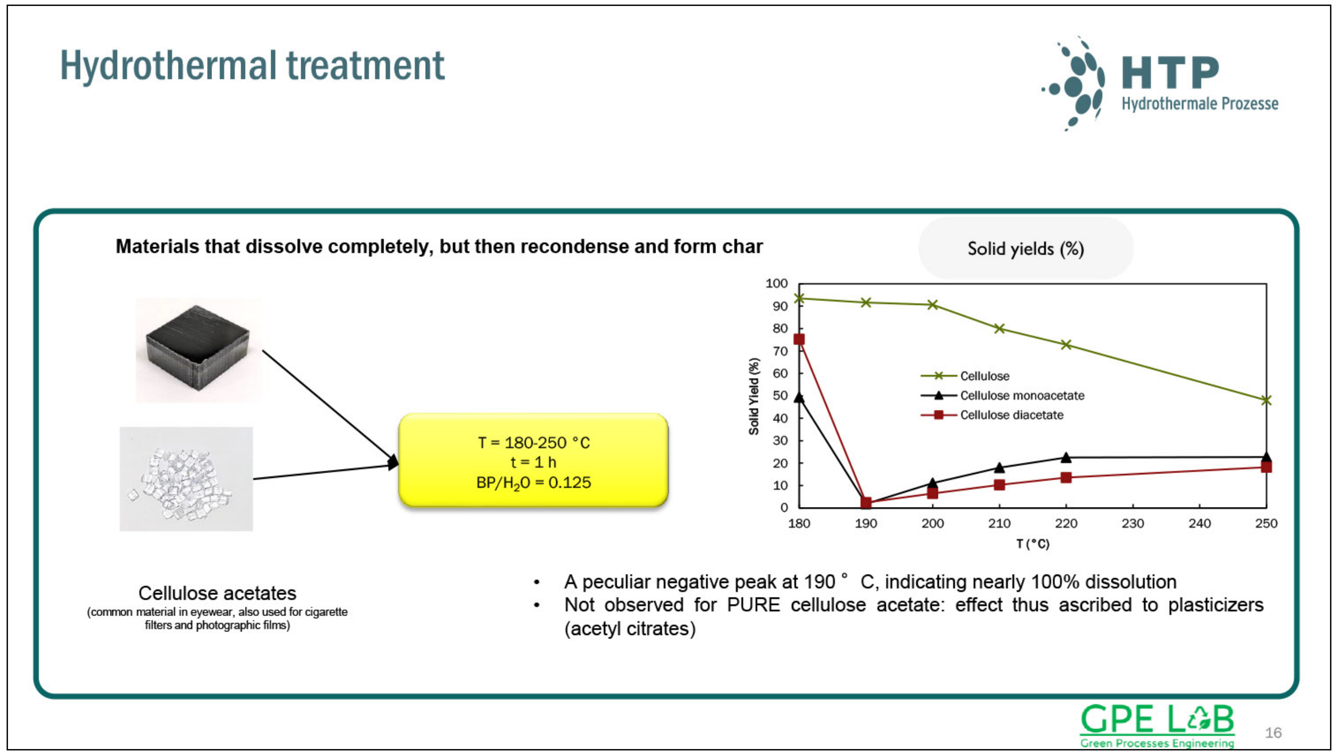
Hydrothermal treatment
HTP
Hydrothermale Prozesse
Materials that dissolve completely, but then recondense and form char
Solid yields (%)
T = 180-250 °C
t = 1 h
BP/H$_2$O = 0.125
Cellulose
Cellulose monoacetate
Cellulose diacetate
Solid Yield (%)
T (°C)
Cellulose acetates
(common material in eyewear, also used for cigarette filters and photographic films)
• A peculiar negative peak at 190 °C, indicating nearly 100% dissolution
• Not observed for PURE cellulose acetate: effect thus ascribed to plasticizers (acetyl citrates)
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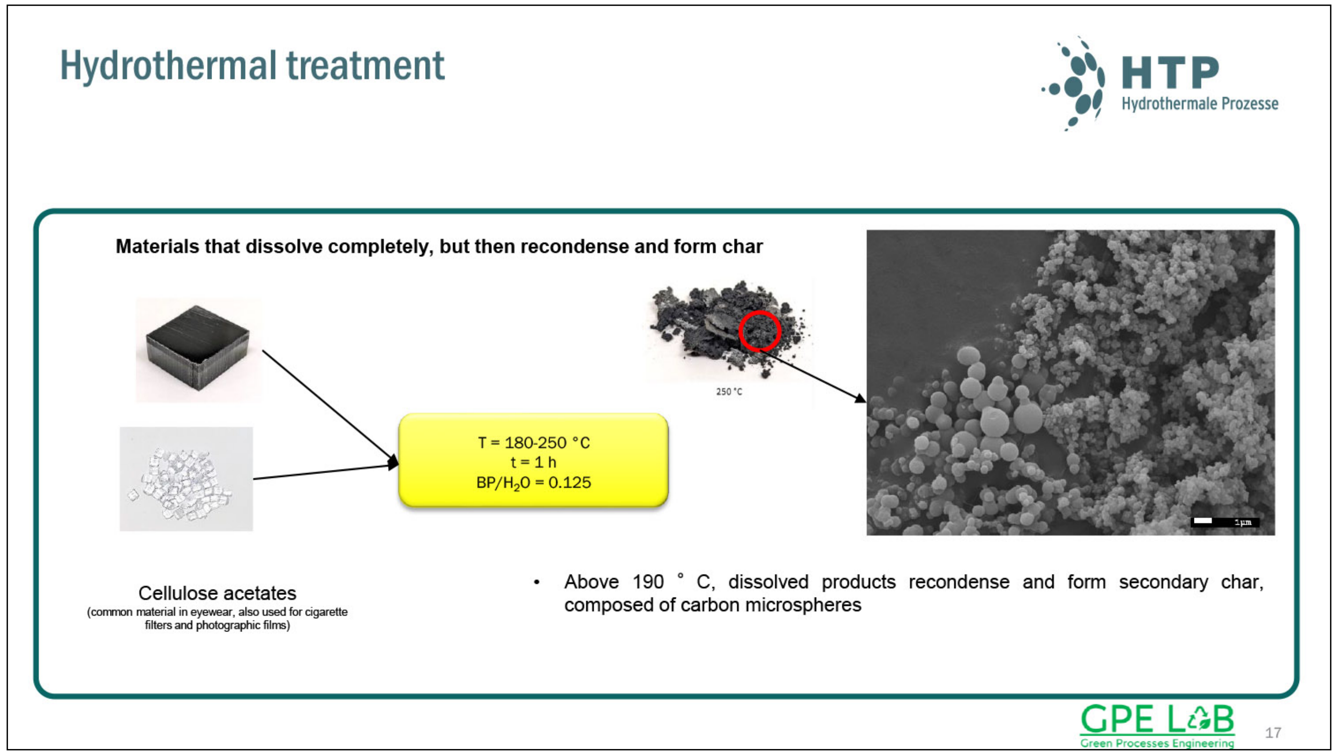
Hydrothermal treatment
HTP
Hydrothermale Prozesse
Materials that dissolve completely, but then recondense and form char
T = 180-250 °C
t = 1 h
BP/H$_2$O = 0.125
Cellulose acetates
(common material in eyewear, also used for cigarette filters and photographic films)
• Above 190 °C, dissolved products recondense and form secondary char, composed of carbon microspheres
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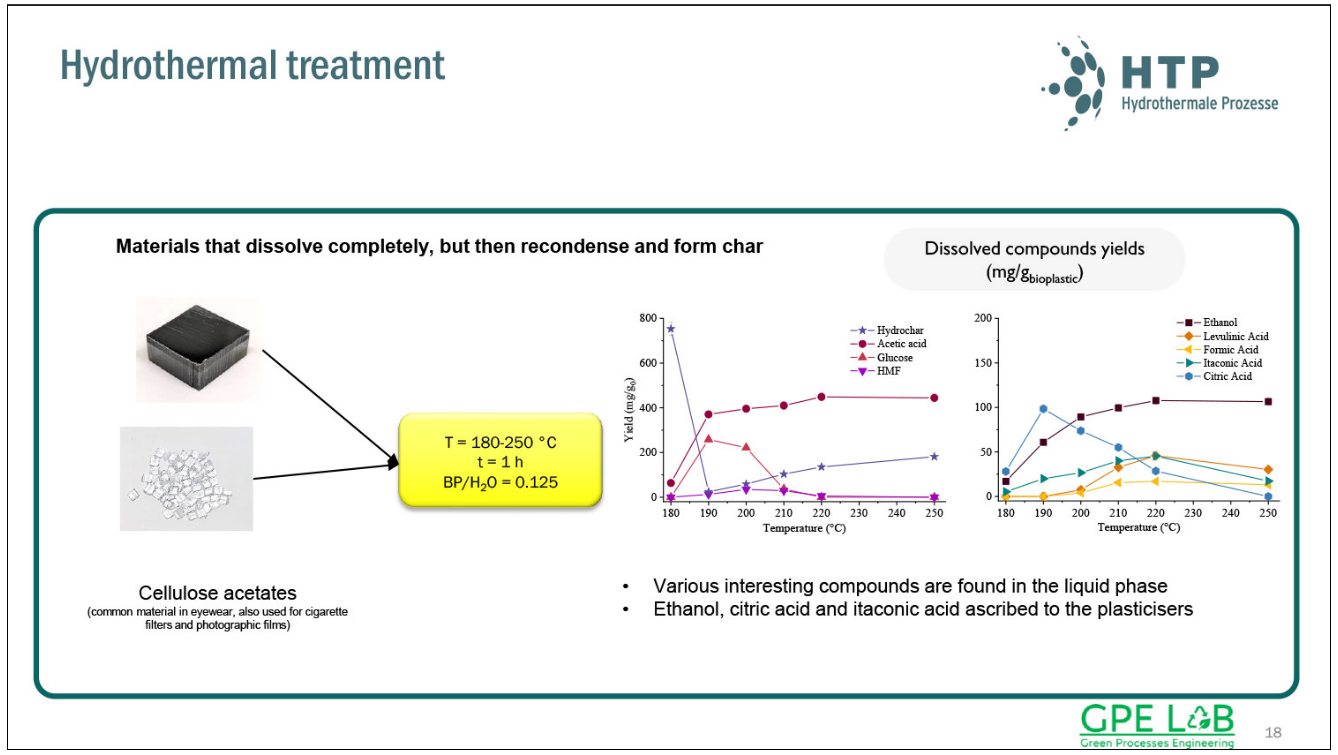
Hydrothermal treatment
HTP
Hydrothermale Prozesse
Materials that dissolve completely, but then recondense and form char
Dissolved compounds yields (mg/g$_{bioplastic}$)
T = 180-250 °C
t = 1 h
BP/H$_2$O = 0.125
Hydrochar
Acetic acid
Glucose
HMF
Ethanol
Levulinic Acid
Formic Acid
Itaconic Acid
Citric Acid
Temperature (°C)
Cellulose acetates
(common material in eyewear, also used for cigarette filters and photographic films)
• Various interesting compounds are found in the liquid phase
• Ethanol, citric acid and itaconic acid ascribed to the plasticisers
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# CONTENTS



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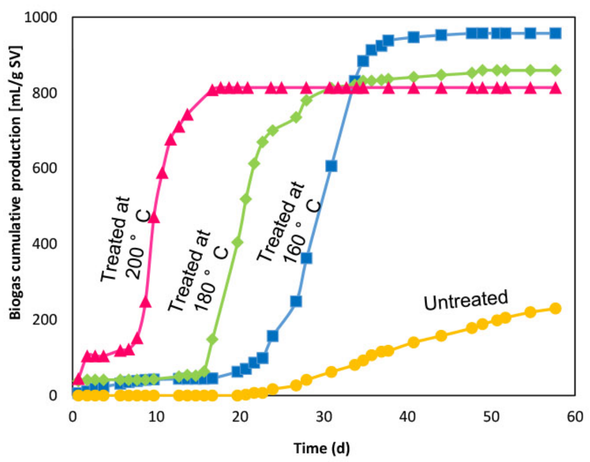
## What are the possible applications?

- Feeding the HT products to **anaerobic digestion**: notably higher biogas yields and rates

Biogas production over time
cPLA and its HT products

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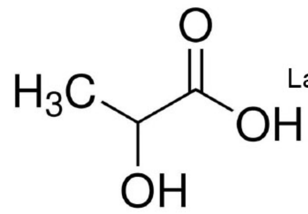
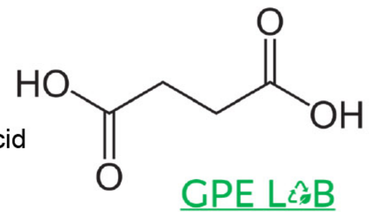
## What are the possible applications?

- Feeding the HT products to **anaerobic digestion**: notably higher biogas yields and rates
- Recovery of monomers (**chemical recycling**): valid for PLA and PBS.



Lactic acid



Succinic acid

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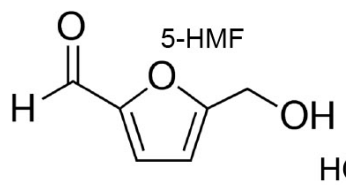
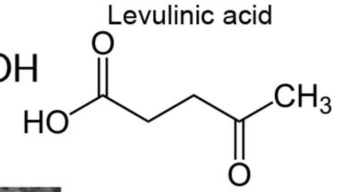
## What are the possible applications?

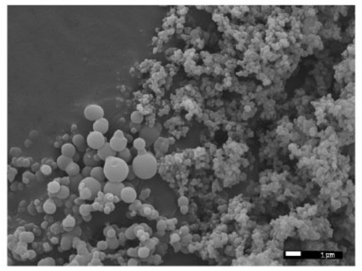
- Feeding the HT products to **anaerobic digestion**: notably higher biogas yields and rates
- Recovery of monomers (**chemical recycling**): valid for PLA and PBS.
- Recovery of valuable materials (**upcycling**): platform chemicals and advanced carbons.

5-HMF



Levulinic acid





Carbon microspheres

22


What are the possible applications?
Feeding the HT products to anaerobic digestion: notably higher biogas yields and rates
Recovery of monomers (chemical recycling): valid for PLA and PBS.
Recovery of valuable materials (upcycling): platform chemicals and advanced carbons.
Separation of bioplastics and traditional plastics.
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Green Processes Engineering
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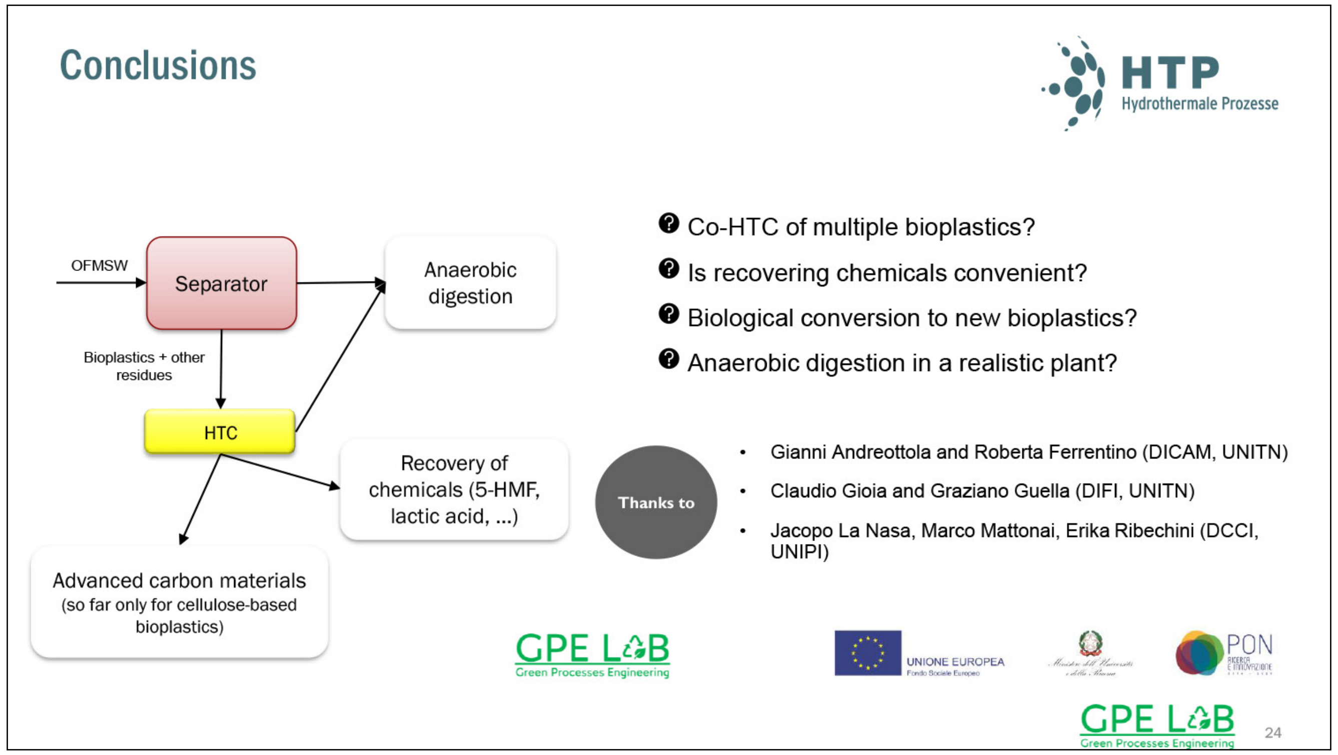
Conclusions
OFMSW
Separator
Anaerobic digestion
Bioplastics + other residues
HTC
Recovery of chemicals (5-HMF, lactic acid, ...)
Advanced carbon materials (so far only for cellulose-based bioplastics)
Co-HTC of multiple bioplastics?
Is recovering chemicals convenient?
Biological conversion to new bioplastics?
Anaerobic digestion in a realistic plant?
Thanks to
Gianni Andreottola and Roberta Ferrentino (DICAM, UNITN)
Claudio Gioia and Graziano Guella (DIFI, UNITN)
Jacopo La Nasa, Marco Mattonai, Erika Ribechini (DCCI, UNIPI)
UNIONE EUROPEA
PON
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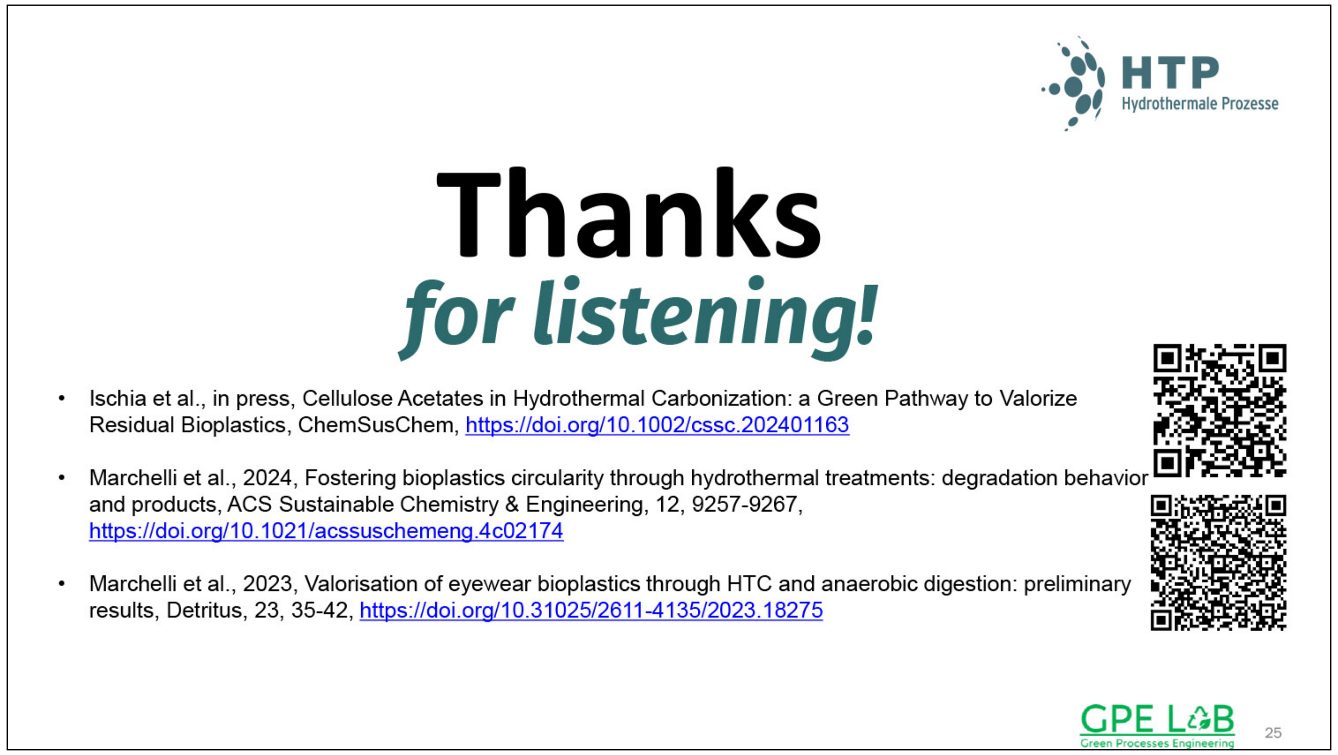
HTP
Hydrothermale Prozesse
Thanks
for listening!
Ischia et al., in press, Cellulose Acetates in Hydrothermal Carbonization: a Green Pathway to Valorize Residual Bioplastics, ChemSusChem, https://doi.org/10.1002/cssc.202401163
Marchelli et al., 2024, Fostering bioplastics circularity through hydrothermal treatments: degradation behavior and products, ACS Sustainable Chemistry & Engineering, 12, 9257-9267, https://doi.org/10.1021/acssuschemeng.4c02174
Marchelli et al., 2023, Valorisation of eyewear bioplastics through HTC and anaerobic digestion: preliminary results, Detritus, 23, 35-42, https://doi.org/10.31025/2611-4135/2023.18275
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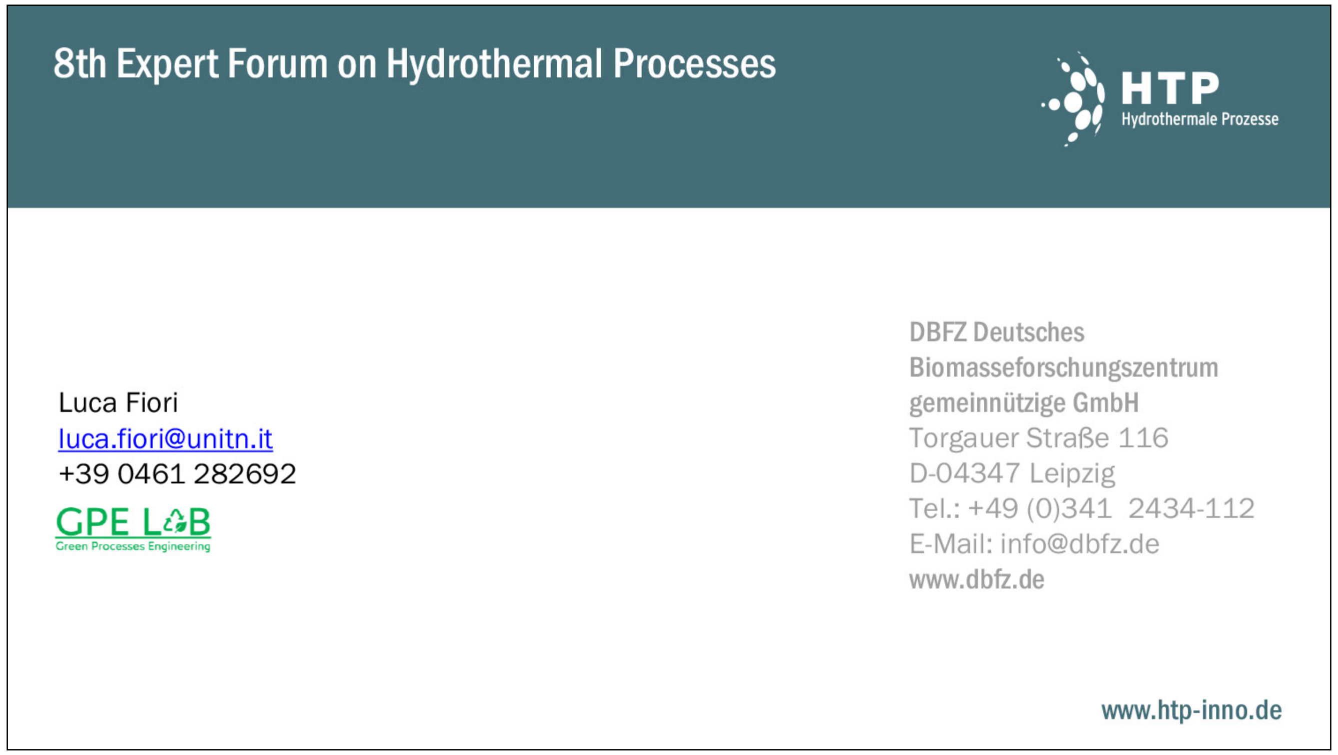
8th Expert Forum on Hydrothermal Processes
HTP
Hydrothermale Prozesse
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Green Processes Engineering
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www.htp-inno.de

# SESSION II

## PROGRESS ON HYDROTHERMAL LIQUEFACTION (HTL), ECONOMICS AND UP-SCALING OF HYDROTHERMAL PROCESSES

*Neha Shukla, Aarhus University*

# Catalytic hydrothermal liquefaction of PFAS

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E-Mail: ns20@bce.au.dk

**Keywords:** Pollutants, sewage sludge, PFAS, hydrochar, life cycle

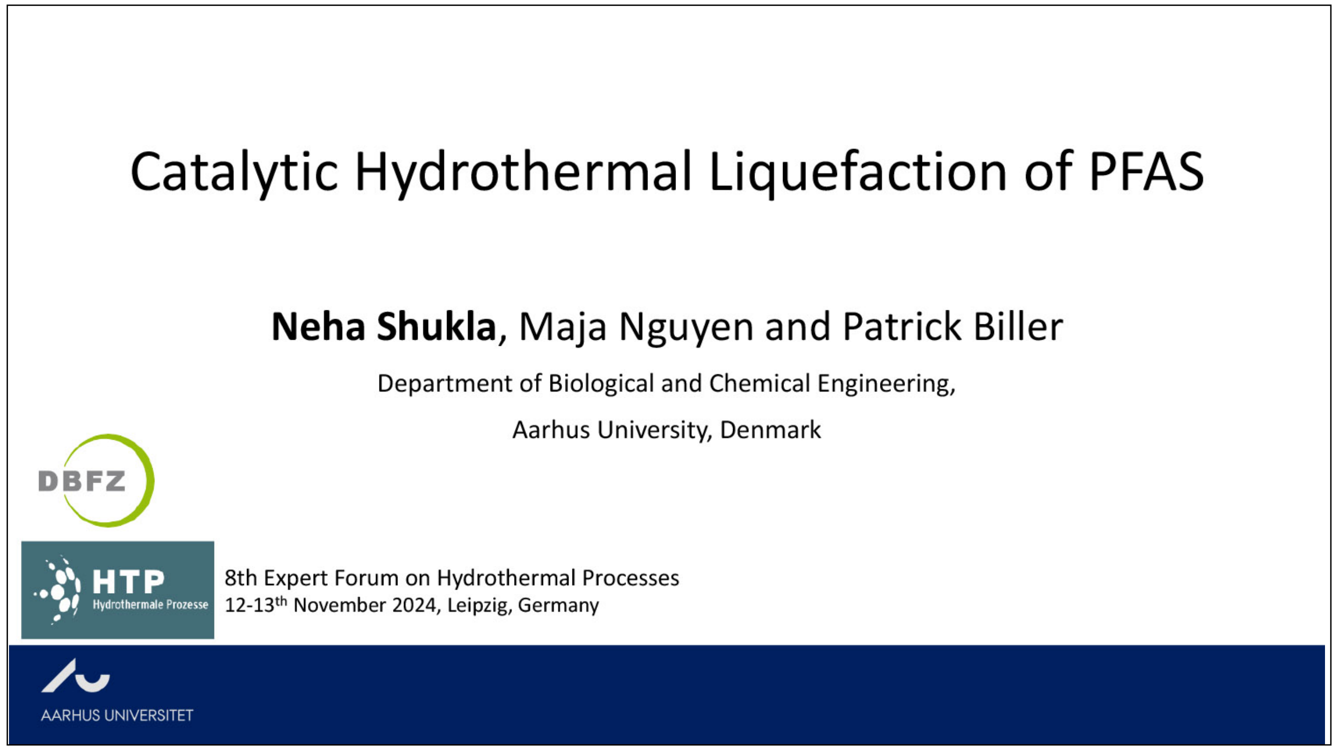
Per- and poly-fluoroalkyl substances (PFAS) are a class of recalcitrant organic pollutants characterized by their environmental persistence and potential adverse health impacts that eventually end up in wastewater treatment plants (WWTPs) where they are sorbed to the sewage sludge. Traditional remediation methodologies for PFAS, encompassing activated carbon adsorption, ion exchange resins, membrane filtration, soil washing, bioremediation, electrochemical oxidation etc, often encounter limitations related to efficacy, cost, and scalability.

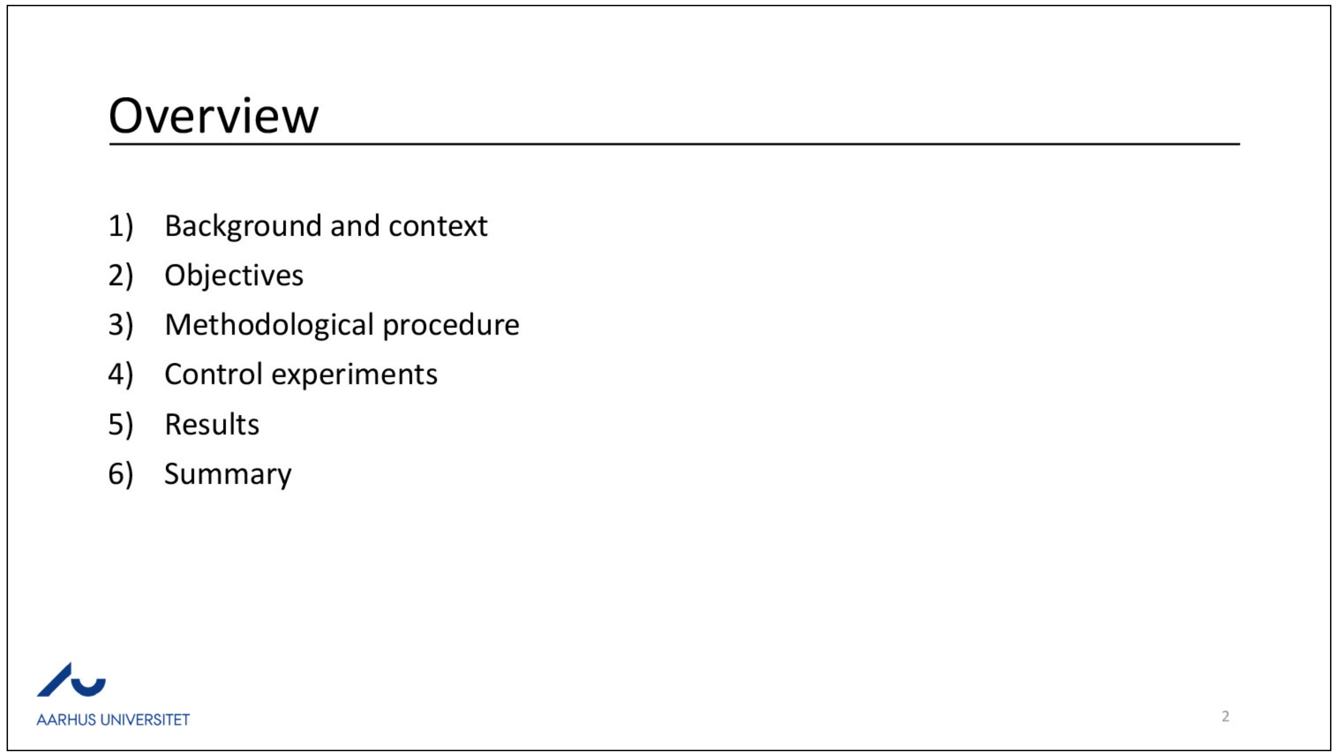
Hydrothermal Liquefaction (HTL) is a promising technology for converting organic compounds into smaller, less harmful molecules under subcritical or supercritical water conditions (200-374 °C, 4-22 MPa). HTL utilizes water as a reaction medium to facilitate the breakdown of complex molecules into smaller, less harmful compounds and potentially valuable hydrocarbons, making it an attractive option for PFAS degradation. PFAS degradation with HTL could be further improved by incorporating catalysts, i.e., catalytic HTL. Therefore, this study aims to degrade the two legacy PFAS compounds, perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA), using spent hydrochar, a byproduct of HTL treatment of sewage sludge, as a catalyst. The influence of operational parameters such as pH, time and catalyst dosage on the efficacy of PFAS destruction was investigated. The results demonstrated > 99% removal of PFOS and PFOA via defluorination, decarboxylation, and hydrolysis. The highest defluorination of PFOS (28.9±0.5 %) and PFOA (41.2±1.9 %) was achieved at 10 wt % spent hydrochar for 1 hour of HTL time. High defluorination of PFOA compared to PFOS could be attributed to the stability of the sulfonate group in PFOS.

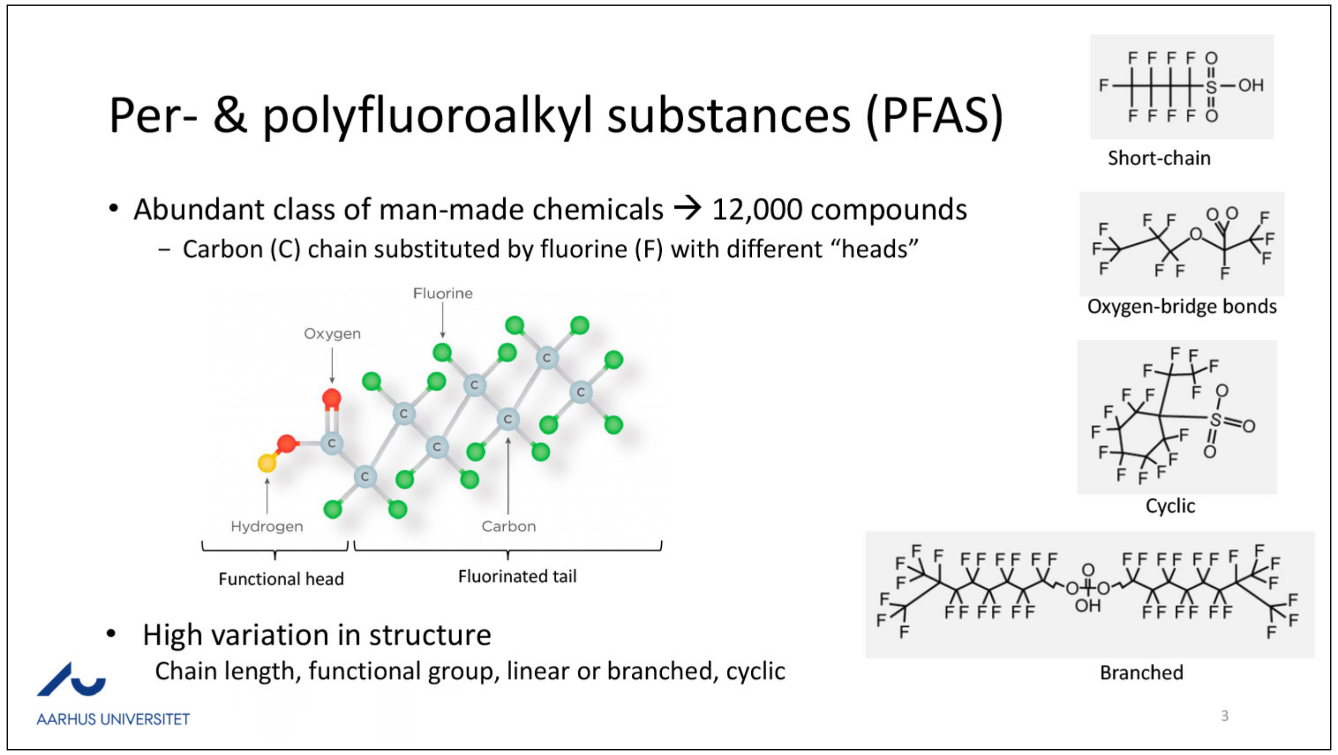
Overall, this study presents a potent and innovative technology for PFAS degradation using spent hydrochar, contributing to a circular lifecycle of sewage sludge and providing a sustainable method for PFAS degradation. This approach integrates well with existing WWTPs, offering a viable pathway for the concurrent treatment of PFAS and other organic pollutants.








Per- & polyfluoroalkyl substances (PFAS)
• Abundant class of man-made chemicals → 12,000 compounds
– Carbon (C) chain substituted by fluorine (F) with different "heads"
Fluorine
Oxygen
Hydrogen
Carbon
Functional head
Fluorinated tail
• High variation in structure
Chain length, functional group, linear or branched, cyclic
Short-chain
Oxygen-bridge bonds
Cyclic
Branched
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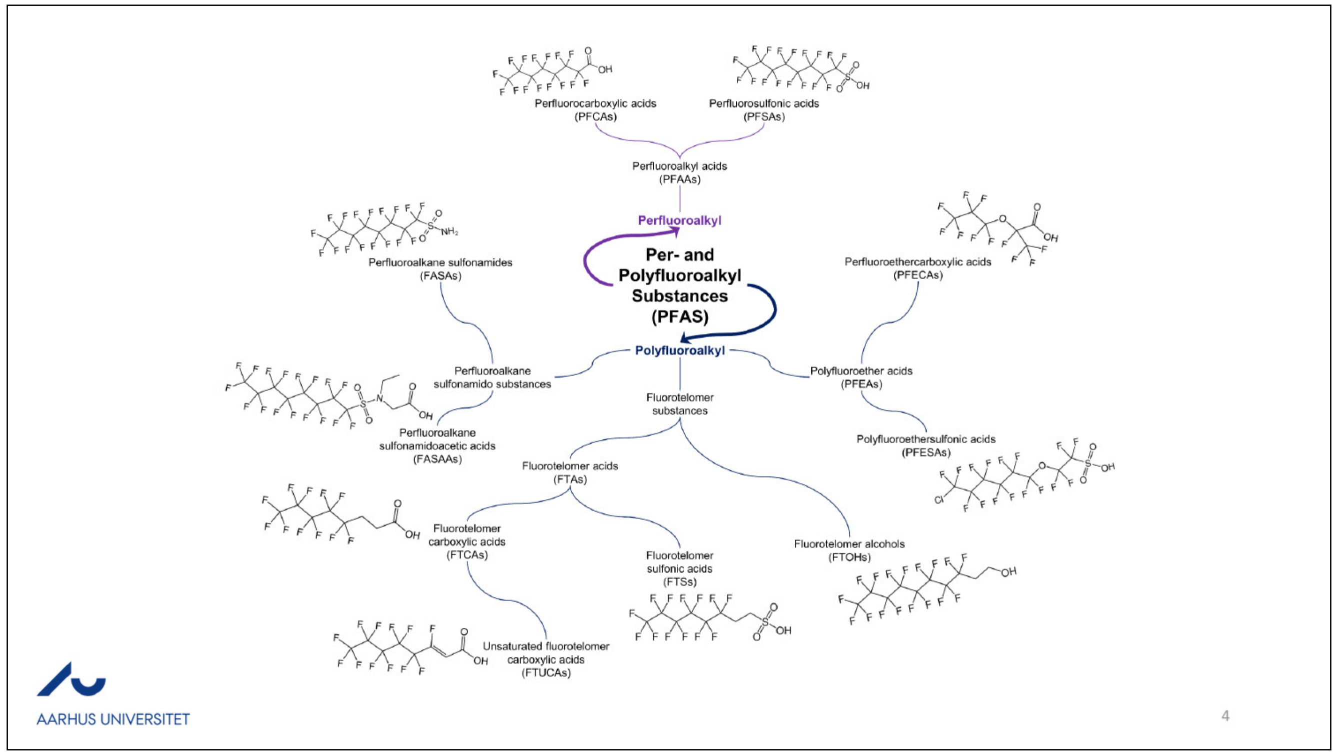
Perfluorocarboxylic acids
(PFCAs)
Perfluorosulfonic acids
(PFSAs)
Perfluoroalkyl acids
(PFAAs)
Perfluoroalkyl
Per- and
Polyfluoroalkyl
Substances
(PFAS)
Polyfluoroalkyl
Perfluoroalkane sulfonamides
(FASAs)
Perfluoroethercarboxylic acids
(PFECAs)
Perfluoroalkane
sulfonamido substances
Polyfluoroether acids
(PFEAs)
Fluorotelomer
substances
Perfluoroalkane
sulfonamidoacetic acids
(FASAAs)
Polyfluoroethersulfonic acids
(PFESAs)
Fluorotelomer acids
(FTAs)
Fluorotelomer
carboxylic acids
(FTCAs)
Fluorotelomer
sulfonic acids
(FTSs)
Fluorotelomer alcohols
(FTOHs)
Unsaturated fluorotelomer
carboxylic acids
(FTUCAs)
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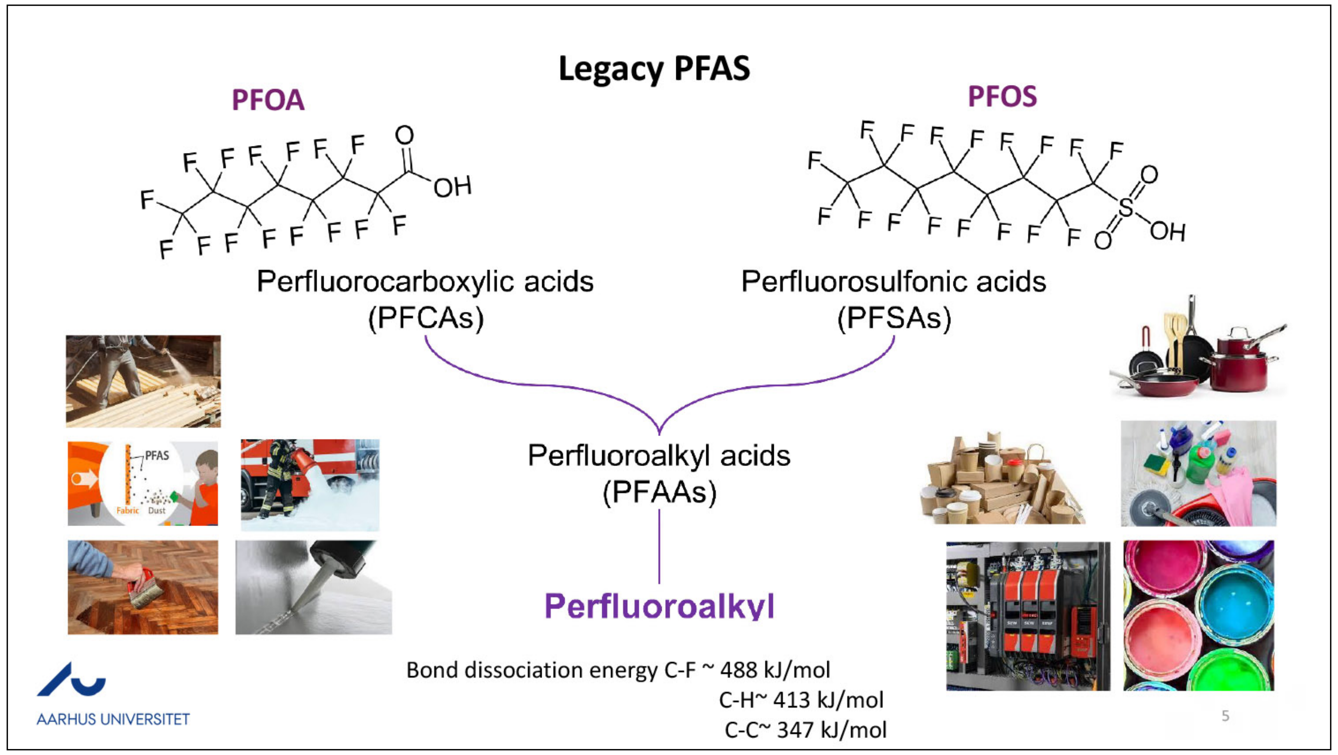
Legacy PFAS
PFOA
PFOS
Perfluorocarboxylic acids
(PFCAs)
Perfluorosulfonic acids
(PFSAs)
Perfluoroalkyl acids
(PFAAs)
Perfluoroalkyl
Bond dissociation energy C-F ~ 488 kJ/mol
C-H~ 413 kJ/mol
C-C~ 347 kJ/mol
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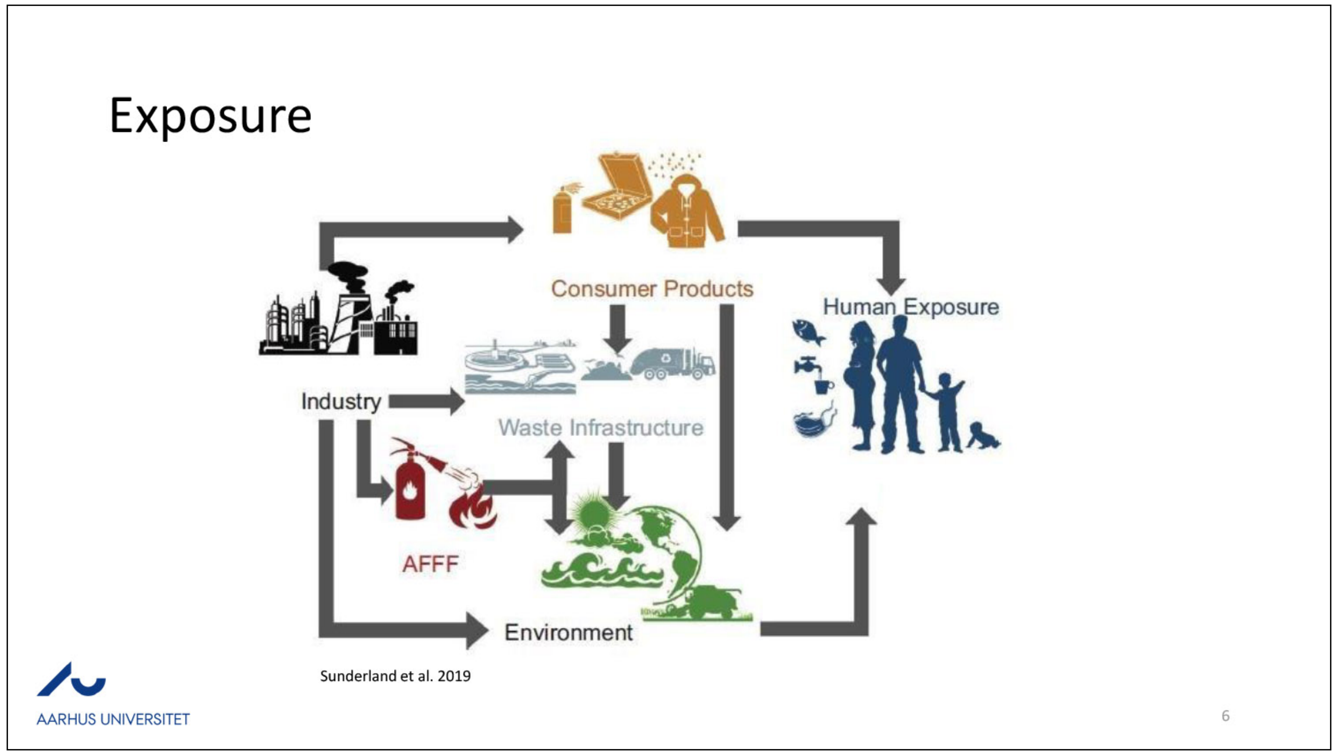
Exposure
Consumer Products
Human Exposure
Industry
Waste Infrastructure
AFFF
Environment
Sunderland et al. 2019
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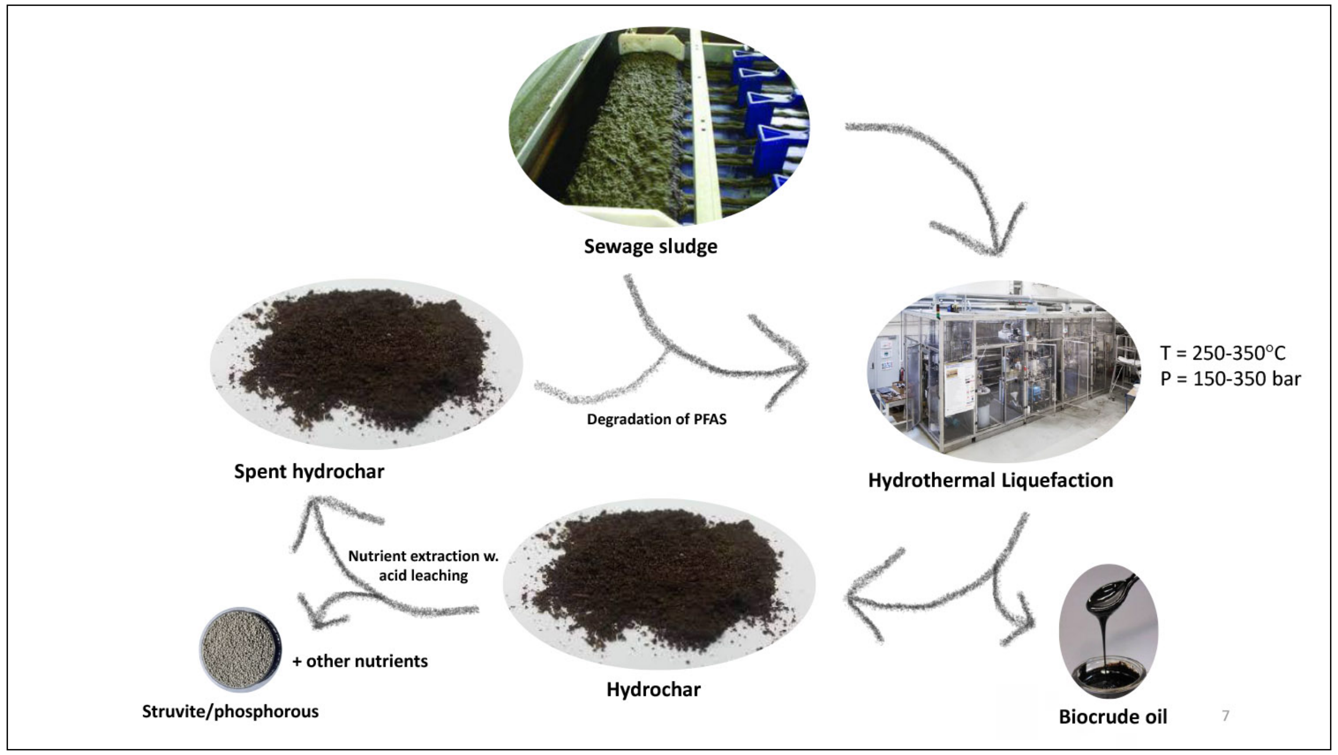
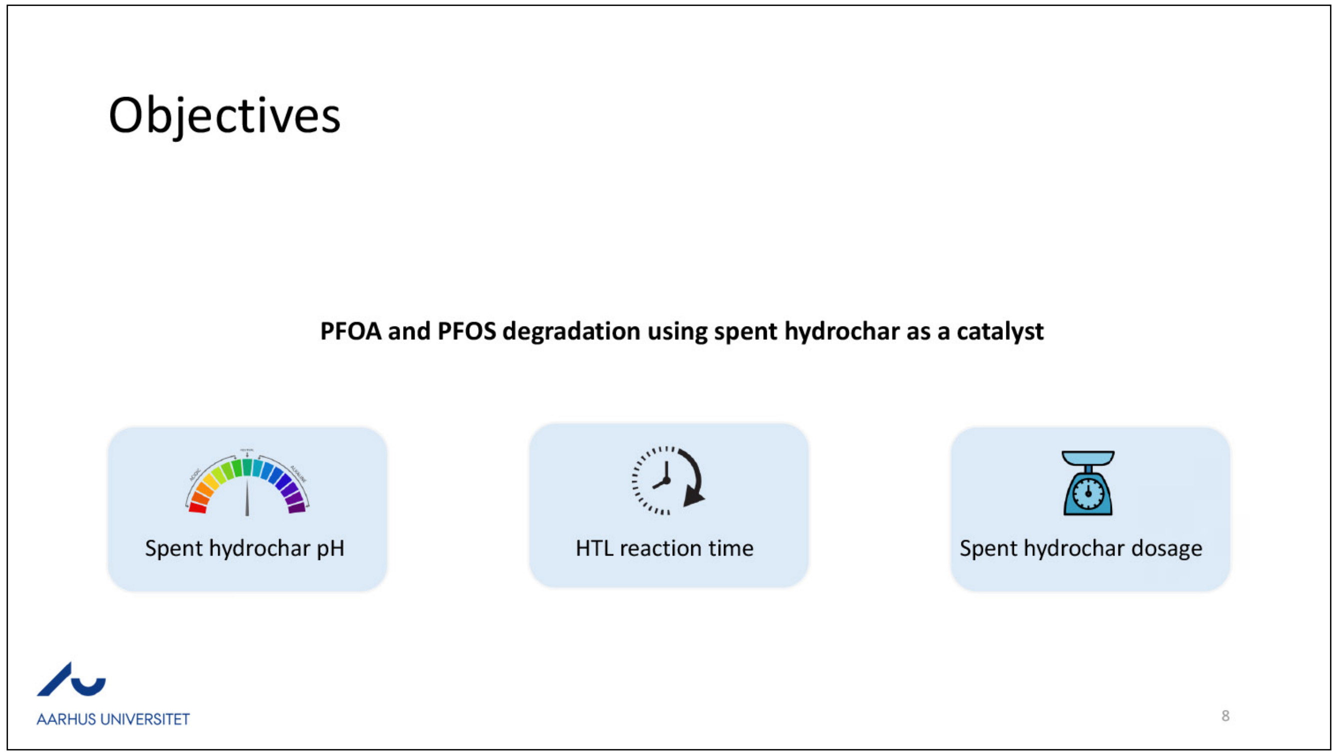

Sewage sludge
Degradation of PFAS
T = 250-350°C
P = 150-350 bar
Spent hydrochar
Hydrothermal Liquefaction
Nutrient extraction w. acid leaching
+ other nutrients
Struvite/phosphorous
Hydrochar
Biocrude oil
7


Objectives
PFOA and PFOS degradation using spent hydrochar as a catalyst
Spent hydrochar pH
HTL reaction time
Spent hydrochar dosage
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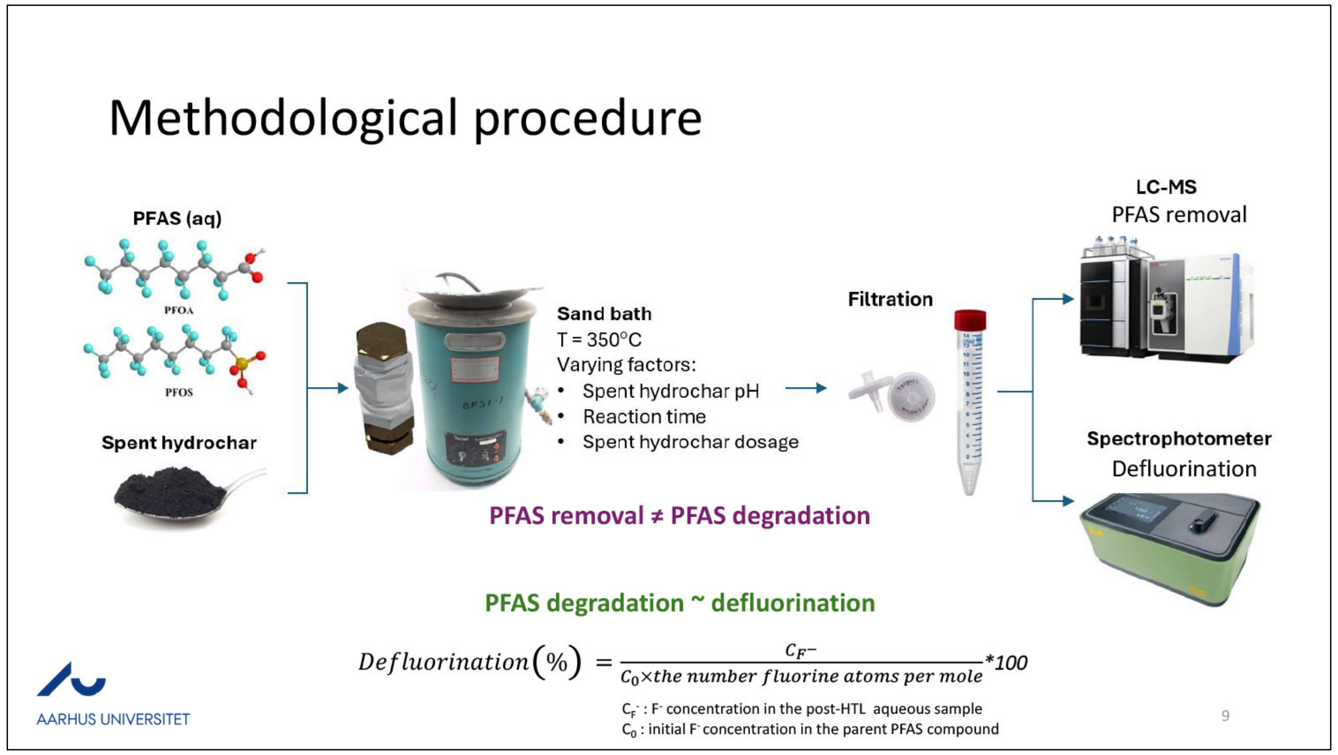
Methodological procedure
PFAS (aq)
PFOA
PFOS
Spent hydrochar
Sand bath
T = 350°C
Varying factors:
• Spent hydrochar pH
• Reaction time
• Spent hydrochar dosage
Filtration
LC-MS
PFAS removal
Spectrophotometer
Defluorination
PFAS removal ≠ PFAS degradation
PFAS degradation ~ defluorination
$Defluorination(\%) = \frac{C_{F^-}}{C_0 \times the\ number\ fluorine\ atoms\ per\ mole} * 100$
$C_{F^-}$ : F⁻ concentration in the post-HTL aqueous sample
$C_0$ : initial F⁻ concentration in the parent PFAS compound
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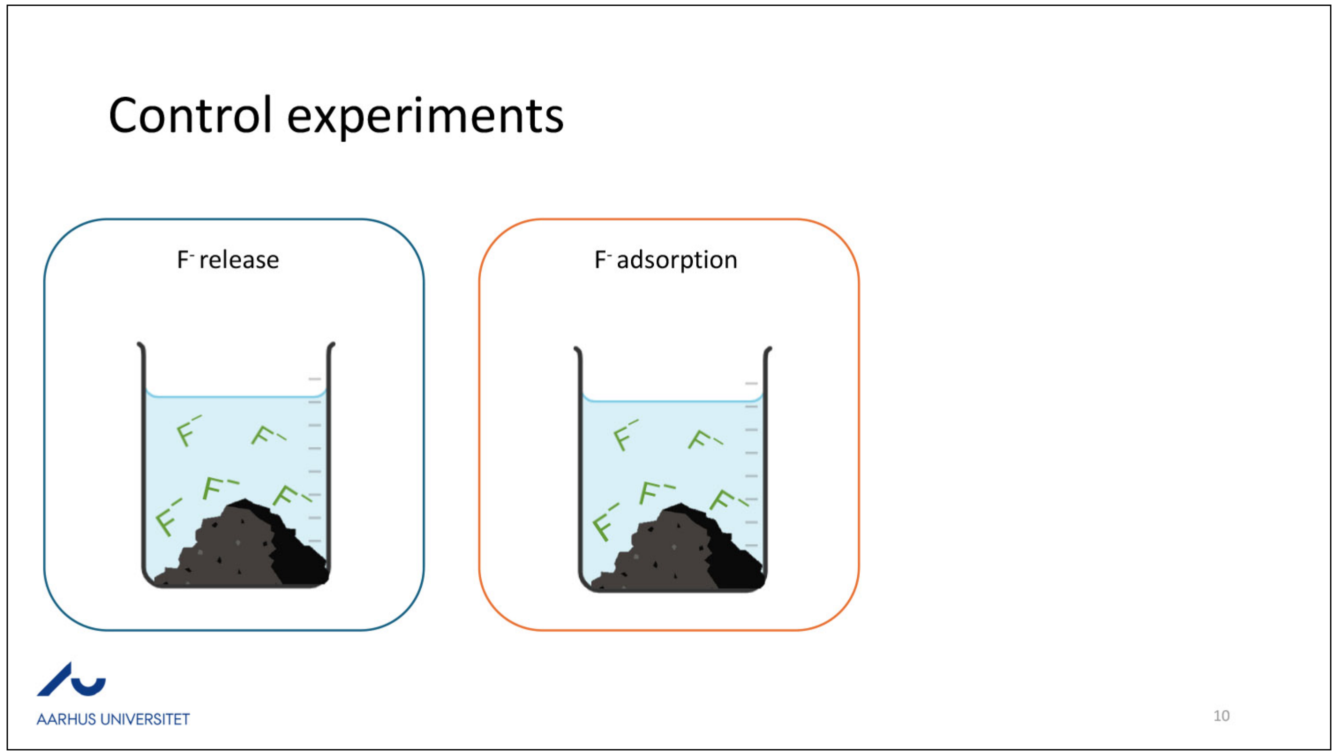
Control experiments
F⁻ release
F⁻ adsorption
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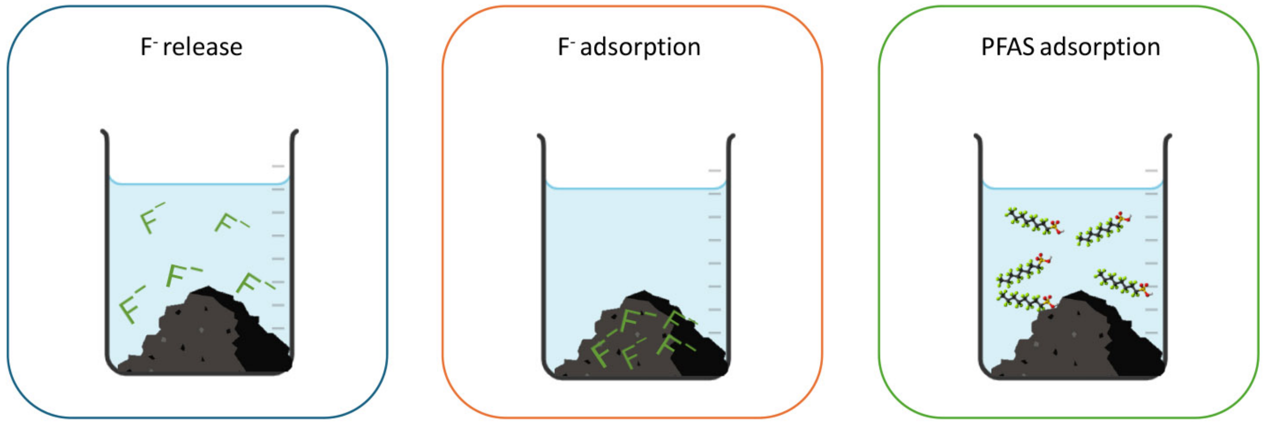
## Control experiments

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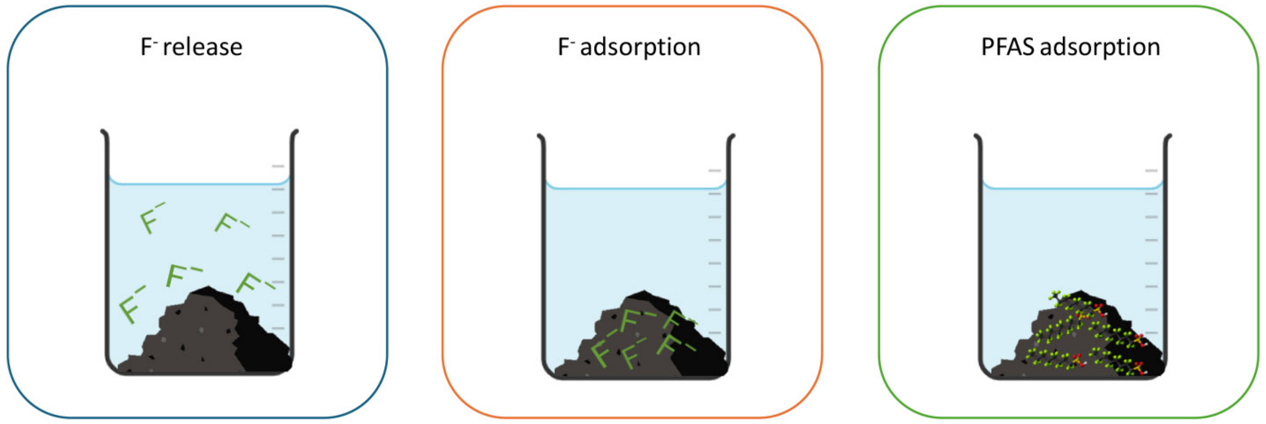
## Control experiments




- Neglible F- release from hydrochar
- High F- and PFAS adsorption by hydrochar

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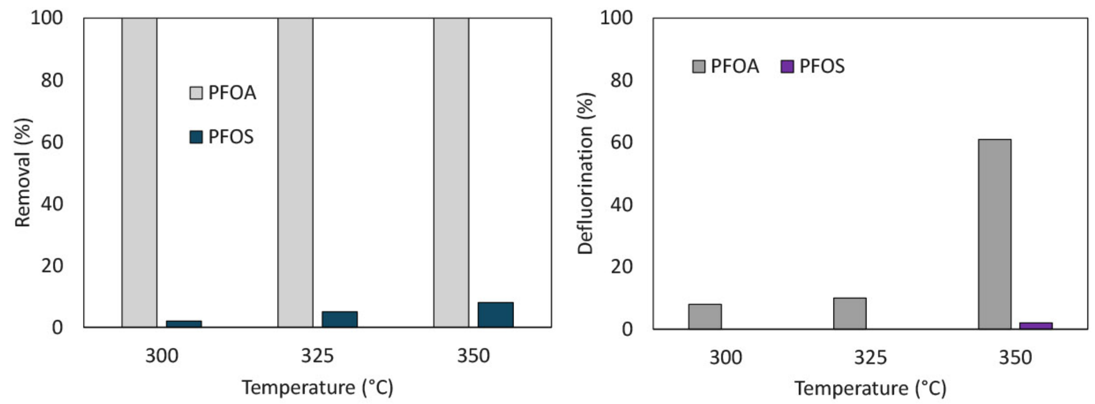
## PFAS removal and defluorination (without hydrochar, 2 hours of HTL)




- Low PFOS removal
- Low defluorination, formation of highly volatile fluorinated alkanes (1H-perfluoroheptane)
- Catalytic HTL ???

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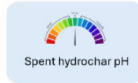
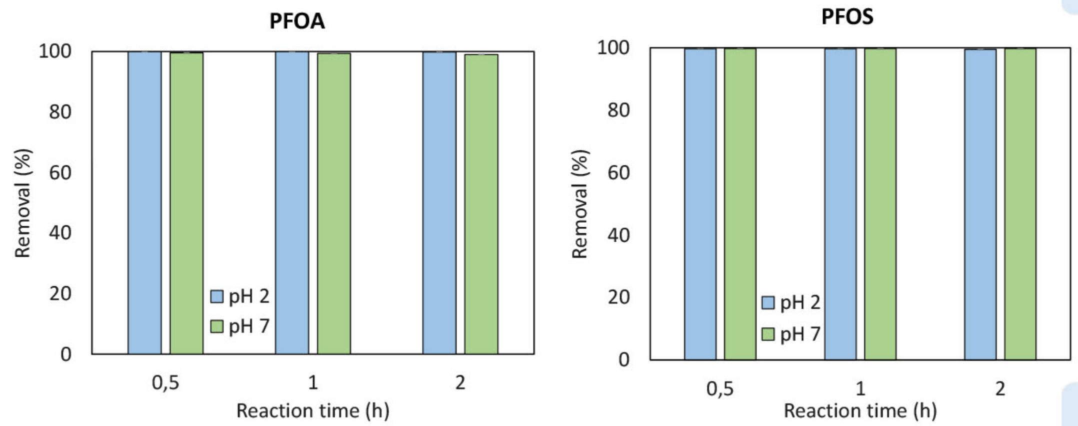
## PFAS removal

350°C, 3 wt% spent hydrochar





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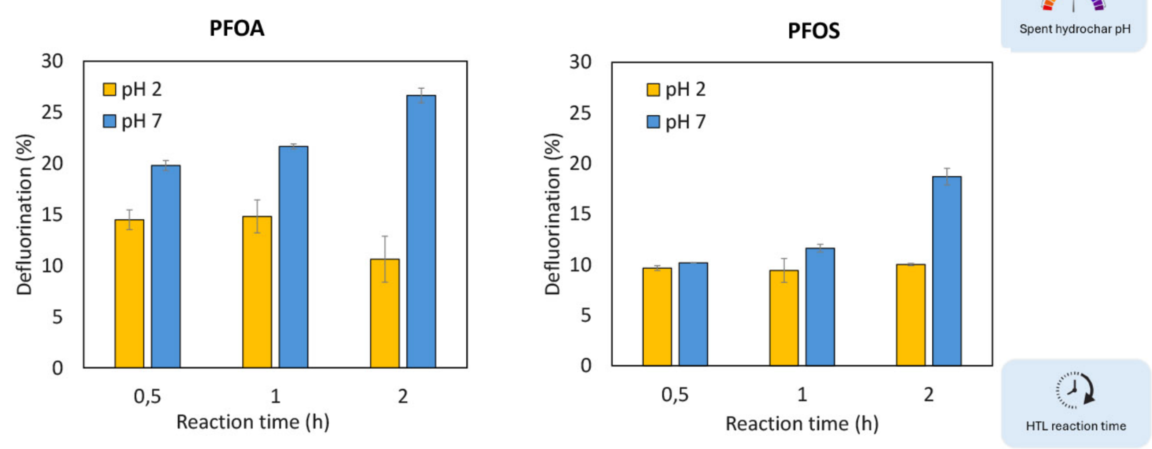
# Defluorination

350°C, 3 wt% spent hydrochar

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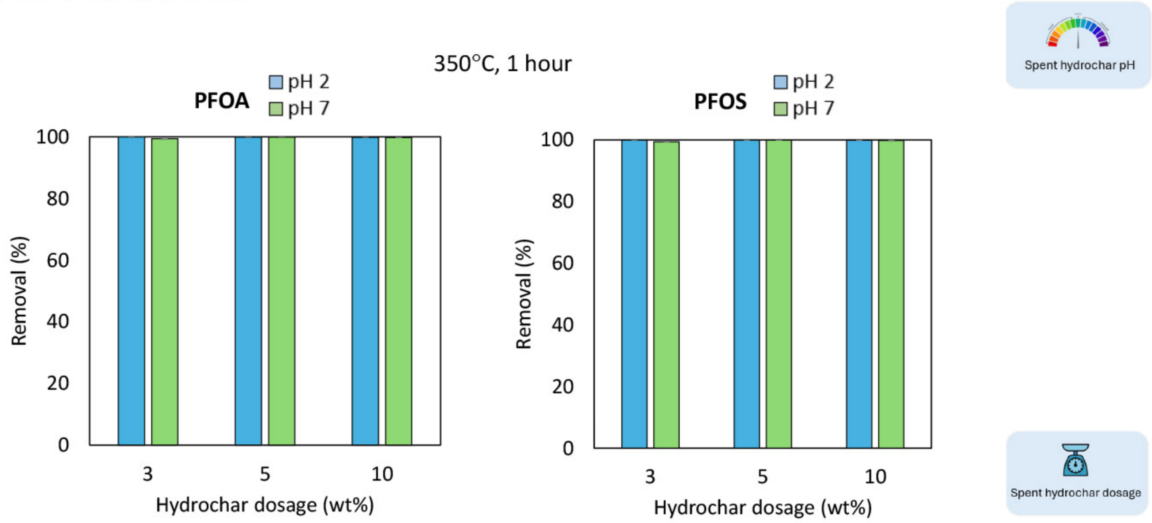
# PFAS removal

350°C, 1 hour

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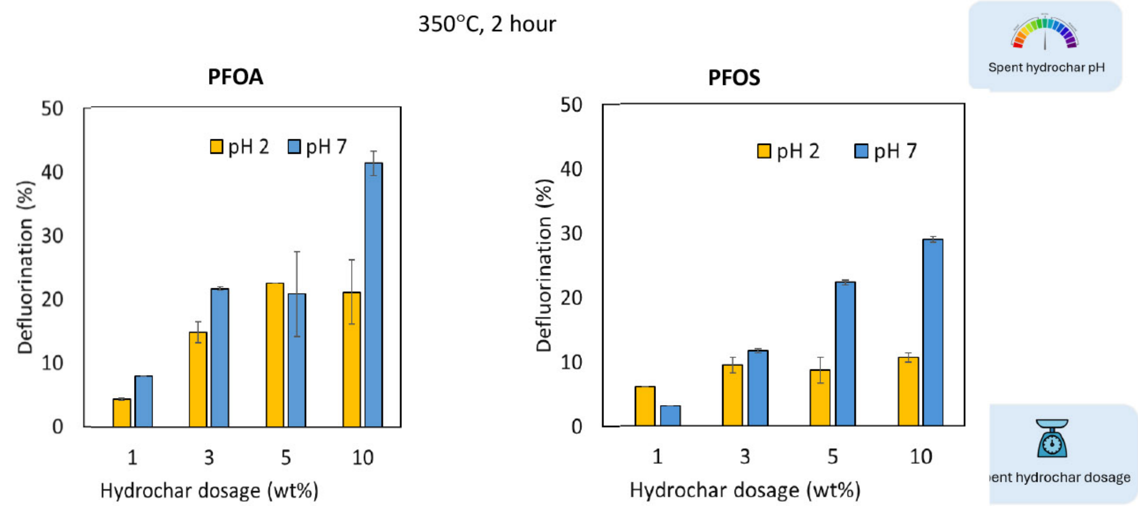
# Defluorination

350°C, 2 hour

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# Take home messages…

- Improved defluorination with spent hydrochar
- Defluorination **increased** with **reaction time** and **spent hydrochar dosage**
  - PFOA > PFOS
  - Spent hydrochar pH 7 > pH 2
  - 10 wt% spent hydrochar (pH 7) in 2 h
  - Highest defluorination of PFOA (41.2±1.9%) PFOS (28.9±0.5%)
- Further research on improved PFAS defluorination and intermediate by-products

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Questions?

Comments?

Collaborations?


Contact
**Neha Shukla**
Post-doc, Department of Biological and Chemical Engineering
Aarhus University, Denmark
ns20@bce.au.dk

erc

EUDP

CBIO
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WATEC
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19

*Carolin Eva Schuck, Aarhus University*

# Continuous wet oxidation of HTL aqueous phase derived from mixture of straw and cattle manure

Caroline Eva Schuck, Konstantinos Anastasakis, Patrick Biller
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8200 Aarhus N, Denmark
E-Mail: cschuck@bce.au.dk

**Keywords:** Wet Oxidation, Hydrothermal Liquefaction, Process Integration

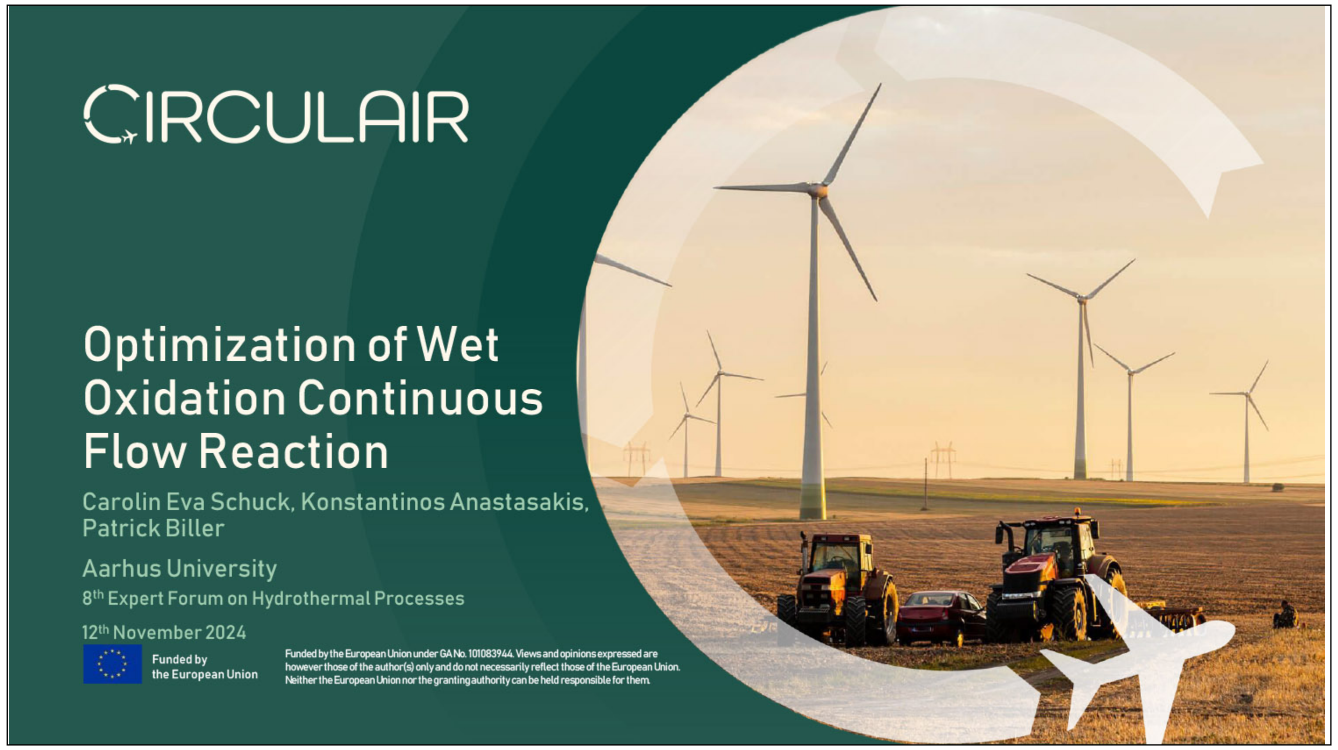
Hydrothermal Liquefaction (HTL) is a thermochemical processing technology that has been receiving increased interest for converting abundant biomass into an organic phase, which can be further upgraded to advanced fuels. However, the challenge of treating the aqueous byproduct needs to be addressed when speaking about further commercialization of this technology. A potential treatment method for HTL aqueous phase (AP) is subcritical non catalytic Wet Oxidation (WO), a hydrothermal wastewater treatment technology for highly polluted and refractory effluents. Organic compounds are oxidized in hot compressed water in the presence of an oxidative atmosphere (e. g. oxygen, air, hydrogen peroxide) to $CO_2$, $H_2O$, and small components (e. g. volatile fatty acids (VFA)) in an exothermic reaction.

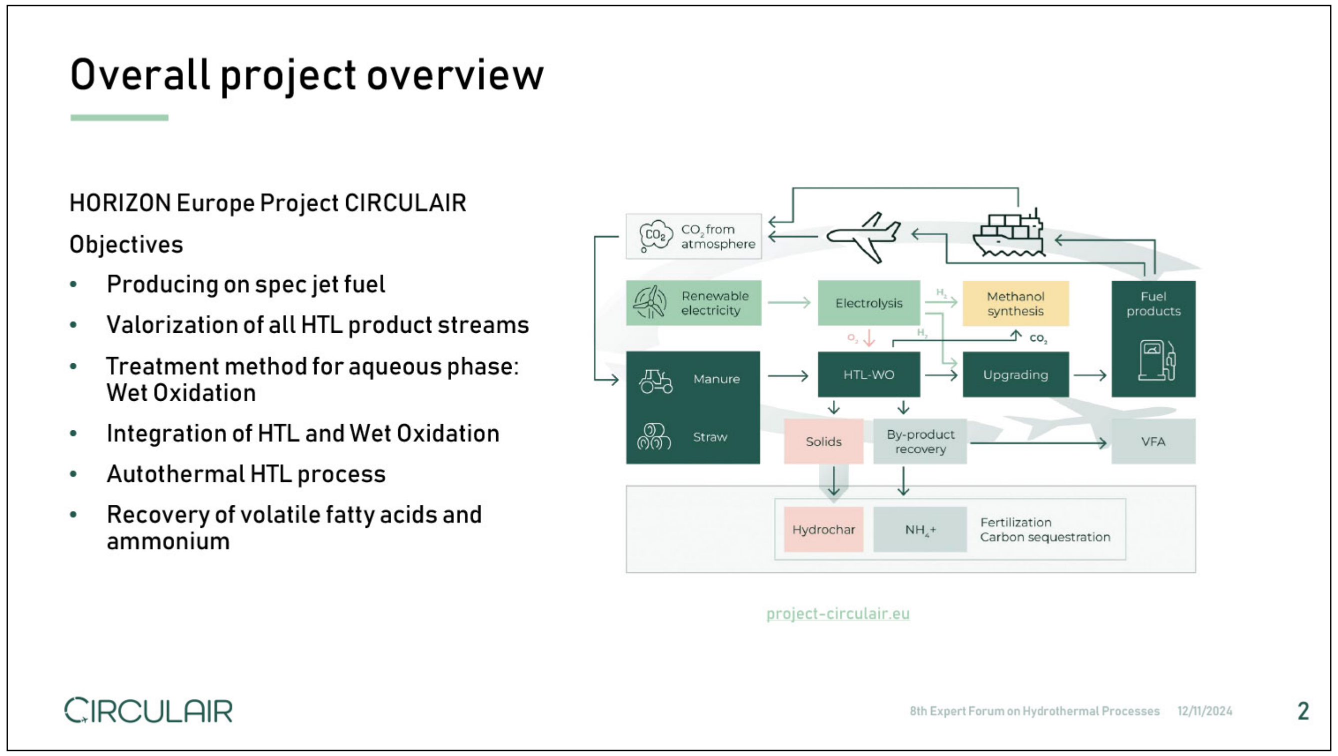
The present study focused on HTL AP derived from a 1:1 mixture of straw and cattle manure feedstock. The investigated WO process was conducted in a continuous flow reactor at temperatures and residence times similar to HTL process (350 °C, 12 43 min). Air was used as $O_2$ source in an equivalent of 0.5 2 times of Chemical Oxygen Demand (COD). Furthermore, a 35 % hydrogen peroxide solution was employed to simulate pure $O_2$ as an alternative to air. The AP before and after WO treatment were characterized by different techniques, to observe changes in chemical oxygen demand (COD), total organic carbon (TOC) and nitrogen (TN), $NH_4$+ and VFA content.

The main goal was to evaluate the oxidation efficiency and heat generation to optimize process conditions. Furthermore, the production of high value VFA and NH4+ in high concentration was favored to create downstream recovery possibilities. Preliminary results show an increasing Chemical Oxygen Demand (COD) removal rate up to 85 % for a residence time of 45 min and stoichiometric air equivalent supply. Furthermore, the relative increase in VFA content of TOC up to 78 % and $NH_4$+ content of TN up to 80 % at 23 min was shown.

In conclusion, WO was successfully applied for the treatment of HTL AP derived from a mixture of cattle manure and straw with high removal of COD and increase of the VFA and ammonium portion in TOC and TN, respectively. Evaluating the results will give rise to determine optimal process conditions to treat the highly contaminated HTL AP while creating possibilities to recover heat and value added chemicals in an integrated HTL WO system.

References:
1. Watson, J., et al., Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability. Progress in Energy and Combustion Science, 2020. 77: p. 100819.
2. Debellefontaine, H. and J.N. Foussard, Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe. Waste Management, 2000. 20(1): p. 15-25.

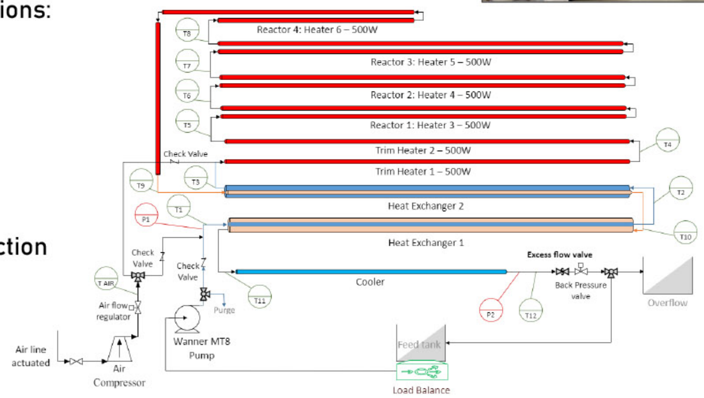


# WetOx plant at Aarhus University

Continuous flow bench-scale reactor

- Material: Sanicro35 pipes and SS316 fittings
- Reactor volume: 880mL
- Tubular system divided into seven sections:
  - AP feed system
  - Air compression system
  - Heat exchanger
  - Trim heater
  - Main reactor
  - Cooler
  - Take-off system with product collection

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# Experimental campaign

Feedstock: HTL aqueous phase derived from 1:1 cattle manure and straw mixture (325°C, 50kg/h, 14% DM)

Reaction conditions

- Residence time 12 – 45 min
- Stoichiometric $O_2$ equivalent 0.5 – 2
- $O_2$ source: air, 35% $H_2O_2$
- Temperature 350 - 365°C

Analysis performed for HTL- and WetOx aqueous phase

- Chemical Oxygen Demand
- Total Carbon/Total Nitrogen
- Ammonium content
- Volatile fatty acid content

CIRCULAIR



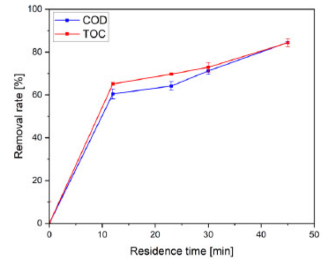


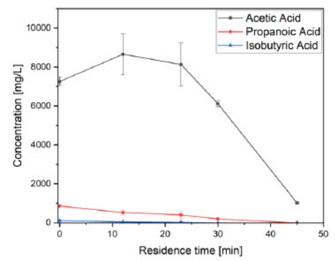


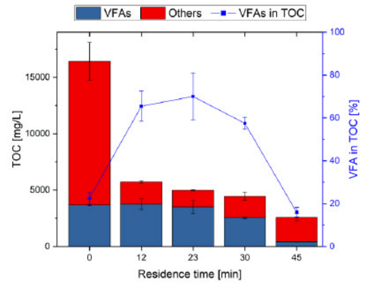
# Effect of residence time

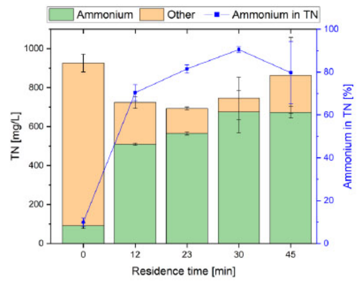
Reaction conditions

Varied residence time at 350°C and stoichiometric supply of air

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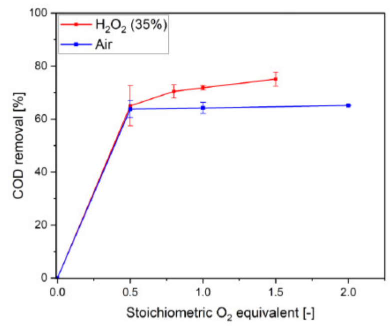
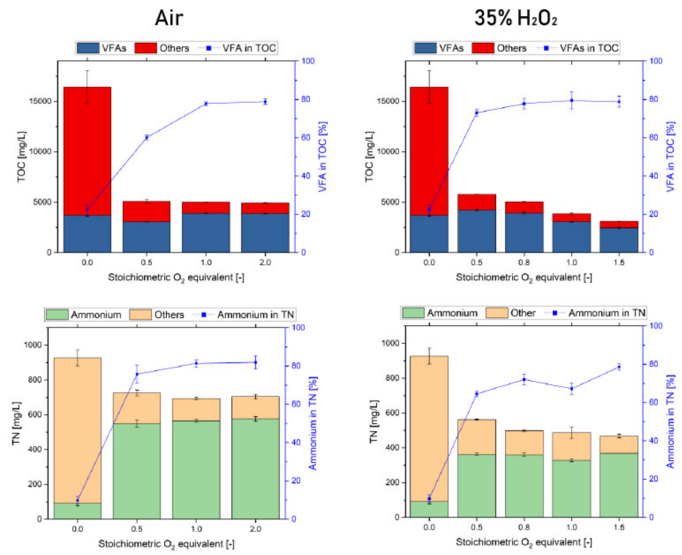
# Effect of supplied oxygen and applied oxidant

Reaction conditions

Varied stoichiometric equivalents supplied by air or 35% $H_2O_2$ at 23 min and 350°C

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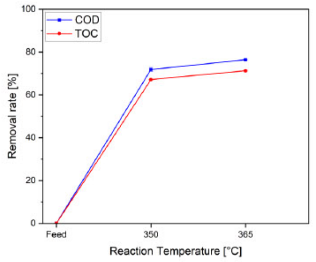
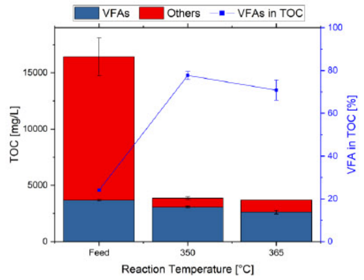
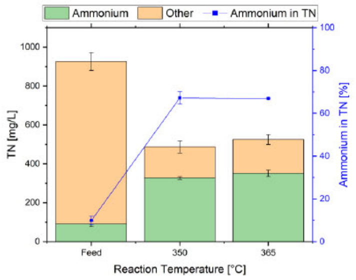
## Effect of reaction temperature

Reaction conditions

Varied reaction temperature at stoichiometric oxygen equivalent supplied by 35% $H_2O_2$ at 23min

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## Conclusion

- High COD and TOC removal achieved at residence times and temperatures similar to HTL
- COD removal increases with increasing reaction condition severity
- Intermediate products degrade at severe conditions
- Supply of increasing oxygen equivalent in form of air shows little effect to COD removal and increase of VFA and ammonium share
- Supply of 35% $H_2O_2$ shows higher oxidation efficiency compared to air
- Higher reaction temperature shows little improvement to COD and TOC removal and increase of VFA and ammonium share

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Bauhaus Luftfahrt The Aviation Think Tank
AARHUS UNIVERSITET
University of Hohenheim
Universidad Complutense Madrid
TOPSOE
Circlia Nordic
eni
RISE

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*Niels Dögnitz, Deutsches Biomasseforschungszentrum*

## Could HTL pathways be economically viable for sustainable aviation fuel?

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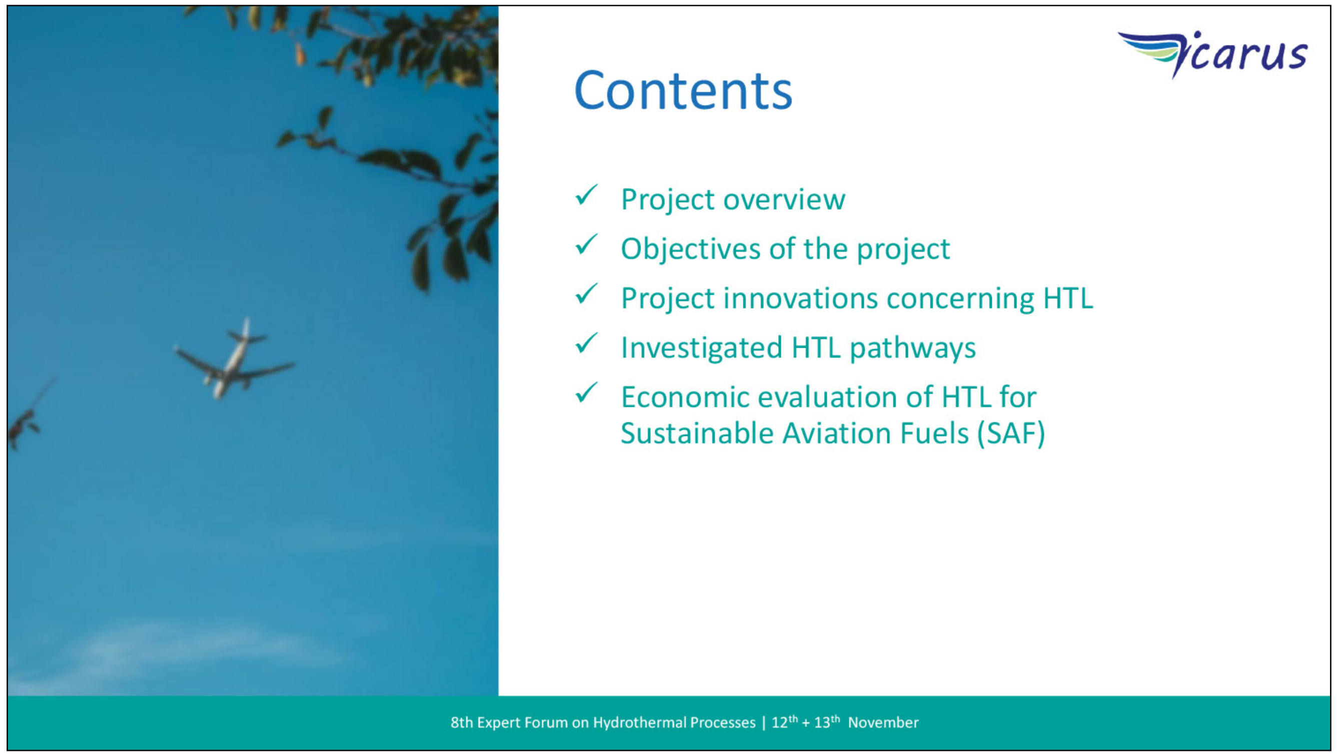
**Keywords:** Sustainable aviation fuels, hydrothermal liquefaction, cost comparison, ICARUS, specific production costs

All forecasts for aviation indicate that the sector will continue to grow with increasing demand for fuel, which will, as one measure, require increased production of sustainable aviation fuels (SAF). Various approaches have been discussed, tested and proven using all types of biomass and waste products. However, there are still many challenges and opportunities for optimisation, including the upgrading of the resulting products. This leads to very different statements regarding process design, efficiency and the need for auxiliary materials and process energy for each of the respective process routes.

Based on the HTL pathway studied in ICARUS (International cooperation for sustainable aviation biofuels, EU project funded under GA No. 101122303), a dedicated data collection of existing techno-economic assessments was applied to SAF production chains. This includes criteria such as Technology Readiness Level (TRL) and Fuel Readiness Level (FRL), as well as other Key Process Indicators (KPIs) related to technical and economic aspects. For the economic aspects, for example, SAF's production costs and market prices are reviewed. The economic analysis is important because it considers all major cost items along the supply chain from raw material supply to finished product, with a particular focus on the HTL stage.

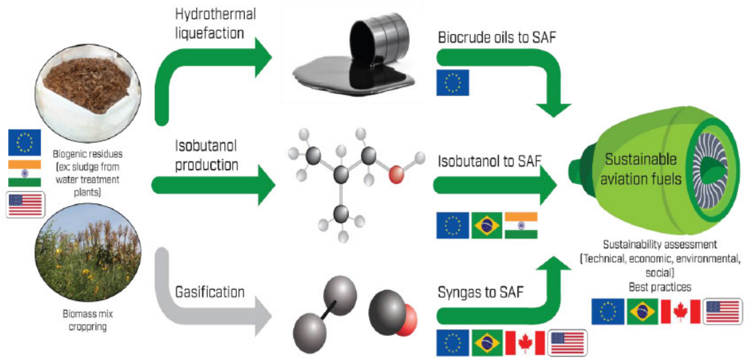




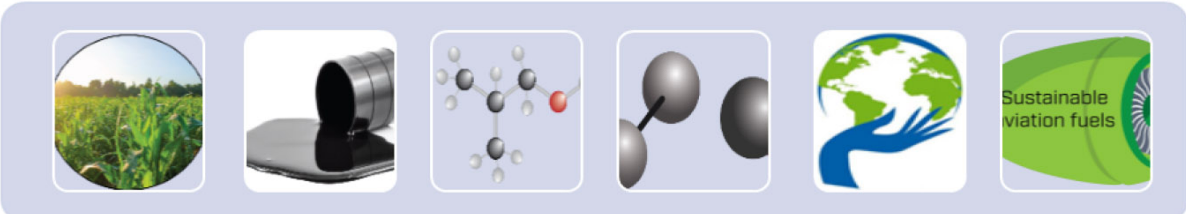
## Project overview

The ultimate objective is to develop **best practices** (based on improved innovative technologies) **and concepts** (founded on market access knowledge) along three entire value chains for accelerating the scale-up of sustainable aviation biofuels production worldwide.






## Project overview




| FEEDSTOCK | BIOCRUDE OILS - SAF | ISOBUTANOL - SAF | SYNGAS - SAF | ASSESSMENTS | BEST PRACTICES |
|---|---|---|---|---|---|
| CRES, UNIBO, BIOREF, LNEG, NEVIS ICRISAT, NDSU* | BIOREF, DBFZ, LNEG, SINTEF, | EHU, LNEG, BIOREF, TNO, NY, AVIONIC, SENAI-CIMATEC | TNO, EHU, PETROGAL, UDS, NREL* SENAI R/N, | NTNU, LNEG, DBFZ, CRES, NEVIS, KM, RSB, UDS, SENAIR/N NREL* | SINTEF, ALL |







## Objectives of the project

- ✓ Evaluate framework conditions for SAF development in Europe and Mission Innovation countries along major value chains
- ✓ Scale up selected technologies to address challenges preventing market deployment
- ✓ Increase cost-effectiveness and sustainability of large-scale sustainable biofuel production through Life Cycle Analysis
- ✓ Create future best practices and concepts for entire value chains based on experiences from Europe and Mission Innovation countries
- ✓ Disseminate and exploit ICARUS activities and results among international stakeholders, end-users, general public



## Project innovations concerning HTL

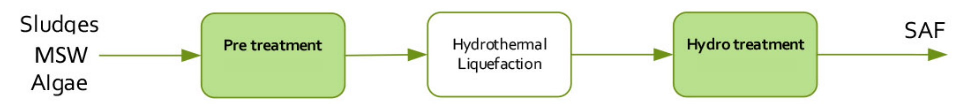
**INNOVATION PILLAR 2: Biocrude oils to SAF value chain**

**SPECIFIC NEED:** To demonstrate optimal catalyst ensemble for the bio-oil hydrotreatment

**OUTCOME**: N removal technology for improving biocrude oils quality

**Technical novelty beyond the state of the art:**

- Improvement of feedstock pretreatment and HTL processing to reduce the nitrogen in the biocrude prior hydrotreating.
- Creation of an innovative catalyst bed to simplify the hydrotreatment process




**R&I maturity - TRL evolution:** TRL 3/4 to TRL 5.

# Investigated HTL pathways

Icarus

**Selection of the papers considered in the project context:**

- ✓ Dissection of the complete value chain from biomass to SAF
- ✓ Project-relevant biomasses (algae, residues/waste, lignocellulose-containing biomass)
- ✓ Comprehensive economic balance
- ✓ Publication within the last few years

36 peer-reviewed-papers with 46 individual results

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# Investigated HTL pathways

Icarus

- ✓ Overview of the 46 results and the specifications in the parameters under consideration

| Specific raw material | Number of results | Location | Number of results | Product | Number of results |
|---|---|---|---|---|---|
| Algae | 19 | US | 18 | Gasoline and diesel mix | 12 |
| Sewage sludge | 9 | unknown | 16 | Diesel substitute | 11 |
| Forestry residues | 9 | Europe | 3 | SAF | 10 |
| Straw | 2 | UK | 3 | Bio-Crude | 3 |
| Food waste | 2 | Brazil | 2 | Gasoline substitute | 3 |
| Manure | 2 | Canada | 1 | Upgraded biocrude | 3 |
| Miscanthus | 1 | Finland | 1 | Bio-Oil | 2 |
| Sugar cane residues | 1 | Netherlands | 1 | Marine biofuel | 2 |
| Lignin | 1 | Sweden | 1 | | |

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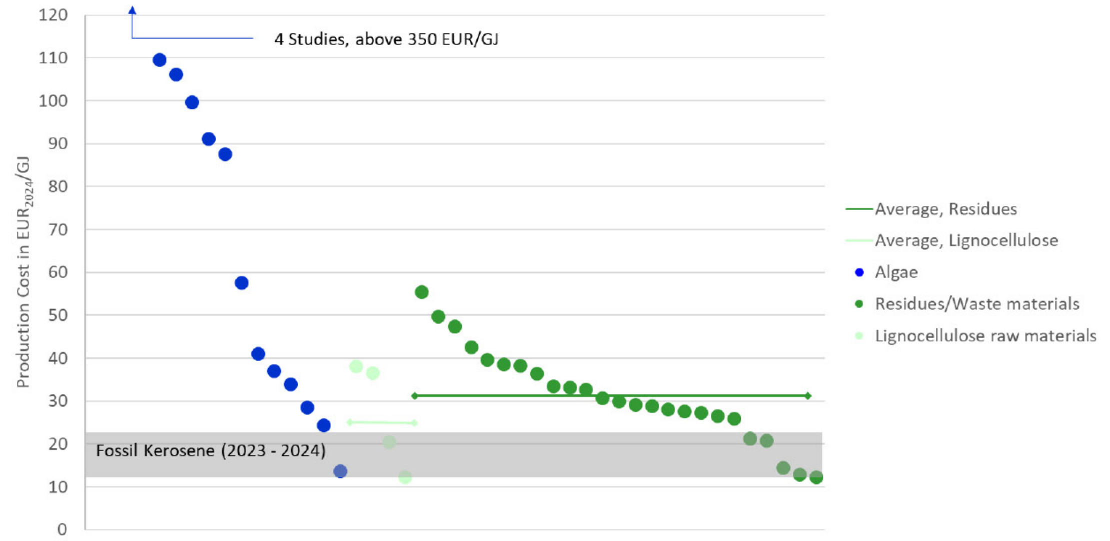
# Economic evaluation of HTL for SAF

Icarus

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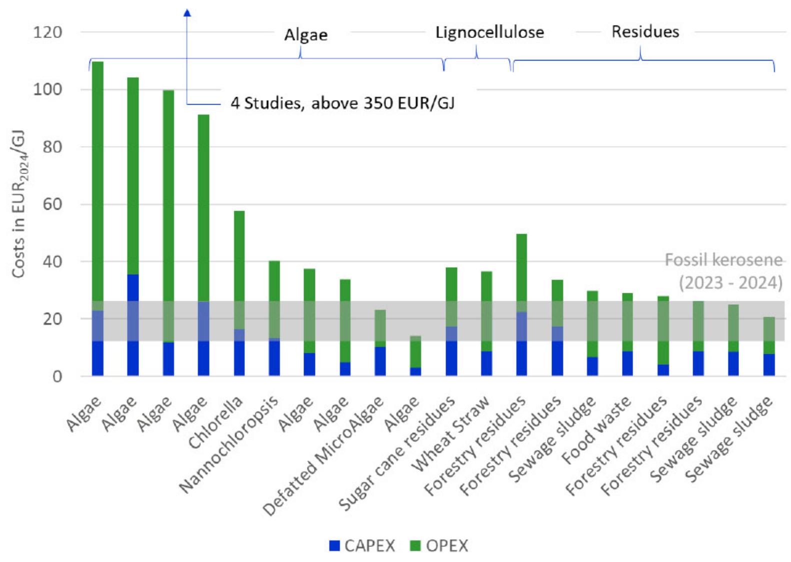
# Economic evaluation of HTL for SAF

Icarus




- ✓ Very high OPEX due to high raw material costs
- ✓ Specific to Algae pathways
- ✓ Comparable CAPEX results

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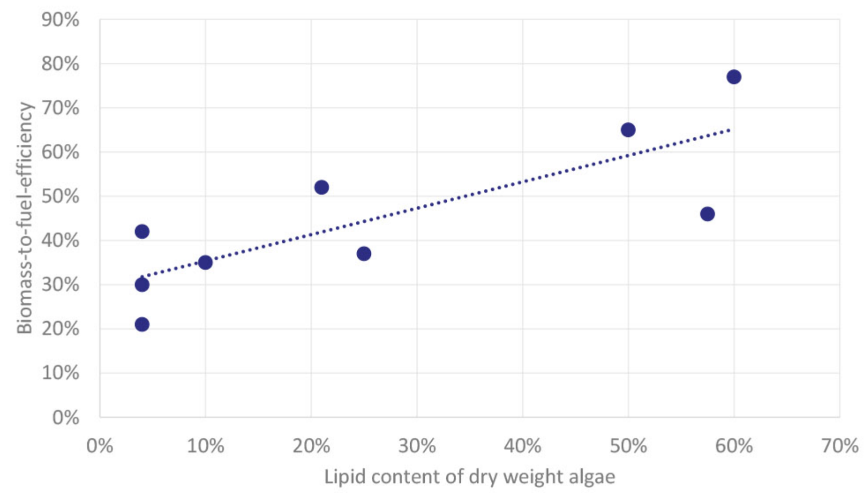
## Economic evaluation of HTL for SAF




- ✓ Biomass-to-fuel-efficiency is the energetic efficiency of the usable biomass that ends up in the energy content of the product
- ✓ Increasing lipid content boosts biocrude yield leading to higher Biomass-to-fuel efficiency
- ✓ A high lipid content can be achieved due to the acid pretreatment, fermentation and HTL aqueous phase application

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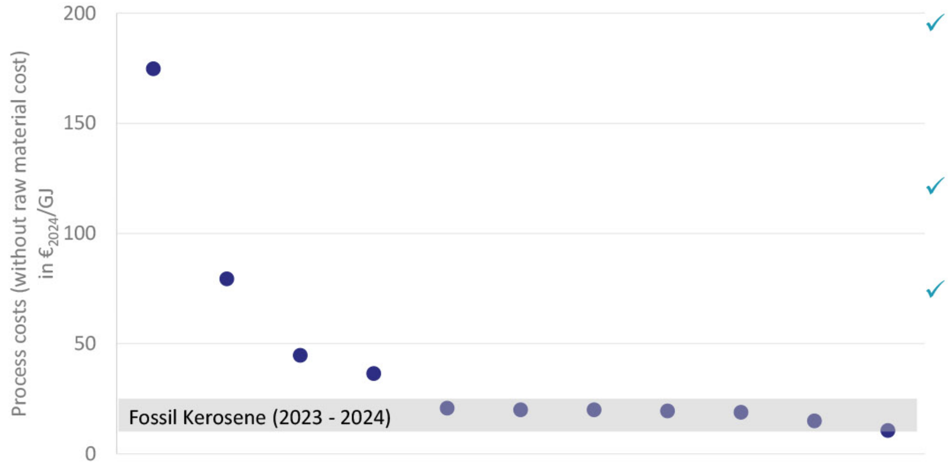
## Economic evaluation of HTL for SAF




- ✓ Most studies are within a certain range, so the results are actually comparable.
- ✓ But without biomass already higher than fossil costs
- ✓ With low and good available biomass, reasonable to high cost.

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## Economic evaluation of HTL for SAF

**To sum up:**

- ✓ HTL pathways are economically viable for sustainable aviation fuel
- ✓ Variability of results mainly due to raw material costs
- ✓ Process costs mainly comparable but still relatively high
- ✓ Focus on waste and residues therefore economically very feasible (among other reasons)
- ✓ Project will evaluate further data and produce own results on SAF costs.

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## Thank you for your attention

www.icarus-biojet.eu/

Partners

Associated Partners

ICARUS has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement no. 101122303

*Christian Klüpfel, Deutsches Biomasseforschungszentrum*

# Techno-economic assessment of a biorefinery concept consisting of AD and HTL

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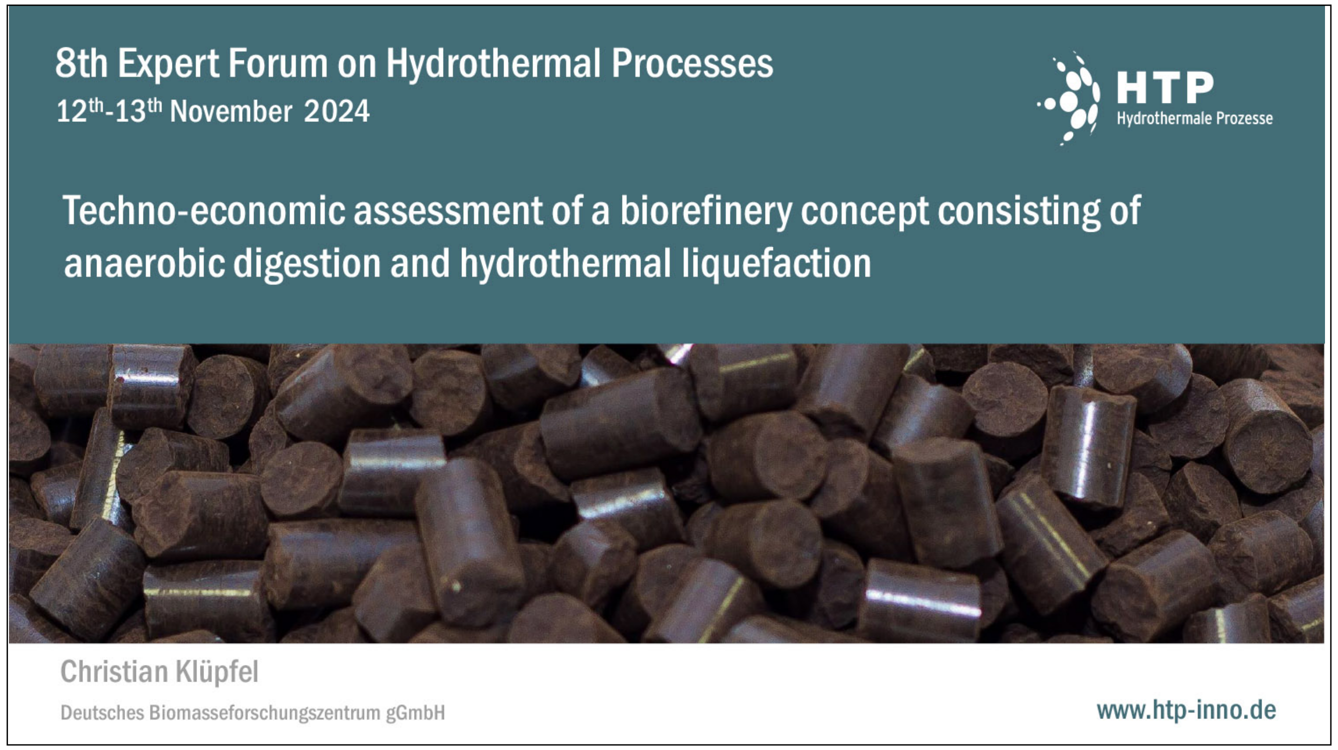
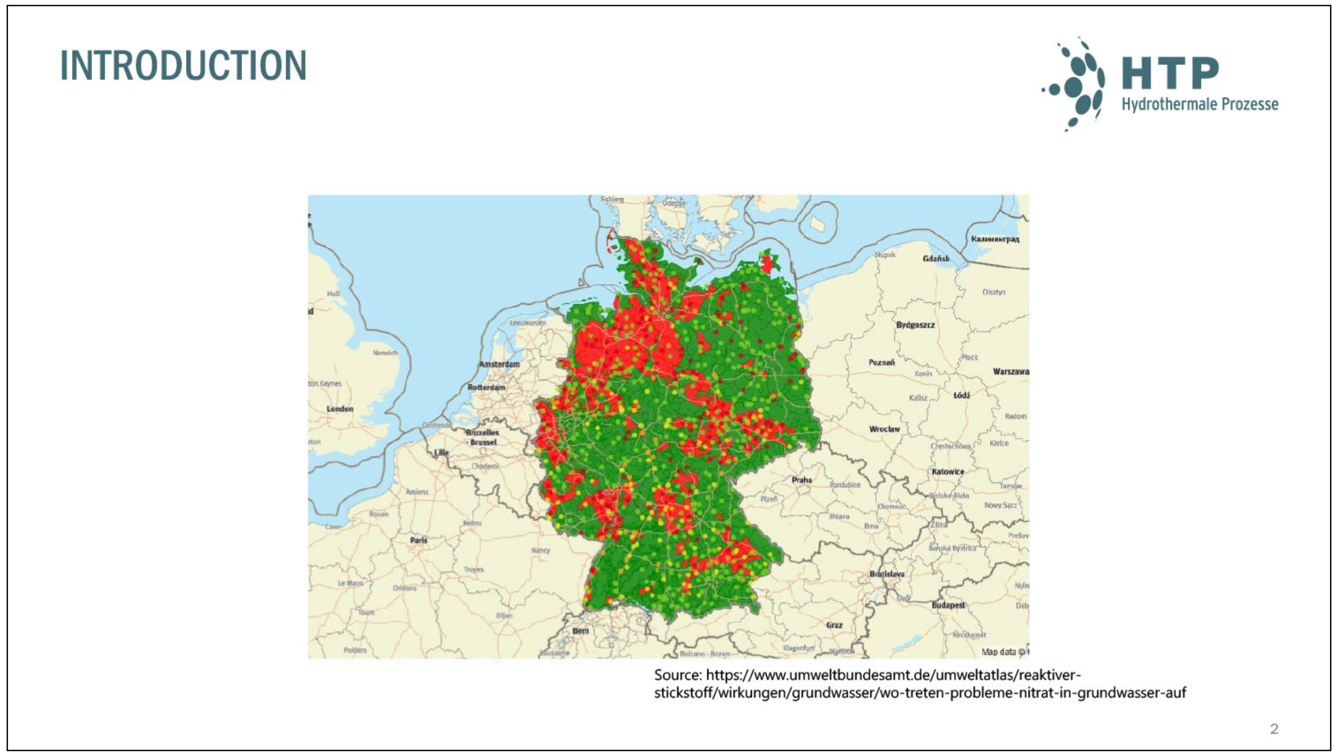
**Keywords:** Hydrothermal liquefaction; waste valorization; Anaerobic digestion; techo-economic assessment; Biofuels

The increasing global energy demand combined with the growing global population requires technology to sustainably provide energy. Arguably the most established scheme to convert wet waste biomass to energy is anaerobic digestion (AD) to produce biogas. One of the process's main challenges is the side product, commonly termed digestate, which still contains vast amounts of energy and carbon, around 50 % of the original biomass. State-of-the-art utilization is the application to agricultural land, yet the amount which can be brought out to the fields is limited by law due to overfertilization and GHG emissions. This leads to storing and transportation, oftentimes rendering the process uneconomical. Innovative treatment methods are required to overcome these obstacles and improve both energy extraction and nutrient recycling while minimizing environmental impact.

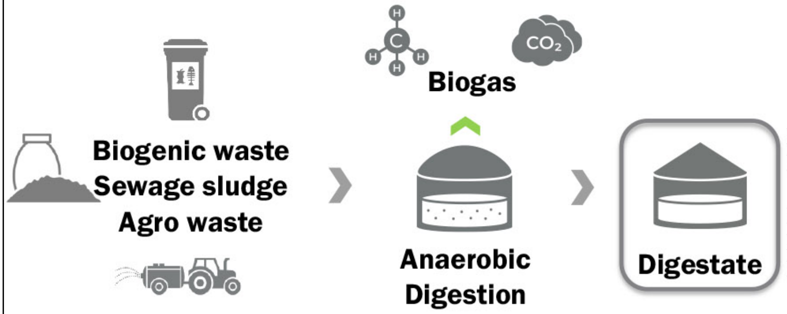
Hydrothermal liquefaction (HTL) can be used as an alternative technology to treat and valorize digestate. At near-critical conditions (647 K, 22 MPa), biomass decomposes and recombines to form an energy-dense biocrude, an aqueous phase (AP) rich in small organic molecules and a nutrient- and carbon-rich hydrochar. This study compares the HTL behavior by means of mass- and energy balances of three digestates: A digested sewage sludge, straw/manure digestate and digested biogenic waste as well as their respective undigested feedstocks. Generally, higher biocrude yield and thus energy recovery is found when using the undigested biomass, yet the overall energy recovery is higher when using the digestate, highlighting synergies of the two processes. High nutrient recovery in the solid residue suggests its utilization as a carbon sink and soil amender. The experimental data was used to inform a process model using Aspen Plus ® software and a sensitivity analysis with regards to mass flow, input total solids (TS) and processing temperature was performed. Based on the equipment dimensioning, factorial methods were used to estimate CAPEX and OPEX of the two biorefining schemes 1) AD + HTL and 2) HTL plant to produce biocrude as the main energy product. The results highlight different paths for the investigated scenarios.

This presentation comparatively investigates the hydrothermal process for the utilization of digestate and waste biomass. This process can help solve a disposal problem that is particularly urgent in regions with intensive livestock farming and at the same time create a renewable fuel, i.e., the biocrude. A process model is developed on the basis of experimental results and used to techno-economically assess the process and highlight, which added-value process is suitable and economical for which biomass.



## INTRODUCTION




- Nutrient and carbon rich side product
- Land application causes GHG emissions and can lead to over fertilization
- Logistics and storage are cost intensive
- Little energetic utilization
- 31 $Mt_{DM}$ in EU in 2022[1]

[1]European Biogas Association (2023). Statistical Report 2023. https://www.europeanbiogas.eu/eba-statistical-report-2023/.

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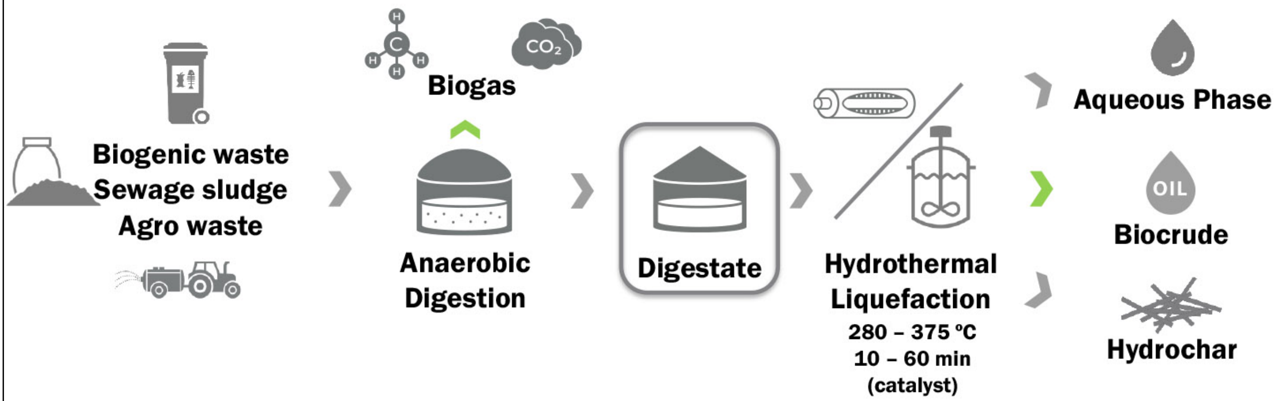
## INTRODUCTION

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## MATERIALS & METHODS

- **Materials:** Sewage sludge (SS), Biogenic waste (BW), Straw/manure (SM) and their respective digestates (D)
  → **six biomass in total**
- **Biogas data** collected from plant operators
- **Experimental method:** HTL at 300, 325, 350 °C for 20 min in 20 mL batch autoclaves; separation by centrifugation, followed by DCM extraction
- **Analytics:** Proximate analysis and ICP of biomasses; ultimate analysis of biomass, biocrude and hydrochar; COD, TOC, TN of HTL aqueous phase

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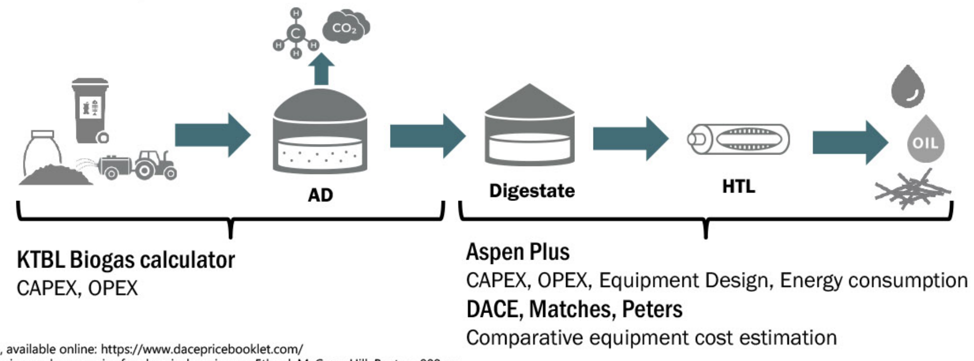
## MATERIALS & METHODS

### Modeling and cost estimation approach

- **Simulation of HTL** with Aspen Plus v14
- **Equipment price estimation and comparison** with APEA, DACE[2], Peters[3], Matches[4] and KTBL[5]
- Calculation of **production cost** according to VDI Guideline 6025
- Biomethane sales price from DENA




[2]DACE price booklet (2024), available online: https://www.dacepricebooklet.com/
[3]Peters et al. (2004) Plant design and economics for chemical engineers, 5th ed. McGraw-Hill, Boston, 988 pp.
[4]Matches (2024), available online: https://www.matche.com/
[5]KTBL (2024) KTBL Biogasrechner, available online: https://daten.ktbl.de/biogas/startseite.do

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## MATERIALS & METHODS
### Aspen Model

HTP Hydrothermale Prozesse

- **Aspen plus v.14**
- **Equation of state:** Soave-Redlich-Kwong
- **Scale:** 10 kt/a and 250 kt/a
- Biomass, digestates and hydrochar as **non conventional solid** based on analytics.
- Biocrude and AP as **mixture of organic compounds** found in GC-MS to fit elemental composition

| Analysis | SM | SMD | Hydrochar |
|---|---|---|---|
| **Proximate** | | | |
| Ash [%] | 11.1 | 18.25 | 34.6 |
| **Ultimate** | | | |
| C [%] | 47.95 | 43.8 | 48.12 |
| H [%] | 5.38 | 5.44 | 3.82 |
| N [%] | 1.28 | 1.71 | 2.12 |
| S [%] | 0.27 | 0.37 | 0.46 |
| O [%] | 34.02 | 30.43 | 13.00 |
| **Sulfanate** | | | |
| Organic [%] | 88.9 | 81.75 | 65.37 |

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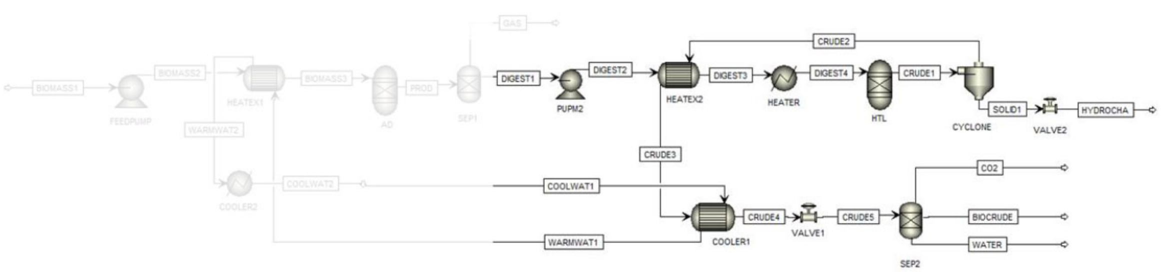
## MATERIALS & METHODS
### Aspen Plus flow sheet

HTP Hydrothermale Prozesse

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## RESULTS
### Mass and energy balance

HTP Hydrothermale Prozesse

| Feedstock | Process | $T_{HTL}$ [°C] | $Y_{Methane}$ [Ma.%] | $ER_{Methane}$ [%] | $Y_{Biocrude}$ [Ma.%] | $ER_{Biocrude}$ [%] | $ER_{total}$ [%] |
|---|---|---|---|---|---|---|---|
| Sewage sludge | AD + HTL | 300 | 14.45 | 47.86 | 13.02% | 28.64% | 62.87% |
| | | 325 | | | 12.81% | 30.27% | 63.72% |
| | | 350 | | | 12.58% | 30.43% | 63.80% |
| | HTL | 300 | - | - | 15.60% | 31.83% | - |
| | | 325 | | | 17.09% | 32.31% | - |
| | | 350 | | | 19.19% | 39.28% | - |
| Straw/ manure | AD + HTL | 300 | 10.09 | 28.96 | 20.50% | 32.36% | 48.59% |
| | | 325 | | | 19.68% | 33.23% | 49.11% |
| | | 350 | | | 19.08% | 34.71% | 50.01% |
| | HTL | 300 | - | - | 21.07% | 32.35% | - |
| | | 325 | | | 23.53% | 37.15% | - |
| | | 350 | | | 22.59% | 36.40% | - |
| Biogenic waste | AD + HTL | 300 | 3.05 | 10.38 | 9.75% | 21.33% | 27.79% |
| | | 325 | | | 9.30% | 20.90% | 27.43% |
| | | 350 | | | 10.52% | 20.87% | 27.41% |
| | HTL | 300 | - | - | 14.66% | 27.26% | - |
| | | 325 | | | 15.04% | 29.81% | - |
| | | 350 | | | 15.96% | 31.91% | - |

x 1.6 - 2

x 1.5

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## RESULTS
### Preliminary economic assessment – minimum fuel selling price (MFSP)

HTP Hydrothermale Prozesse

| Feedstock | Process | $T_{HTL}$ [°C] | Biomethane sales €/y | CAPEX € | Annuity €/y | OPEX €/y | Total deficit €/y | MFSP €/kg | MFSP €/GJ |
|---|---|---|---|---|---|---|---|---|---|
| Sewage sludge | AD + HTL | 300 | 514,739 | 6.003.809 | 777.521 | 2.108.474 | 2.371.256 | **13,60** | **449,08** |
| | | 325 | | 6.045.815 | 782.961 | 2.112.806 | 2.381.027 | **13,89** | **426,60** |
| | | 350 | | 6.179.512 | 800.275 | 2.124.226 | 2.409.762 | **14,30** | **429,51** |
| | HTL | 300 | - | 3.167.483 | 410.203 | 2.043.214 | 2.453.417 | **7,49** | **218,98** |
| | | 325 | | 3.214.020 | 416.230 | 2.045.034 | 2.461.264 | **6,86** | **216,46** |
| | | 350 | | 3.321.291 | 430.122 | 2.052.814 | 2.482.936 | **6,16** | **179,61** |
| Straw/ manure | AD + HTL | 300 | 1,814,274 | 5.644.040 | 730.929 | 1.694.026 | 610.681 | **2,35** | **81,89** |
| | | 325 | | 5.941.064 | 769.395 | 1.695.937 | 651.058 | **2,61** | **85,03** |
| | | 350 | | 6.161.967 | 798.003 | 1.704.582 | 688.311 | **2,85** | **86,06** |
| | HTL | 300 | - | 2.816.341 | 364.729 | 1.635.540 | 2.000.269 | **4,83** | **141,14** |
| | | 325 | | 3.094.428 | 400.743 | 1.637.797 | 2.038.540 | **4,41** | **139,10** |
| | | 350 | | 3.374.034 | 436.953 | 1.657.608 | 2.094.561 | **4,72** | **137,46** |
| Biogenic waste | AD + HTL | 300 | 559,483 | 5.581.124 | 722.781 | 1.631.134 | 1.794.432 | **10,32** | **316,20** |
| | | 325 | | 5.820.600 | 753.794 | 1.632.590 | 1.826.901 | **11,00** | **328,60** |
| | | 350 | | 6.144.169 | 795.698 | 1.654.593 | 1.890.808 | **10,07** | **340,55** |
| | HTL | 300 | - | 2.859.074 | 370.263 | 1.583.830 | 1.954.094 | **6,67** | **219,88** |
| | | 325 | | 3.054.388 | 395.557 | 1.596.570 | 1.992.127 | **6,62** | **204,97** |
| | | 350 | | 3.381.542 | 437.925 | 1.608.955 | 2.046.881 | **6,41** | **196,77** |

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## RESULTS
### Scale-up and cost comparison

- **Scale-up to 250 kt/a** of biomass performed for economically most viable cases (by tonnage):
  - Straw/manure @ 325 °C
    → 4.41 €/kg
  - Straw/manure digestate @ 300 °C
    → 2.35 €/kg
- Comparative equipment cost estimation for **heat exchanger, pump and reactor** using DACE, Peters and Matches
- Prices were adapted with **CEPCI** factor if necessary

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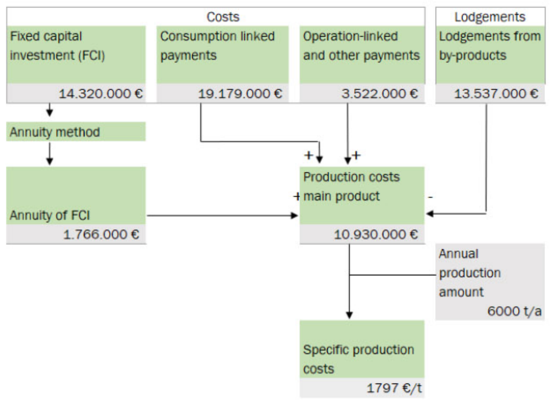
## Sensitivity analysis
### Properties & assumptions

- **Aspen Plus Economic Analyzer** provides relatively high cost estimation compared to other methods
- Mean of DACE, Peters and Matches aligned well and was used to estimate **equipment cost** for HTL
- **Inconel (Alloy 625)** was used for high temperature equipment for its high temperature corrosion resistance
- **Operating cost** was calculated using Peters plant capacity estimation
- **Process water** treatment cost is based on the Leipzger Wasserwerke price list for COD, TOC and TNB

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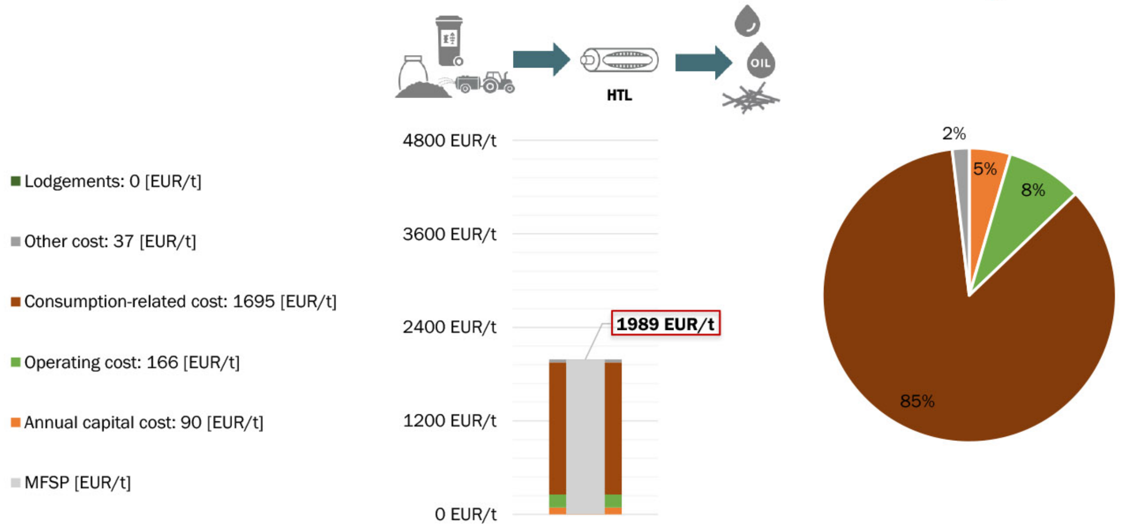
## Sensitivity analysis
### HTL

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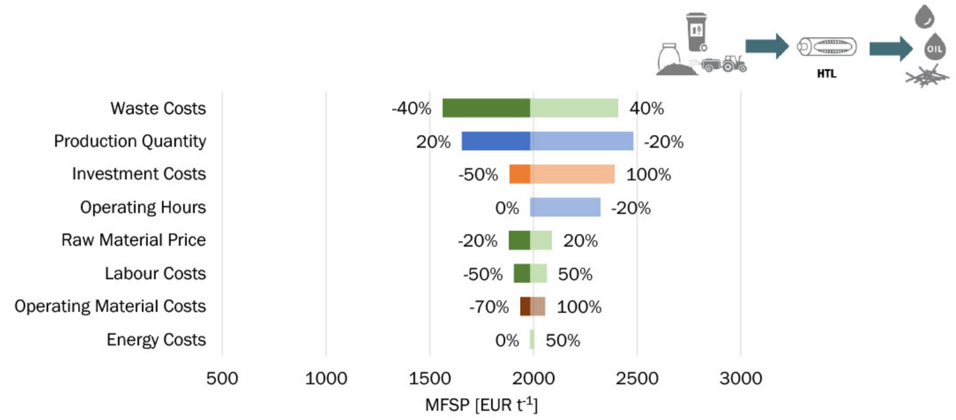
## Sensitivity analysis
### HTL




- **Production quantity, waste and investment** as main price drivers
- **Labor cost, raw material price** have a lower and **energy cost** an almost negligible influence

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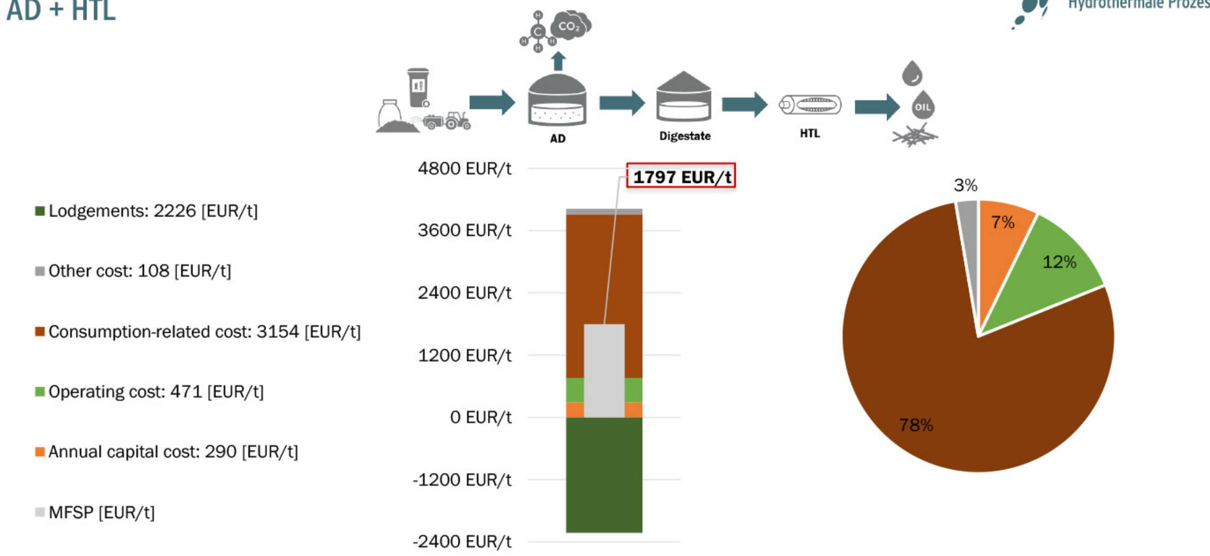
## Sensitivity analysis

### AD + HTL

HTP Hydrothermale Prozesse

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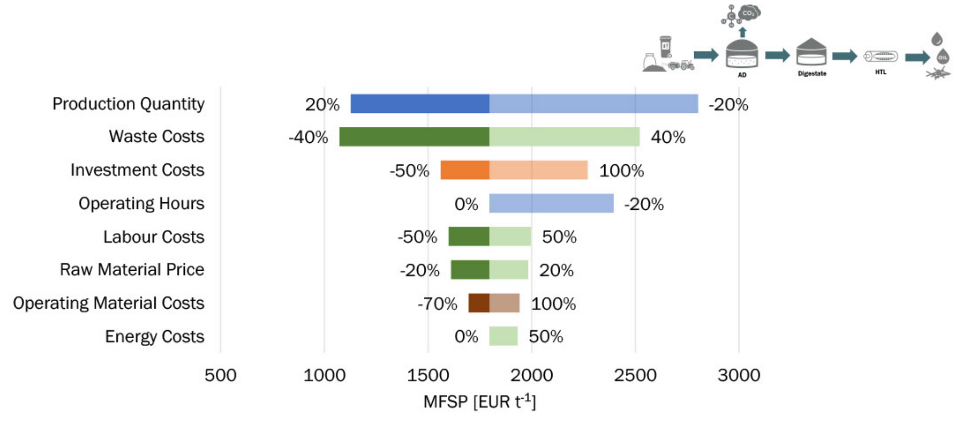
## Sensitivity analysis

### AD + HTL

HTP Hydrothermale Prozesse




- **Production quantity, waste and investment** as main price drivers similar to AD + HTL

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## Conclusion

HTP Hydrothermale Prozesse

- Combination of AD + HTL can make sense **energetically** depending on the scenario.
- Aspen Plus Economic Analyzer seems unreliable and **generally gives high estimations** compared to other established estimation methods.
- Sensitivity analysis reveals **similar cost structure** and price drivers when comparing AD + HTL and HTL.
- **Process water treatment / waste cost** found to be the crucial economic barrier.
- Combination of AD and HTL can allow for a **lower MFSP** of biocrude while significantly increasing the energetic exploitation of the biomass.

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## 8th Expert Forum on Hydrothermal Processes

HTP Hydrothermale Prozesse

### Thank you for your attention!


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www.htp-inno.de

*Philipp Knötig, Deutsches Biomasseforschungszentrum*

## From waste to renewable methane and secondary products – The role of HT processes in a pilot scale biorefinery

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**Keywords:** Renewable methane, pilot plant, biorefinery, hydrothermal pre-treatment, hydrothermal carbonization

At DBFZ Leipzig, a pilot plant was developed and installed able to produce 819–930 m3/a (0.59–0.67 t/a) of renewable methane, 5–7 t/a of solid and liquid fertiliser as well as around 2 t/a hydrochar. In addition, it is aimed for complete avoidance of waste streams, thus recycling process water streams within the plant. The process is intensely monitored, highly automated and continuously operated in a 1000 m2 experimental area. The plant follows a holistic biorefinery approach and is composed of different state-of-the-art and innovative processes, such as methanation, fermentation, hydrothermal processes and several separation units. The process is fed with 7–8 t/a biogenic residues/wastes and 2000–2900 m3/a (0.18–0.26 t/a) green hydrogen.

The pilot plant is part of a project called Pilot-SBG addressing important topics such as the cascaded use of biomass, circular economy, sector coupling, $CO_2$ reduction as well as decentralised and regional energy production.

One of the highlights is the use of two hydrothermal processes. First, a mild hydrothermal pre-treatment is applied before the fermentation process allowing for an increased accessibility of digestible material for the microorganisms. Second, a more severe hydrothermal carbonization is applied generating additional products and increasing the overall business case for the biorefinery concept.

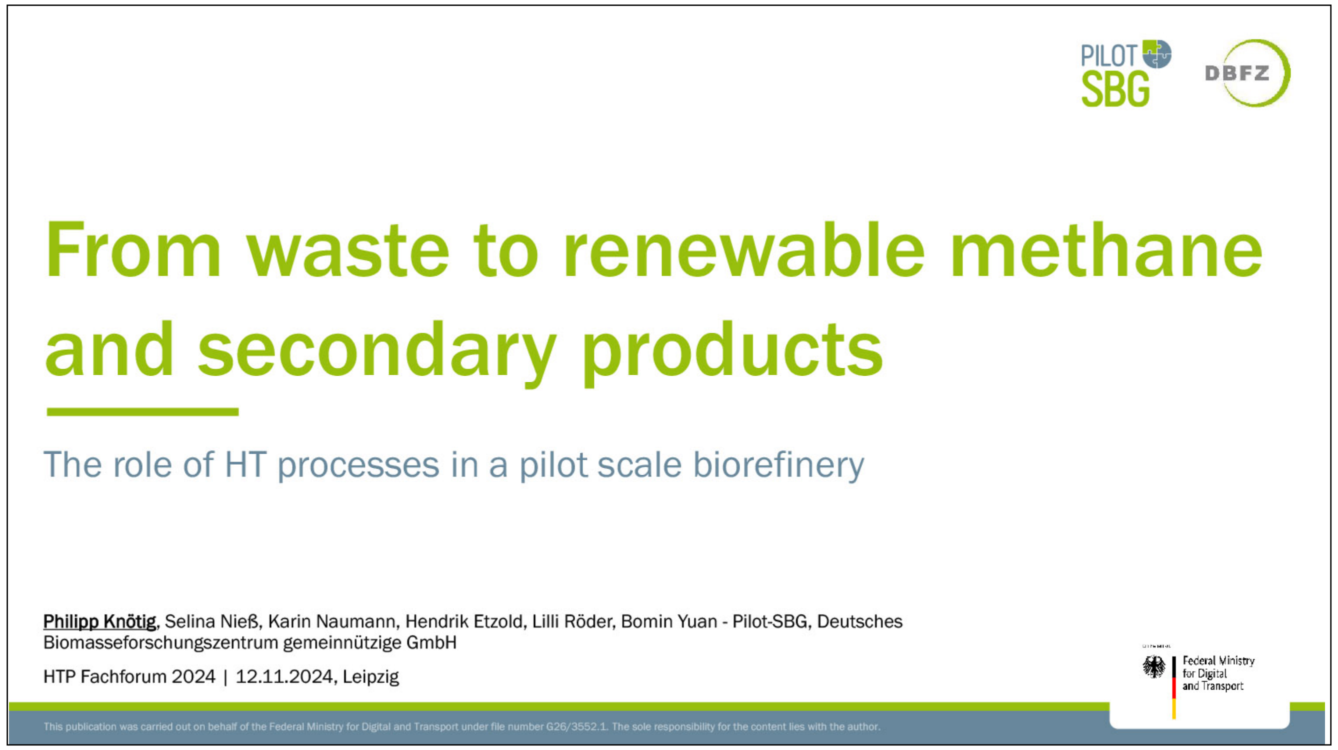
The plant data is reproduced in a digital twin allowing for even deeper studies in regards to demand side management analyses and chemical process optimisation, which are used for the publication of long-lasting, robust and economically competitive commercial-size plant concepts. Based on preliminary lab-scale investigations and intensive literature reviews, a first commercial-scale concept was developed based on agricultural residues. At the moment, the commercial-size concept for the urban waste streams is developed. Looking into the potential of hydrochars in regards to quota trading from carbon capture applications is an essential part of this.

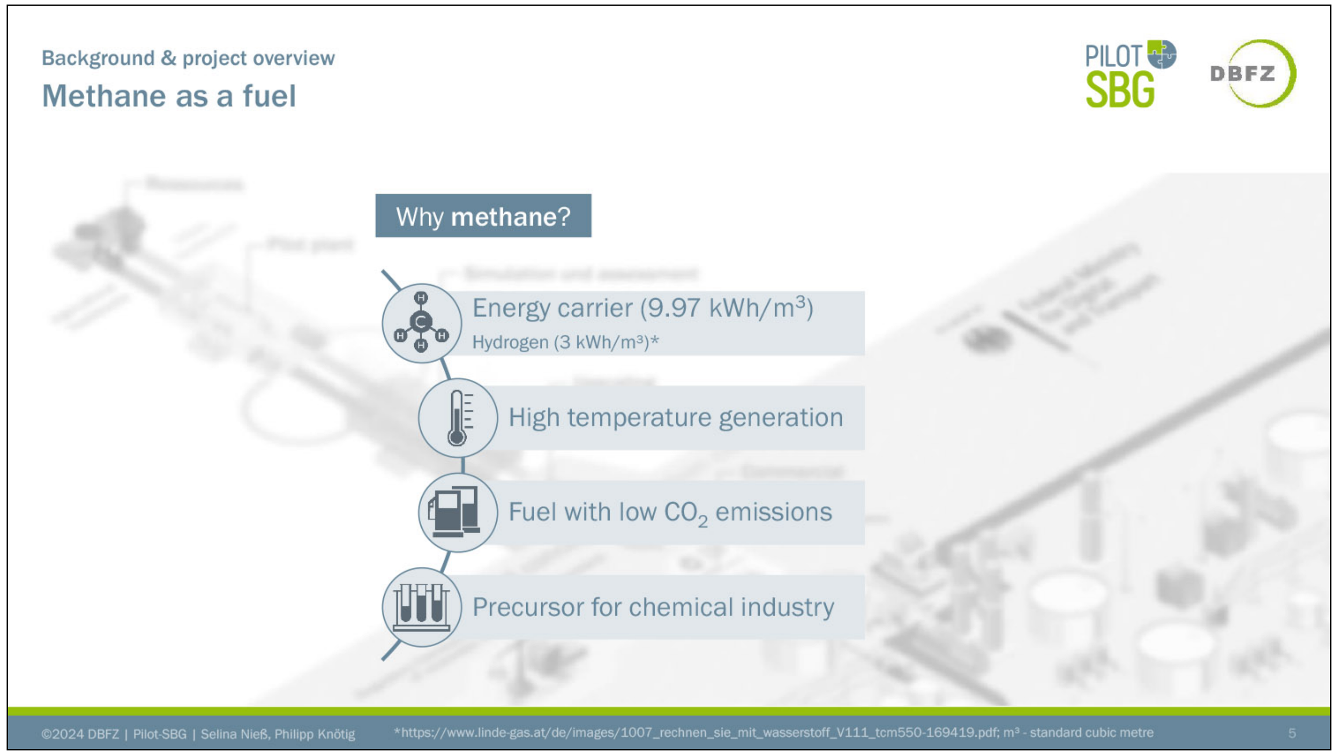
Both commercial-size concepts will be validated, updated as well as improved through the real time data from the pilot plant. We are in a progressed state of the commissioning process. Active research on the hydrothermal equipment is scheduled to begin in Q3/2024.

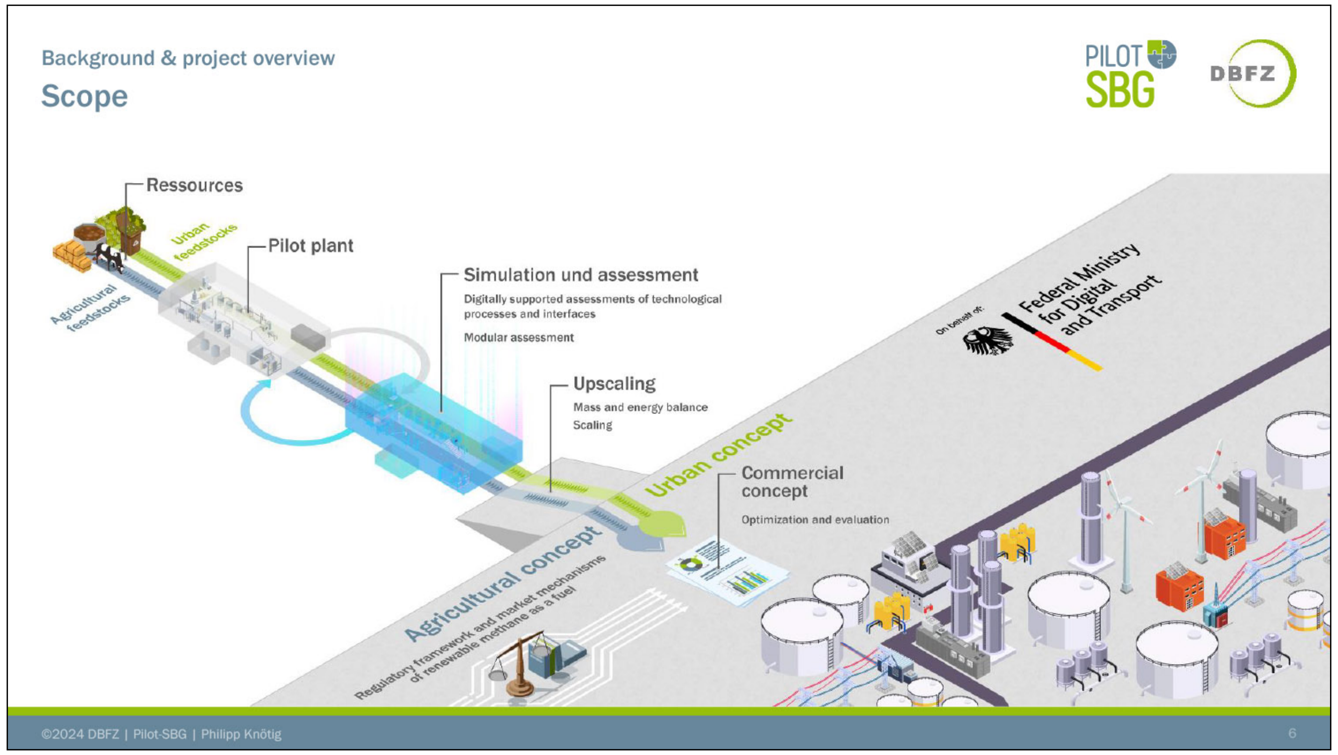
More insights into the project Pilot-SBG and its additional fields of research will be granted at https://www.dbfz.de/pilot-sbg.









Background & project overview
Methane as a fuel
PILOT SBG
DBFZ
Why methane?
Energy carrier (9.97 kWh/m³)
Hydrogen (3 kWh/m³)*
High temperature generation
Fuel with low CO₂ emissions
Precursor for chemical industry
©2024 DBFZ | Pilot-SBG | Selina Nieß, Philipp Knötig
*https://www.linde-gas.at/de/images/1007_rechnen_sie_mit_wasserstoff_V111_tcm550-169419.pdf; m³ - standard cubic metre
5


Background & project overview
Scope
PILOT SBG
DBFZ
Ressources
Pilot plant
Urban feedstocks
Agricultural feedstocks
Simulation und assessment
Digitally supported assessments of technological processes and interfaces
Modular assessment
Upscaling
Mass and energy balance
Scaling
Commercial concept
Optimization and evaluation
Urban concept
Agricultural concept
Regulatory framework and market mechanisms of renewable methane as a fuel
Federal Ministry for Digital and Transport
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6






Background & project overview
Scope
PILOT SBG
DBFZ
LNG
Efficiencies
Emissions
Economics
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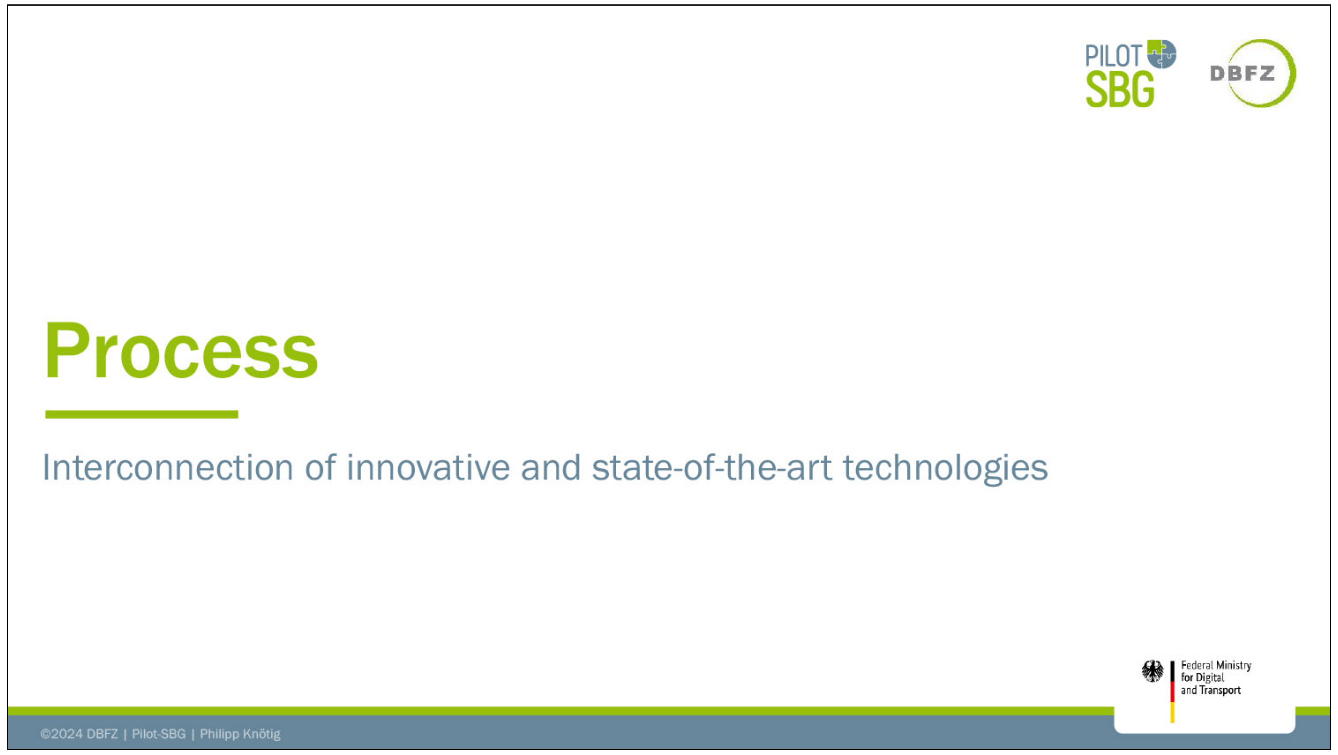
7


PILOT SBG
DBFZ
Process
Interconnection of innovative and state-of-the-art technologies
Federal Ministry for Digital and Transport
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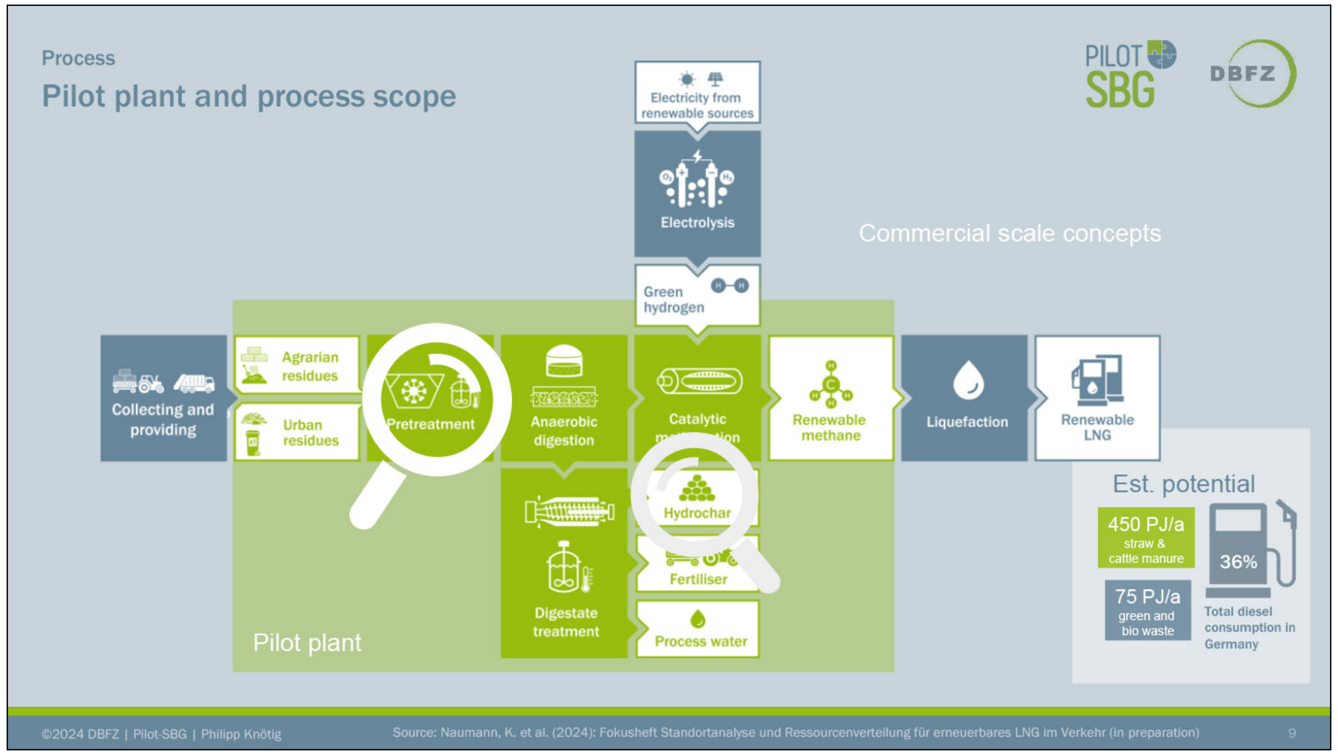
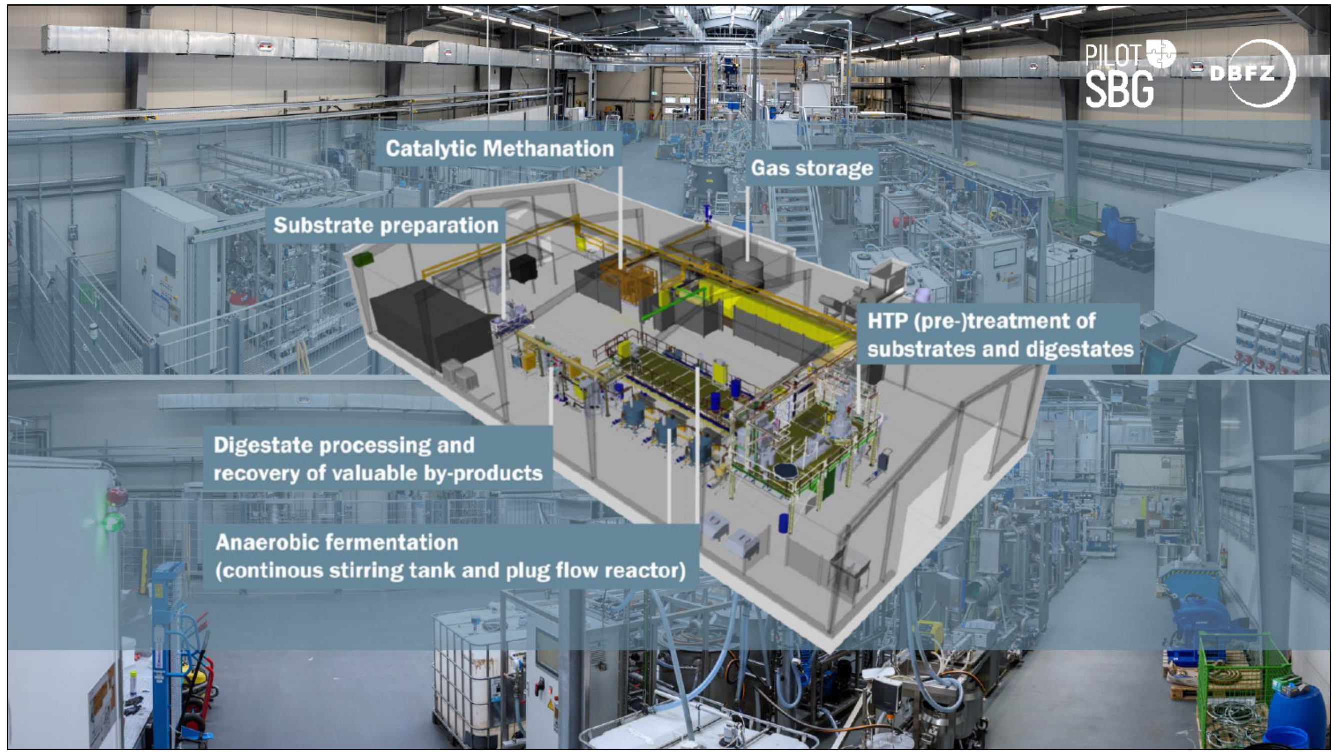
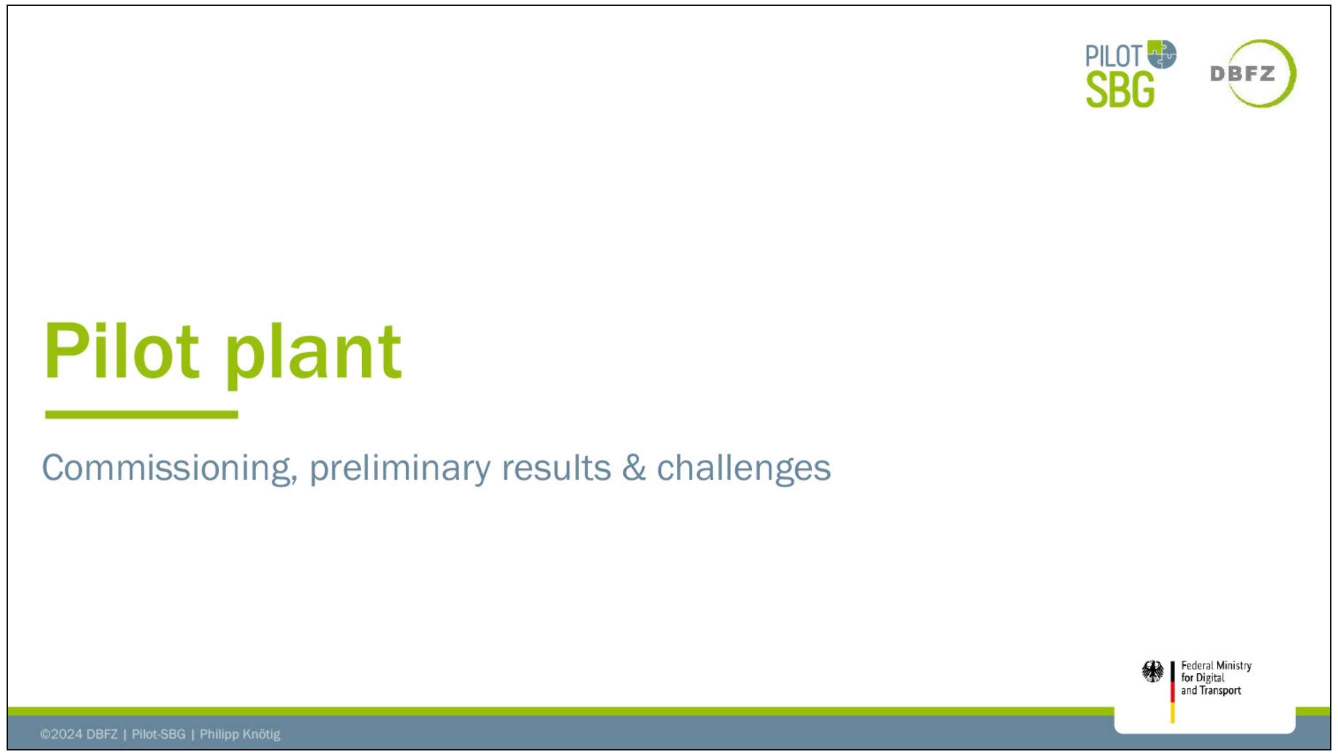

Process
Pilot plant and process scope
PILOT SBG
DBFZ
Electricity from renewable sources
Electrolysis
Commercial scale concepts
Green hydrogen
Collecting and providing
Agrarian residues
Urban residues
Pretreatment
Anaerobic digestion
Catalytic
Renewable methane
Liquefaction
Renewable LNG
Hydrochar
Fertiliser
Digestate treatment
Process water
Pilot plant
Est. potential
450 PJ/a straw & cattle manure
75 PJ/a green and bio waste
36%
Total diesel consumption in Germany
©2024 DBFZ | Pilot-SBG | Philipp Knötig
Source: Naumann, K. et al. (2024): Fokusheft Standortanalyse und Ressourcenverteilung für erneuerbares LNG im Verkehr (in preparation)
9


PILOT SBG
DBFZ
Catalytic Methanation
Gas storage
Substrate preparation
HTP (pre-)treatment of substrates and digestates
Digestate processing and recovery of valuable by-products
Anaerobic fermentation (continous stirring tank and plug flow reactor)


PILOT SBG
DBFZ
Pilot plant
Commissioning, preliminary results & challenges
Federal Ministry for Digital and Transport
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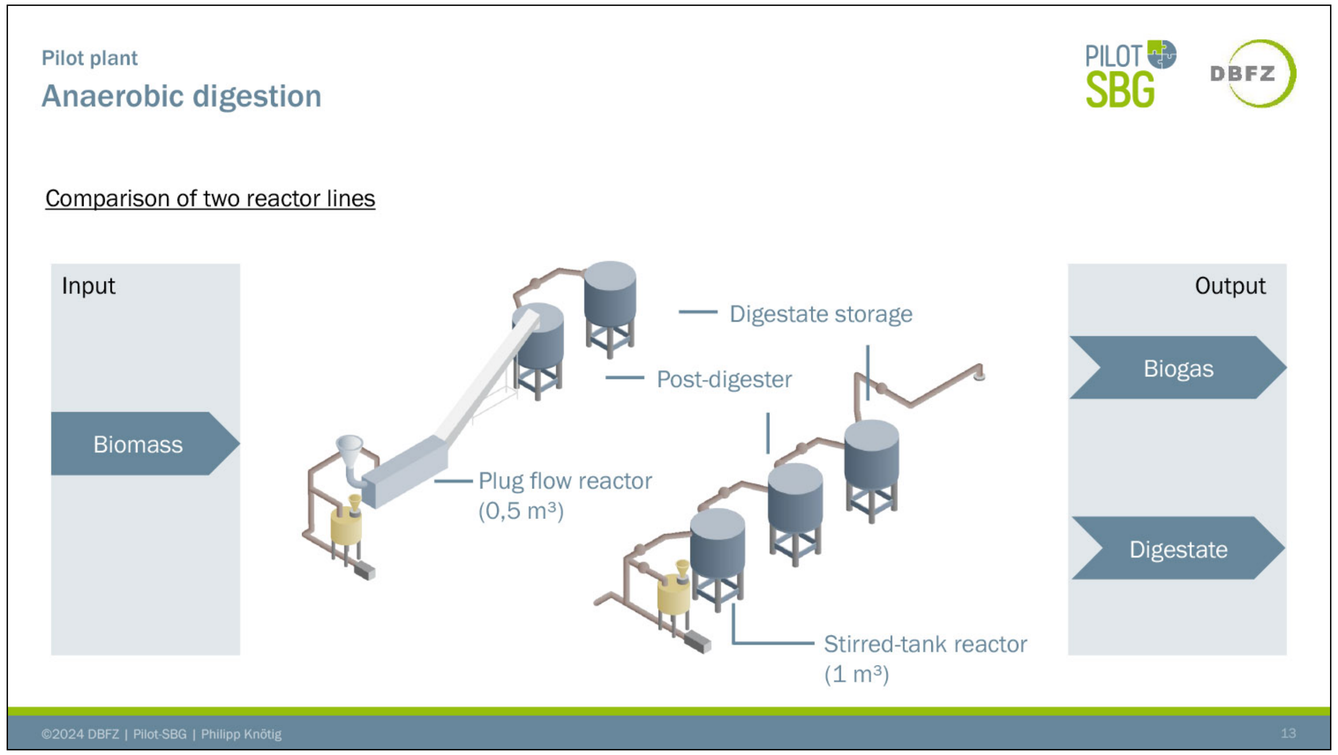
PILOT SBG
DBFZ
Anaerobic fermentation | Line 2
Anaerobic fermentation | Line 1


Pilot plant
Anaerobic digestion
PILOT SBG
DBFZ
Comparison of two reactor lines
Input
Biomass
Digestate storage
Post-digester
Plug flow reactor
(0,5 m³)
Stirred-tank reactor
(1 m³)
Output
Biogas
Digestate
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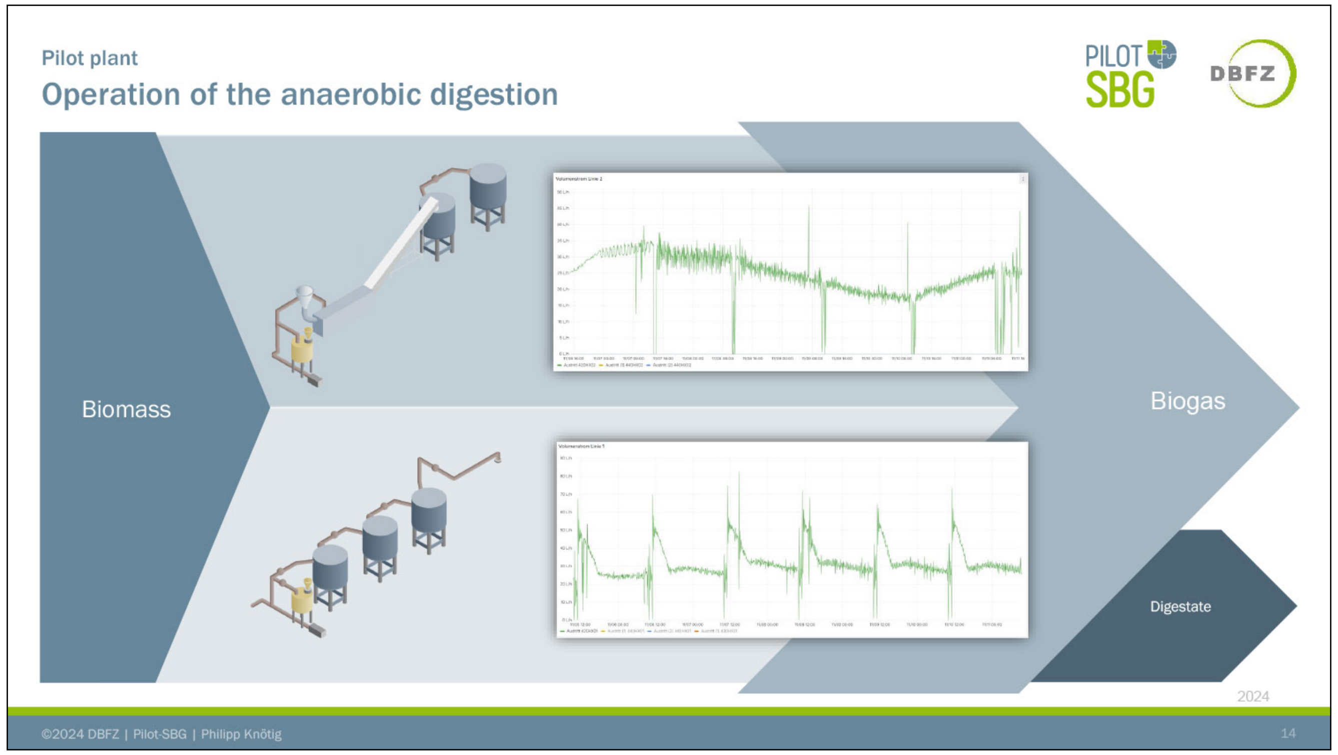
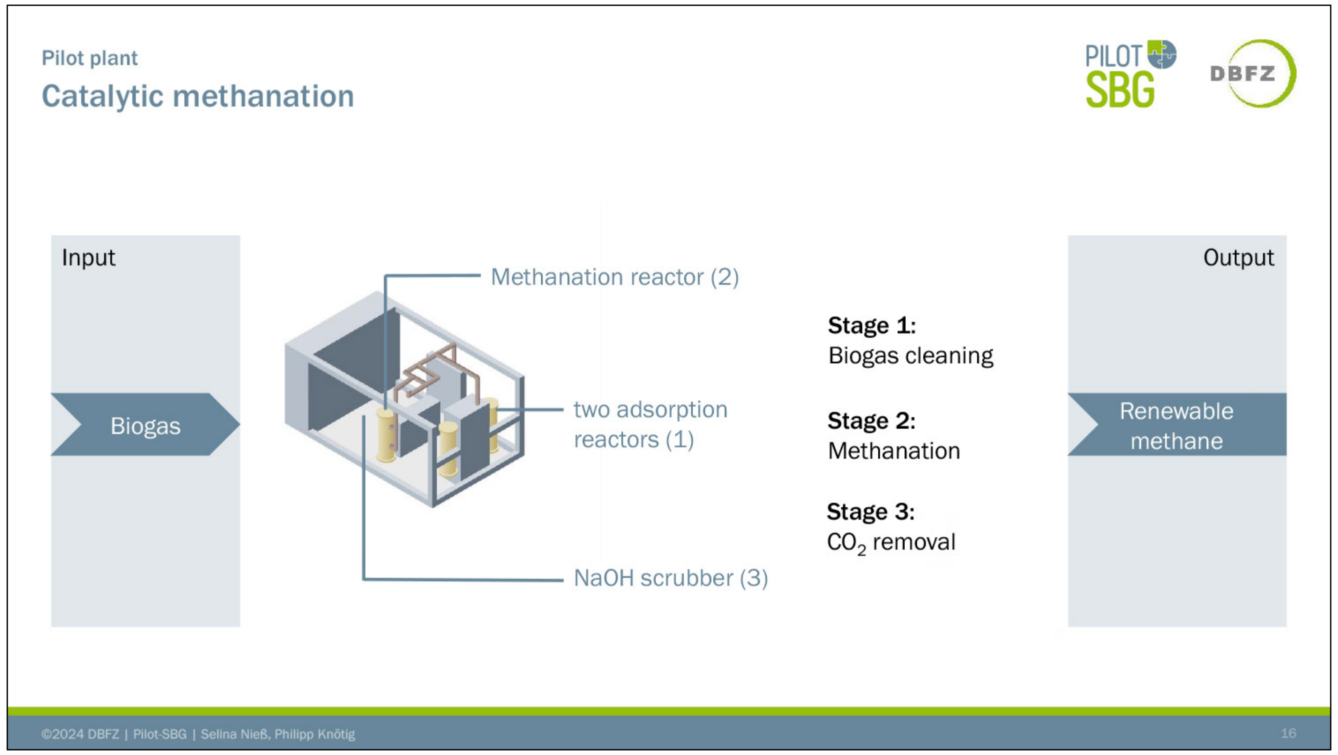
Methanation
Gas storage & flare
PILOT SBG
DBFZ
Methanation


Pilot plant
Operation of the anaerobic digestion
PILOT SBG
DBFZ
Biomass
Biogas
Digestate
2024
©2024 DBFZ | Pilot-SBG | Philipp Knötig
14


Pilot plant
Catalytic methanation
PILOT SBG
DBFZ
Input
Biogas
Methanation reactor (2)
two adsorption
reactors (1)
NaOH scrubber (3)
Stage 1:
Biogas cleaning
Stage 2:
Methanation
Stage 3:
CO2 removal
Output
Renewable
methane
©2024 DBFZ | Pilot-SBG | Selina Nieß, Philipp Knötig
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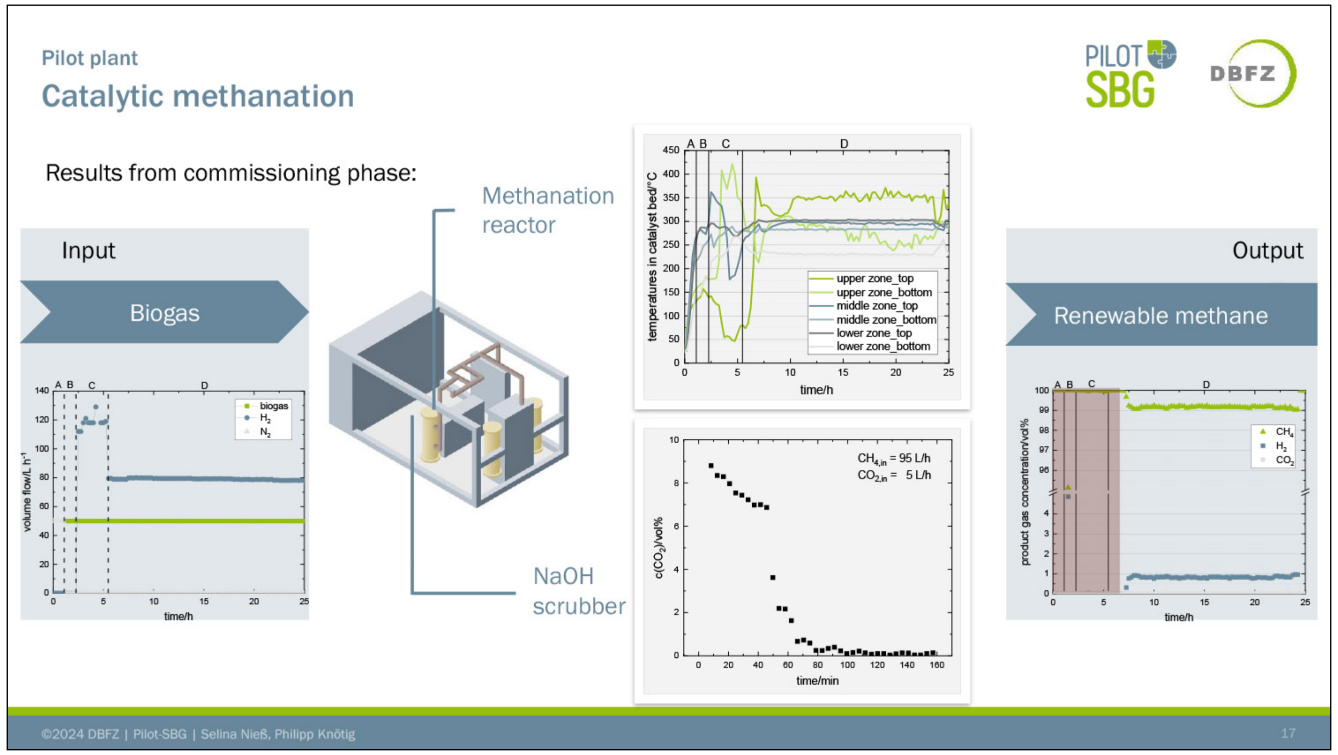
Pilot plant
Catalytic methanation
PILOT SBG
DBFZ
Results from commissioning phase:
Input
Biogas
Methanation reactor
NaOH scrubber
Output
Renewable methane
time/h
time/min
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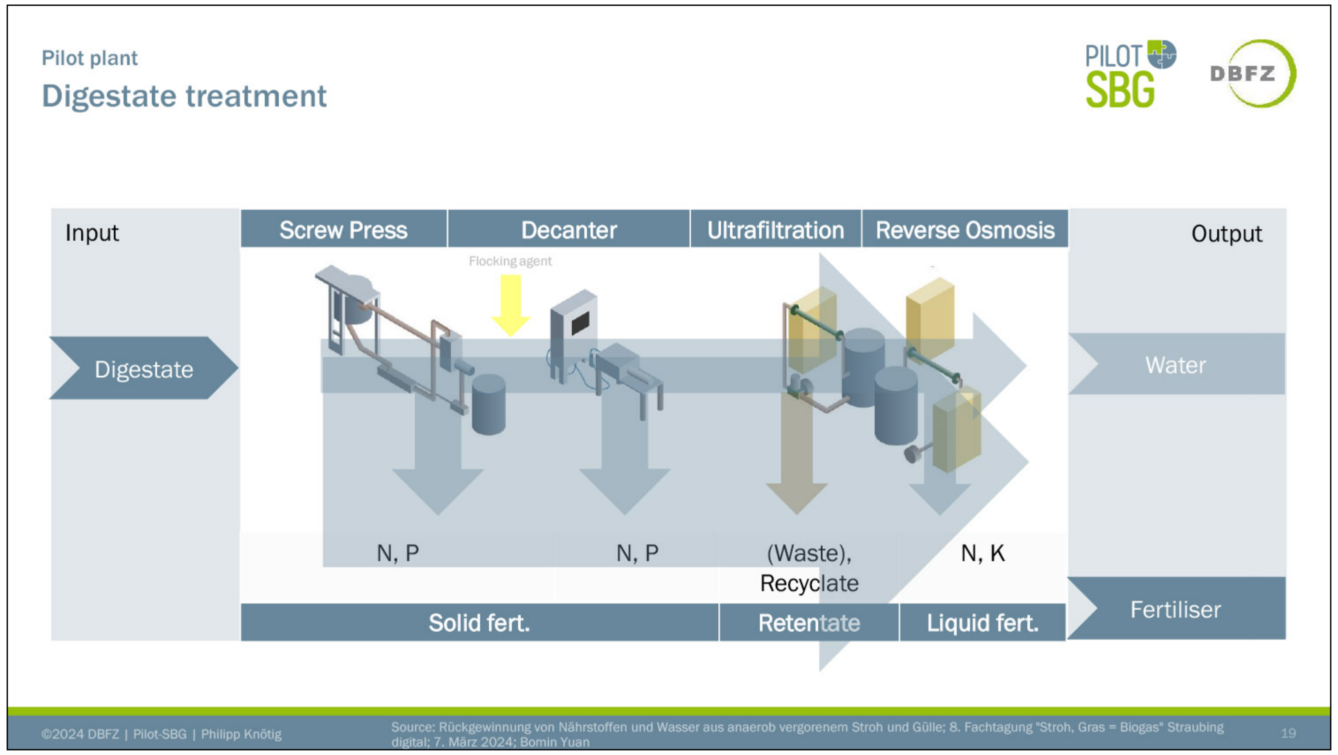
PILOT SBG
DBFZ
Digestate treatment
Digestate treatment






Pilot plant
Digestate treatment
PILOT SBG
DBFZ
Input
Screw Press
Decanter
Ultrafiltration
Reverse Osmosis
Output
Digestate
Water
N, P
N, P
(Waste), Recyclate
N, K
Solid fert.
Retentate
Liquid fert.
Fertiliser
©2024 DBFZ | Pilot SBG | Philipp Knötig
Source: Rückgewinnung von Nährstoffen und Wasser aus anaerob vergorenem Stroh und Gülle; 8. Fachtagung "Stroh, Gras = Biogas" Straubing digital; 7. März 2024; Bomin Yuan
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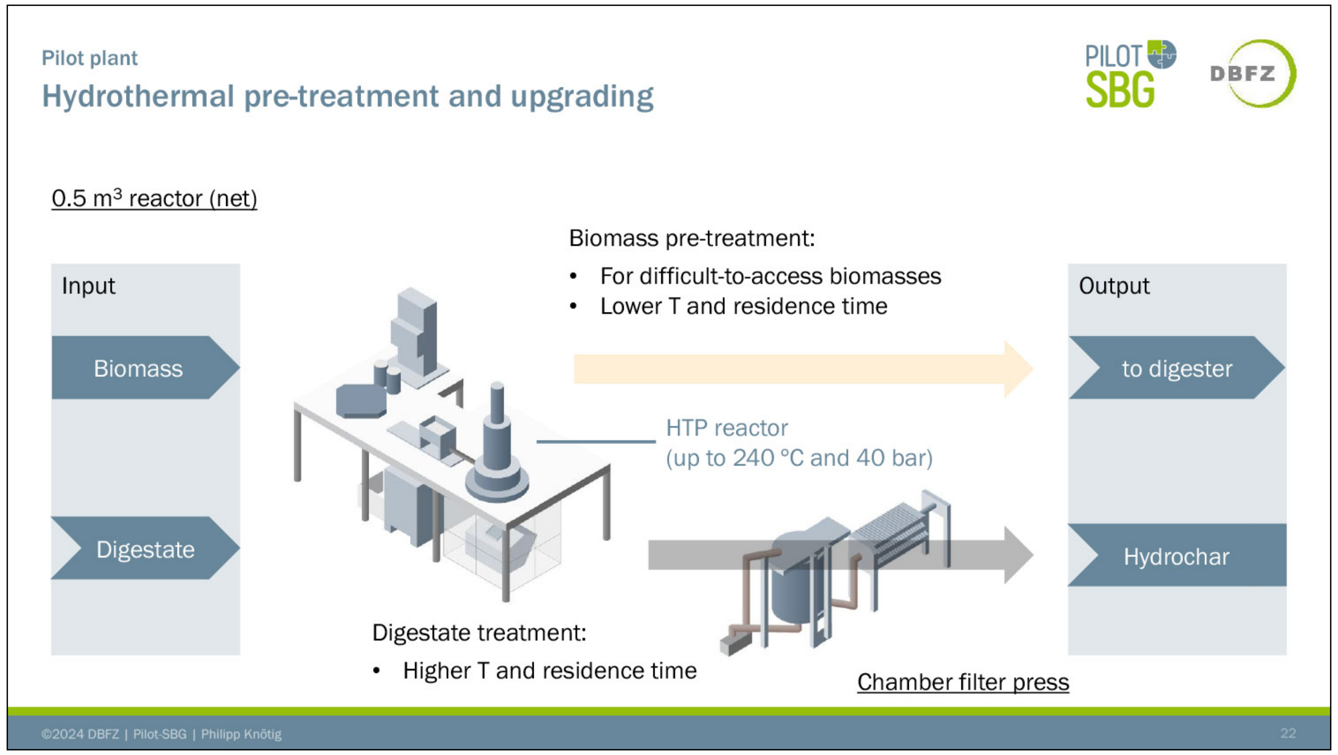
Pilot plant
Digestate treatment
PILOT SBG
DBFZ
Results from commissioning phase:
27%
19%
Input
Output
Digestate
Water
Fertiliser
8%
8%
4%
7%
1%
3%
0%
*TS in %
©2024 DBFZ | Pilot SBG | Philipp Knötig
20


PILOT SBG
DBFZ
Hydrothermal (pre-)treatment


Pilot plant
Hydrothermal pre-treatment and upgrading
PILOT SBG
DBFZ
0.5 m³ reactor (net)
Biomass pre-treatment:
• For difficult-to-access biomasses
• Lower T and residence time
Input
Biomass
Digestate
Output
to digester
Hydrochar
HTP reactor
(up to 240 °C and 40 bar)
Digestate treatment:
• Higher T and residence time
Chamber filter press
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Pilot plant
Hydrothermal pre-treatment and upgrading, commissioning
PILOT SBG
DBFZ
Input
Straw, manure, small branch cuttings, water (TS 15-20%)
Output
HTC slurry
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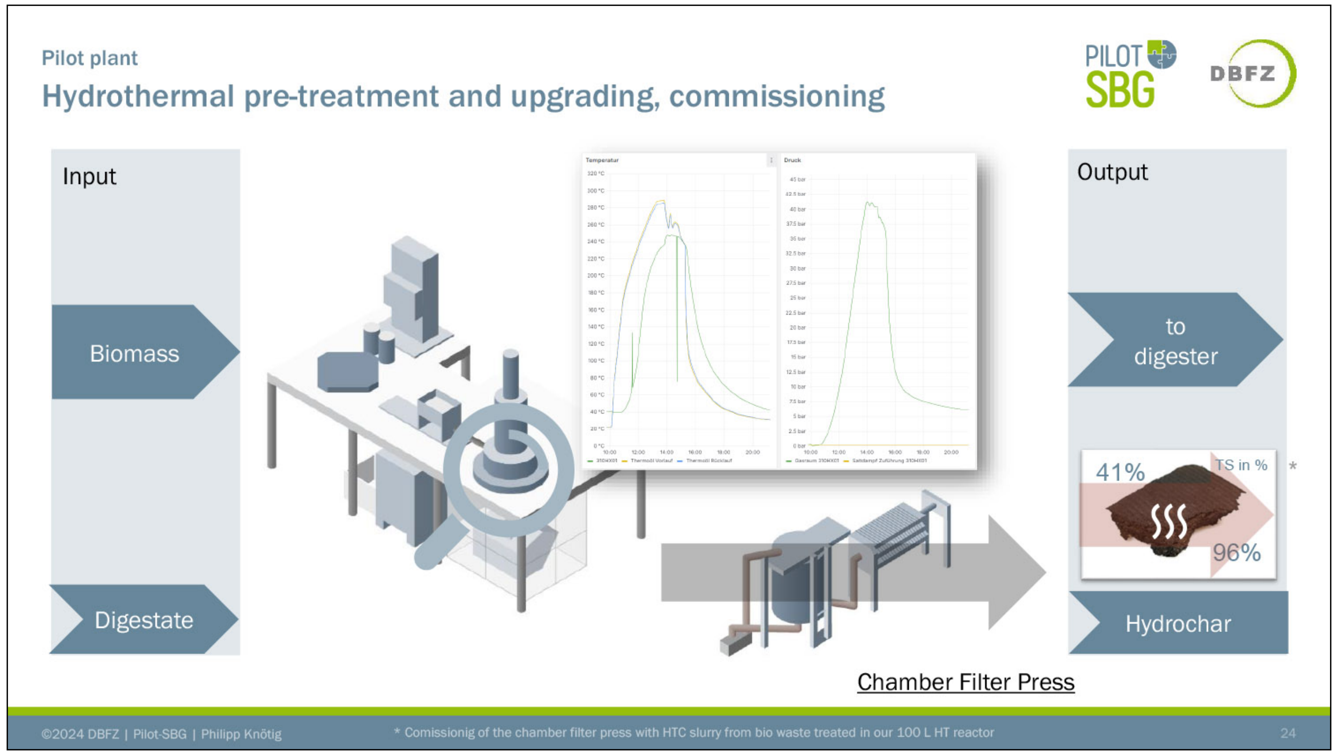
* Straw, manure, small branch cuttings; ** Comissionig of the chamber filter press with HTC slurry from bio waste treated in our 100 L HT reactor
23


Pilot plant
Hydrothermal pre-treatment and upgrading, commissioning
PILOT SBG
DBFZ
Input
Biomass
Digestate
Output
to digester
41%
TS in %
96%
*
Hydrochar
Chamber Filter Press
©2024 DBFZ | Pilot-SBG | Philipp Knötig
* Comissionig of the chamber filter press with HTC slurry from bio waste treated in our 100 L HT reactor
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PILOT SBG
DBFZ
Scale-Up
and commercial scale concept
Federal Ministry for Digital and Transport
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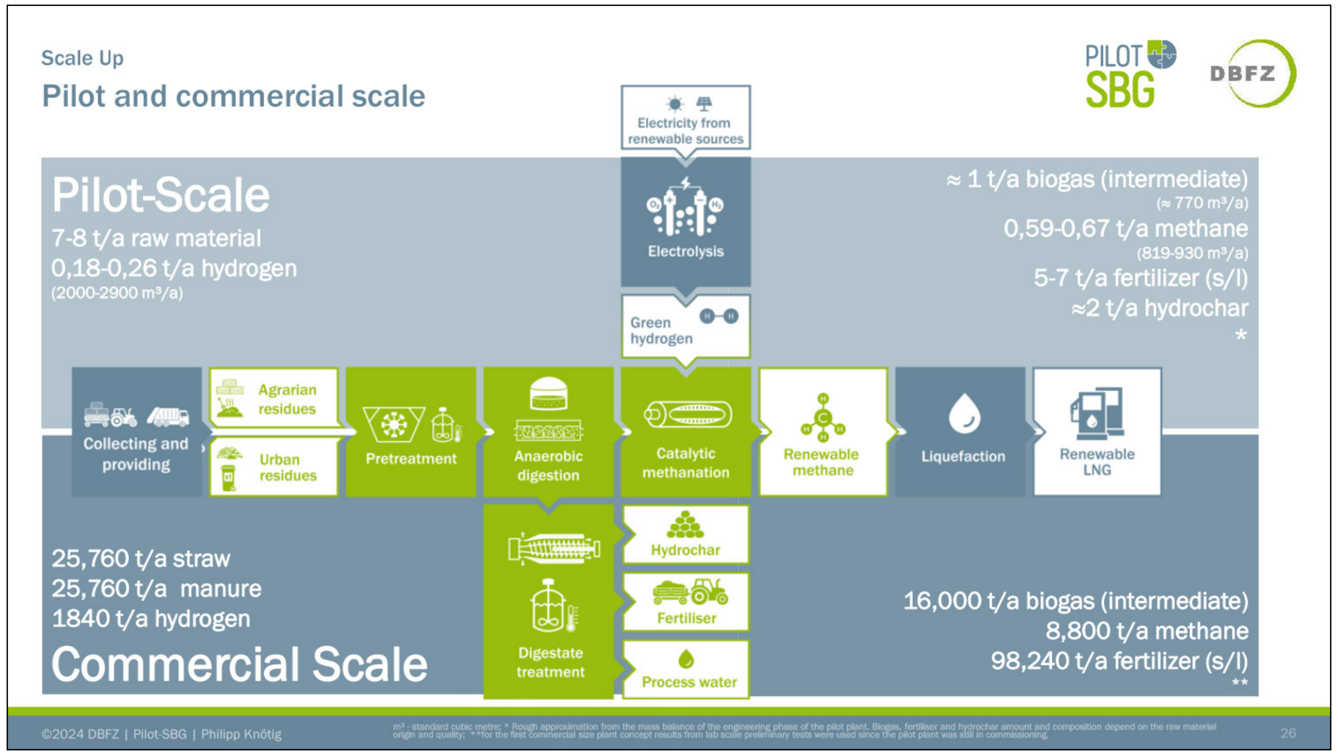
Scale Up
Pilot and commercial scale
PILOT SBG
DBFZ
Electricity from renewable sources
Electrolysis
Green hydrogen
Pilot-Scale
7-8 t/a raw material
0,18-0,26 t/a hydrogen
(2000-2900 m³/a)
≈ 1 t/a biogas (intermediate)
(≈ 770 m³/a)
0,59-0,67 t/a methane
(819-930 m³/a)
5-7 t/a fertilizer (s/l)
≈2 t/a hydrochar
*
Collecting and providing
Agrarian residues
Urban residues
Pretreatment
Anaerobic digestion
Catalytic methanation
Renewable methane
Liquefaction
Renewable LNG
Digestate treatment
Hydrochar
Fertiliser
Process water
25,760 t/a straw
25,760 t/a manure
1840 t/a hydrogen
Commercial Scale
16,000 t/a biogas (intermediate)
8,800 t/a methane
98,240 t/a fertilizer (s/l)
**
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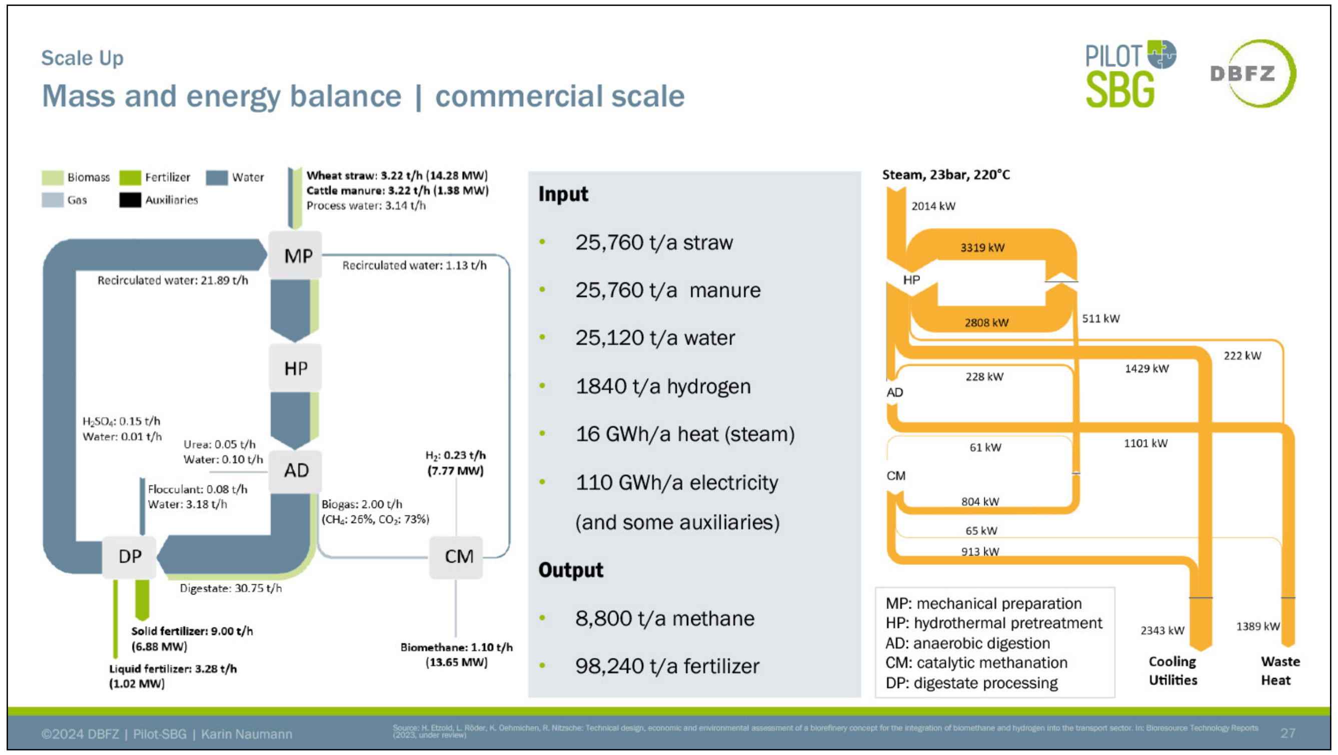
Scale Up
Mass and energy balance | commercial scale
PILOT SBG
DBFZ
Biomass
Fertilizer
Water
Gas
Auxiliaries
Wheat straw: 3.22 t/h (14.28 MW)
Cattle manure: 3.22 t/h (1.38 MW)
Process water: 3.14 t/h
MP
HP
AD
CM
DP
Recirculated water: 21.89 t/h
Recirculated water: 1.13 t/h
Digestate: 30.75 t/h
Solid fertilizer: 9.00 t/h (6.88 MW)
Liquid fertilizer: 3.28 t/h (1.02 MW)
Biogas: 2.00 t/h
Biomethane: 1.10 t/h (13.65 MW)
Input
25,760 t/a straw
25,760 t/a manure
25,120 t/a water
1840 t/a hydrogen
16 GWh/a heat (steam)
110 GWh/a electricity
(and some auxiliaries)
Output
8,800 t/a methane
98,240 t/a fertilizer
Steam, 23bar, 220°C
2014 kW
3319 kW
2808 kW
511 kW
222 kW
1429 kW
228 kW
61 kW
1101 kW
804 kW
65 kW
913 kW
2343 kW
1389 kW
Cooling Utilities
Waste Heat
MP: mechanical preparation
HP: hydrothermal pretreatment
AD: anaerobic digestion
CM: catalytic methanation
DP: digestate processing
©2024 DBFZ | Pilot-SBG | Karin Naumann
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[German version only]
Focus booklets in the Pilot-SBG project
Download:
Renewable methane in transport
Methanation
Anaerobic fermentation
Example concept for the provision of renewable LNG
Infrastructure for renewable methane in transport
Market analysis and greenhouse gas quota for renewable methane in transportation
www.dbfz.de/pilot-sbg


Interested?
Contact me!
PILOT SBG
DBFZ
Philipp Knötig
Department Biorefinery
Scientific and Technical Coordinator of the pilot plant Pilot-SBG
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www.dbfz.de/pilot-sbg
Bioresources and hydrogen to methane as fuel

*Alfons Kuhles, Bundesverband HTC e.V.*

# Actual overview of HTP in Europe

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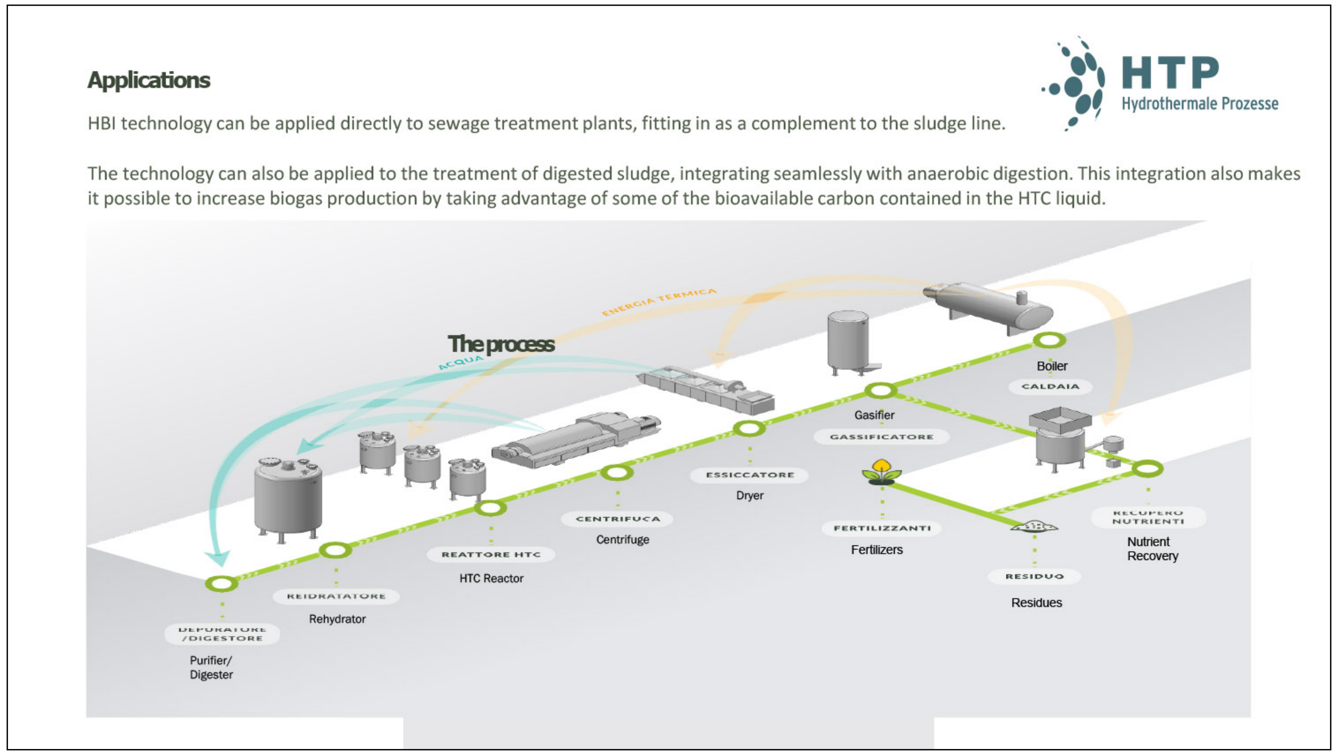
**Keywords:** bluFlux, htc technology, overview, HTCycle

The board of BV-HTC e.V. is actually trying to get an overview about the still existing companies who are commercially engaged in HTC or VTC or PTC. The results will be presented in November in Leipzig.



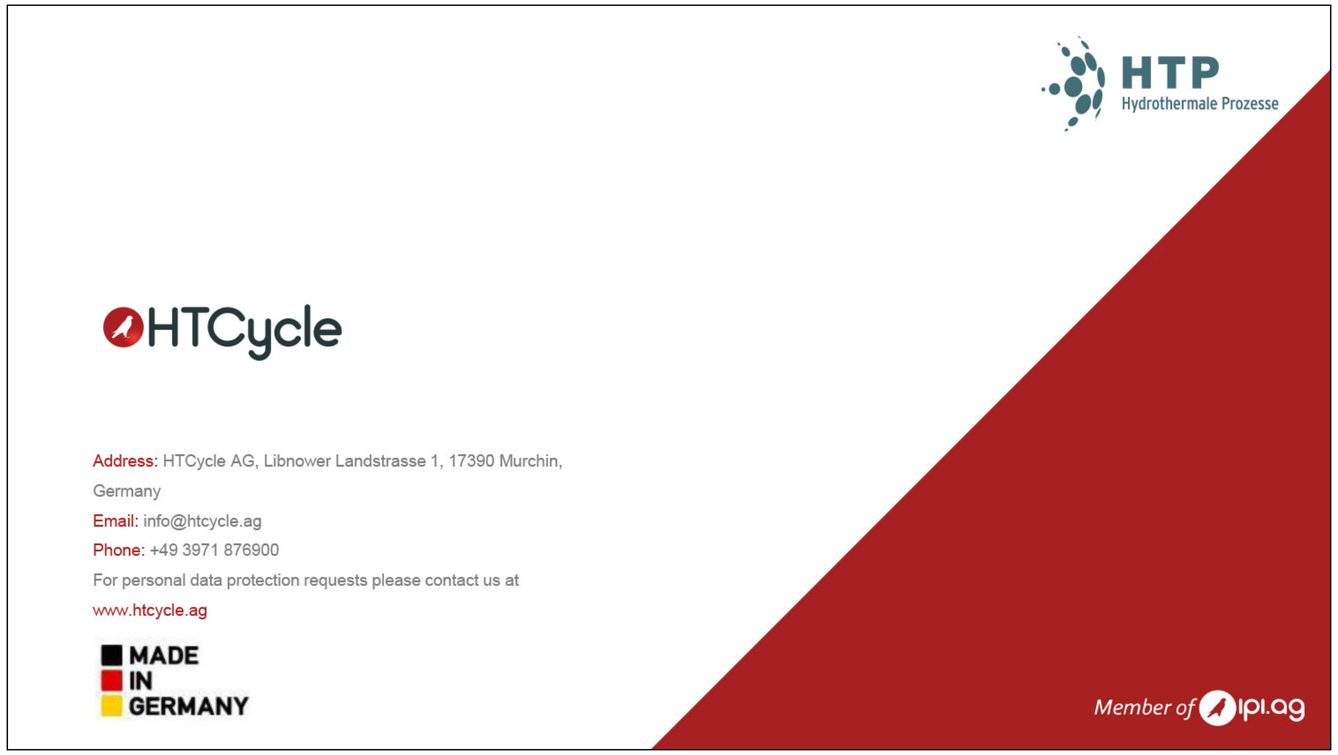


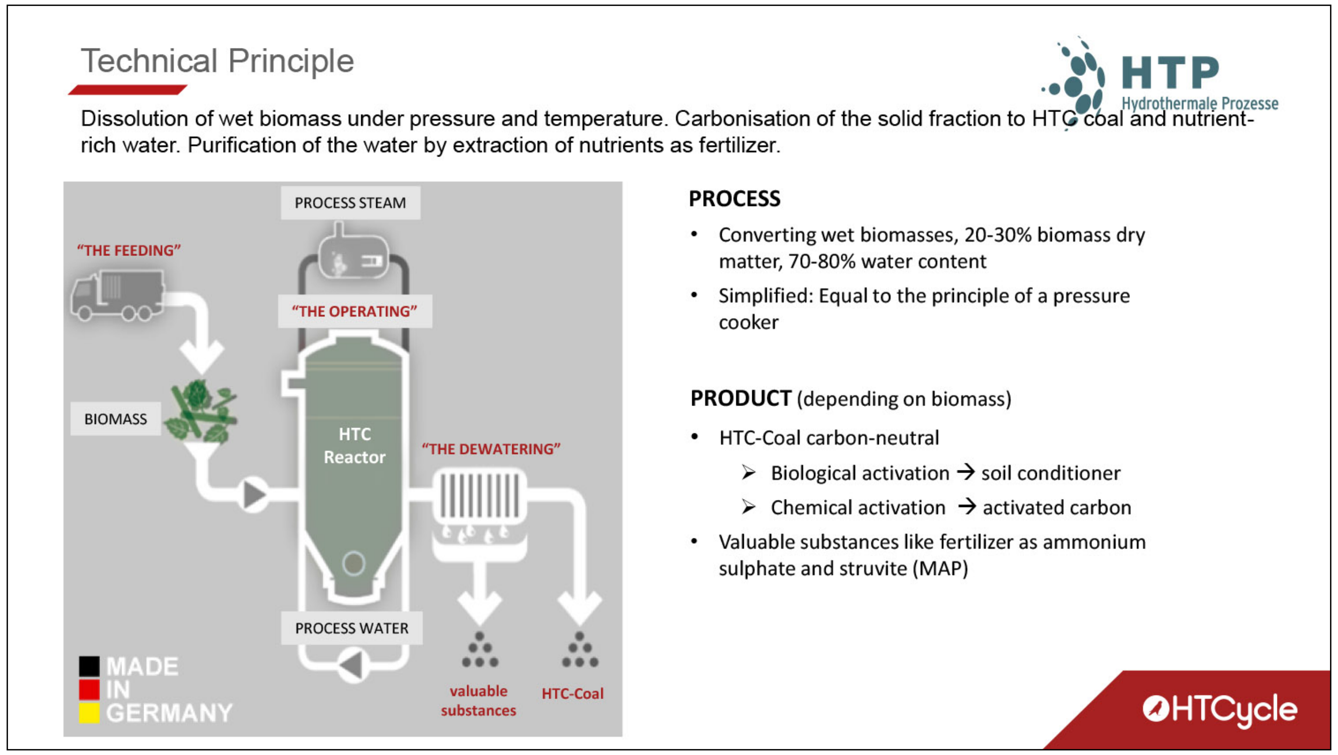


Applications
HTP Hydrothermale Prozesse
HBI technology can be applied directly to sewage treatment plants, fitting in as a complement to the sludge line.
The technology can also be applied to the treatment of digested sludge, integrating seamlessly with anaerobic digestion. This integration also makes it possible to increase biogas production by taking advantage of some of the bioavailable carbon contained in the HTC liquid.
The process
Boiler
CALDAIA
Gasifier
GASSIFICATORE
ESSICCATORE
Dryer
CENTRIFUGA
Centrifuge
FERTILIZZANTI
Fertilizers
RECUPERO NUTRIENTI
Nutrient Recovery
REATTORE HTC
HTC Reactor
RESIDUO
Residues
REIDRATATORE
Rehydrator
DEPURATORE /DIGESTORE
Purifier/ Digester

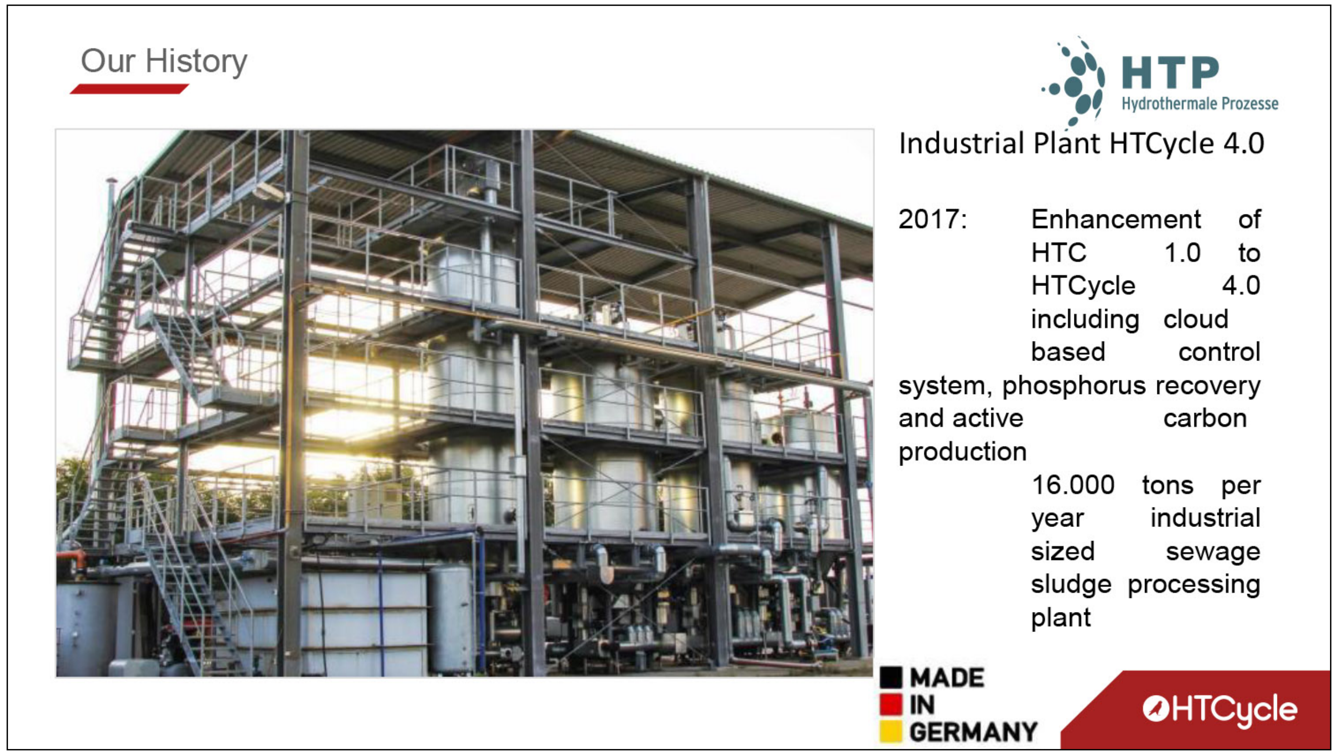

HTP Hydrothermale Prozesse
HBI
Eva

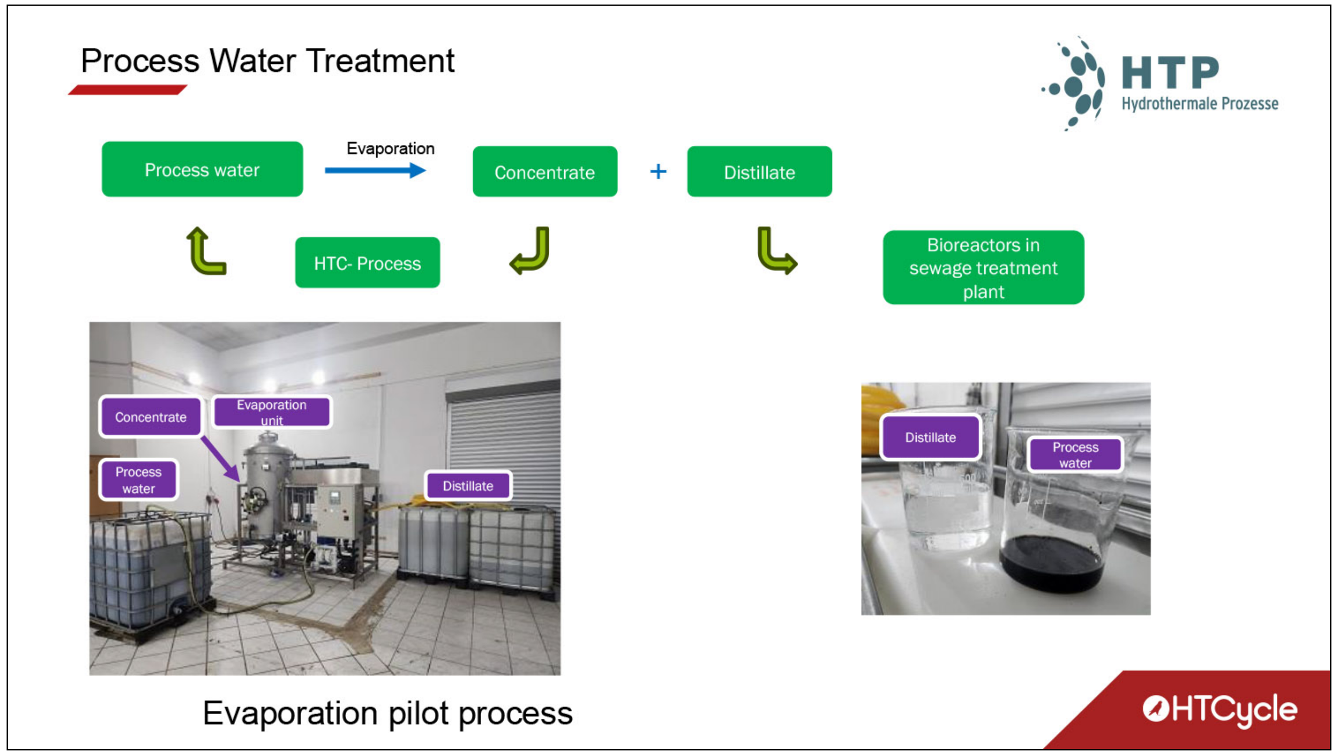


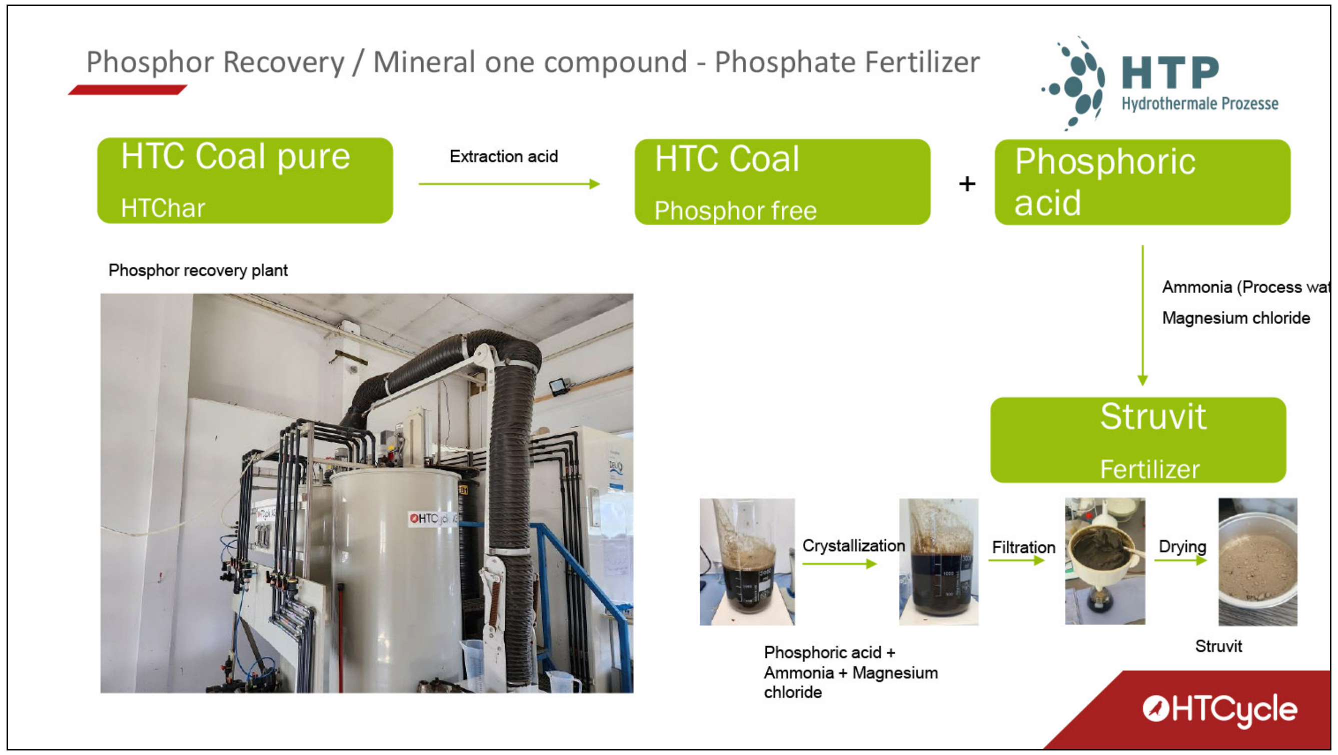


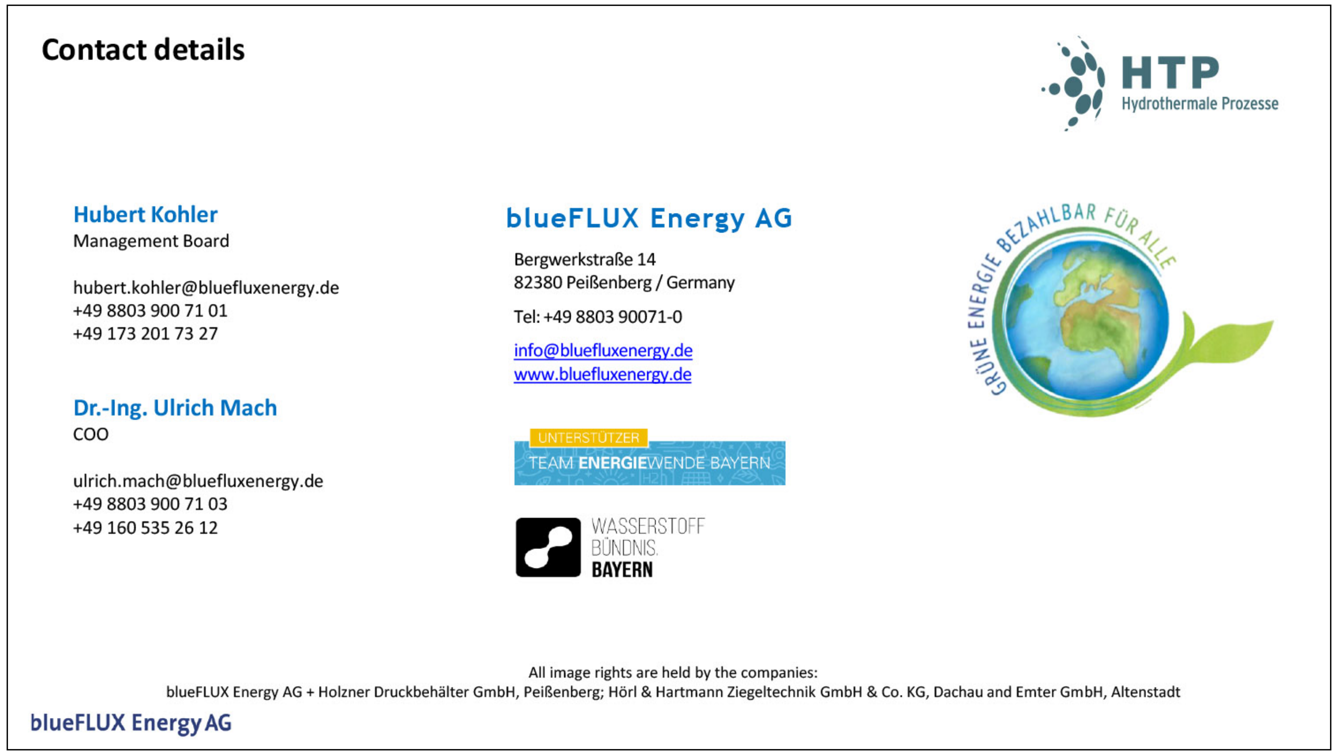

HTP Hydrothermale Prozesse
HTCycle
Address: HTCycle AG, Libnower Landstrasse 1, 17390 Murchin, Germany
Email: info@htcycle.ag
Phone: +49 3971 876900
For personal data protection requests please contact us at
www.htcycle.ag
MADE IN GERMANY
Member of ipi.ag


Technical Principle
HTP Hydrothermale Prozesse
Dissolution of wet biomass under pressure and temperature. Carbonisation of the solid fraction to HTC coal and nutrient-rich water. Purification of the water by extraction of nutrients as fertilizer.
PROCESS STEAM
"THE FEEDING"
"THE OPERATING"
BIOMASS
HTC Reactor
"THE DEWATERING"
PROCESS WATER
valuable substances
HTC-Coal
MADE IN GERMANY
PROCESS
Converting wet biomasses, 20-30% biomass dry matter, 70-80% water content
Simplified: Equal to the principle of a pressure cooker
PRODUCT (depending on biomass)
HTC-Coal carbon-neutral
Biological activation → soil conditioner
Chemical activation → activated carbon
Valuable substances like fertilizer as ammonium sulphate and struvite (MAP)
HTCycle


Our History
HTP
Hydrothermale Prozesse
Industrial Plant HTCycle 4.0
2017: Enhancement of HTC 1.0 to HTCycle 4.0 including cloud based control system, phosphorus recovery and active carbon production
16.000 tons per year industrial sized sewage sludge processing plant
MADE IN GERMANY
HTCycle


Process Water Treatment
HTP
Hydrothermale Prozesse
Process water
Evaporation
Concentrate
+
Distillate
HTC- Process
Bioreactors in sewage treatment plant
Concentrate
Evaporation unit
Process water
Distillate
Distillate
Process water
Evaporation pilot process
HTCycle


Phosphor Recovery / Mineral one compound - Phosphate Fertilizer
HTP
Hydrothermale Prozesse
HTC Coal pure
HTChar
Extraction acid
HTC Coal
Phosphor free
+
Phosphoric acid
Phosphor recovery plant
Ammonia (Process wat
Magnesium chloride
Struvit
Fertilizer
Crystallization
Filtration
Drying
Phosphoric acid +
Ammonia + Magnesium chloride
Struvit
HTCycle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GRÜNE ENERGIE BEZAHLBAR FÜR ALLE
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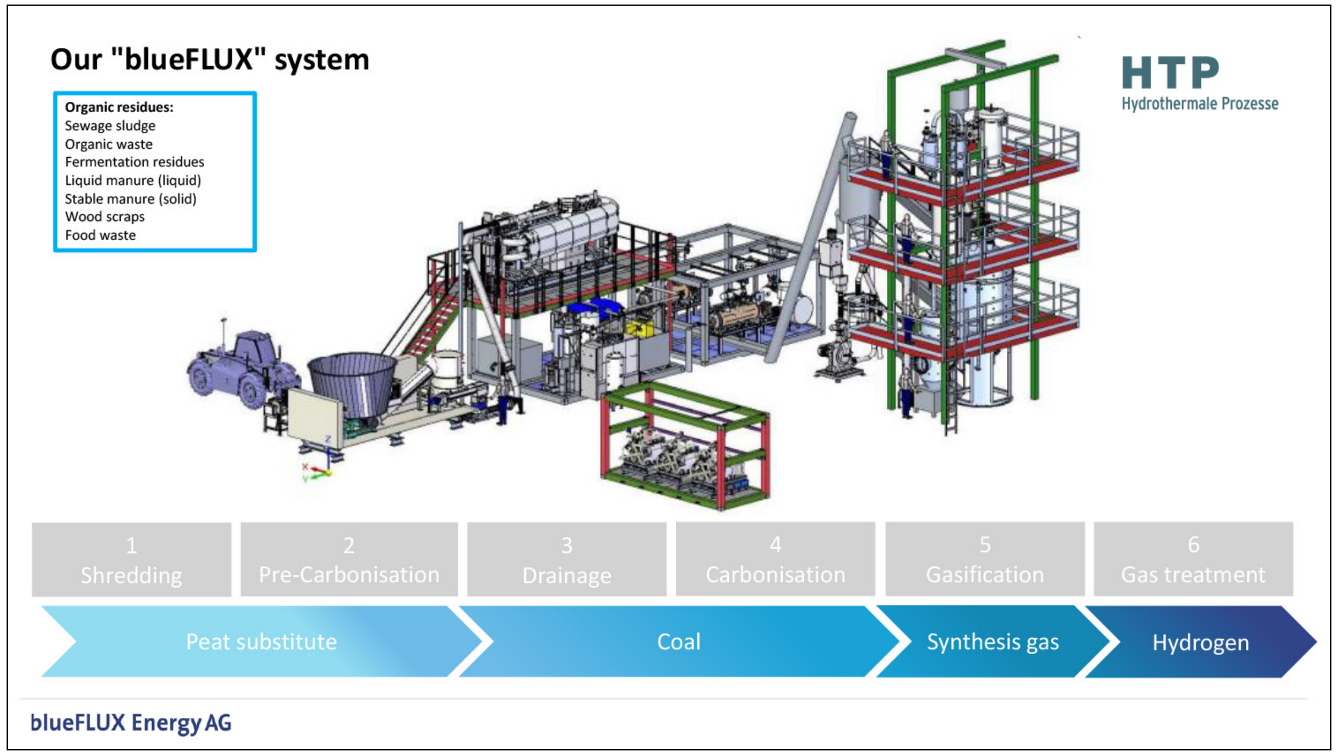
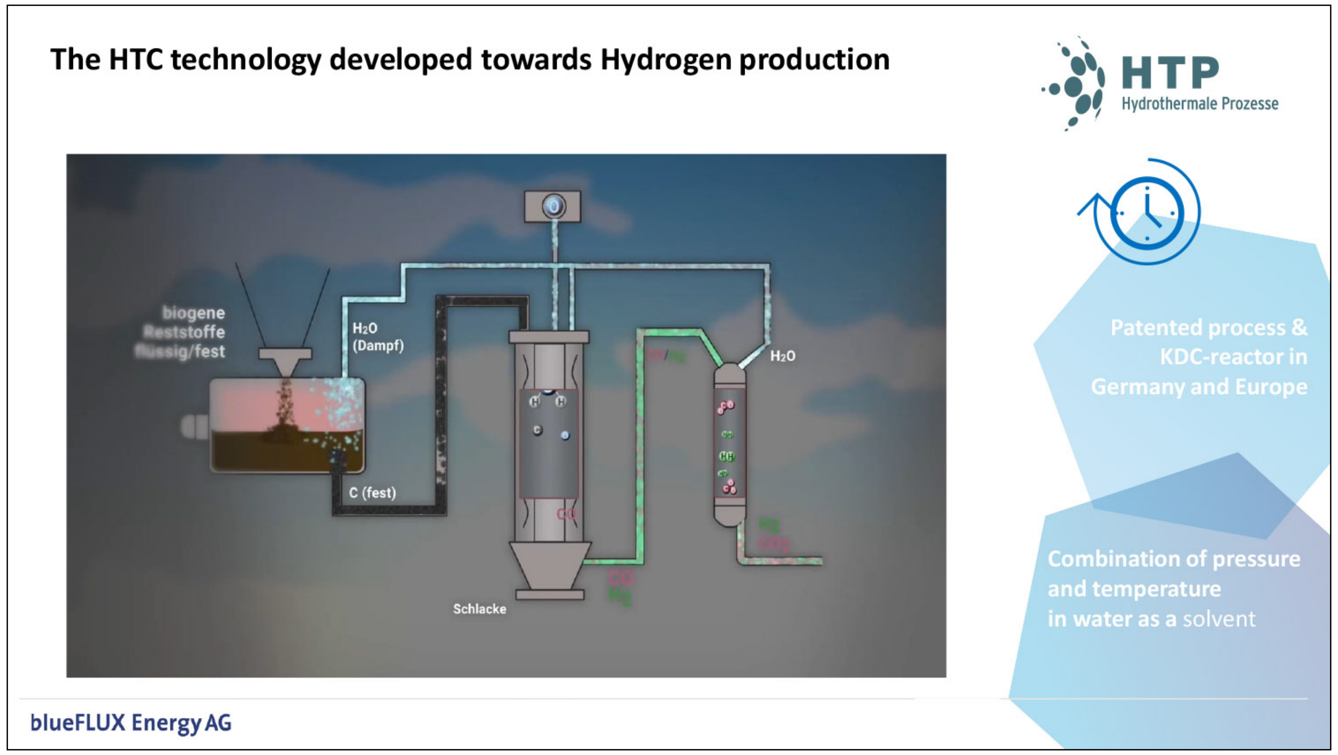
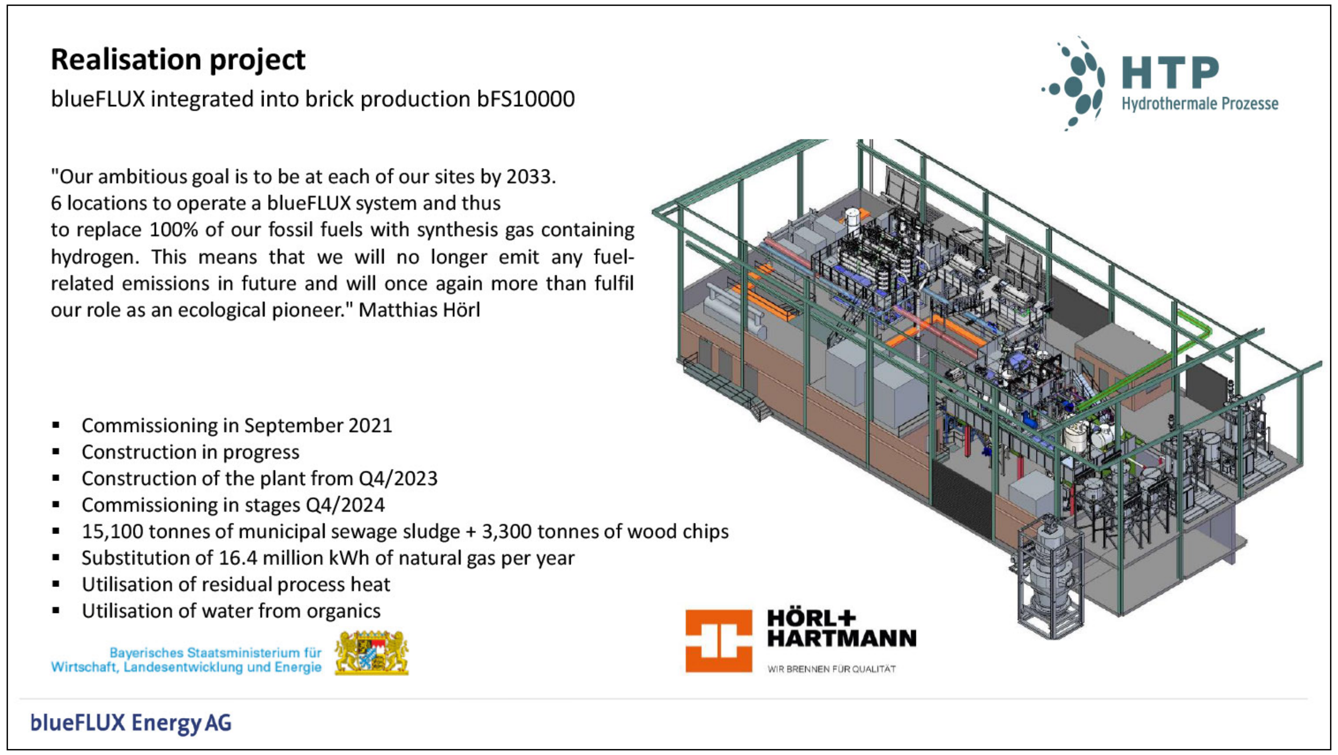
blueFLUX Energy AG

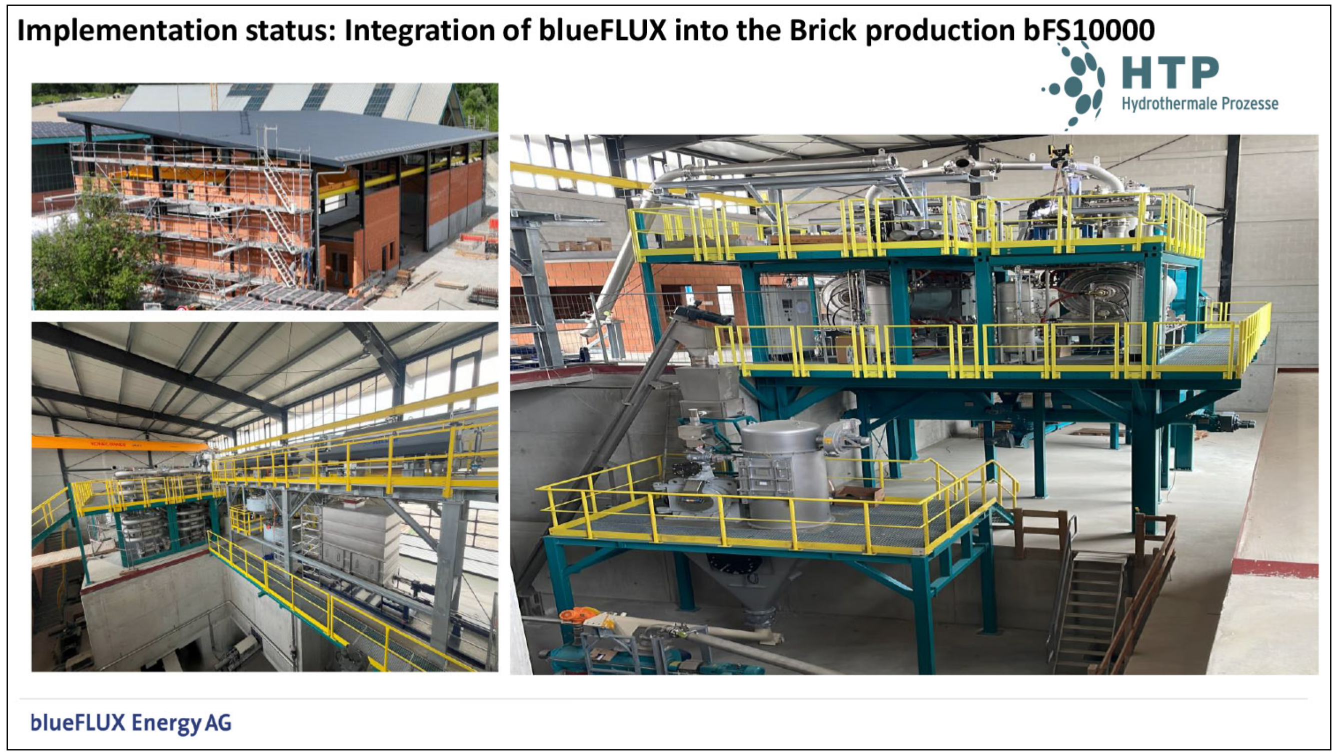

Our "blueFLUX" system
HTP
Hydrothermale Prozesse
Organic residues:
Sewage sludge
Organic waste
Fermentation residues
Liquid manure (liquid)
Stable manure (solid)
Wood scraps
Food waste
1 Shredding
2 Pre-Carbonisation
3 Drainage
4 Carbonisation
5 Gasification
6 Gas treatment
Peat substitute
Coal
Synthesis gas
Hydrogen
blueFLUX Energy AG


The HTC technology developed towards Hydrogen production
HTP
Hydrothermale Prozesse
biogene Reststoffe flüssig/fest
H2O (Dampf)
C (fest)
Schlacke
H2O
Patented process & KDC-reactor in Germany and Europe
Combination of pressure and temperature in water as a solvent
blueFLUX Energy AG






Realisation project
blueFLUX integrated into brick production bFS10000
HTP
Hydrothermale Prozesse
"Our ambitious goal is to be at each of our sites by 2033.
6 locations to operate a blueFLUX system and thus
to replace 100% of our fossil fuels with synthesis gas containing hydrogen. This means that we will no longer emit any fuel-related emissions in future and will once again more than fulfil our role as an ecological pioneer." Matthias Hörl
▪ Commissioning in September 2021
▪ Construction in progress
▪ Construction of the plant from Q4/2023
▪ Commissioning in stages Q4/2024
▪ 15,100 tonnes of municipal sewage sludge + 3,300 tonnes of wood chips
▪ Substitution of 16.4 million kWh of natural gas per year
▪ Utilisation of residual process heat
▪ Utilisation of water from organics
Bayerisches Staatsministerium für Wirtschaft, Landesentwicklung und Energie
HÖRL+ HARTMANN
WIR BRENNEN FÜR QUALITÄT
blueFLUX Energy AG


Implementation status: Integration of blueFLUX into the Brick production bFS10000
HTP
Hydrothermale Prozesse
blueFLUX Energy AG

## Actual Overview HTP in Europe according circumstances

HTP Hydrothermale Prozesse

- Election in the USA
- Climate Change -> Valencia et.al.
- Economical Crisis especially in D
- Unemployment especially in D
- Competition worldwide
- $CO_2$ Taxes
- Political crisis especially in D

Alfons Kuhles Bundesverband Hydrothermale Karbonisierung e.V.

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## 8th Expert Forum on Hydrothermal Processes

HTP Hydrothermale Prozesse

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www.dbfz.de

www.htp-inno.de

# SESSION III

## USE OF HYDROTHERMAL PROCESSES AND ITS PRODUCTS FOR VARIOUS APPLICATIONS

*Luca Fiori, University of Trento*

# Agro-waste to adsorbents by combining HTC, pyrolysis and activation processes

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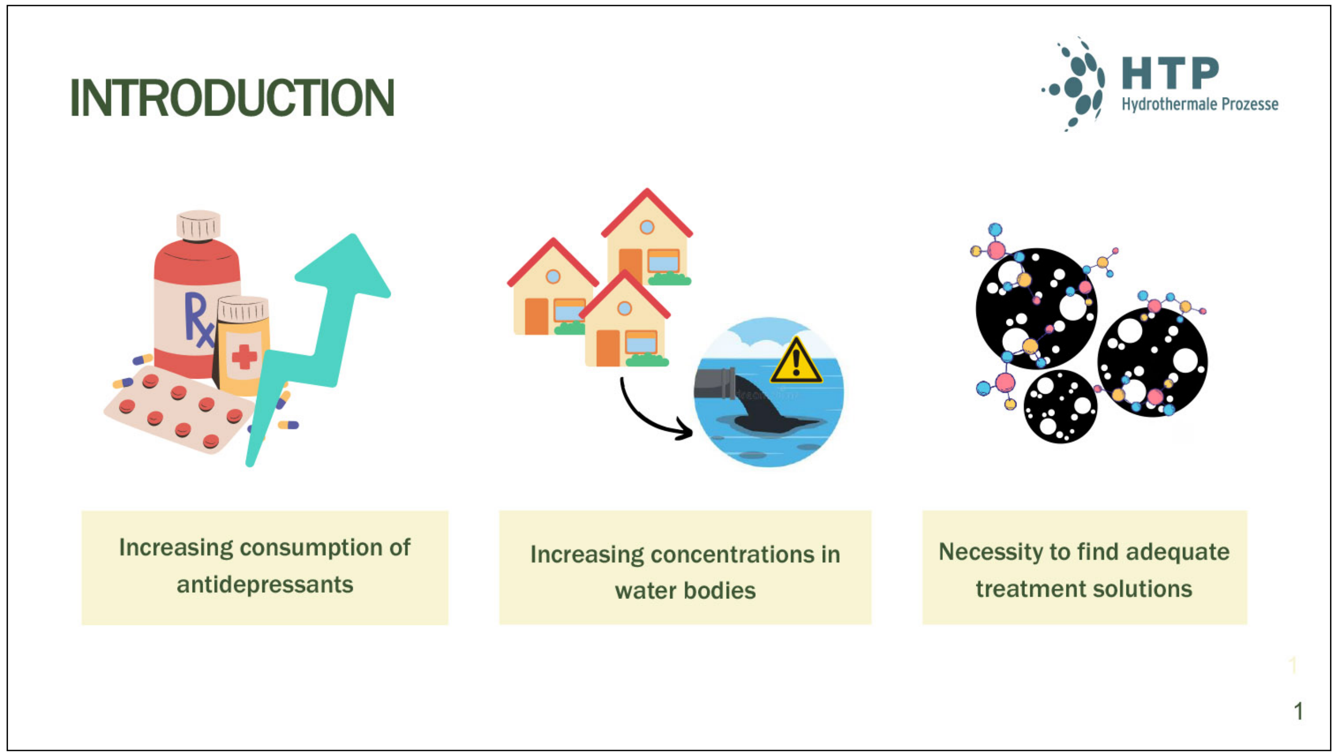
E-Mail: luca.fiori@unitn.it

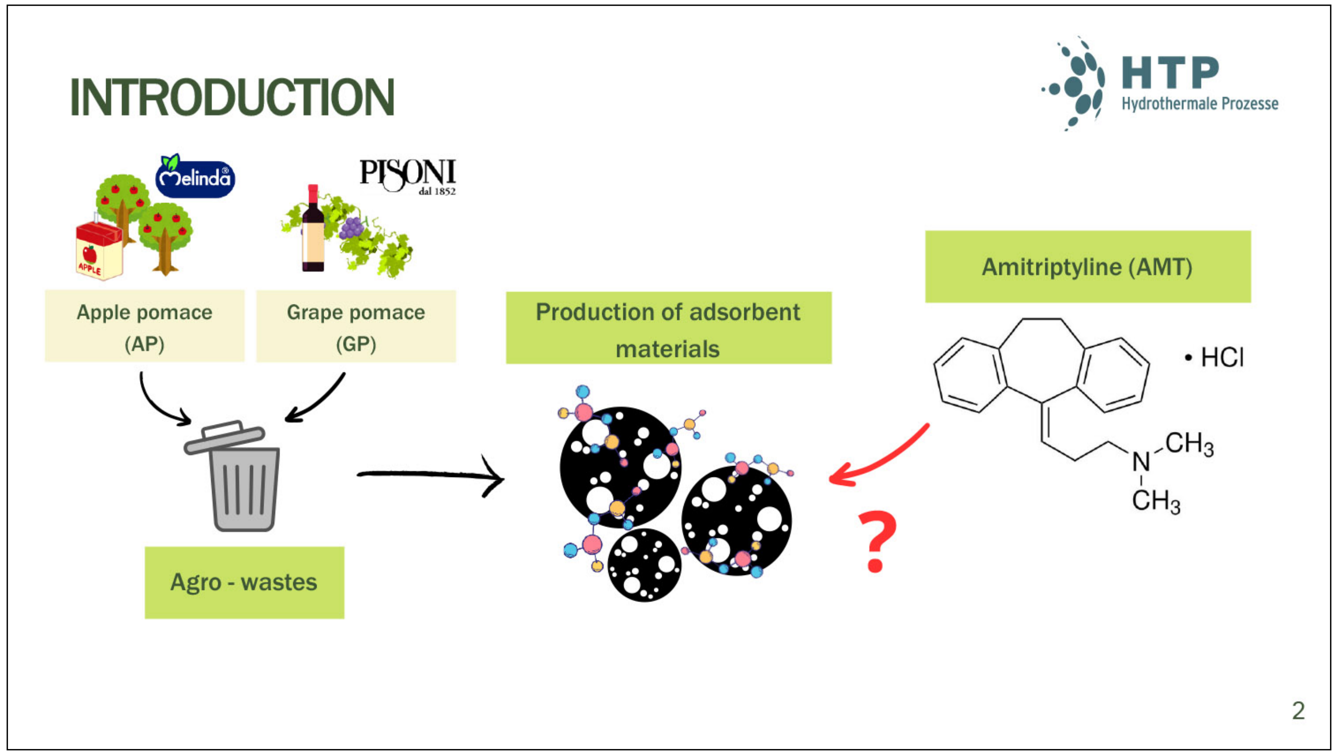
**Keywords:** Grape marc, apple pomace, HTC, pyrolysis, $CO_2$ activation, agricultural waste

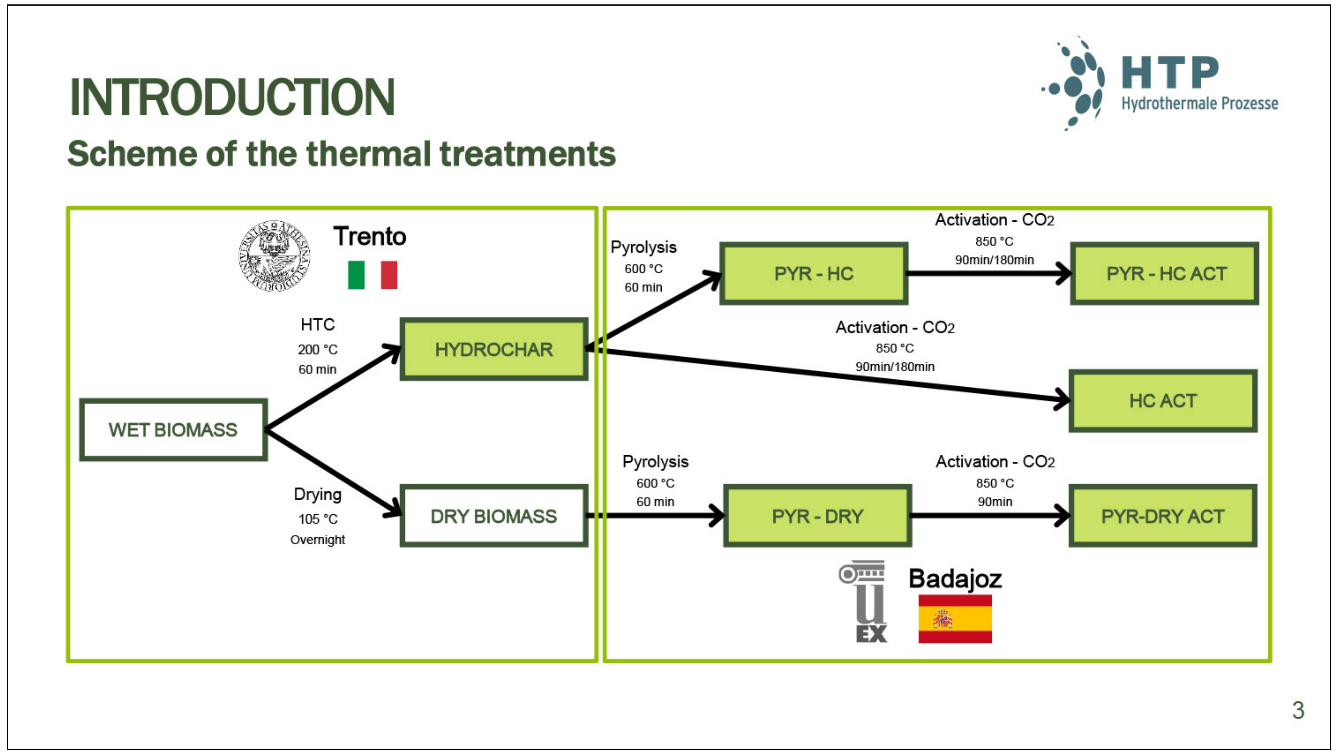
- Two agro-industrial wastes, namely grape marc from winemaking and apple pomace from apple juice production, were used to produce adsorbent media.
- Different processes were utilized for the purpose, as single processes and in combination: HTC, pyrolysis, and $CO_2$ activation.
- The carbonaceous adsorbent media produced were tested for the removal of a pharmaceutical compound (namely, amitriptyline) present in aqueous streams.
- The best results were obtained when using agro-wastes which underwent HTC, pyrolysis and activation in series.





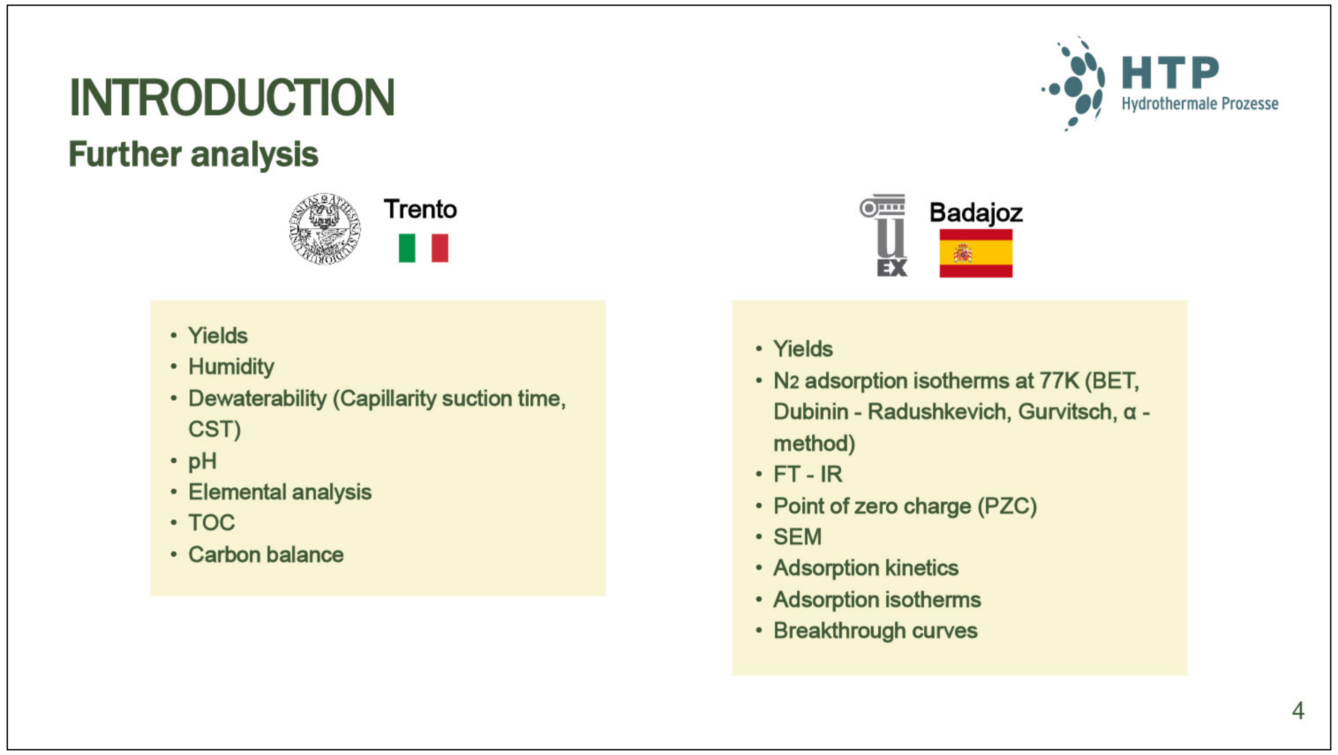



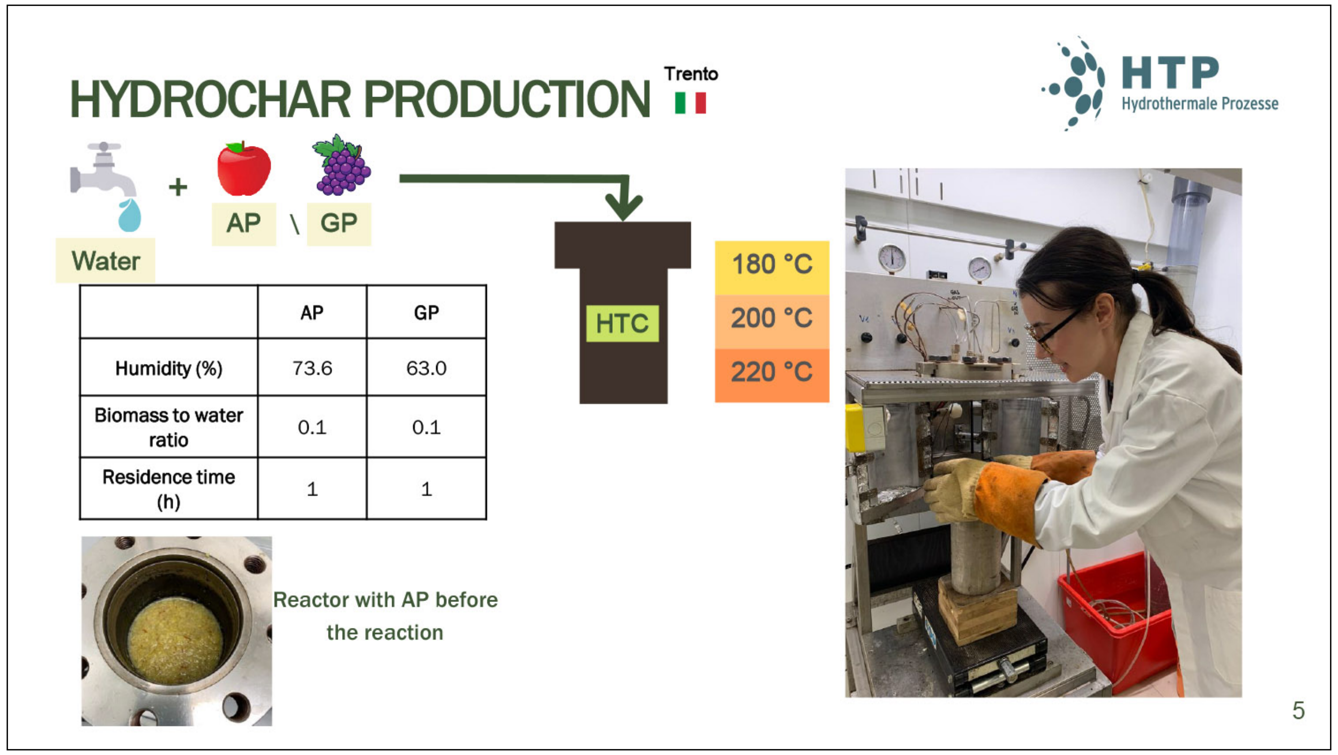


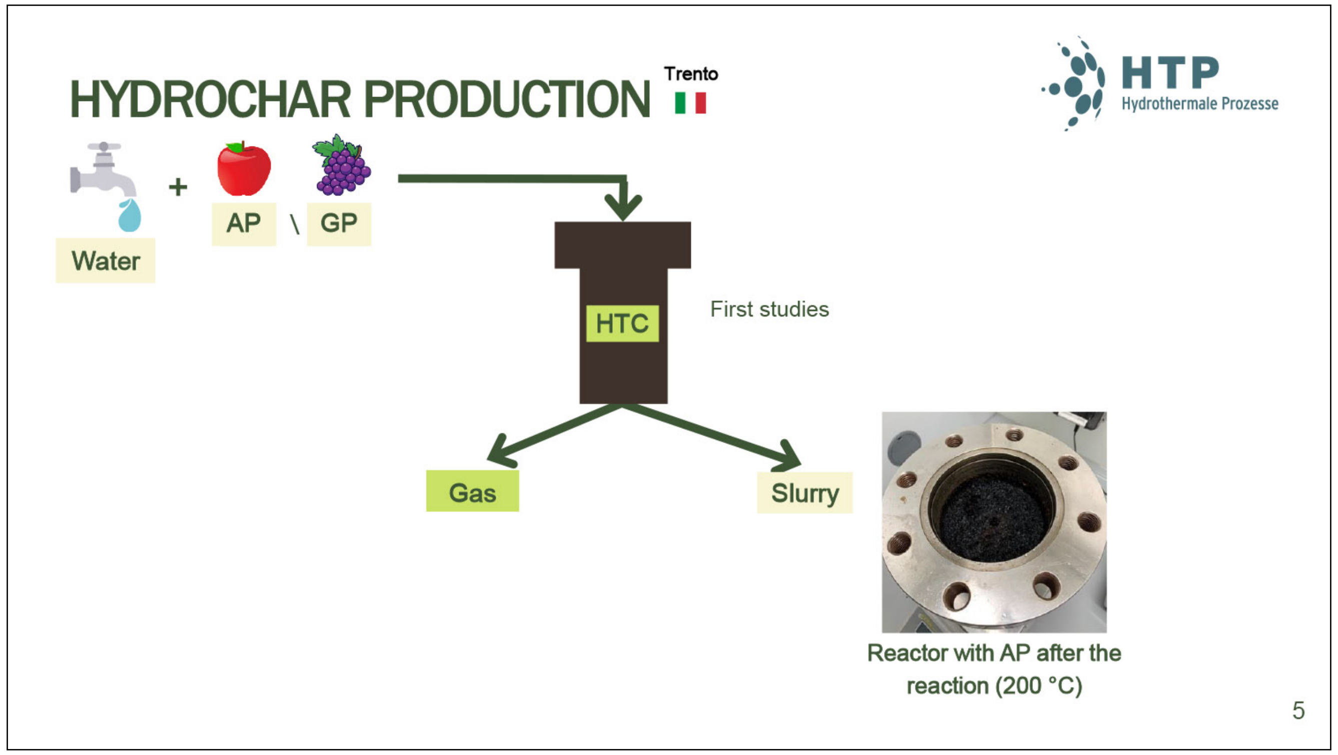


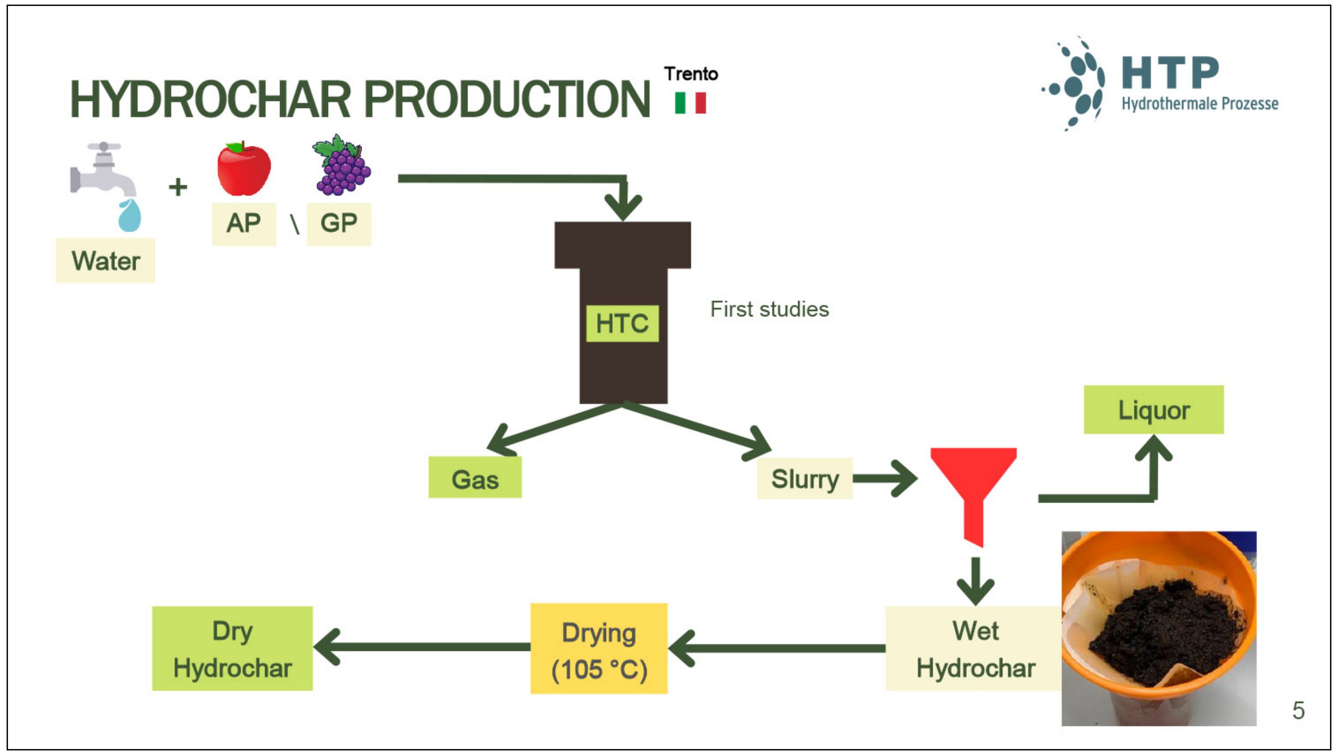


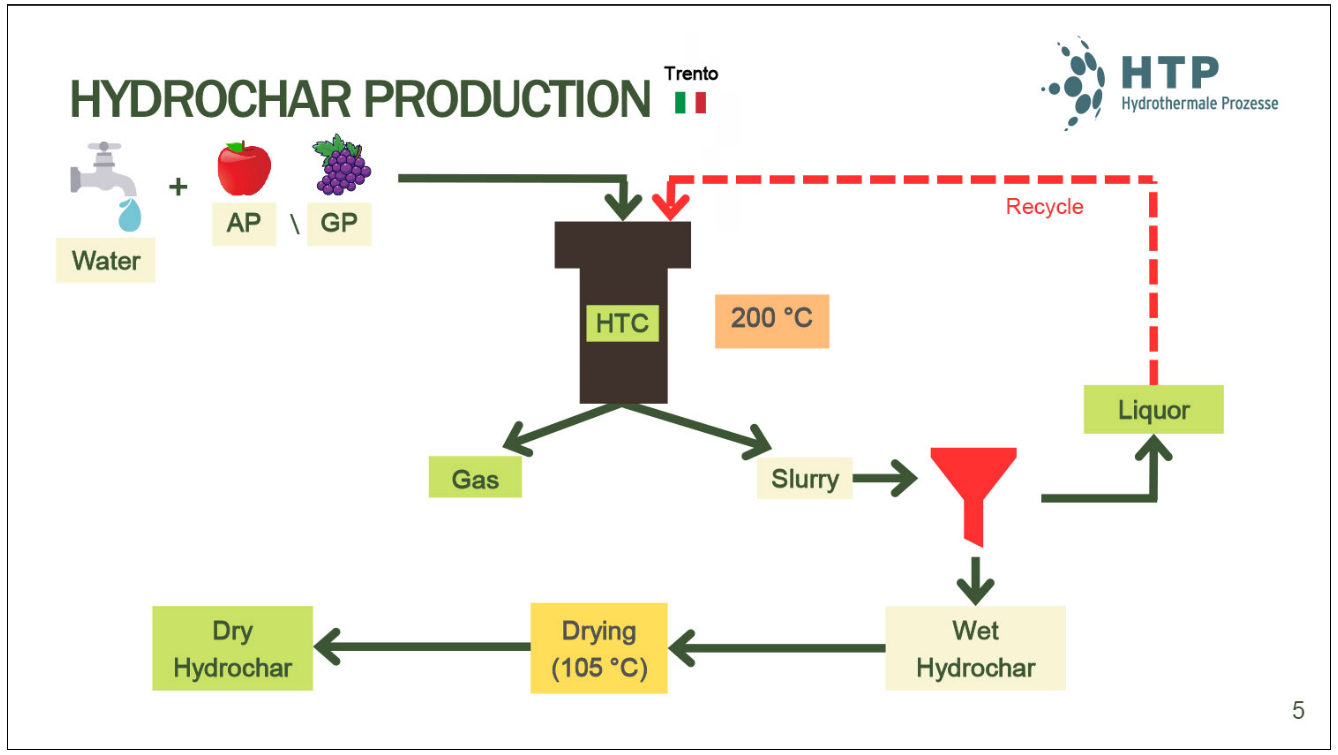

| | AP | GP |
|---|---|---|
| Humidity (%) | 73.6 | 63.0 |
| Biomass to water ratio | 0.1 | 0.1 |
| Residence time (h) | 1 | 1 |

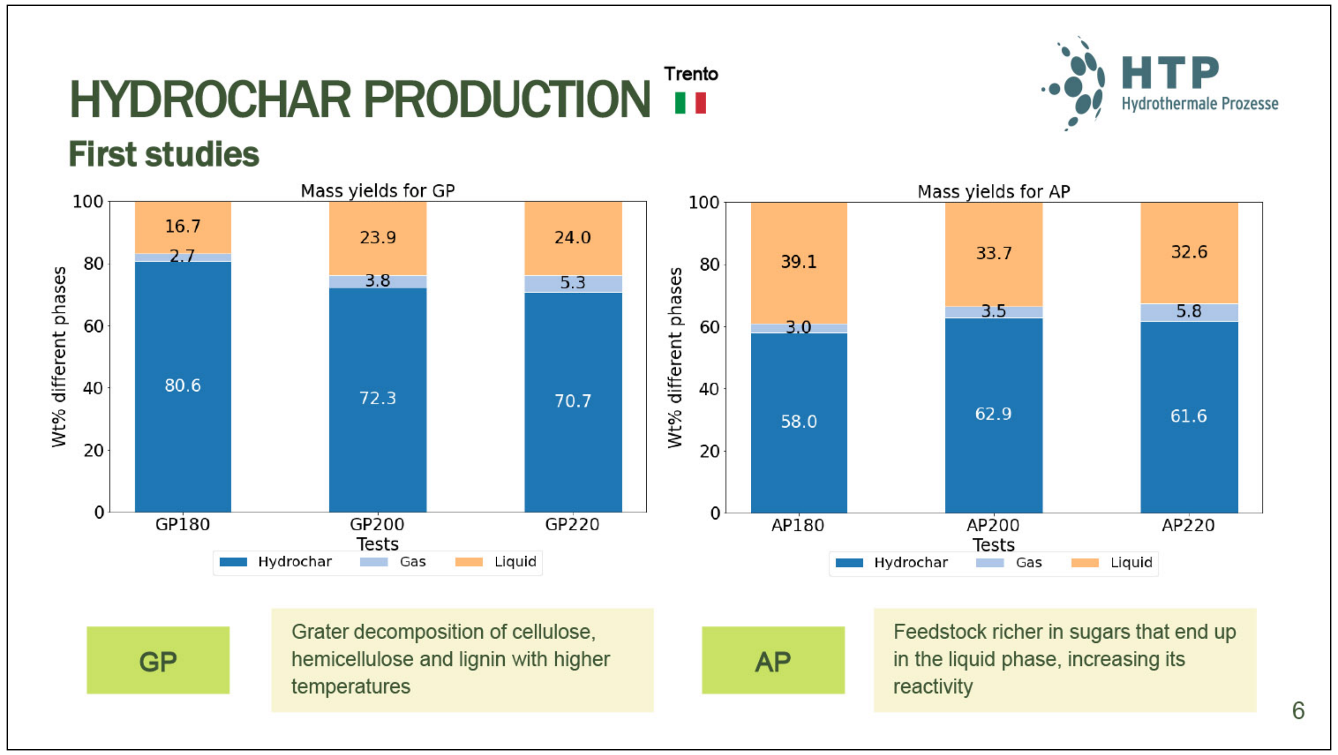

HYDROCHAR PRODUCTION
Trento
HTP
Hydrothermale Prozesse
Water
+
AP
\
GP
HTC
First studies
Gas
Slurry
Reactor with AP after the reaction (200 °C)
5


HYDROCHAR PRODUCTION
Trento
HTP
Hydrothermale Prozesse
Water
+
AP
\
GP
HTC
First studies
Gas
Slurry
Liquor
Dry Hydrochar
Drying (105 °C)
Wet Hydrochar
5






HYDROCHAR PRODUCTION
Trento
HTP
Hydrothermale Prozesse
Water
+
AP
\
GP
Recycle
HTC
200 °C
Liquor
Gas
Slurry
Dry Hydrochar
Drying (105 °C)
Wet Hydrochar
5

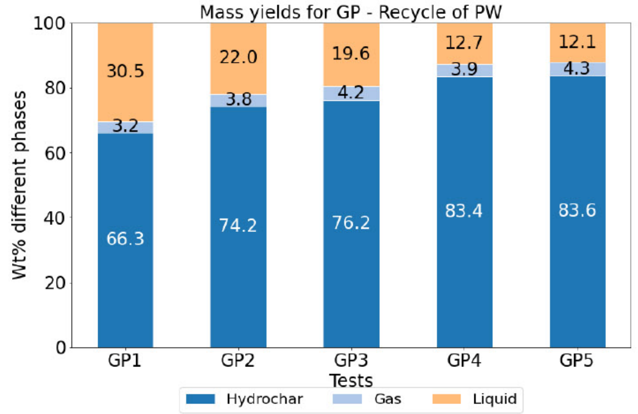

HYDROCHAR PRODUCTION
Trento
HTP
Hydrothermale Prozesse
First studies
Mass yields for GP
Wt% different phases
100
80
60
40
20
0
16.7
2.7
80.6
23.9
3.8
72.3
24.0
5.3
70.7
GP180
GP200
GP220
Tests
Hydrochar
Gas
Liquid
Mass yields for AP
39.1
3.0
58.0
33.7
3.5
62.9
32.6
5.8
61.6
AP180
AP200
AP220
GP
Grater decomposition of cellulose, hemicellulose and lignin with higher temperatures
AP
Feedstock richer in sugars that end up in the liquid phase, increasing its reactivity
6

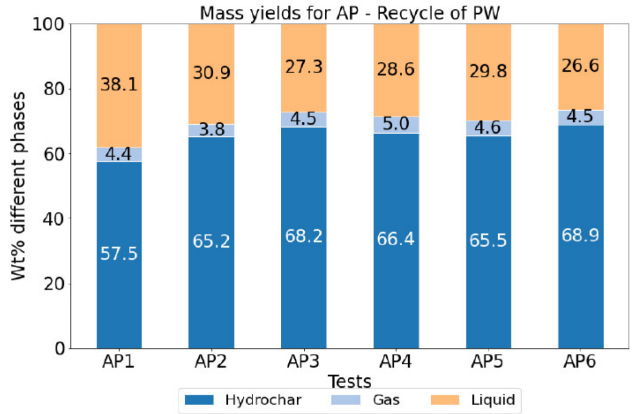
## HYDROCHAR PRODUCTION

Trento

HTP Hydrothermale Prozesse

### Recycle of process water




200 °C | Solid yield ↑ | C% = | 0% = | Ash% ↓

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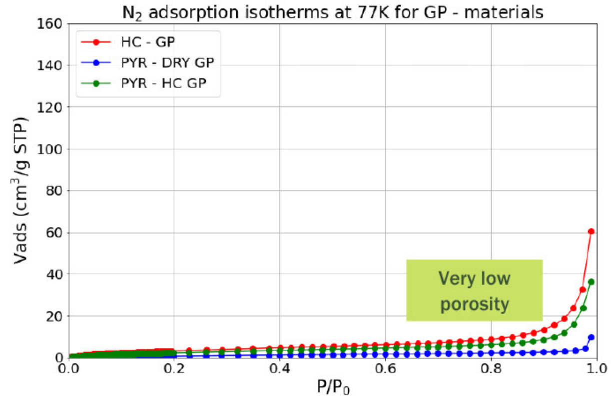
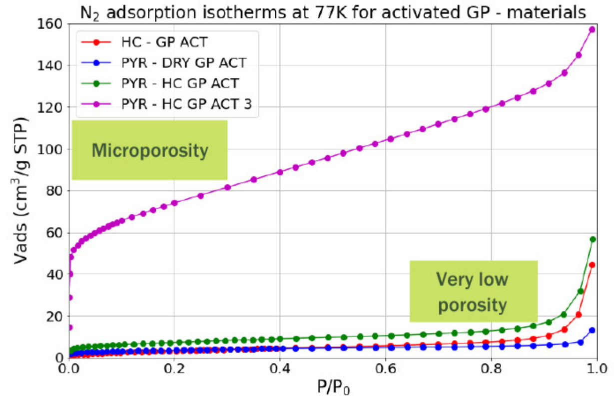
## PRODUCTION OF THE ADSORBENTS

Badajoz

HTP Hydrothermale Prozesse

### Characterization of the materials- GP




**SBET**
- HC - GP : 13 m²/g
- PYR - DRY GP : < 5 m²/g
- PYR - HC GP: 10 m²/g

**SBET**
- HC - GP ACT : 12 m²/g
- PYR - DRY GP ACT: 12 m²/g
- PYR - HC GP ACT: 25 m²/g
- **PYR - HC GP ACT 3: 250 m²/g**

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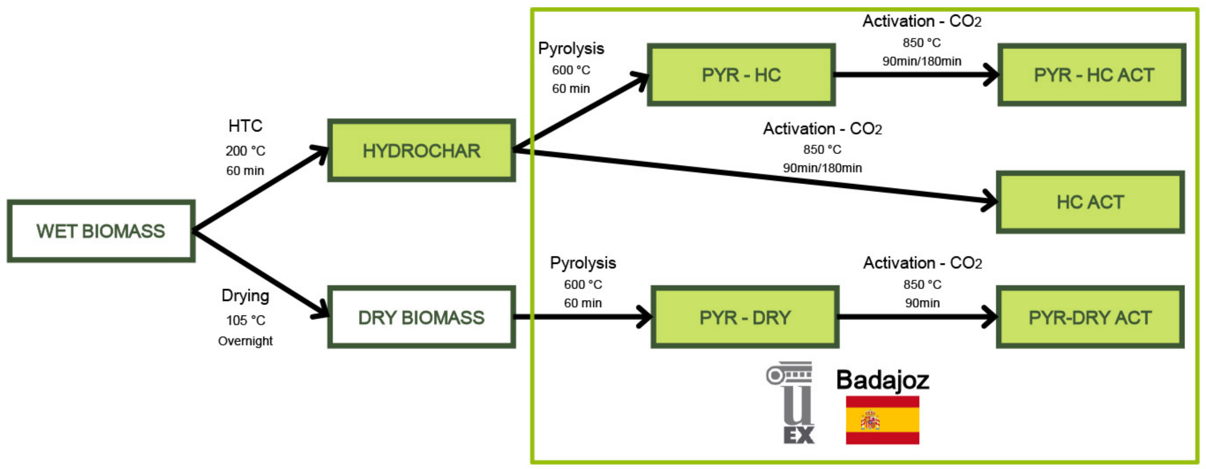
## PRODUCTION OF THE ADSORBENTS

HTP Hydrothermale Prozesse

### Scheme of the thermal treatments



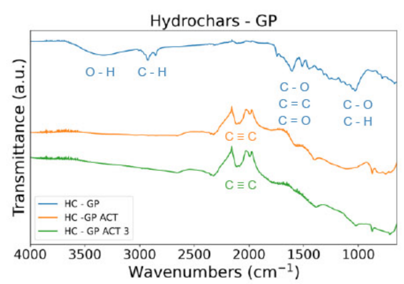

8

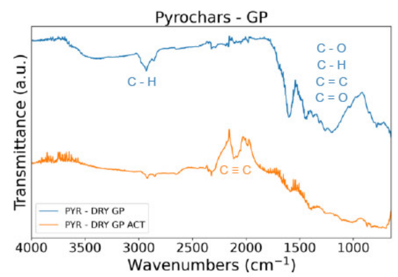
## PRODUCTION OF THE ADSORBENTS

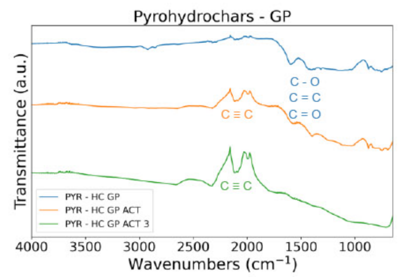
Badajoz

HTP Hydrothermale Prozesse

### Characterization of the materials- GP




| Material | PCZ |
|---|---|
| HC - GP | 6.92 |
| PYR - DRY GP | 10.04 |
| PYR - HC GP | 9.46 |
| HC -GP ACT | 8.81 |

| Material | PCZ |
|---|---|
| PYR - DRY GP ACT | 10.02 |
| PYR - HC GP ACT | 8.95 |
| HC - GP ACT 3 | 9.76 |
| PYR - HC GP ACT 3 | 9.88 |

- FT - IR: acid groups and aromatic rings
- PZC: all the materials have a basic PZC

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## PRODUCTION OF THE ADSORBENTS

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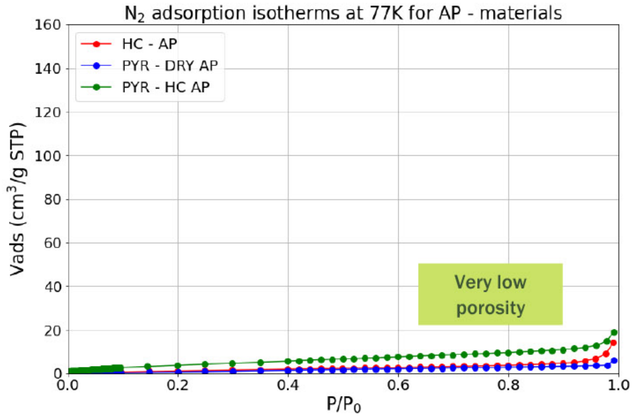
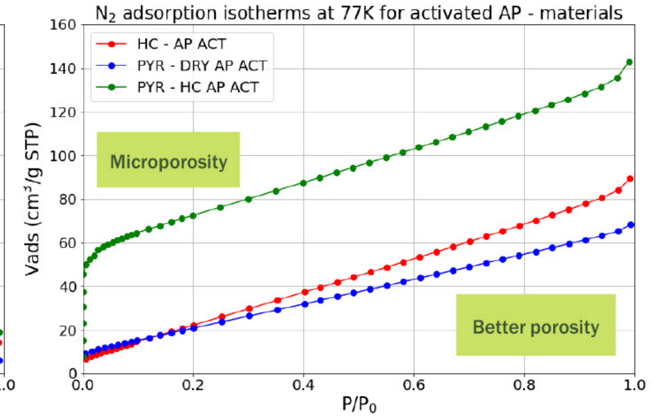
HTP Hydrothermale Prozesse

### Characterization of the materials- AP




**SBET**
- HC - AP : <5 m²/g
- PYR - DRY AP : < 5 m²/g
- PYR - HC AP: 8 m²/g

**SBET**
- HC - AP ACT : 98 m²/g
- PYR - DRY AP ACT: 84 m²/g
- **PYR - HC AP ACT: 245 m²/g**

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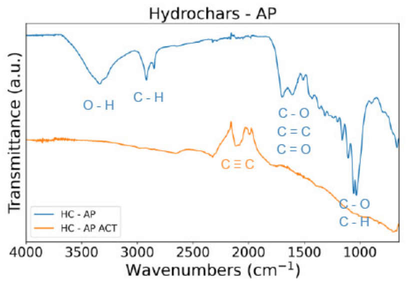
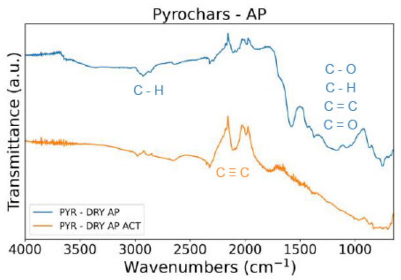
## PRODUCTION OF THE ADSORBENTS

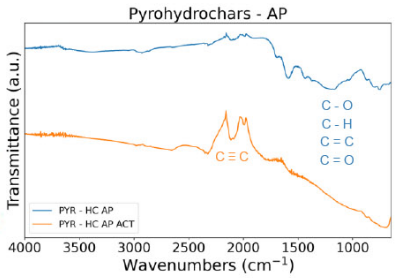
Badajoz

HTP Hydrothermale Prozesse

### Characterization of the materials - AP




| Material | PCZ |
|---|---|
| HC - AP | 8.47 |
| PYR - DRY AP | 8.52 |
| PYR - HC AP | 7.81 |

| Material | PCZ |
|---|---|
| HC - AP ACT | 7.48 |
| PYR - DRY AP ACT | 7.72 |
| PYR – HC AP ACT | 8.31 |

- FT - IR: acid groups and aromatic rings
- PZC: all the materials have a basic PZC

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## PRODUCTION OF THE ADSORBENTS

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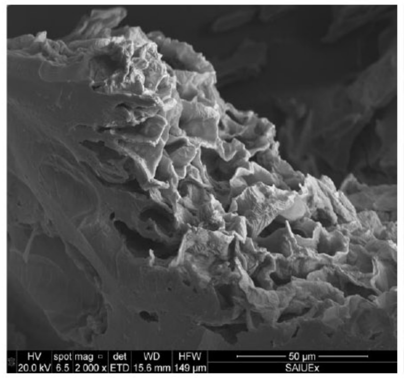
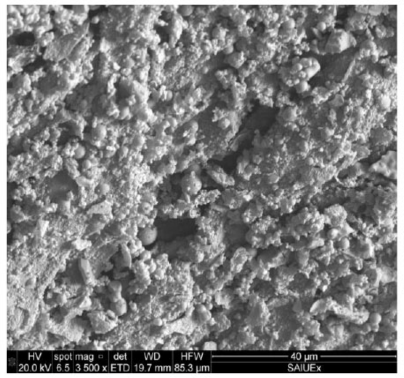
HTP Hydrothermale Prozesse

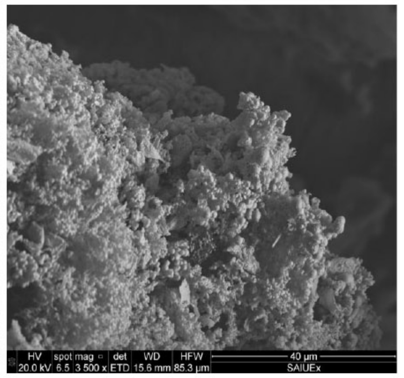
### SEM



**PYR - DRY AP**



**PYR - HC AP ACT**



**PYR - HC GP ACT 3**

**Microspheres** on the surface of the materials subjected to HTC

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## PRODUCTION OF THE ADSORBENTS

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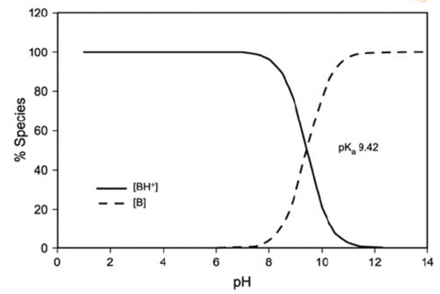
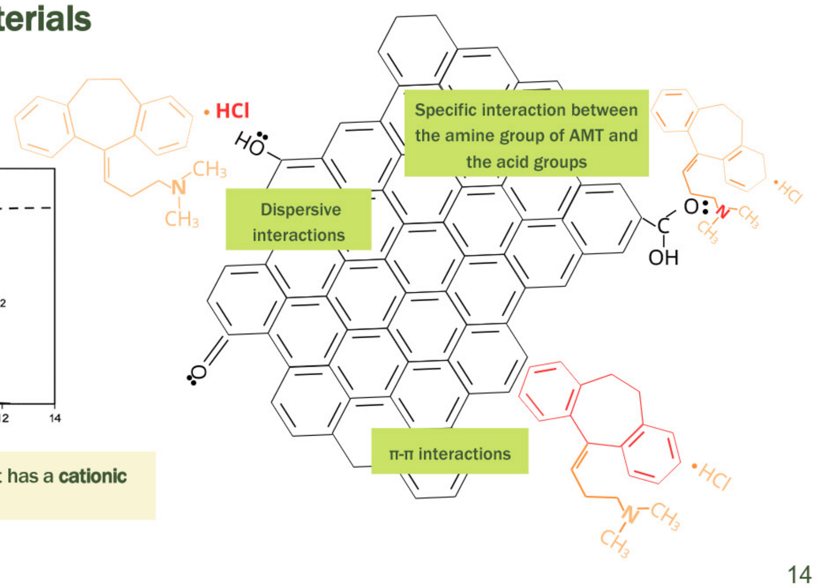
HTP Hydrothermale Prozesse

### Characterization of the materials




**Amitriptyline** has a **pKa = 9.4**, which means it has a **cationic form** at neutral pH

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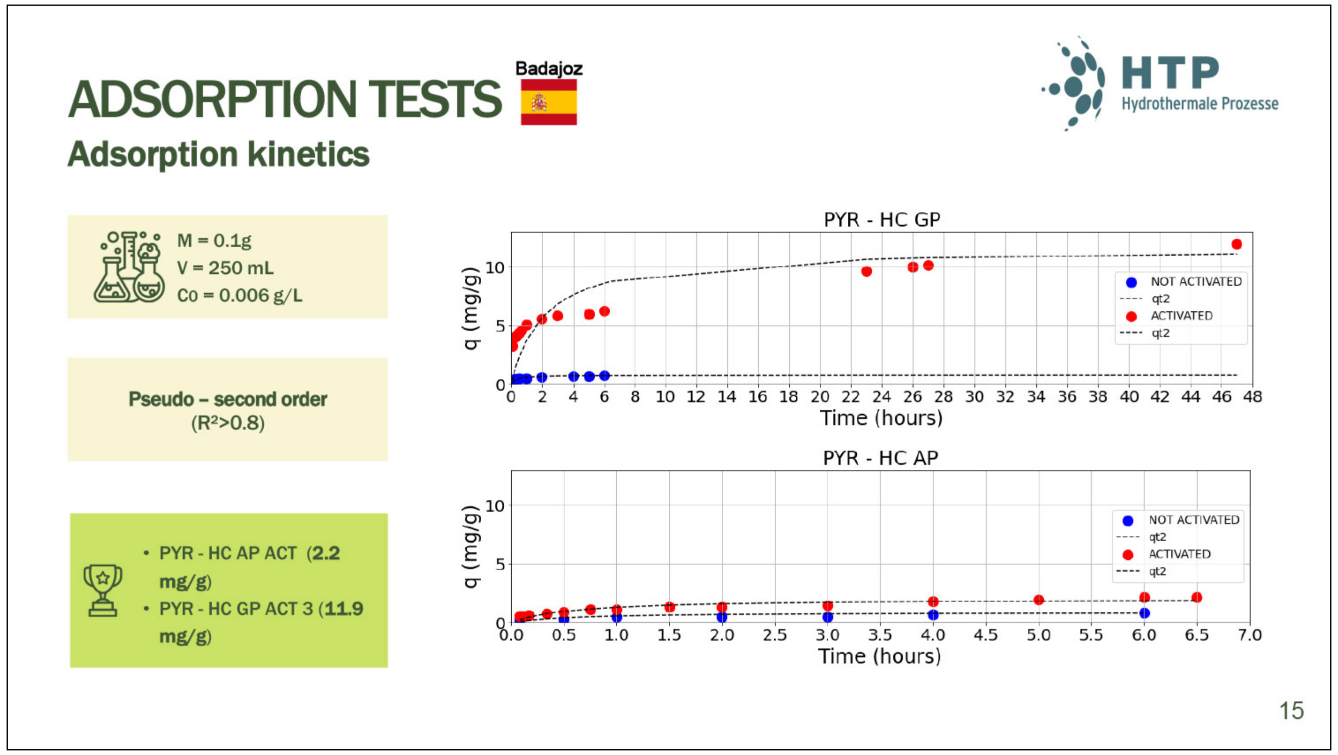
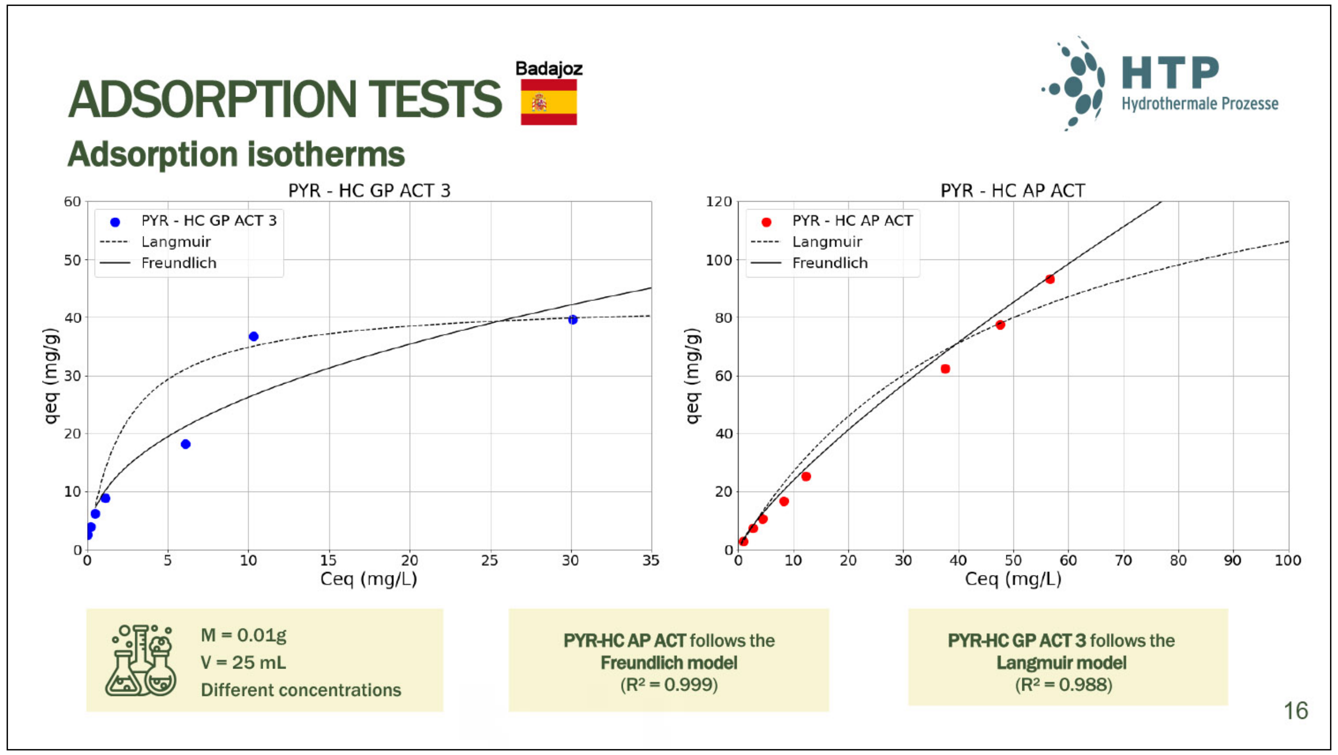
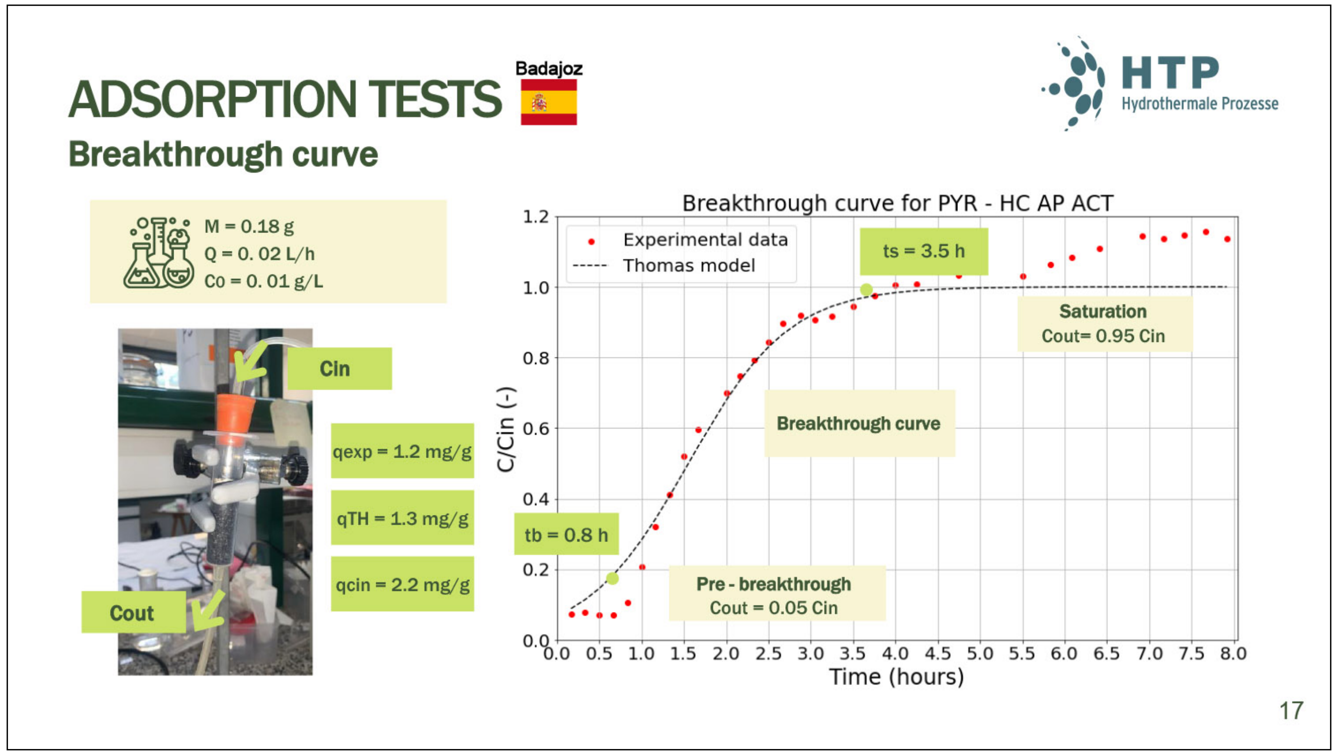
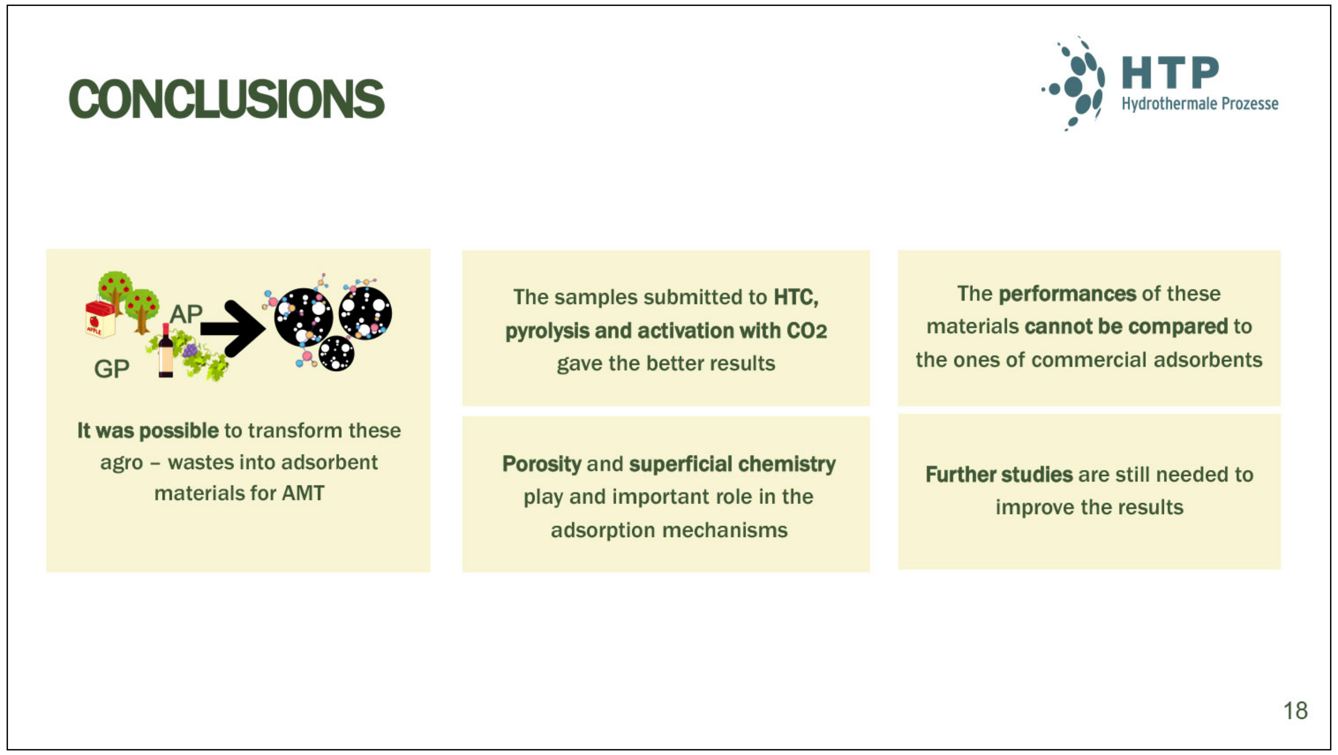

ADSORPTION TESTS
Badajoz
Adsorption kinetics
HTP Hydrothermale Prozesse
M = 0.1g
V = 250 mL
Co = 0.006 g/L
Pseudo – second order
(R²>0.8)
PYR - HC AP ACT (2.2 mg/g)
PYR - HC GP ACT 3 (11.9 mg/g)
PYR - HC GP
q (mg/g)
Time (hours)
NOT ACTIVATED
qt2
ACTIVATED
qt2
PYR - HC AP
q (mg/g)
Time (hours)
NOT ACTIVATED
qt2
ACTIVATED
qt2
15


ADSORPTION TESTS
Badajoz
Adsorption isotherms
HTP Hydrothermale Prozesse
PYR - HC GP ACT 3
PYR - HC GP ACT 3
Langmuir
Freundlich
qeq (mg/g)
Ceq (mg/L)
PYR - HC AP ACT
PYR - HC AP ACT
Langmuir
Freundlich
qeq (mg/g)
Ceq (mg/L)
M = 0.01g
V = 25 mL
Different concentrations
PYR-HC AP ACT follows the Freundlich model
(R² = 0.999)
PYR-HC GP ACT 3 follows the Langmuir model
(R² = 0.988)
16






ADSORPTION TESTS
Badajoz
Breakthrough curve
HTP Hydrothermale Prozesse
M = 0.18 g
Q = 0. 02 L/h
Co = 0. 01 g/L
Cin
Cout
qexp = 1.2 mg/g
qTH = 1.3 mg/g
qcin = 2.2 mg/g
Breakthrough curve for PYR - HC AP ACT
Experimental data
Thomas model
ts = 3.5 h
Saturation
Cout= 0.95 Cin
Breakthrough curve
tb = 0.8 h
Pre - breakthrough
Cout = 0.05 Cin
C/Cin (-)
Time (hours)
17


CONCLUSIONS
HTP Hydrothermale Prozesse
AP
GP
It was possible to transform these agro – wastes into adsorbent materials for AMT
The samples submitted to HTC, pyrolysis and activation with CO2 gave the better results
The performances of these materials cannot be compared to the ones of commercial adsorbents
Porosity and superficial chemistry play and important role in the adsorption mechanisms
Further studies are still needed to improve the results
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HTP Hydrothermale Prozesse

# THANK YOU VERY MUCH

8th Expert Forum on Hydrothermal Processes

HTP Hydrothermale Prozesse

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www.htp-inno.de

*Lisa Röver, Deutsches Biomasseforschungszentrum*

## RegioH2O – Implementing activated hydrochar in a water purification cascade of municipal wastewater for safe and multifunctional reuse

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**Keywords:** Activated carbon, Water treatment, sewage sludge treatment, phosphor recycling, hydrothermal pretreatment

Regio$H_2O$ is developing a nature-based technology for efficient decentralized wastewater recycling for irrigation in order to improve the resilience of urban and rural areas to increasing water scarcity. Components of the innovative system are an aerated constructed wetland with an integrated vegetation layer and an adsorber derived from hydrothermal processing of sewage sludge for the removal of trace substances. The focus lays on the usage of greywater, which implies domestic wastewater without fecal contamination. To make the cities more water resilient, greywater treatment and reuse can be a sustainable solution to prevent discharge of greywater into the environment and reduce the import of freshwater into cities.

Therefore, an aerated vertical-flow constructed wetland will be built serving as the first water purification step. It consists of a glasshouse growing reeds, gravel, and an aeration system in the wetland bed (Rahman et al. 2023). Afterwards, the water is sent through a sand filter and undergoes a disinfection via UV-light or the treatment with hydrogen peroxide. An additional water purification step using sustainable activated hydrochar on the basis of sewage sludge is added. After the water purification, the water is used for watering plants. The main target of the project is a significant reduction of pollutants by the applied purification steps.

The circular use of sewage sludge is a main goal, since a by-product of industrial wastewater treatment would then be reused for the purification of greywater. Hydrothermal carbonization offers benefits in the form of a better mechanical dewatering compared to the initial feedstock and an increase in carbon content beneficial for the subsequent activation of the material.

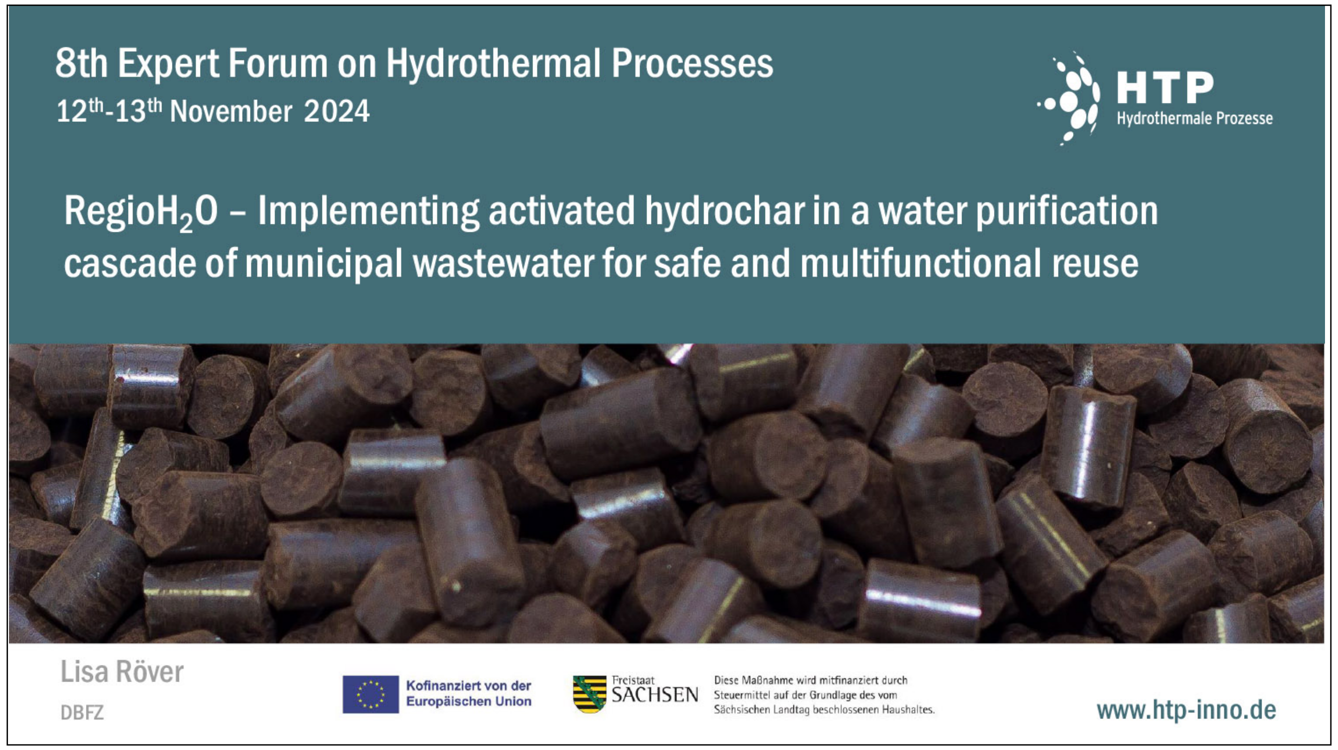
The hydrothermal reactions will be carried out under acidic conditions using citric acid for an additional look into the nutrient recycling by means of phosphorus. The nutrient depleted hydrochar is then thermally activated. This will be tailored according to the sorption needs by a variation of temperature, heating rate, holding time, and gas composition. This talk is to present the general concept of the project and the significance of hydrothermal carbonization within the overall process.

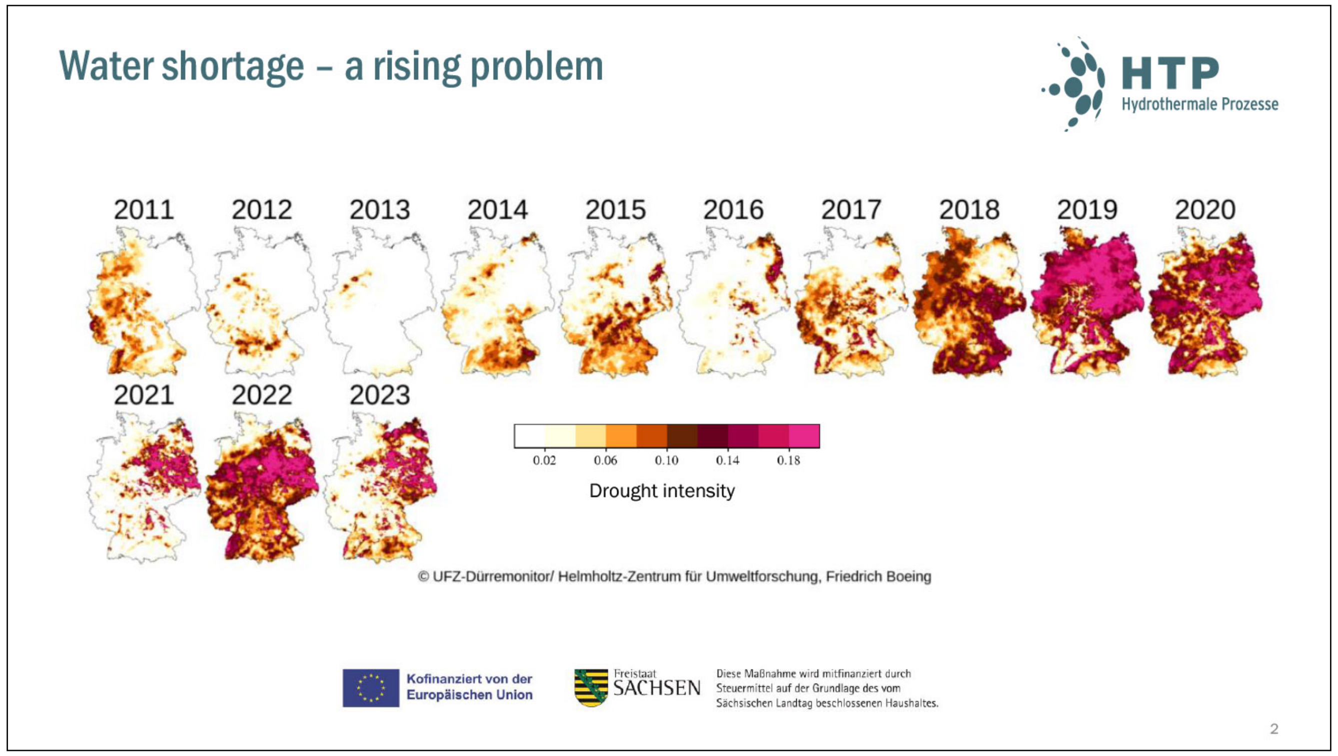
References:

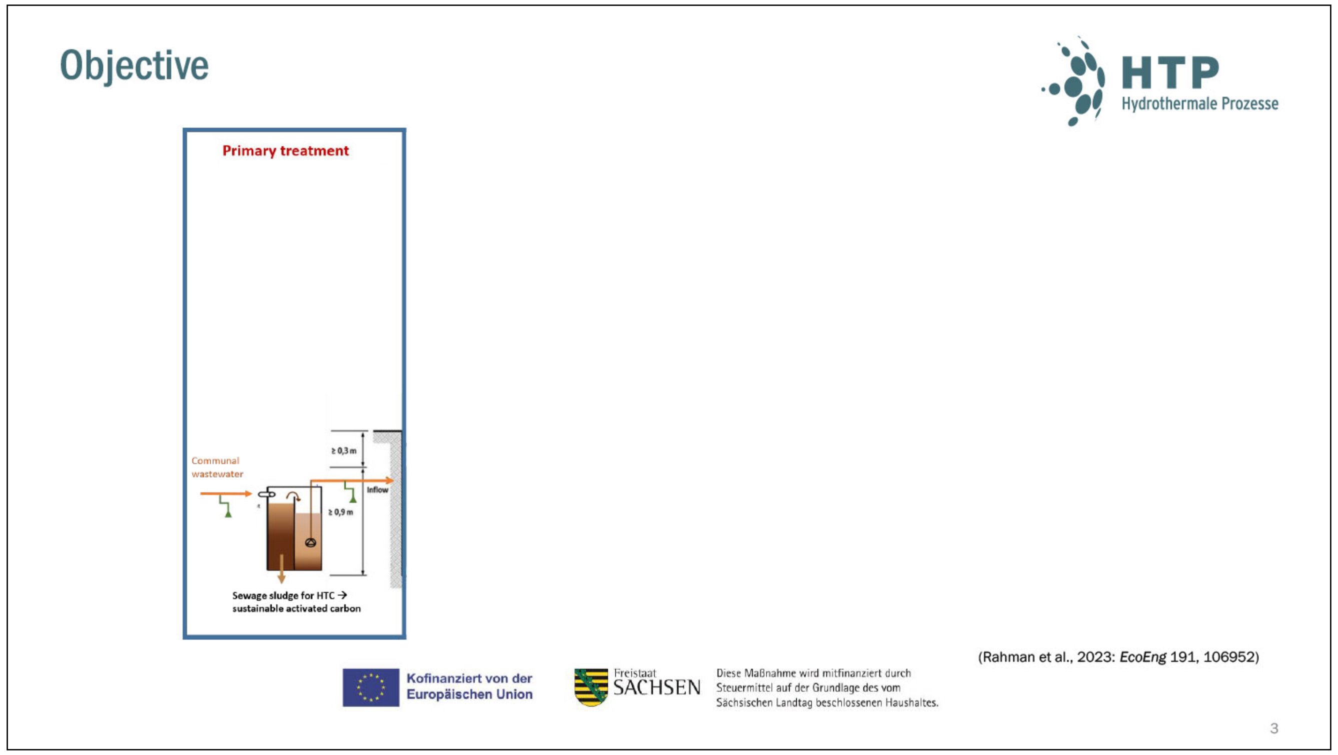
Rahman, Khaja Zillur; Al Saadi, Shamsa; Al Rawahi, Mohammed; Knappe, Jan; van Afferden, Manfred; Moeller, Lucie et al. (2023): A multi-functional nature-based solution (NBS) for greywater treatment and reuse at the same plot. In: Ecological Engineering 191, S. 106952. DOI: 10.1016/j.ecoleng.2023.106952.

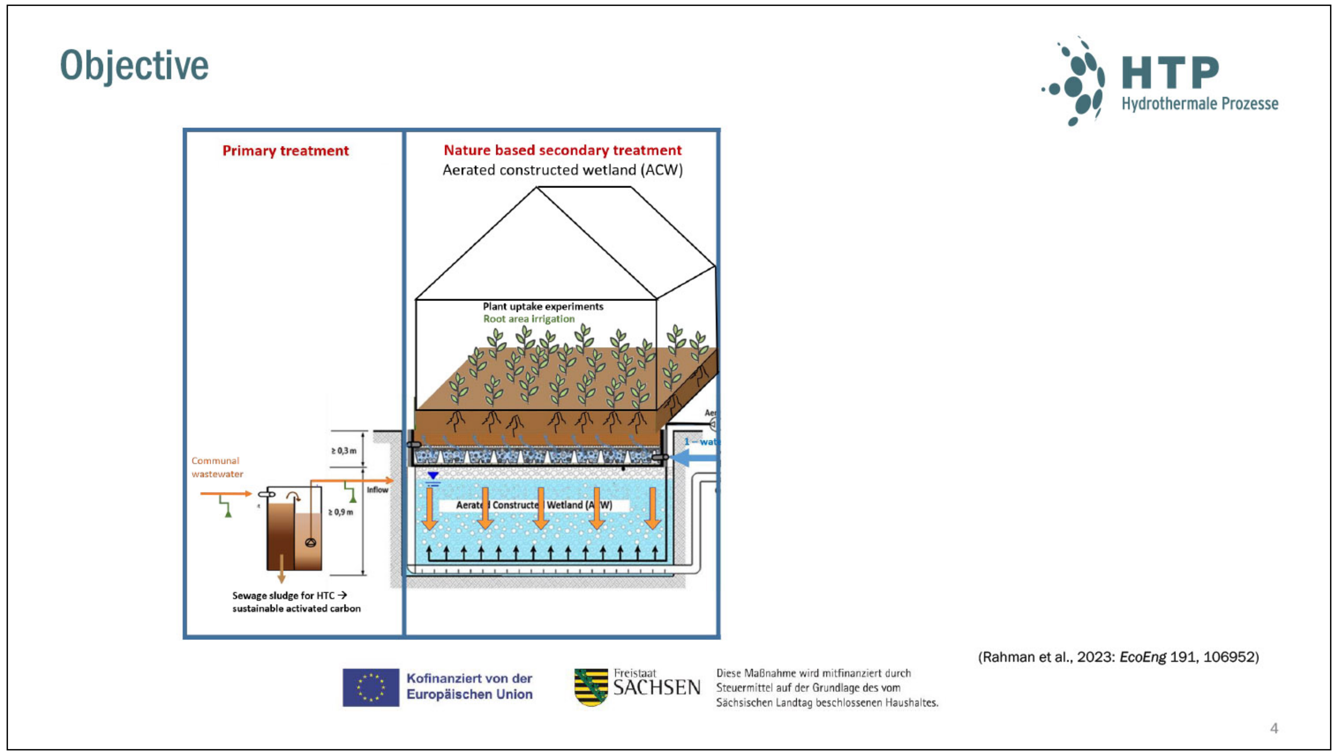







Objective
HTP
Hydrothermale Prozesse
Primary treatment
Communal wastewater
Sewage sludge for HTC →
sustainable activated carbon
(Rahman et al., 2023: EcoEng 191, 106952)
Kofinanziert von der Europäischen Union
Freistaat SACHSEN
Diese Maßnahme wird mitfinanziert durch Steuermittel auf der Grundlage des vom Sächsischen Landtag beschlossenen Haushaltes.
3


Objective
HTP
Hydrothermale Prozesse
Primary treatment
Nature based secondary treatment
Aerated constructed wetland (ACW)
Plant uptake experiments
Root area irrigation
Communal wastewater
Sewage sludge for HTC →
sustainable activated carbon
(Rahman et al., 2023: EcoEng 191, 106952)
Kofinanziert von der Europäischen Union
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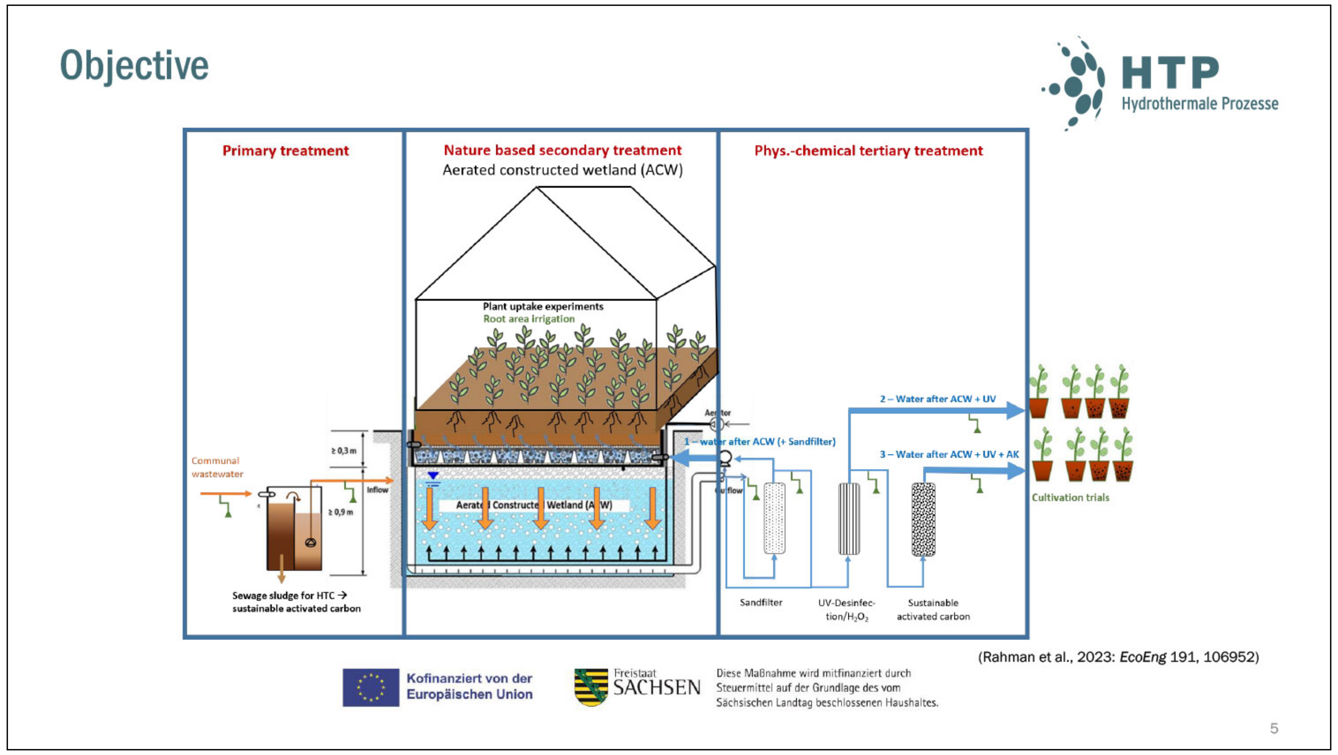
Diese Maßnahme wird mitfinanziert durch Steuermittel auf der Grundlage des vom Sächsischen Landtag beschlossenen Haushaltes.
4






Objective
HTP
Hydrothermale Prozesse
Primary treatment
Nature based secondary treatment
Aerated constructed wetland (ACW)
Phys.-chemical tertiary treatment
Plant uptake experiments
Root area irrigation
2 – Water after ACW + UV
3 – Water after ACW + UV + AK
Cultivation trials
Sandfilter
UV-Desinfection/$H_2O_2$
Sustainable activated carbon
Communal wastewater
Sewage sludge for HTC →
sustainable activated carbon
(Rahman et al., 2023: EcoEng 191, 106952)
Kofinanziert von der Europäischen Union
Freistaat SACHSEN
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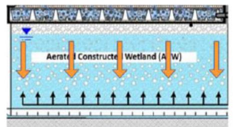
5


Test field at BDZ Leipzig – small wastewater treatment plant
HTP
Hydrothermale Prozesse
Plant uptake experiments
Root area irrigation
Kofinanziert von der Europäischen Union
Freistaat SACHSEN
Diese Maßnahme wird mitfinanziert durch Steuermittel auf der Grundlage des vom Sächsischen Landtag beschlossenen Haushaltes.
6

## Long-term implementation

HTP Hydrothermale Prozesse

- Reduction of water loss, sub-surface irrigation
- Reduce over-reliance on freshwater
- Create green spaces in urban landscapes, enrich biodiversity
- Application in public parks, spaces between office buildings, backyard gardens, holiday homes, golf courses etc.

(Rahman et al., 2023: *EcoEng* 191, 106952)

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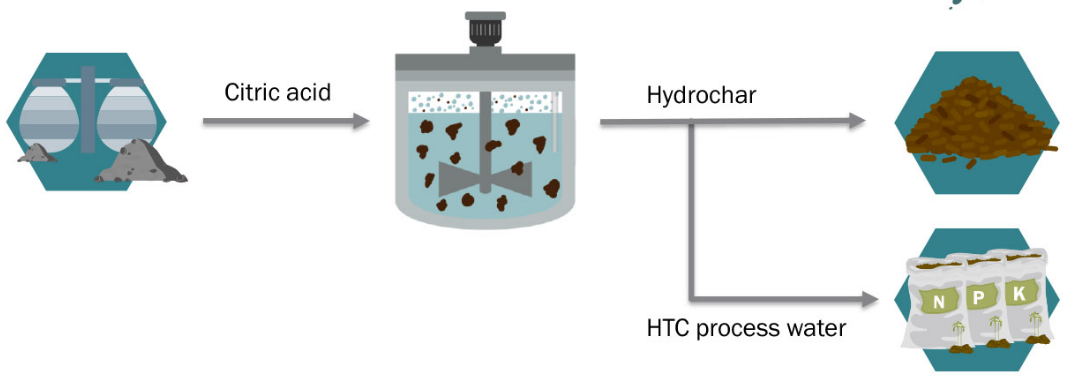
7

## Hydrothermal carbonization for activated carbon

HTP Hydrothermale Prozesse




296 g sewage sludge + 63 g citric acid (s) → 120 g hydrochar (50 % DM) + 155 g process water

Lab results pending

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Freistaat SACHSEN
Diese Maßnahme wird mitfinanziert durch Steuermittel auf der Grundlage des vom Sächsischen Landtag beschlossenen Haushaltes.

8





## Experiment design

HTP Hydrothermale Prozesse

- Instead of varying process parameters we will vary the substrates
- Sludges with biological and chemical P-removal at the WWTP will be examined
  - Cow Manure + sewage sludge
  - Seasonal biomass + sewage sludge
  - Lignocellulosic biomass + sewage sludge
- All experiments at 230 °C, 120 min with addition of 1 mol citric acid/kg sewage sludge

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Freistaat SACHSEN
Diese Maßnahme wird mitfinanziert durch Steuermittel auf der Grundlage des vom Sächsischen Landtag beschlossenen Haushaltes.

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## Subsequent activation from the project partner UFZ

HTP Hydrothermale Prozesse

- 3 different temperatures (800, 850, 900 °C) and 2 activation holding time (1 h and 4 h) were tested
- Activation conducted with steam and $N_2$ flow of 200 mL/min, elevated steam levels of 5-7% were also tested
- Sorption tests with PMOCs (2 PFAS, 2 pharmaceuticals, 1 tire wear additive) are being conducted
- The chars will be characterized for their pore volume (meso- and microporosity), specific surface area and elemental composition

Kofinanziert von der Europäischen Union
Freistaat SACHSEN
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Acknowledgements
HTP
Hydrothermale Prozesse
Funding:
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Freistaat
SACHSEN
SAB
Project team:
Technical Biogeochemistry, UFZ
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Systemic Environmental Biotechnology, UFZ
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Environmental Analytical Chemistry. UFZ
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Exposure Science, UFZ
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Biorefineries, DBFZ
Lisa Röver, Dr. Benjamin Herklotz
Kofinanziert von der Europäischen Union
Freistaat SACHSEN
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Freistaat SACHSEN
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*Gabriel Gerner, ZHAW Zurich University of Applied Sciences*

## New improvements in phosphatic fertilizer production and process water treatment using freeze concentration

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**Keywords:** Hydrothermal carbonisation, digested sewage sludge, hydrochar, nutrient recovery, recycling fertilizer, ion exchanger, process water treatment, freeze concentration

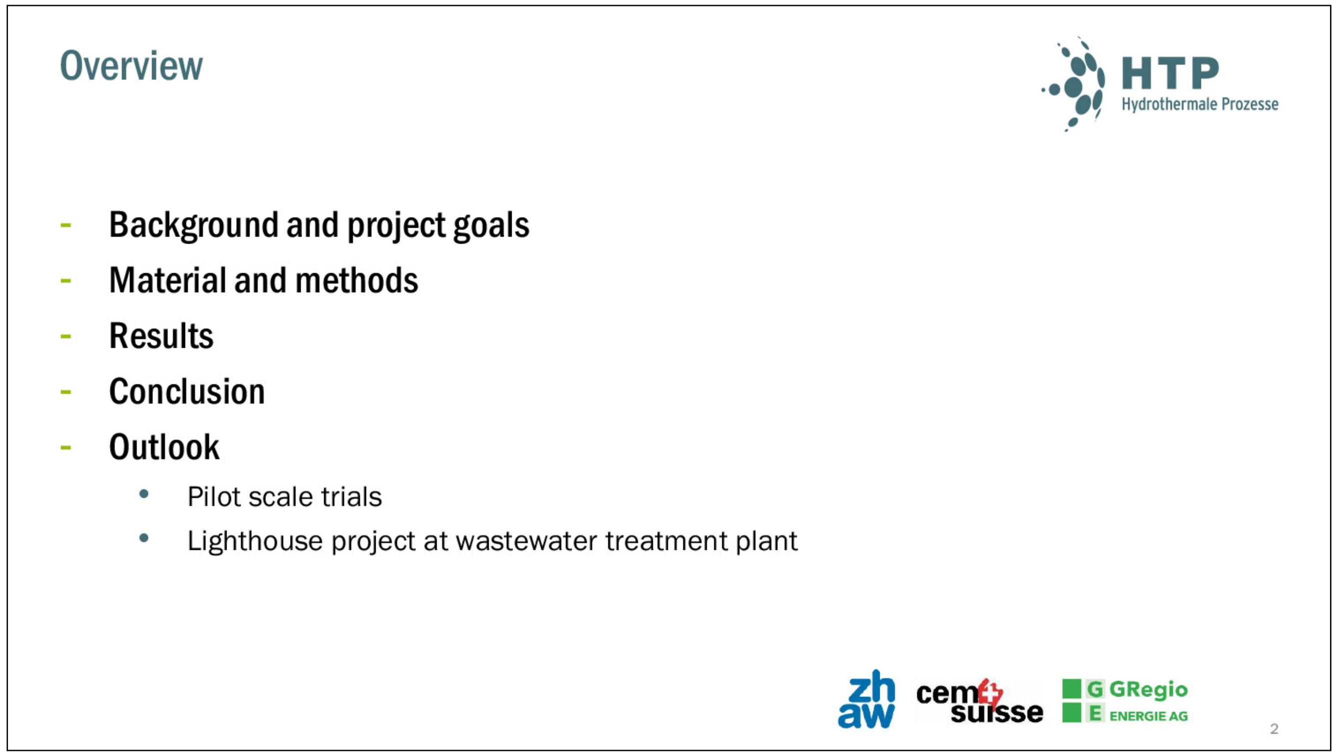
In recent years, there have been promising developments in the hydrothermal carbonisation (HTC) of sewage sludge and the potential to recover phosphorus and nitrogen from such waste streams. In this study, the HTC of digested sewage sludge (DSS) was investigated for the downstream production of heavy metal (HM)-free fertilizer and the usage of freeze concentration as a novel technology for process water treatment.

Phosphorus (P) was extracted from the hydrochar directly after the HTC treatment by acid leaching. To obtain clean fertilizer, phosphatic acid extracts were first treated with ion-exchange resins to remove dissolved HM, as well as phosphorus precipitating agents (i.e., aluminum and iron). Over 98 % of the aluminum (Al) and 97 % of the iron (Fe) could be removed in a single treatment step. The purified extract was then used for the precipitation of HM-free struvite crystals, with P-recovery rates exceeding 89%. Compared to the mono-incineration of sewage sludge with P-recovery from the ash, HTC treatment enables also the recovery of nitrogen and the utilisation of the remaining hydrochar as a climate-neutral energy source. It is therefore a key technology in the utilisation of moist biomass for achieving the global goal of a circular economy.

The HTC process consists of two main products, hydrochar and process water. While hydrochar is the product of interest, process water (PW) makes up the largest share and is very rich in dissolved organic compounds and nitrogen. Compared to evaporation or membrane separation, freeze concentration is a promising technology for concentrating solutes from PW. Separation experiments resulted in the recovery of over 90 % of the dissolved compounds in the concentrate. In our study, the concentrate was later utilized as an ammonium source for struvite precipitation, and the subsequent aerobic digestion of the remaining ice water resulted in an 85 % reduction in chemical oxygen demand (COD) in 15 days.





## Background and project goals

### Swiss legislation

- Ordinance on the Avoidance and the Disposal of Waste (ADWO[1])
  - Article 15: Phosphorus (P) recovery from municipal wastewater, sewage sludge, or residual ash form incinerated sewage sludge
  - P-recovery from sewage sludge mandatory from 2026.
- Chemical Risk Reduction Ordinance (ORRChem[2])
  - Annex 2.6 Number 2.2.2.2: Requirements for recycling fertilizer

Source:
[1] www.fedlex.admin.ch/eli/cc/2015/891/en
[2] www.fedlex.admin.ch/eli/cc/2005/478/en
[3] www.fedlex.admin.ch/eli/cc/1984/1122_1122_1122/en

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## Background and project goals

### Swiss legislation

- Environmental Protection Act (EAP[3])
  - New update March 15th 2024 for material recycling
  - Article 30d
    - Recovery of phosphorus from sewage sludge, animal & bone meal and food waste
    - Recovery of nitrogen from wastewater treatment plants
    - Returning phosphorus to the economic cycle (e.g. fertilizer, phophoric acid)
    - Usage of sewage sludge as substitute fuel if complied with requirements

Source:
[1] www.fedlex.admin.ch/eli/cc/2015/891/en
[2] www.fedlex.admin.ch/eli/cc/2005/478/en
[3] www.fedlex.admin.ch/eli/cc/1984/1122_1122_1122/en

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## Background and project goals

### Main goals

- Improvement of the process for acid leaching
- Innovative process water treatment
- Production of a compliant fertilizer
- Optimization of material recycling and waste reduction
  - Recovery of phosphorus (P), nitrogen (N), carbon (C), aluminum (Al) and iron (Fe)
  - Production of a climate-neutral fuel

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## Materials and methods

- Experimental setup
  - Hydrothermal carbonization of digested sewage sludge
  - Sedimentation of hydrochar and decantation of process water
  - Acidification of thickened slurry for P-recovery and purification of acid extract with ion exchange resin
  - Process water treatment with freeze concentration and N-recovery
  - Precipitation of struvite fertilizer


Image source: Gerner et al. 2023. Hydrothermal Carbonization of Sewage Sludge: New Improvements in Phosphatic Fertilizer Production and Process Water Treatment Using Freeze Concentration. Energies 2023, 16, 7027. https://doi.org/10.3390/en16207027

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## Materials and methods

- **Sedimentation and acid extraction**
  - Before acid addition, the slurry was thickened by decanting the supernatant in order to reduce the dilution effect
  - Sulphuric acid was added to thickened hydrochar slurry and acid extract was separated
- **Purification of acid extract**
  - Preliminary tests on a selection of ion exchange resins, the influence of pH and the P concentration were conducted
  - Selected cation exchange resin was tested for the concentration effect of the acid extract
-

Image source: Gerner et al. 2023. Hydrothermal Carbonization of Sewage Sludge: New Improvements in Phosphatic Fertilizer Production and Process Water Treatment Using Freeze Concentration. Energies 2023, 16, 7027. https://doi.org/10.3390/en16207027

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## Materials and methods

- **Freeze concentration**
  - Preserves volatile compounds and reduces corrosion
  - No filters causing fouling
  - Less energy consumption than evaporation-concentration
  - Recovery of dissolved organic compounds and nitrogen
  - Testing the separability of the process water (determination of distribution coefficient k)
- **Fertilizer production**
  - Precipitation of struvite by mixing phosphorus-containing acid extract and nitrogen-containing, concentrated process water


Image source: Gerner et al. 2023. Hydrothermal Carbonization of Sewage Sludge: New Improvements in Phosphatic Fertilizer Production and Process Water Treatment Using Freeze Concentration. Energies 2023, 16, 7027. https://doi.org/10.3390/en16207027

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## Results

### Products: Phosphorus and nitrogen distribution

| | Nutrient Content and Recovery | | | | |
|---|---|---|---|---|---|
| | P | N | K | Mg | Ca |
| | [mg kg⁻¹] | [mg kg⁻¹] | [mg kg⁻¹] | [mg kg⁻¹] | [mg kg⁻¹] |
| DSS | 33,613 (-) | 42,066 (-) | 1489 (-) | 3353 (-) | 33,064 (-) |
| HTC-HC | 17,798 (35.6) | 29,529 (47.1) | [1] 1347 (60.7) | [1] 2133 (42.7) | [1] 45,856 (93.1) |
| | [mg L⁻¹] | [mg L⁻¹] | [mg L⁻¹] | [mg L⁻¹] | [mg L⁻¹] |
| HTC-PW | 17.9 (0.1) | 6797 (25.6) | 146 (15.5) | 64 (3.0) | 536 (2.6) |
| HTC-PAE | 12,681 (72.2) | 7030 (32.0) | 199 (25.6) | 931 (53.1) | 556 (3.2) |

Image source: Gerner et al. 2023. Hydrothermal Carbonization of Sewage Sludge: New Improvements in Phosphatic Fertilizer Production and Process Water Treatment Using Freeze Concentration. Energies 2023, 16, 7027. https://doi.org/10.3390/en16207027

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## Results

### Products: Precipitant (Al, Fe) and heavy metal distribution

| | Precipitants | | Heavy Metal Content | | | | |
|---|---|---|---|---|---|---|---|
| | Fe [mg kg⁻¹] | Al [mg kg⁻¹] | Ni [mg kg⁻¹] | Cu [mg kg⁻¹] | Zn [mg kg⁻¹] | Cd [mg kg⁻¹] | Pb [mg kg⁻¹] |
| DSS | 74,091 | 53,446 | 18 | 242 | 583 | <1 | 15 |
| HTC-HC | 49,863 | 32,649 | [1] 23 | 360 | 783 | <1 | 23 |
| | [mg L⁻¹] | [mg L⁻¹] | [mg L⁻¹] | [mg L⁻¹] | [mg L⁻¹] | [mg L⁻¹] | [mg L⁻¹] |
| HTC-PW | 367 | 16 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| HTC-PAE | 22,970 | 18,150 | 1.8 | <0.1 | 35.2 | <0.1 | <0.1 |

Image source: Gerner et al. 2023. Hydrothermal Carbonization of Sewage Sludge: New Improvements in Phosphatic Fertilizer Production and Process Water Treatment Using Freeze Concentration. Energies 2023, 16, 7027. https://doi.org/10.3390/en16207027

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## Results

HTP Hydrothermale Prozesse

- **Purification of acid extract**
  - Break through of Fe and Al with 1:10 dilution, and 60% loss of P
  - High recovery with 1:50 and 1:100 dilution
  - Cation-exchange resin has high affinity for Al and Fe with high recovery and 100% passage of P

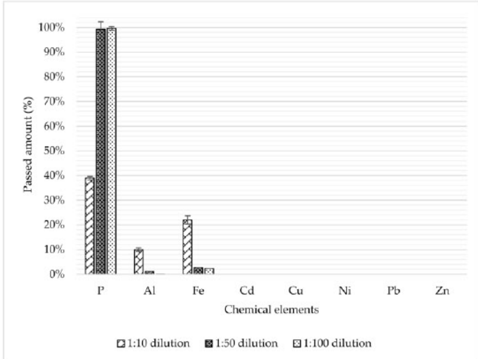


Image source: Gerner et al. 2023. Hydrothermal Carbonization of Sewage Sludge: New Improvements in Phosphatic Fertilizer Production and Process Water Treatment Using Freeze Concentration. Energies 2023, 16, 7027. https://doi.org/10.3390/en16207027

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## Results

HTP Hydrothermale Prozesse

- **Freeze concentration**
  - Low freezing compounds collected on the surface and could be removed with the first meltwater
  - Recovery of clean ice at the end of the melting process
  - Evaluation of bottle
    - Volume: min. amount of 500mL
    - Shape: cone shape neck for better rinsing effect of ice

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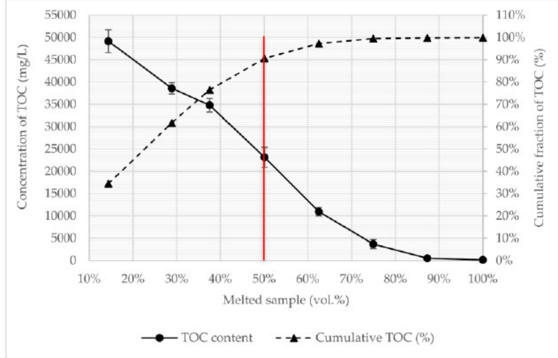
## Results

HTP Hydrothermale Prozesse

- **Freeze concentration**
  - At 50 vol.% melted sample (red line), the cumulative TOC and TN fractions reached 90 and 95%, respectively
  - A k-value of 0.145 was achieved, which showed a good separation of impurities
  - Further tests in a pilot plant are required to maximize recovery

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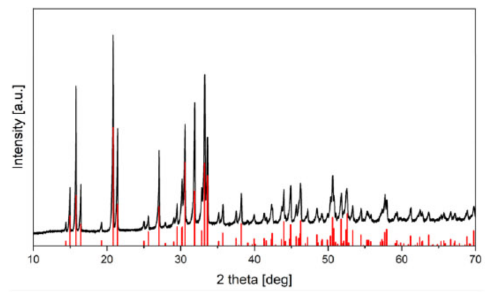
## Results

HTP Hydrothermale Prozesse

- **Struvite fertilizer**
  - Concentrated PW was the only nitrogen source
  - P-recovery for struvite precipitation over 90% , with a total P-recovery of 64-70%
  - Concentration of nickel, copper, zinc, cadmium and lead were bellow the Swiss threshold values for mineral recycling fertilizer
  - XRD patterns from struvite precipitate matched closely with ICDD reference

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## Conclusion

- Advantage of decantation of excess process water (PW):
  - Prevents contamination of PW with heavy metals
  - PW can be treated by freeze concentration, aerobic or anaerobic digestion
  - Increases phosphorus concentration in acid extract
- Purification of acid extract allows the recovery of precipitants like Fe and Al for reuse
- High separability of PW was achieved by freeze concentration
- Hydrochar can be further used as substitute fuel
- Compared to mono-incineration of sewage sludge:
  - No waste residue are sent on landfill
  - Nitrogen and carbon can be recovered as well

Image source: Gerner et al. 2023. Hydrothermal Carbonization of Sewage Sludge: New Improvements in Phosphatic Fertilizer Production and Process Water Treatment Using Freeze Concentration. Energies 2023, 16, 7027. https://doi.org/10.3390/en16207027

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## Outlook – Pilot scale trial with freeze concentration

- End of 2024 are pilot scale trials planned with a pilot plant from Sulzer
- Treatment of 1 $m^3$ of process water from sewage sludge
- Investigaton of the separation performance and characterization of products

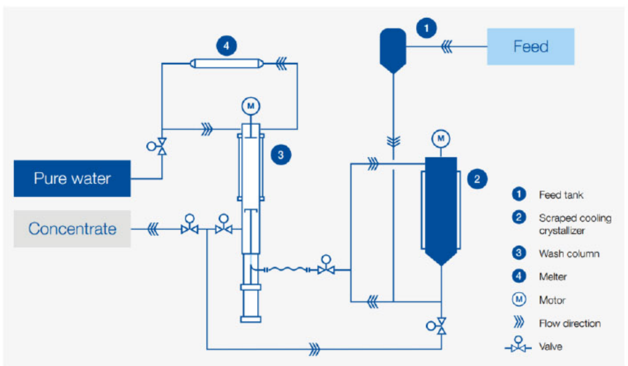


Image source: Brochure ‚Pilot plant Freeze concentration' from Sulzer (E10623 en 11.2019)

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## Outlook – Lighthouse project

- Pilot plant planned at wastewater treatment plant in Buchs SG, Switzerland
- Phosphorus recovery from thickened HTC-slurry
- Nitrogen recovery from digester water and centrate
- Carbon recovery in hydrochar

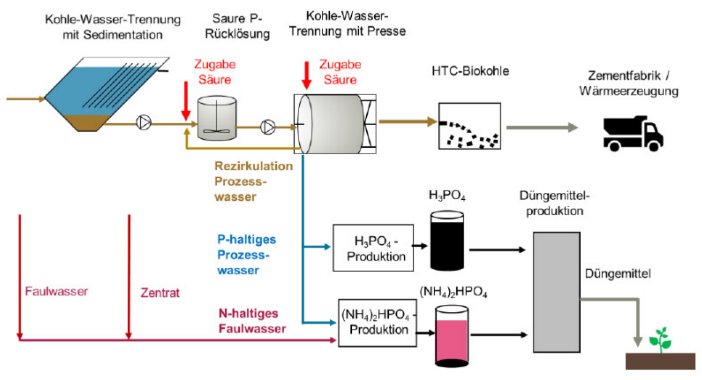


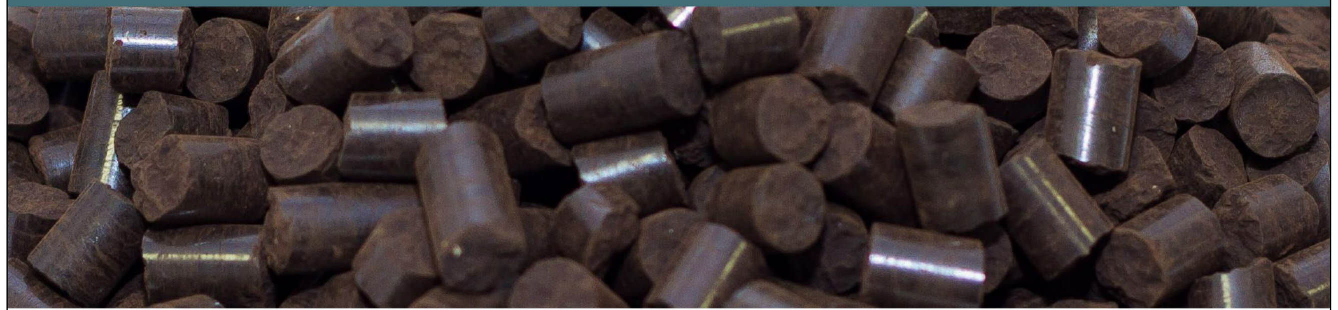

Image source: Gautschi et al. 2024. HTC-Verfahren auf der ARA Buchs (SG) – Klärschlamm in Biokohle umwandeln und gleichzeitig Phosphor zurückgewinnen. Aqua&Gas 2024, 11.

17

## 8th Expert Forum on Hydrothermal Processes

12th-13th November 2024

### Thank you for your attention!



Institute of Natural Resource Sciences, ZHAW

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## 8th Expert Forum on Hydrothermal Processes

HTP Hydrothermale Prozesse

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www.htp-inno.de

## References

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- Gerner et al. 2023. Hydrothermal Carbonization of Sewage Sludge: New Improvements in Phosphatic Fertilizer Production and Process Water Treatment Using Freeze Concentration. Energies 2023, 16, 7027. https://doi.org/10.3390/en16207027
- Gautschi et al. 2024. HTC-Verfahren auf der ARA Buchs (SG) – Klärschlamm in Biokohle umwandeln und gleichzeitig Phosphor zurückgewinnen. Aqua&Gas 2024, 11.


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## Project partner

HTP Hydrothermale Prozesse

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This research project was financially supported by the Association of the Swiss Cement Industry (cemsuisse).

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*Giulia Ischia, Max Planck Institute of Colloids and Interfaces*

# From hydrothermal carbonization to humification for soil carbon sequestration

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**Keywords:** Soil health, biomacromolecules, carbon sinks, hydrothermal humification, hydrochar

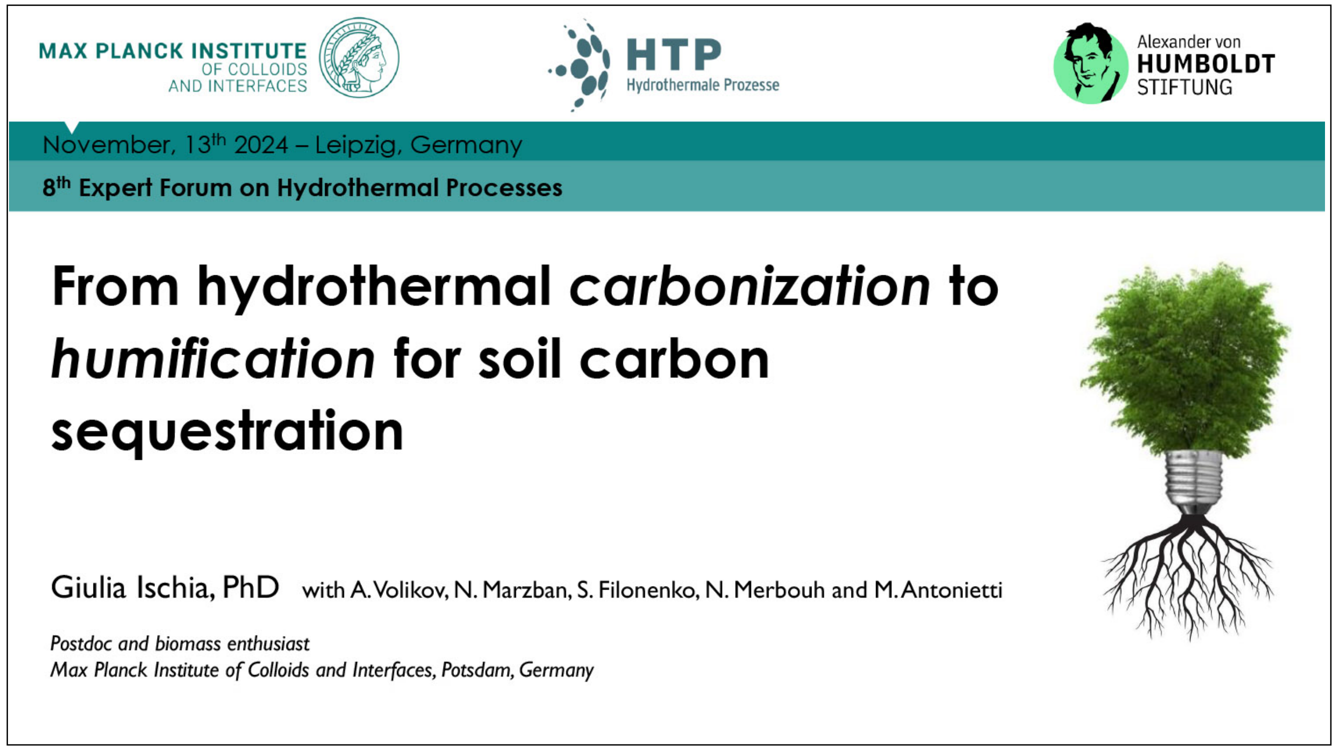
How can we produce recalcitrant organic matter while improving soil health? Inspiration can come from natural humic substances, the complex biomacromolecules that form via biomass degradation, often referred to as “black gold” for their capacity to act as carbon sinks and regulate soil health. Recently, a novel technique called hydrothermal humification (HTH) has been developed to synthesize this humic matter from biomass under a pH-regulated hydrothermal environment.

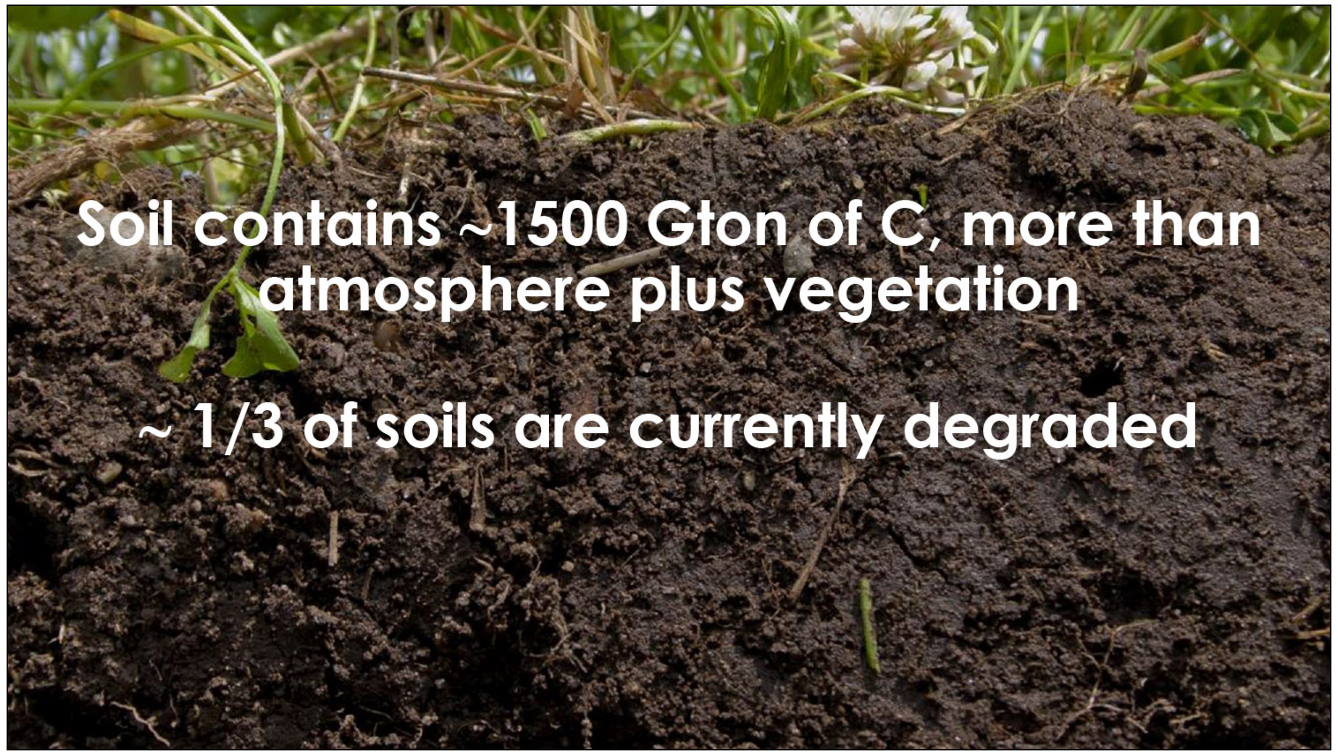
This conversion process differs from classical hydrothermal carbonization (HTC) only by a pH modification. This work provides chemical insights into this emerging field of research. Several substrates (glucose, cellulose, lignin, and wood) were hydrothermally treated under progressively varying pH conditions, transitioning from HTC to HTH. The resulting products – hydrochar, liquid phases, and humic substances – were thoroughly characterized using liquid chromatography, solid-state NMR, and analysis of composition and morphology.

The results show that alkaline conditions trigger retro-aldol splitting, forming acidic species that neutralize the environment. These species then partially condense with furans (formed from the pH drop), resulting in the formation of polymeric linear humic and fulvic acids with minimal non-solid residues (< 2 % mass yield). The data diverge from HTC products, instead rich in furans and leading to hydrochar. These findings allowed for the construction of reaction pathways, highlighting the shift from HTC to HTH and elucidating the differences between these processes. Finally, the artificial humic substances were compared with their natural counterparts, demonstrating their similarity in recalcitrance and their potential for soil carbon sequestration and soil health regulation.







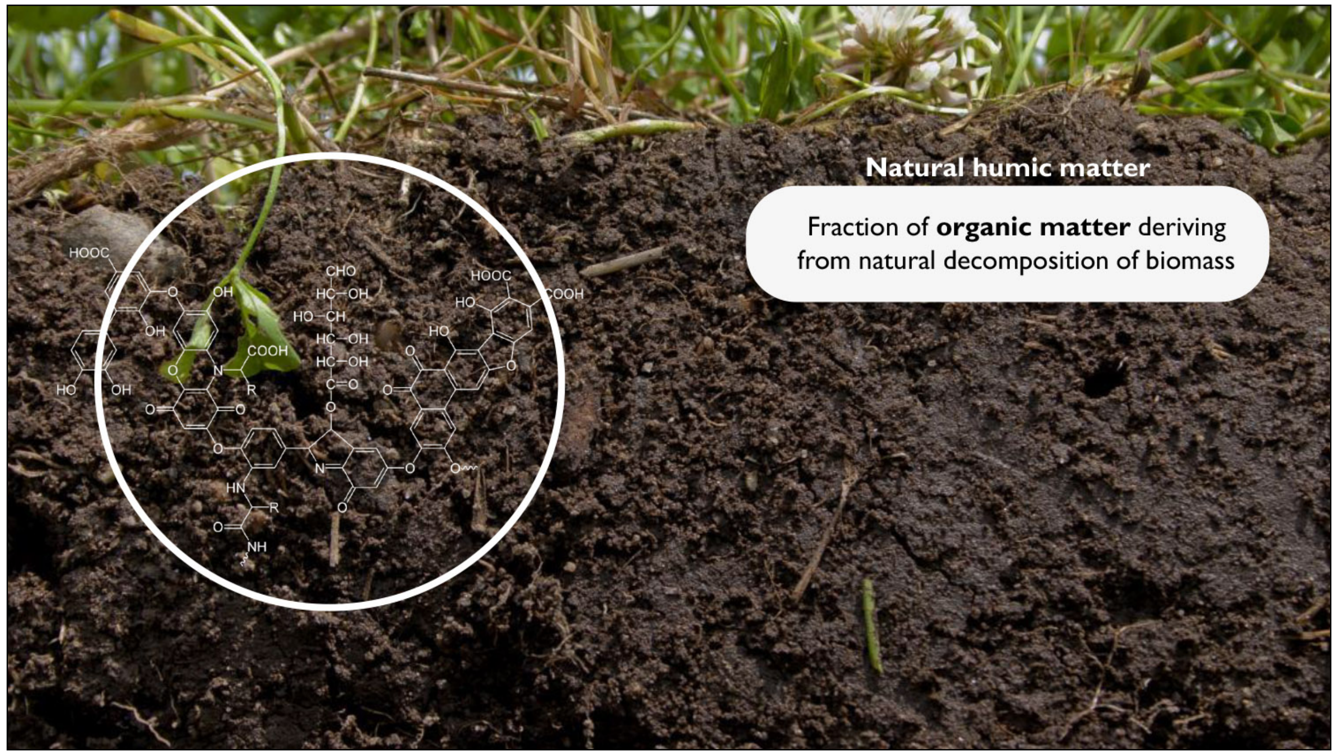



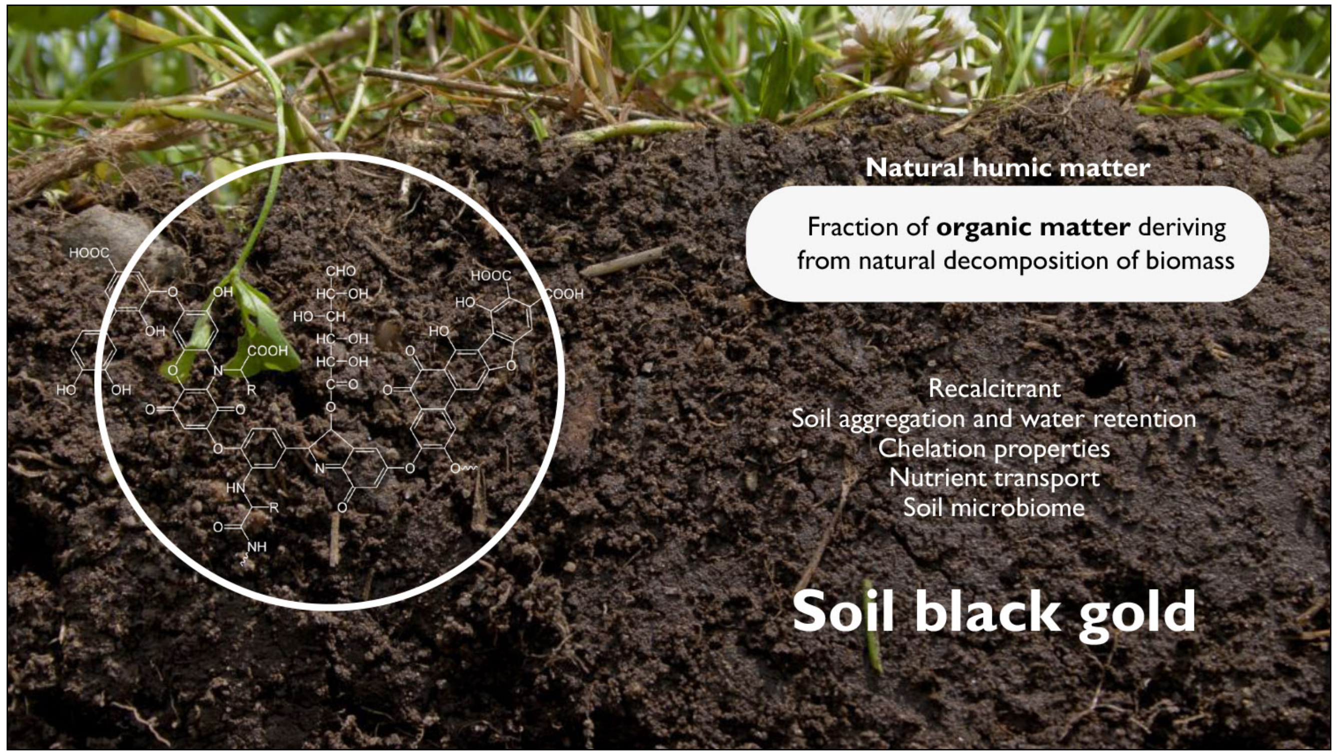


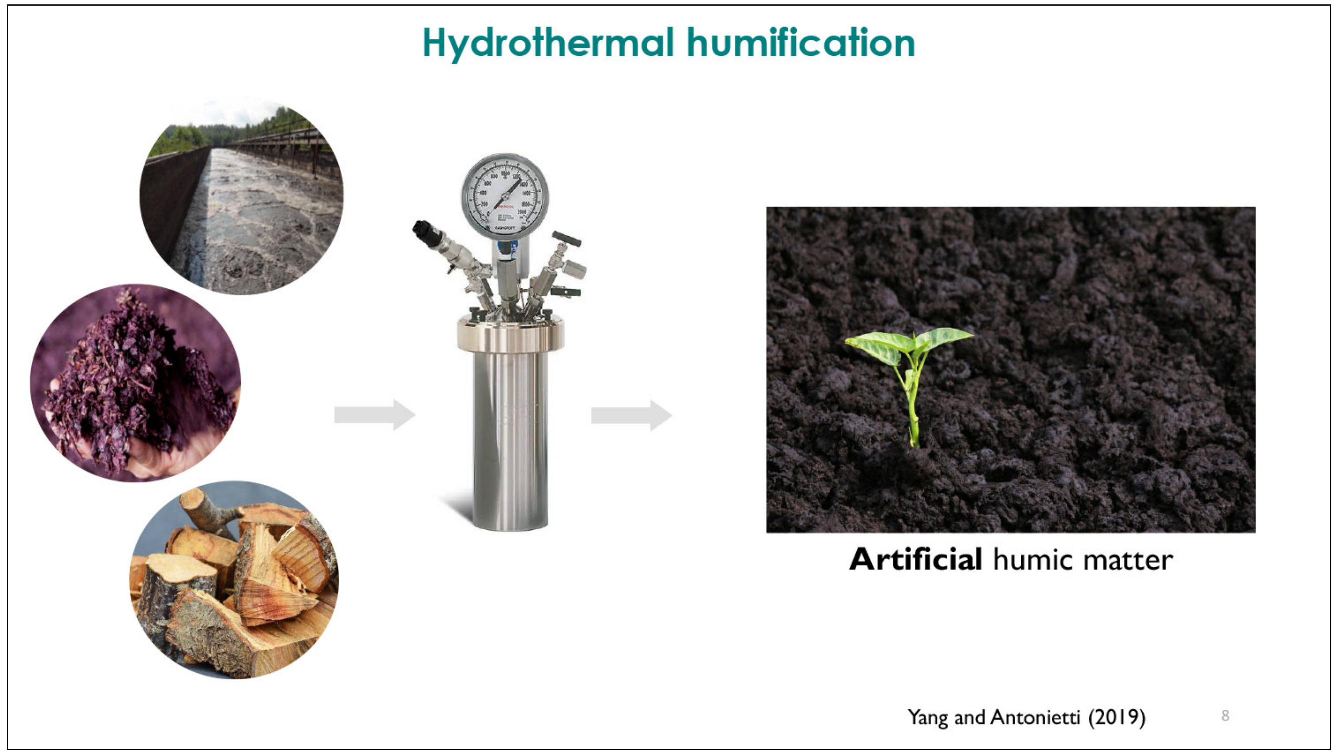




## What is natural humic matter?

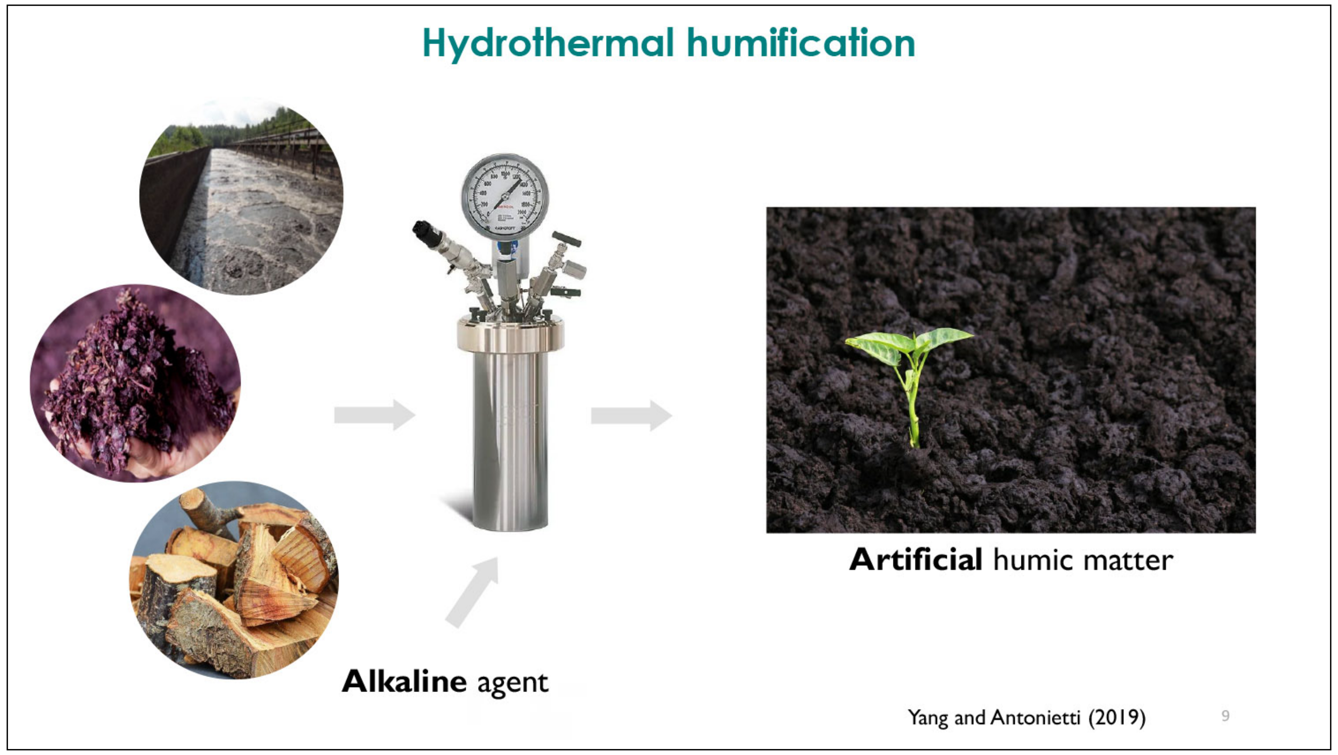


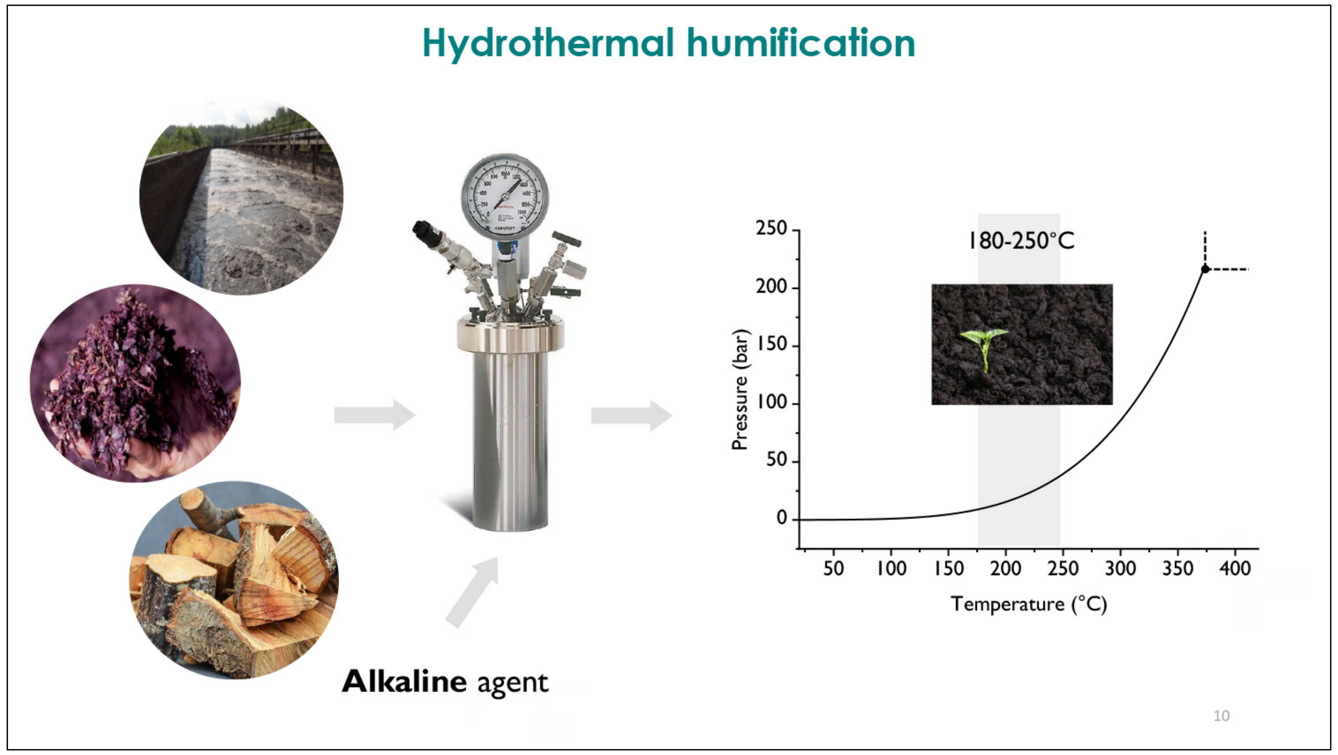

Natural humic matter
Fraction of **organic matter** deriving from natural decomposition of biomass
Recalcitrant
Soil aggregation and water retention
Chelation properties
Nutrient transport
Soil microbiome
Soil black gold

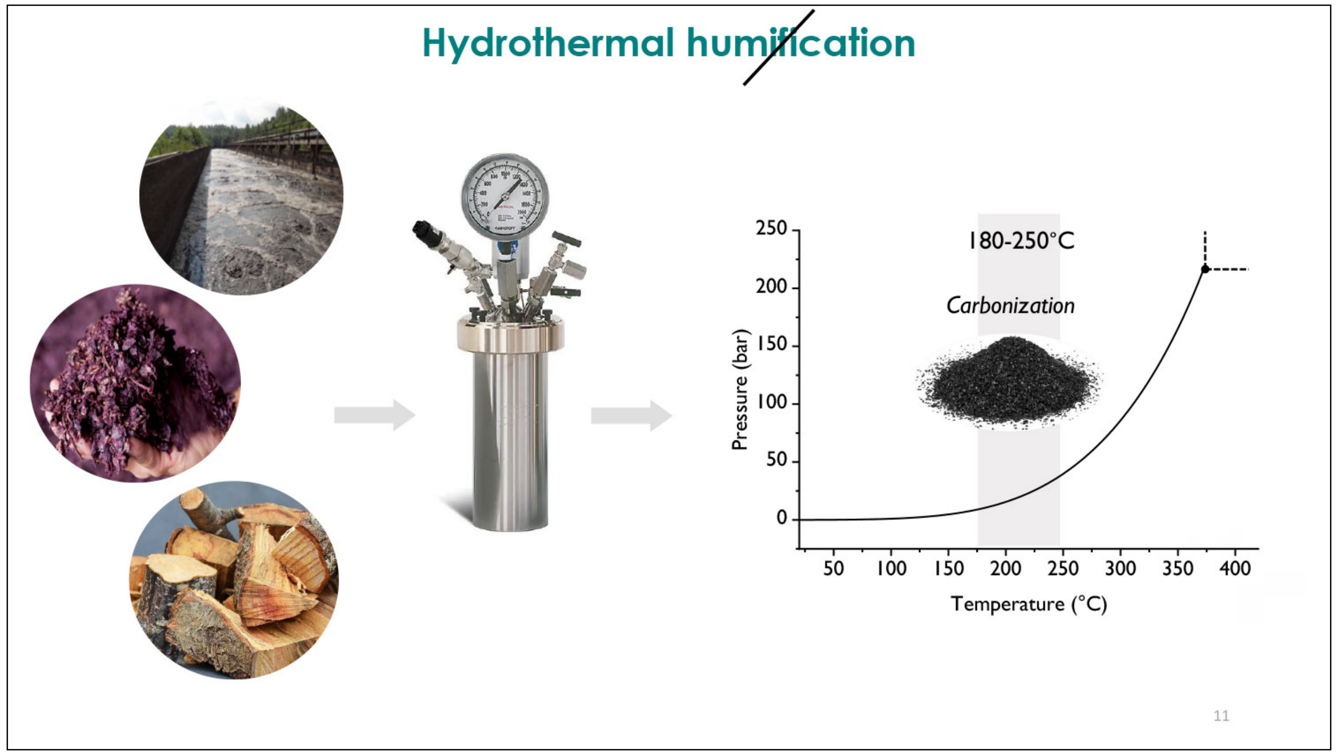

Hydrothermal humification
**Artificial** humic matter
Yang and Antonietti (2019)
8



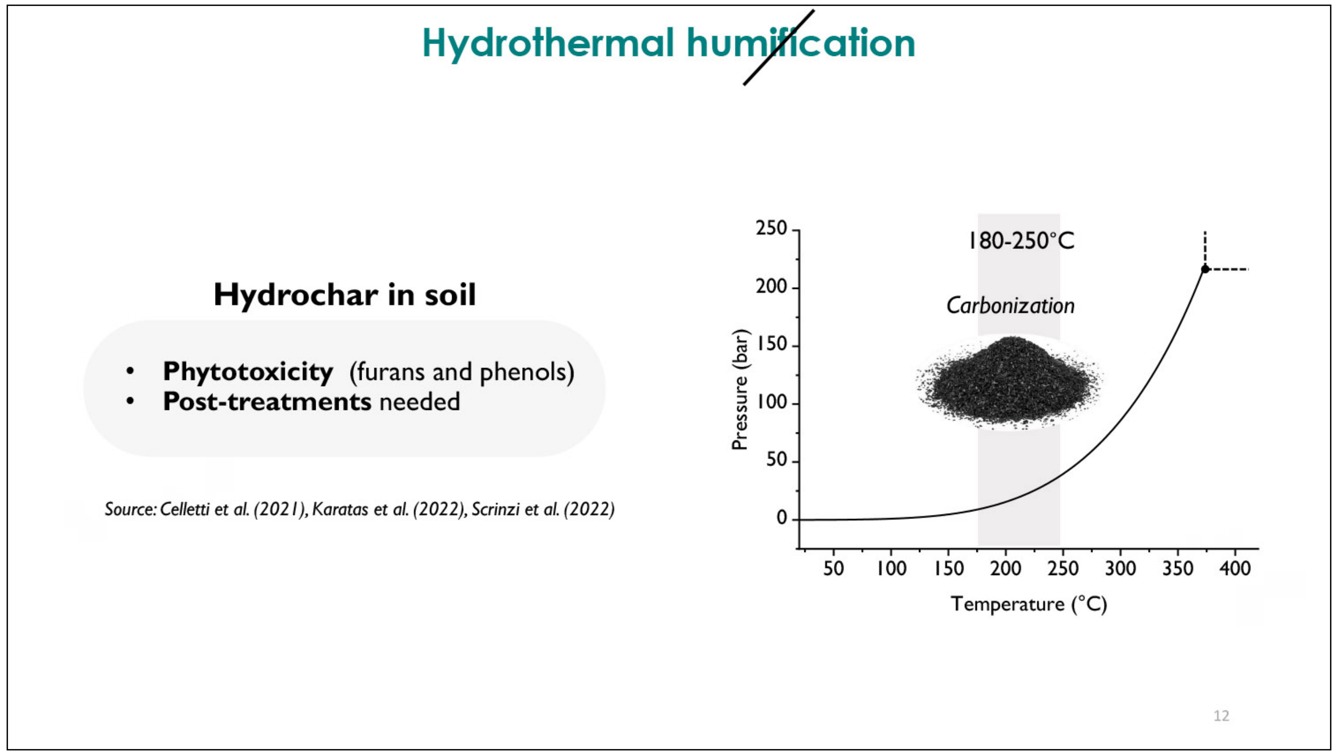


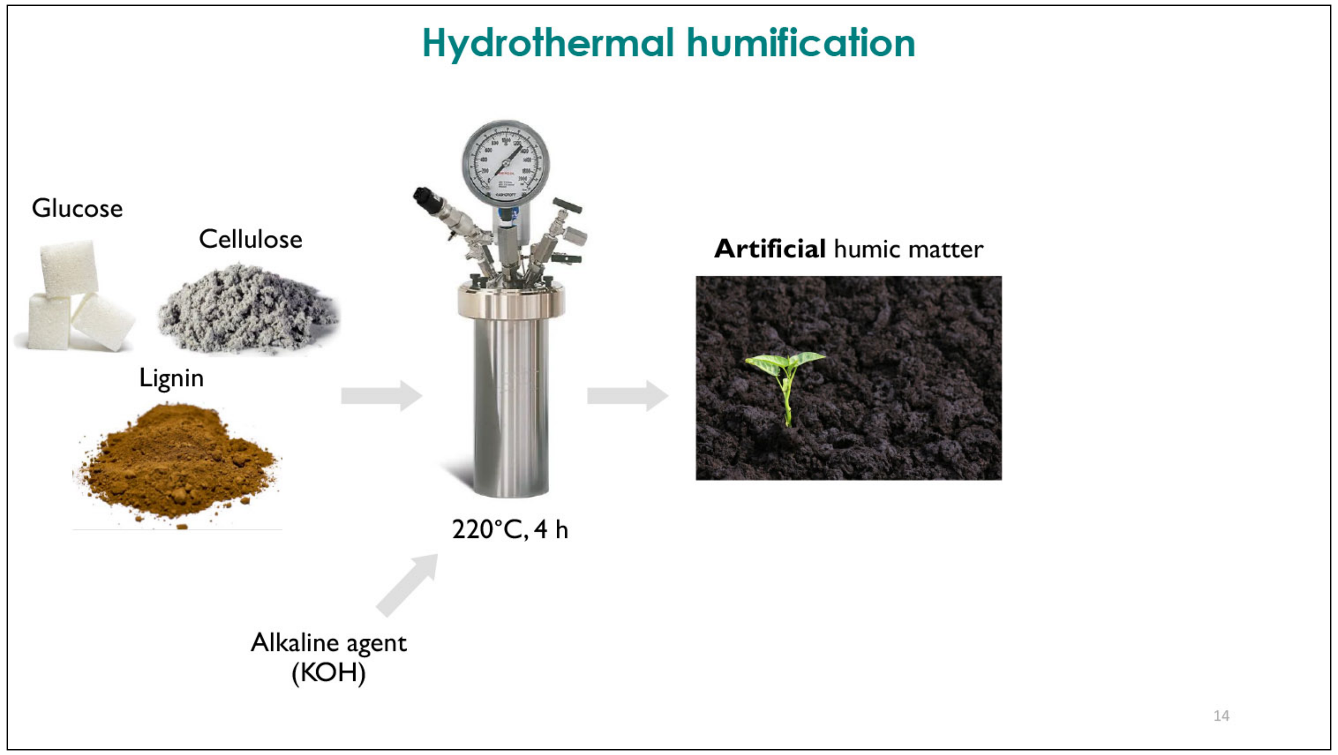

Hydrothermal humification
**Artificial** humic matter
**Alkaline** agent
Yang and Antonietti (2019)
9

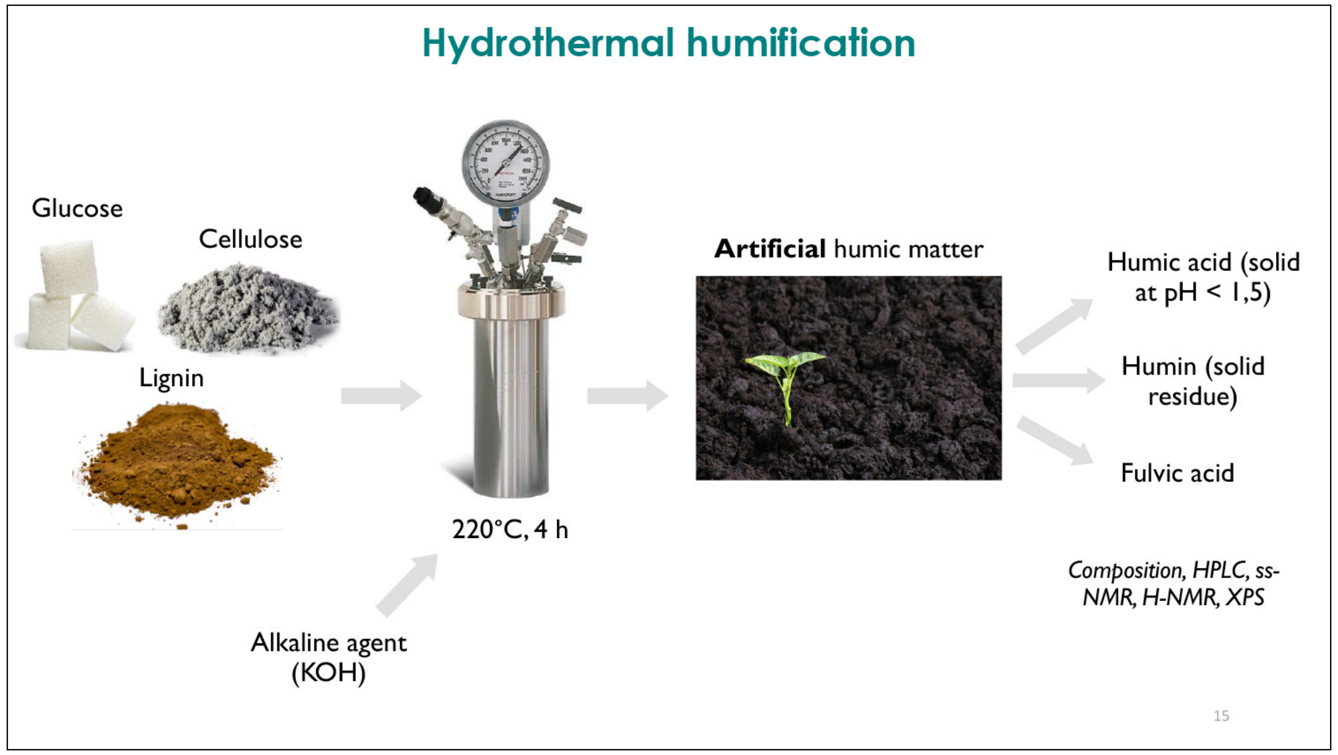

Hydrothermal humification
180-250°C
Pressure (bar)
0
50
100
150
200
250
Temperature (°C)
50
100
150
200
250
300
350
400
**Alkaline** agent
10

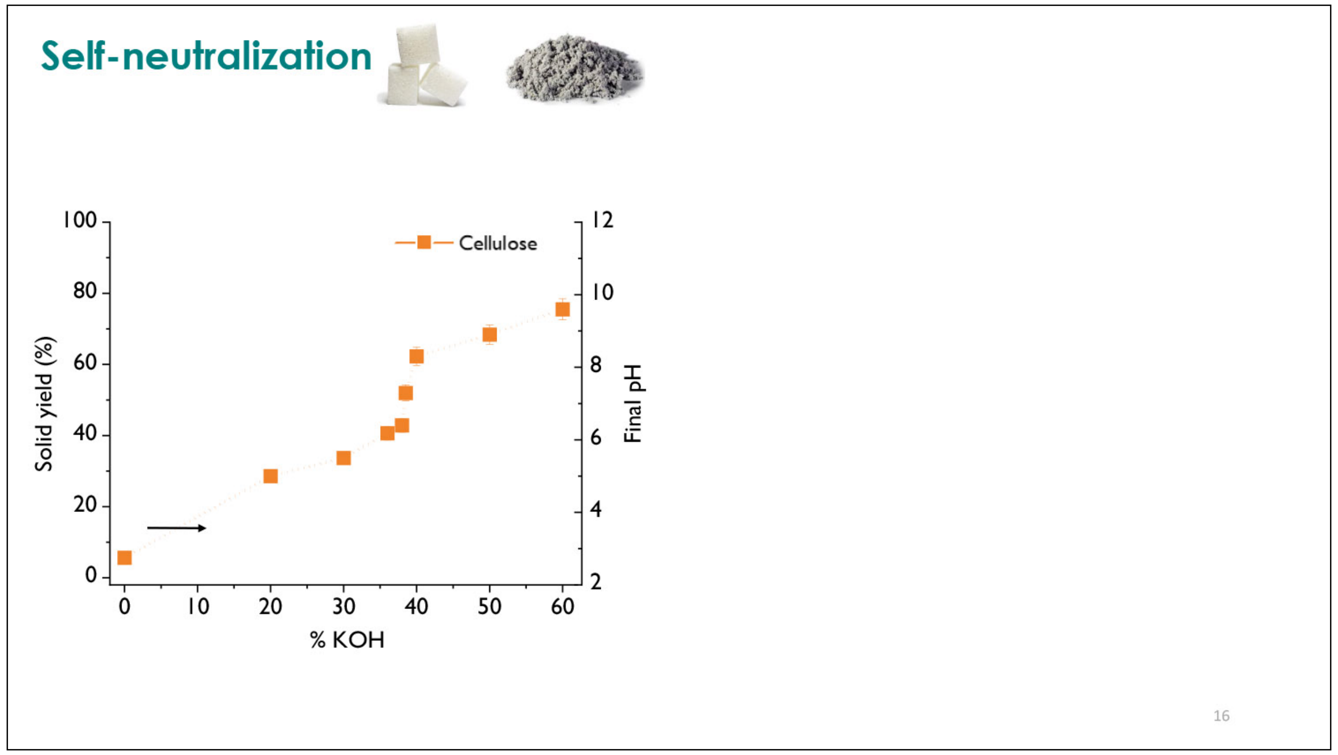

Hydrothermal humification
180-250°C
Carbonization
Pressure (bar)
0
50
100
150
200
250
50
100
150
200
250
300
350
400
Temperature (°C)
11


Why is different?


Hydrothermal humification
Hydrochar in soil
• Phytotoxicity (furans and phenols)
• Post-treatments needed
Source: Celletti et al. (2021), Karatas et al. (2022), Scrinzi et al. (2022)
180-250°C
Carbonization
Pressure (bar)
0
50
100
150
200
250
50
100
150
200
250
300
350
400
Temperature (°C)
12

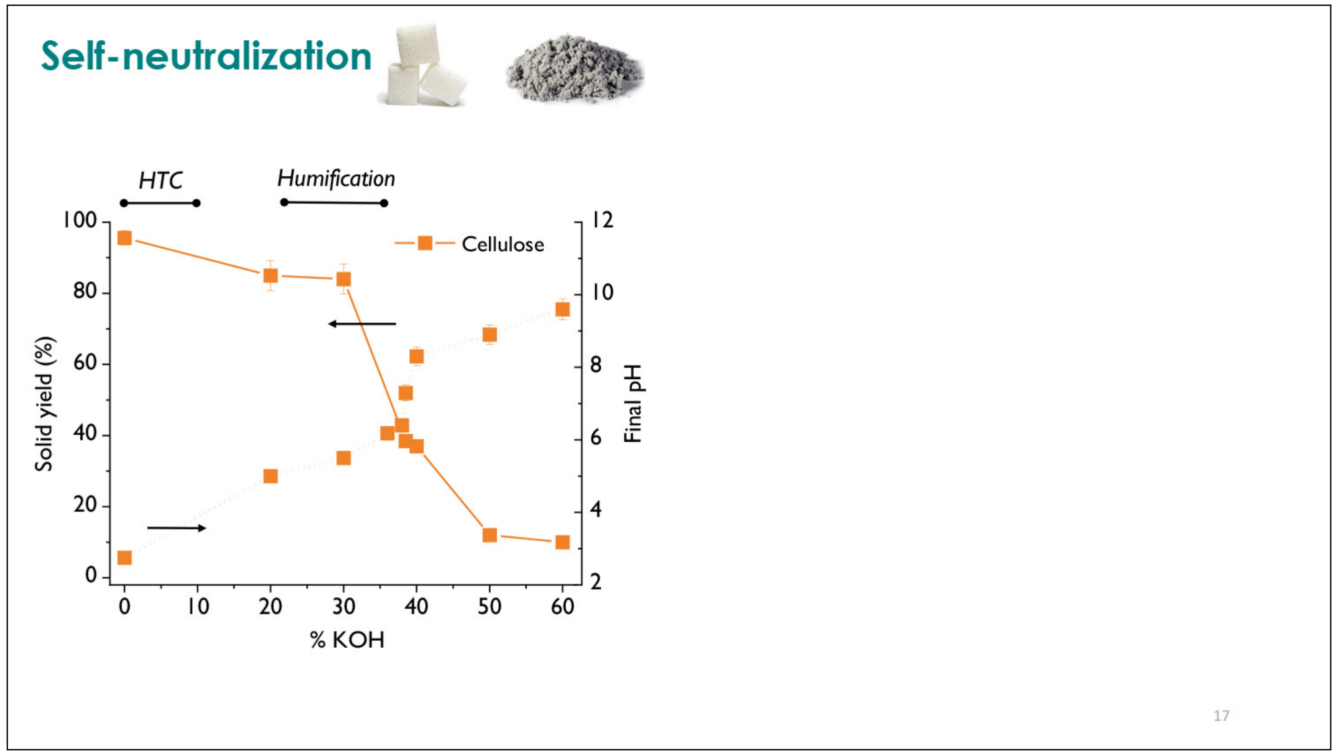

Hydrothermal humification
Glucose
Cellulose
Lignin
220°C, 4 h
Alkaline agent
(KOH)
Artificial humic matter
14

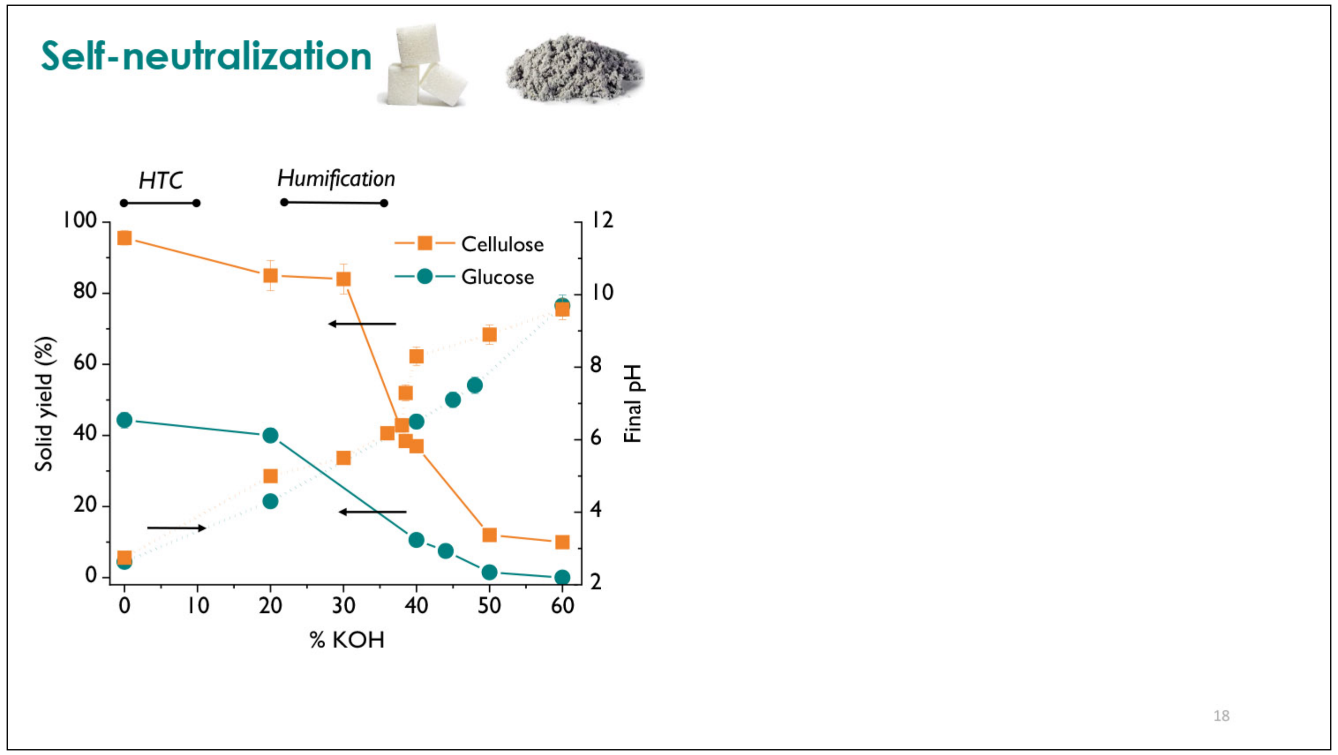

Hydrothermal humification
Glucose
Cellulose
Lignin
220°C, 4 h
Alkaline agent
(KOH)
Artificial humic matter
Humic acid (solid
at pH < 1,5)
Humin (solid
residue)
Fulvic acid
Composition, HPLC, ss-
NMR, H-NMR, XPS
15


Self-neutralization
Cellulose
Solid yield (%)
Final pH
% KOH
16

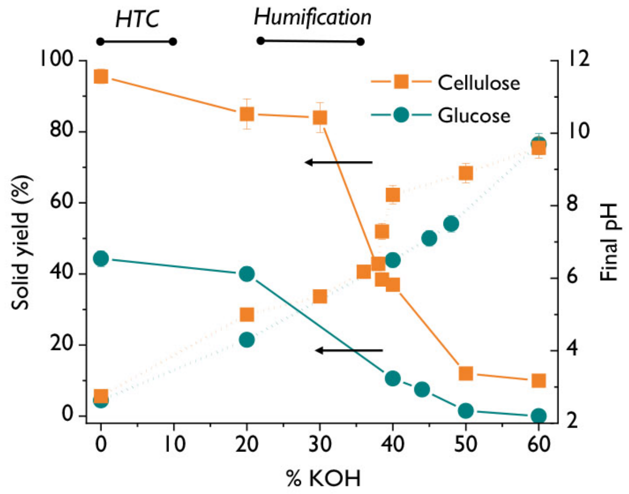




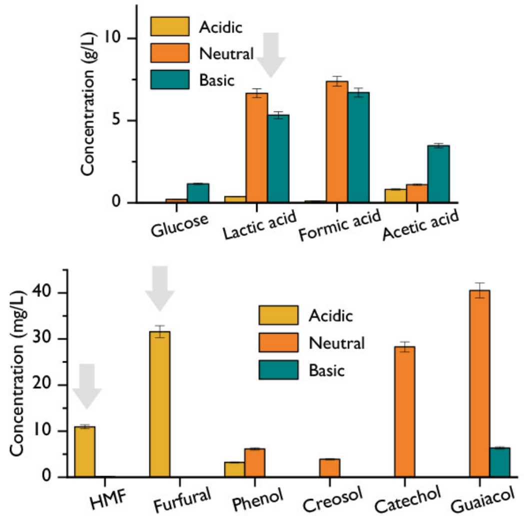

Self-neutralization
HTC
Humification
Cellulose
Solid yield (%)
Final pH
% KOH
17


Self-neutralization
HTC
Humification
Cellulose
Glucose
Solid yield (%)
Final pH
% KOH
18

## Self-neutralization




Liquid phase from cellulose (HPLC)

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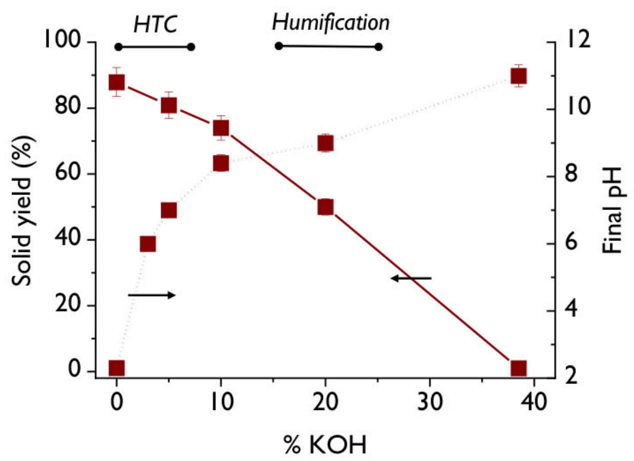
## Self-neutralization

Solid yield and pH



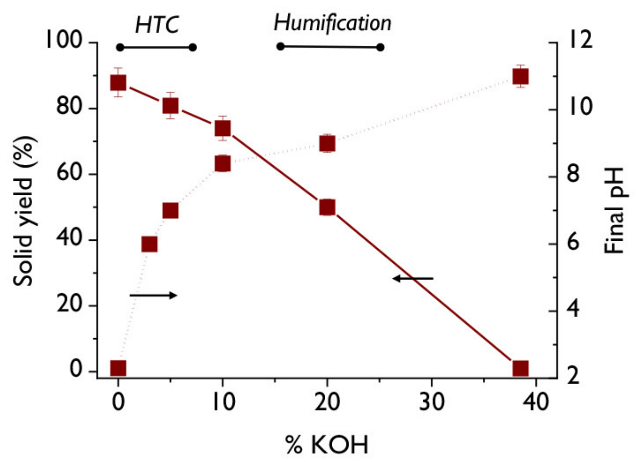

20



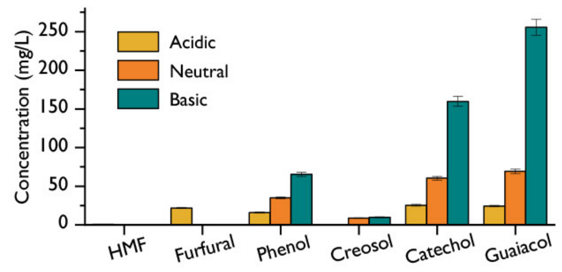


## Self-neutralization

Solid yield and pH



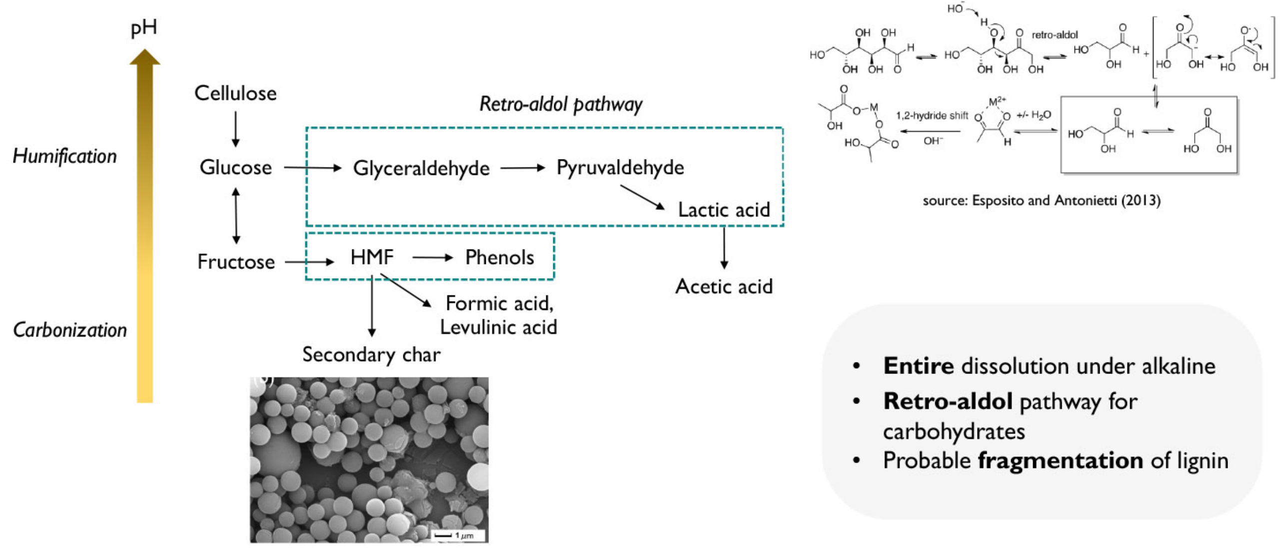

Liquid phase (HPLC)




- **Entire** dissolution under alkaline
- Probable **fragmentation**

21

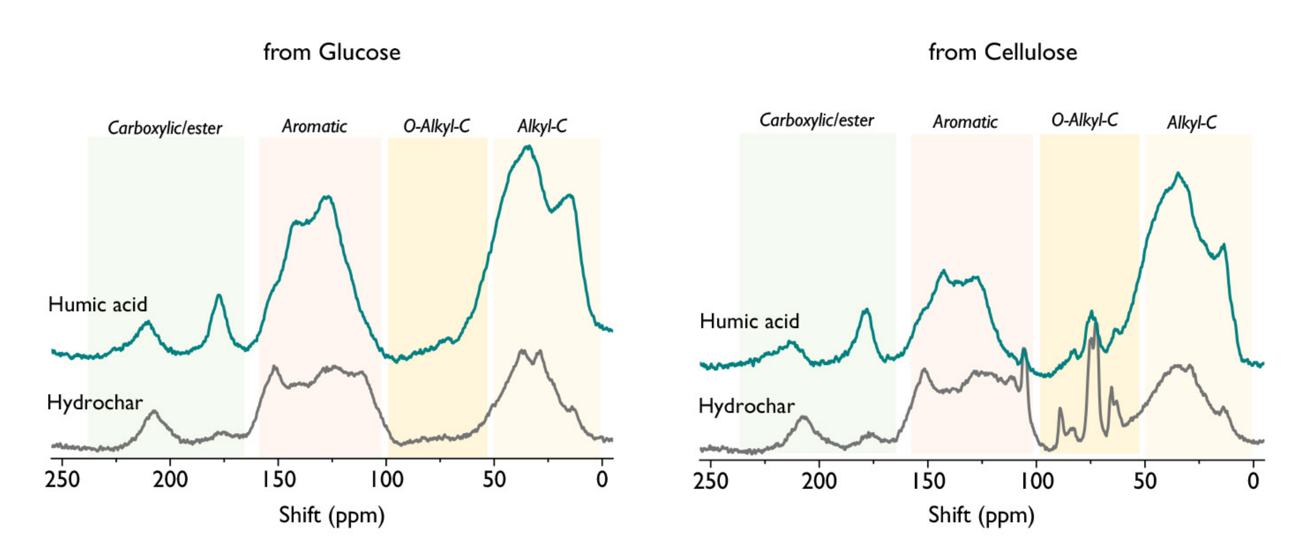
## Pathways




- **Entire** dissolution under alkaline
- **Retro-aldol** pathway for carbohydrates
- Probable **fragmentation** of lignin

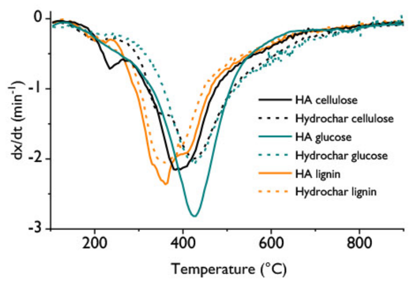
22

## Solid state NMR



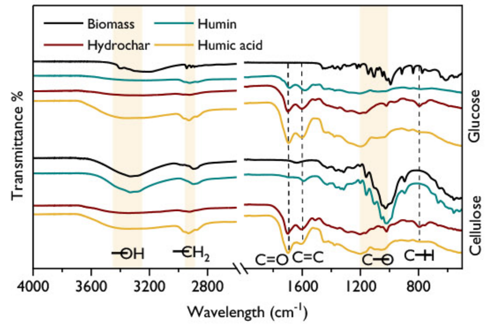

## Other data

DTG curves

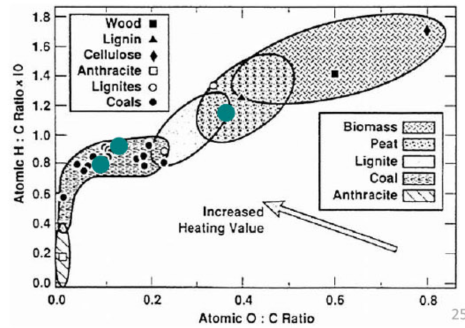


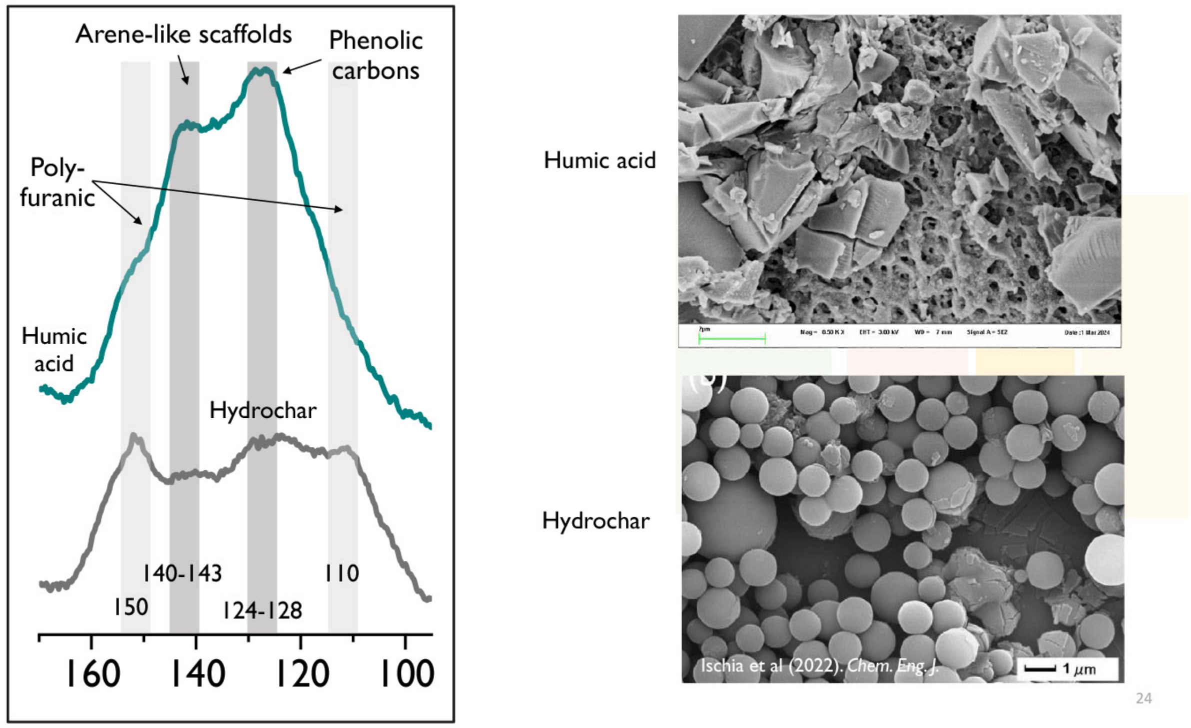

| Substrate | Final pH | Yield (%) | Elemental (wt.%) C | Elemental (wt.%) H | Elemental (wt.%) O* | TGA res (%) |
|---|---|---|---|---|---|---|
| Glucose | HA neutral | 1.2 | 64.6 | 5.5 | 30 | 44.8 |
| | HA alkaline | 3.1 | 78.1 | 5.9 | 15.1 | 47.1 |
| | Hydrochar | 44.3 | 67.9 | 5.6 | 26.6 | 66.5 |
| Cellulose | HA neutral | 1.1 | 63.4 | 5.8 | 30.8 | 50.9 |
| | HA alkaline | 3.2 | 76.2 | 6.6 | 16.4 | 42.0 |
| | Hydrochar | 50.2 | 69.3 | 4.6 | 26.2 | 49.5 |
| Lignin | HA neutral | 80.1 | 62.6 | 5.2 | 32.2 | 49.0 |
| | HA alkaline | 98.1 | 79.6 | 6.1 | 13.6 | 53.3 |
| | Hydrochar | 87.9 | 68.9 | 5.6 | 25.2 | 46.2 |

FTIR

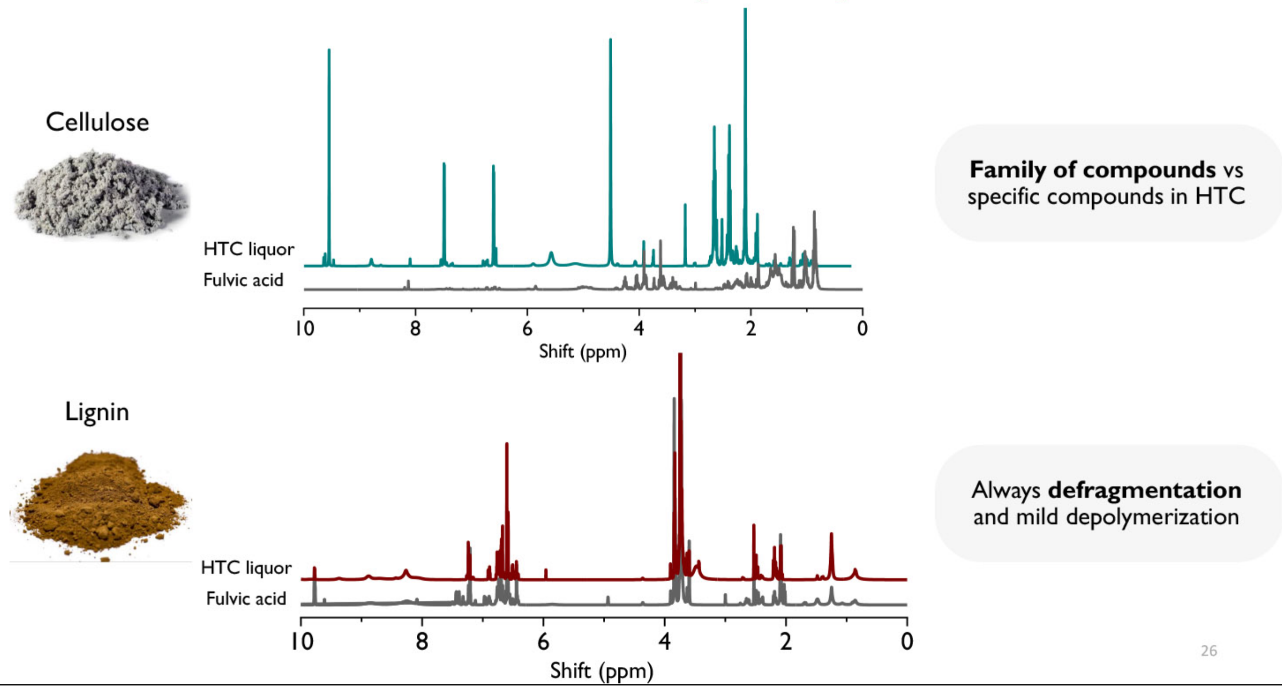


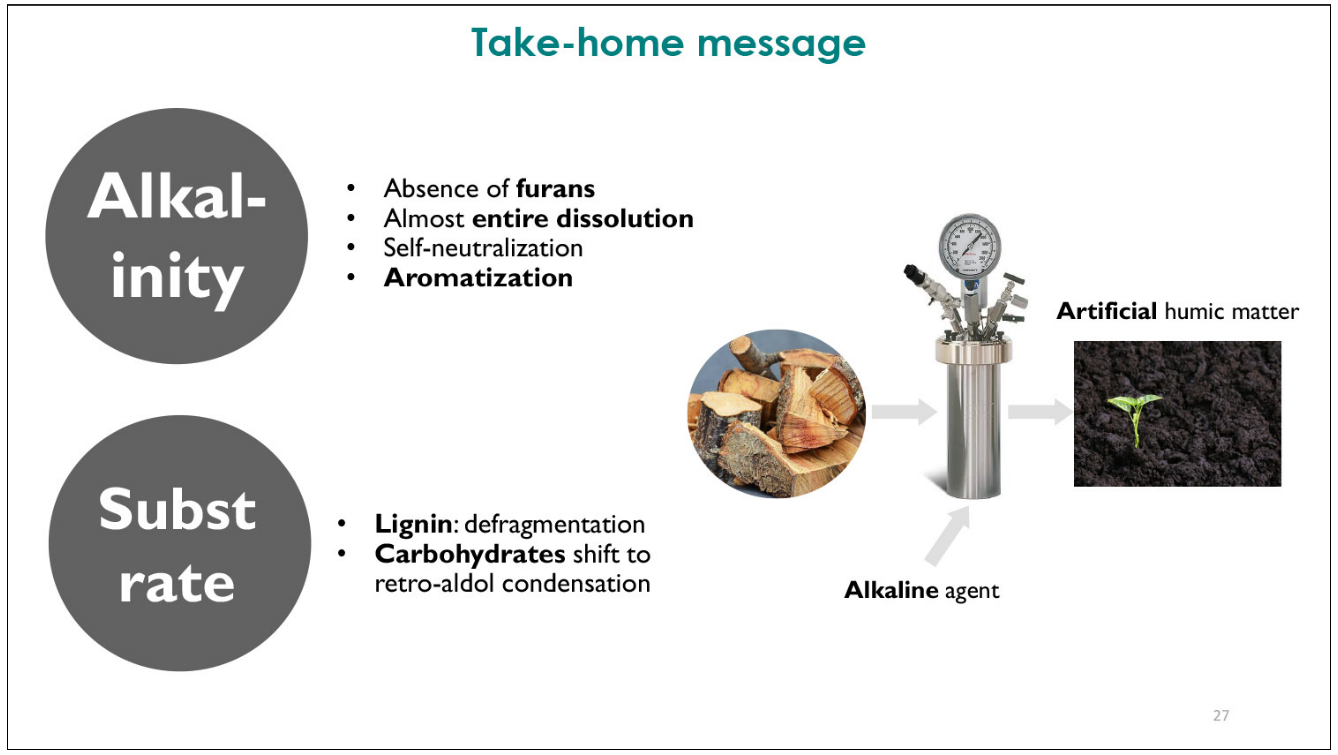

Humic acids on Van Kreleven

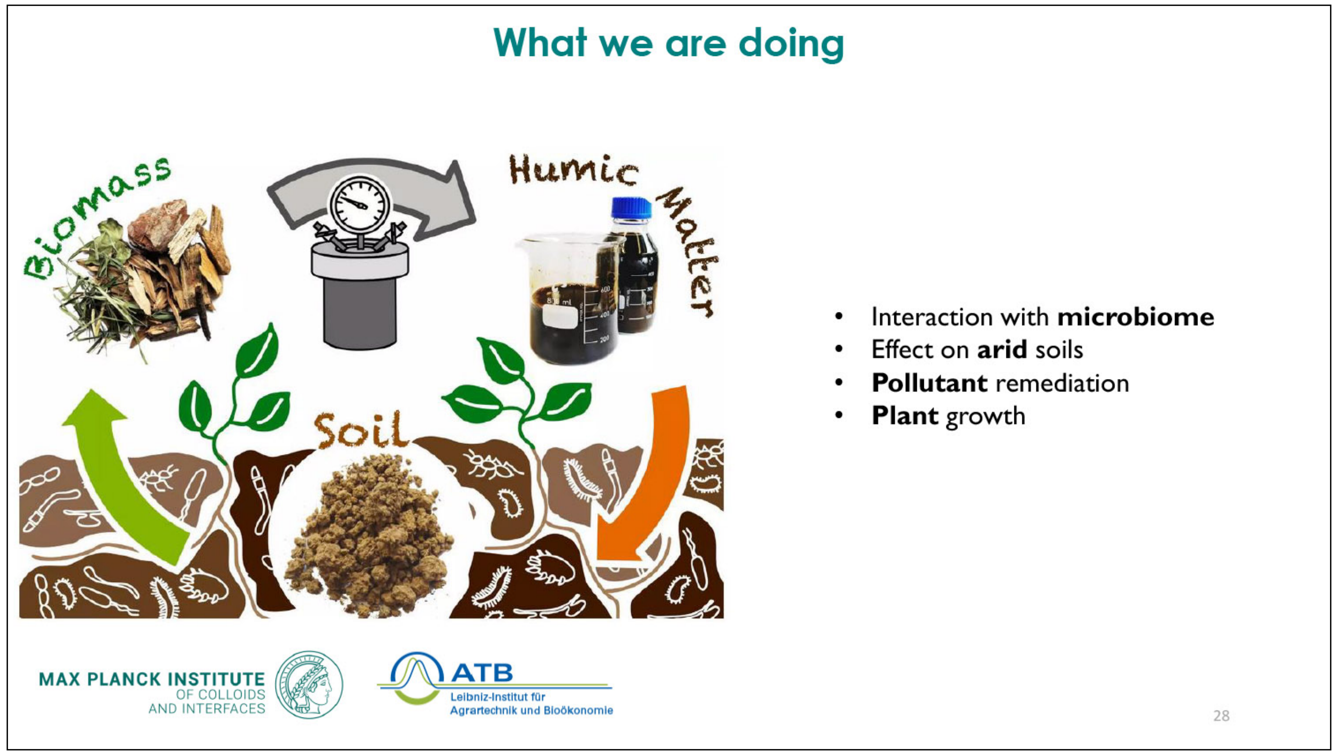



## Fulvic acids (H-NMR)




Take-home message
Alkal-inity
Absence of furans
Almost entire dissolution
Self-neutralization
Aromatization
Artificial humic matter
Subst rate
Lignin: defragmentation
Carbohydrates shift to retro-aldol condensation
Alkaline agent
27


What we are doing
Biomass
Humic Matter
Soil
Interaction with microbiome
Effect on arid soils
Pollutant remediation
Plant growth
MAX PLANCK INSTITUTE OF COLLOIDS AND INTERFACES
ATB Leibniz-Institut für Agrartechnik und Bioökonomie
28






What we are doing
Biomass
Humic Matter
Soil
MPI humic matter webpage
MAX PLANCK INSTITUTE OF COLLOIDS AND INTERFACES
ATB Leibniz-Institut für Agrartechnik und Bioökonomie
with A. Volikov, K. Pakzad., T. Seemann and M. Antonietti
with D. Höfle and A. Abdelfattah
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Thanks!!
Questions?
HTP Hydrothermale Prozesse
E-mail: giulia.ischia@mpikg.mpg.de
Alexander von HUMBOLDT STIFTUNG

*Lisa Röver, Deutsches Biomasseforschungszentrum*

## HYTORF II – Production of a hydrochar-based peat substitute

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**Keywords:** peat substitute, soil amendment, horticulture, green cuttings, hydrothermal conversion

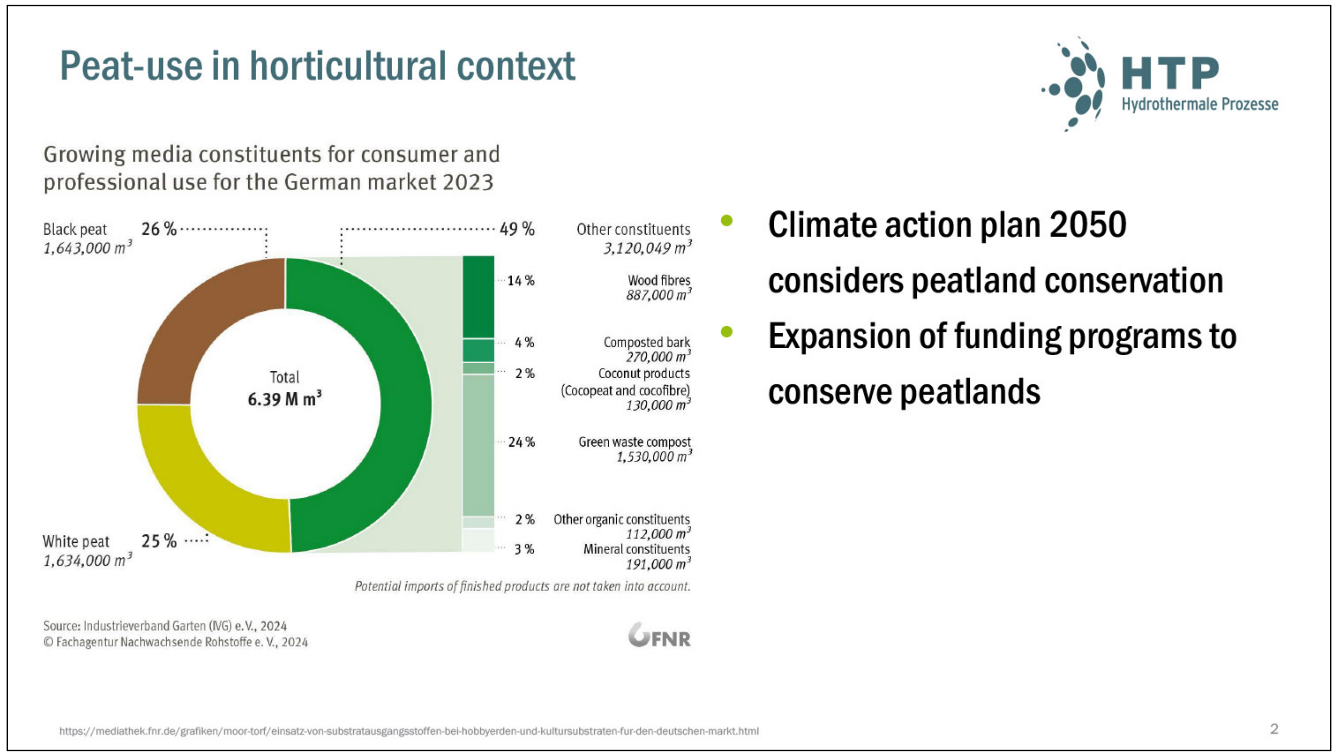
The German government's Climate Action Plan 2050 includes measures to reduce the use of peat in hobby soils and growing media. The regulations are initially voluntary, but are recognized by the substrate industry. Therefore, research must be conducted on peat substitutes which are ecologically and economically feasible. HYTORF II aims at the use of biogenic residual materials and its hydrothermal conversion to obtain a peat substitute of high quality in terms of nutrient and salt content, degradation stability, and a stable N-balance. The biomass used here is green cuttings from flowering meadows.

Experiments in lab-scale were conducted and showed promising properties of water retention and growth. The optimal conditions were a relatively mild hydrothermal conversion of 150 °C and 30 min holding time. To research the performance of this peat substitute under real conditions in soil mixtures, approx. 3 tons of hydrochar will be produced by HTCycle AG. These will then be dewatered to a water content of 50 % and subsequently mixed with soil by Störk GmbH. Detailed results and the upscaling will be presented.

This is the first approach of a hydrothermally produced peat substitute at an industrial scale. Next steps include the testing of the soil in growing experiments, hydro-physical experiments, and having a look into the aging and storage behavior. Additionally, this production is used for a detailed economic and ecological assessment of the production and the overall process.

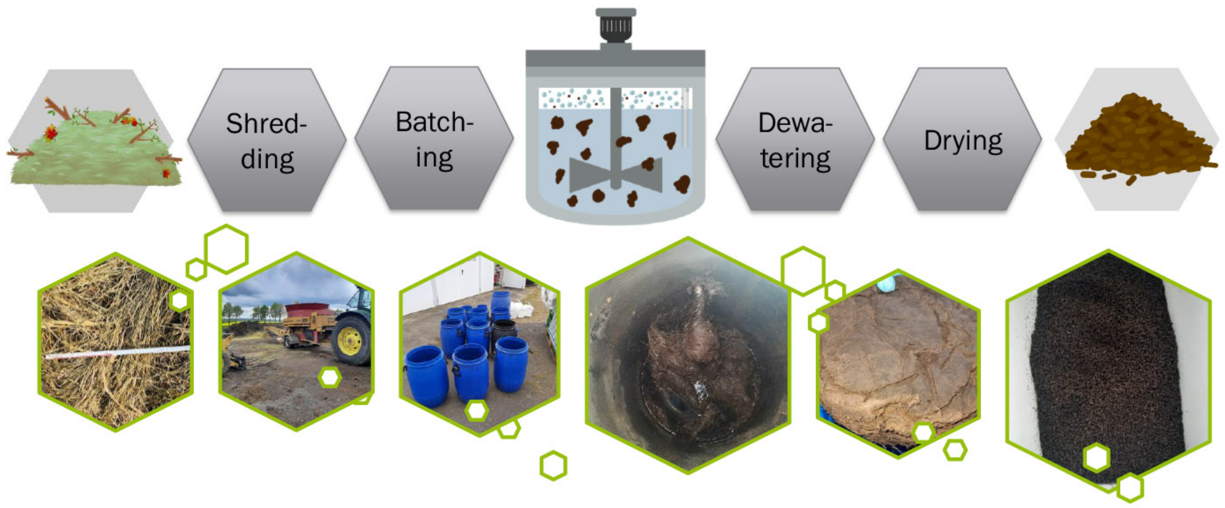




## HYTORF II – hydrochar based peat substitute

HTP Hydrothermale Prozesse




3

## Small scale experiments: Influence of the HTC on the appearance

HTP Hydrothermale Prozesse

4





## Hydrochar based peat substitutes Challenges and solutions

HTP Hydrothermale Prozesse

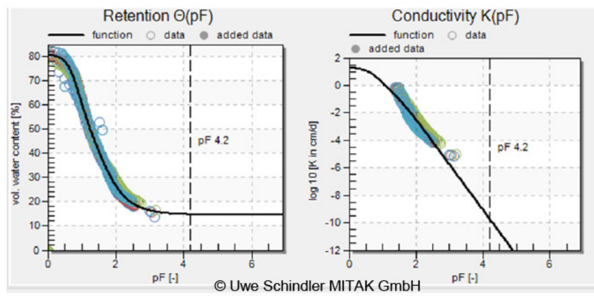
- **Previous project had some issues that were addressed within this project**
- **Major problem: Mold during storage was limited by drying the hydrochar and an inertisation during transport**
  - Experts opinion: fermentation or composting of the hydrochar is needed to stop molding
- **Nitrogen-distribution**
- **Phytotoxicity of the process water remaining in the hydrochar**
  - Washing the hydrochar, but difficult for upscaling

5

## Peat substitutes quality testing

HTP Hydrothermale Prozesse

### Water retention

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### Phytotoxicity

© Josef Schlaghecken

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# Upscaling

7

## Production of ca. 3 t of peat substitute


- Mild HTC-conditions
  - 150 °C, 30 min
  - DM in the reactor ca. 5 %
- DM content of the resulting hydrochar: 50 %

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Large scale production of peat substitutes

## Challenges

- Feeding system for a large batch reactor is pump based
  - Difficulties for fibre-rich substrates
- Clogging of the pipes
- Shredding of the fibre-rich substrates with residual moisture content to a small length
- Timewise: Production ready for the vegetative period

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## Next steps in 2025

- Mixing the hydrochar with other peat substitutes in order to produce a substrate for cultivation
- Testing the substrate with plant cultivation
- Storage tests for the mixed substrate
- Aging behavior for the mixed substrate

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## 8th Expert Forum on Hydrothermal Processes

HTP Hydrothermale Prozesse

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*Chau Huyen Dang, Leibniz Institute for Agricultural Engineering and Bioeconomy*

# Co-HTC using coffee by-products to recover carbon and nutrients for soil amendment

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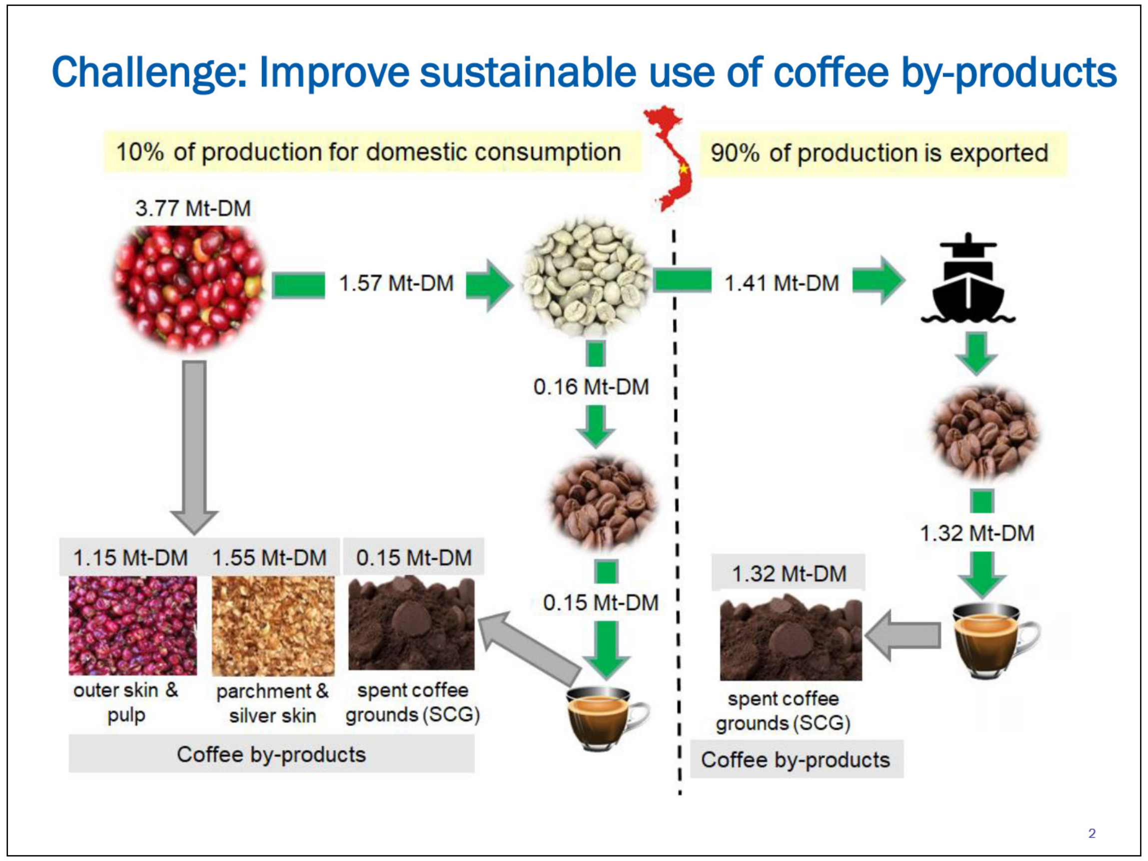
**Keywords:** Coffee beans, fertiliser, hydrochar, soil improvement, HTC products

Two types of coffee by-products can be produced regionally in coffee-growing countries from the processing of coffee berries to coffee beans, depending on whether a wet or dry method is used. A similar amount of dry residue is generated in both types of coffee berry processing methods, i.e. approximately 1 kgDM of by-products per kgDM green coffee beans, however the type, handling and treatment requirements for the residues are different. In Vietnam, the processing sector is transitioning from dry to wet methods to improve the quality of the coffee beans, therefore, the amount of wet residues (e.g. pulp, mucilage, accompanied by wastewaters) being produced is increasing, alongside dry coffee husks. Incorrect disposal of the wet, biologically unstable, by-products can cause phytosanitary and environmental impacts, besides wasting their potential as a source of carbon and nutrients NPK that can be utilized for fertilizing coffee farms.

In this study, the use of the co-hydrothermal carbonization process (Co-HTC) is being investigated to treat the two types of by-products simultaneously into carbon-rich material (hydrochar) to recover carbon and nutrients NPK for use as soil amendments. Experiments were carried out using a definitive screening design with six process variables to determine the influence of co-HTC conditions on the hydrochar properties, as well as the optimal process setting for obtaining the ideal recovery of carbon and nutrient applied as soil amendments afterward. The process conditions that were varied included: temperature (160 – 240 °C), holding time (1 – 5 h), pH value (7 – 13), solid content (15 – 25 wt%-db), agitation (0 – 200 rpm), and by-product mixture (from 100 % dry to 100 % wet). The changes in the hydrochars produced were evaluated in terms of their carbon and nutrient content.

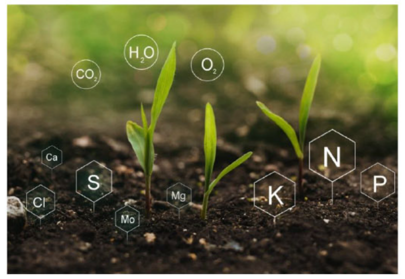
The presentation will discuss the potential of substituting hydrochar from coffee by-products for fertilizer on coffee farms. In addition, based on interviews of local stakeholders on their willingness to use the HTC products, an assessment of the socio-economic impacts of deploying such systems in the coffee sector will be presented.

## Research questions

**Co-HTC conversion and Carbon and Nutrients (NPK) Recovery**

- Can co-hydrothermal carbonization (co-HTC) improve the recovery of carbon and nutrients (NPK) from coffee berry by-products?
- Which co-HTC parameters significantly influence the recovery of carbon and nutrients (NPK)?
- How do CNPK substitute the demand of CNPK for coffee farms in every season?

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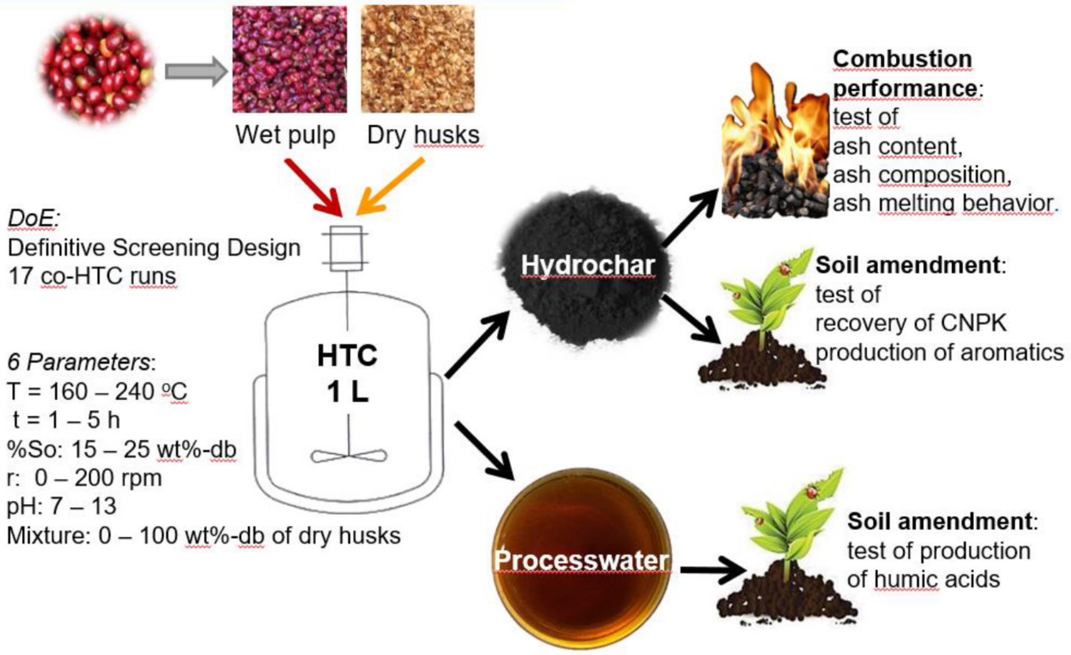
## Material and Methods

Berry by-products: from berries to beans








## Methodology

*DoE - Definitive Screening Design:* 6 parameters varied, 17 HTC/co-HTC runs

| Runs | | Codes* | | Moisture | HTC process parameters | | | | | | SF |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Hydrochars HC_ | Process water PW_ | [wt%] | %So [wt%-db] | T [°C] | t [h] | A [rpm] | pH [-] | Mix [wt%-db] | [-] |
| 1 | P_200_1_pH7 | HCP_200_1_pH7 | PWP_200_1_pH7 | 74.24 | 15.25 | 200 | 1 | 0 | 7 | 0 | 5 |
| 2 | H_160_1_pH13 | HCH_160_1_pH13 | PWH_160_1_pH13 | 7.57 | 15.24 | 160 | 1 | 200 | 13 | 100 | 4 |
| 3 | M_160_1_pH7 | HCM_160_1_pH7 | PWM_160_1_pH7 | 60.08 | 24.99 | 160 | 1 | 200 | 7 | 50 | 4 |
| 4 | H_200_5_pH13 | HCH_200_5_pH13 | PWH_200_5_pH13 | 7.41 | 25.26 | 200 | 5 | 200 | 13 | 100 | 5 |
| 5 | H_240_1_pH7 | HCH_240_1_pH7 | PWH_240_1_pH7 | 7.45 | 24.99 | 240 | 1 | 100 | 7 | 100 | 6 |
| 6 | H_160_5_pH10 | HCH_160_5_pH10 | PWH_160_5_pH10 | 7.49 | 25.02 | 160 | 5 | 0 | 10 | 100 | 4 |
| 7 | P_240_3_pH13 | HCP_240_3_pH13 | PWP_240_3_pH13 | 74.49 | 25.24 | 240 | 3 | 200 | 13 | 0 | 6 |
| 8 | H_240_1_pH13 | HCH_240_1_pH13 | PWH_240_1_pH13 | 7.49 | 20.25 | 240 | 1 | 0 | 13 | 100 | 6 |
| 9 | P_160_5_pH13 | HCP_160_5_pH13 | PWP_160_5_pH13 | 74.88 | 15.22 | 160 | 5 | 100 | 13 | 0 | 4 |
| 10 | M_240_5_pH13 | HCM_240_5_pH13 | PWM_240_5_pH13 | 59.53 | 14.98 | 240 | 5 | 0 | 13 | 50 | 7 |
| 11 | P_160_1_pH13 | HCP_160_1_pH13 | PWP_160_1_pH13 | 74.65 | 25.09 | 160 | 1 | 0 | 13 | 0 | 4 |
| 12 | P_160_5_pH7 | HCP_160_5_pH7 | PWP_160_5_pH7 | 74.28 | 20.22 | 160 | 5 | 200 | 7 | 0 | 4 |
| 13 | M_200_3_pH10 | HCM_200_3_pH10 | PWM_200_3_pH10 | 59.5 | 20.01 | 200 | 3 | 100 | 10 | 50 | 5 |
| 14 | H_240_5_pH7 | HCH_240_5_pH7 | PWH_240_5_pH7 | 7.27 | 15.12 | 240 | 5 | 200 | 7 | 100 | 7 |
| 15 | H_160_3_pH7 | HCH_160_3_pH7 | PWH_160_3_pH7 | 7.46 | 14.99 | 160 | 3 | 0 | 7 | 100 | 4 |
| 16 | P_240_1_pH10 | HCP_240_1_pH10 | PWP_240_1_pH10 | 74.45 | 15.08 | 240 | 1 | 200 | 10 | 0 | 6 |
| 17 | P_240_5_pH10 | HCP_240_5_pH7 | PWP_240_5_pH7 | 74.58 | 24.97 | 240 | 5 | 0 | 7 | 0 | 7 |

P indicates HTC runs with only wet pulp (mixture of 0 wt%-db); H indicates HTC runs with only dry husk (mixture of 100 wt%-db); M indicates HTC runs using a mixture of 50 wt%-db of wet pulp and 50 wt%-db of dry husk. SF = severity factor.

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## Results _ *Difficulties on dewartering the final products*

| Case 1 separated hydrochars | Case 2 unseparated hydrochars |
|---|---|
| Case 1 includes all 17 separated hydrochars (vacuum filtration and pressed) for the modeling analysis in order to gain insight into effects on the physical and chemical properties. Further experiments with more consistent separation (e.g. centrifugation) would be needed to develop more quantitative trends. | Case 2 includes the 9 hydrochars separated by vacuum filtration and the 8 slurries (of the hard-to-separate hydrochars mainly from the wet pulp at low temperatures) to evaluate the results to be expected at real coffee processing plants considering practical operating conditions. |

**Separated HC**

**Unseparated HC**

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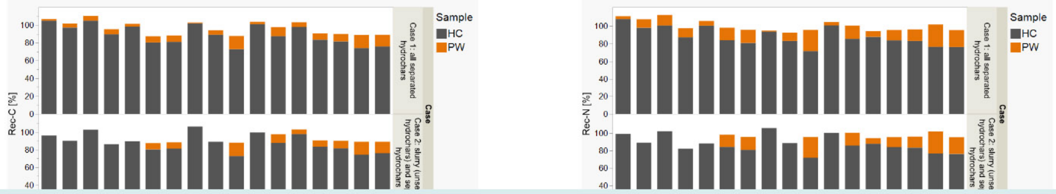
## Results _ *Distribution of CNPK in final products*



Recoveries of C and N in the hydrochars: 71 – 100 % for all process conditions, mixtures, and cases.
The evaluation of P and K-recoveries shows more variability between feedstocks and process conditions.

- The P recovery: temperature and pH dependencies (highest values found at 240 °C and more neutral pH (7, 10), but different from feedstock type (up to 110 % for wet pulp, up to 84 % for dry husks).
- The K recovery in HCs is lower than the others due to its highly water soluble property. The high value are found for runs at 240 °C (using dry husks 22 - 50 % depending on pH) and the 50% mixture (28 %).

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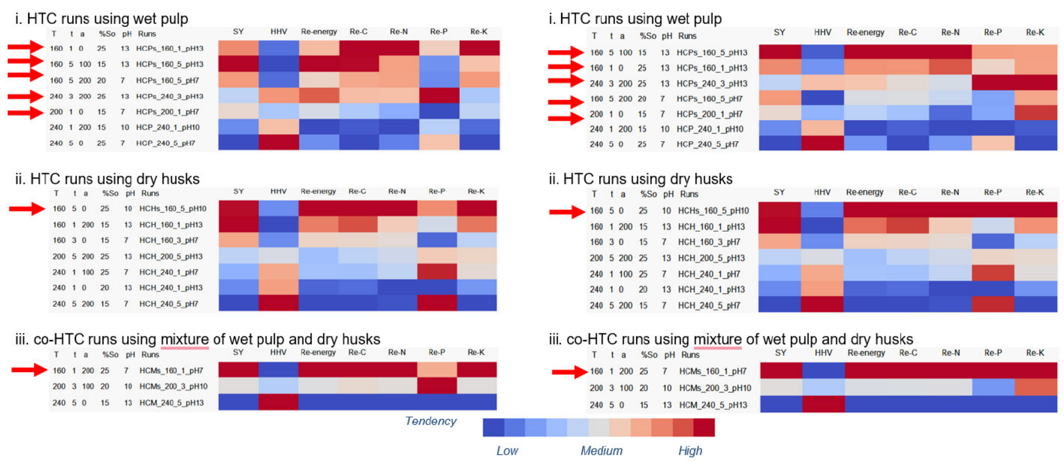
## Results _ *Distribution of CNPK in final products*

| Case 1 separated hydrochars | Case 2 unseparated hydrochars |
|---|---|



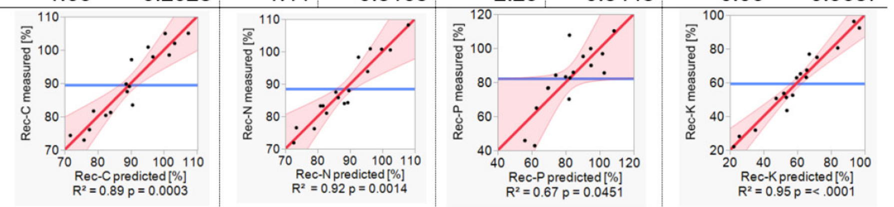

8





## Results _ Significant effect of input process parameters

| Parameter estimates | Rec-C [%] | | Rec-N [%] | | Rec-P [%] | | Rec-K [%] | |
|---|---|---|---|---|---|---|---|---|
| | *slope* | *p* | *slope* | *p* | *slope* | *p* | *slope* | *p* |
| *Intercept* | 89.58 | <.0001 | 80.85 | <.0001 | 82.22 | <.0001 | 59.55 | <.0001 |
| T [°C] | -9.50 | <.0001 | -7.61 | 0.0001 | 2.15 | 0.5678 | -16.51 | <.0001 |
| t [h] | -1.30 | 0.3105 | 0.52 | 0.6497 | 1.23 | 0.7416 | -5.07 | 0.0087 |
| a [rpm] | 1.57 | 0.2277 | 4.38 | 0.0045 | 6.29 | 0.1152 | 3.30 | 0.0601 |
| %So [wt%-db] | 2.98 | 0.0350 | -4.70 | 0.0030 | 7.27 | 0.0741 | 9.15 | 0.0002 |
| mix [wt%-db] | -3.93 | 0.0092 | 1.11 | 0.3497 | -12.75 | 0.0058 | -9.74 | <.0001 |
| pH [-] | 1.66 | 0.2028 | 1.11 | 0.5165 | -2.29 | 0.5443 | 0.06 | 0.9687 |
| Plot (Measured vs Predicted) | | | | | | | | |




Blue line = null hypothesis (that the response is independent of the factors); Red line = alternative hypothesis (that the response depends on the factors); Light red zone = confidence region

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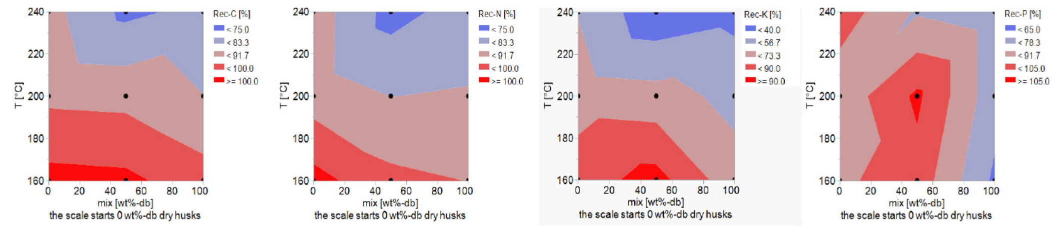
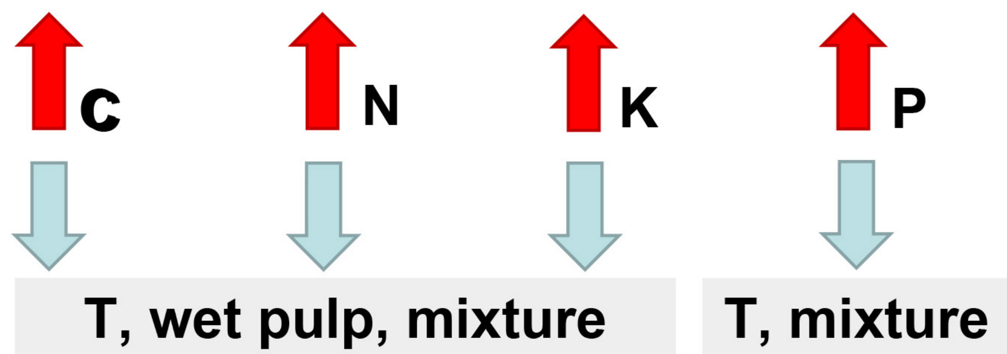
## Results _ Significant effect of input process parameters

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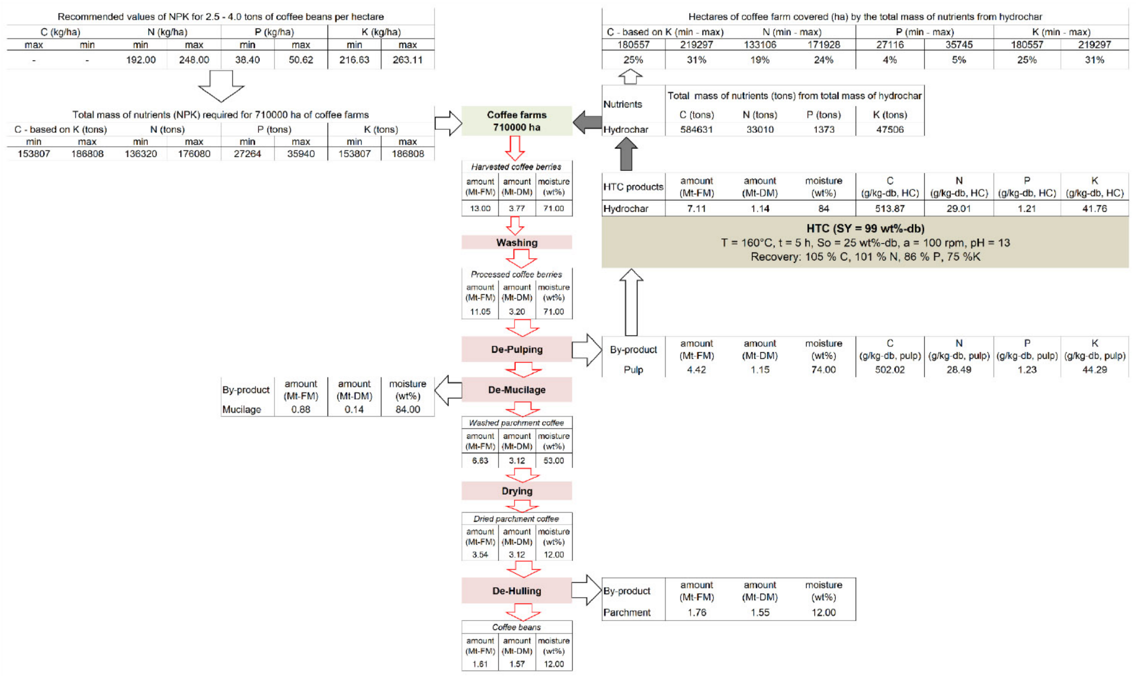
## Results _ Fertilizing CNPK from hydrochar to coffee farms

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## Conclusions

These findings indicate that high recoveries of C, N, P, and K can be achieved in hydrochars from coffee berry by-products.

- Especially the unseparated slurries produced at low temperatures from wet pulp achieved good recoveries (> 80 % for CNP and > 50 % for K), which makes them interesting for recycling the elements to agricultural fields.
- Even the separated hydrochars have high values for C and N recoveries (> 80 %) under most conditions and feedstocks.
- Unfortunately, P and K recoveries are inversely related in the separated hydrochars, higher temperatures increase P recovery but diminish Rec-K.
- Such a well-mixed slurry could be used directly to distribute the elements evenly around the coffee plants, or aggregated and dried into pellets before spreading.
- Further experiments are recommended to determine if the higher recovery of P and K in hydrochars from wet pulp than from dry husks is only due to the poorer separation of process water and to clarify the effect of pH. The results of the additional experiments can then be used to determine if the mixture of wet pulp and dry husks can improve this recovery more than dry husks alone.

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Leibniz-Institut für Agrartechnik und Bioökonomie

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HDang@atb-potsdam.de

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Leibniz Association

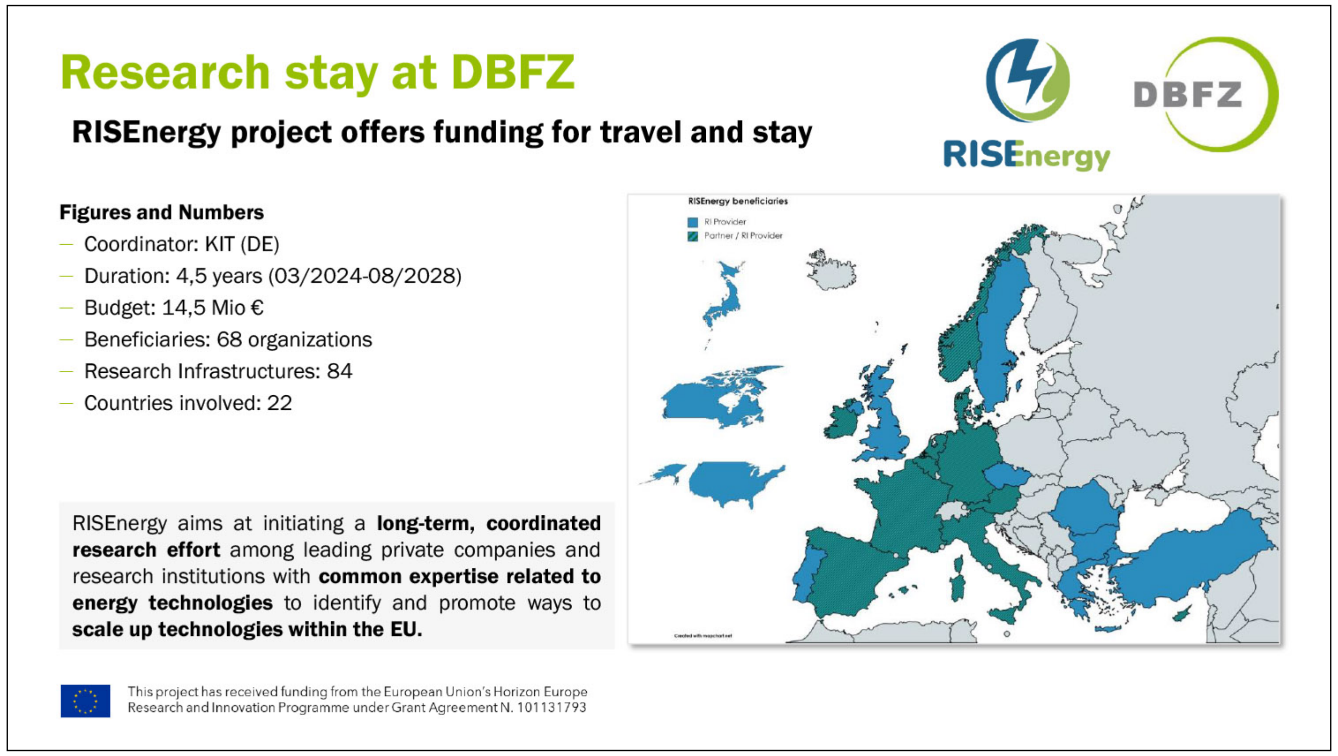
# ANNEX

## Research stay at DBFZ










## Host

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### Our Mission

The DBFZ was founded in 2008 by the former Federal Ministry of Food, Agriculture and Consumer Protection (BMELV) with the aim of establishing a central research institution for all relevant fields of bioenergy research and to network the results of the very diverse German research landscape in this sector. The scientific mission of the DBFZ is to provide comprehensive scientific support for the efficient integration of biomass as a valuable resource for sustainable energy supply within the framework of applied research. This mission encompasses technical, ecological, economic, social and energy management aspects along the entire process chain (from production to supply and utilisation). The development of new processes, procedures and concepts is accompanied and supported by the DBFZ in close co-operation with industrial partners. At the same time, there is close networking with public German research in the agricultural, forestry and environmental sectors, as well as with European and international institutions. Based on this broad research background, the DBFZ also develops scientifically sound decision-making aids for policymakers.






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