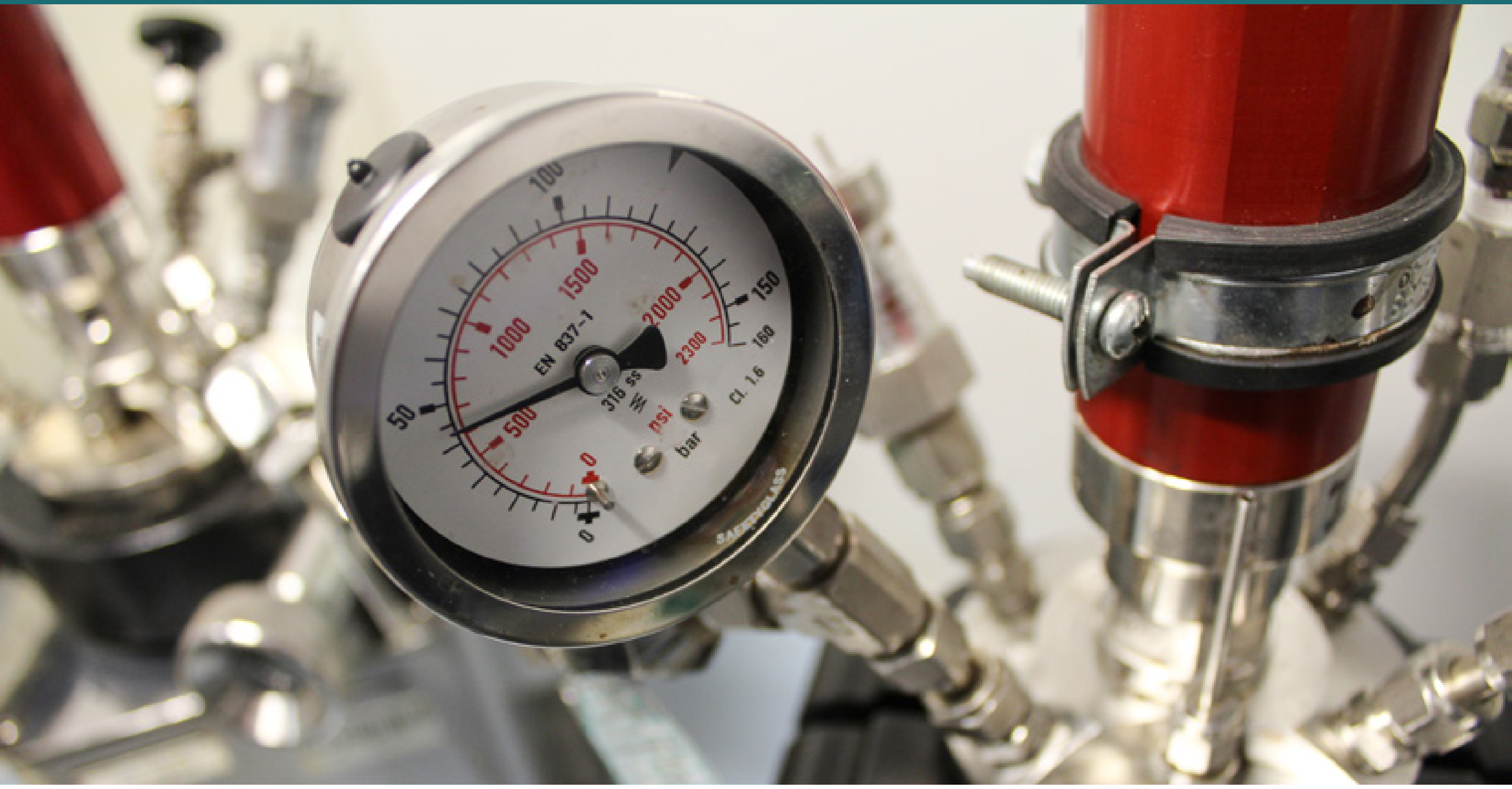
HTP-Fachforum

Hydrothermale Prozesse zur stofflichen und energetischen Wertschöpfung

25./26. NOVEMBER 2020 | LEIPZIG, DBFZ



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HTP
Hydrothermale Prozesse

IMPRESSUM

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Gestaltung: Stefanie Bader, Beate Kämpf / **DTP:** Beate Kämpf

HTP-Fachforum 2020

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SESSION III

FRAGEN ZUR DEMONSTRATION UND ANWENDUNG

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TECHNOLOGIEBEWERTUNG HYDROTHERMALER VERFAHREN

Grußwort

Sehr geehrte Teilnehmende des HTP-Fachforums 2020,

wir danken Ihnen herzlich für Ihre Teilnahme und Ihr Engagement zum diesjährigen 6. Fachforum Hydrothermale Prozesse 2020. Mit Ihrem Interesse und Ihrem wertvollem Input haben Sie wesentlich zum Erfolg der Veranstaltung beigetragen. Anders als üblich haben wir uns aufgrund der derzeitigen Corona-Situation virtuell – im wahrsten Sinne des Wortes – zusammengeschaltet und vernetzt. In insgesamt sechs Sessions wurden verschiedenste Themen und Forschungsansätze aus allen Bereichen der hydrothermalen Prozesse vorgestellt. Ein besonderer Fokus lag dabei in diesem Jahr auf internationalen Aktivitäten rund um die hydrothermale Verflüssigung von Biomasse. Nationales und internationales Feedback hat uns erreicht. Insgesamt 70 Teilnehmende aus 10 verschiedenen Ländern waren vertreten, vorwiegend aus wissenschaftlichen und wirtschaftlichen Bereichen.

Neben einer Vielzahl von Referent*innen zu den unterschiedlichsten Aspekten der hydrothermalen Prozesse durften wir u. a. Prof. Dr. Andrea Kruse von der Universität Hohenheim als Keynote-Speakerin begrüßen. In ihrer Präsentation stellte sie Wasser als außergewöhnliches Reaktionsmedium und Reaktionspartner dar. Wie gewohnt war dieser Blick auf die Grundlagen unseres Arbeitsgebietes wieder sehr anregend und hat viele Aspekte, die unsere tägliche Arbeit betreffen, noch einmal wissenschaftlich auf den Punkt gebracht.

Im vorliegenden Tagungsreader präsentieren wir Ihnen die eingereichten Abstracts und Folien zum Nachlesen. Wir danken Ihnen für Ihre Teilnahme und verbleiben mit den besten Grüßen. Bis zum nächsten Mal!

M. Klemm

Dr. Marco Klemm, DBFZ

Opening Session

Prof. Dr. Andrea Kruse, Universität Hohenheim

Wasser als außergewöhnliches Arbeitsmedium – „ein magisches Lösungsmittel“

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E-Mail: **andrea_kruse@uni-hohenheim.de**

Unter hydrothermalen Verfahren werden Prozesse verstanden, die in Wasser unter erhöhten Temperaturen und Drücken entstehen. Die meisten hydrothermalen Verfahren, im engeren Sinne dieses Begriffes alle, verlaufen in flüssigem Wasser, d.h. unter einem Druck, der höher als der Dampfdruck ist. Je nach Temperatur können mittels hydrothermaler Prozesse feste, flüssige und gasförmige Brennstoffe oder Plattform-Chemikalien hergestellt werden. Dabei ergeben sich deutliche Unterschiede zu trockenen Verfahren. Beispielsweise sind die notwendigen Temperaturen niedriger und die Selektivitäten höher. Zudem können Reaktionen durchgeführt werden, die bei trockenen, thermochemischen Umwandlungen nicht möglich sind, beispielsweise die Methan-Erzeugung im selben Reaktor wie die Biomasse-Umwandlung und die Herstellung von Plattform-Chemikalien wie Hydroxymethylfurfural. Diese Variationsbreite der Produkte und die hohen Selektivitäten sind eine Folge der Veränderung der Eigenschaften des Wassers als Funktion der Temperatur. Wasser unter normalen Bedingungen ein polares Lösungsmittel, das Salze sehr gut und unpolare organische Substanzen sehr schlecht löst. Mit steigender Temperatur erhöht sich zunächst das Ionenprodukt um einige Größenordnungen. Dies ist eine wesentliche Grundvoraussetzung für die hydrothermale Karbonisierung bzw. hydrothermale Verflüssigung. Bei der hydrothermalen Karbonisierung sorgt das flüssige Wasser als Lösungsmittel dafür, das ionische Reaktionen bei relativ hohen Temperaturen (180 – 220°C) ermöglicht, durchgeführt werden. Es ist die Eliminierung von Wasser kombiniert mit der anschließenden Polymerisation, die zu der Bildung der sauerstoffarmen Hydrokohle führt. Neure Untersuchungen zeigen, das zunächst hier zunächst eine flüssige Phase gebildet werden kann, die dann zur Hydrokohle wird. Mit steigender Temperatur nimmt die relative statische Dielektrizitätszahl ab. Diese Veränderung der Lösungsmitteleigenschaft führt letztendlich dazu, dass bei der hydrothermalen Verflüssigung während der Reaktion keine zweite flüssige Phase ausfällt, sodass keine Polymerisation zu Hydrokohle mehr stattfindet. So zumindest die Hypothese. Dies und andere Erkenntnisse zur Rolle des Wassers werden im Vortrag diskutiert.


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Wasser als außergewöhnliches Arbeitsmedium – „ein magisches Lösungsmittel“

Andrea Kruse, Dennis Jung

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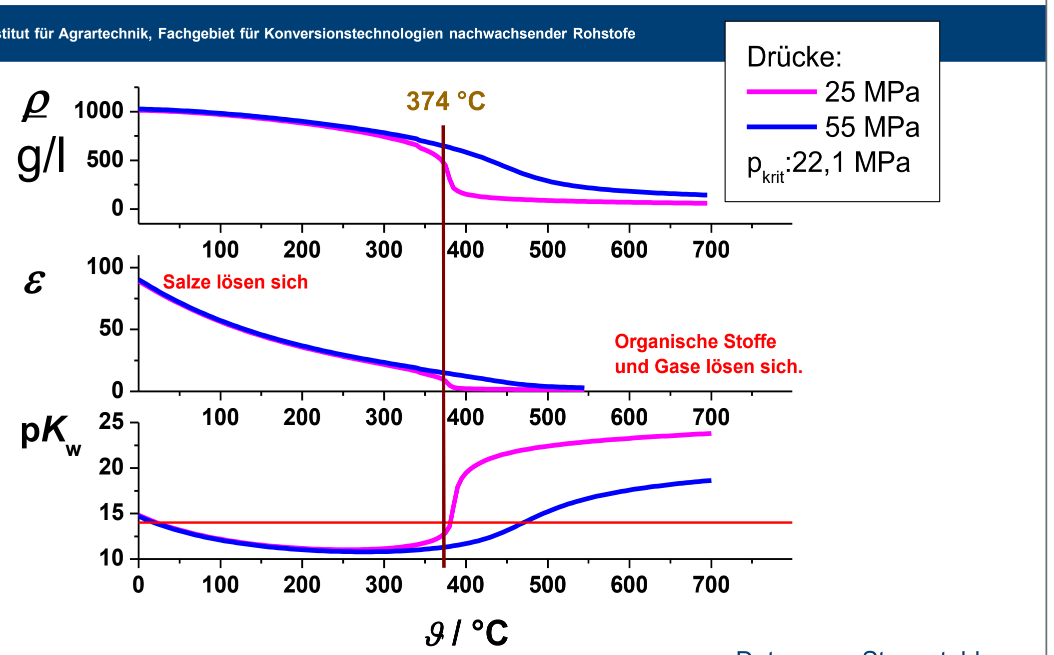

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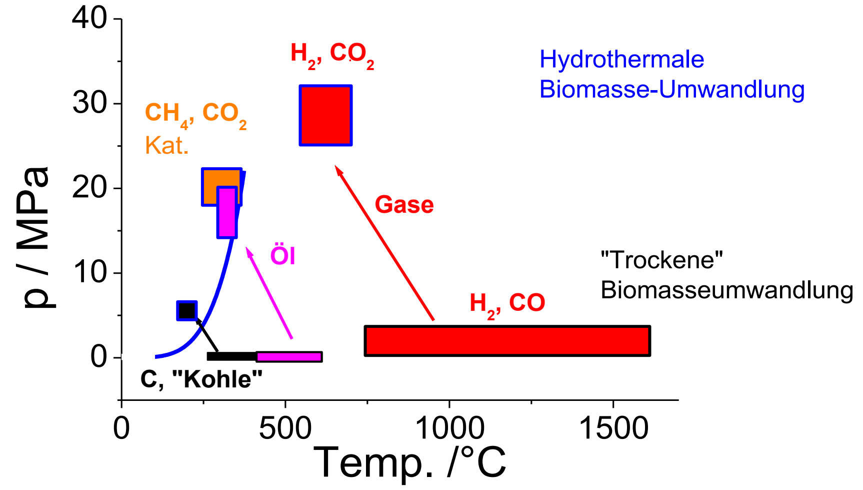
Vergleich: Trockene und nasse Biomasse-Umwandlung



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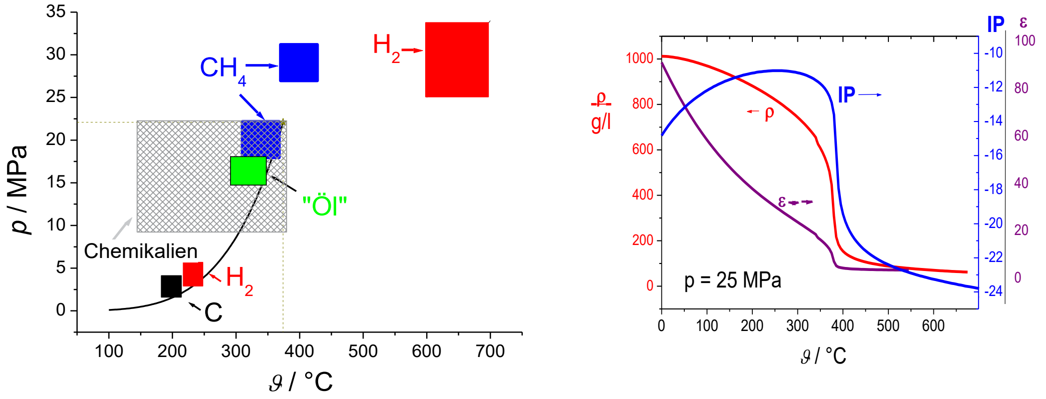
Hydrothermale Biomasse-Umwandlungen



A. Kruse, E. Dinjus; *J. Supercrit. Fluids* **2007**, *39*, 362.
A. Kruse, E. Dinjus; *J. Supercrit. Fluids* **2007**, *41*, 361.
A. Kruse; *Biofuels, Bioproducts & Biorefining* **2008**, *2*, 415.

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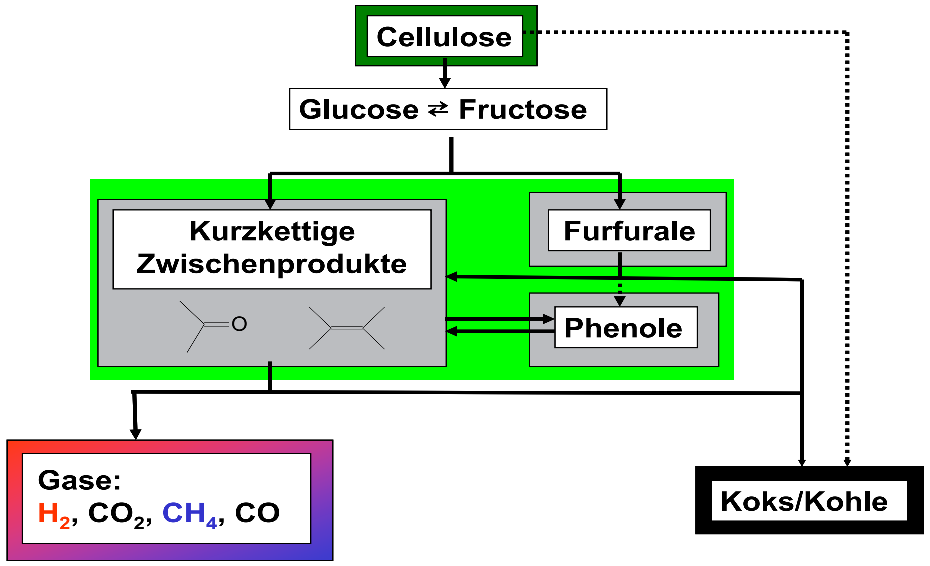


Cellulose

Glucose ⇄ Fructose

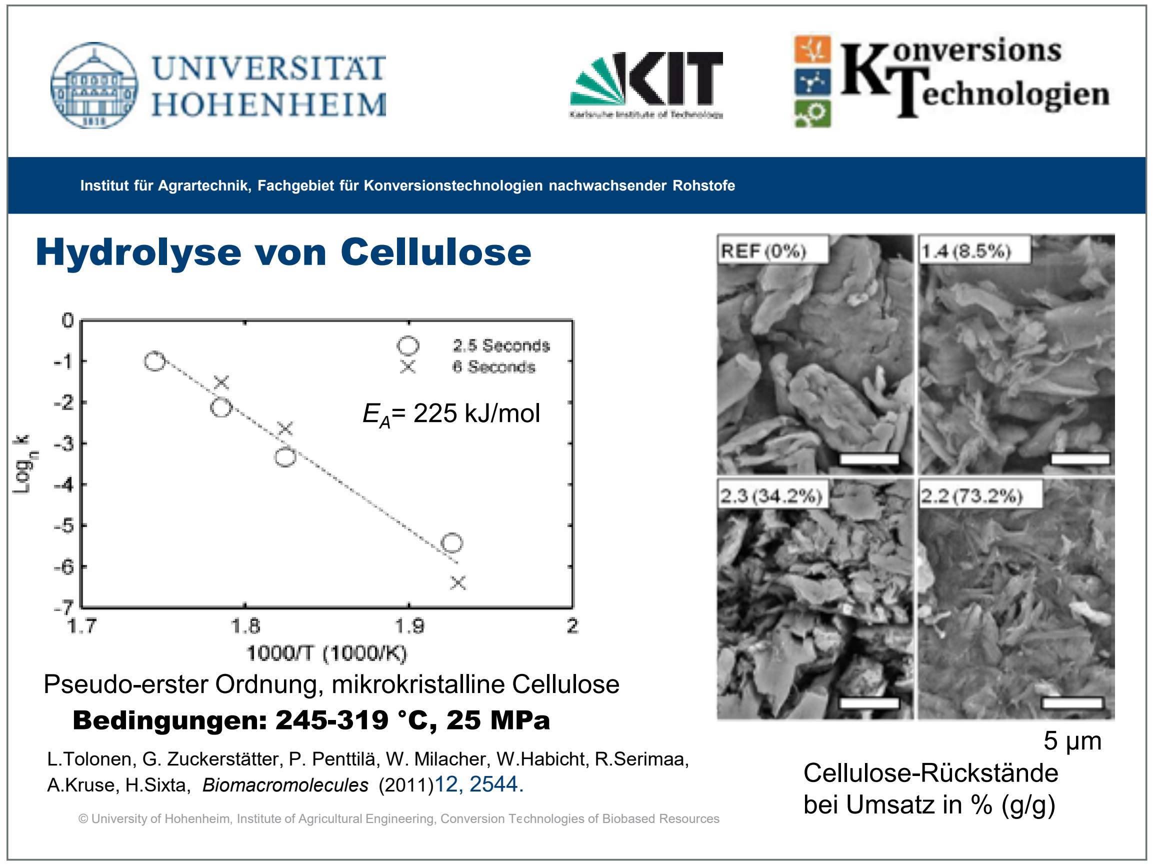
Kurzkettige Zwischenprodukte

Furfurale

Phenole

Gase:
H_2, CO_2, CH_4, CO

Koks/Kohle



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Hydrolyse von Cellulose

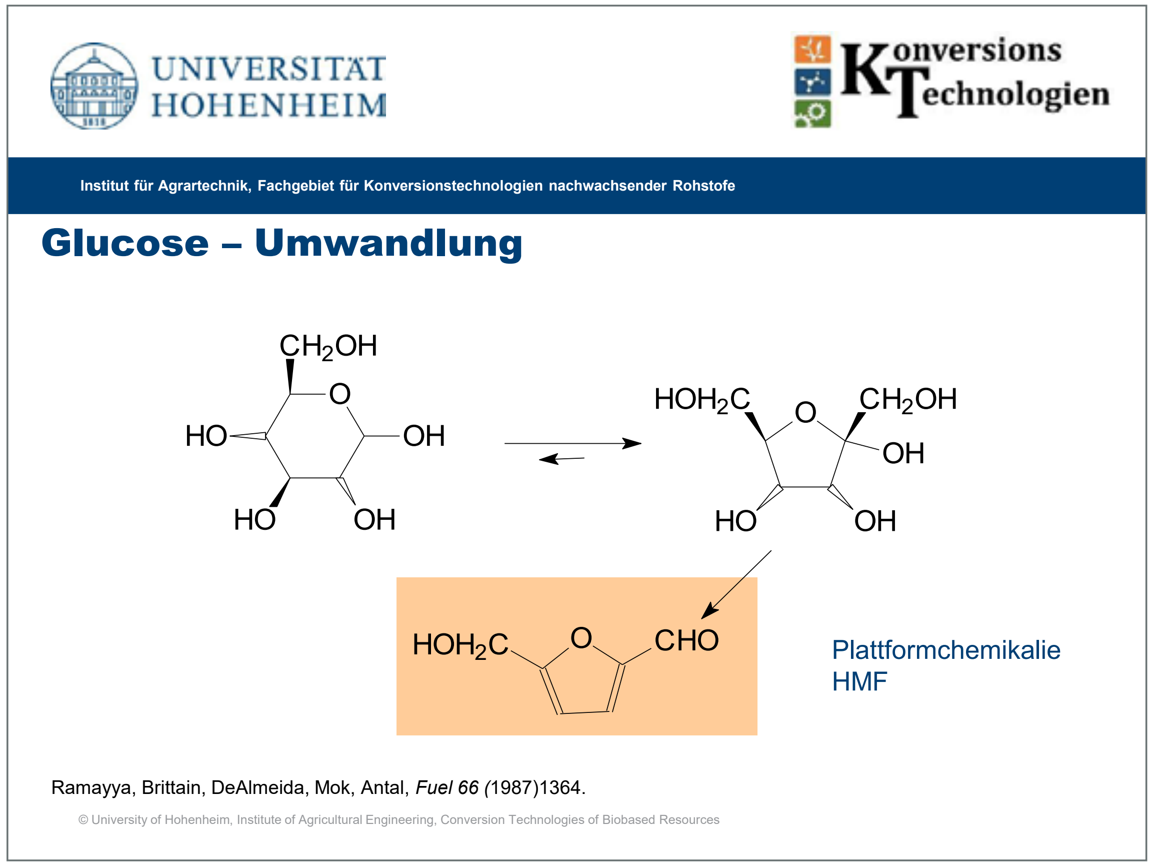
Pseudo-erster Ordnung, mikrokristalline Cellulose

Bedingungen: 245-319 °C, 25 MPa

L.Tolonen, G. Zuckerstätter, P. Penttilä, W. Milacher, W.Habicht, R.Serimaa, A.Kruse, H.Sixta, *Biomacromolecules* (2011)12, 2544.

5 µm

Cellulose-Rückstände bei Umsatz in % (g/g)



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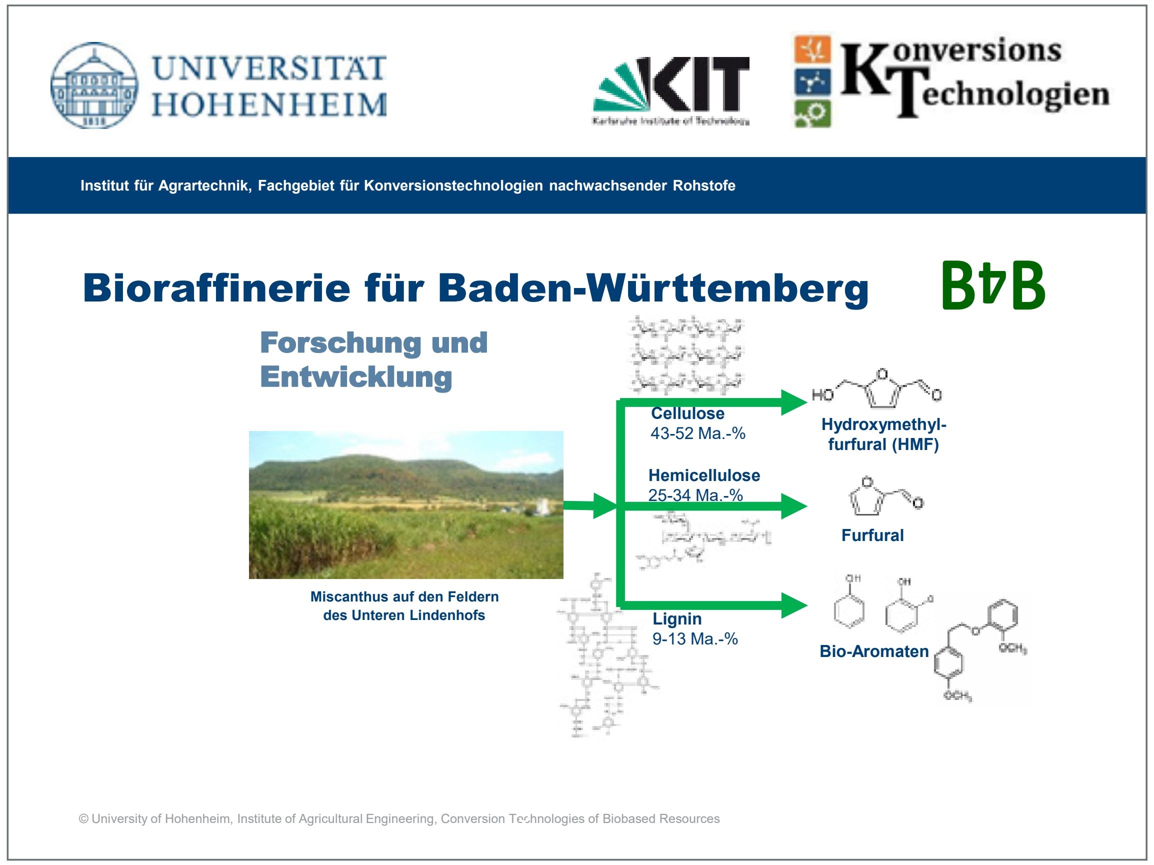
Glucose – Umwandlung

Plattformchemikalie HMF

Ramayya, Brittain, DeAlmeida, Mok, Antal, *Fuel 66* (1987)1364.



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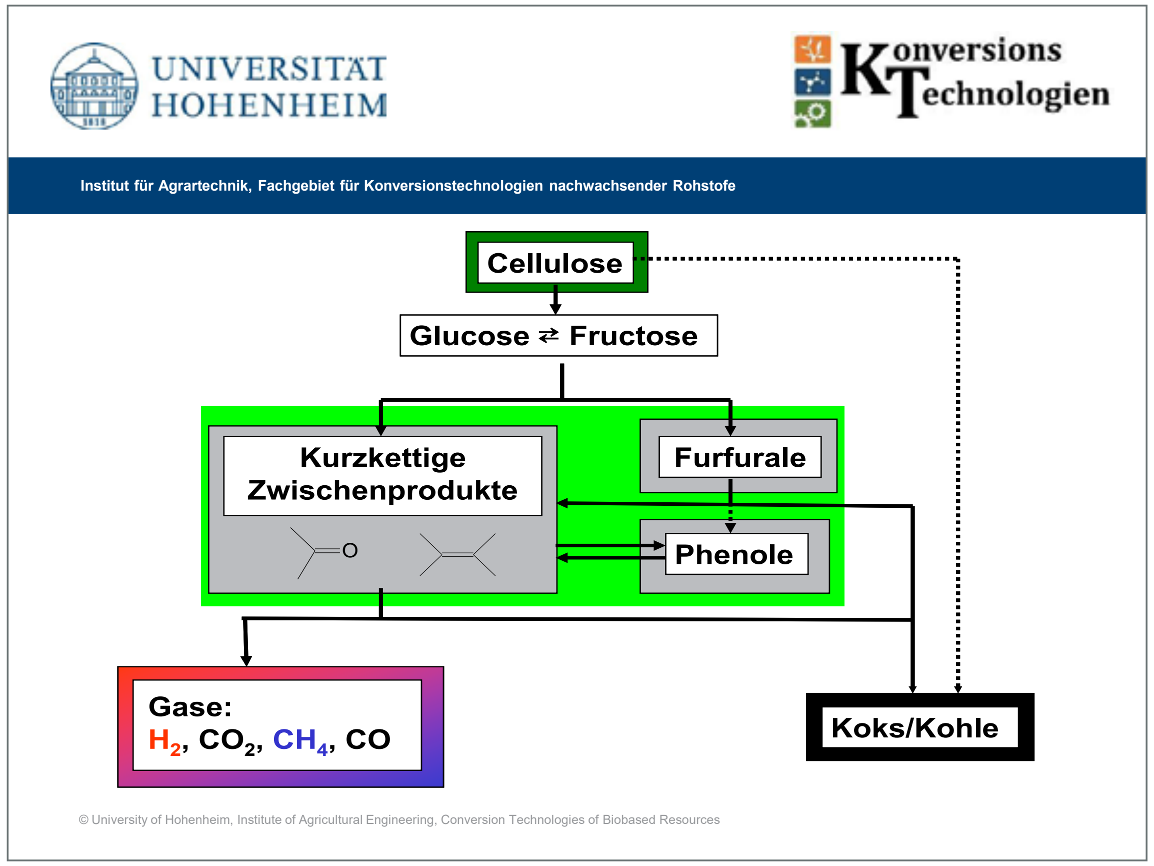
Bioraffinerie für Baden-Württemberg

Forschung und Entwicklung

Miscanthus auf den Feldern des Unteren Lindenhofs



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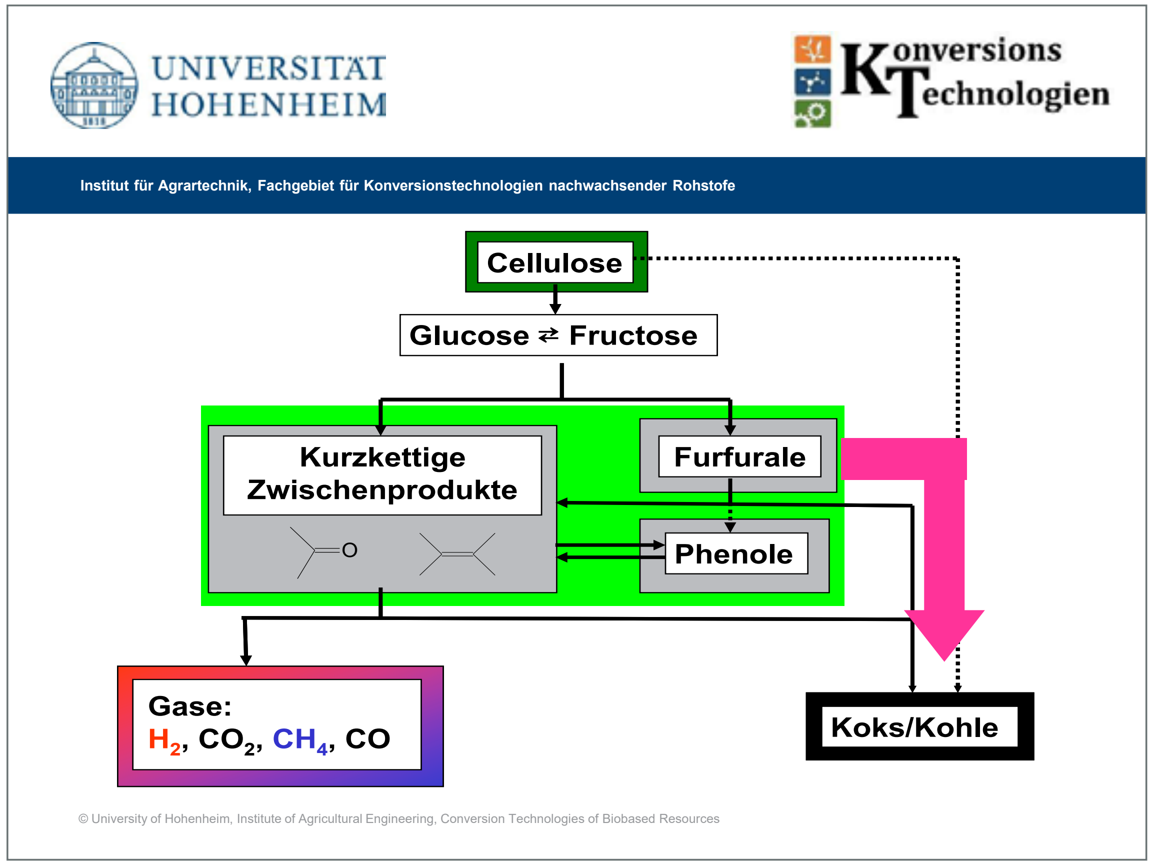

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Cellulose

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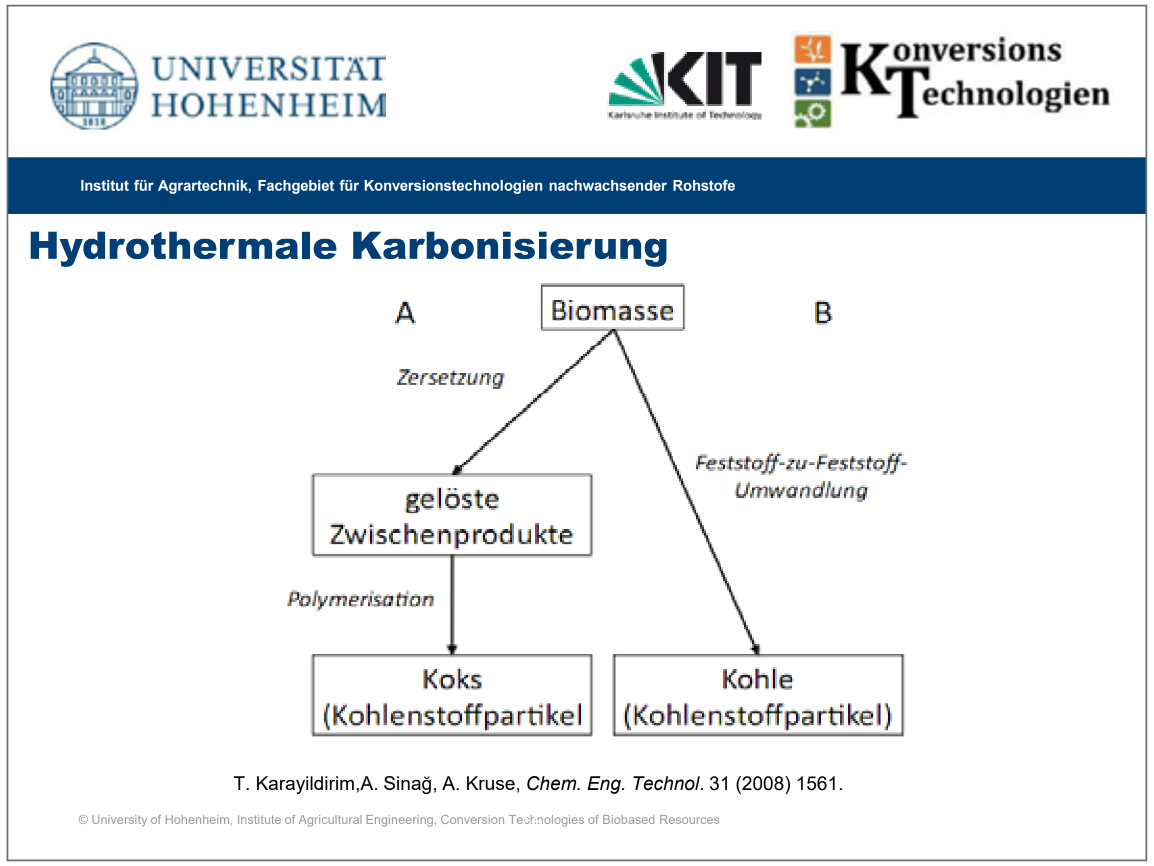

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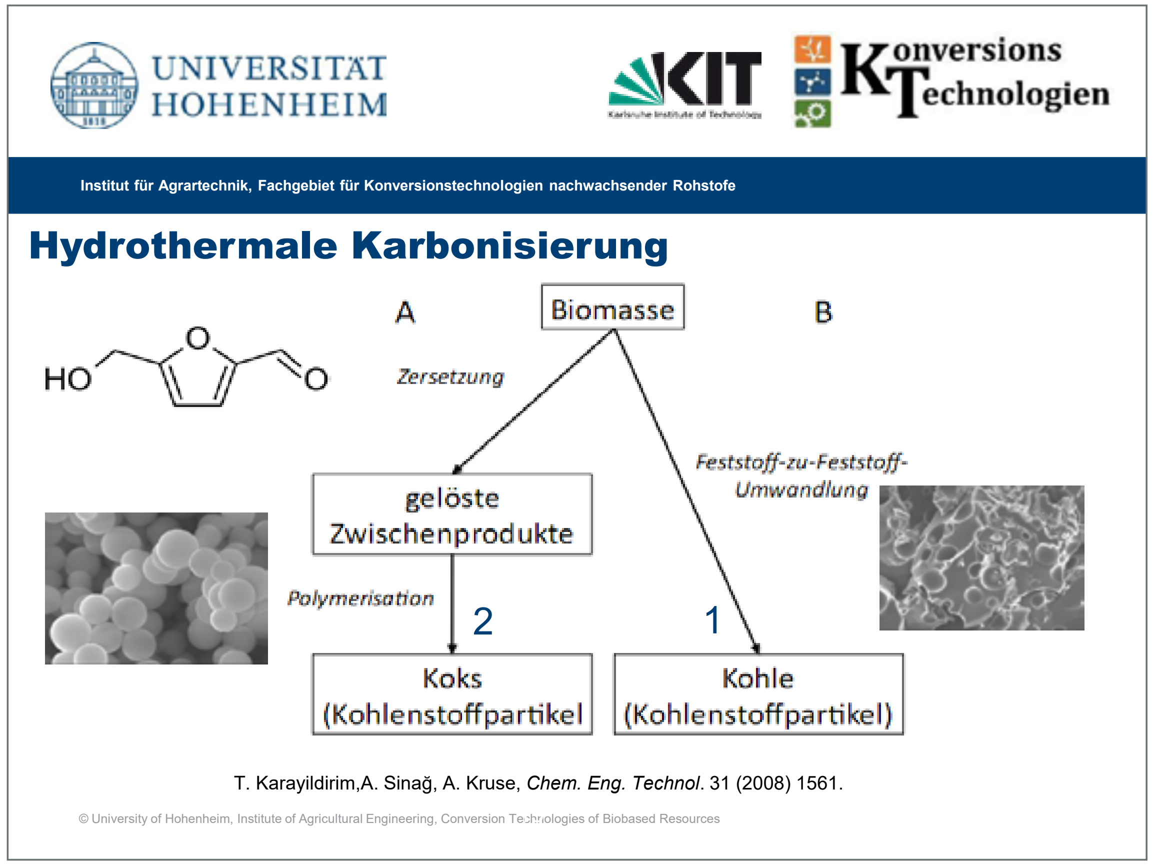
Hydrothermale Karbonisierung

A
Biomasse
B
Zersetzung
gelöste Zwischenprodukte
Feststoff-zu-Feststoff-Umwandlung
Polymerisation
Koks (Kohlenstoffpartikel
Kohle (Kohlenstoffpartikel)

T. Karayildirim,A. Sinağ, A. Kruse, *Chem. Eng. Technol.* 31 (2008) 1561.



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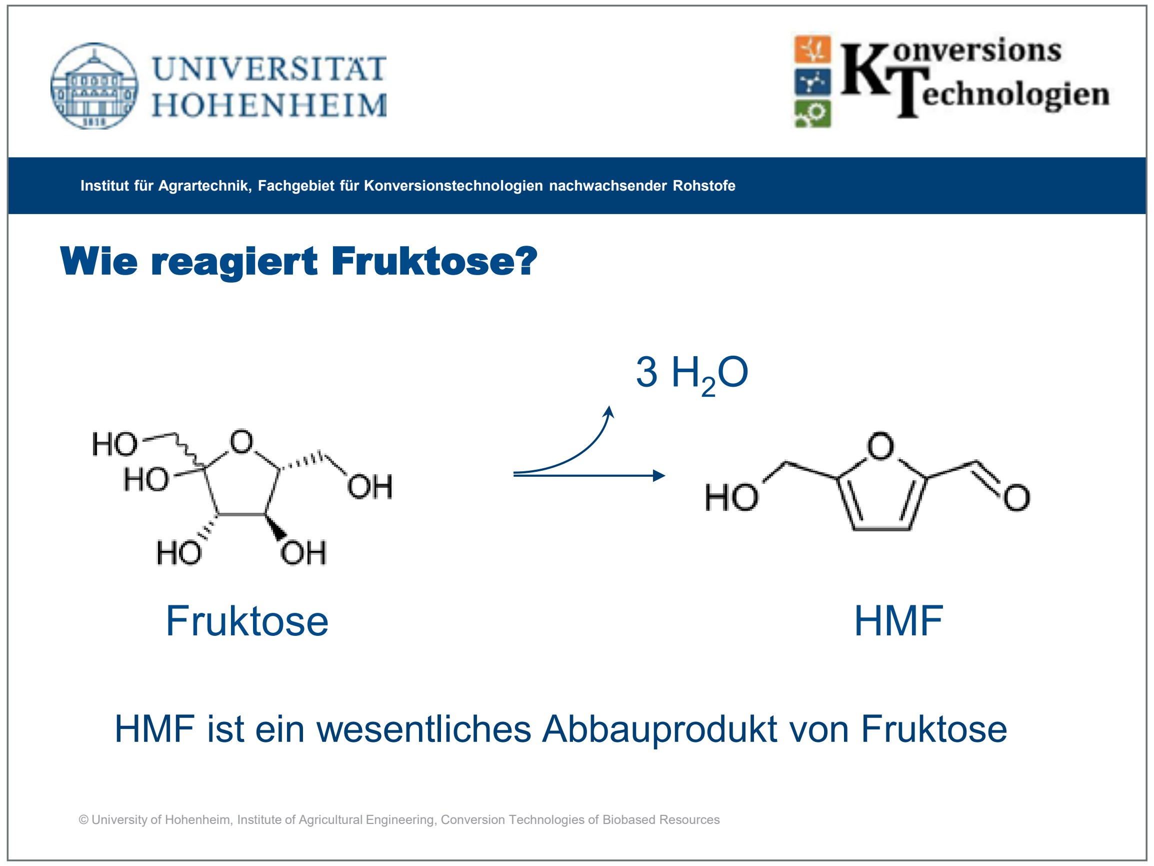
Hydrothermale Karbonisierung

A
Biomasse
B
Zersetzung
gelöste Zwischenprodukte
Feststoff-zu-Feststoff-Umwandlung
Polymerisation
2
1
Koks (Kohlenstoffpartikel
Kohle (Kohlenstoffpartikel)

T. Karayildirim,A. Sinağ, A. Kruse, *Chem. Eng. Technol.* 31 (2008) 1561.



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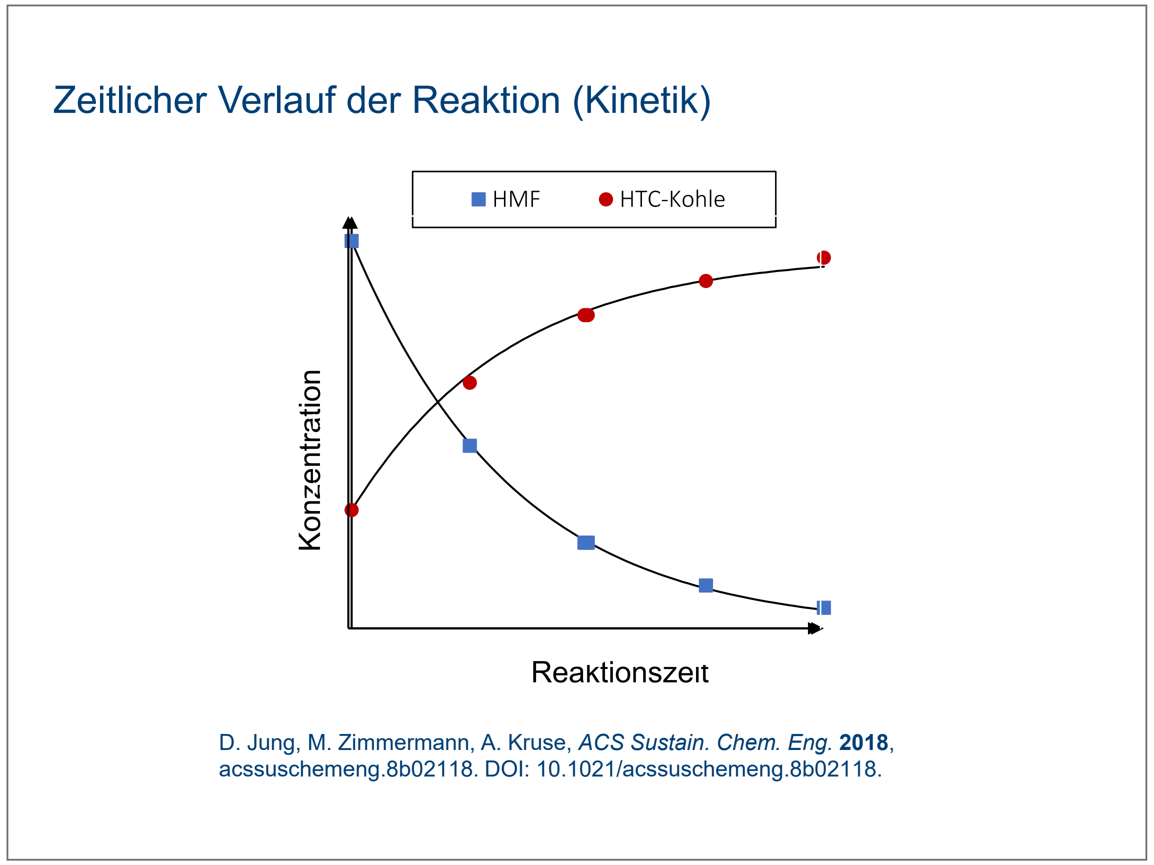
Wie reagiert Fruktose?

3 H_2O

Fruktose

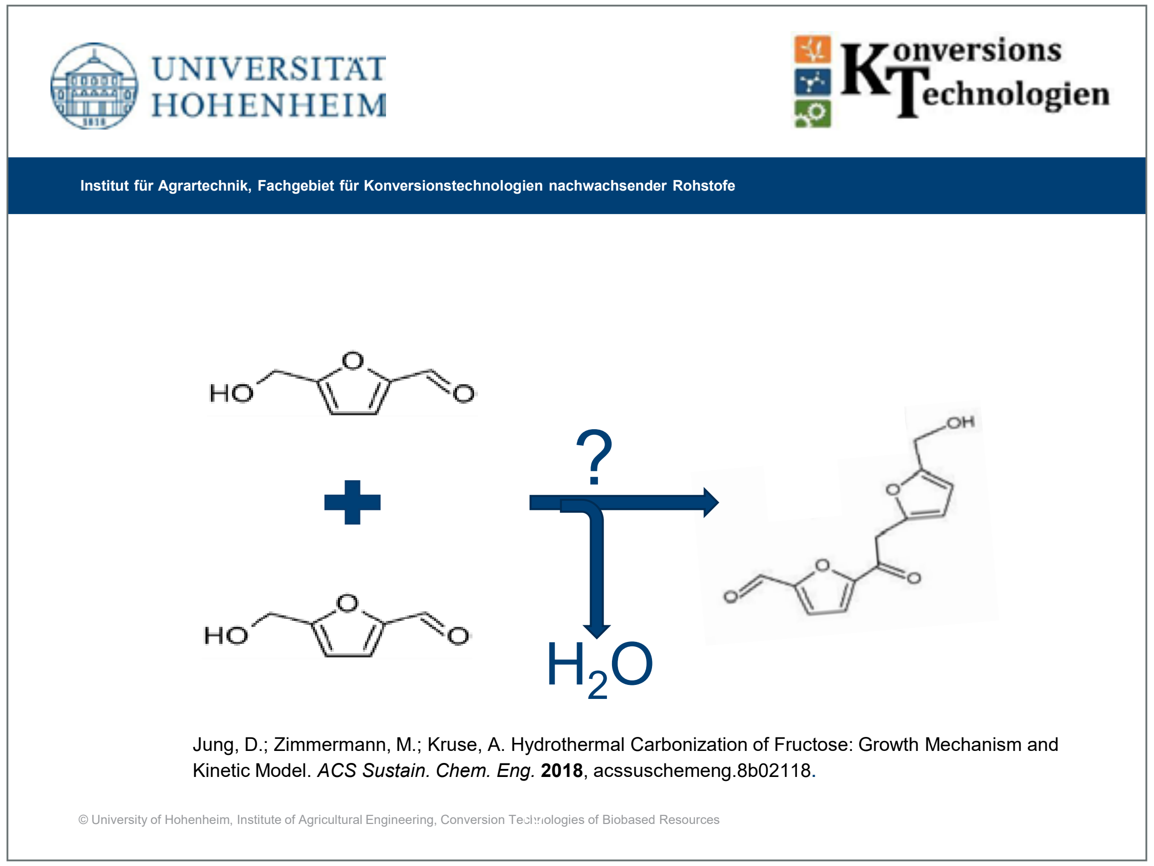
HMF

HMF ist ein wesentliches Abbauprodukt von Fruktose



Zeitlicher Verlauf der Reaktion (Kinetik)

D. Jung, M. Zimmermann, A. Kruse, *ACS Sustain. Chem. Eng.* **2018**, acssuschemeng.8b02118. DOI: 10.1021/acssuschemeng.8b02118.



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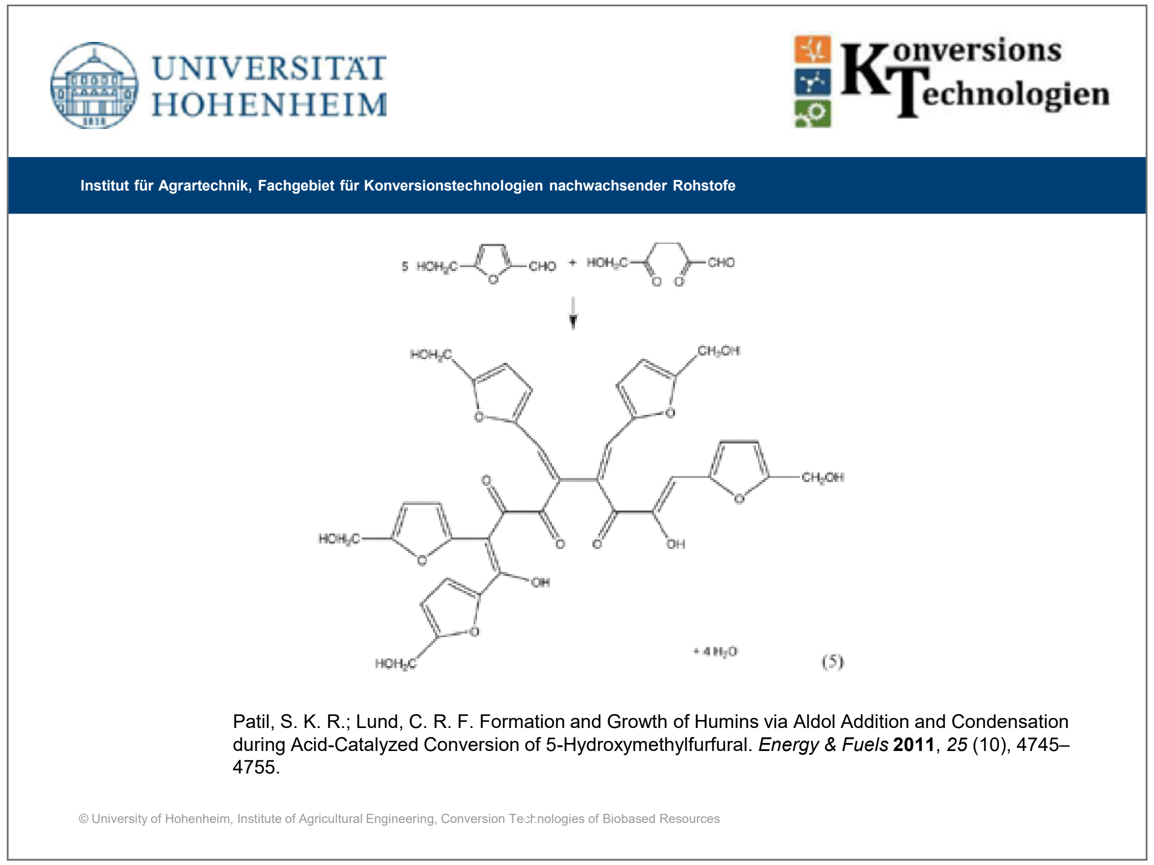
Jung, D.; Zimmermann, M.; Kruse, A. Hydrothermal Carbonization of Fructose: Growth Mechanism and Kinetic Model. *ACS Sustain. Chem. Eng.* **2018**, acssuschemeng.8b02118.



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Patil, S. K. R.; Lund, C. R. F. Formation and Growth of Humins via Aldol Addition and Condensation during Acid-Catalyzed Conversion of 5-Hydroxymethylfurfural. *Energy & Fuels* **2011**, *25* (10), 4745–4755.

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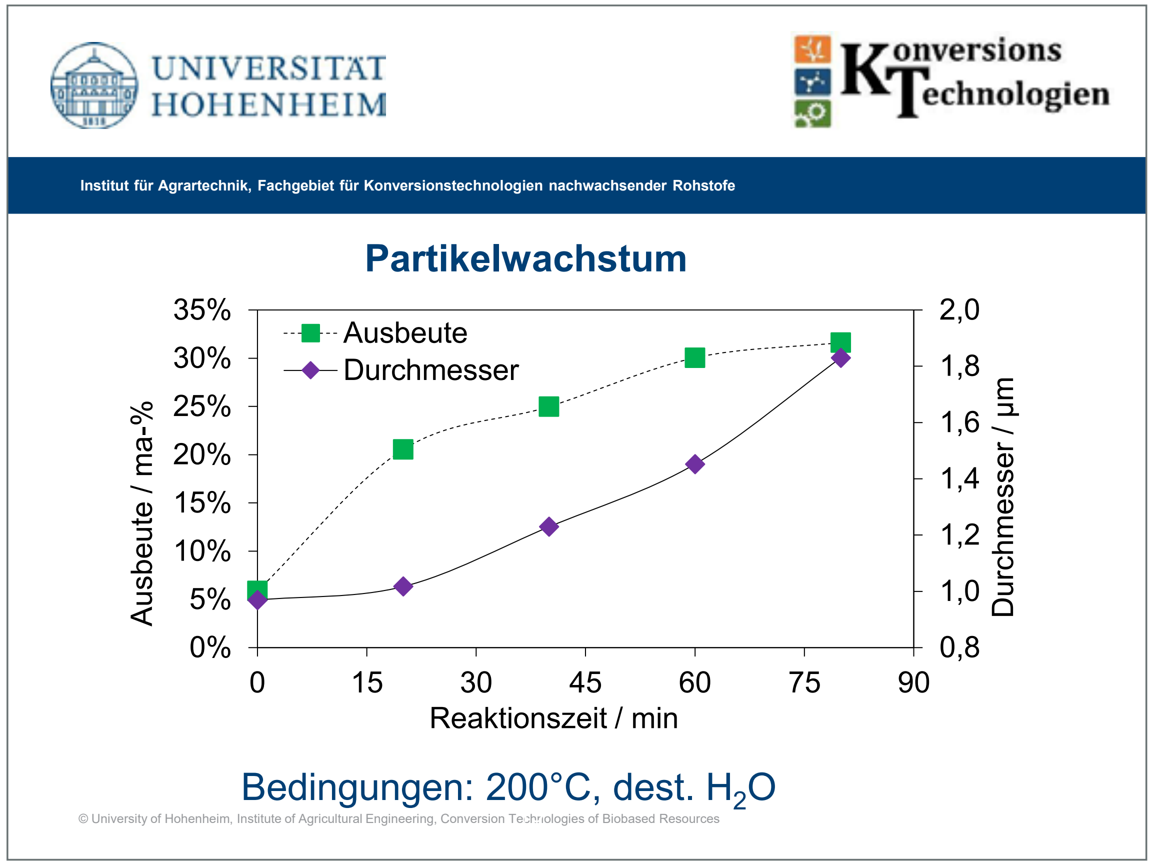
Wie entstehen diese Strukturen?



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Partikelwachstum

Bedingungen: 200°C, dest. H_2O

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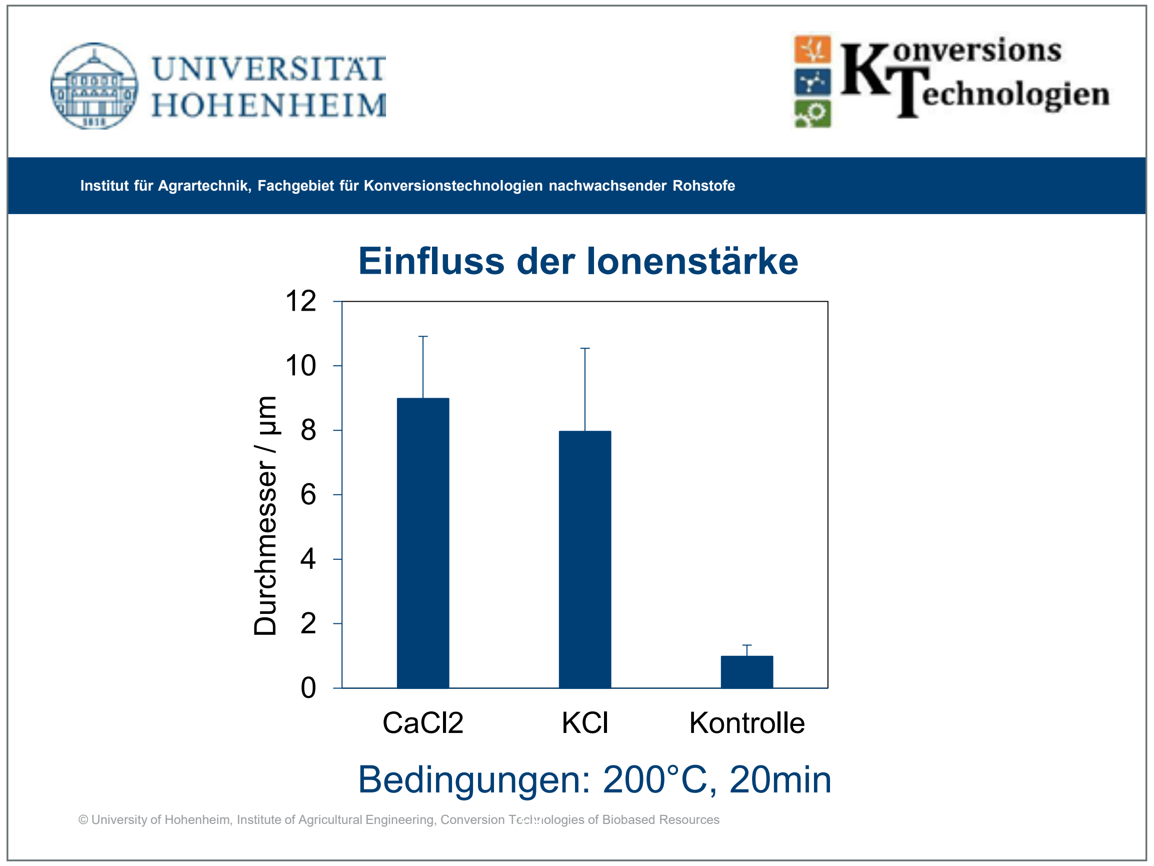

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Einfluss der Ionenstärke

Bedingungen: 200°C, 20min

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Wissenschaftsjahr 2020|21

BIOÖKONOMIE

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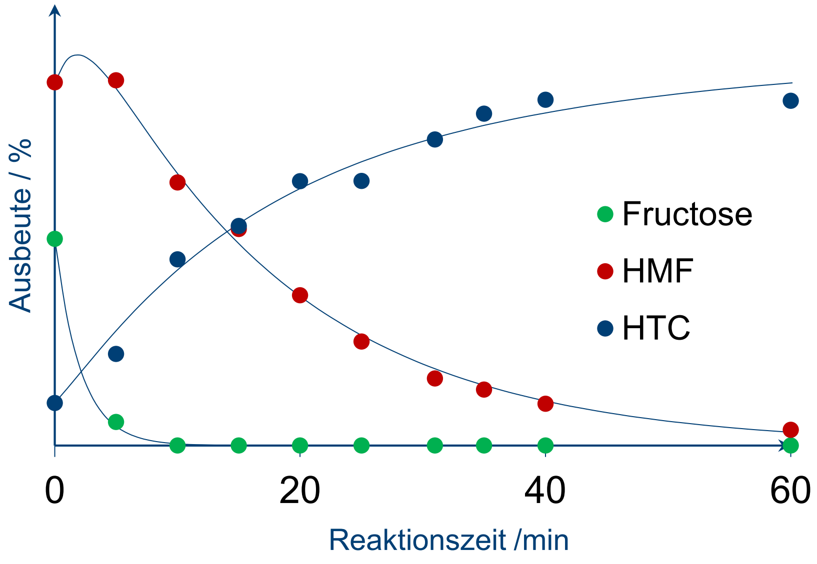
1818

Anhang

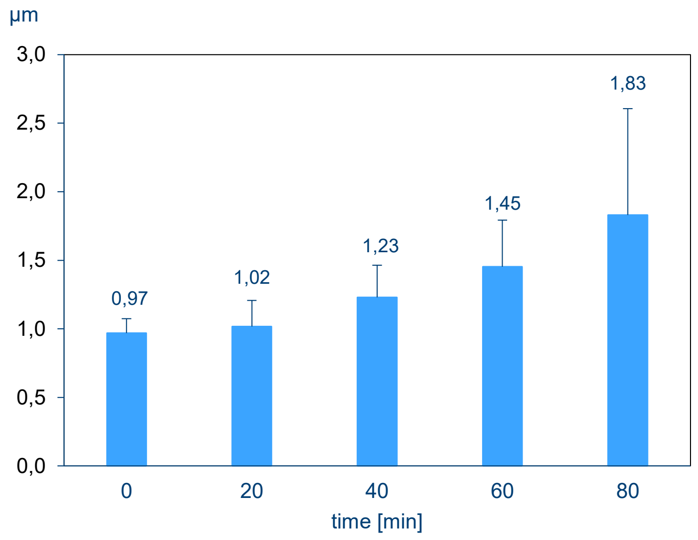
Hydrothermal Karbonisierung bei 200°C

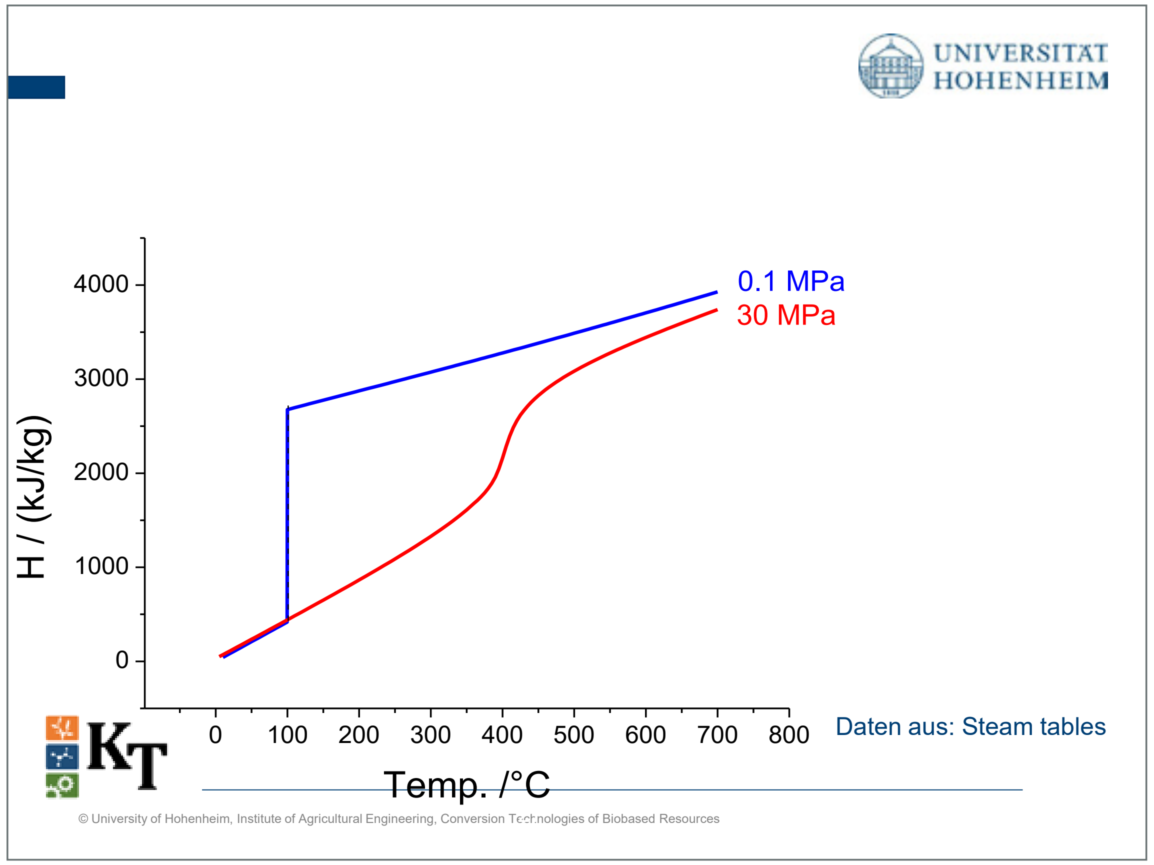


Experimenteller Aufbau

- Fruktose + dest. (H_2O) + Salze oder Säuren
- Mikro-Autoklaven mit 12ml Volumen
- Ausgedienter Gaschromatograph
- Temperatur 150 und 200°C

Partikeldurchmesser





Daten aus: Steam tables

Poster Speed Presentation

Elisabeth Kleiber, Hochschule Anhalt

Thermische Behandlung von HTC-Kohle in Drehtrommeln

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Tel.: +49 (0)349 6672546
E-Mail: **elisabeth.kleiber@hs-anhalt.de**

Die Verwertung von ungenutzter Biomasse wird aufgrund des stetig steigenden globalen Energiebedarfs und damit verbundener CO_2-Emissionen immer bedeutsamer. Insbesondere hydrothermal karbonisierte Biomasse erfährt einen vielfältigen Einsatz in verschiedenen Industriezweigen. So wird sie beispielsweise in der Landwirtschaft als Bodenhilfsstoff, in der Umwelttechnik als Adsorptionsmittel, im Bauwesen als Zuschlagsstoff sowie in Kraftwerken und Industriefeuerungen als Energieträger vorgesehen. Um einen effizienten Einsatz als hydrothermal karbonisierte Kohle (HTC-Kohle) zu gewährleisten, wird die Kohle im letzten Aufbereitungsschritt thermisch nachbehandelt. Hierzu liegen im Schrifttum bisher keine Untersuchungen vor.

Zielstellung ist es daher die thermische Aufbereitung von HTC-Kohle in einer Drehtrommel zu analysieren. Sowohl am Einzelpartikel als auch im Schüttungskollektiv soll die Phänomenologie beschreibbar gemacht werden. Hierfür werden thermogravimetrische Untersuchungen an einer Laborthermowaage (Netzsch STA 449 F3 Jupiter) zur Bestimmung der Trocknungskinetik und des Zersetzungsverhaltens durchgeführt. Die Analyse von Freisetzungsraten organischer Verbindungen sowie des Selbstentzündungsverhaltens der HTC-Kohle sind hierbei wesentlicher Bestandteil. Die schüttungsdynamischen Analysen werden an Batchdrehtrommeln mit Durchmessern von D = 0,3 m bis 1,0 m durchgeführt. Hierbei werden insbesondere die Partikelgeschwindigkeiten, Mischintensitäten und Segregationseffekte mittels einer Ultrahochauflösenden Kamera (Panasonic Lumix DC-GH5) sowie einer Hochgeschwindigkeitskamera (IDT XS-1440p PCIe 2.0) bestimmt. Dabei soll der Einfluss der Partikeleigenschaften (Partikelgröße, -form, -dichte), der Betriebsbedingungen (Temperatur, Drehzahl, Füllungsgrad, Gaskonditionierung) und der apparativen Parameter (Mischintensität, Förderfähigkeit) auf die Trocknungskinetik untersucht werden. Daraus ableitend sollen in weiterführenden Arbeiten die optimalen Prozessbedingungen und das konstruktive Design der verfahrenstechnischen Anlagen festgelegt werden, damit eine hinreichende Produktqualität gewährleistet werden kann.

Dr. Thomas Heinrich, Leibniz-Institut für Agrartechnik und Bioökonomie

Thermochemical Conversion of Grass to Biochar: A Comparison of Process Dependence

Thomas Heinrich, Judy Libra, Thomas Hoffmann
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Max-Eyth-Allee 100
14469 Potsdam
E-Mail: **theinrich@atb-potsdam.de**

Upon heating biomass the natural constituents decompose with one of the products being solid highly carbonaceous char. Char from biomass, although produced for millennia, has only recently received attention for its potential application as a soil amendment (so-called biochar) in agriculture. Many studies have shown that a multitude of biomass feedstocks and various thermochemical conversion processes may yield biochars, which could provide substantial benefits to farmland. Due to the inhomogeneity of the biomass feedstock and the wide range of potential product distributions (between gaseous, liquid and solid products) from its thermochemical conversion the unconditional validity of ameliorating properties of char remain questionable. This leads to the necessity of experimental validation of the char properties from various processes and parameter settings (e.g. peak temperature) for soil application. Protocols, such as the European Biochar Certificate (EBC), have been developed to classify the properties of chars for the application as biochar. In this certificate biochar produced, not only from wood but from all types of biomass, via pyrolysis are considered. It excludes other potential technologies to produce biochar.

Therefore, in the present study the properties of biochars produced via hydrothermal carbonisation (HTC), and pyrolysis in an inert as well as in a limited air environment are analysed and compared with values considered in the EBC. While all three processes are thermochemical and produce a solid char, many differences exist. The media plays a vital role. In HTC and pyrolysis biomass is converted anaerobe, while the addition even of limited amounts of air influence the pyrolysis processes substantially. In low air pyrolysis and HTC, air and water, respectively, act as reactants, while only pyrolysis reactions occur in an inert environment. However, all three processes are substantially temperature dependent and may yield a product suitable for the use as soil amendment. Especially the product carbon, hydrogen and oxygen contents are substantially process dependent. While in Pyrolysis the ash constituents largely remain in the solid product, they may be released into the process water in HTC. This could be beneficial in case of heavy metals but also detrimental to the biochar application in case of nutrients. Here differences and benefits of the utilised technologies with regard to the biochar composition in the context of the EBC are investigated. The feedstock in the present study is grass from extensively managed areas in the National Unteres Odertal, Germany.

Thermochemical Conversion of Grass to Biochar: A Comparison of Process Dependence

Heinrich, Thomas, Libra, Judy, Hoffmann, Thomas

HTP
Hydrothermale Prozesse

6. HTP-Fachforum
25./26. November 2020

FEEDSTOCK

- Late harvest of grass with high value for biodiversity in the Lower Oder Valley National Park
- Total area of 10,500 ha including 4,190 ha of managed grasslands within a polder system [1]

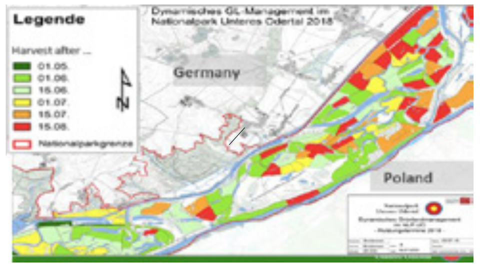

Figure 1: Management of agricultural utilisation of grassland areas in the Lower Oder Valley National Park.

THERMOCHEMICAL CONVERSION TECHNOLOGIES

In the project three technologies are evaluated:

- Hydrothermal Carbonisation (water)
- Pyrolysis (nitrogen)
- Pyrolysis (air)

Figure 1: Reactors: HTC (left), pyrolysis-N2 (middle), pyrolysis-air (right).

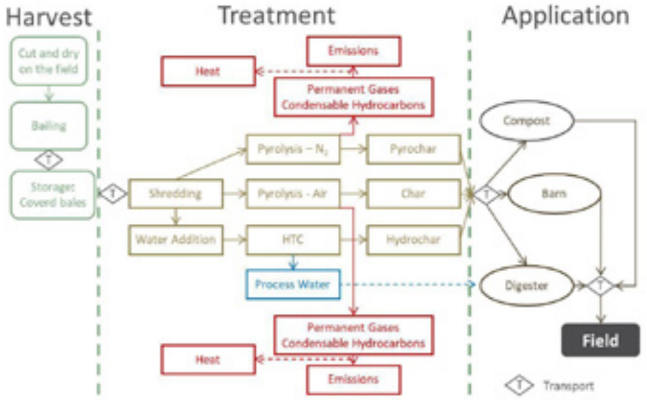

Figure 2: Options for process flow design.

BIOCHAR PROPERTIES

Char produced from plant material that is used as a soil amendment is called biochar. Results from preliminary experiments with the grass are presented in Table 1.

Some important properties for its evaluation are:

- Physical: Surface area, particle size, etc.
- Interactions: Water holding capacity, etc.
- Potential toxins: PAHs, PCB, PCDD, etc.

APPLICATION

Three options for application are being considered:

- Bedding material in cow barns
- Anaerobic digestion
- Co-composting
- (Direct application to the field is currently prohibited in Germany)

Field application with manure / digestate / compost:

- To least profitable, sandy soils in the surrounding area

Table 1: Comparison of preliminary data from grass biochars to EBC guidelines [2].

	CHO (molar ratio)		Heavy Metals (mg · kg^{-1})								pH	Conductivity
	H/C	O/C	Pb	Cd	Cu	Ni	Hg	Zn	Cr	As		(mS · cm^{-1})
EBC Guidelines Class I	$< 0.70^1$	$<0.40^2$	< 10.00	< 1.00	< 100.00	< 30.00	< 0.10	< 400.00	< 80.00	< 2.00		
Grass	1.29	0.59									6.20	
Hydrochar – 220°C	0.85	0.35	nd	0.03	3.34	2.18	-	21. 02	0.80	-	4.36	6.23
Pyrochar N_2 – 450°C	0.52	0.11	0.96	0.28	19.31	4.87	-	185.51	3.99	-	8.04	30.68
Pyrochar Air – 650°C	0.39	0.04	0.90	0.36	25.46	2.62	-	231.35	1.42	-	9.83	53.50

$^1 H/C_{org}$; $^2 O/C_{org}$

[1] Vössing, A. et. al. (2009) Nationalpark-Jahrbuch Unteres Odertal.
[2] The European Biochar Certificat: www.european-biochar.org.

ATB
Leibniz-Institut für Agrartechnik und Bioökonomie

GO-GRASS

This project has received funding from the European Union’s Horizon 2020 research and Innovation programme under grant agreement **N°862674**.

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Hydrothermal liquefaction of waste biomass

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The increasing scarcity of fossil resources and the climate crisis associated with their use require sustainable solutions for supplying global energy needs. Waste biomass is a promising, renewable carbon resource. In recent years, various thermochemical processes have been applied for refining biomass, including pyrolysis, gasification, and hydrothermal processes (HTP). However, compared to other thermochemical processes, HTP have the advantage that wet biomasses do not need to be dried, since water is required as a reaction medium. One process that offers a promising path for the energetic and material exploitation of wet biomass is hydrothermal liquefaction (HTL). Biocrude obtained from HTL is a potential fuel precursor. HTL has been studied for various feedstocks, such as algae, (ligno-)cellulosic biomass, sewage sludge and manure, while digestate requires further investigation. Integrating HTL into the biogas process promises to create a value product from waste while retaining the nutrient load for fertilization. This doctorate aims to highlight the influence of parameters such as digestate feedstock, digestion time, temperature, pH, catalyst on 1) the biocrude yield and composition and 2) the nutrient distribution and recycling.

Hydrothermal liquefaction of waste biomass

Christian Klüpfel, Jakob Köchermann, Benjamin Wirth

HTP Hydrothermale Prozesse

6. HTP-Fachforum
25./26. November 2020

Introduction

The increasing scarcity of fossil fuels coupled with growing world population calls for renewable solutions for meeting global energy needs. The project “Pilot-SBG“ seeks to improve the production of methane from biogenic residues, by-products and wastes by opening up hitherto untapped resources and optimizing the utilization of developed resources. This is to be achieved by combining established processes (see Figure 1).

In this context, hydrothermal liquefaction (HTL) shall be used to treat the product of anaerobic digestion. Hydrothermal liquefaction is the thermochemical conversion of wet biomass in hot, compressed water. It is typically performed in subcritical conditions (T = 523 – 647 K, p = 4 – 22 MPa). First, biomass is depolymerized by hydrolysis, the monomers further decompose by decarboxylation and dehydration and subsequently recombine by polymerization and polycondensation. This yields an energy-dense biocrude, an aqueous fraction rich in nutrients, a gas-phase mainly comprised of CO_2 and a solid fraction containing hydrochar as well as insoluble components. Benefits of implementation include the creation of a renewable fuel, recycling of nutrients and sterilization of a potentially pathogenic biomass in a single, one-step process (see Figure 2).

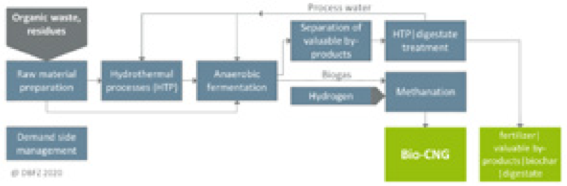

Figure 1: Main process steps in the plant concept.

PILOT SBG

Federal Ministry of Transport and Digital Infrastructure

Materials and Methods

As a first step, an SOP for HTL experiments will be established. For this purpose, bomb-type batch reactors will be procured. Experiments with wet biomass and catalysts will be conducted in a fluidized sand bath. After cooling the reactor, the products are separated and analysed via elemental analysis, GC-MS, HPLC, TKN, ICP and TGA. This will enable to set up mass and energy balances and investigate the influence of process parameters and feedstock composition on the products. Based on this data, suitable reaction conditions can be determined to achieve optimal fuel properties and nutrient separation.

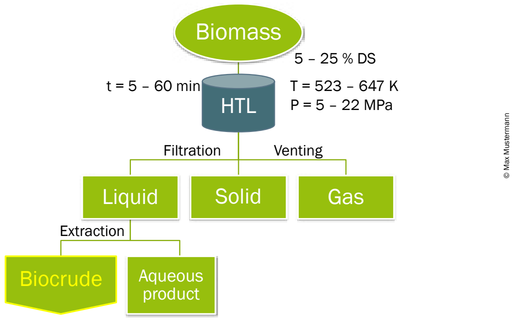

Figure 2: HTL process and downstreaming.

Outlook

Following these screenings, this thesis aims to address the following points:

- Influence of feedstock, temperature, time and catalyst on product distribution and composition
- Optimizing biocrude yield
- Kinetic modelling and prediction of optimal reaction conditions
- Investigate the exploitation of process water

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Mats Hultman, Neste Corporation

The role of the biofuels in future sustainable traffic

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The climate change, and the related global warming, are the challenges of our life time. To combat these, many countries aim to become carbon-neutral in up-coming decades. This is a challenging goal that calls for extensive measures – especially for transportation.

Even though energy policies focus on cutting down emissions by using a variety of means, debate concerning transportation and the powertrain of cars has ended up in a situation that concentrates on the confrontation between emission reduction technologies, such as renewable fuels, electricity and gas.

This is a wrong point of departure.

Throughout the history of modern transportation, we have become used to considering the combustion engine, fuels and fossil raw materials in an identical manner. However, this no longer holds true today. In EU, there is no such as 100% fossil road transportation fuel on market, if we look annual averages. Each member states have obligations to use certain amount of biofuels in their fuel pools – and these obligations are increasing towards 2030 (e.g. 30% mandate in Finland 2030).

It is often forgotten in public debate about different power trains, which focuses on confrontation, that biofuels are already the most efficient and socio-economically the most affordable way of reducing road traffic emissions. The truthful comparison of different solutions is not ambiguous. When aspiring towards more climatea-friendly solutions, all emissions during the vehicle's life cycle must be taken into consideration from the manufacturing to the recycling.

Many of us may be surprised by the results of comparing the emissions of electric and diesel cars during their life cycle, which is about 200,000 kilometers, based on different energy sources. An electric vehicle running with 100% wind power may easily sound like the best solution. However, when comparing life cycle emissions, a diesel car running with 100% renewable fuel can be even better alternative in view of emissions. Although a 100% renewable fuel may not always be a realistic alternative, higher blending rates are also an efficient step in view of combating climate change.

We must point out at the same time, however, that biofuels alone cannot address the climate challenge in road traffic, but we also need other means, such as electrification. Continuous comparisons and confrontations between different alternatives are one of the reasons why pursuing a sensible climate policy is so challenging. Let us return to the vastness of the original challenge, i.e. the climate crisis. None of the alternatives available will be sufficient alone, especially not according to the required schedule. Remaining to focus on a single solution would be a grave mistake. aThe necessary technical breakthroughs already exist or are, at least, very close. All we have to do is to create an operating environment and culture that allow us to make optimum use of technologies to combat climate change.

The role of the biofuels in future sustainable traffic

Mats Hulman, Neste Corporation, Head of OEM partnerships
Teemu Sarjovaara, Neste Corporation, Head of R&D

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Climate change is the main driver for transportation regulation that defines the future landscape for us, but is not telling the whole truth

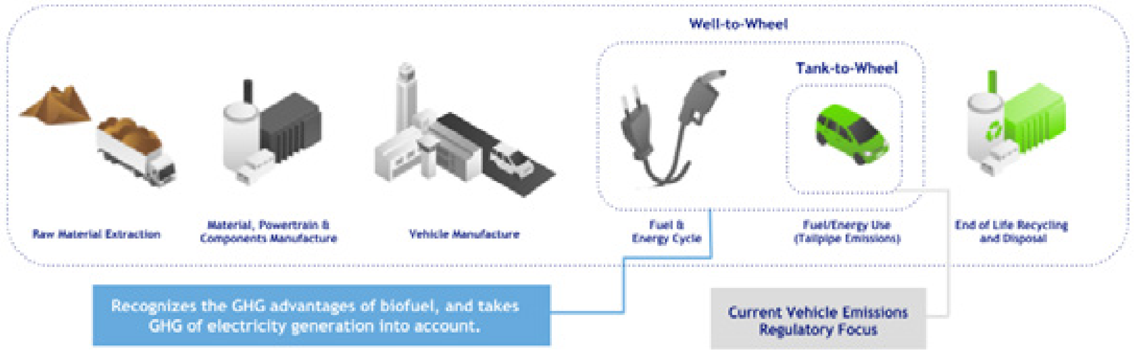

Fig 1. The true vehicle Life Cycle GHG emission sources

Taking the true life cycle emissions into account changes the "picture" dramatically

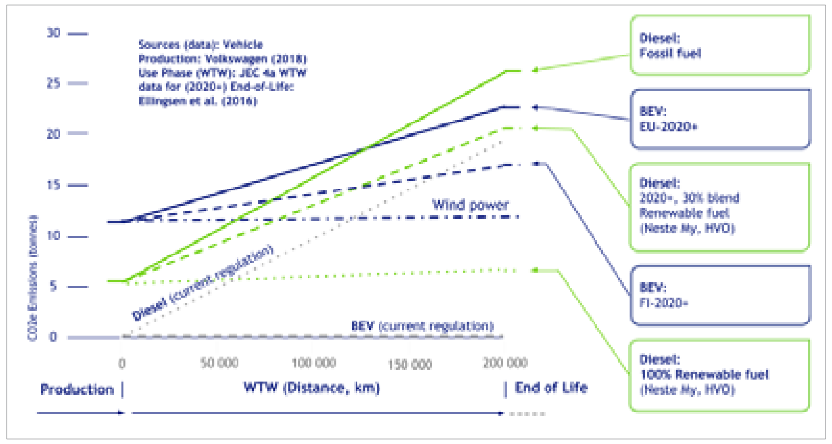

Fig. 2: Medium sized car's life cycle GHG emissionwith diffrent powertrains and fuel or energy

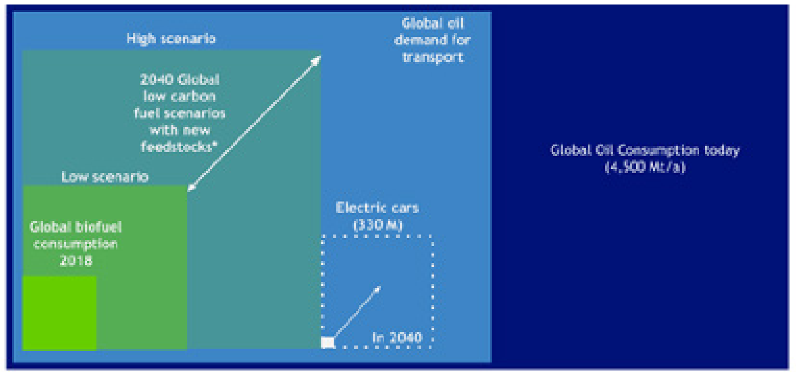

Fig. 3: The availability scenarios of diffrent ways to decarbonize transportation. * New feedstocks: Waste and residue fats and oils, waste plastic, municipal solid waste, lignocellosic biomass, algae and PtX. Source: Neste based on IEA, UNDP, ExxonMobil and others

The decarbonization challenge is huge and every solution is needed and should be exploited to the maximum.

Low carbon fuels are a truly scalable and system level solution to reduce GHG emissions!

To fully utilize this potential, we need favorable regulation that recognizes their potential.

NESTE

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Lars Thomsen, Aarhus University

Pilot-scale Hydrothermal liquefaction of sewage sludge: Energy considerations and the fate of micropollutants

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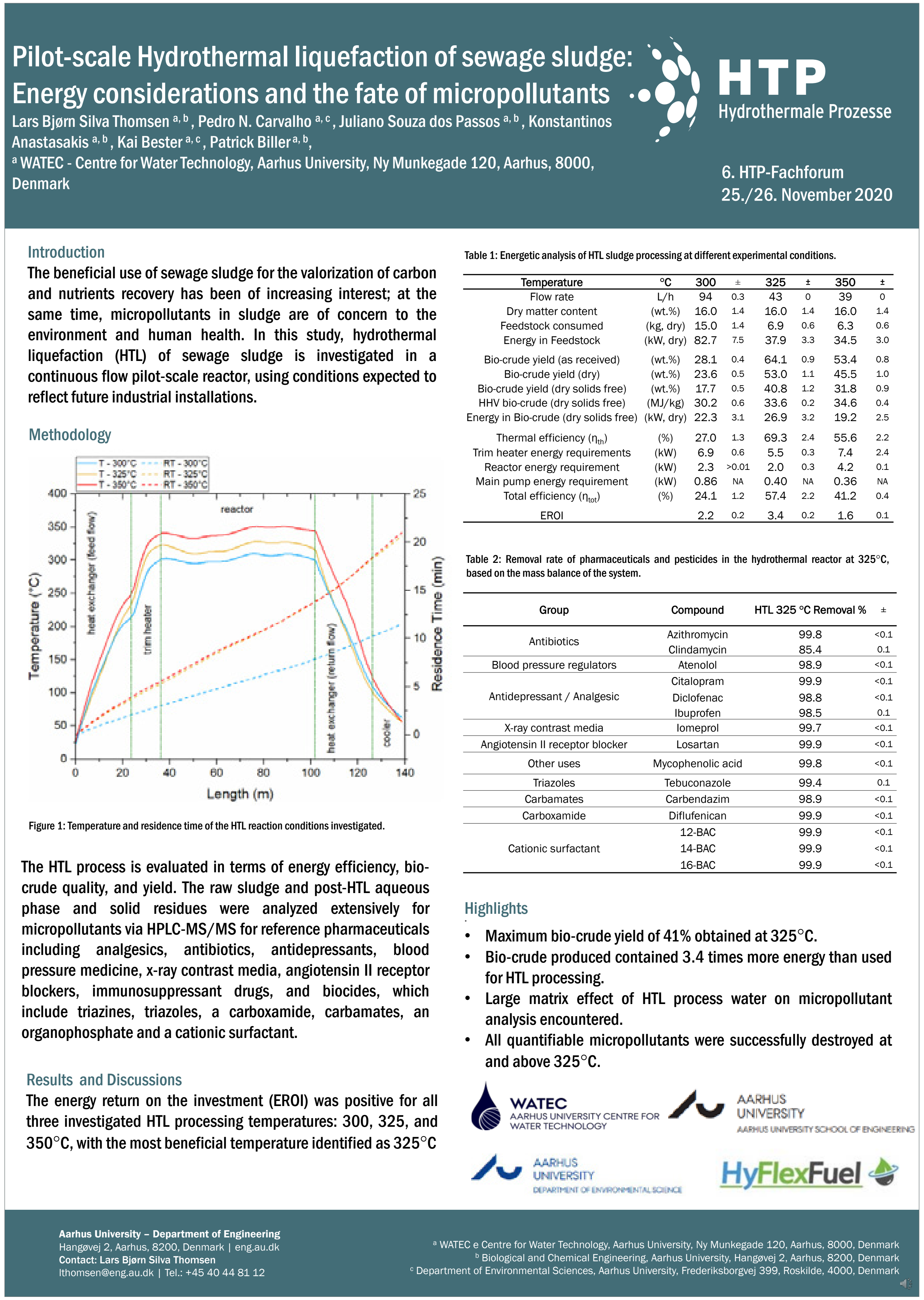
The beneficial use of sewage sludge for the valorization of carbon and nutrients recovery has been of increasing interest; at the same time, micropollutants in sludge are of concern to the environment and human health. In this study, hydrothermal liquefaction (HTL) of sewage sludge is investigated in a continuous flow pilot-scale reactor, using conditions expected to reflect future industrial installations. The HTL process is evaluated in terms of energy efficiency, bio-crude quality, and yield. The raw sludge and post-HTL aqueous phase and solid residues were analyzed extensively for micropollutants via HPLC-MS/MS for reference pharmaceuticals including analgesics, antibiotics, antidepressants, blood pressure medicine, x-ray contrast media, angiotensin II receptor blockers, immunosuppressant drugs, and biocides, which include triazines, triazoles, a carboxamide, carbamates, an organophosphate and a cationic surfactant. The results show that the energy return on the investment (EROI) was positive for all three investigated HTL processing temperatures: 300, 325, and 350 °C, with the most beneficial temperature identified as 325 °C. The HTL aqueous phase and solids' analysis indicates that the HTL process is a suitable technology for the destruction of micropollutants. However, the large matrix effect of the HTL aqueous phase affected the analyses, and only 9 from 30 pharmaceuticals and 5 out of 7 biocides products analyzed can be stated with certainty that was destroyed successfully (over 98% removal). The antidepressant citalopram showed to be slightly recalcitrant at 300 °C with 87% removal; however, it was destroyed at temperatures ≥325 °C (>99% removal). Overall, the results advocate that HTL is a suitable technology for energy-efficient and value-added sewage sludge treatment, enabling micropollutants' destruction.



Pilot-scale Hydrothermal liquefaction of sewage sludge: Energy considerations and the fate of micropollutants

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HTP
Hydrothermale Prozesse

6. HTP-Fachforum
25./26. November 2020

Introduction

The beneficial use of sewage sludge for the valorization of carbon and nutrients recovery has been of increasing interest; at the same time, micropollutants in sludge are of concern to the environment and human health. In this study, hydrothermal liquefaction (HTL) of sewage sludge is investigated in a continuous flow pilot-scale reactor, using conditions expected to reflect future industrial installations.

Methodology

Figure 1: Temperature and residence time of the HTL reaction conditions investigated.

The HTL process is evaluated in terms of energy efficiency, bio-crude quality, and yield. The raw sludge and post-HTL aqueous phase and solid residues were analyzed extensively for micropollutants via HPLC-MS/MS for reference pharmaceuticals including analgesics, antibiotics, antidepressants, blood pressure medicine, x-ray contrast media, angiotensin II receptor blockers, immunosuppressant drugs, and biocides, which include triazines, triazoles, a carboxamide, carbamates, an organophosphate and a cationic surfactant.

Results and Discussions

The energy return on the investment (EROI) was positive for all three investigated HTL processing temperatures: 300, 325, and 350°C, with the most beneficial temperature identified as 325°C

Table 1: Energetic analysis of HTL sludge processing at different experimental conditions.

Temperature	°C	300	±	325	±	350	±
Flow rate	L/h	94	0.3	43	0	39	0
Dry matter content	(wt.%)	16.0	1.4	16.0	1.4	16.0	1.4
Feedstock consumed	(kg, dry)	15.0	1.4	6.9	0.6	6.3	0.6
Energy in Feedstock	(kW, dry)	82.7	7.5	37.9	3.3	34.5	3.0
Bio-crude yield (as received)	(wt.%)	28.1	0.4	64.1	0.9	53.4	0.8
Bio-crude yield (dry)	(wt.%)	23.6	0.5	53.0	1.1	45.5	1.0
Bio-crude yield (dry solids free)	(wt.%)	17.7	0.5	40.8	1.2	31.8	0.9
HHV bio-crude (dry solids free)	(MJ/kg)	30.2	0.6	33.6	0.2	34.6	0.4
Energy in Bio-crude (dry solids free)	(kW, dry)	22.3	3.1	26.9	3.2	19.2	2.5
Thermal efficiency (η_{th})	(%)	27.0	1.3	69.3	2.4	55.6	2.2
Trim heater energy requirements	(kW)	6.9	0.6	5.5	0.3	7.4	2.4
Reactor energy requirement	(kW)	2.3	>0.01	2.0	0.3	4.2	0.1
Main pump energy requirement	(kW)	0.86	NA	0.40	NA	0.36	NA
Total efficiency (η_{tot})	(%)	24.1	1.2	57.4	2.2	41.2	0.4
EROI		2.2	0.2	3.4	0.2	1.6	0.1

Table 2: Removal rate of pharmaceuticals and pesticides in the hydrothermal reactor at 325°C, based on the mass balance of the system.

Group	Compound	HTL 325 °C Removal %	±
Antibiotics	Azithromycin	99.8	<0.1
	Clindamycin	85.4	0.1
Blood pressure regulators	Atenolol	98.9	<0.1
Antidepressant / Analgesic	Citalopram	99.9	<0.1
	Diclofenac	98.8	<0.1
	Ibuprofen	98.5	0.1
X-ray contrast media	Iomeprol	99.7	<0.1
Angiotensin II receptor blocker	Losartan	99.9	<0.1
Other uses	Mycophenolic acid	99.8	<0.1
Triazoles	Tebuconazole	99.4	0.1
Carbamates	Carbendazim	98.9	<0.1
Carboxamide	Diflufenican	99.9	<0.1
Cationic surfactant	12-BAC	99.9	<0.1
	14-BAC	99.9	<0.1
	16-BAC	99.9	<0.1

Highlights

- Maximum bio-crude yield of 41% obtained at 325°C.
- Bio-crude produced contained 3.4 times more energy than used for HTL processing.
- Large matrix effect of HTL process water on micropollutant analysis encountered.
- All quantifiable micropollutants were successfully destroyed at and above 325°C.

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Hydrothermale Verflüssigung I

Dr. Anne Roubaud, Commissariat à l'Energie Atomique et aux Energies Alternatives

Industrial CO_2 sequestration for biofuel production through micro-algae hydrothermal liquefaction

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This work presented below is part of a French integrated program, VASCO$_2$, for the development of a process route from CO_2 capture of industrial fumes through micro-algae cultivation to third generation biodiesel production. Within this project, CO_2 remediation was done by direct injection of industrial fumes in micro-algae cultivation open ponds. Several raceways were installed on different industrial sites in the Fos-sur-Mer industrial zone with two different size 10 and 160 m^2. Growth of a natural consortium of micro-algae was compared in sea water and industrial water. One of the bottleneck of this process route is that aquatic biomass is growing in highly diluted media (biomass concentration ~0.1-1 g/L DW). The first step is to harvest and concentrate the biomass to obtain an algae paste with 10w%dry matter. The harvesting step is done using the vacuum airlift process up to ~1-10 g/L DW, followed by a concentration step by centrifugation. To transform this highly wet biomass, hydrothermal conversion is better suited than dry routes, avoiding the energy consuming drying step. It converts organic matters into a black sticky oil that is often called a green crude or biocrude. Algae biomass is made of different kinds of natural polymers (lipids, proteins, carbohydrates). Under hydrothermal conditions, the natural polymers are deconstructed and transformed. The resulting biocrude has a reduced oxygen mass content compared to the initial biomass. Hence, its energetic content is higher. The natural microalgae consortium was harvested from the different raceways on industrial sites from Fos / mer and from Ifremer station at Palavas. The first lots were converted in a batch reactor due to small quantities and following harvests of larger size (5 to 10 Kg of algae paste at 8 to 12 % wt of dry matter) were converted into our continuous pilot. The selected operating conditions were 300 °C, 150 bar (continuous) or 90 bar (batch). The hydrothermal liquefaction continuous pilot is designed to work up to 350 °C and 200 bar with a flow rate between 0.5 and 2.5 L/h. This biocrude can be further separated into a bio-oil and a solid fraction named char. Bio-oil higher heating values obtained were between 35 and 38 MJ/kg with a carbon content between 74 and 78 w%. The carbon conversion yield into biocrude was between 48 and 70 % regarding to the different algae harvest batches and cultivation conditions.

In conclusion, micro-algae were cultivated successfully at pilot scale in sufficient quantities and quality to allow continuous operation. Conversion rates were determined for different algae batches from different sites and for different seasons. Feasibility of continuous operation for hydrothermal liquefaction was validated for the pilot as well as efficiency of conversion into a biocrude with an interesting energetic content. Production of algal biomass and biocrude wass validated for every time of the year and for every industrial site.

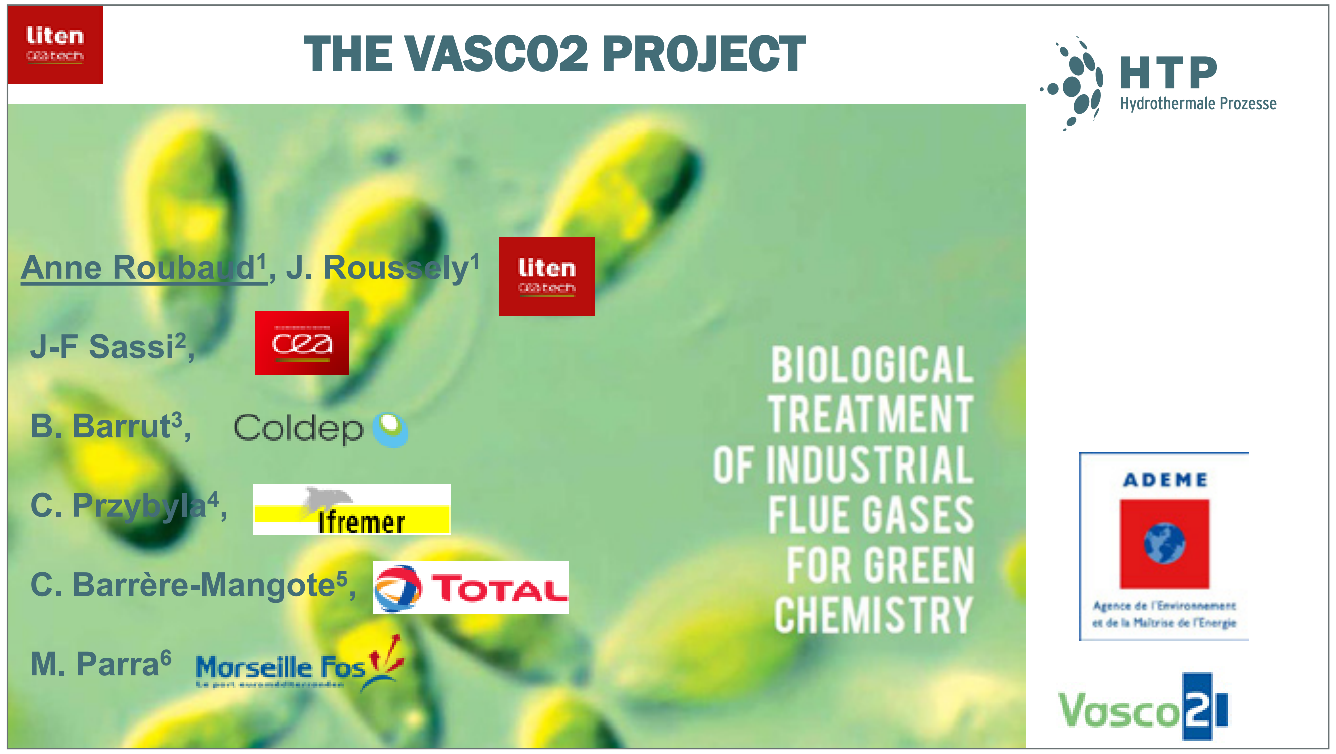
6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

Industrial CO_2 sequestration for biofuel production through microalgae hydrothermal liquefaction

Anne ROUBAUD
CEA LITEN

www.htp-inno.de



THE VASCO2 PROJECT

HTP Hydrothermale Prozesse

Anne Roubaud[1], J. Roussely[1]
J-F Sassi[2],
B. Barrut[3],
C. Przybyla[4],
C. Barrère-Mangote[5],
M. Parra[6]

BIOLOGICAL TREATMENT OF INDUSTRIAL FLUE GASES FOR GREEN CHEMISTRY

ADEME Agence de l'Environnement et de la Maîtrise de l'Energie

Vasco2

FOS industrial zone

HTP Hydrothermale Prozesse

Solamat Merex SARPI VEOLIA

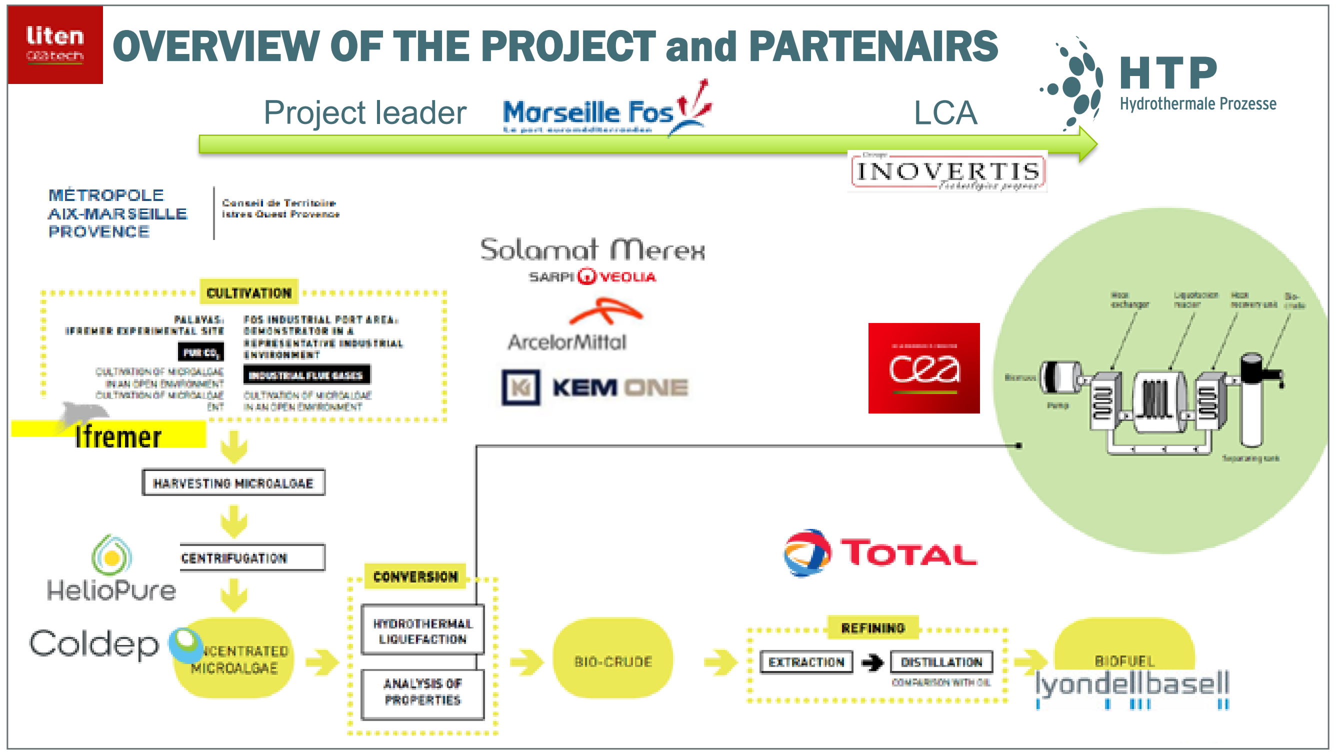
ArcelorMittal

KEM ONE

Marseille

ZIP de Fos

Vasco2



OVERVIEW OF THE PROJECT and PARTENAIRS

HTP Hydrothermale Prozesse

Project leader Marseille Fos LCA INOVERTIS

MÉTROPOLE AIX-MARSEILLE PROVENCE | Conseil de Territoire Istres Ouest Provence

CULTIVATION

PALAVAS: IFREMER EXPERIMENTAL SITE

PUR CO2

CULTIVATION OF MICROALGAE IN AN OPEN ENVIRONMENT

CULTIVATION OF MICROALGAE ENT

FOS INDUSTRIAL PORT AREA: DEMONSTRATOR IN A REPRESENTATIVE INDUSTRIAL ENVIRONMENT

INDUSTRIAL FLUE GASES

CULTIVATION OF MICROALGAE IN AN OPEN ENVIRONMENT

Ifremer

HARVESTING MICROALGAE

CENTRIFUGATION

CONCENTRATED MICROALGAE

HelioPure

Coldep

CONVERSION

HYDROTHERMAL LIQUEFACTION

ANALYSIS OF PROPERTIES

BIO-CRUDE

REFINING

EXTRACTION → DISTILLATION

COMPARISON WITH OIL

BIOFUEL

Solamat Merex SARPI VEOLIA

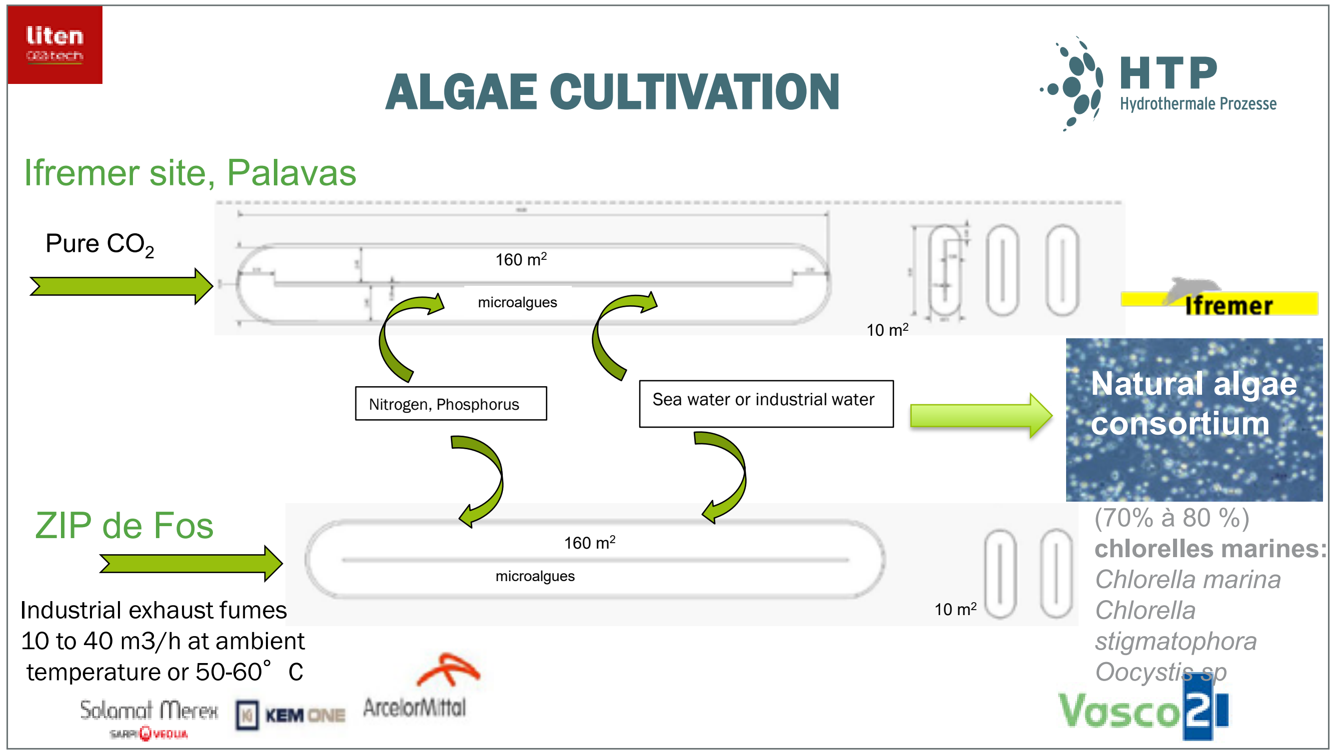
ArcelorMittal

KEM ONE

cea

TOTAL

lyondellbasell



ALGAE CULTIVATION

HTP Hydrothermale Prozesse

Ifremer site, Palavas

Pure CO_2

Nitrogen, Phosphorus

Sea water or industrial water

Ifremer

Natural algae consortium

ZIP de Fos

Industrial exhaust fumes 10 to 40 m3/h at ambient temperature or 50-60° C

(70% à 80 %) **chlorelles marines:** *Chlorella marina* *Chlorella stigmatophora* *Oocystis sp*

Solamat Merex SARPI VEOLIA

KEM ONE

ArcelorMittal

Vasco2

ALGAE CULTIVATION

HTP Hydrothermale Prozesse

Ifremer PALAVAS

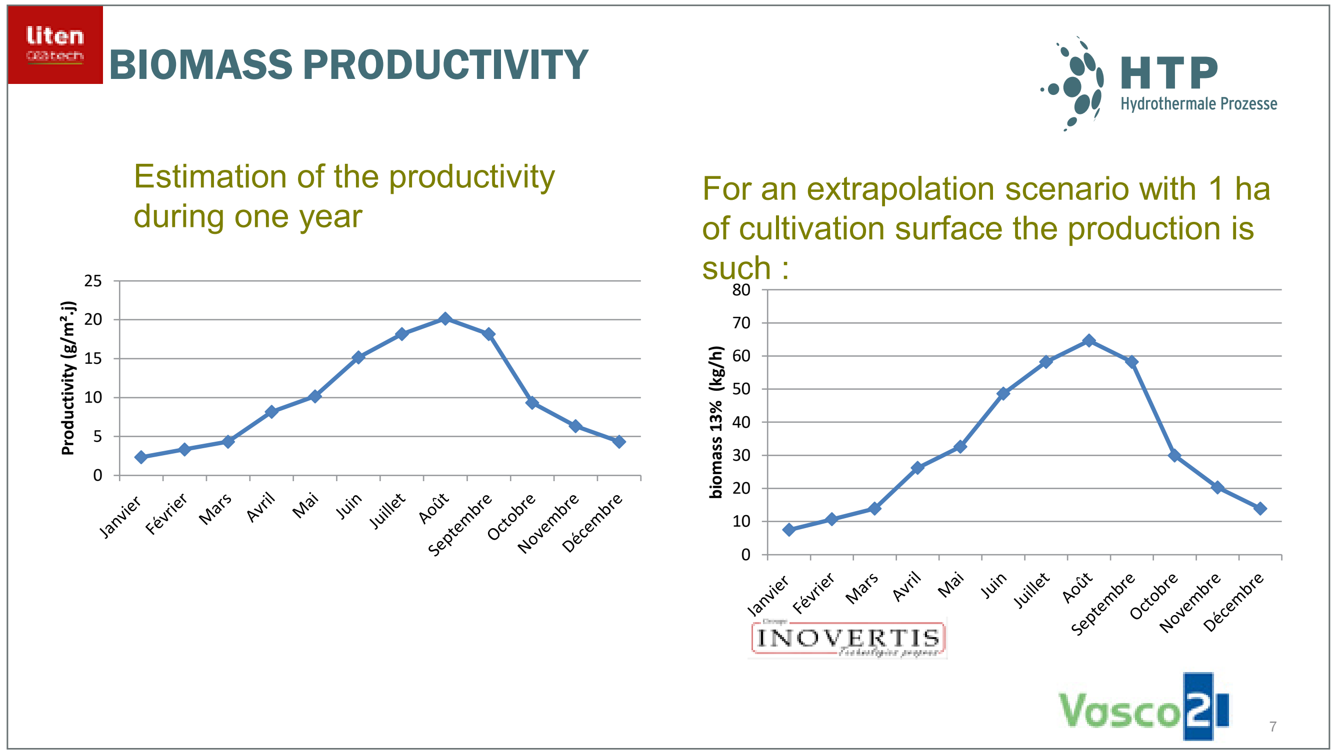
FOS / mer

Coldep

HelioPure

Crédit DroneStudio/Ifremer

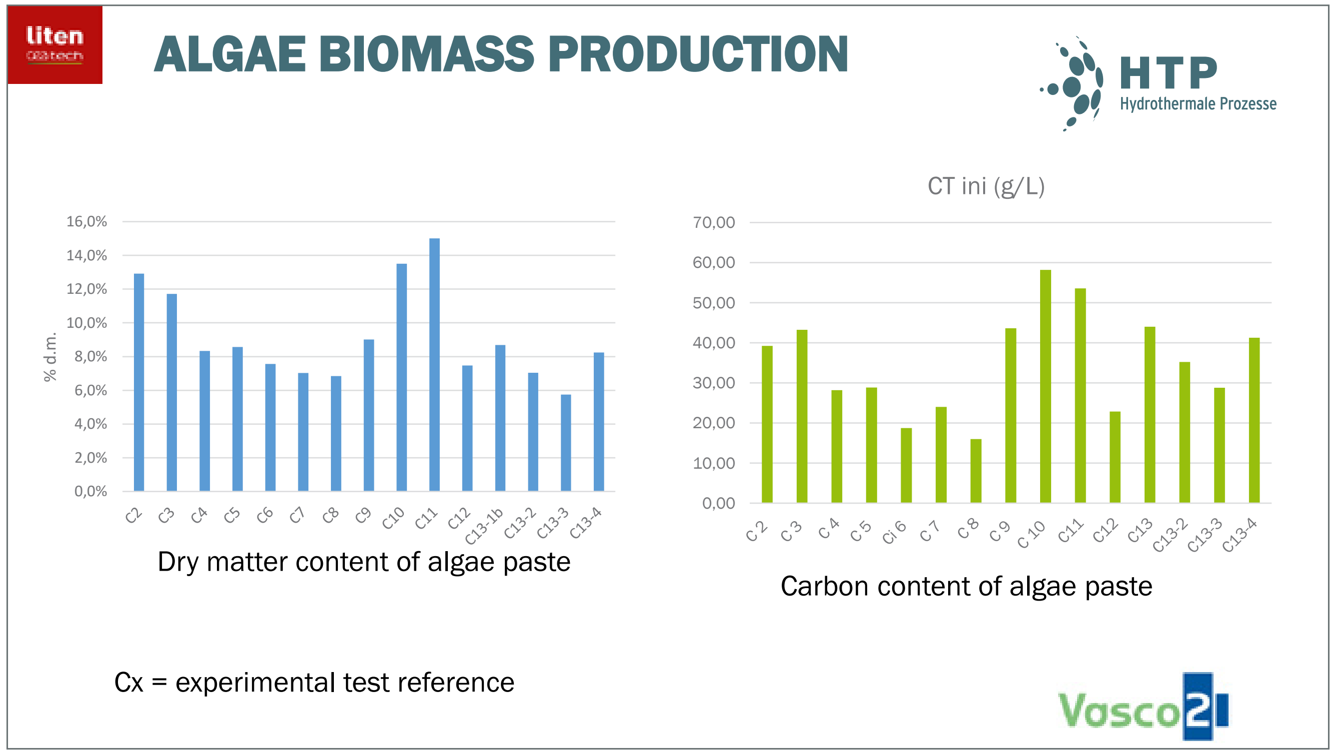
Vasco2



BIOMASS PRODUCTIVITY

Estimation of the productivity during one year

For an extrapolation scenario with 1 ha of cultivation surface the production is such :

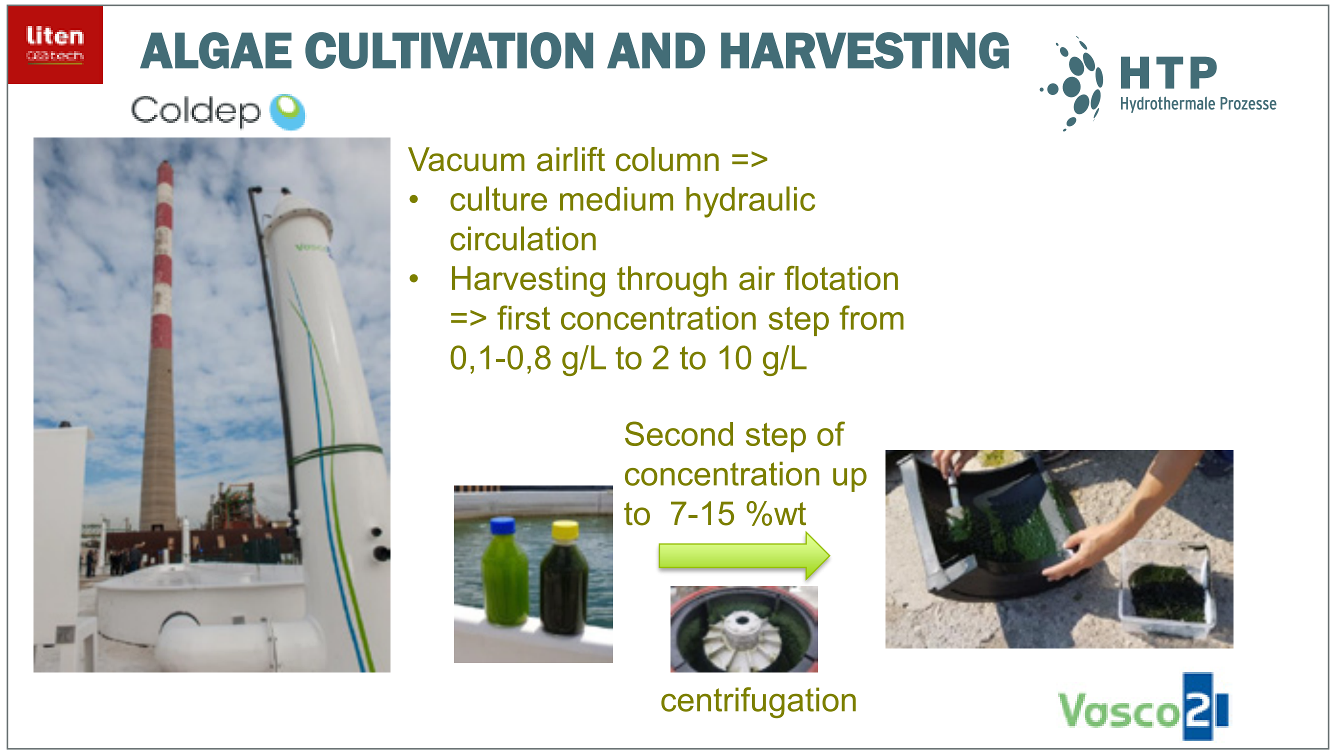


ALGAE BIOMASS PRODUCTION

Dry matter content of algae paste

Carbon content of algae paste

Cx = experimental test reference



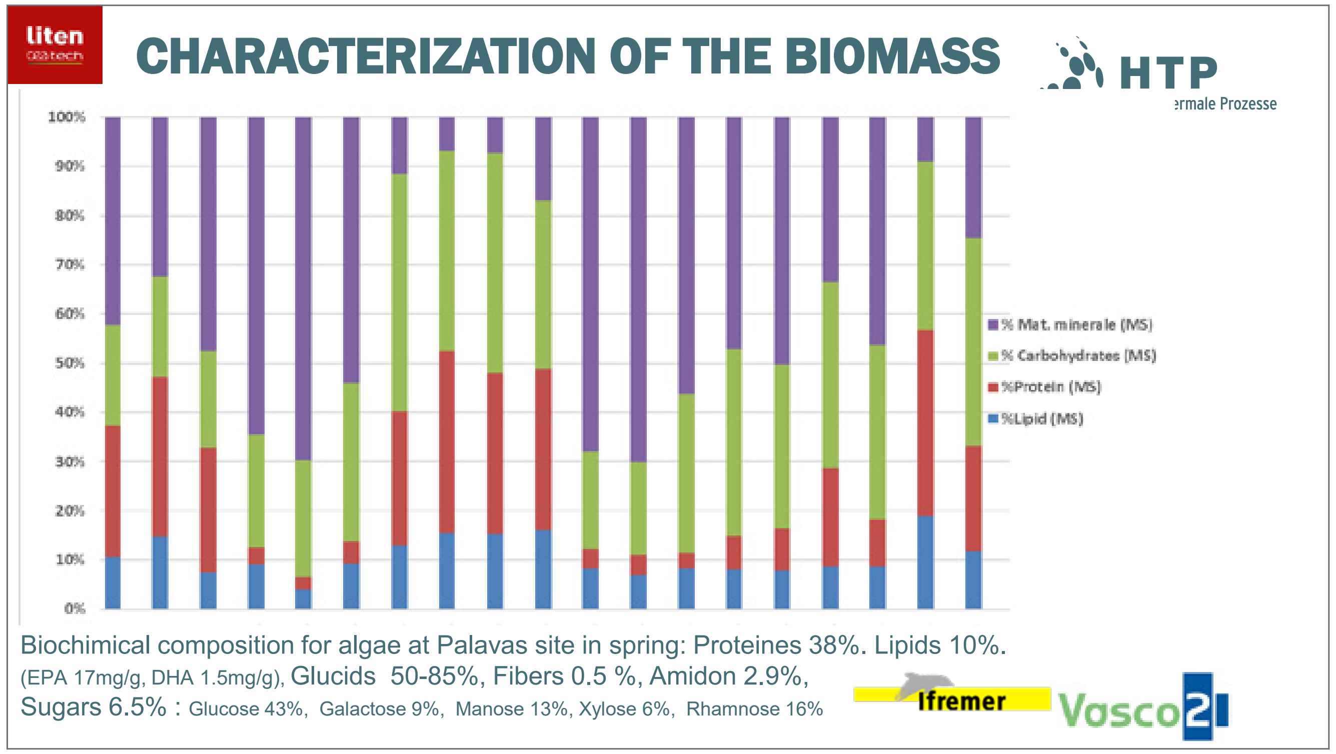
ALGAE CULTIVATION AND HARVESTING

Vacuum airlift column =>

- culture medium hydraulic circulation
- Harvesting through air flotation => first concentration step from 0,1-0,8 g/L to 2 to 10 g/L

Second step of concentration up to 7-15 %wt

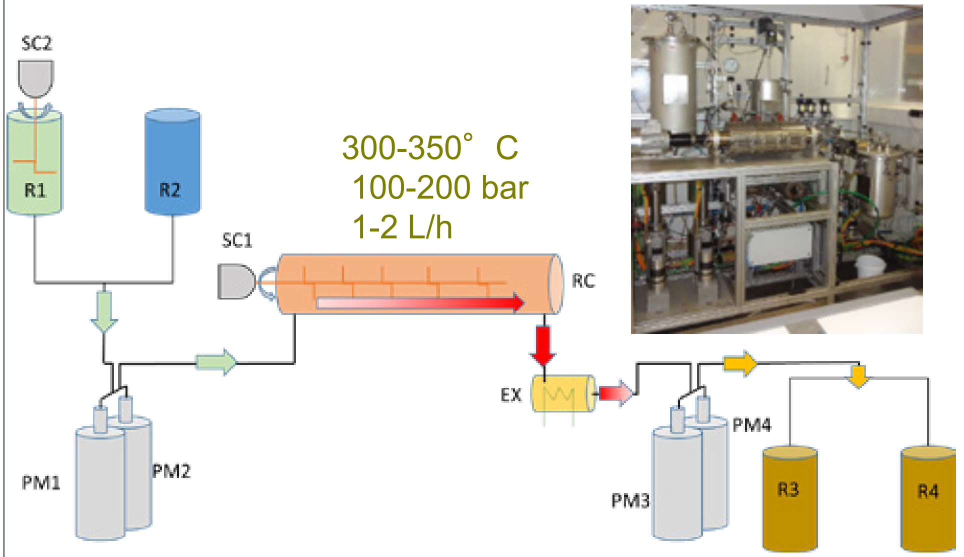
centrifugation



CHARACTERIZATION OF THE BIOMASS

Biochimical composition for algae at Palavas site in spring: Proteines 38%. Lipids 10%. (EPA 17mg/g, DHA 1.5mg/g), Glucids 50-85%, Fibers 0.5 %, Amidon 2.9%, Sugars 6.5% : Glucose 43%, Galactose 9%, Manose 13%, Xylose 6%, Rhamnose 16%

CONVERSION THROUGH HYDROTHERMAL LIQUEFACTION



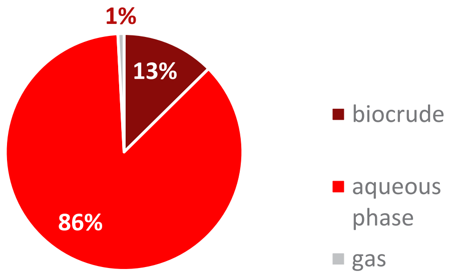
300-350° C
100-200 bar
1-2 L/h

R1, R2 : water and biomass reservoirs
PM1, PM2 : feeding pumps
PM3, PM4 : pressure regulation pumps
R3, R4 : product recovery reservoirs
RC : conversion reactor
EX : heat exchanger
SC1, SC2 : stirrers

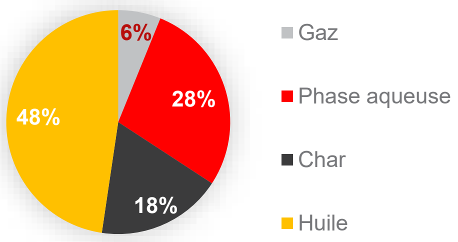
CONVERSION EFFICIENCY AND PRODUCTS DISTRIBUTION

Algae paste with 8,2 % d.m. (and 16,3 % wt of mineral matter)

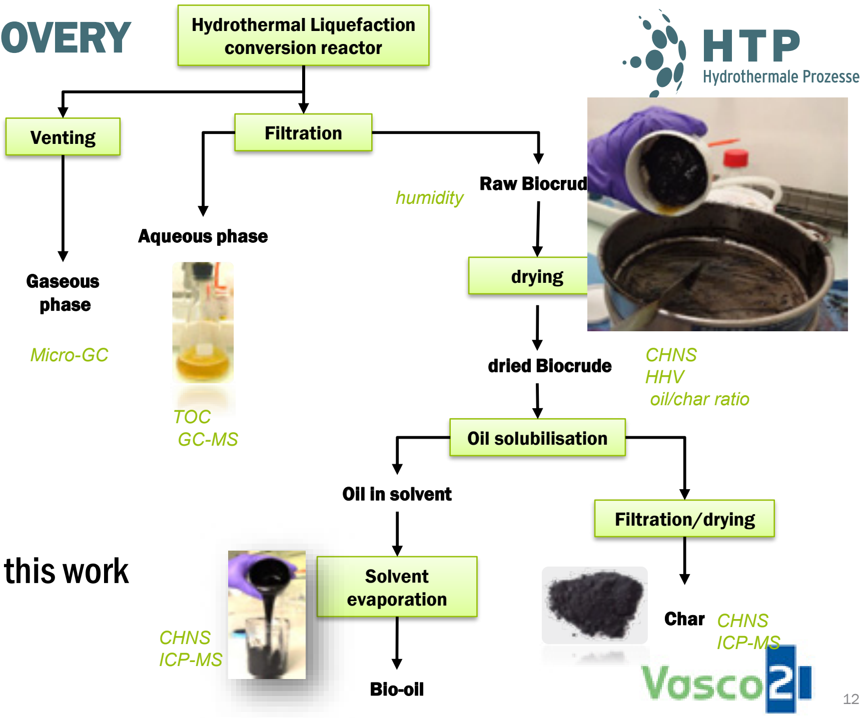
Example weight distribution



Example Carbone distribution



PRODUCTS RECOVERY



Hydrothermal Liquefaction conversion reactor

Venting

Gaseous phase

Micro-GC

Filtration

Aqueous phase

TOC
GC-MS

Raw Biocrud

humidity

drying

dried Biocrude

CHNS
HHV
oil/char ratio

Oil solubilisation

Oil in solvent

Solvent evaporation

CHNS
ICP-MS

Bio-oil

Filtration/drying

Char *CHNS*
ICP-MS

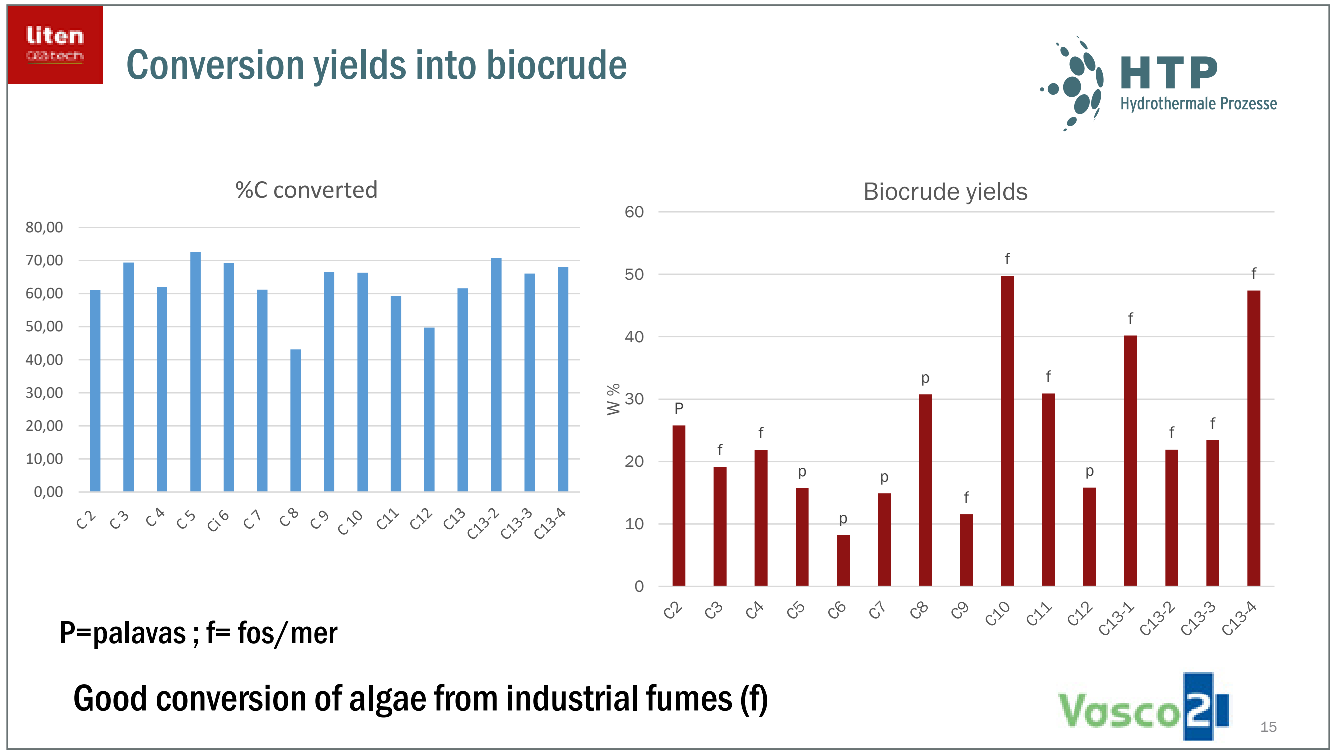
Solvent used is toluene is this work

Production resume

algae paste converted (g)	site	harvest month	culltivation medium	weight of biocrude* produced (g)
4000	P	6	sea water	140
2869	F	5	sea water	70
3400	F	8	sea water	66
7900	P	8	sea water	106
8000	P	9	sea water	63
12400	P	4	sea water	180
8500	P	5	sea water	190
9710	F	7	soft water	176
5305	F	7	soft water	1042
2605	F	7 to 10	sea water	408
8000	P	1 to 5	sea water	283
12000	F	12	soft water	1333
8300	F	12	soft water	463
6255	F	12	soft water	204
9980	F	12	soft water	1203

P=palavas ; f= fos/mer

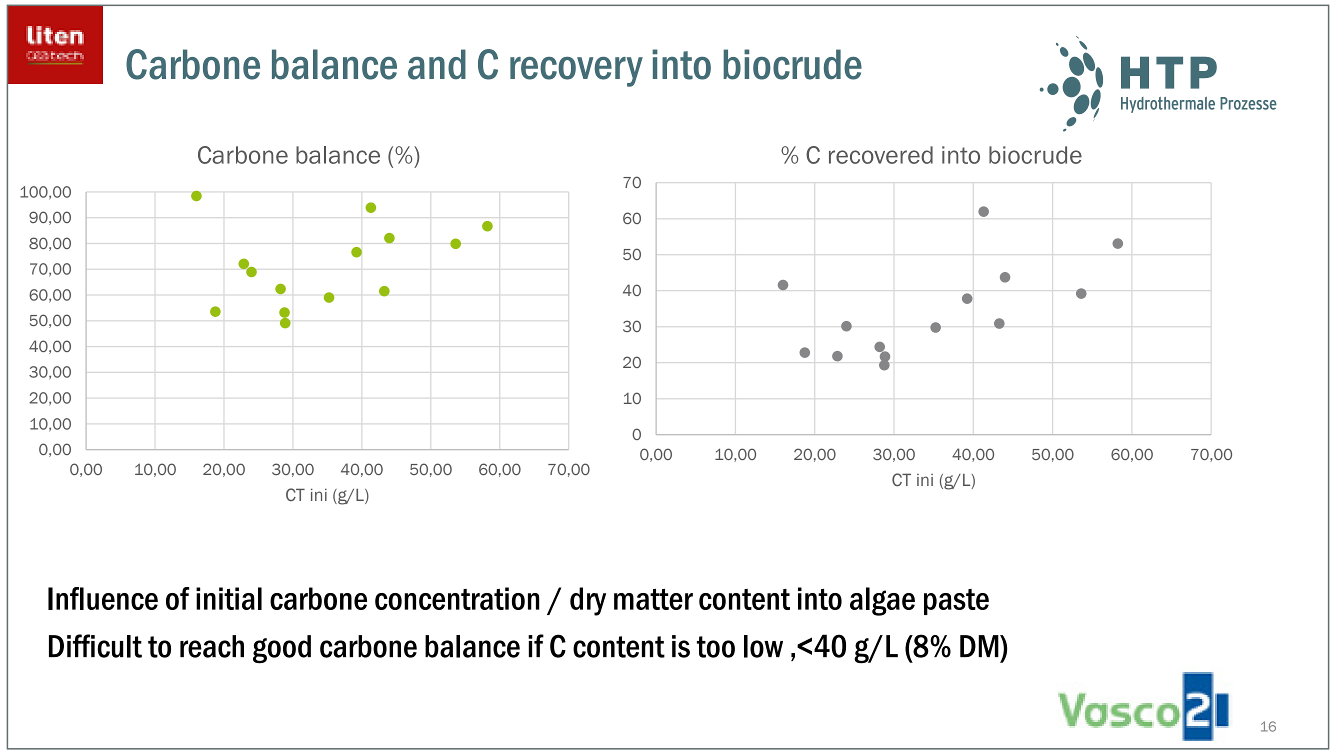
* Wet biocrude



Conversion yields into biocrude

P=palavas ; f= fos/mer

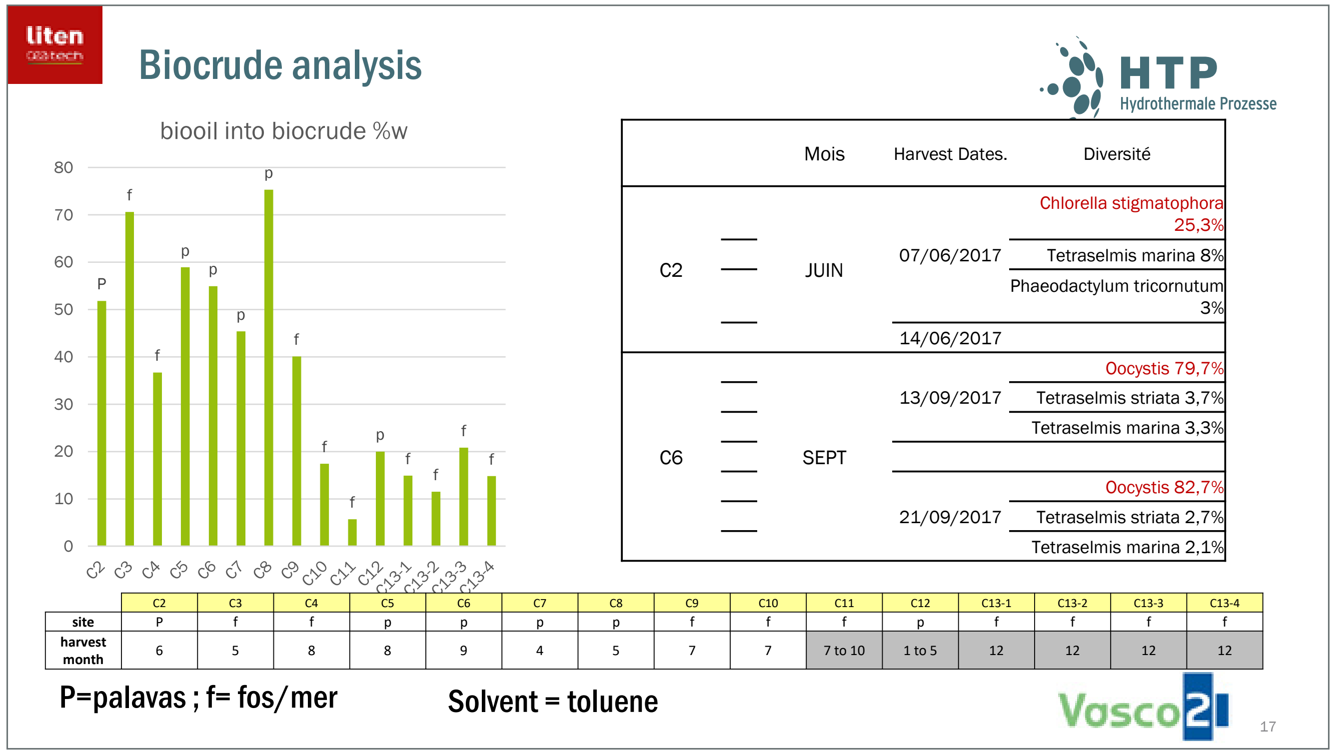
Good conversion of algae from industrial fumes (f)



Carbone balance and C recovery into biocrude

Influence of initial carbone concentration / dry matter content into algae paste

Difficult to reach good carbone balance if C content is too low ,<40 g/L (8% DM)



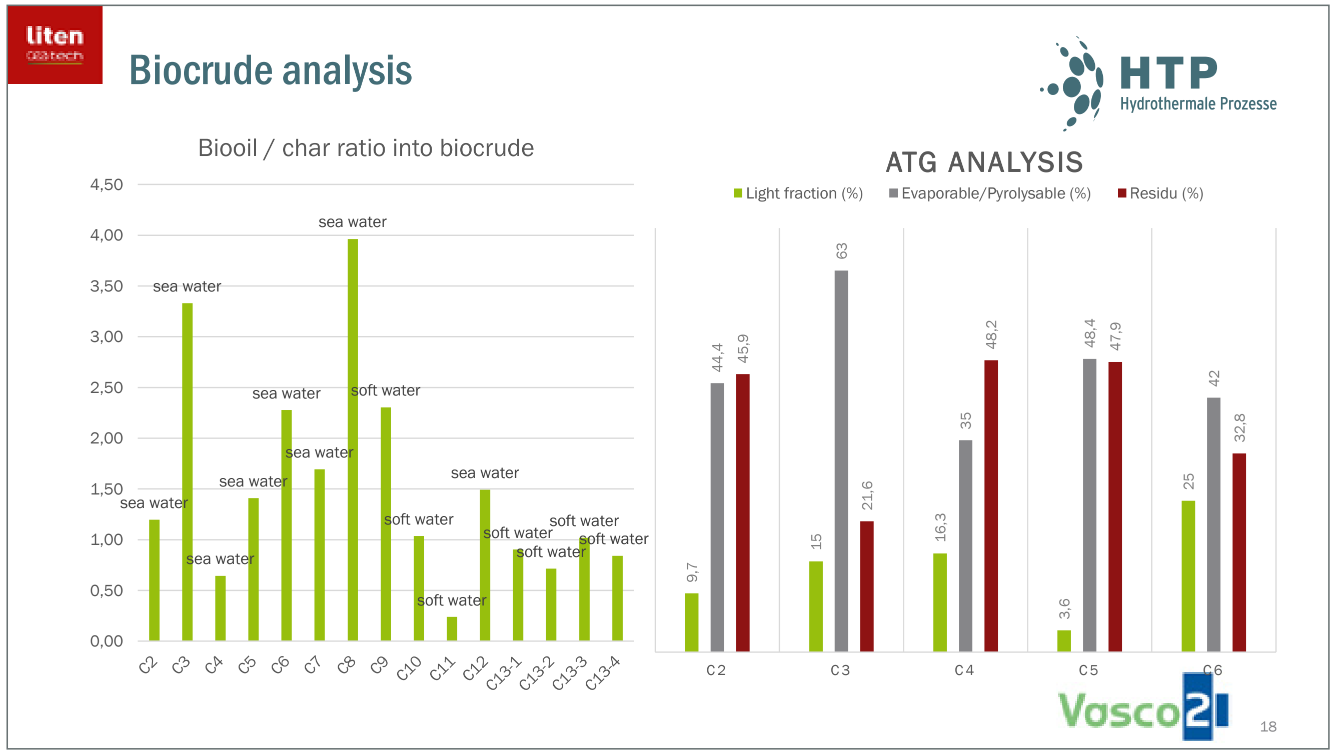
Biocrude analysis

		Mois	Harvest Dates.	Diversité
C2		JUIN	07/06/2017	Chlorella stigmatophora 25,3%
				Tetraselmis marina 8%
				Phaeodactylum tricornutum 3%
			14/06/2017	
C6		SEPT	13/09/2017	Oocystis 79,7%
				Tetraselmis striata 3,7%
				Tetraselmis marina 3,3%
			21/09/2017	Oocystis 82,7%
				Tetraselmis striata 2,7%
				Tetraselmis marina 2,1%

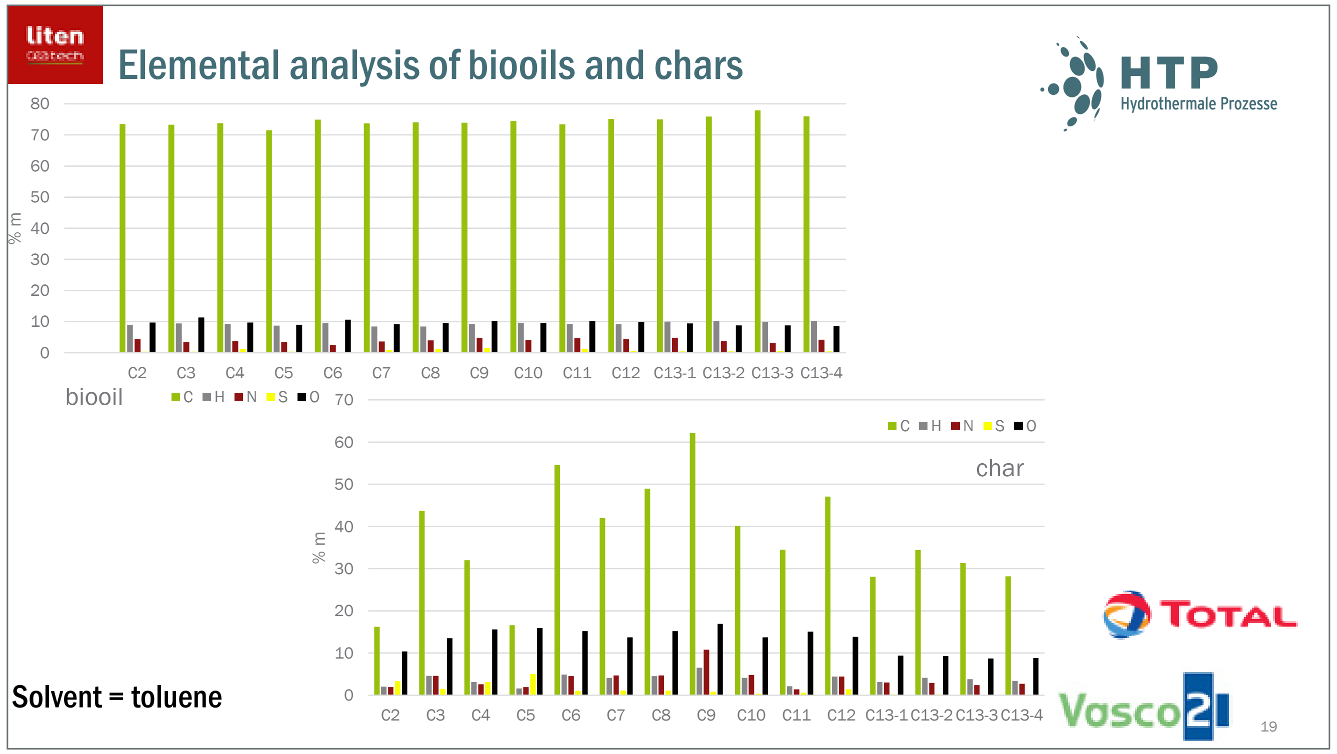
	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13-1	C13-2	C13-3	C13-4
site	P	f	f	p	p	p	p	f	f	f	p	f	f	f	f
harvest month	6	5	8	8	9	4	5	7	7	7 to 10	1 to 5	12	12	12	12

P=palavas ; f= fos/mer

Solvent = toluene

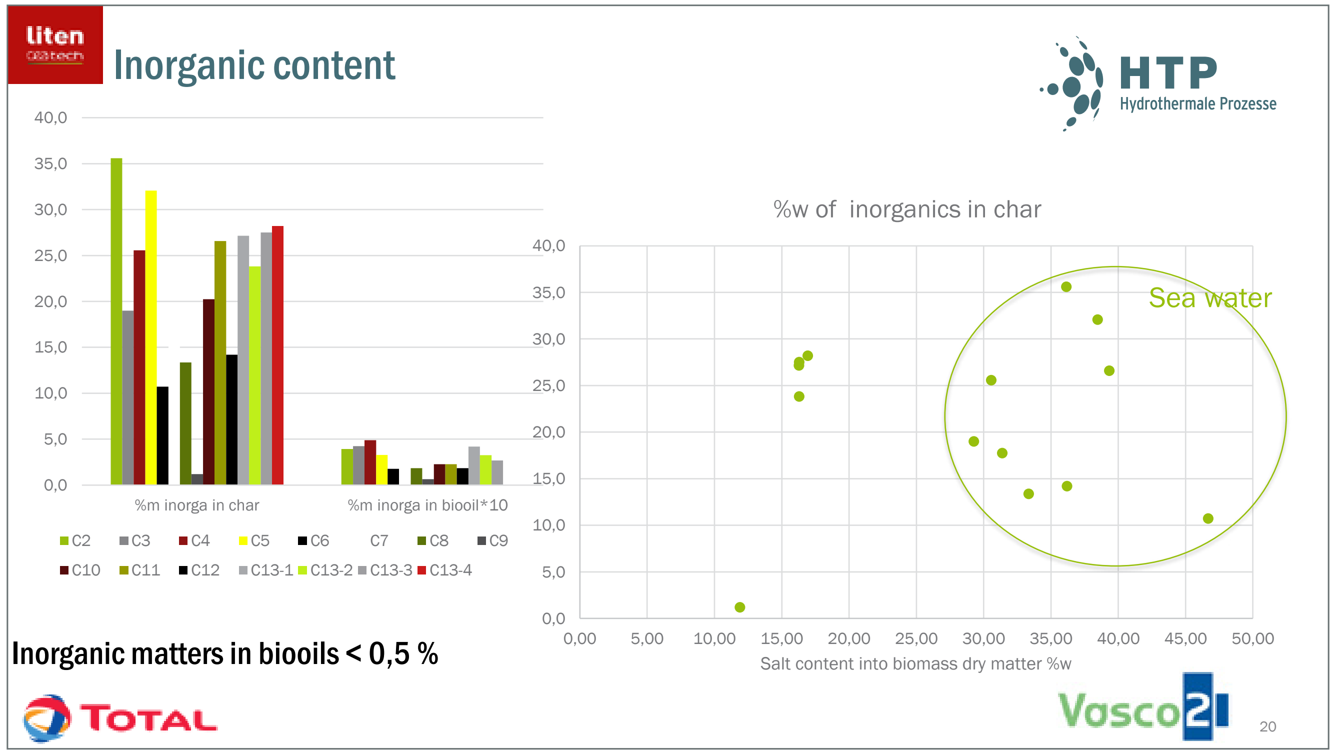


Biocrude analysis



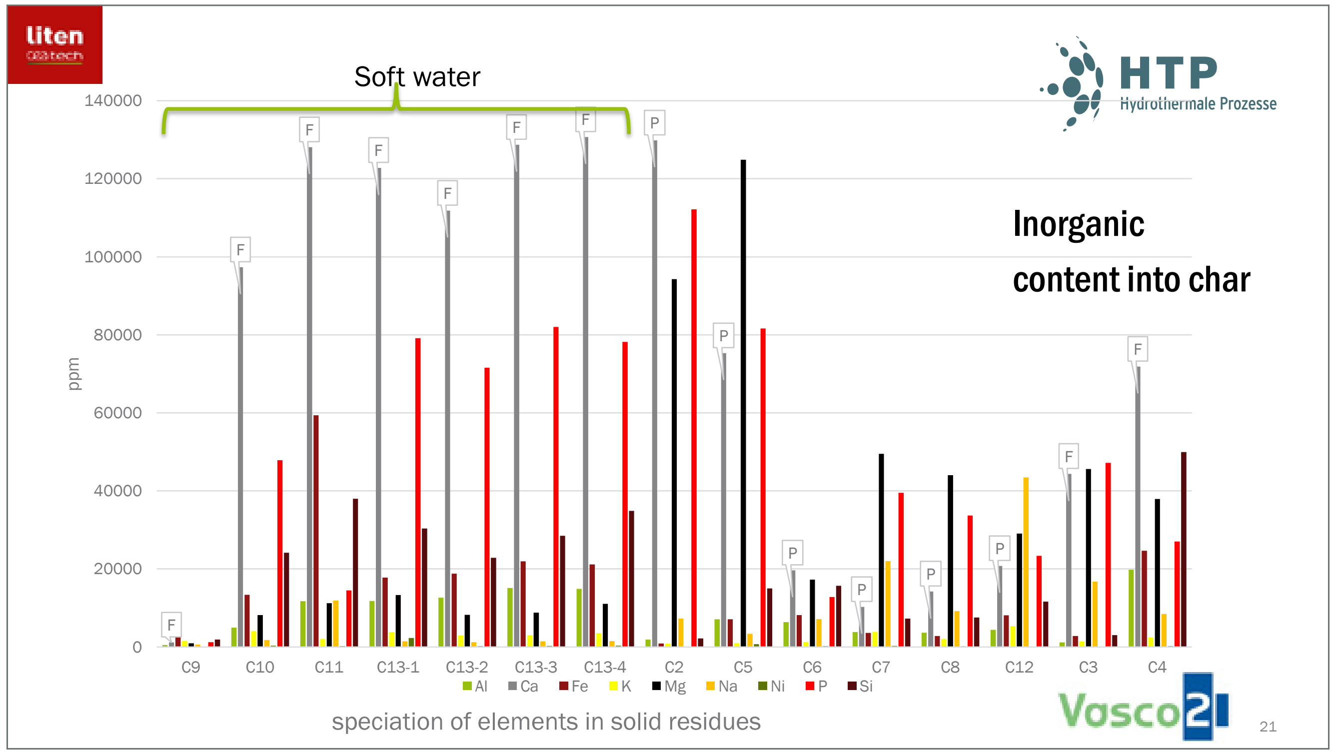
Elemental analysis of biooils and chars

Solvent = toluene



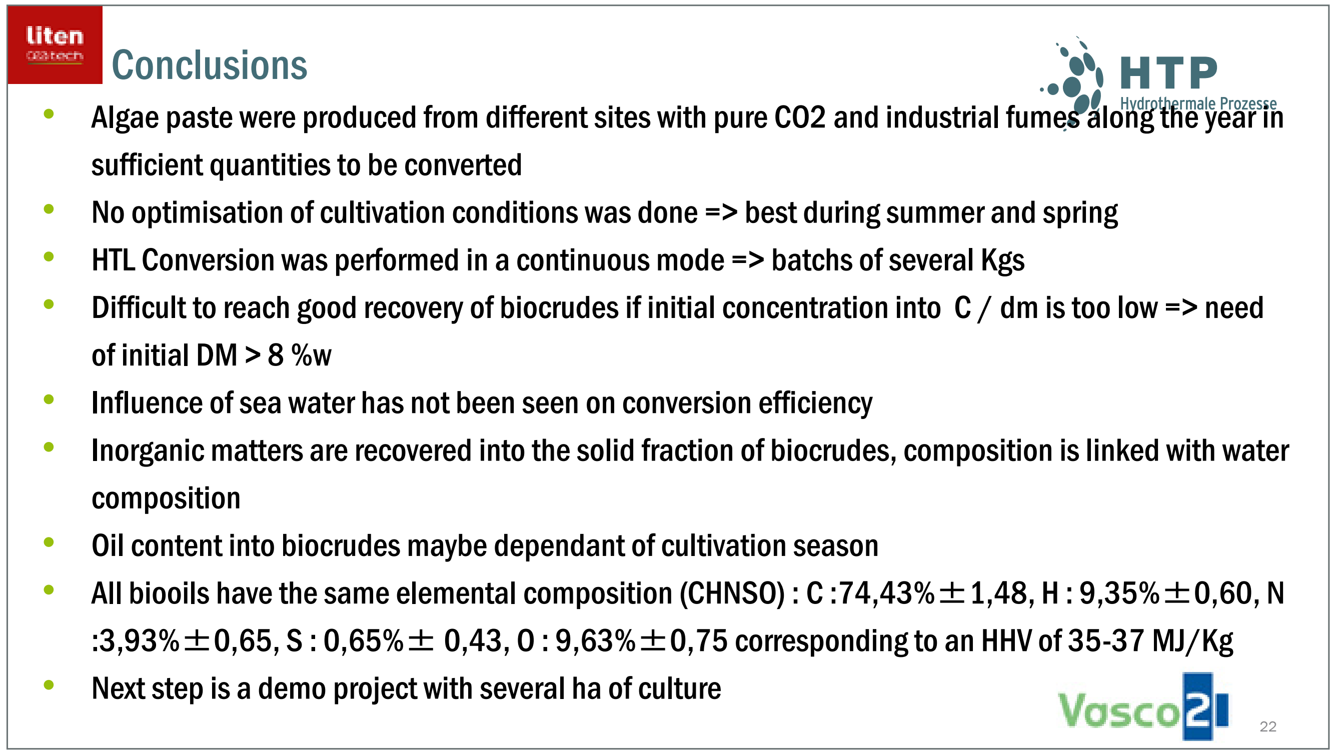
Inorganic content

Inorganic matters in biooils < 0,5 %



Inorganic content into char

speciation of elements in solid residues



Conclusions

- Algae paste were produced from different sites with pure CO2 and industrial fumes along the year in sufficient quantities to be converted
- No optimisation of cultivation conditions was done => best during summer and spring
- HTL Conversion was performed in a continuous mode => batchs of several Kgs
- Difficult to reach good recovery of biocrudes if initial concentration into C / dm is too low => need of initial DM > 8 %w
- Influence of sea water has not been seen on conversion efficiency
- Inorganic matters are recovered into the solid fraction of biocrudes, composition is linked with water composition
- Oil content into biocrudes maybe dependant of cultivation season
- All biooils have the same elemental composition (CHNSO) : C :74,43%±1,48, H : 9,35%±0,60, N :3,93%±0,65, S : 0,65%± 0,43, O : 9,63%±0,75 corresponding to an HHV of 35-37 MJ/Kg
- Next step is a demo project with several ha of culture

6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

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Dr. Guillaume Boissonnet, Commissariat à l‘Energie Atomique et aux Energies Alternatives

Hydrothermal liquefaction and gasification process assessments applied to different kind of resources

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Wet organic wastes (sewage sludge from municipal water treatment or food wastes) or algae are organic resources with a very high water content and a quite interesting carbon, hydrogen and energy content in their dry matter. The high water content makes incineration or gasification inefficient. It is then preferred to convert them through hydrothermal processes, to produces either organic liquids or gas. Hydrothermal liquefaction (HTL) converts organic matter in hot compressed water into a hydrophobic oily residue. HTL increases the energy content of the organic matter while facilitating its separation. The conversion takes place at temperatures between 300 and 400 °C and at pressures above the saturation pressure to assure that the reaction mixture remain liquid. Hydrothermal Gasification (HTG or Supercritical gasification) converts organic matter in hot compressed water into a gas containing mainly CH_4 or H_2 (depending of temperature conditions) and CO_2. The conversion takes place at temperatures between 600 and 800 °C and at pressures below the water critical point. This paper presents the analysis of different resources such as sewage sludges, algae and food wastes processed though HTG and HTL. The assessment criteria are mass yield and energy efficiency and economics (investments, operating costs and production cost) This paper presents the results of hydrothermal experiments at different conditions and for different sewage sludges, food wastes and algae. Under HTL conditions, bio-oil yields of 25 to 50 % are achievable. The analysis are both elemental and in terms of fibres, lipids and proteins. From the results, we show that sludge produced by the digestion process is less interesting as a resource as it contains too much ash. In the whole bio-oil, we also differentiate the oil produced in the HTL reactions from the oil naturally present (and converted) in the sludge.Under HTG conditions, gas yields range from X to X. The H_2 and CH_4 composition are considered. The results highlight the necessity of a strong energy integration to make these processes profitable in terms of energy. The economic assessment shows the level of profitability of HTL processes. It also show that an economic equilibrium is more difficult to achieve with HTG processes, due to a much more high investment linked to extreme conditions of the process. This work shows how HTL liquefaction can make a difference in the processing of sewage sludge and food waste. Three different sewage sludges from two municipal water treatment works were studied: mixed sludge from a small sewage plant with a one-step treatment, activated sludge from the aeration basin of a large treatment plant and digested sludge from a methanisation unit. HTL can significantly increase the energetic value of sewage sludge with a relatively simple process. It also shows, under which specific conditions and in what context, HTG process could be relevant.

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Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HYDROTHERMAL LIQUEFACTION AND GASIFICATION PROCESSES.
ASSESSMENTS APPLIED TO DIFFERENT KIND OF RESOURCES.

Guillaume Boissonnet, Geert Haarlemmer, Stéphane Colasson, Morgane Briand, Cyril Bourasseau,
Thierry Chataing, Vincent Lacroix Julien Roussely, Anne Roubaud, Gilles Ratel
CEA Grenoble - France

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Introduction

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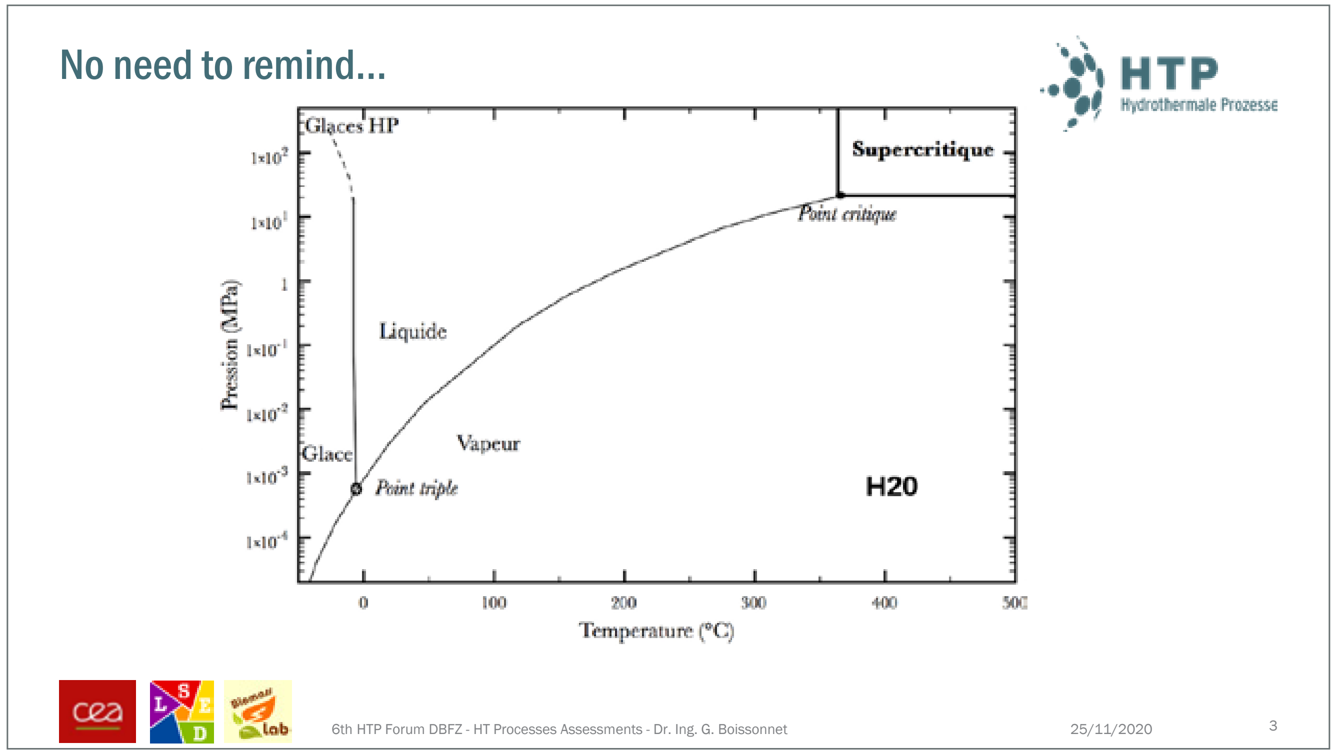
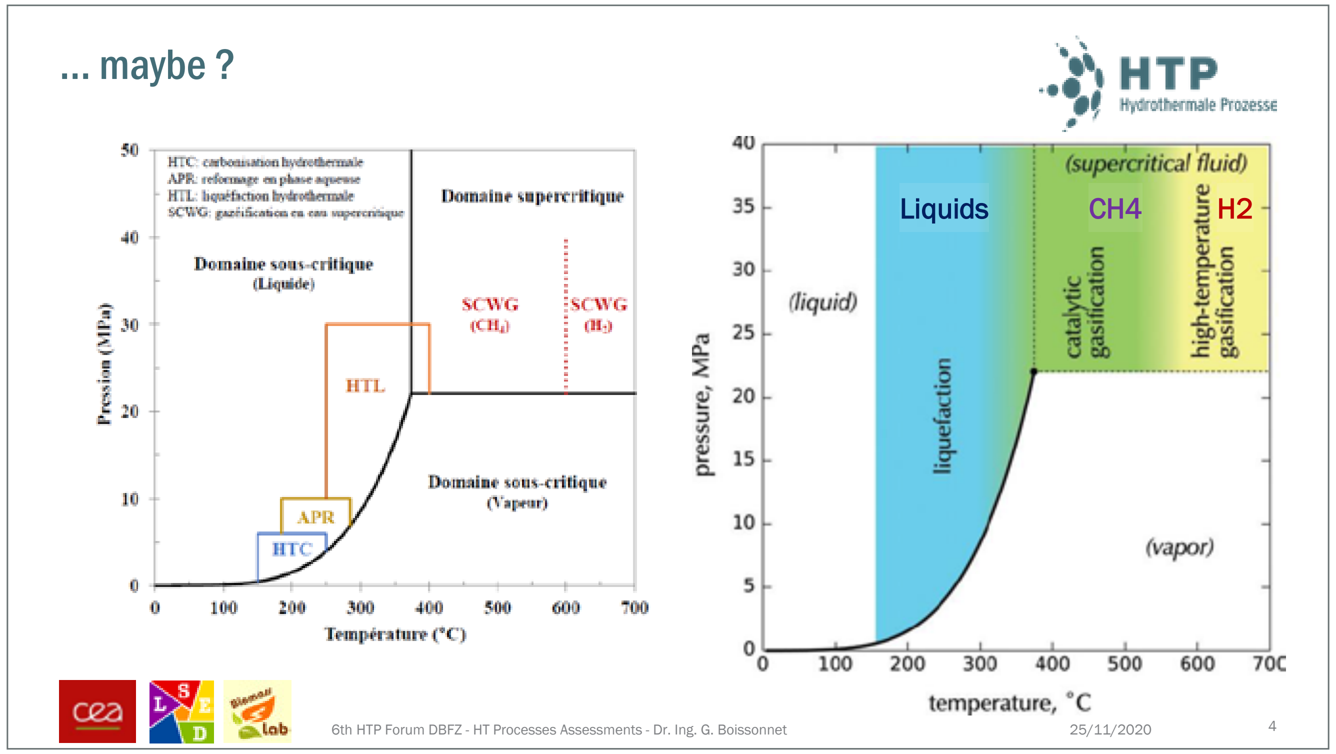


No need to remind...



... maybe ?

Advantages and Constraints

Way to produce
- Liquids approaching fossil crude-oil
- CH4 or H2 with low pollutants

Way to recover
- Salts
- Nitrogen under mineral form

Process risks linked to
- Pressure
- Corrosion
- Metal weakening
- Plugging

Objectives of the studies

Balances and economic assessments of several processes
- Several resources: algae, sludge, agricultural and food industry residues, wood
- Several conditions: sub and supercritical
- Several products: liquids, CH4 and H2

Assessments
- Energy and material balances
- Energy integration
- Process / Technology improvement
- CAPEX and OPEX estimation
- Economics (LCOP, LCOE)

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Thermodynamics
A Water content issue

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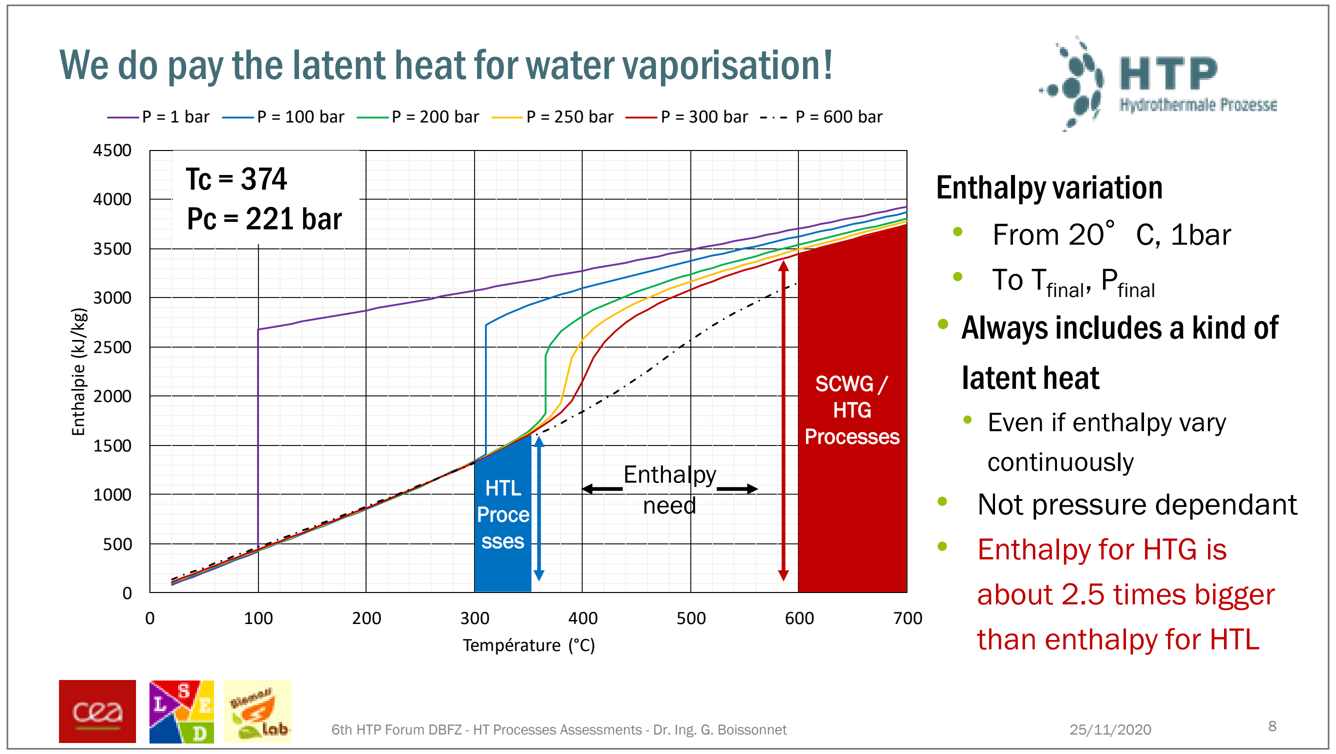
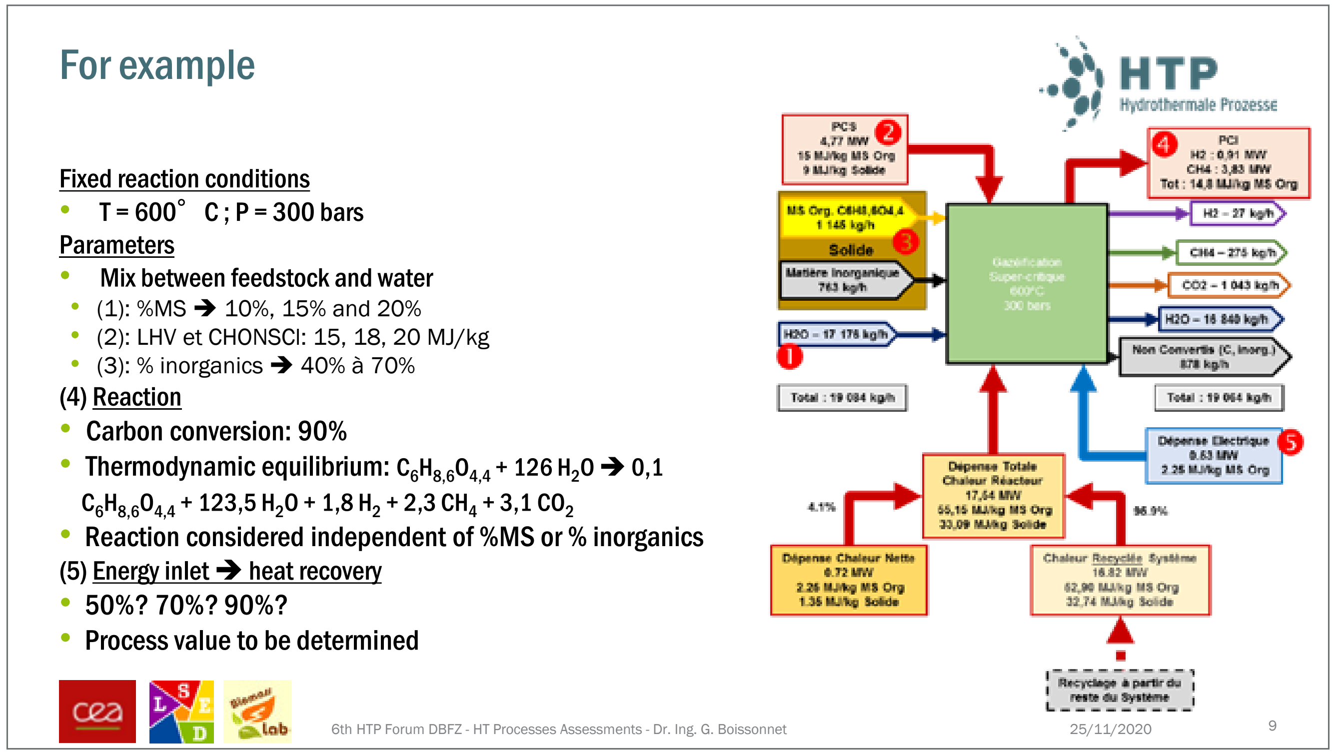


We do pay the latent heat for water vaporisation!

Enthalpy variation

- From 20° C, 1bar
- To T_{final}, P_{final}

- Always includes a kind of latent heat
  - Even if enthalpy vary continuously
- Not pressure dependant
- Enthalpy for HTG is about 2.5 times bigger than enthalpy for HTL



For example

Fixed reaction conditions

- T = 600° C ; P = 300 bars

Parameters

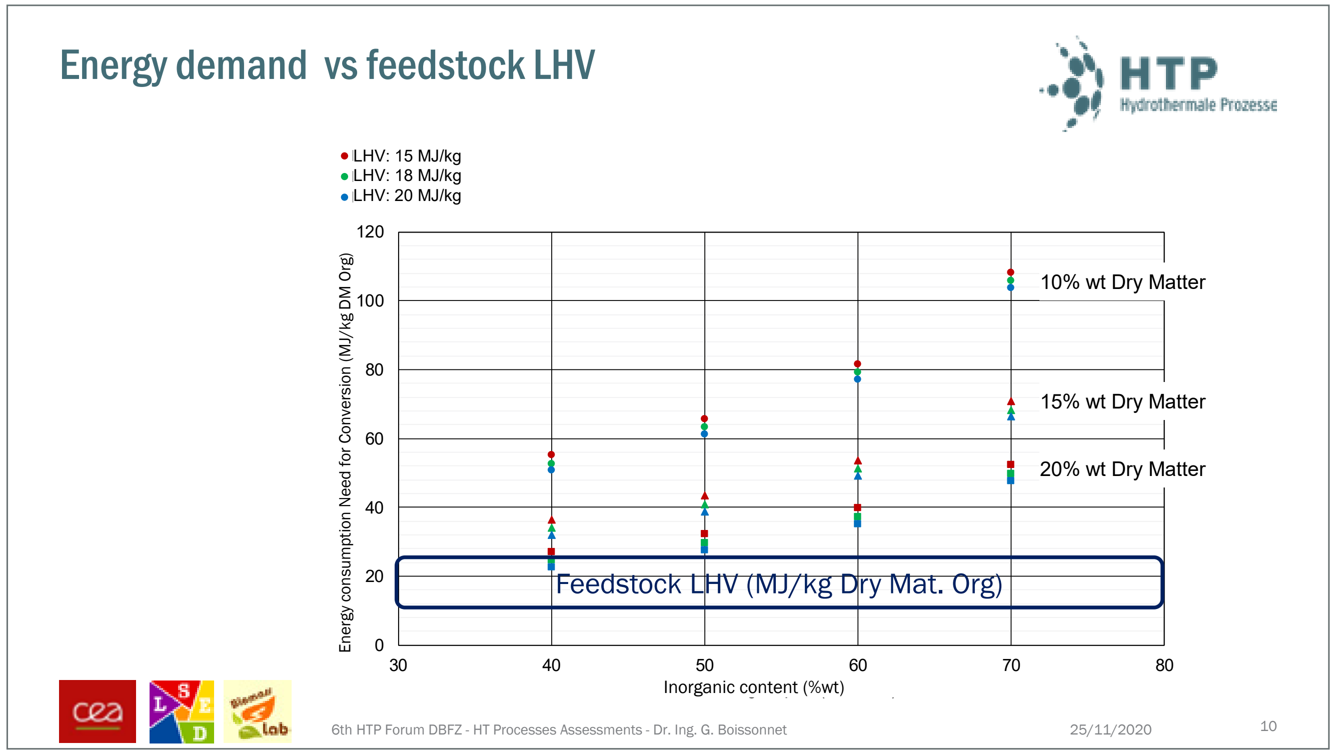
- Mix between feedstock and water
- (1): %MS ➔ 10%, 15% and 20%
- (2): LHV et CHONSCl: 15, 18, 20 MJ/kg
- (3): % inorganics ➔ 40% à 70%

(4) Reaction

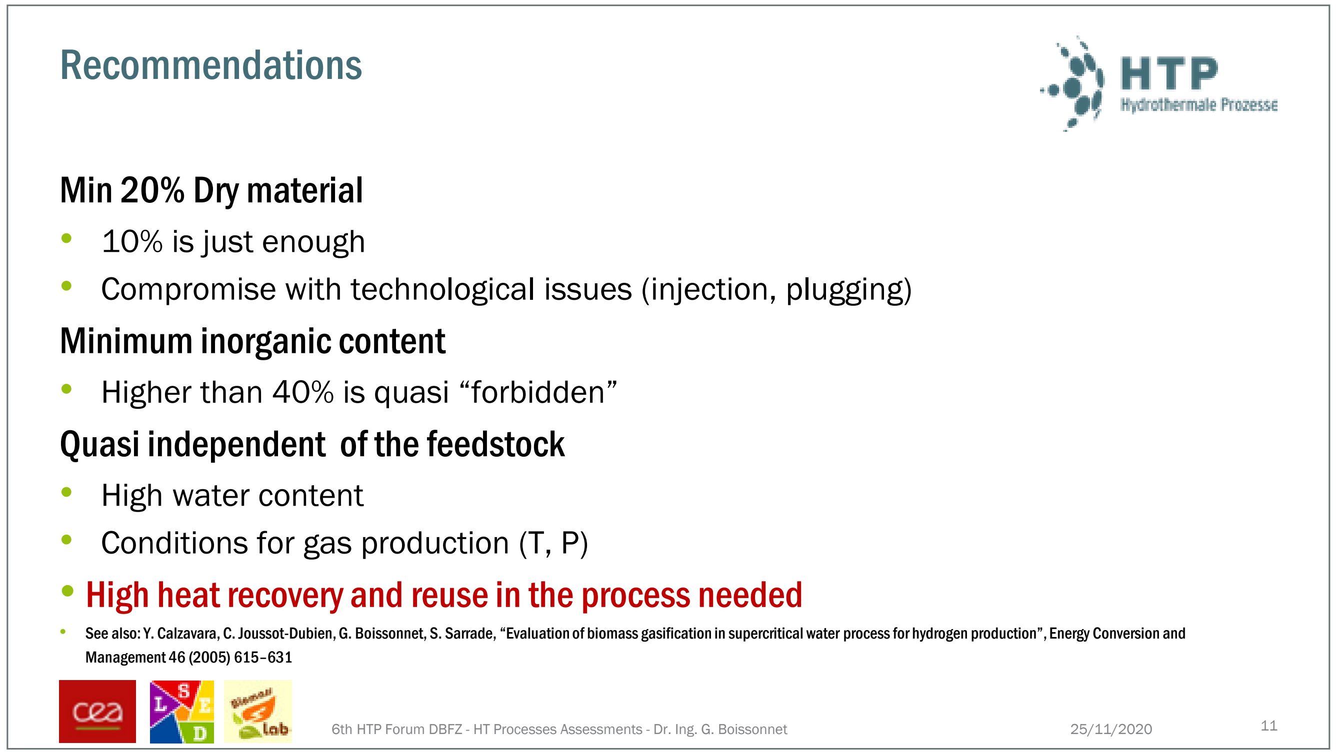
- Carbon conversion: 90%
- Thermodynamic equilibrium: $C_6H_{8,6}O_{4,4} + 126\ H_2O \rightarrow 0{,}1\ C_6H_{8,6}O_{4,4} + 123{,}5\ H_2O + 1{,}8\ H_2 + 2{,}3\ CH_4 + 3{,}1\ CO_2$
- Reaction considered independent of %MS or % inorganics

(5) Energy inlet ➔ heat recovery

- 50%? 70%? 90%?
- Process value to be determined



Energy demand vs feedstock LHV



Recommendations

HTP Hydrothermale Prozesse

Min 20% Dry material

- 10% is just enough
- Compromise with technological issues (injection, plugging)

Minimum inorganic content

- Higher than 40% is quasi "forbidden"

Quasi independent of the feedstock

- High water content
- Conditions for gas production (T, P)
- **High heat recovery and reuse in the process needed**
- See also: Y. Calzavara, C. Joussot-Dubien, G. Boissonnet, S. Sarrade, "Evaluation of biomass gasification in supercritical water process for hydrogen production", Energy Conversion and Management 46 (2005) 615–631

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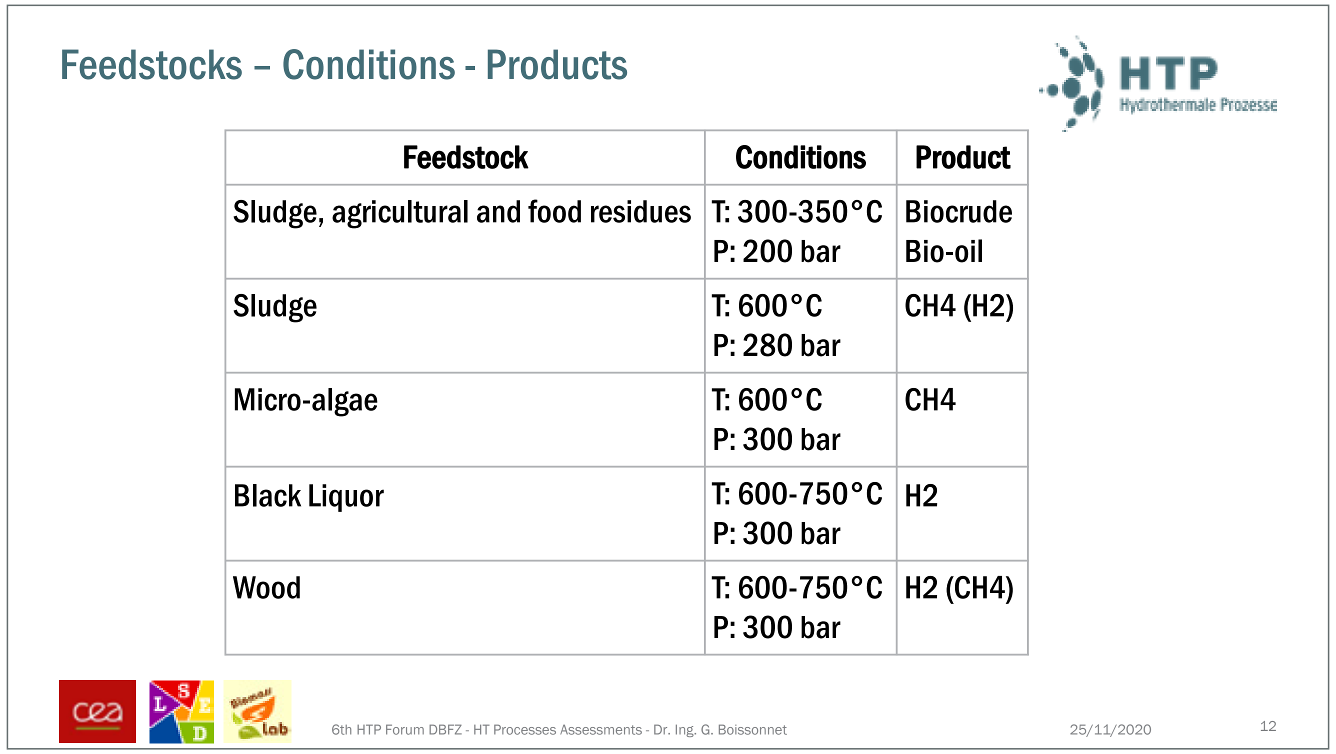

Feedstocks – Conditions - Products

HTP Hydrothermale Prozesse

Feedstock	Conditions	Product
Sludge, agricultural and food residues	T: 300-350°C P: 200 bar	Biocrude Bio-oil
Sludge	T: 600°C P: 280 bar	CH4 (H2)
Micro-algae	T: 600°C P: 300 bar	CH4
Black Liquor	T: 600-750°C P: 300 bar	H2
Wood	T: 600-750°C P: 300 bar	H2 (CH4)

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SCWG to produce CH4 and H2
A question of energy integration

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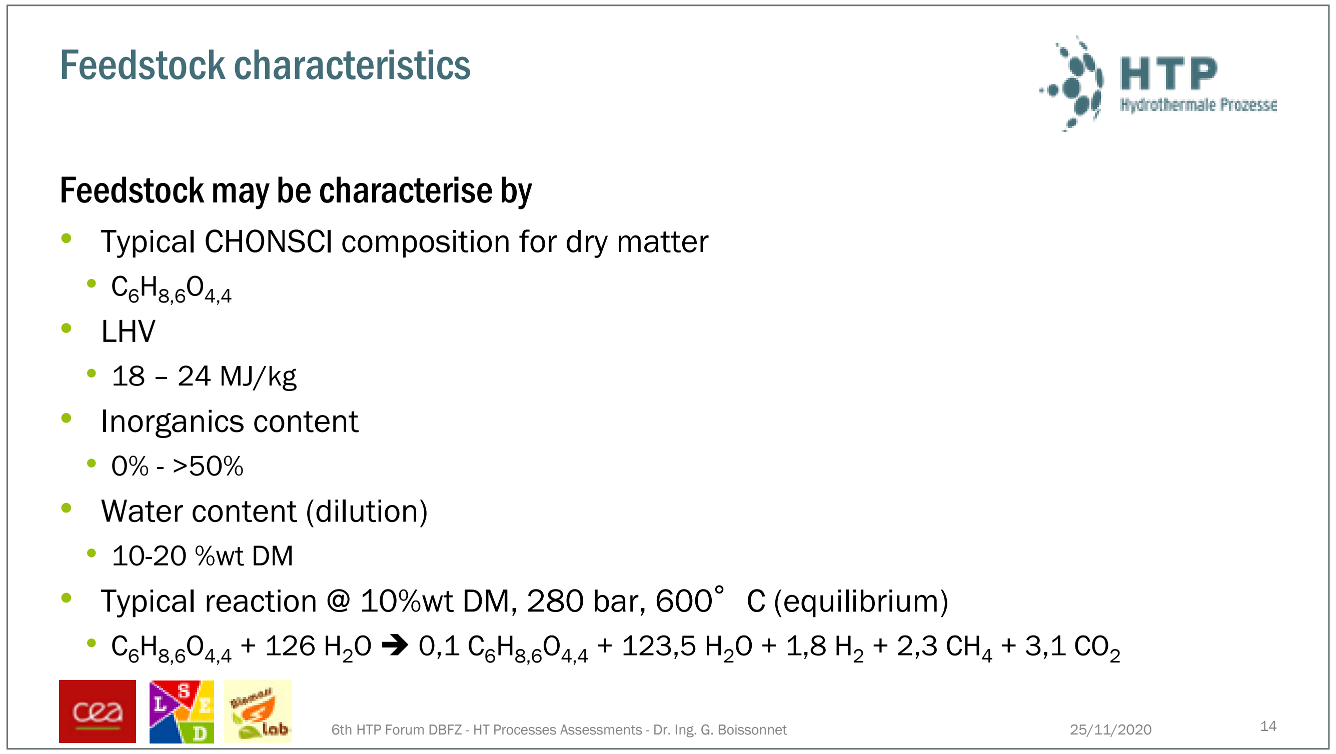

Feedstock characteristics

HTP Hydrothermale Prozesse

Feedstock may be characterise by

- Typical CHONSCl composition for dry matter
  - $C_6H_{8,6}O_{4,4}$
- LHV
  - 18 – 24 MJ/kg
- Inorganics content
  - 0% - >50%
- Water content (dilution)
  - 10-20 %wt DM
- Typical reaction @ 10%wt DM, 280 bar, 600˚ C (equilibrium)
  - $C_6H_{8,6}O_{4,4} + 126\ H_2O \rightarrow 0,1\ C_6H_{8,6}O_{4,4} + 123,5\ H_2O + 1,8\ H_2 + 2,3\ CH_4 + 3,1\ CO_2$

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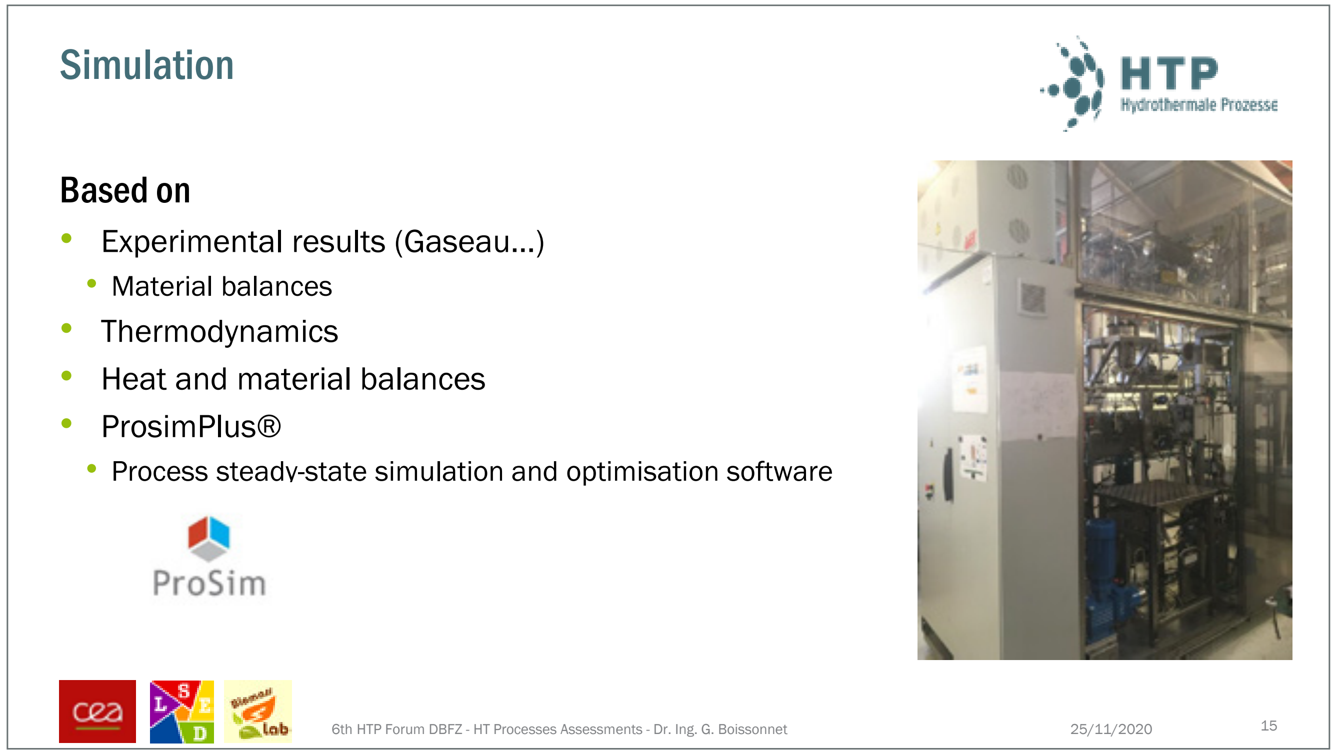

Simulation

Based on

- Experimental results (Gaseau…)
  - Material balances
- Thermodynamics
- Heat and material balances
- ProsimPlus®
  - Process steady-state simulation and optimisation software

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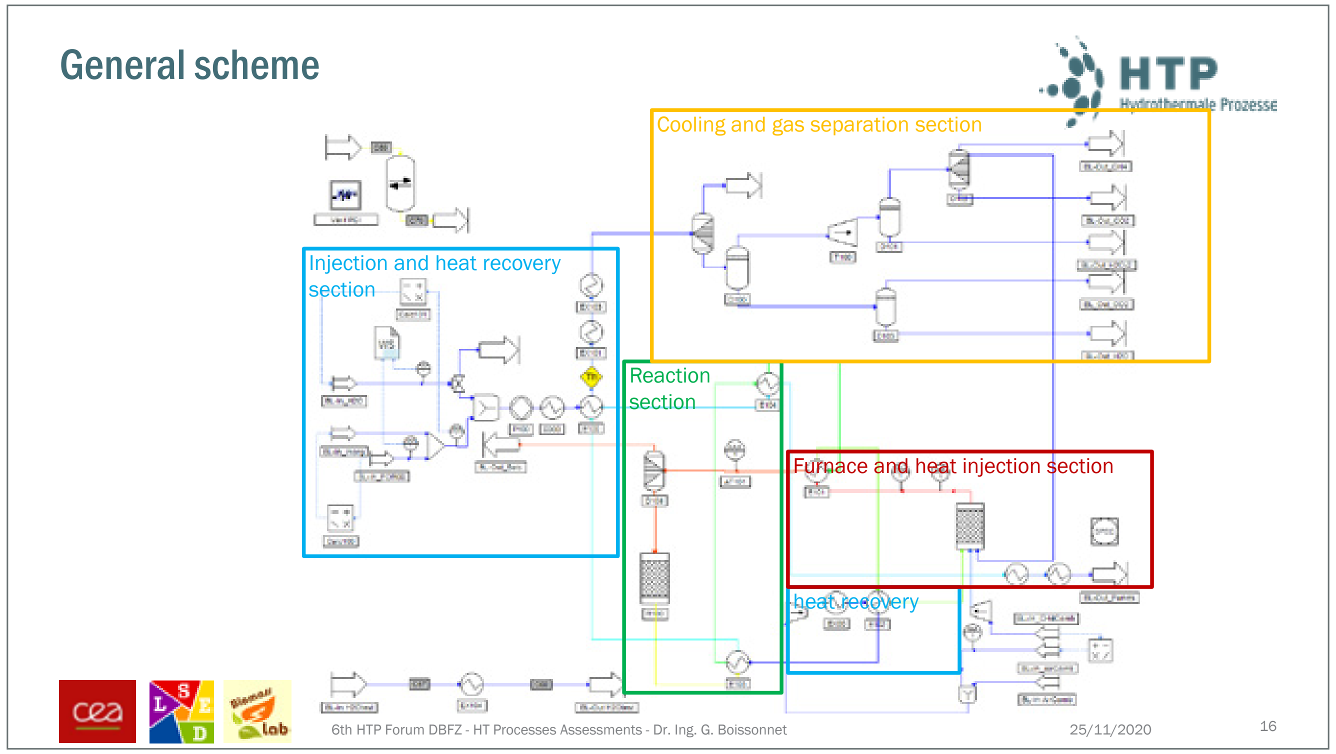

General scheme

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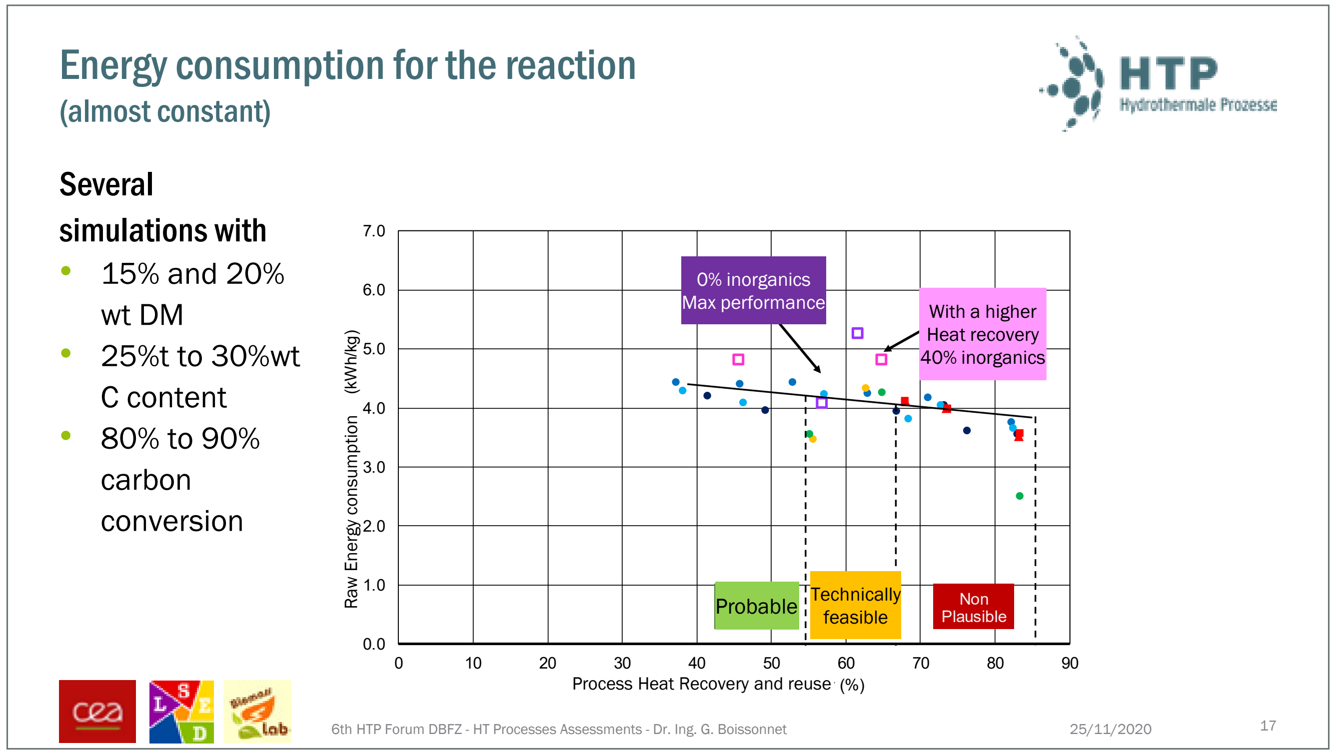

Energy consumption for the reaction
(almost constant)

Several simulations with

- 15% and 20% wt DM
- 25%t to 30%wt C content
- 80% to 90% carbon conversion

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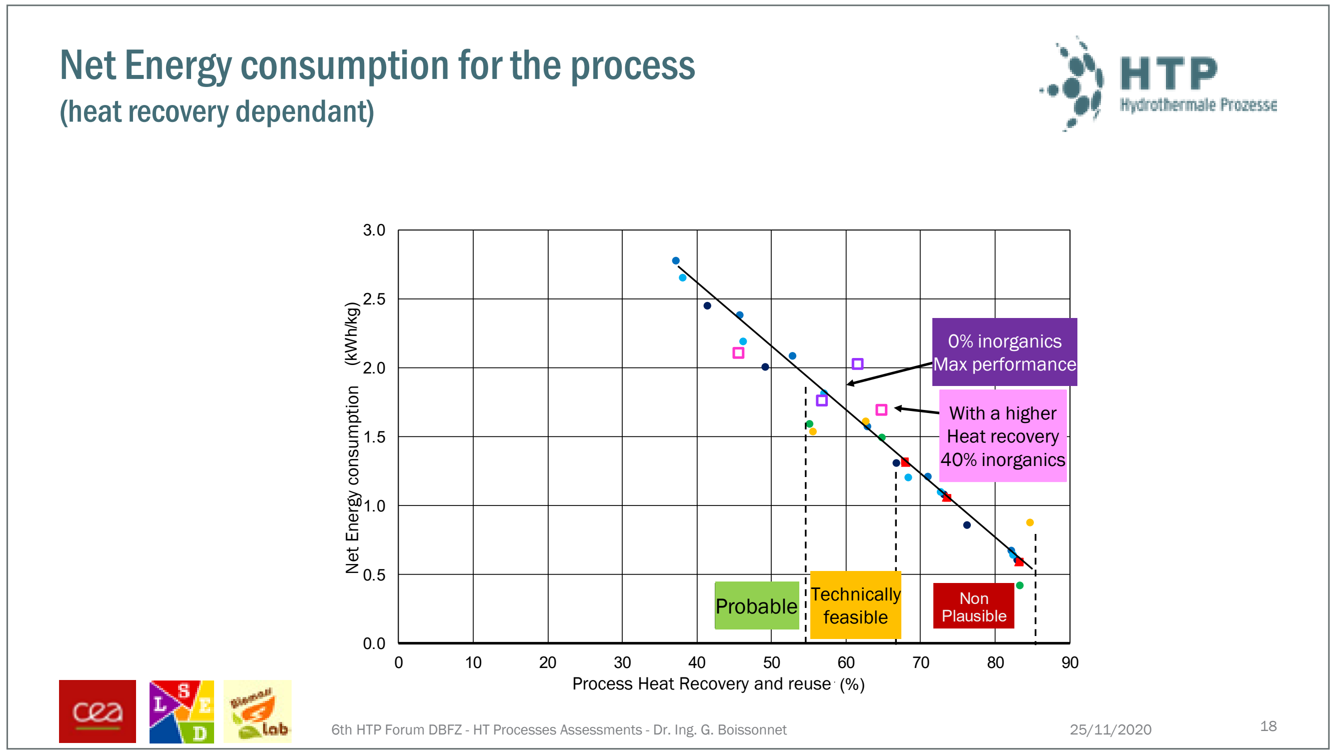

Net Energy consumption for the process
(heat recovery dependant)

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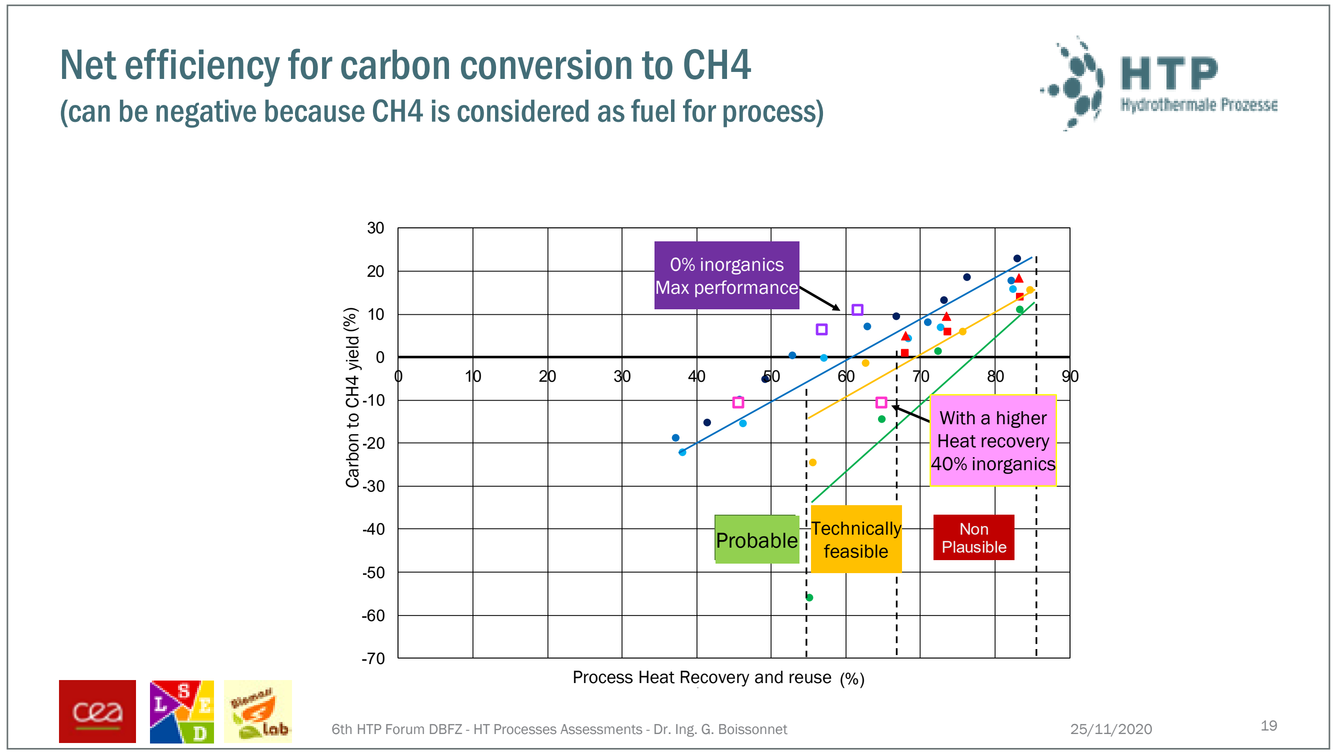

Net efficiency for carbon conversion to CH4

(can be negative because CH4 is considered as fuel for process)

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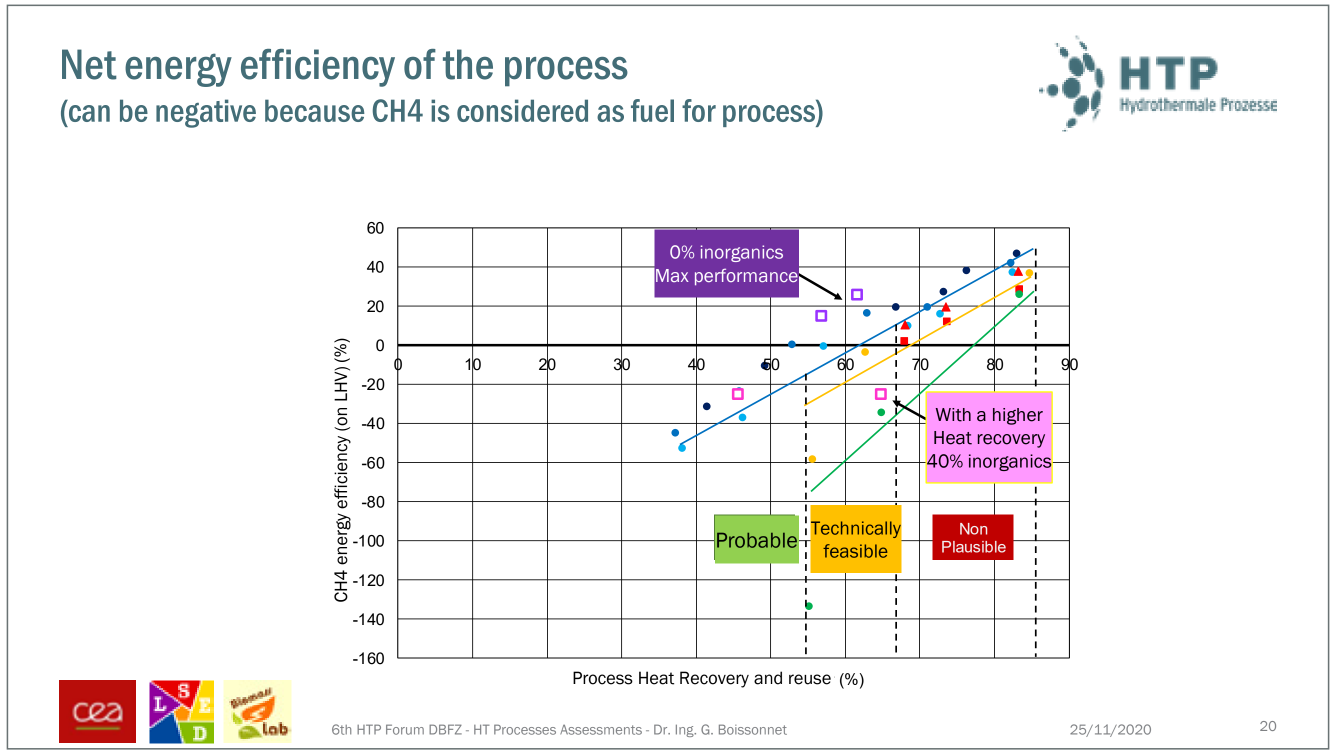

Net energy efficiency of the process

(can be negative because CH4 is considered as fuel for process)

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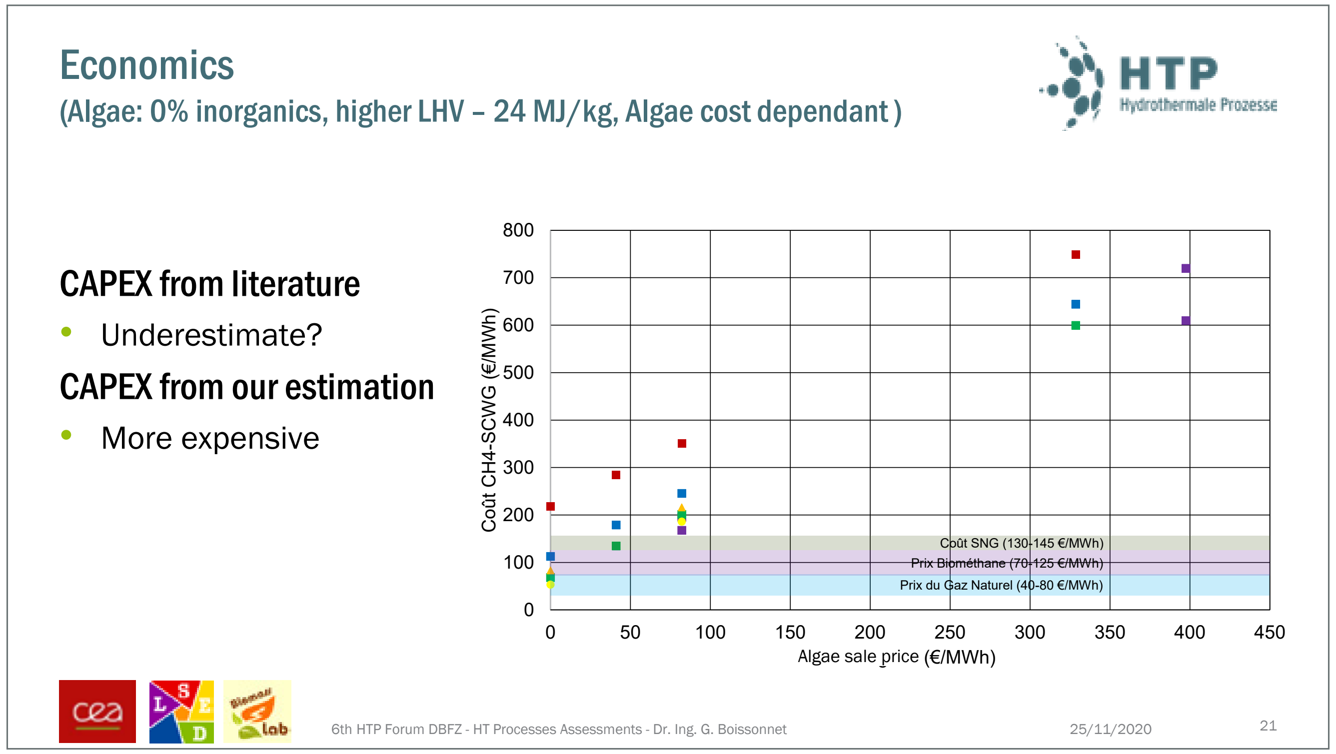

Economics

(Algae: 0% inorganics, higher LHV – 24 MJ/kg, Algae cost dependant)

CAPEX from literature

- Underestimate?

CAPEX from our estimation

- More expensive

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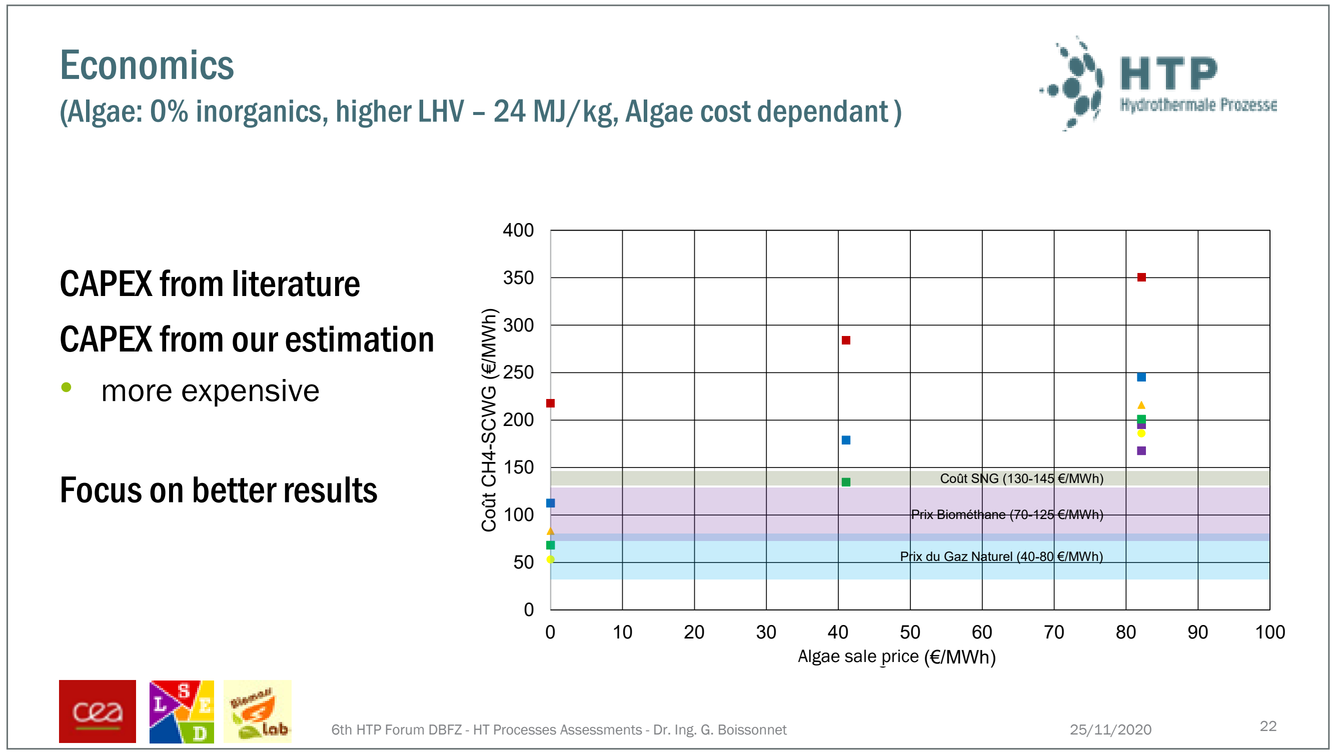

Economics

(Algae: 0% inorganics, higher LHV – 24 MJ/kg, Algae cost dependant)

CAPEX from literature

CAPEX from our estimation

- more expensive

Focus on better results

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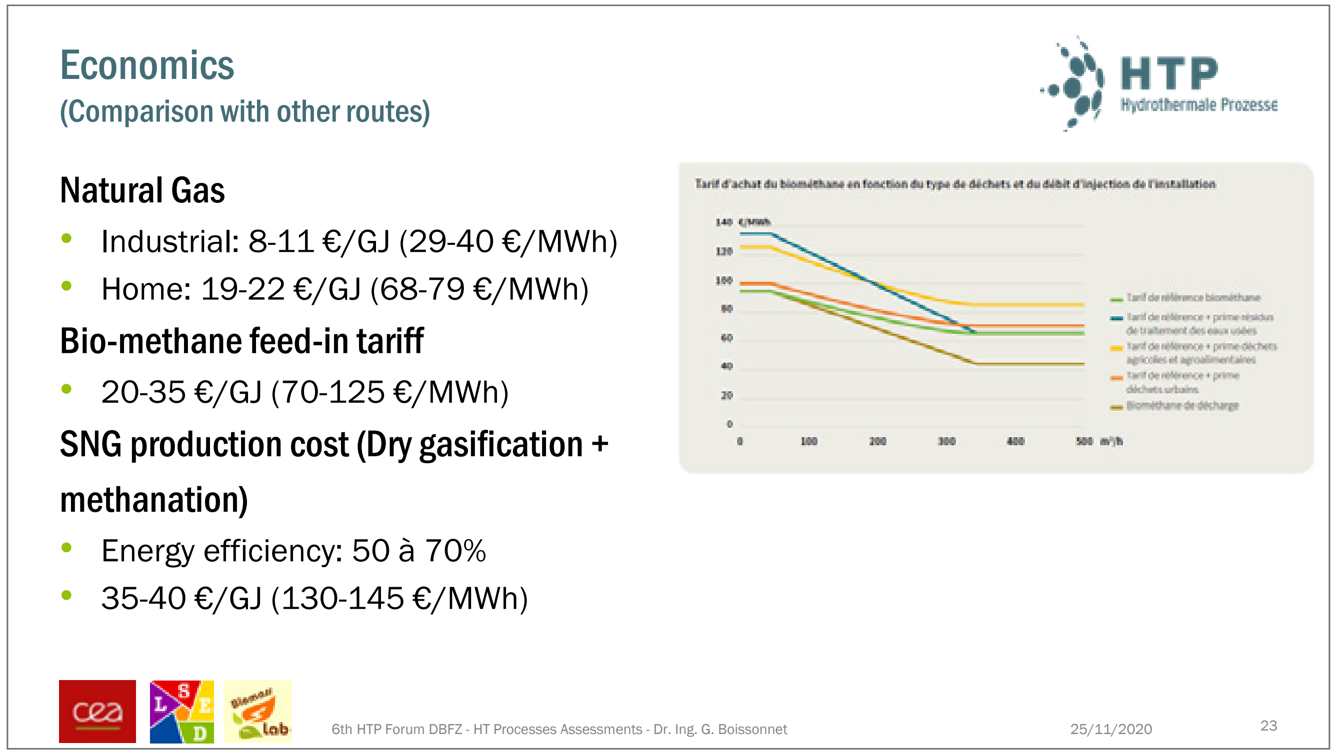

Economics

(Comparison with other routes)

Natural Gas

- Industrial: 8-11 €/GJ (29-40 €/MWh)
- Home: 19-22 €/GJ (68-79 €/MWh)

Bio-methane feed-in tariff

- 20-35 €/GJ (70-125 €/MWh)

SNG production cost (Dry gasification + methanation)

- Energy efficiency: 50 à 70%
- 35-40 €/GJ (130-145 €/MWh)

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HtL Processes
CAPEX and yield related

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Particular case of wood SCWG

- **Low overall process performances**
- **Better solutions with dry gasification**
- Balances and economics

- See also: Y. Calzavara, C. Joussot-Dubien, G. Boissonnet, S. Sarrade, "Evaluation of biomass gasification in supercritical water process for hydrogen production", Energy Conversion and Management 46 (2005) 615–631

Product		CH4	H2	H2 + CH4
Temperature	°C	600	750	730
Conditions		Equilib.	Equilib.	Experiments
% DM	%	20	10	10
Production de CH4	%wt	25	25	27
Process efficiency (negative when produced CH4 is subtracted for process heating after integration)	%	46.37	1.84	-83.09
Net process efficiency	%	65.5	50.9	22.9

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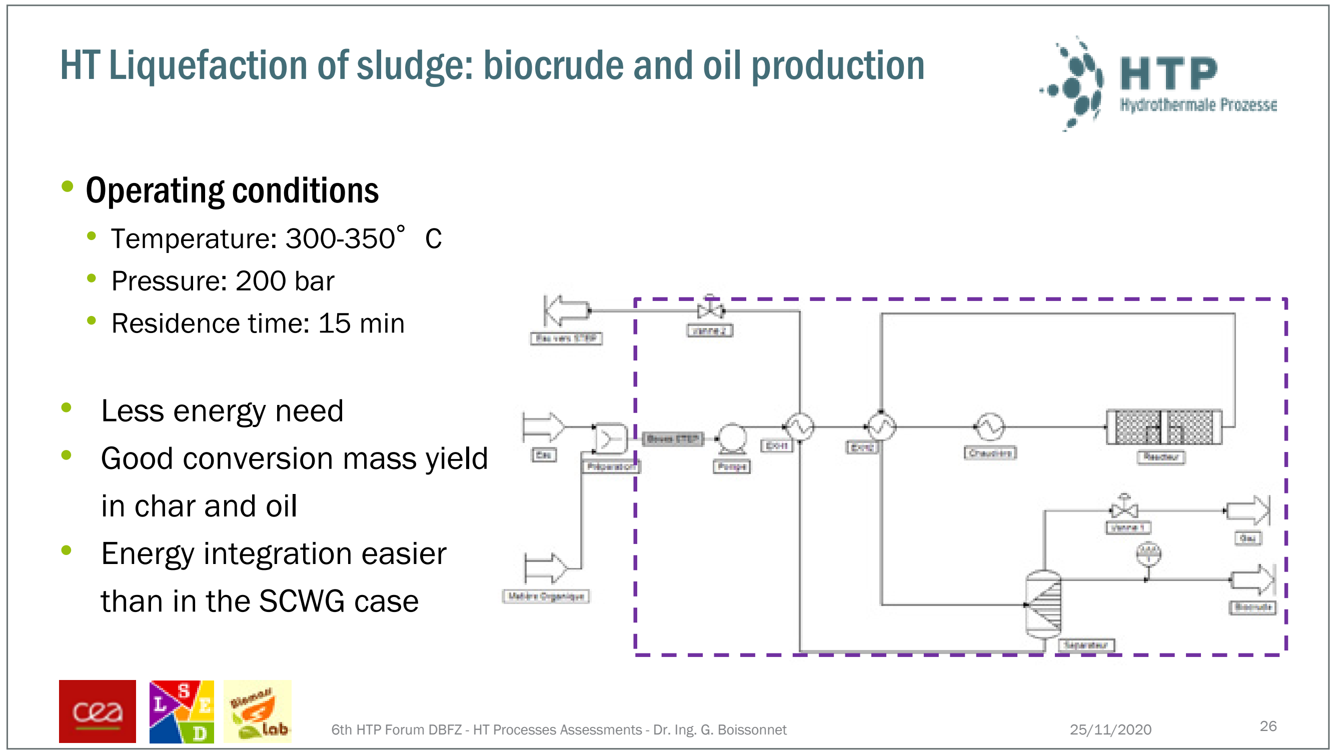

HT Liquefaction of sludge: biocrude and oil production

- **Operating conditions**
  - Temperature: 300-350° C
  - Pressure: 200 bar
  - Residence time: 15 min
- Less energy need
- Good conversion mass yield in char and oil
- Energy integration easier than in the SCWG case

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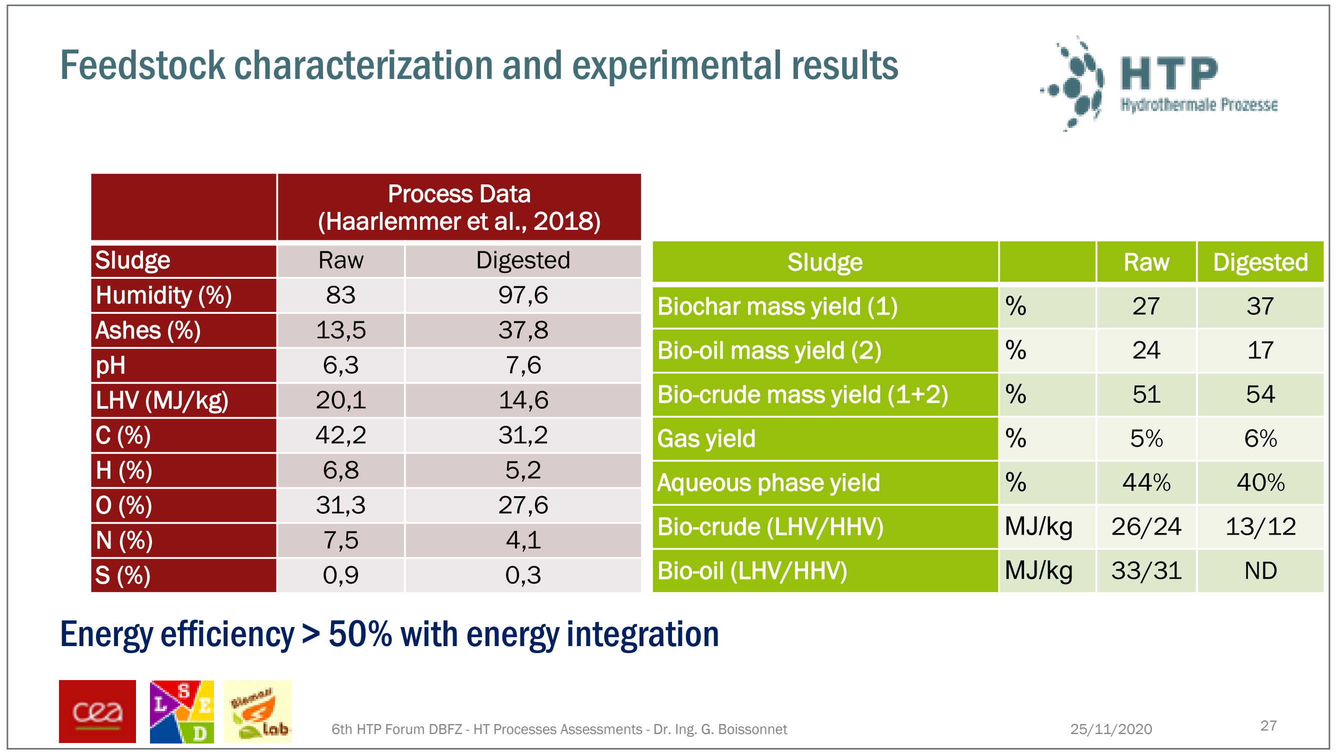

Feedstock characterization and experimental results

	Process Data (Haarlemmer et al., 2018)	
Sludge	Raw	Digested
Humidity (%)	83	97,6
Ashes (%)	13,5	37,8
pH	6,3	7,6
LHV (MJ/kg)	20,1	14,6
C (%)	42,2	31,2
H (%)	6,8	5,2
O (%)	31,3	27,6
N (%)	7,5	4,1
S (%)	0,9	0,3

Sludge		Raw	Digested
Biochar mass yield (1)	%	27	37
Bio-oil mass yield (2)	%	24	17
Bio-crude mass yield (1+2)	%	51	54
Gas yield	%	5%	6%
Aqueous phase yield	%	44%	40%
Bio-crude (LHV/HHV)	MJ/kg	26/24	13/12
Bio-oil (LHV/HHV)	MJ/kg	33/31	ND

Energy efficiency > 50% with energy integration

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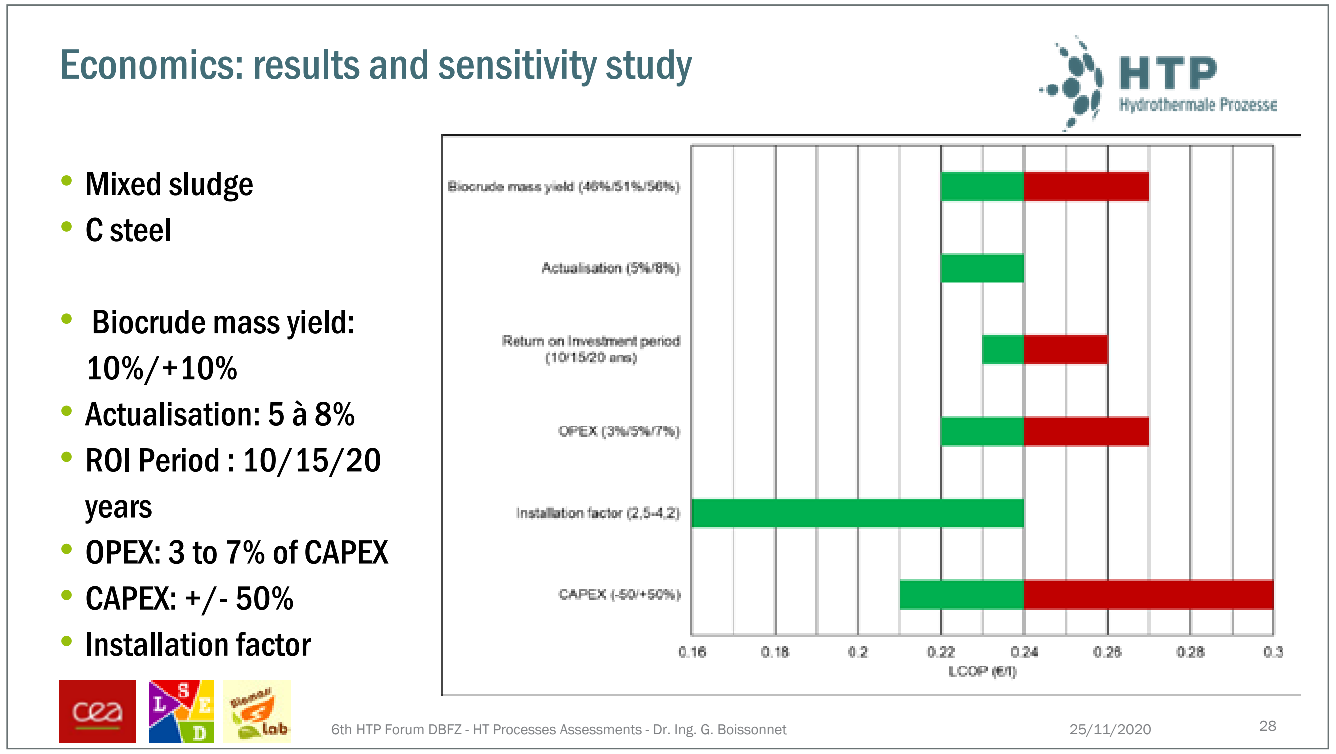

Economics: results and sensitivity study

- Mixed sludge
- C steel

- Biocrude mass yield: 10%/+10%
- Actualisation: 5 à 8%
- ROI Period : 10/15/20 years
- OPEX: 3 to 7% of CAPEX
- CAPEX: +/- 50%
- Installation factor

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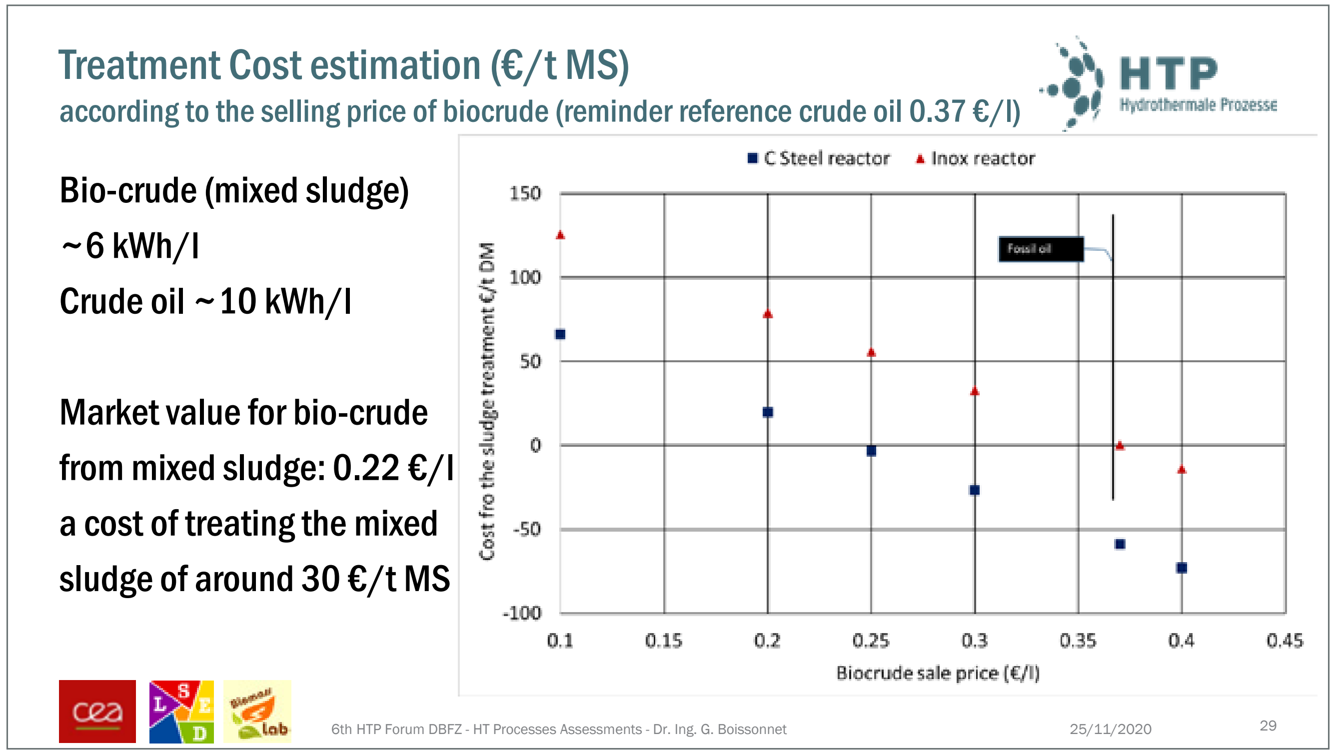

Treatment Cost estimation (€/t MS)

according to the selling price of biocrude (reminder reference crude oil 0.37 €/l)

Bio-crude (mixed sludge) ~6 kWh/l

Crude oil ~10 kWh/l

Market value for bio-crude from mixed sludge: 0.22 €/l a cost of treating the mixed sludge of around 30 €/t MS

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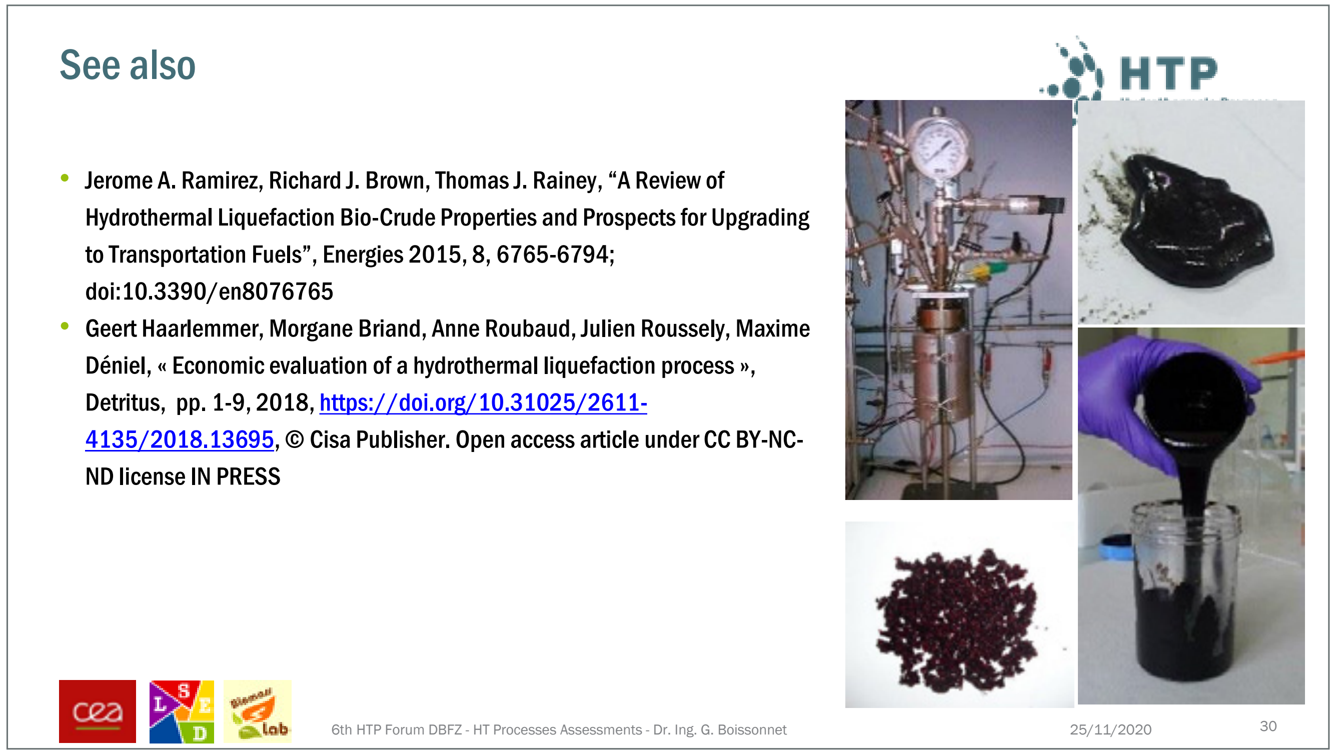

See also

- Jerome A. Ramirez, Richard J. Brown, Thomas J. Rainey, "A Review of Hydrothermal Liquefaction Bio-Crude Properties and Prospects for Upgrading to Transportation Fuels", Energies 2015, 8, 6765-6794; doi:10.3390/en8076765
- Geert Haarlemmer, Morgane Briand, Anne Roubaud, Julien Roussely, Maxime Déniel, « Economic evaluation of a hydrothermal liquefaction process », Detritus, pp. 1-9, 2018, https://doi.org/10.31025/2611-4135/2018.13695, © Cisa Publisher. Open access article under CC BY-NC-ND license IN PRESS

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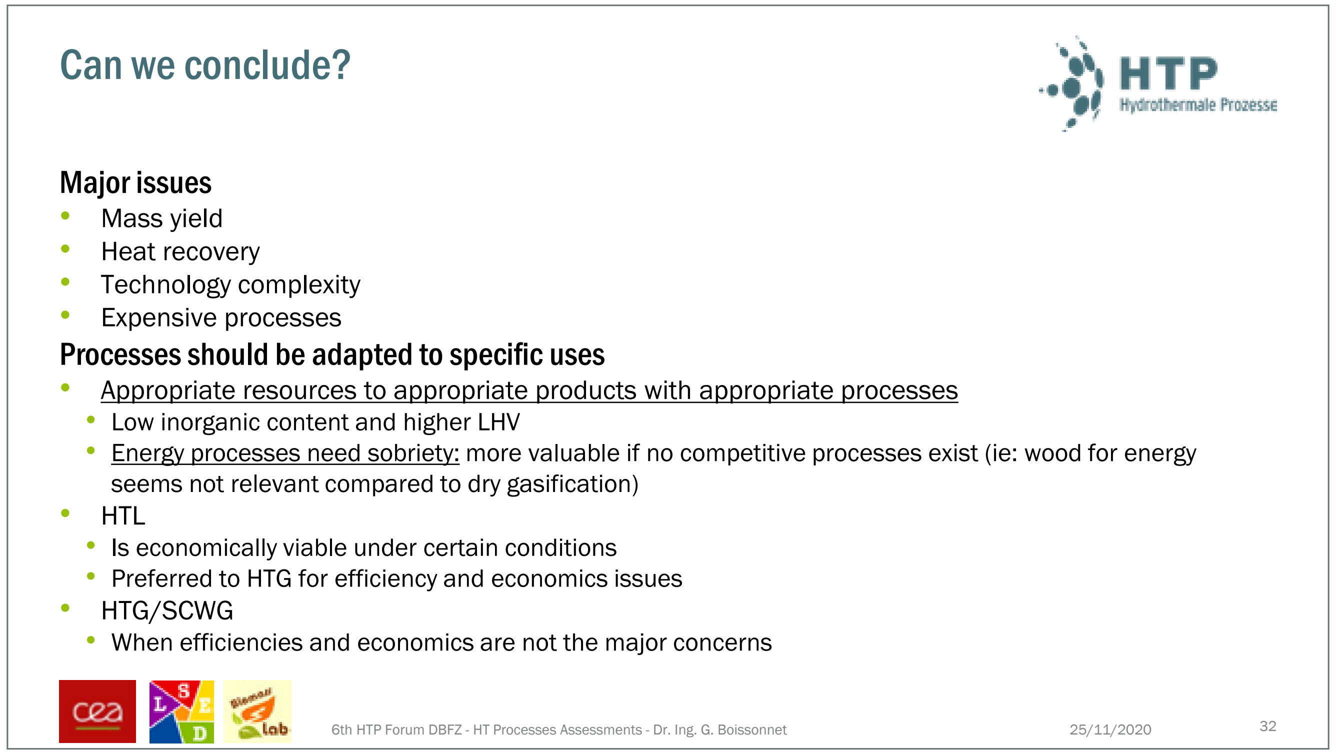
6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Some conclusions...

www.htp-inno.de



Can we conclude?

Major issues
- Mass yield
- Heat recovery
- Technology complexity
- Expensive processes

Processes should be adapted to specific uses
- Appropriate resources to appropriate products with appropriate processes
  - Low inorganic content and higher LHV
  - Energy processes need sobriety: more valuable if no competitive processes exist (ie: wood for energy seems not relevant compared to dry gasification)
- HTL
  - Is economically viable under certain conditions
  - Preferred to HTG for efficiency and economics issues
- HTG/SCWG
  - When efficiencies and economics are not the major concerns

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Valentin Blatteiger, Bauhaus Luftfahrt e.V.

The HyFlexFuel project – Sustainable fuel production via hydrothermal liquefaction of various organic feedstock

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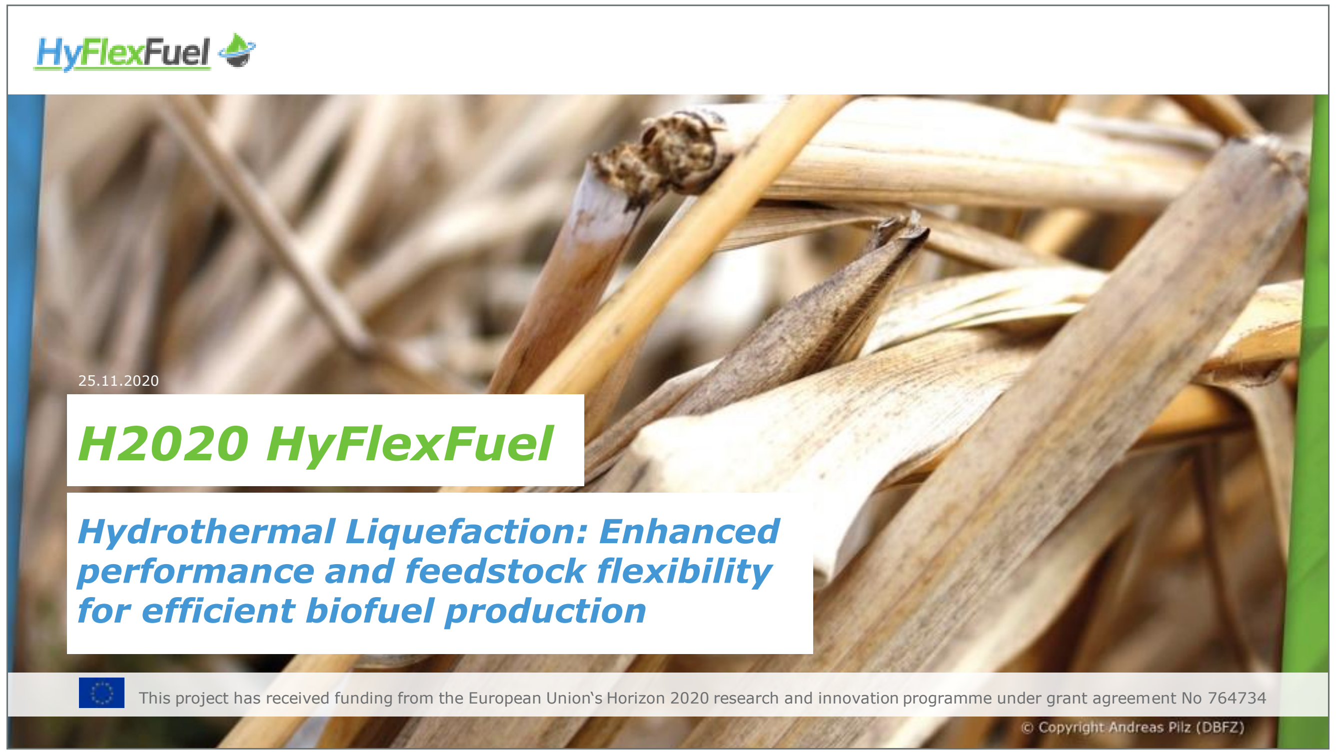
The European research project HyFlexFuel is focused on sustainable liquid transportation fuels production via hydrothermal liquefaction of various organic feedstocks. The HyFlexFuel project aims to develop the main process steps of a HTL-based fuel production chain and to demonstrate their technical viability under relevant operational conditions. The project implementation covers the production of biocrudes in a pilot-scale continuous HTL plant, the subsequent upgrading of the biocrudes to final fuels via catalytic hydrotreatment, as well as the valorisation of residual process streams for energy and nutrient recovery. We introduce to the key results from the first three years of the HyFlexFuel project and highlight the roles of the individual consortium partners. In the main part of this contribution, we discuss the findings from the system analyses within HyFlexFuel. We introduce to a numerical system model for the HTL production pathway. The model approximates the complex chemical composition of various organic feedstock by a reduced set of model compounds. The conversion of these model compounds via HTL and catalytic hydrotreatment, towards a mixture of liquid hydrocarbon fuel products is evaluated in Aspen Plus. Likewise, the modelling considers the treatment of the HTL process water via catalytic hydrothermal gasification and/or anaerobic digestion, and a potential nutrient recovery from HTL solids and process waters in form of a marketable fertilizer product. This feedstock specific process model lays the basis for an evaluation of the economic viability in terms of projected fuel production costs, and for an assessment of the environmental performance with respect to several indicators including life cycle greenhouse gas emissions. The results from the economic and environmental analyses lay the basis for a comparison of the HTL pathway with other renewable fuel production options, the latter discussion will focus on jet fuel as a main target product of the HyFlexFuel project. We identify early implementation perspectives for the most suitable feedstocks in specific regions, and discuss the challenges and opportunities towards a broad application of HTL for large volume production of renewable fuels.

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



HyFlexFuel

25.11.2020

H2020 HyFlexFuel

Hydrothermal Liquefaction: Enhanced performance and feedstock flexibility for efficient biofuel production

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

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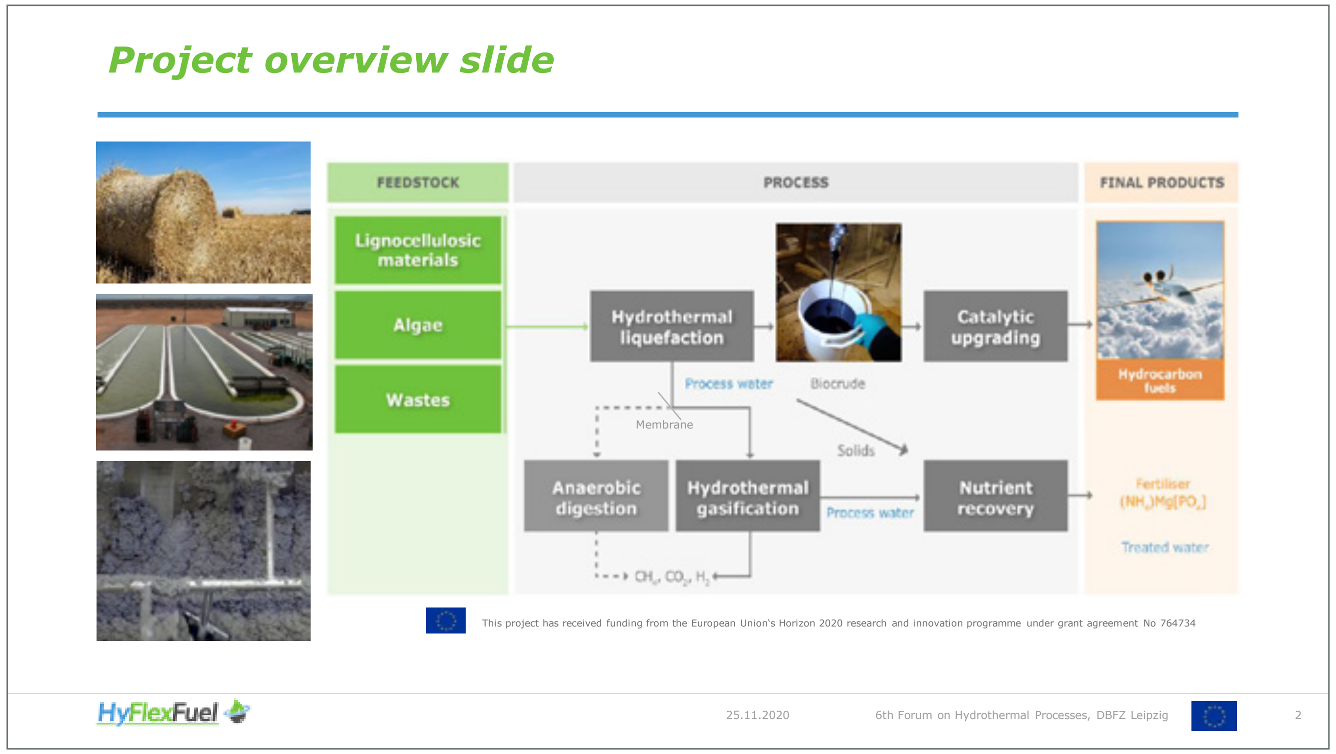

Project overview slide

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

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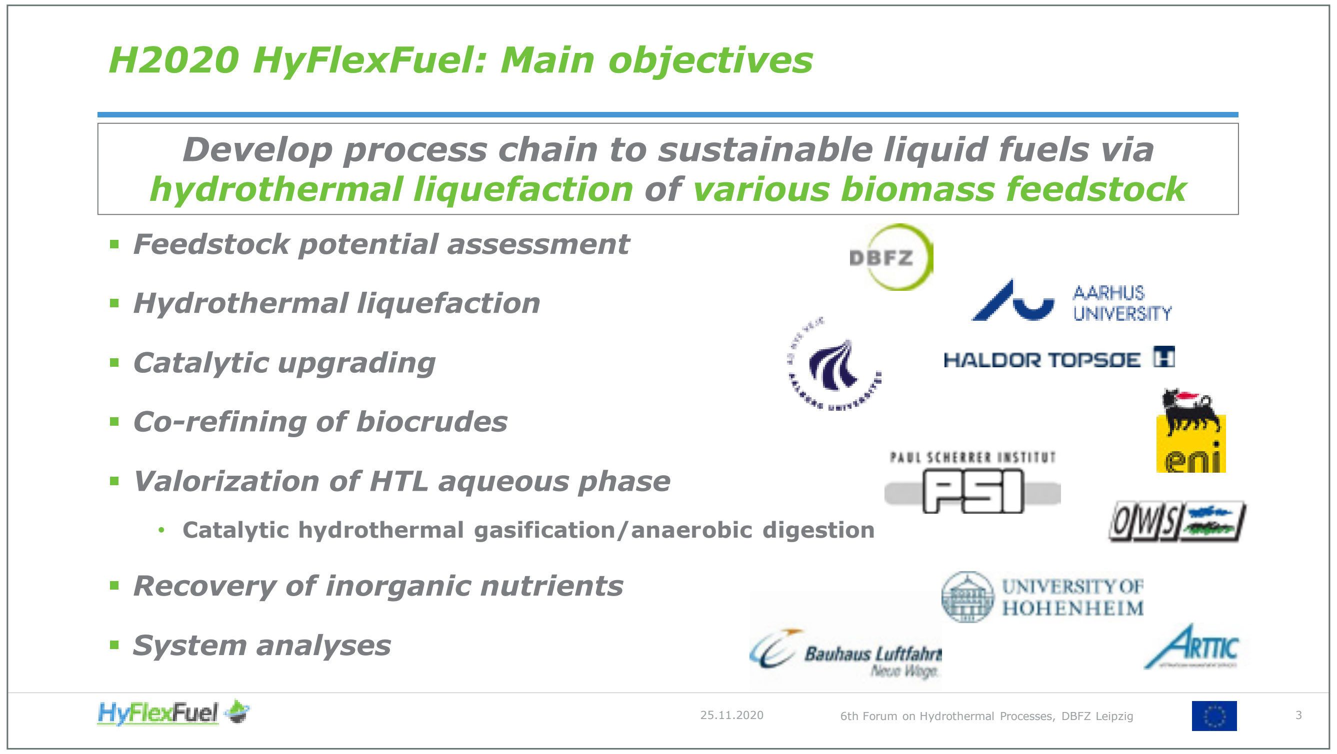
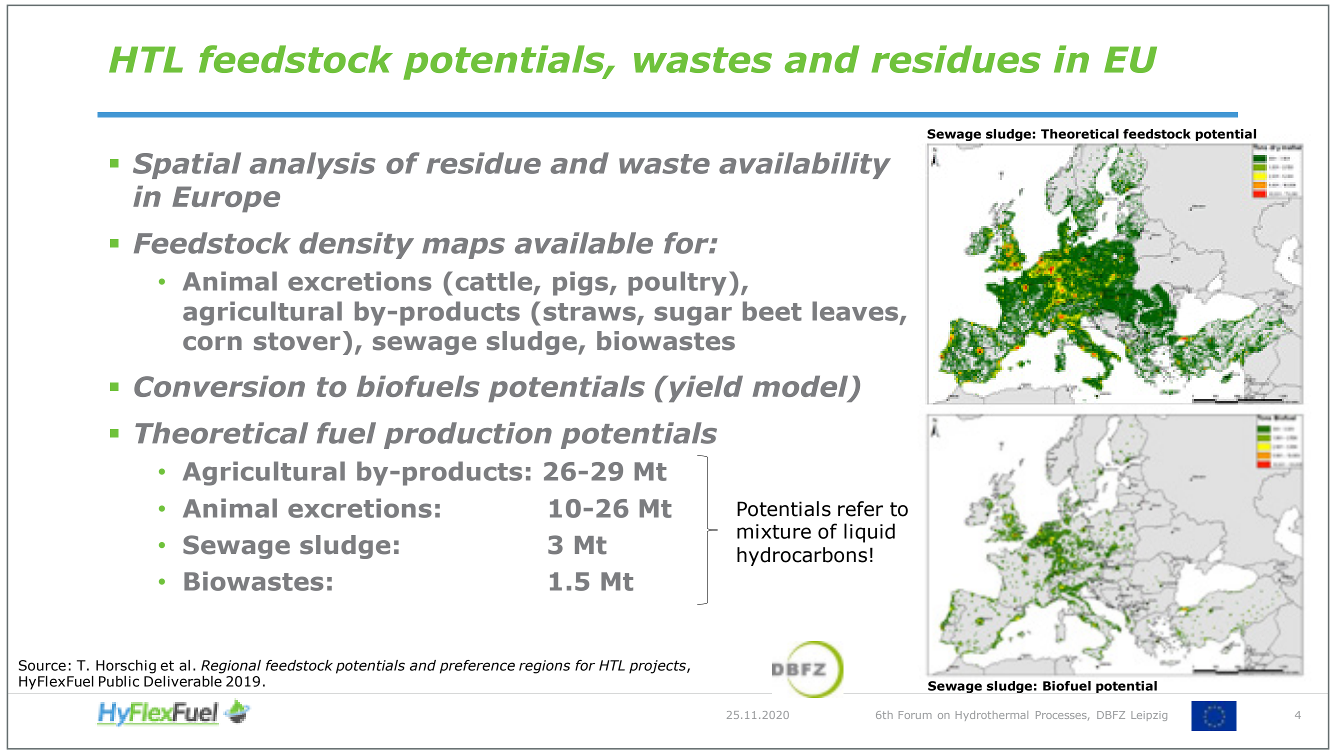


H2020 HyFlexFuel: Main objectives

Develop process chain to sustainable liquid fuels via hydrothermal liquefaction of various biomass feedstock

- Feedstock potential assessment
- Hydrothermal liquefaction
- Catalytic upgrading
- Co-refining of biocrudes
- Valorization of HTL aqueous phase
  - Catalytic hydrothermal gasification/anaerobic digestion
- Recovery of inorganic nutrients
- System analyses



HTL feedstock potentials, wastes and residues in EU

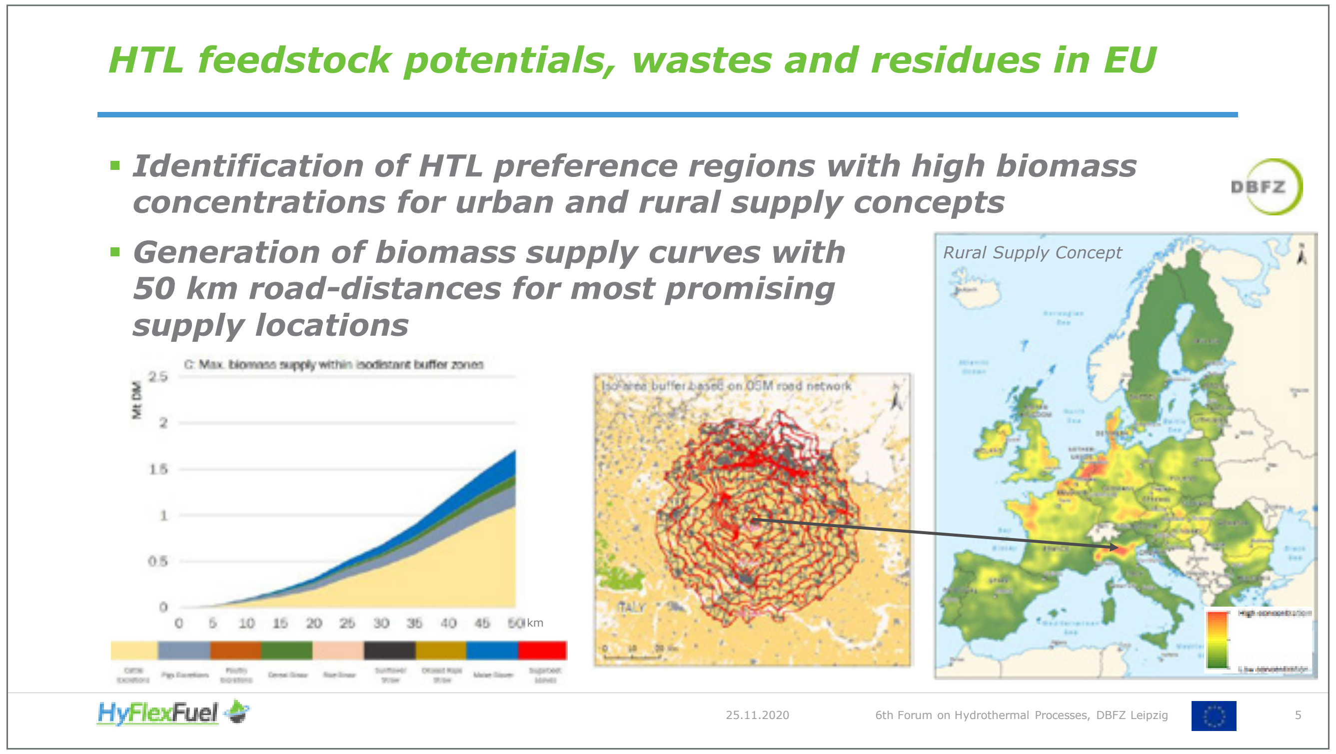
- Spatial analysis of residue and waste availability in Europe
- Feedstock density maps available for:
  - Animal excretions (cattle, pigs, poultry), agricultural by-products (straws, sugar beet leaves, corn stover), sewage sludge, biowastes
- Conversion to biofuels potentials (yield model)
- Theoretical fuel production potentials
  - Agricultural by-products: 26-29 Mt
  - Animal excretions: 10-26 Mt
  - Sewage sludge: 3 Mt
  - Biowastes: 1.5 Mt

Potentials refer to mixture of liquid hydrocarbons!

Sewage sludge: Theoretical feedstock potential

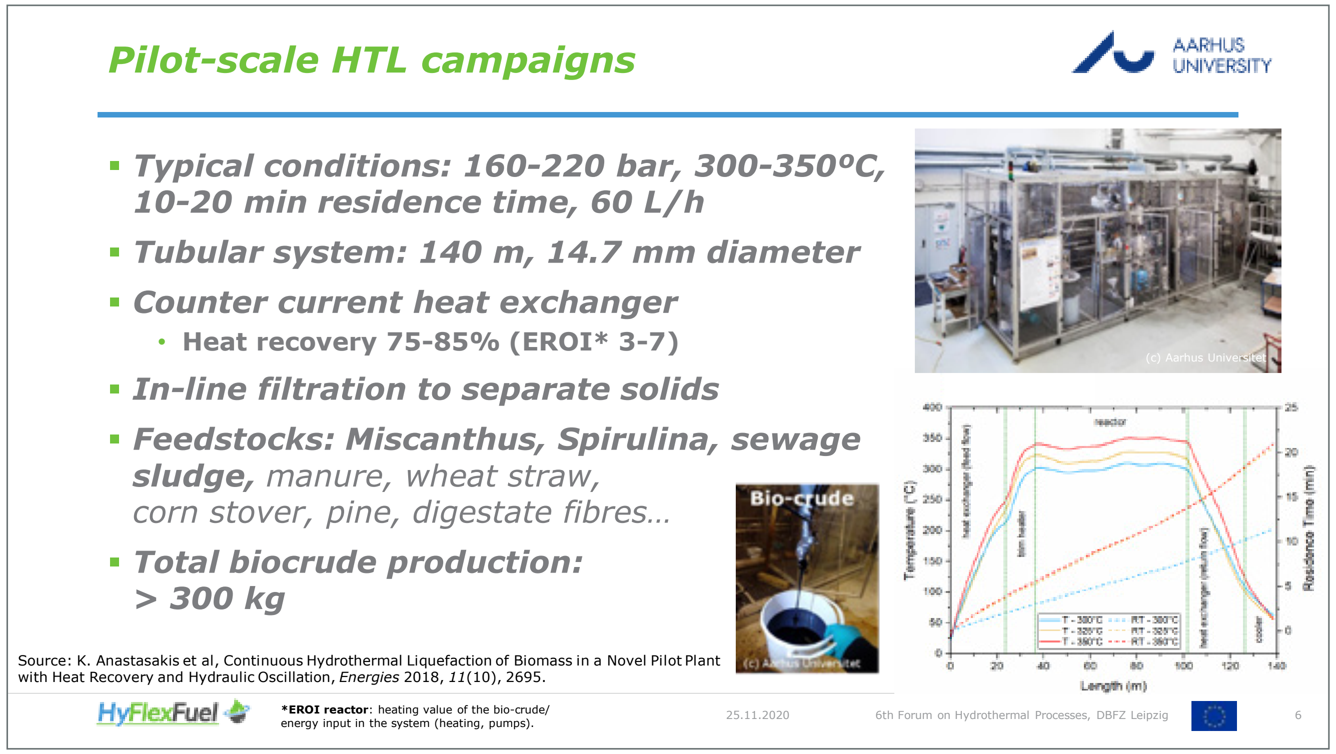
Sewage sludge: Biofuel potential

Source: T. Horschig et al. *Regional feedstock potentials and preference regions for HTL projects*, HyFlexFuel Public Deliverable 2019.



HTL feedstock potentials, wastes and residues in EU

- Identification of HTL preference regions with high biomass concentrations for urban and rural supply concepts
- Generation of biomass supply curves with 50 km road-distances for most promising supply locations

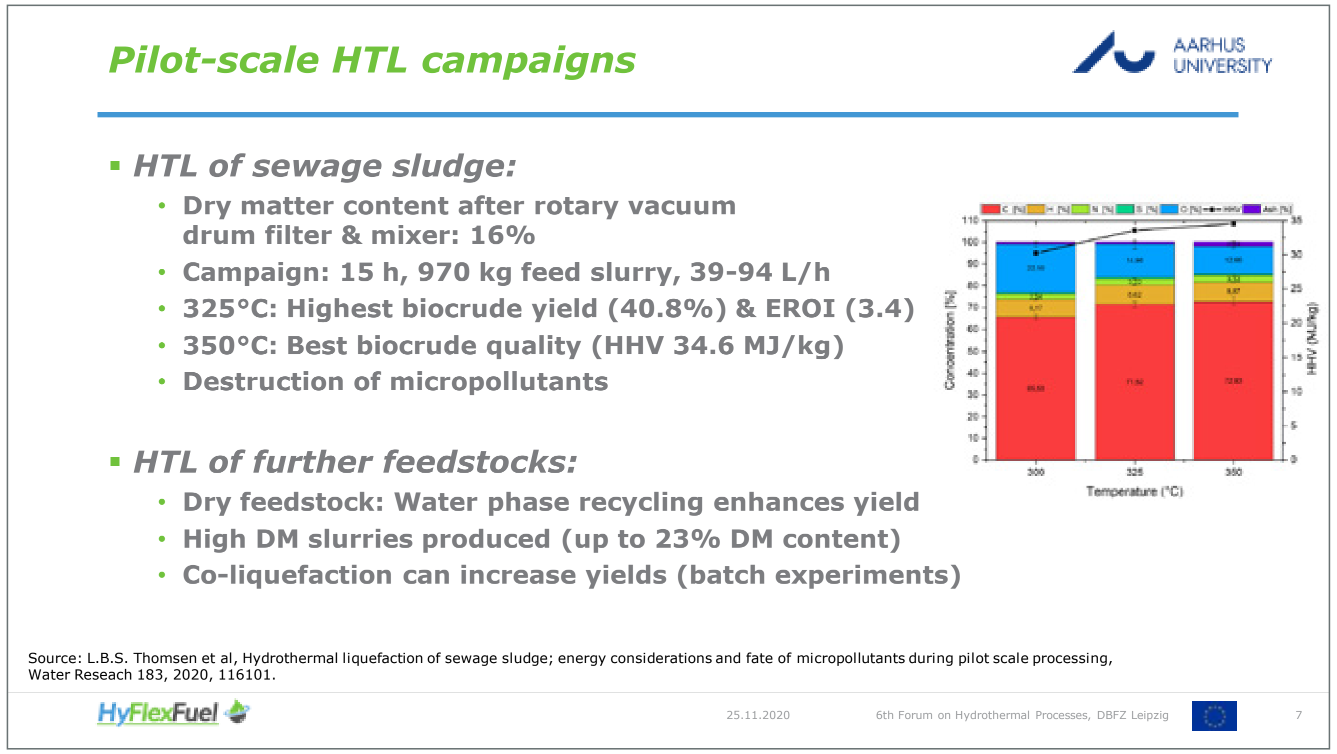


Pilot-scale HTL campaigns

- Typical conditions: 160-220 bar, 300-350ºC, 10-20 min residence time, 60 L/h
- Tubular system: 140 m, 14.7 mm diameter
- Counter current heat exchanger
  - Heat recovery 75-85% (EROI* 3-7)
- In-line filtration to separate solids
- Feedstocks: Miscanthus, Spirulina, sewage sludge, *manure, wheat straw, corn stover, pine, digestate fibres…*
- Total biocrude production: > 300 kg

Source: K. Anastasakis et al, Continuous Hydrothermal Liquefaction of Biomass in a Novel Pilot Plant with Heat Recovery and Hydraulic Oscillation, *Energies* 2018, *11*(10), 2695.

***EROI reactor**: heating value of the bio-crude/ energy input in the system (heating, pumps).



Pilot-scale HTL campaigns

AARHUS UNIVERSITY

- **HTL of sewage sludge:**
  - Dry matter content after rotary vacuum drum filter & mixer: 16%
  - Campaign: 15 h, 970 kg feed slurry, 39-94 L/h
  - 325°C: Highest biocrude yield (40.8%) & EROI (3.4)
  - 350°C: Best biocrude quality (HHV 34.6 MJ/kg)
  - Destruction of micropollutants
- **HTL of further feedstocks:**
  - Dry feedstock: Water phase recycling enhances yield
  - High DM slurries produced (up to 23% DM content)
  - Co-liquefaction can increase yields (batch experiments)

Source: L.B.S. Thomsen et al, Hydrothermal liquefaction of sewage sludge; energy considerations and fate of micropollutants during pilot scale processing, Water Reseach 183, 2020, 116101.

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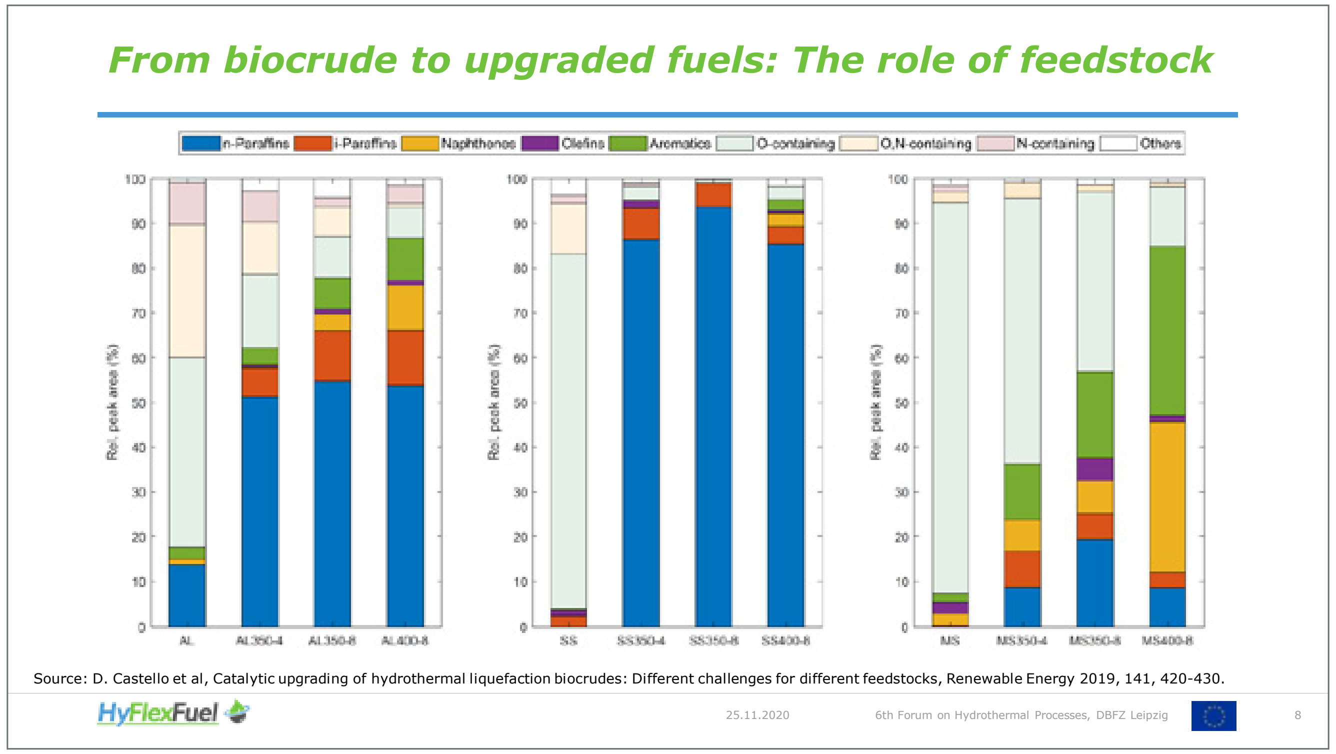

From biocrude to upgraded fuels: The role of feedstock

Source: D. Castello et al, Catalytic upgrading of hydrothermal liquefaction biocrudes: Different challenges for different feedstocks, Renewable Energy 2019, 141, 420-430.

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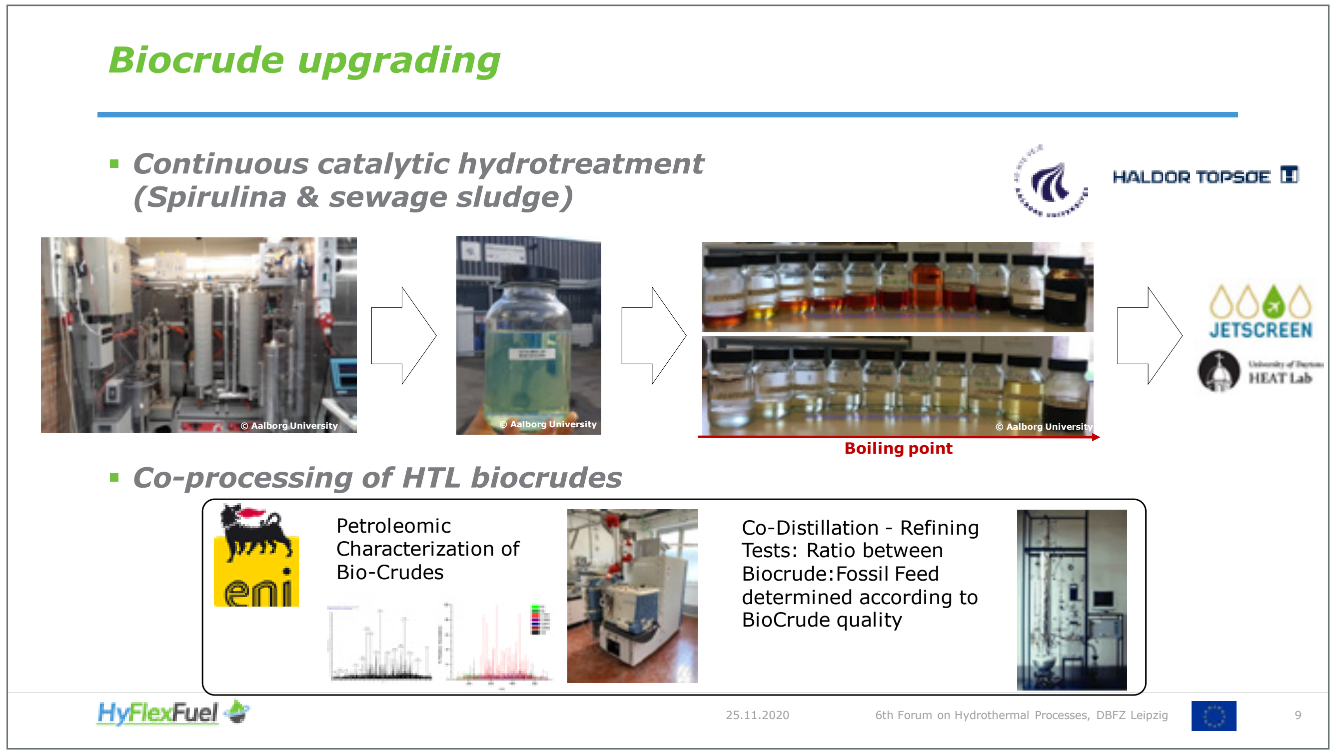

Biocrude upgrading

- ***Continuous catalytic hydrotreatment (Spirulina & sewage sludge)***

HALDOR TOPSOE

- ***Co-processing of HTL biocrudes***

eni

Petroleomic Characterization of Bio-Crudes

Co-Distillation - Refining Tests: Ratio between Biocrude:Fossil Feed determined according to BioCrude quality

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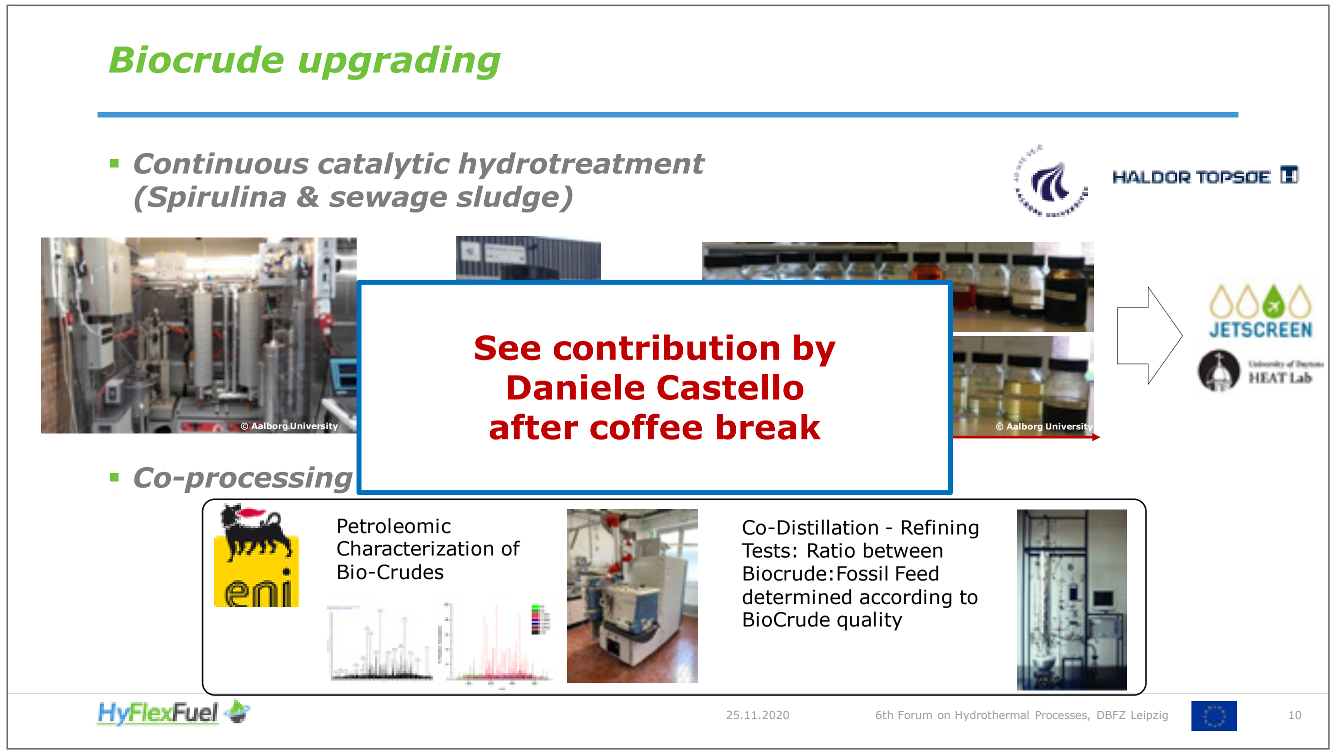

Biocrude upgrading

- ***Continuous catalytic hydrotreatment (Spirulina & sewage sludge)***

HALDOR TOPSOE

See contribution by Daniele Castello after coffee break

- ***Co-processing***

eni

Petroleomic Characterization of Bio-Crudes

Co-Distillation - Refining Tests: Ratio between Biocrude:Fossil Feed determined according to BioCrude quality

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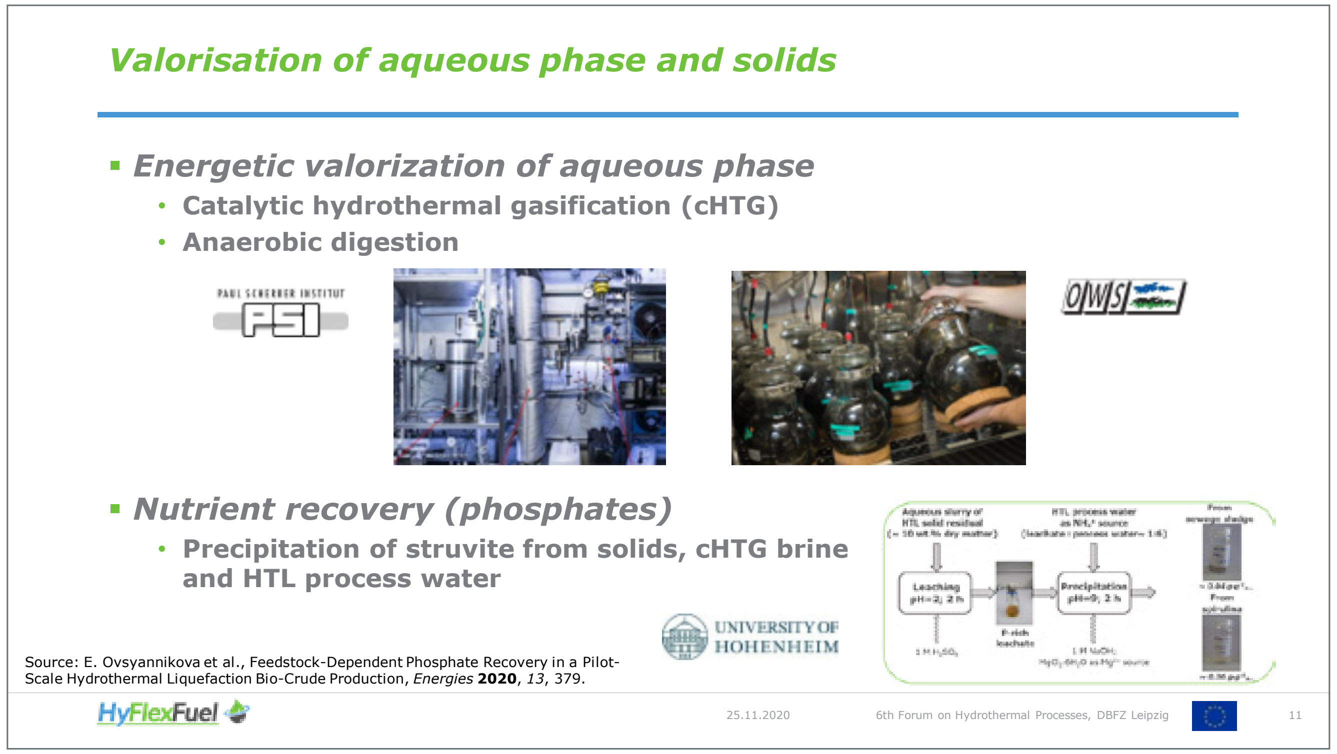
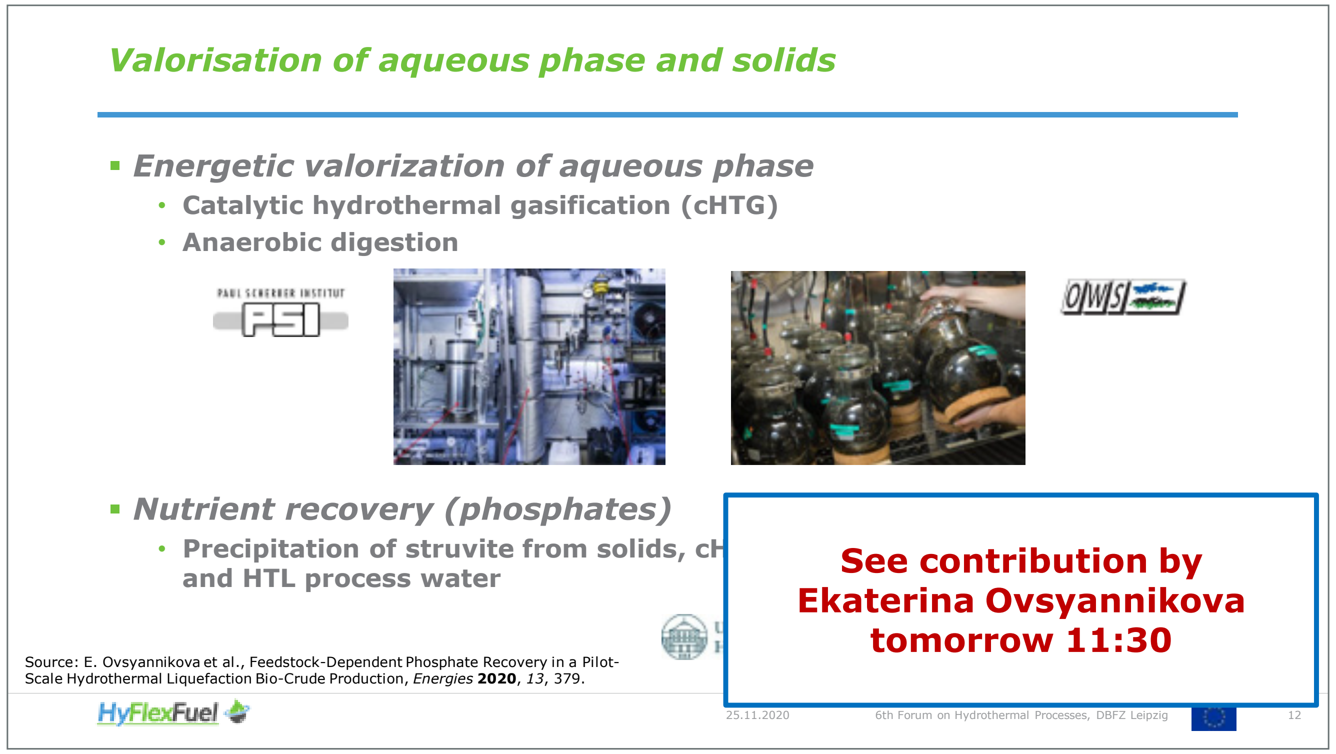


Valorisation of aqueous phase and solids

- **Energetic valorization of aqueous phase**
  - Catalytic hydrothermal gasification (cHTG)
  - Anaerobic digestion
- **Nutrient recovery (phosphates)**
  - Precipitation of struvite from solids, cHTG brine and HTL process water

Source: E. Ovsyannikova et al., Feedstock-Dependent Phosphate Recovery in a Pilot-Scale Hydrothermal Liquefaction Bio-Crude Production, *Energies* **2020**, *13*, 379.



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  - Catalytic hydrothermal gasification (cHTG)
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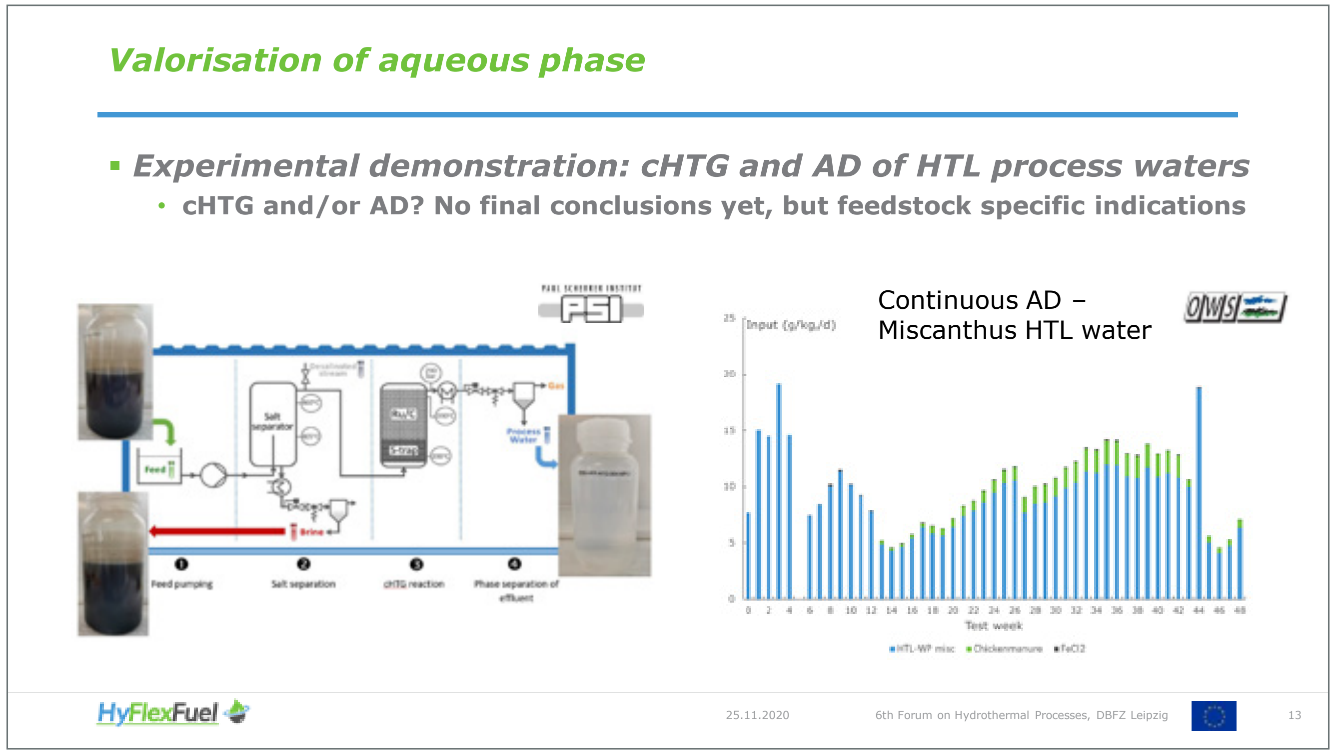
- **Nutrient recovery (phosphates)**
  - Precipitation of struvite from solids, cH
  - and HTL process water

See contribution by Ekaterina Ovsyannikova tomorrow 11:30

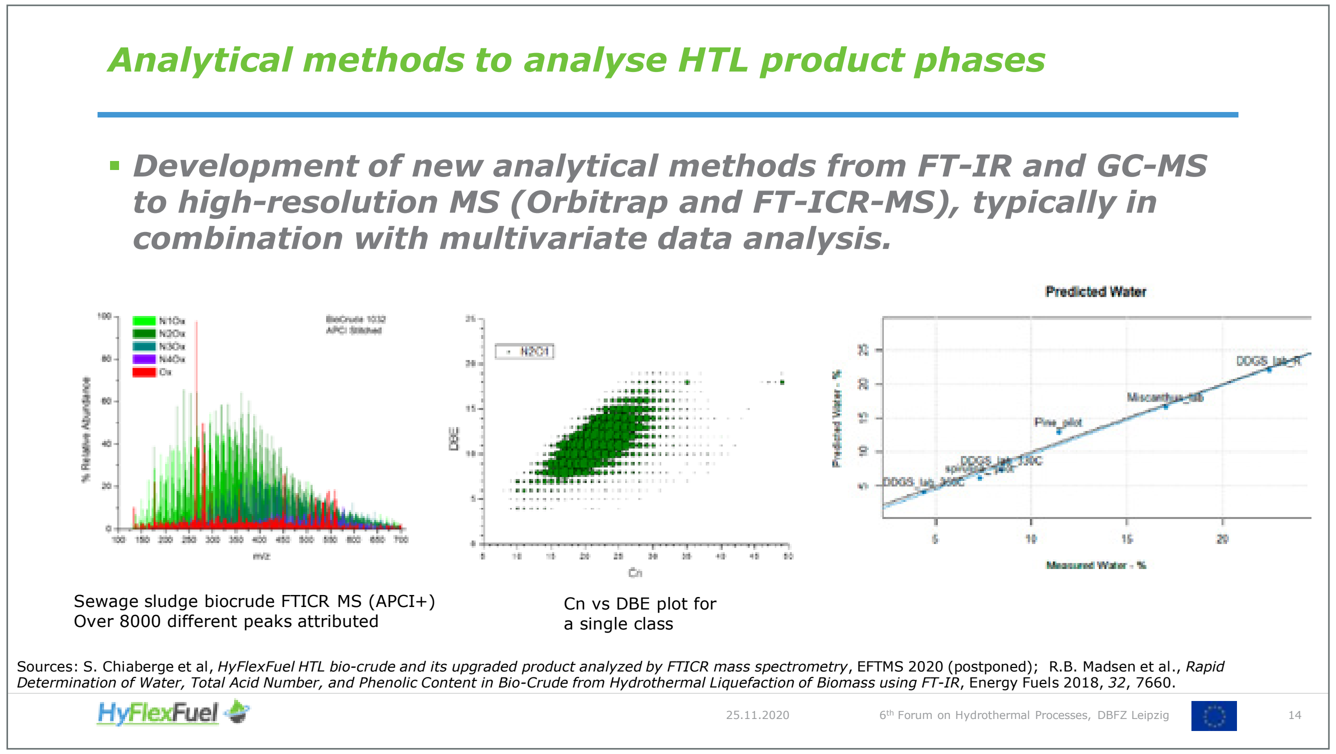
Source: E. Ovsyannikova et al., Feedstock-Dependent Phosphate Recovery in a Pilot-Scale Hydrothermal Liquefaction Bio-Crude Production, *Energies* **2020**, *13*, 379.



Valorisation of aqueous phase

- **Experimental demonstration: cHTG and AD of HTL process waters**
  - cHTG and/or AD? No final conclusions yet, but feedstock specific indications

Continuous AD – Miscanthus HTL water



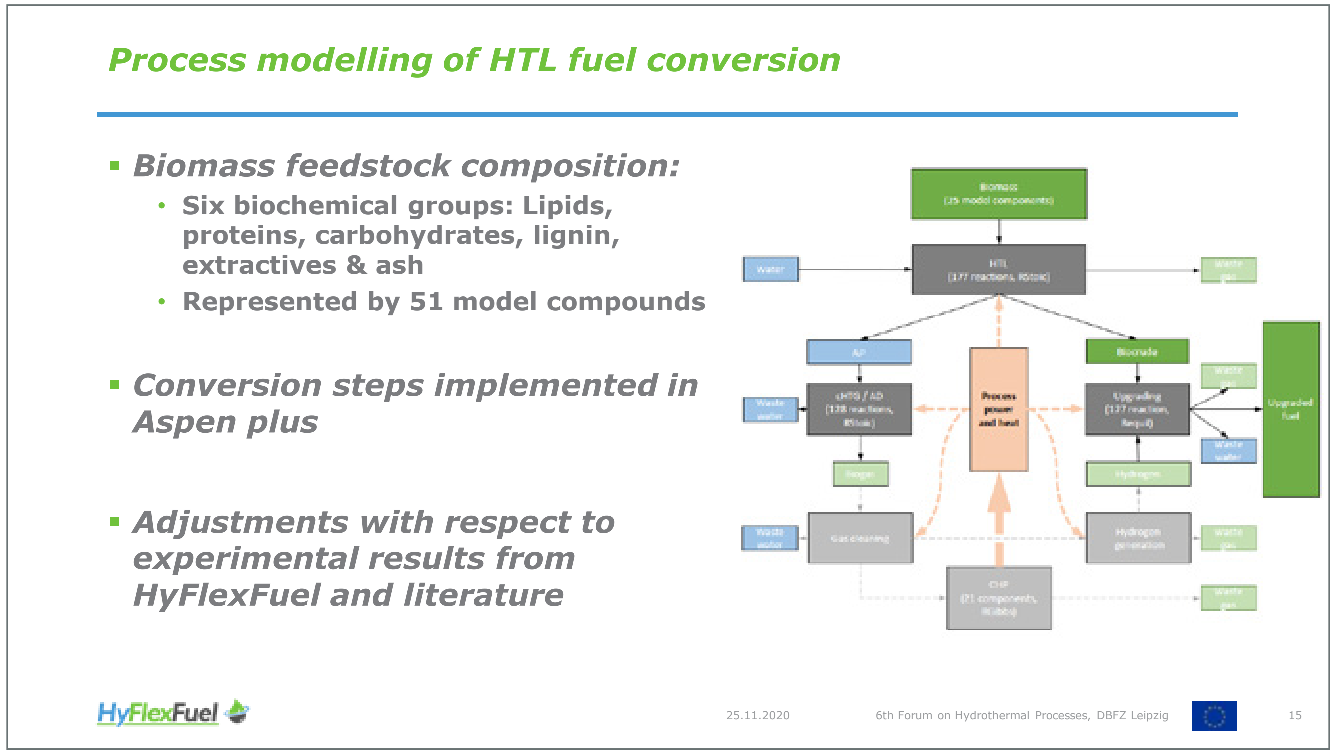
Analytical methods to analyse HTL product phases

- **Development of new analytical methods from FT-IR and GC-MS to high-resolution MS (Orbitrap and FT-ICR-MS), typically in combination with multivariate data analysis.**

Sewage sludge biocrude FTICR MS (APCI+)
Over 8000 different peaks attributed

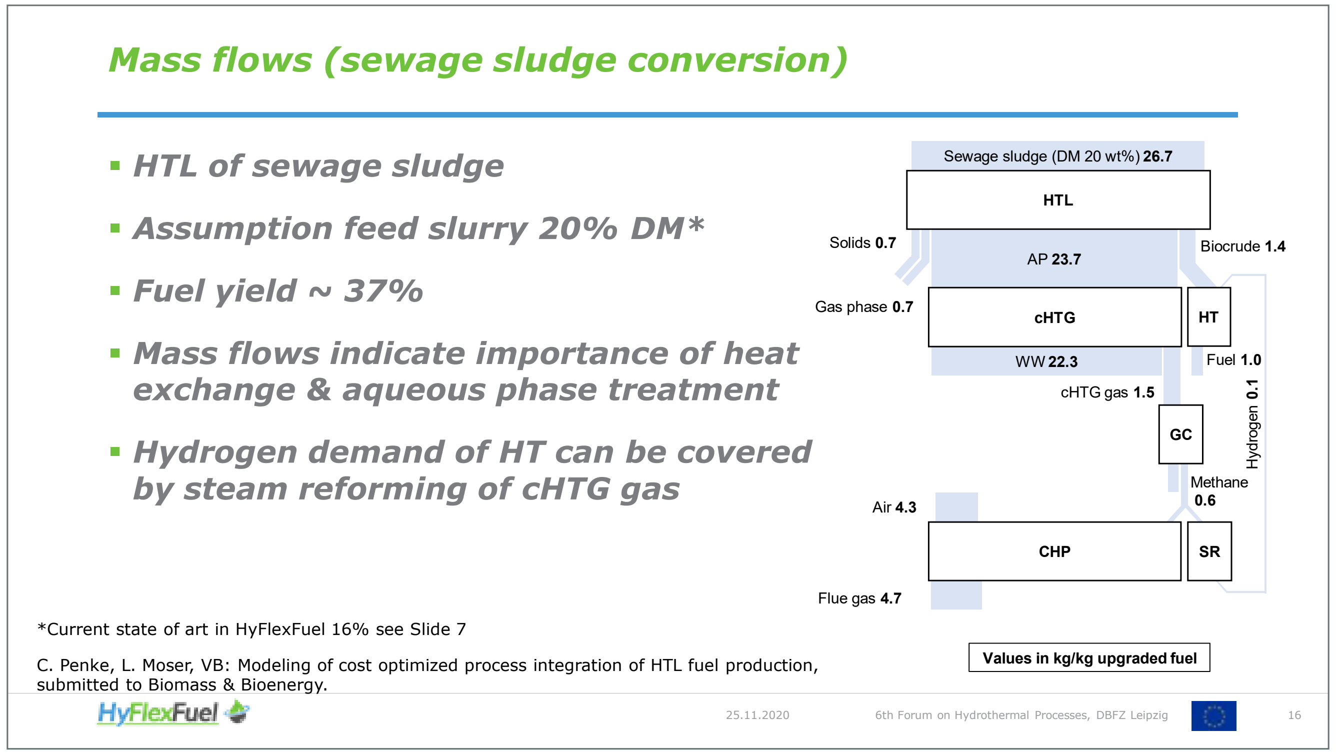
Cn vs DBE plot for
a single class

Sources: S. Chiaberge et al, *HyFlexFuel HTL bio-crude and its upgraded product analyzed by FTICR mass spectrometry*, EFTMS 2020 (postponed); R.B. Madsen et al., *Rapid Determination of Water, Total Acid Number, and Phenolic Content in Bio-Crude from Hydrothermal Liquefaction of Biomass using FT-IR*, Energy Fuels 2018, 32, 7660.



Process modelling of HTL fuel conversion

- ***Biomass feedstock composition:***
  - **Six biochemical groups: Lipids, proteins, carbohydrates, lignin, extractives & ash**
  - **Represented by 51 model compounds**
- ***Conversion steps implemented in Aspen plus***
- ***Adjustments with respect to experimental results from HyFlexFuel and literature***

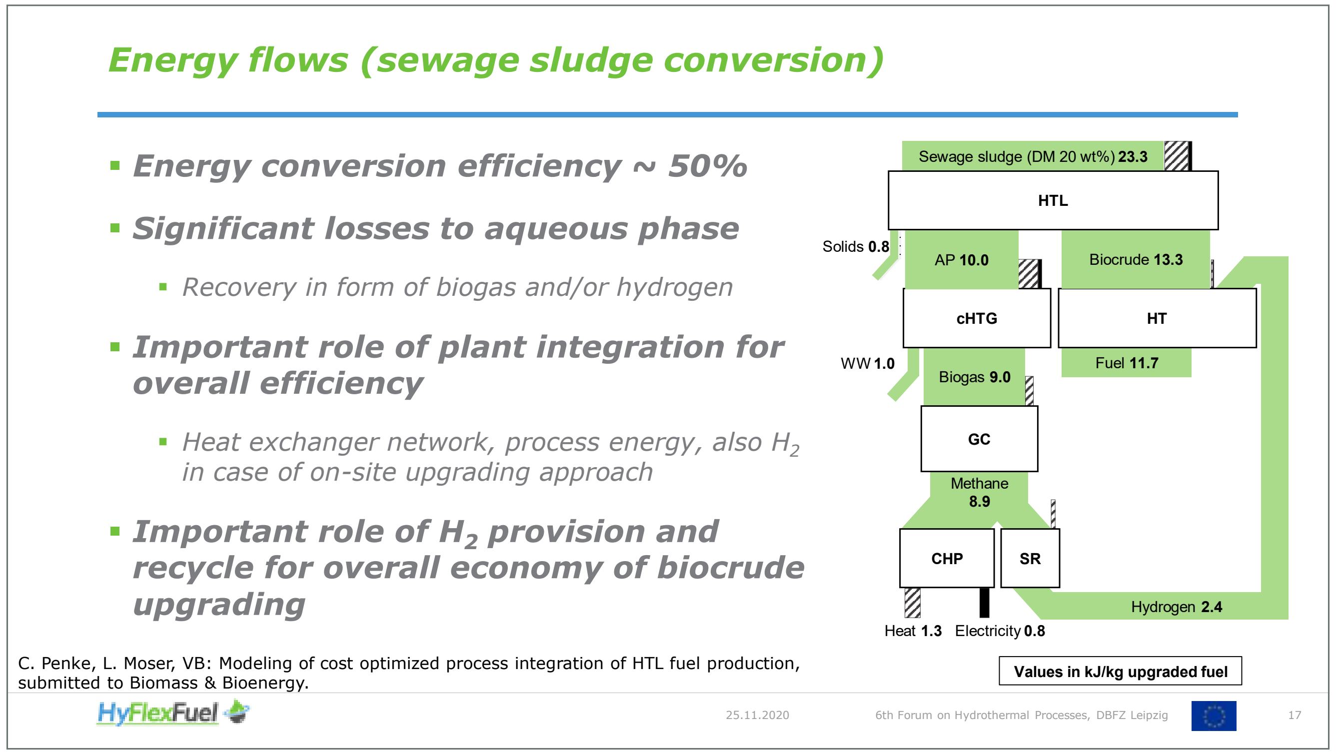


Mass flows (sewage sludge conversion)

- ***HTL of sewage sludge***
- ***Assumption feed slurry 20% DM****
- ***Fuel yield ~ 37%***
- ***Mass flows indicate importance of heat exchange & aqueous phase treatment***
- ***Hydrogen demand of HT can be covered by steam reforming of cHTG gas***

*Current state of art in HyFlexFuel 16% see Slide 7

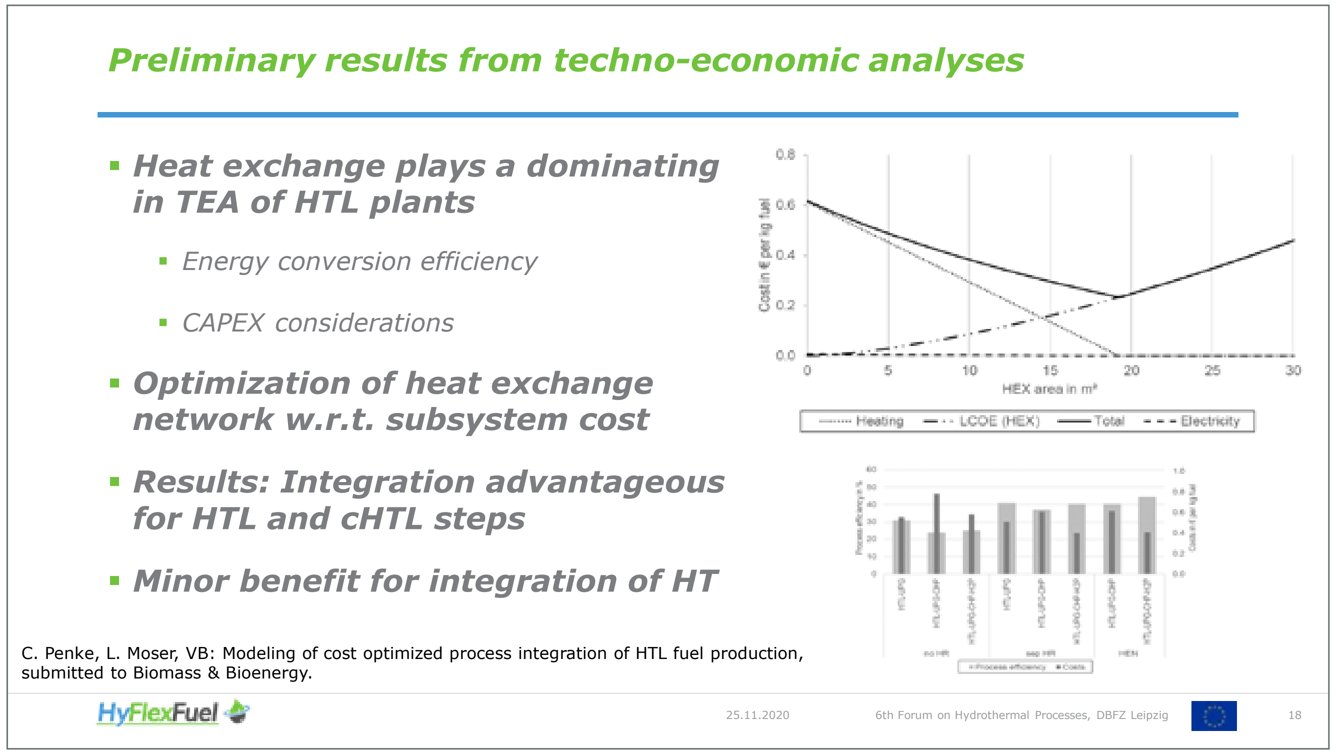
C. Penke, L. Moser, VB: Modeling of cost optimized process integration of HTL fuel production, submitted to Biomass & Bioenergy.



Energy flows (sewage sludge conversion)

- ***Energy conversion efficiency ~ 50%***
- ***Significant losses to aqueous phase***
  - *Recovery in form of biogas and/or hydrogen*
- ***Important role of plant integration for overall efficiency***
  - *Heat exchanger network, process energy, also H_2 in case of on-site upgrading approach*
- ***Important role of H_2 provision and recycle for overall economy of biocrude upgrading***

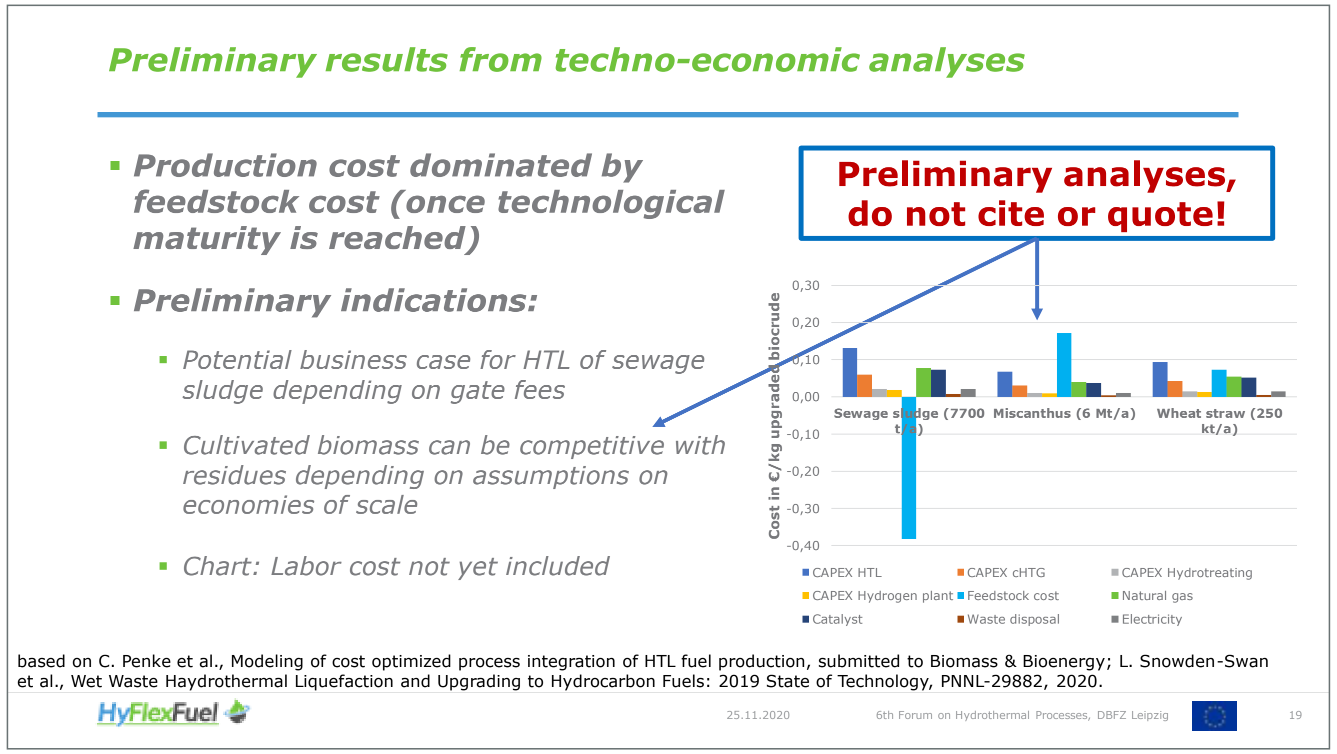
C. Penke, L. Moser, VB: Modeling of cost optimized process integration of HTL fuel production, submitted to Biomass & Bioenergy.



Preliminary results from techno-economic analyses

- ***Heat exchange plays a dominating in TEA of HTL plants***
  - *Energy conversion efficiency*
  - *CAPEX considerations*
- ***Optimization of heat exchange network w.r.t. subsystem cost***
- ***Results: Integration advantageous for HTL and cHTL steps***
- ***Minor benefit for integration of HT***

C. Penke, L. Moser, VB: Modeling of cost optimized process integration of HTL fuel production, submitted to Biomass & Bioenergy.



Preliminary results from techno-economic analyses

- *Production cost dominated by feedstock cost (once technological maturity is reached)*
- *Preliminary indications:*
  - *Potential business case for HTL of sewage sludge depending on gate fees*
  - *Cultivated biomass can be competitive with residues depending on assumptions on economies of scale*
  - *Chart: Labor cost not yet included*

Preliminary analyses, do not cite or quote!

based on C. Penke et al., Modeling of cost optimized process integration of HTL fuel production, submitted to Biomass & Bioenergy; L. Snowden-Swan et al., Wet Waste Haydrothermal Liquefaction and Upgrading to Hydrocarbon Fuels: 2019 State of Technology, PNNL-29882, 2020.

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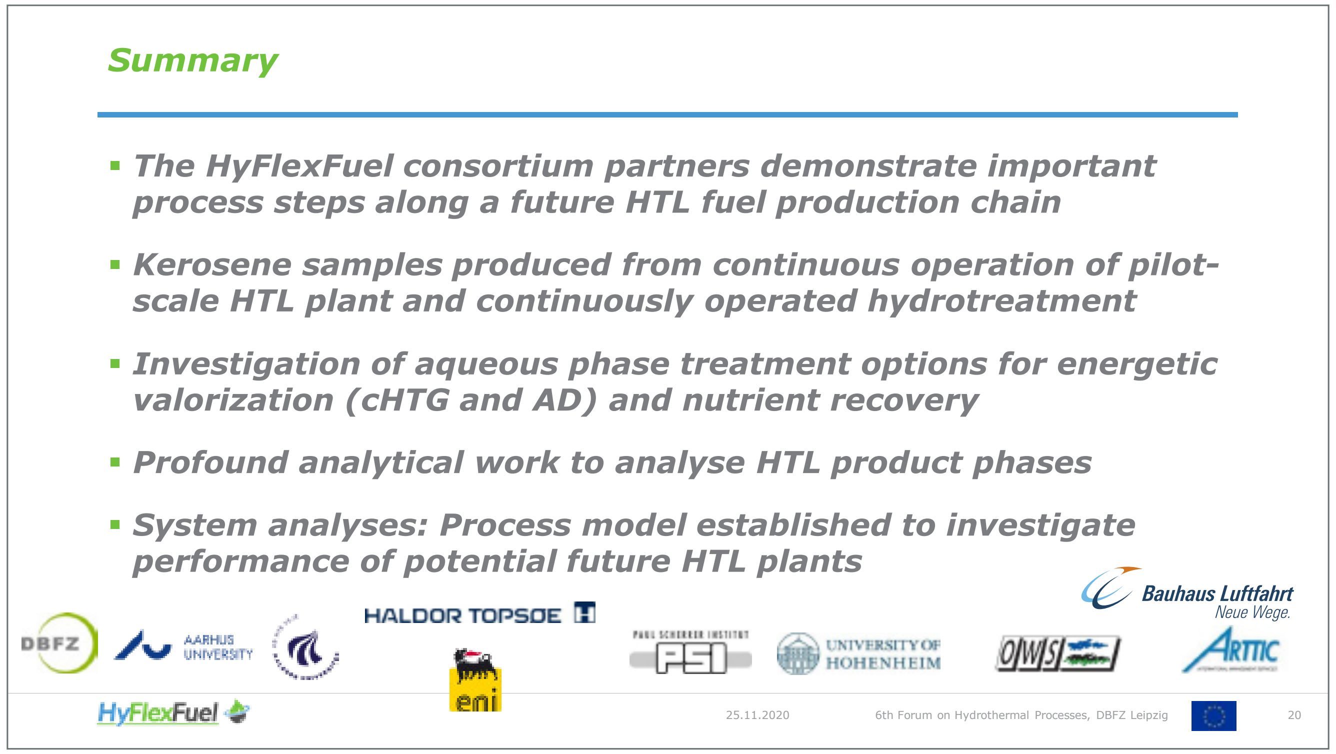

Summary

- ***The HyFlexFuel consortium partners demonstrate important process steps along a future HTL fuel production chain***
- ***Kerosene samples produced from continuous operation of pilot-scale HTL plant and continuously operated hydrotreatment***
- ***Investigation of aqueous phase treatment options for energetic valorization (cHTG and AD) and nutrient recovery***
- ***Profound analytical work to analyse HTL product phases***
- ***System analyses: Process model established to investigate performance of potential future HTL plants***

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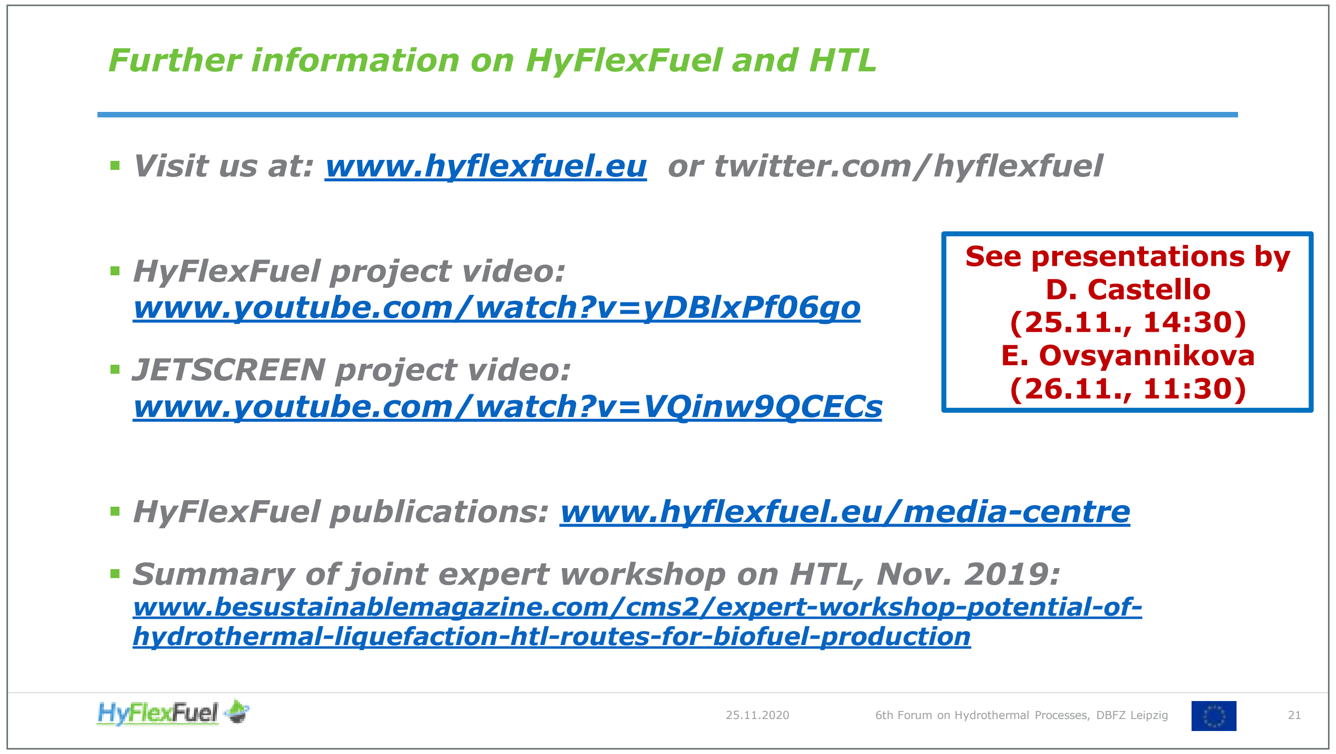

Further information on HyFlexFuel and HTL

- ***Visit us at: www.hyflexfuel.eu or twitter.com/hyflexfuel***
- ***HyFlexFuel project video: www.youtube.com/watch?v=yDBlxPf06go***
- ***JETSCREEN project video: www.youtube.com/watch?v=VQinw9QCECs***
- ***HyFlexFuel publications: www.hyflexfuel.eu/media-centre***
- ***Summary of joint expert workshop on HTL, Nov. 2019: www.besustainablemagazine.com/cms2/expert-workshop-potential-of-hydrothermal-liquefaction-htl-routes-for-biofuel-production***

See presentations by D. Castello (25.11., 14:30) E. Ovsyannikova (26.11., 11:30)

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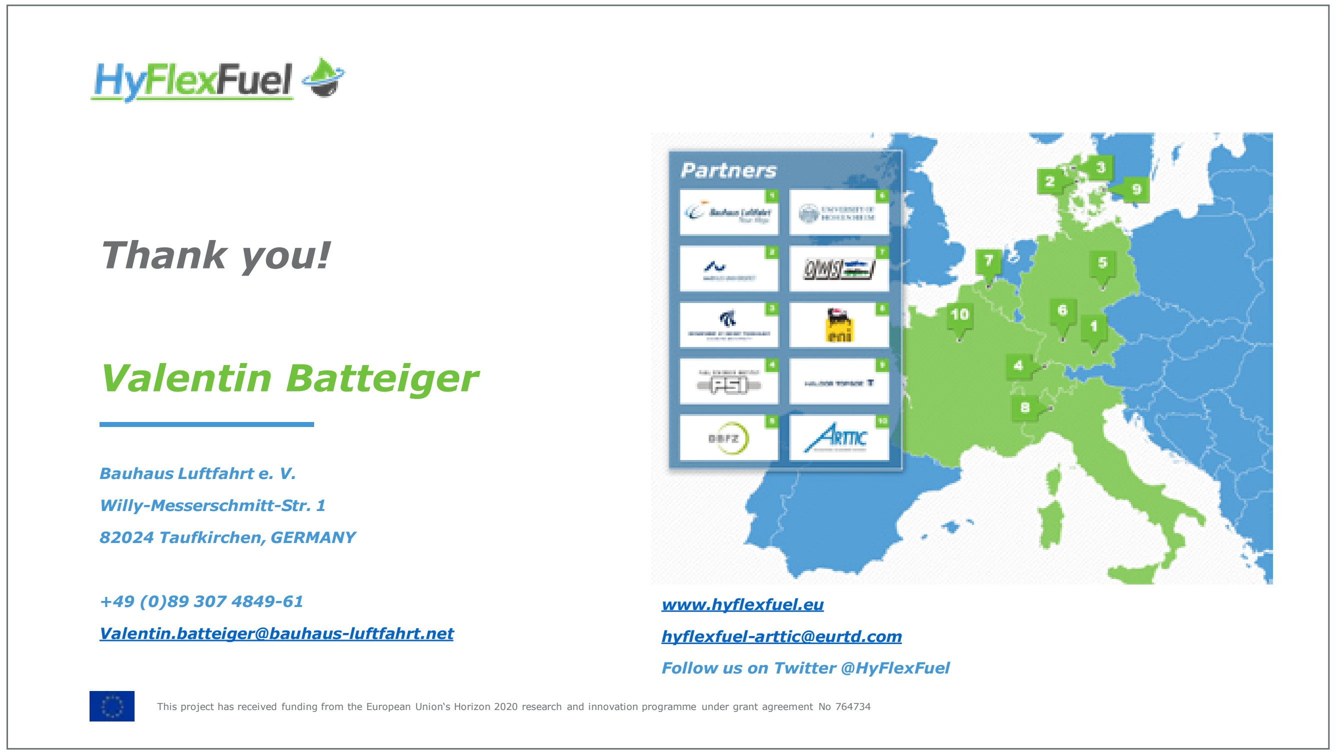

HyFlexFuel

Thank you!

Valentin Batteiger

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

Hydrothermale Verflüssigung II

Dr. Daniele Castello, Aalborg University

From HTL biocrude to drop-in biofuels: achievements and perspectives on catalytic upgrading

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Biocrude from hydrothermal liquefaction (HTL) of biomass cannot be utilized as-it-is as a fuel for most applications in the transportation field. Indeed, its properties, especially in terms of viscosity and very high content of heteroatoms (mainly oxygen and nitrogen), make an upgrading step necessary. Indeed, these characteristics of biocrude result in poor miscibility with traditional fossil fuels and in poor combustion properties, which are both strong limitations to the use of this product.

Catalytic hydroprocessing is the most promising process for biocrude upgrading, involving treatment with hydrogen at high pressure, in the presence of a suitable catalyst. This process has been widely applied to fossil oil refining, and therefore it can be considered a mature technology. However, biocrude poses new and exciting challenges, which are not commonly experienced when processing fossil streams. This is why biocrude hydroprocessing needs specific attention and research.

In this contribution, we present the latest advancements and lessons learned in the catalytic biocrude upgrading activities by the Advanced Biofuels group at Aalborg University, Denmark. Thanks to the experimental facilities available at our group (microbatch reactors, as well as a continuous lab-scale 2-stage hydrotreater) a number of experimental results were obtained with biocrudes from different origins, including algal biomass and sewage sludge. Several challenges are associated with biocrude hydroprocessing, such as dealing with biocrude thermal instability at high temperature and achieving a good degree of denitrogenation. In this presentation, we will highlight how they can be successfully addressed, leading to effective and reliable operations in view of a commercial implementation of the process. Finally, we also present the results of the fractional distillation of the upgraded biocrudes, which is the final step required for the production of real drop-in fuels. A complete characterization of the obtained fractional cuts reveals the high potential towards the production of transportation fuels, including gasoline, jet-fuel and diesel. Correct hydroprocessing is therefore of vital importance to allow the utilization of HTL products as fuels in the existing technological context, thus representing a concrete way to promote renewables in the transportation field.

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Dr. Ursel Hornung, Karlsruher Institut für Technologie

Strategien für die hydrothermale Verflüssigung von Klärschlamm aus energetischer Sicht

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Weltweit fällt Klärschlamm fällt in großen Mengen an, in Europa jährlich rund 10 Mio. t in China 20 Mio. t und in den USA 49 Billionen bezogen auf die Trockenmasse. Traditionell wurde Klärschlamm in der Landwirtschaft benutzt oder kompostiert, was jedoch Umweltproblemen führte. Daher wurden die gesetzlichen Regeln angepasst und für Klärschlamm müssen heute andere Verwertungsmöglichkeiten gefunden werden. Besonders gängig in Europa ist heute die Verbrennung, die jedoch erfordert, dass der Klärschlamm auf rund 50 % Wasseranteil getrocknet werden muss. Um diesen energetisch aufwendigen Schritt einzusparen, bieten sich hydrothermale Verfahren an. Da Klärschlamm jedoch zu einem 1/3 aus Kohlehydraten und 1/3 aus Proteinen, aber nur zwischen 10 und 15 % Lipide erhält, stellt sich die Frage, ob eine hydrothermale Verflüssigung (HTL) ausreichende Ausbeuten an Biocrude für Kraftstoffanwendungen liefert und wie deren Zusammensetzung gerade in Bezug auf Heteroatome ist. Darüber hinaus wurde noch nie untersucht, ob es sich lohnt den Lipidanteil direkt zu nutzen, bzw. zu Biodiesel zu verestern und die HTL nur für die Verflüssigung des lipidextrahierten Anteils zu verwenden. Betrachtet wird die Energierückgewinnung in Bezug auf die gewonnenen Produkte sowie das Verhältnis der Energie der Produkte zu dem Energiebedarf der Prozesse, dem sogenannten Energieverbrauchsverhältnis (ECR). Damit die Lipide einen Beitrag zum Biocrude durch die HTL haben, müssen höhere Temperaturen angewendet werden, weil sonst die Lipide nur hydrolysiert und nur als Alkohole oder Fettsäuren in der wässrigen Phase vorliegen. In einem gekoppelten Prozess aus Lipidextraktion und Veresterung kann bis zu 98% der Energie des Eisatzstoffes zurückgewonnen werden, allerdings fällt das Energieverbrauchverhältnis ungünstig aus, weil der Energiebedarf für die Extraktion und damit verbundene Trocknung zu hoch ist. In Hinblick auf die Heteroatome wurden die Wechselwirkungen der Proteine mit den Kohlenhydraten sowie mit den Lipiden betrachtet und Reaktionspfade aufgezeigt.

Session I

Grundlagen und Hydrothermale Verfahren zur Produktion von Kohlenstoffmaterialien

Maria Balda, Helmholtz-Zentrum für Umweltforschung GmbH – UFZ

Carbon spheres generated via hydrothermal carbonization of sugar as tailor-made sorbent – Influence of carboxymethyl cellulose as aditive

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Grundwasser ist eines unserer wertvollsten Güter. Besonders, wenn sich zukünftig aufgrund des Klimawandels Dürren häufen, wird es immer wichtiger, bestehende Ressourcen zu erhalten bzw. zu regenerieren. Um das zu erreichen, sind möglichst kostengünstige und einfach umzusetzende Techniken nötig. Aktivkohlepartikel im Mikromaßstab eignen sich für die in situ Sanierung von kontaminierten Grundwasserleitern. Ihre Herstellung ist jedoch aufgrund des aufwändigen Mahlschrittes von größeren zu mikrometerkleinen AK-Körnchen ein kostenintensives Verfahren.

Eine kostengünstigere Alternative könnte die bottom up Synthese mittels hydrothermaler Carbonisierung (HTC) darstellen, da lösliche Kohlenhydrate (wie bspw. Haushaltszucker) unter hydrothermalen Bedingungen naturgemäß sphärische kohlenstoffreiche Partikel im Mikrometerbereich bilden. Diese lassen sich leicht in Wasser redispergieren und bilden auch in elektrolythaltigem Wasser ohne weitere Zusätze stabile Suspensionen. Um die Ausbeute der dispergierbaren, uniformen Partikel zu erhöhen, wird während der HTC eine geringe Menge des Polyelektrolyten Carboxymethylcellulose (CMC) zugesetzt. Die CMC verankert sich dabei vermutlich auf der Oberfläche der frisch gebildeten Sphären und verhindert durch elektrostatische Wechselwirkungen die Aggregation zu größeren Kohlenstoffgebilden.

In dieser Arbeit wurden die Möglichkeiten und Grenzen von CMC als Stabilisierungszusatz während der HTC von Saccharose untersucht. Dafür wurde eine 0,5 molare wässrige Saccharose-Lösung zusammen mit 1 Ma.-% CMC (bezogen auf die Masse des Zuckers) bei verschiedenen Temperaturen und für verschiedene Zeitspannen in einem Autoklaven erhitzt. Anschließend wurden die Suspensionseigenschaften der synthetisierten Partikel sowie ihre Sorptionseigenschaften gegenüber Phenanthren untersucht. Bei Erhitzen der Partikel auf 600 °C in einer inerten Atmosphäre bildeten sich Mikroporen und es wurden spezifische Oberflächen von 300-600 m2/g erhalten. Im Anschluss daran wurden die Auswirkungen der dadurch entstandenen strukturellen Veränderungen der C-Sphären auf das Suspensions- und Sorptionsverhalten charakterisiert.

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Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

Carbon spheres generated via hydrothermal carbonization of sugar as tailor-made sorbent

Influence of carboxymethyl cellulose (CMC) as additive

UFZ

Maria Balda, Anett Georgi, Katrin Mackenzie, Frank-Dieter Kopinke
Helmholtz-Zentrum für Umweltforschung GmbH - UFZ

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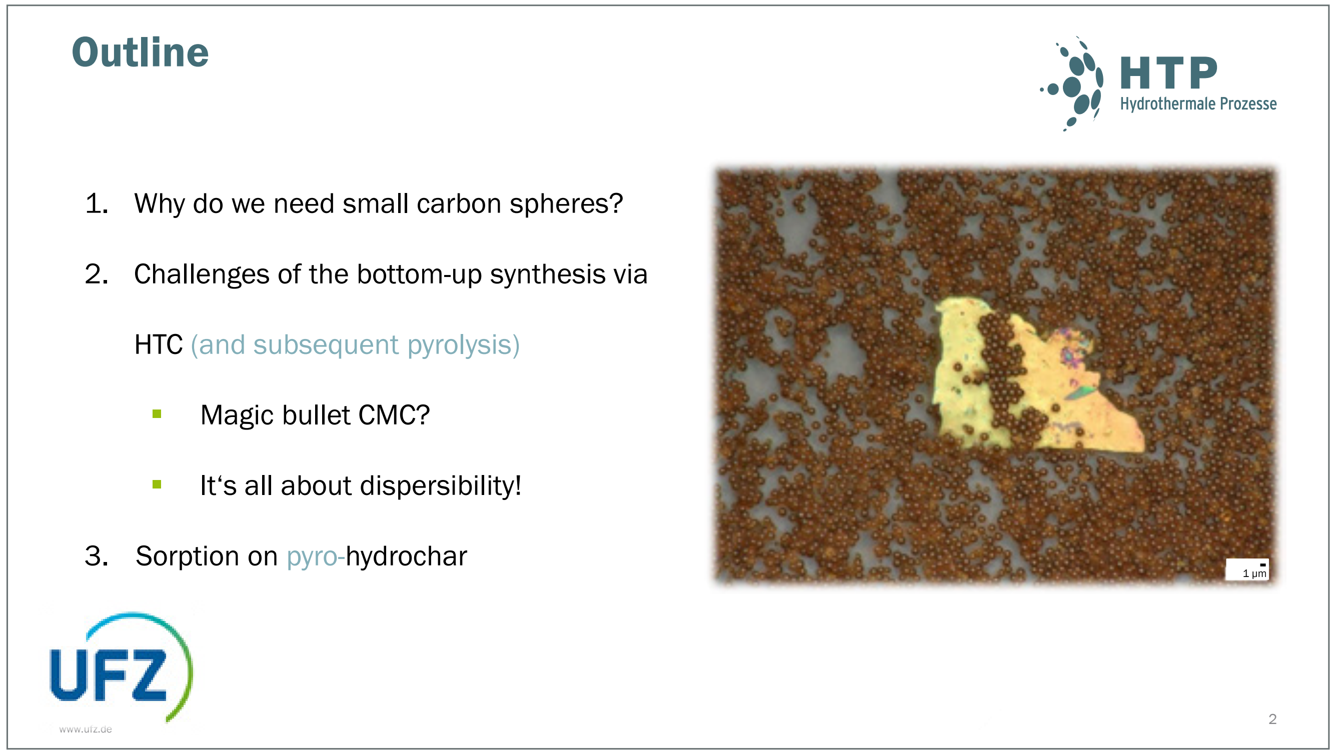

Outline

HTP Hydrothermale Prozesse

1. Why do we need small carbon spheres?
2. Challenges of the bottom-up synthesis via HTC (and subsequent pyrolysis)
   - Magic bullet CMC?
   - It‘s all about dispersibility!
3. Sorption on pyro-hydrochar

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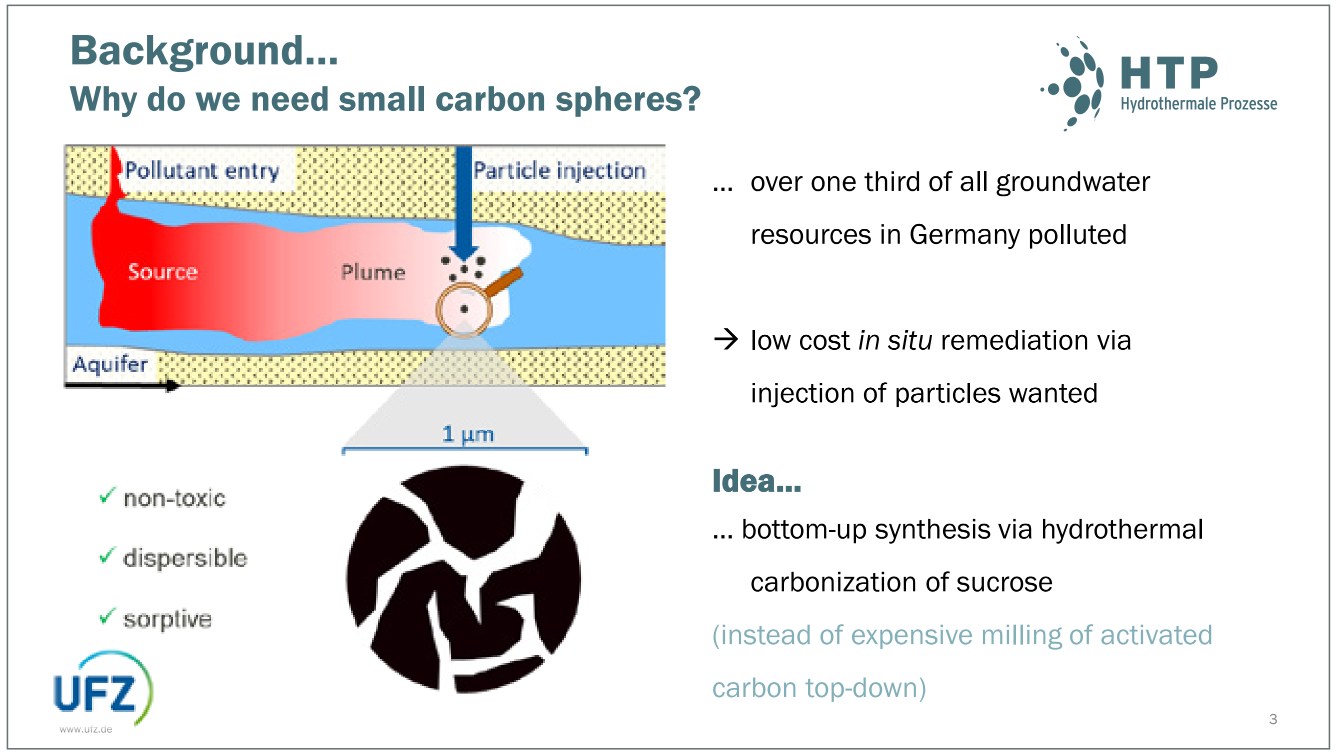

Background…
Why do we need small carbon spheres?

- ✓ non-toxic
- ✓ dispersible
- ✓ sorptive

… over one third of all groundwater resources in Germany polluted

→ low cost *in situ* remediation via injection of particles wanted

Idea…

… bottom-up synthesis via hydrothermal carbonization of sucrose

(instead of expensive milling of activated carbon top-down)

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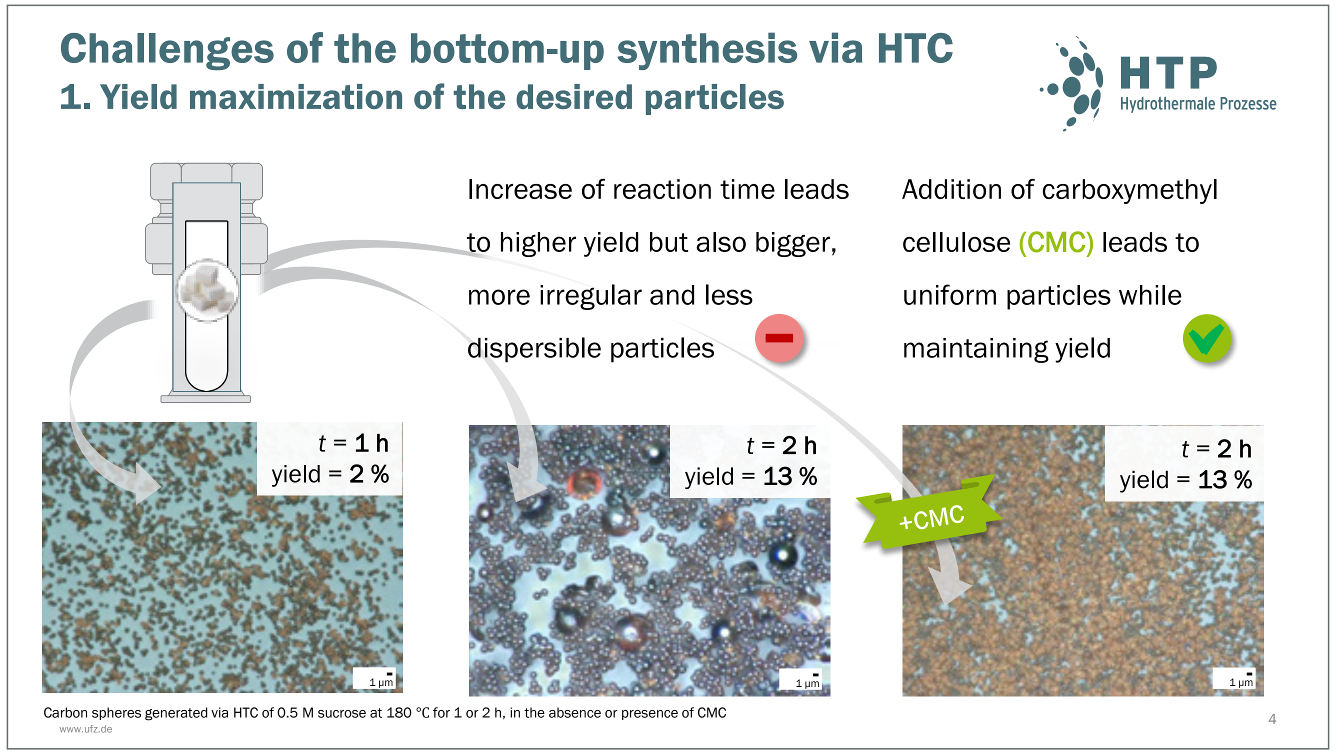

Challenges of the bottom-up synthesis via HTC
1. Yield maximization of the desired particles

Increase of reaction time leads to higher yield but also bigger, more irregular and less dispersible particles ⛔

Addition of carboxymethyl cellulose (CMC) leads to uniform particles while maintaining yield ✓

t = 1 h
yield = 2 %

t = 2 h
yield = 13 %

t = 2 h
yield = 13 %

Carbon spheres generated via HTC of 0.5 M sucrose at 180 °C for 1 or 2 h, in the absence or presence of CMC

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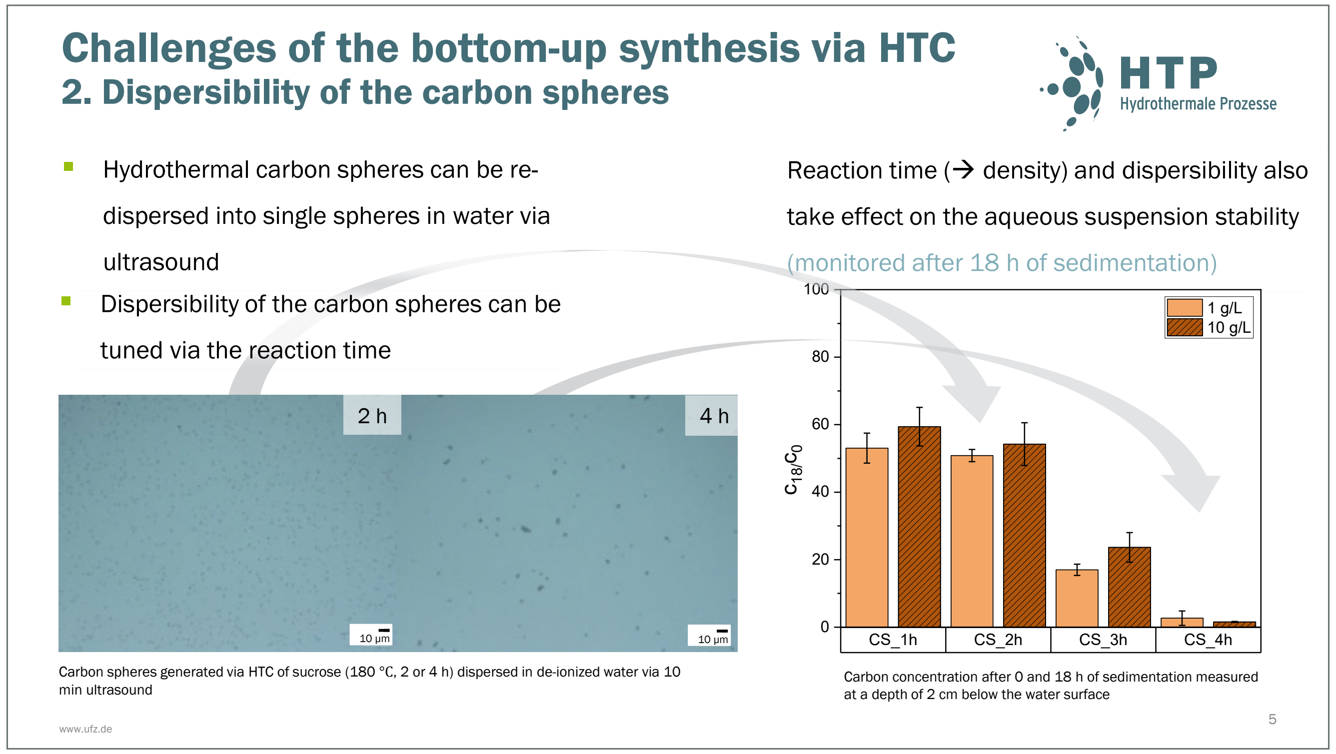

Challenges of the bottom-up synthesis via HTC
2. Dispersibility of the carbon spheres

- Hydrothermal carbon spheres can be re-dispersed into single spheres in water via ultrasound
- Dispersibility of the carbon spheres can be tuned via the reaction time

Reaction time (→ density) and dispersibility also take effect on the aqueous suspension stability (monitored after 18 h of sedimentation)

Carbon spheres generated via HTC of sucrose (180 °C, 2 or 4 h) dispersed in de-ionized water via 10 min ultrasound

Carbon concentration after 0 and 18 h of sedimentation measured at a depth of 2 cm below the water surface

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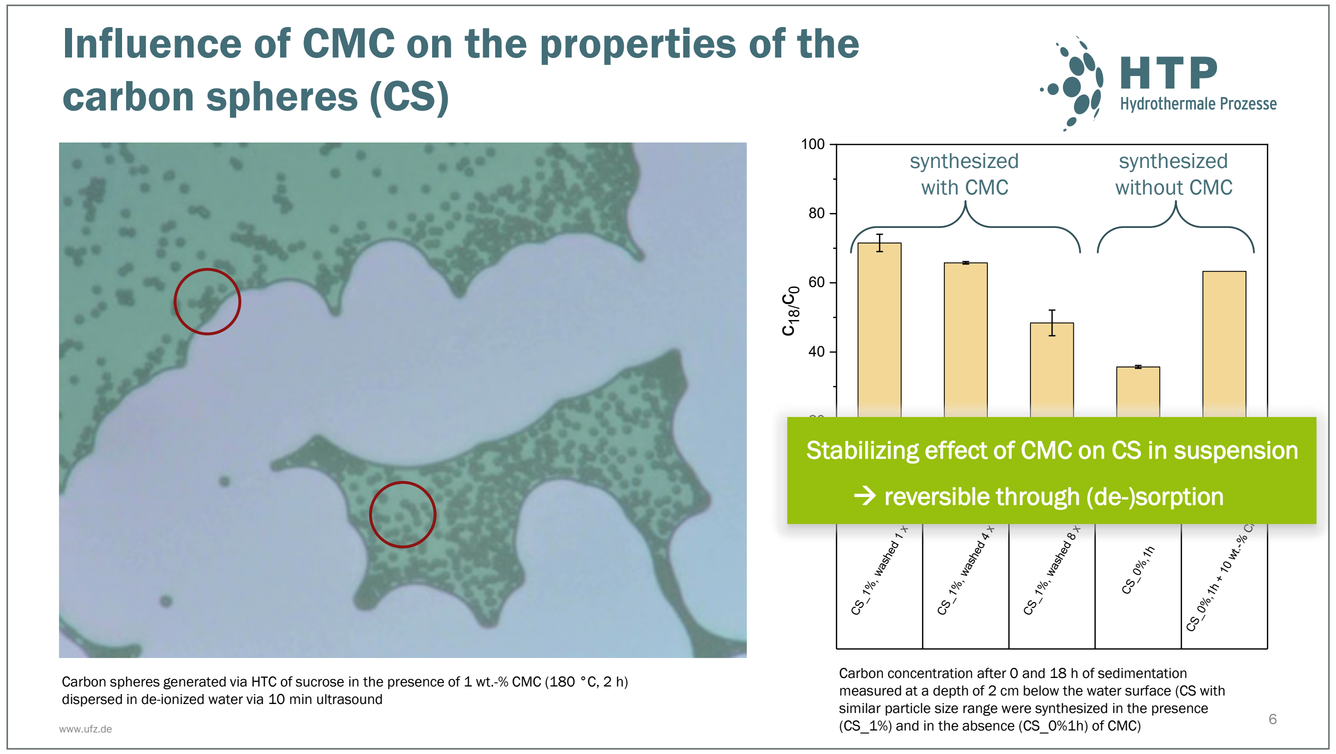

Influence of CMC on the properties of the carbon spheres (CS)

Stabilizing effect of CMC on CS in suspension
→ reversible through (de-)sorption

Carbon spheres generated via HTC of sucrose in the presence of 1 wt.-% CMC (180 °C, 2 h) dispersed in de-ionized water via 10 min ultrasound

Carbon concentration after 0 and 18 h of sedimentation measured at a depth of 2 cm below the water surface (CS with similar particle size range were synthesized in the presence (CS_1%) and in the absence (CS_0%1h) of CMC)

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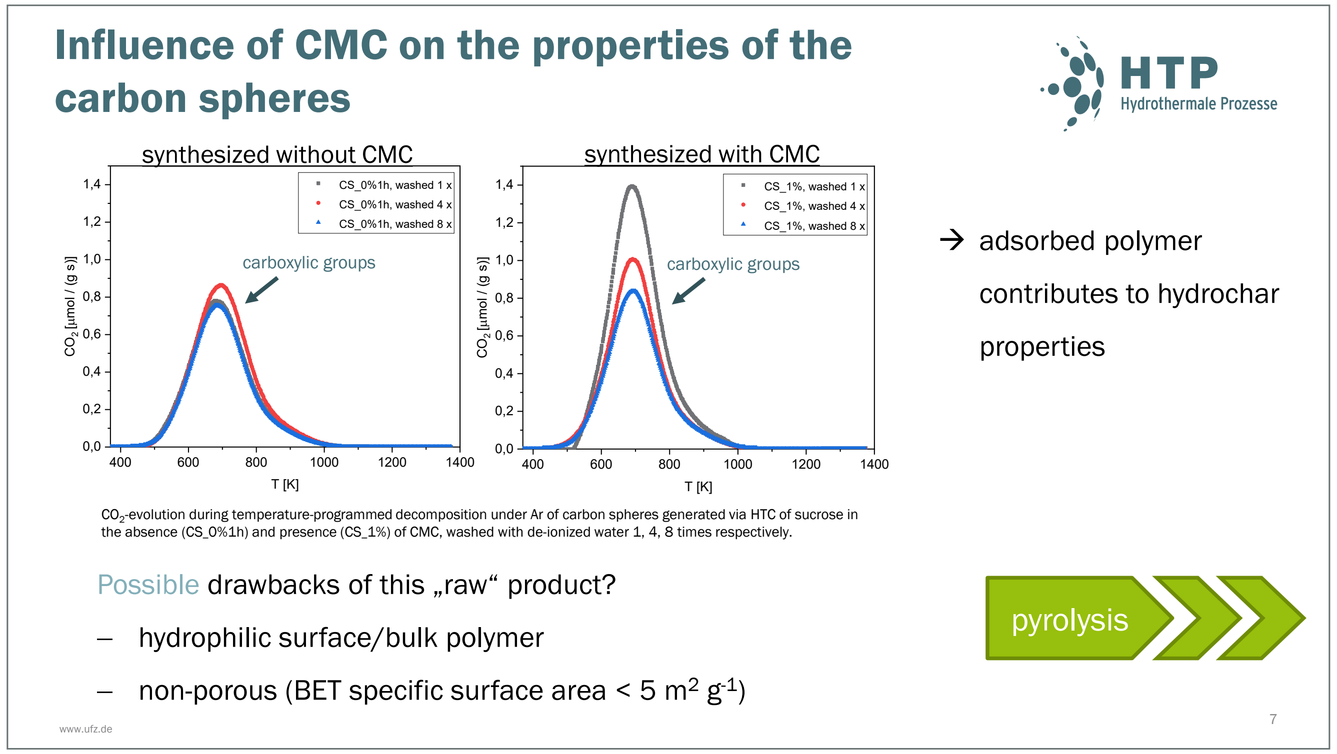


Influence of CMC on the properties of the carbon spheres

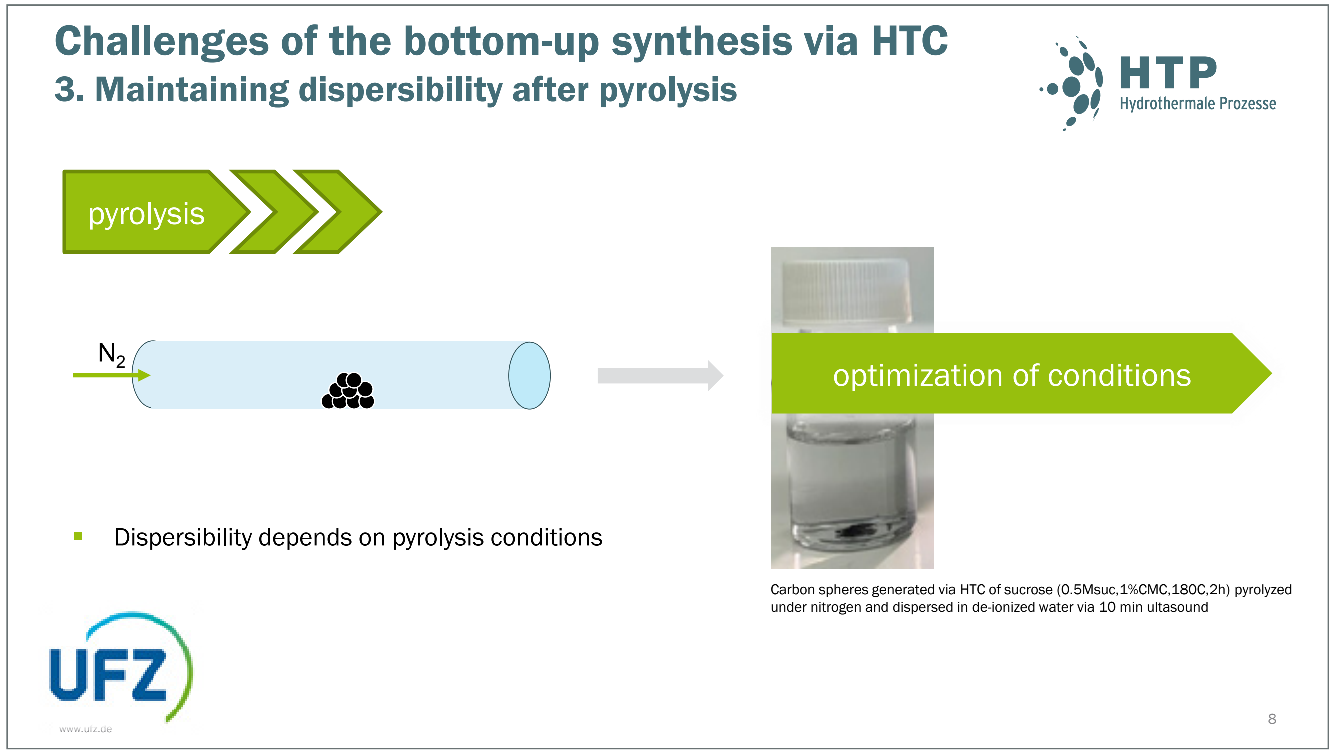
CO_2-evolution during temperature-programmed decomposition under Ar of carbon spheres generated via HTC of sucrose in the absence (CS_0%1h) and presence (CS_1%) of CMC, washed with de-ionized water 1, 4, 8 times respectively.

→ adsorbed polymer contributes to hydrochar properties

Possible drawbacks of this „raw“ product?

- hydrophilic surface/bulk polymer
- non-porous (BET specific surface area < 5 m^2 g^{-1})

pyrolysis

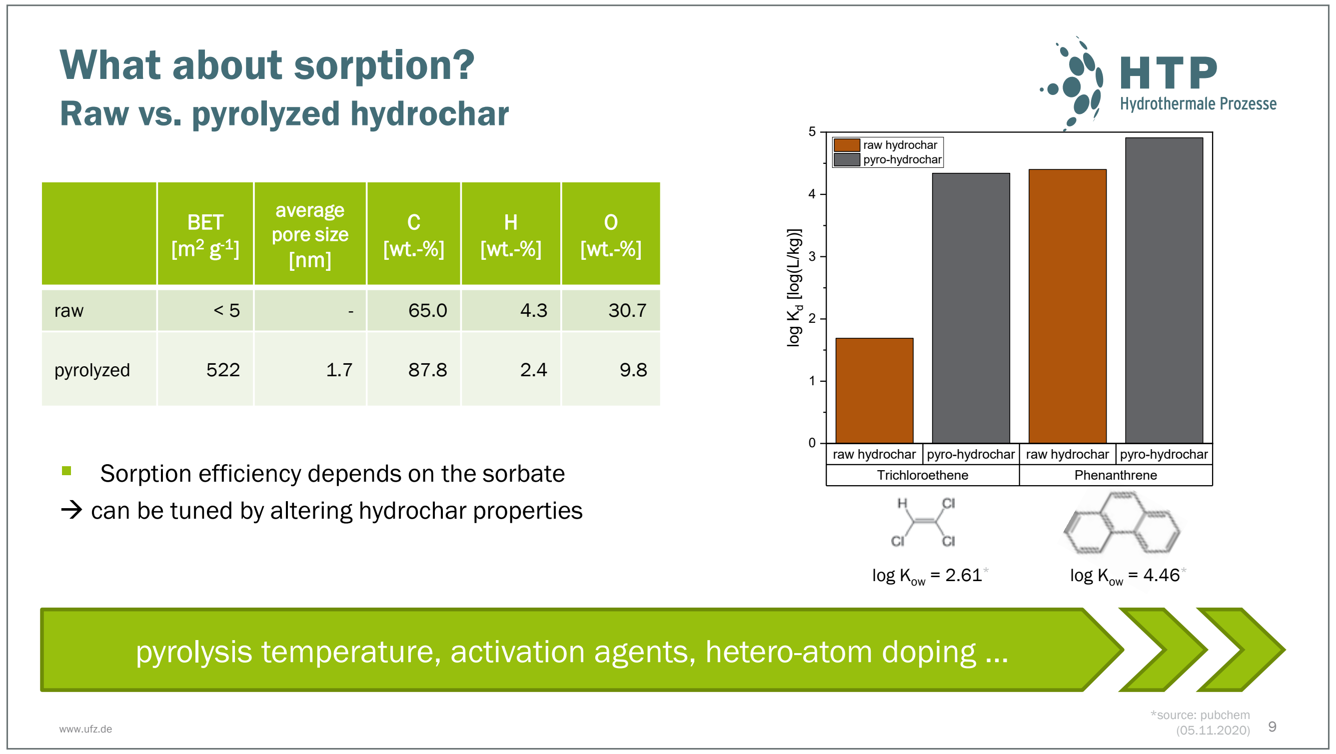


Challenges of the bottom-up synthesis via HTC

3. Maintaining dispersibility after pyrolysis

- Dispersibility depends on pyrolysis conditions

Carbon spheres generated via HTC of sucrose (0.5Msuc,1%CMC,180C,2h) pyrolyzed under nitrogen and dispersed in de-ionized water via 10 min ultasound



What about sorption?

Raw vs. pyrolyzed hydrochar

	BET [m^2 g^{-1}]	average pore size [nm]	C [wt.-%]	H [wt.-%]	O [wt.-%]
raw	< 5	-	65.0	4.3	30.7
pyrolyzed	522	1.7	87.8	2.4	9.8

log K_{ow} = 2.61*

log K_{ow} = 4.46*

- Sorption efficiency depends on the sorbate

→ can be tuned by altering hydrochar properties

pyrolysis temperature, activation agents, hetero-atom doping …

*source: pubchem (05.11.2020)

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UFZ HELMHOLTZ Centre for Environmental Research

Thank you for your attention!

6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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Versatile carbon coating of different substrates via Hydrothermal Carbonization

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Coating of substrates with carbon is usually an energy consuming and expensive process that needs a lot of specialized equipment and know-how. In addition, many of these processes are remote from green and environmental-friendly chemistry. In contrast, Hydrothermal Carbonization (HTC) could be a long sought alternative.

Presumably everyone, who has performed a HTC process of sugars in a non-Teflon®-lined autoclave, knows that it generally involves a lot of effort to clean it afterwards due to carbon-residues on its inner walls. Still, until now, only very little use is made from this supreme feature of HTC.

Coating of macroscopic substrates via hydrothermal carbonization is not as limited as it may seem on first glance. The coating of carbon materials with hydrochar from sugars seems reasonable and has gained more and more attention over the past few years.[1-6] Other macroscopic materials, e.g. metal, ceramics or glass are not that deeply investigated[7-9] and it seems challenging to coat them with carbon.

In this work we present an efficient way of coating of three different "macro"-substrates via HTC by introducing magnetic stirring during the reaction. This aspect is new in terms of hydrothermal-carbon-coating and leads to an even covering of the substrates, independent of used material type and shape.

In a second step, the coated substrates can be further carbonized via a simple thermal treatment, reaching a specific surface area up to 500 m2/g, and thus could be used as adsorbents in technical applications. The coated "macro"-substrates ensure an easy removal of the loaded adsorbent, without time-consuming separation processes and yield losses, while still keeping the favorable properties of sugar-based hydrochars. We additionally present the opportunity of catalytic reactions by adding different metal particles to the coating and the possibility to regenerate used metal-substrates in air via electro-thermal heating.

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Nader Marzban, Leibniz-Institut für Agrartechnik und Bioökonomie e.V.

Prediction of fuel characteristics for hydrochars derived from various biomasses based on feedstock elemental analysis and process operating conditions using the genetic programming

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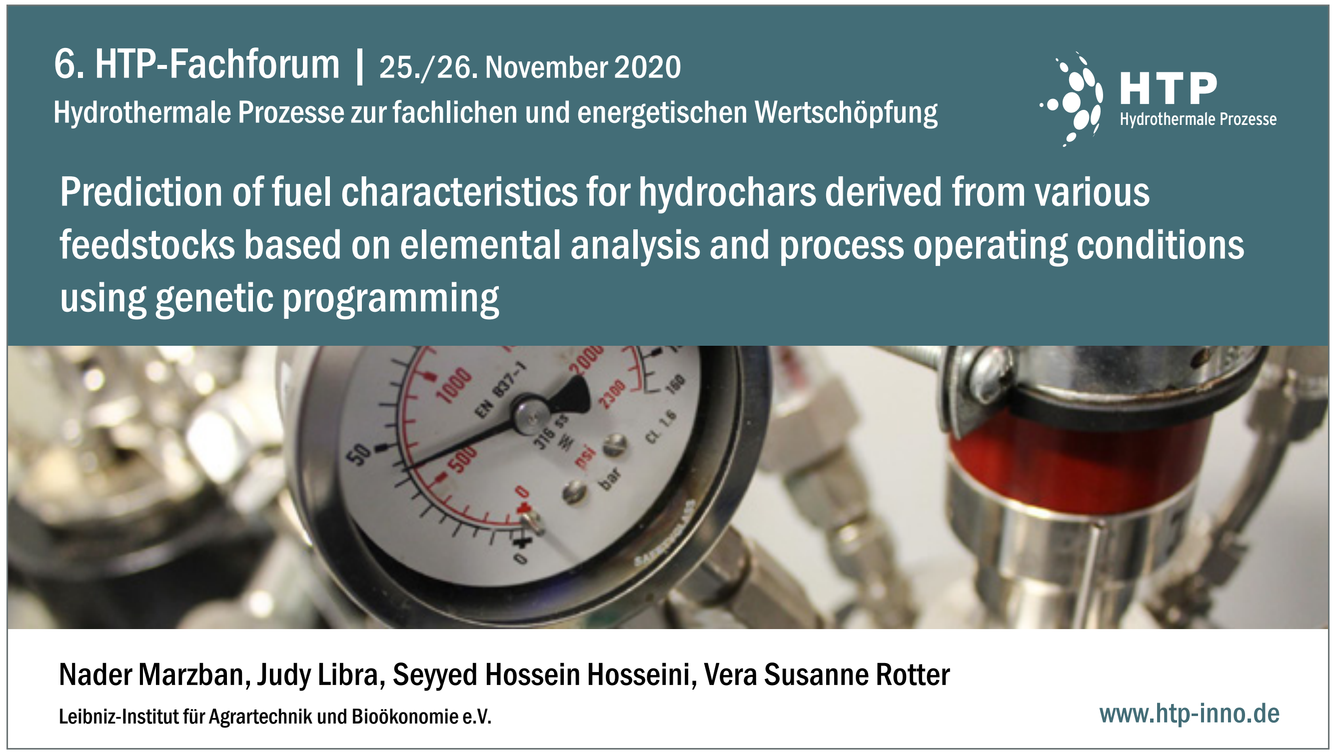
The hydrothermal carbonization (HTC) of wet organic residues can improve their fuel characteristics significantly by reducing the ratio of oxygen to carbon content of the solids, which in turn increases their higher heating value (HHV). However, since solids are lost in the process, assessment of whether the process is beneficial must include an evaluation of the energy yield, which depends on the behavior of the solid yield and change in HHV as a function of the HTC operating conditions. Therefore, correlations which can predict how operating conditions affect the HHV and solid yield are essential. The goal of this work was to develop correlations that can be used to predict the energy yield and energy densification based on a simple elemental analysis of the original biomass and operating conditions.

A graph-based genetic programming method was used to explore the correlations for predicting the HHV and solid yield. The correlations were derived and further validated based on data collected from 26 and 4 literature sources, respectively. Three correlations were introduced which:

1. predict the HHV of feedstock and char by using their elemental analysis,
2. predict the HHV of char by using the HHV of biomass and operating conditions
3. predict the solid yield by using the operating conditions

The first correlation can be used for biomass and chars with widely varying elemental composition (wt%), i.e. 29.93≤ C% ≤72, 2.94 ≤ H% ≤8.32, 0≤ N% ≤10.8, 0≤ S% ≤7.74, 8.6≤ O% ≤54.23, 0≤ Ash% ≤43.92. Compared to previous correlations for HHV published in literature, the proposed correlation has lower error. For measured values ranging from 13.87≤ HHV (MJ/kg) ≤32.21, the correlation offers a low average absolute error (AAE) of 4.7% and bias error (ABE) of 0.18%. To derive the second and third correlations which take operating conditions into account, published values covering a wide range of conditions were analyzed, i.e. 5.76≤ HHV of biomass (MJ/kg) ≤27.4, 0 ≤ holding time (min) ≤2208, 122.7 ≤ temperature (°C) ≤300, 0.0096 ≤ biomass to water ratio ≤0.5. The correlation to predict HHV values deviates from measured values (15.72 ≤ HHV of char (MJ/kg) ≤33.21) with an AAE=6.4% and ABE=0.58%. The third correlation for the solid yield based on the operating conditions was able to predict the measured values (26.9 ≤ solid yield% ≤98.23) with an AAE of 11.93% and ABE of 0.4%. Finally, we can achieve the goal of predicting what type of energy densification and energy yield can be expected for different feedstocks and operating conditions by combining the correlations. Using correlation 1 and 2, energy densification can be predicted (AAE= 6.2 %; ABE=1.7 %), while using the three correlations together, it is possible to predict the energy yield of chars. The values calculated by this method agree well with the measured energy yield (AAE=13.3%; ABE=12.5%).



6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Prediction of fuel characteristics for hydrochars derived from various feedstocks based on elemental analysis and process operating conditions using genetic programming

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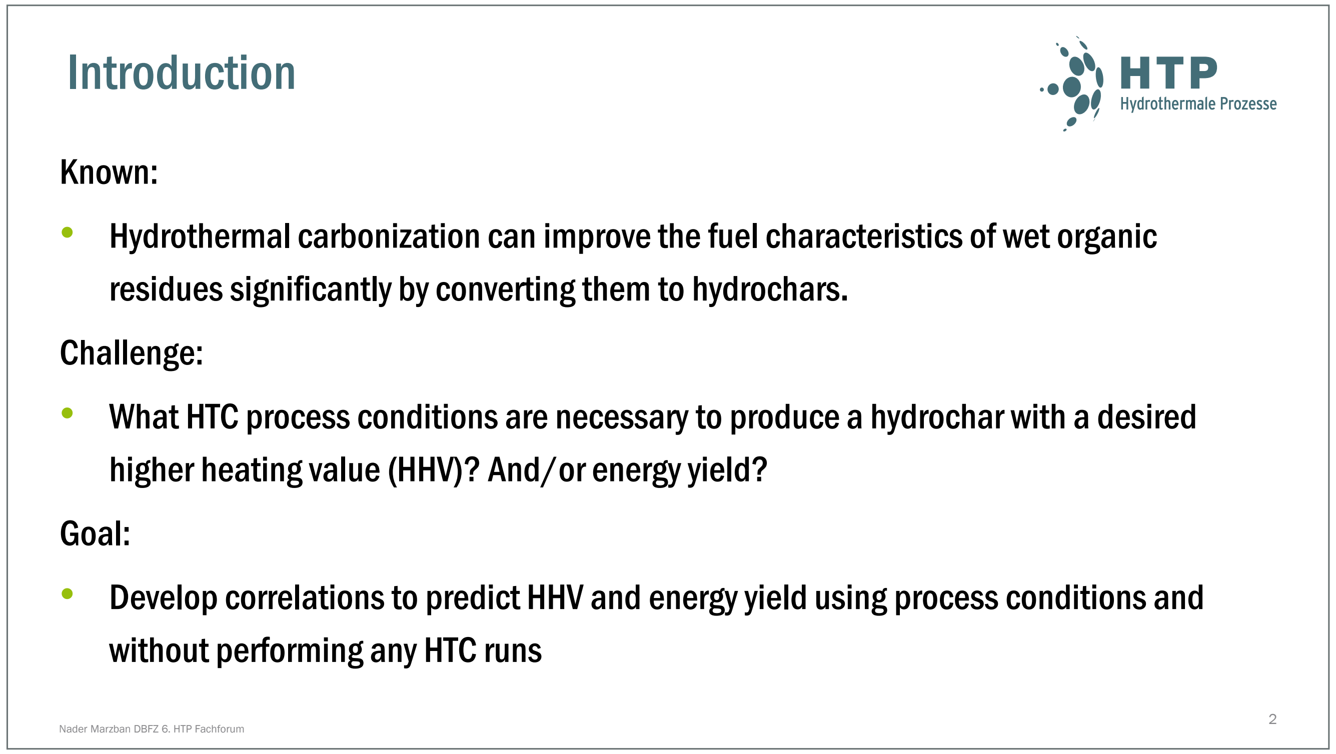

Introduction

Known:

- Hydrothermal carbonization can improve the fuel characteristics of wet organic residues significantly by converting them to hydrochars.

Challenge:

- What HTC process conditions are necessary to produce a hydrochar with a desired higher heating value (HHV)? And/or energy yield?

Goal:

- Develop correlations to predict HHV and energy yield using process conditions and without performing any HTC runs

Nader Marzban DBFZ 6. HTP Fachforum
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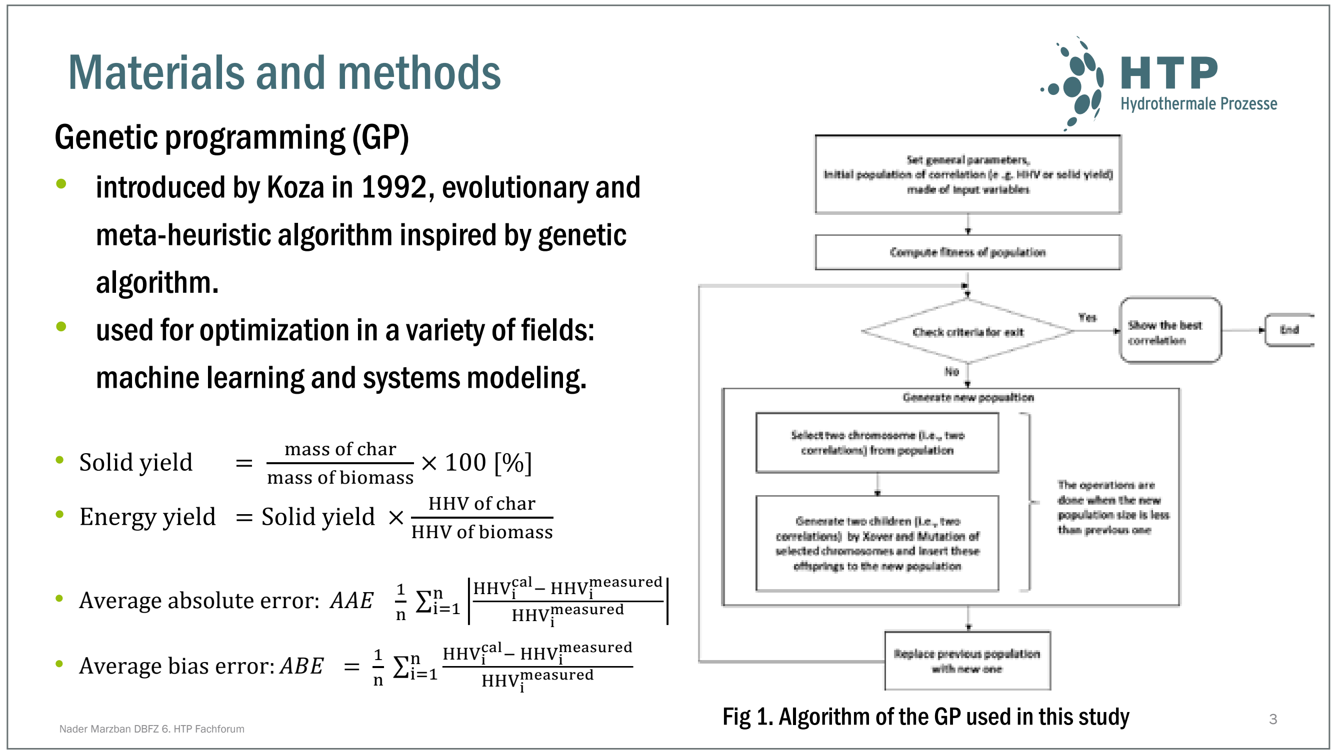


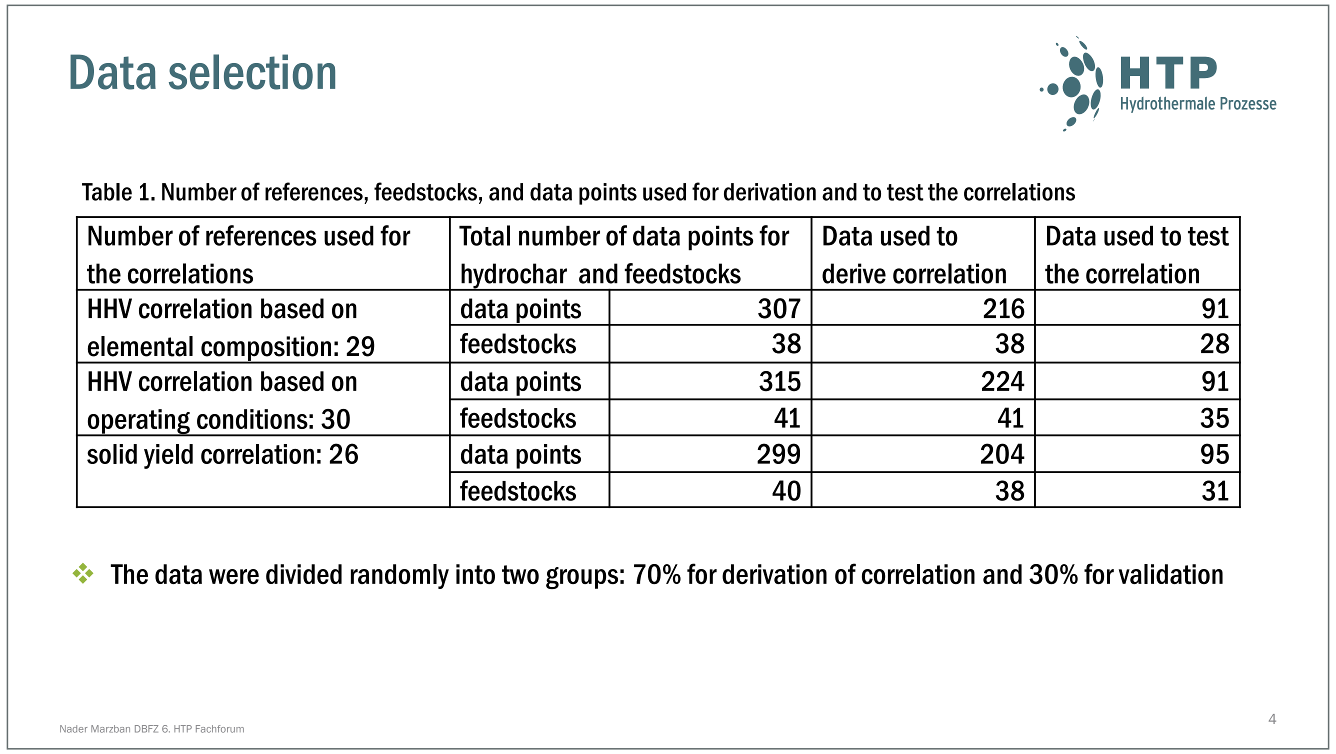
Materials and methods

Genetic programming (GP)

- introduced by Koza in 1992, evolutionary and meta-heuristic algorithm inspired by genetic algorithm.
- used for optimization in a variety of fields: machine learning and systems modeling.

- Solid yield $= \frac{\text{mass of char}}{\text{mass of biomass}} \times 100\ [\%]$
- Energy yield $= \text{Solid yield} \times \frac{\text{HHV of char}}{\text{HHV of biomass}}$
- Average absolute error: $AAE\ \ \frac{1}{n}\sum_{i=1}^{n}\left|\frac{HHV_i^{cal} - HHV_i^{measured}}{HHV_i^{measured}}\right|$
- Average bias error: $ABE = \frac{1}{n}\sum_{i=1}^{n}\frac{HHV_i^{cal} - HHV_i^{measured}}{HHV_i^{measured}}$

Fig 1. Algorithm of the GP used in this study



Data selection

Table 1. Number of references, feedstocks, and data points used for derivation and to test the correlations

Number of references used for the correlations	Total number of data points for hydrochar and feedstocks		Data used to derive correlation	Data used to test the correlation
HHV correlation based on elemental composition: 29	data points	307	216	91
	feedstocks	38	38	28
HHV correlation based on operating conditions: 30	data points	315	224	91
	feedstocks	41	41	35
solid yield correlation: 26	data points	299	204	95
	feedstocks	40	38	31

- The data were divided randomly into two groups: 70% for derivation of correlation and 30% for validation

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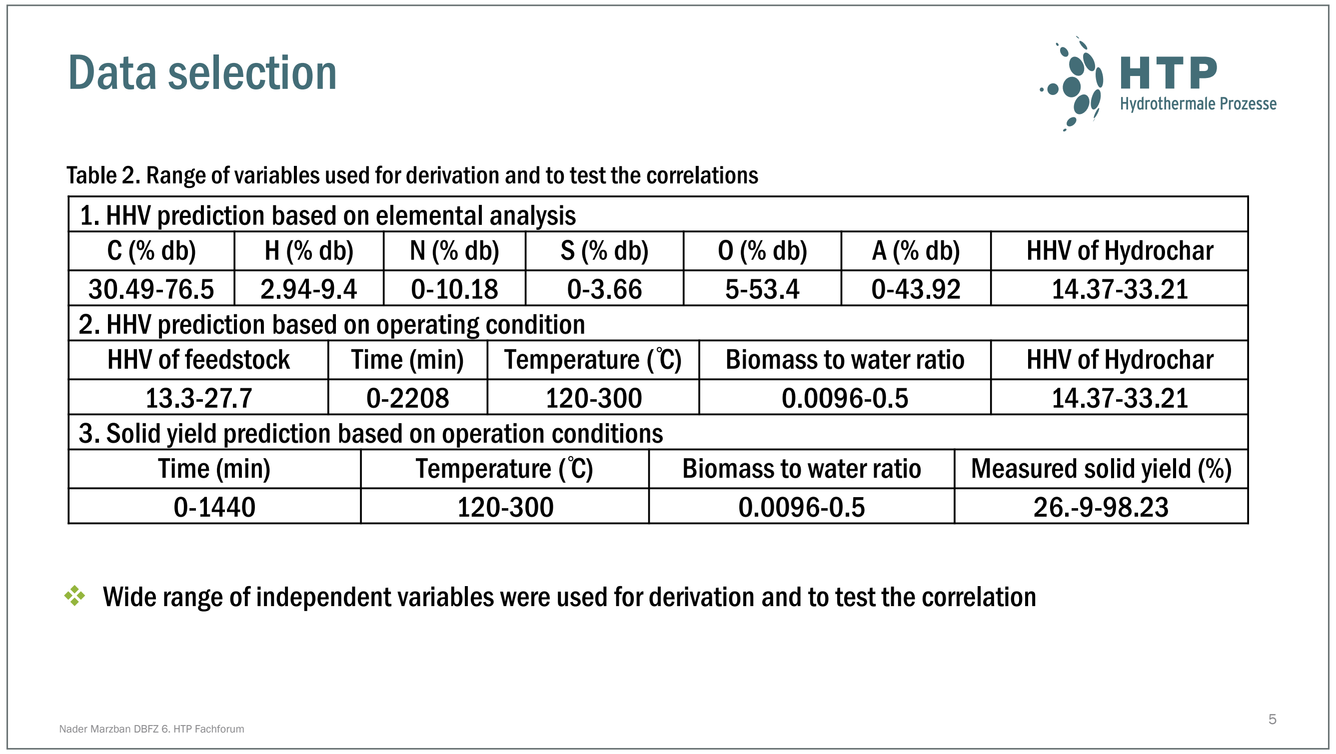
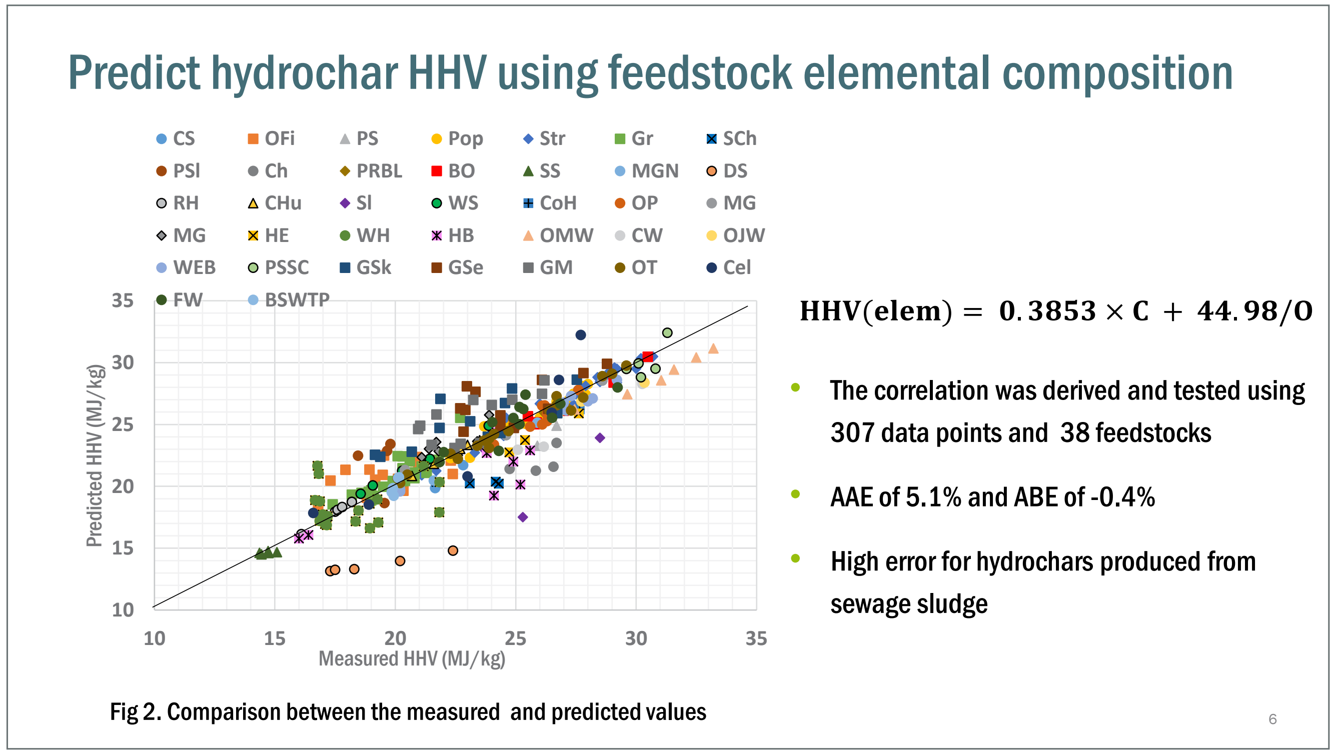


Data selection

Table 2. Range of variables used for derivation and to test the correlations

1. HHV prediction based on elemental analysis						
C (% db)	H (% db)	N (% db)	S (% db)	O (% db)	A (% db)	HHV of Hydrochar
30.49-76.5	2.94-9.4	0-10.18	0-3.66	5-53.4	0-43.92	14.37-33.21
2. HHV prediction based on operating condition						
HHV of feedstock	Time (min)	Temperature (℃)	Biomass to water ratio	HHV of Hydrochar		
13.3-27.7	0-2208	120-300	0.0096-0.5	14.37-33.21		
3. Solid yield prediction based on operation conditions						
Time (min)	Temperature (℃)	Biomass to water ratio	Measured solid yield (%)			
0-1440	120-300	0.0096-0.5	26.-9-98.23			

- Wide range of independent variables were used for derivation and to test the correlation



Predict hydrochar HHV using feedstock elemental composition

Fig 2. Comparison between the measured and predicted values

$$HHV(elem) = 0.3853 \times C + 44.98/O$$

- The correlation was derived and tested using 307 data points and 38 feedstocks
- AAE of 5.1% and ABE of -0.4%
- High error for hydrochars produced from sewage sludge

Sensitivity analysis of correlation

$$\mathbf{HHV(elem) = 0.3853 \times C + 44.98/O}$$

Variable	Sensitivity	% Positive	Positive Magnitude	% Negative	% Negative Magnitude
C	0.93554	100%	0.93554	0%	0
O	0.20707	0%	0	100%	0.20707

- Increase in C leads to increase in the HHV.
- Increase in O leads to decrease in the HHV.
- The effect of carbon is bigger than the effect of oxygen on HHV
- Experimental data also show the same influence of O and C on HHV

Comparison with other correlations from literature

- None of the previous works were developed based on hydrochar.
- Most older works focused on coal, while correlations after 1978 were developed for different types of biomasses.
- Comparison to previous correlations shows the lowest error for HHV prediction of hydrochar from the new correlation.
- It includes only terms for carbon and oxygen and is less complex than the recent correlations developed for biomasses.
- The correlation developed in this study can also be used to predict the HHV of biomass.

Predict hydrochar HHV from operating conditions and feedstock HHV

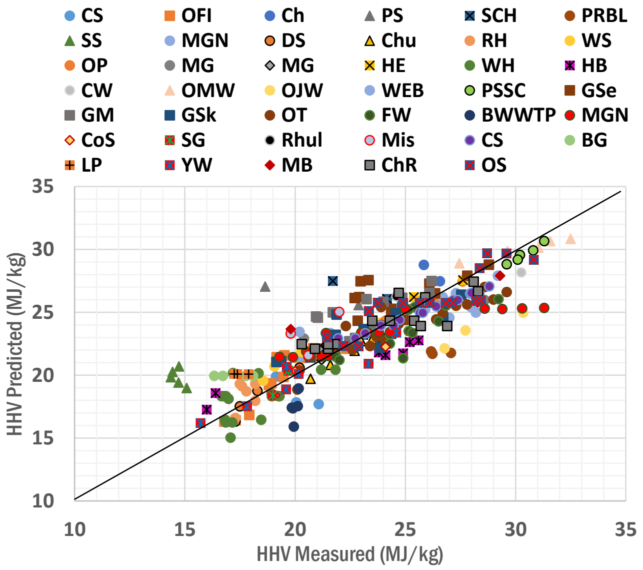


Fig 3. Comparison between measured and predicted values

$$\mathbf{HHV\ (op) = HHV_{FS} + \frac{0.51}{R + 0.65\ HHV_{FS} - 10.93} + \frac{T + 0.0003\ t\ T - 143.3}{HHV_{FS}}}$$

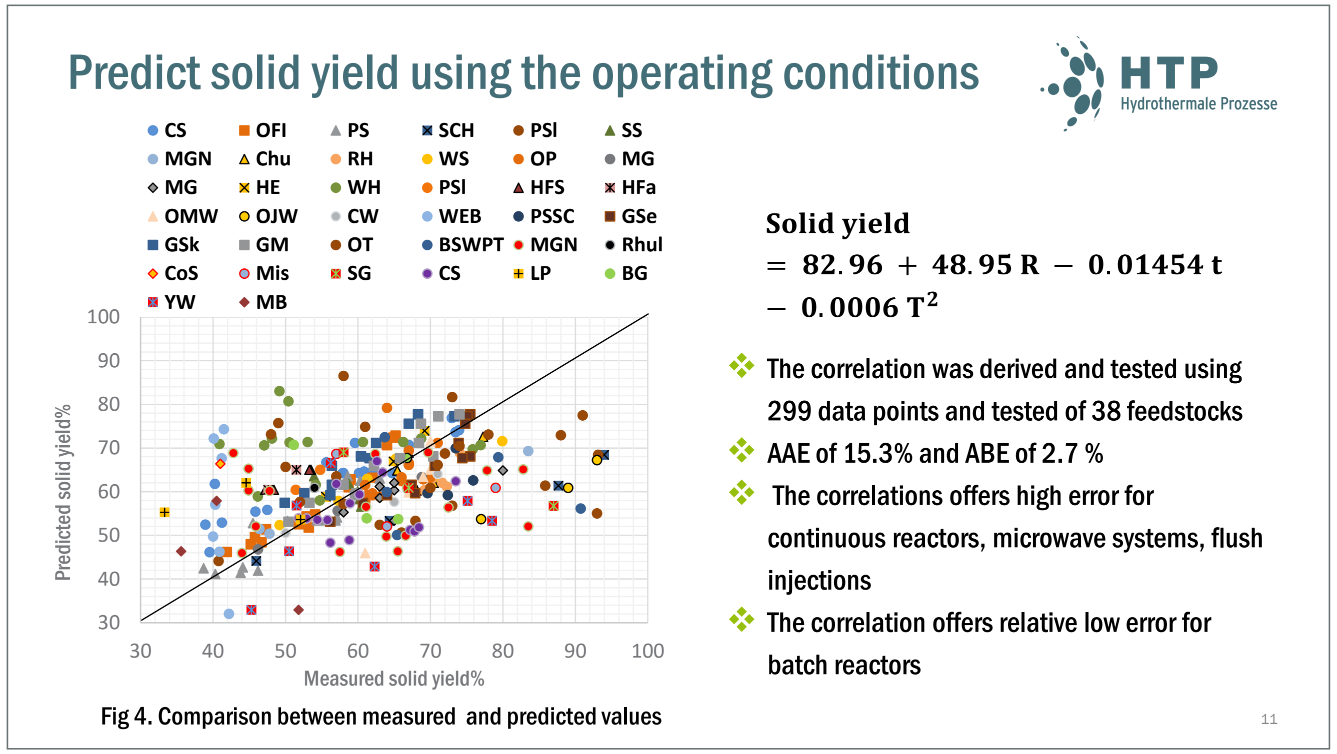
- The correlation was derived and tested using 315 data points and 41 feedstocks
- AAE of 6.5% and ABE of 1.2%
- Low error for batch reactors, but high error for microwave systems and flush injection of slurry

Sensitivity analysis of correlation

$$\mathbf{HHV\ (op) = HHV_{FS} + \frac{0.51}{R + 0.65\ HHV_{FS} - 10.93} + \frac{T + 0.0003\ t\ T - 143.3}{HHV_{FS}}}$$

Variable	Sensitivity	% Positive	Positive Magnitude	% Negative	% Negative Magnitude
HHV of feedstock	21.538	70%	18.639	30%	28.228
Temperature	0.50306	100%	0.50306	0%	0
Time	0.24094	100%	0.24094	0%	0
Biomass to water ratio	6.093	8%	30.307	92%	4.8448

- The HHV of feedstock, temperature and time have the positive effect on HHV
- The effect of HHV of feedstock is bigger than the rest of operating parameters
- The biomass to water ratio, has negative effect on HHV

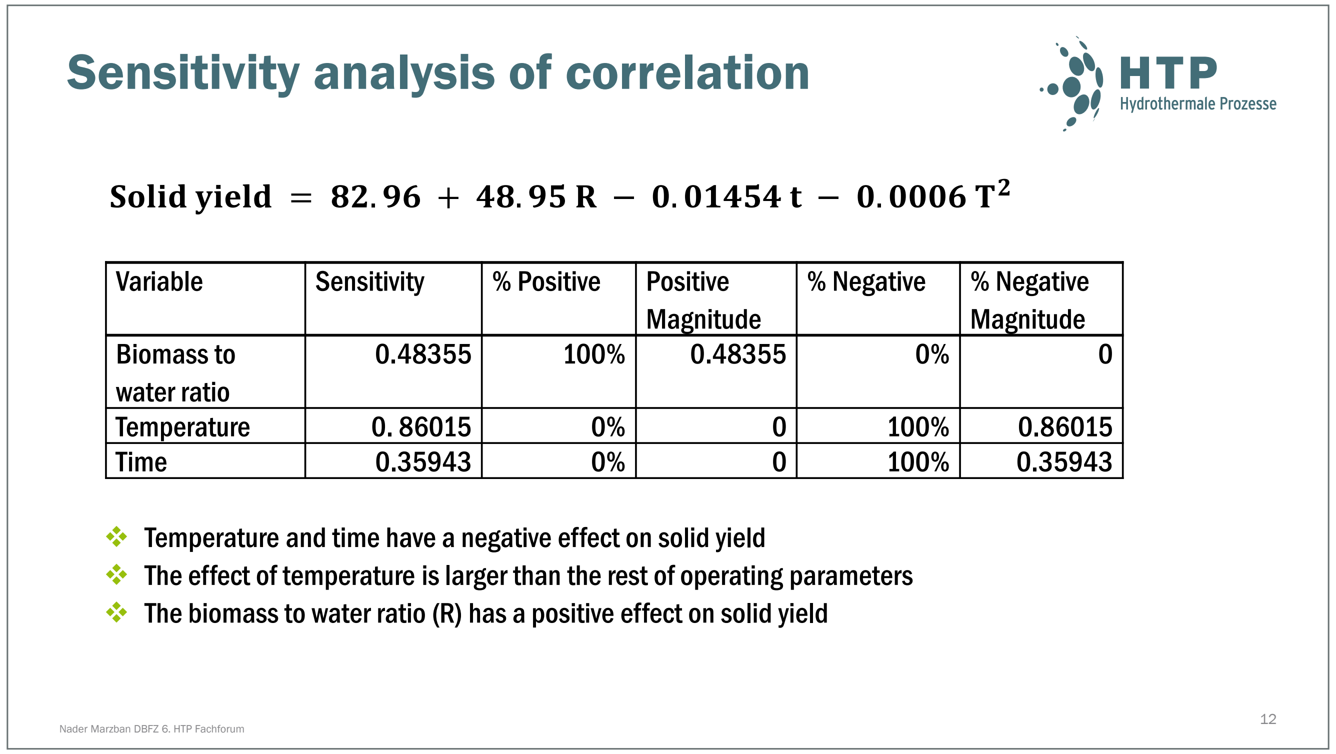


Predict solid yield using the operating conditions

Fig 4. Comparison between measured and predicted values

$$\text{Solid yield} = 82.96 + 48.95\,R - 0.01454\,t - 0.0006\,T^2$$

- The correlation was derived and tested using 299 data points and tested of 38 feedstocks
- AAE of 15.3% and ABE of 2.7 %
- The correlations offers high error for continuous reactors, microwave systems, flush injections
- The correlation offers relative low error for batch reactors



Sensitivity analysis of correlation

$$\text{Solid yield} = 82.96 + 48.95\,R - 0.01454\,t - 0.0006\,T^2$$

Variable	Sensitivity	% Positive	Positive Magnitude	% Negative	% Negative Magnitude
Biomass to water ratio	0.48355	100%	0.48355	0%	0
Temperature	0. 86015	0%	0	100%	0.86015
Time	0.35943	0%	0	100%	0.35943

- Temperature and time have a negative effect on solid yield
- The effect of temperature is larger than the rest of operating parameters
- The biomass to water ratio (R) has a positive effect on solid yield

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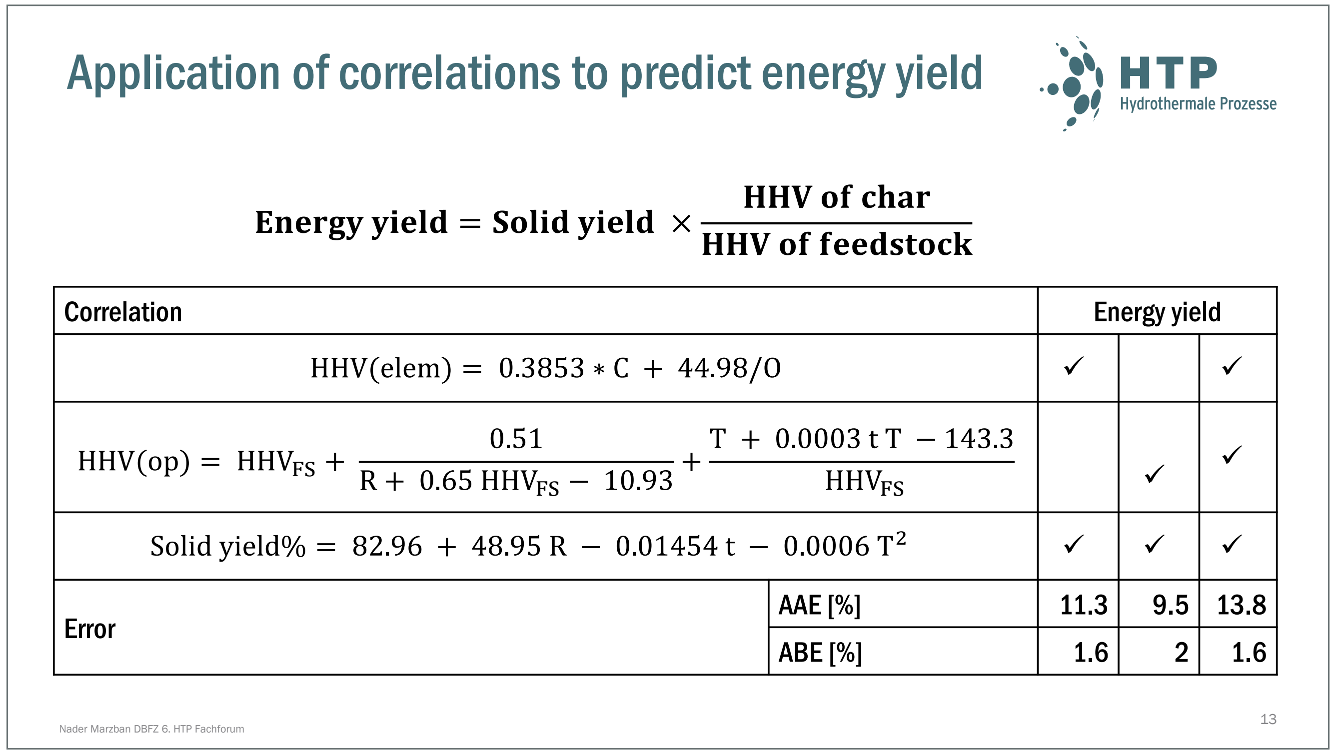
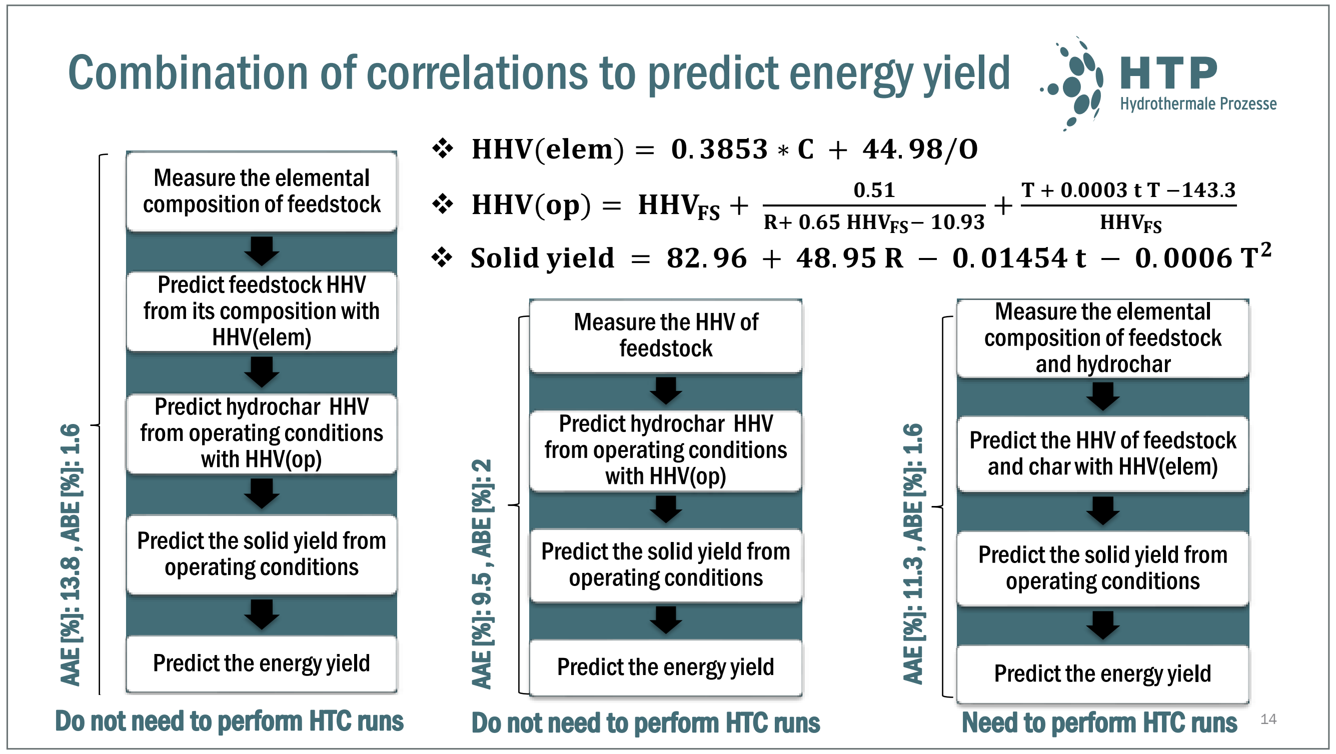


Application of correlations to predict energy yield

$$\text{Energy yield} = \text{Solid yield} \times \frac{\text{HHV of char}}{\text{HHV of feedstock}}$$

Correlation		Energy yield		
$HHV(elem) = 0.3853 * C + 44.98/O$		✓		✓
$HHV(op) = HHV_{FS} + \frac{0.51}{R + 0.65\,HHV_{FS} - 10.93} + \frac{T + 0.0003\,t\,T - 143.3}{HHV_{FS}}$			✓	✓
$\text{Solid yield\%} = 82.96 + 48.95\,R - 0.01454\,t - 0.0006\,T^2$		✓	✓	✓
Error	AAE [%]	11.3	9.5	13.8
	ABE [%]	1.6	2	1.6



Combination of correlations to predict energy yield

- $HHV(elem) = 0.3853 * C + 44.98/O$
- $HHV(op) = HHV_{FS} + \frac{0.51}{R + 0.65\,HHV_{FS} - 10.93} + \frac{T + 0.0003\,t\,T - 143.3}{HHV_{FS}}$
- $\text{Solid yield} = 82.96 + 48.95\,R - 0.01454\,t - 0.0006\,T^2$

Measure the elemental composition of feedstock
Predict feedstock HHV from its composition with HHV(elem)
Predict hydrochar HHV from operating conditions with HHV(op)
Predict the solid yield from operating conditions
Predict the energy yield

AAE [%]: 13.8 , ABE [%]: 1.6

Do not need to perform HTC runs

Measure the HHV of feedstock
Predict hydrochar HHV from operating conditions with HHV(op)
Predict the solid yield from operating conditions
Predict the energy yield

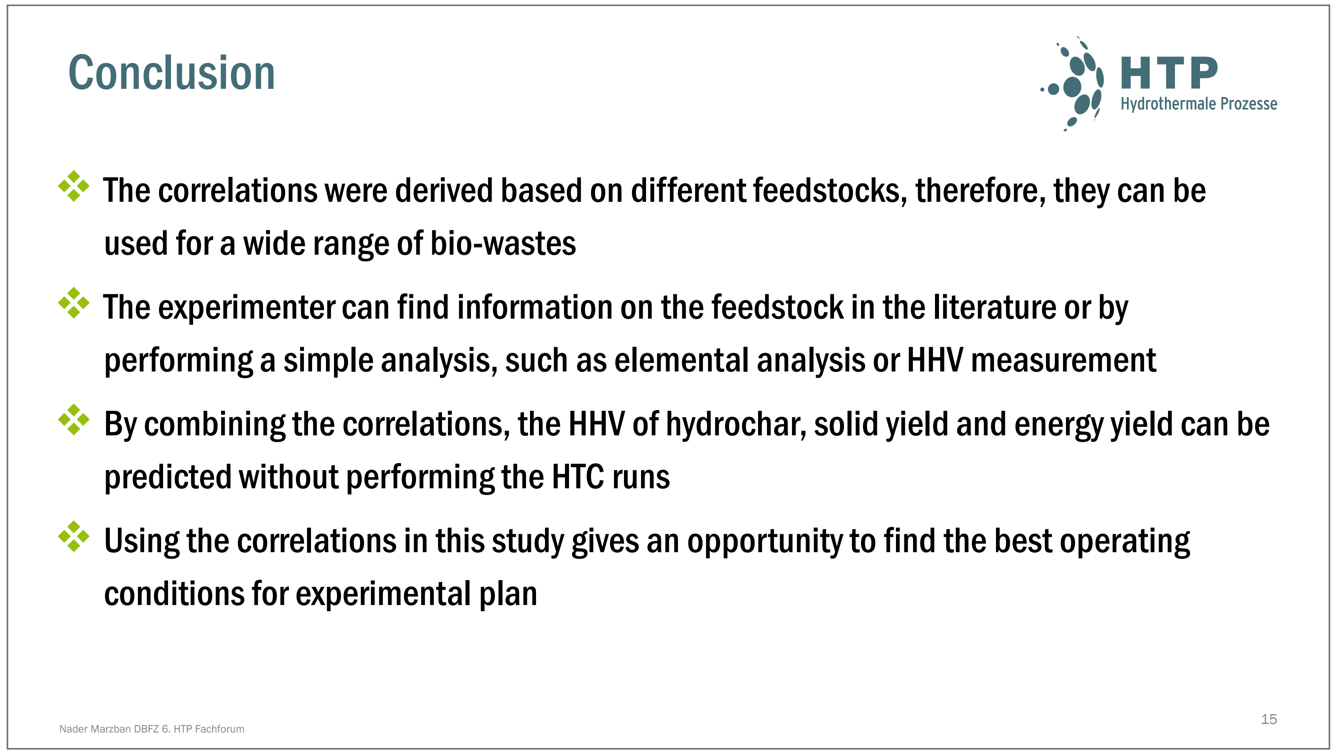
AAE [%]: 9.5 , ABE [%]: 2

Do not need to perform HTC runs

Measure the elemental composition of feedstock and hydrochar
Predict the HHV of feedstock and char with HHV(elem)
Predict the solid yield from operating conditions
Predict the energy yield

AAE [%]: 11.3 , ABE [%]: 1.6

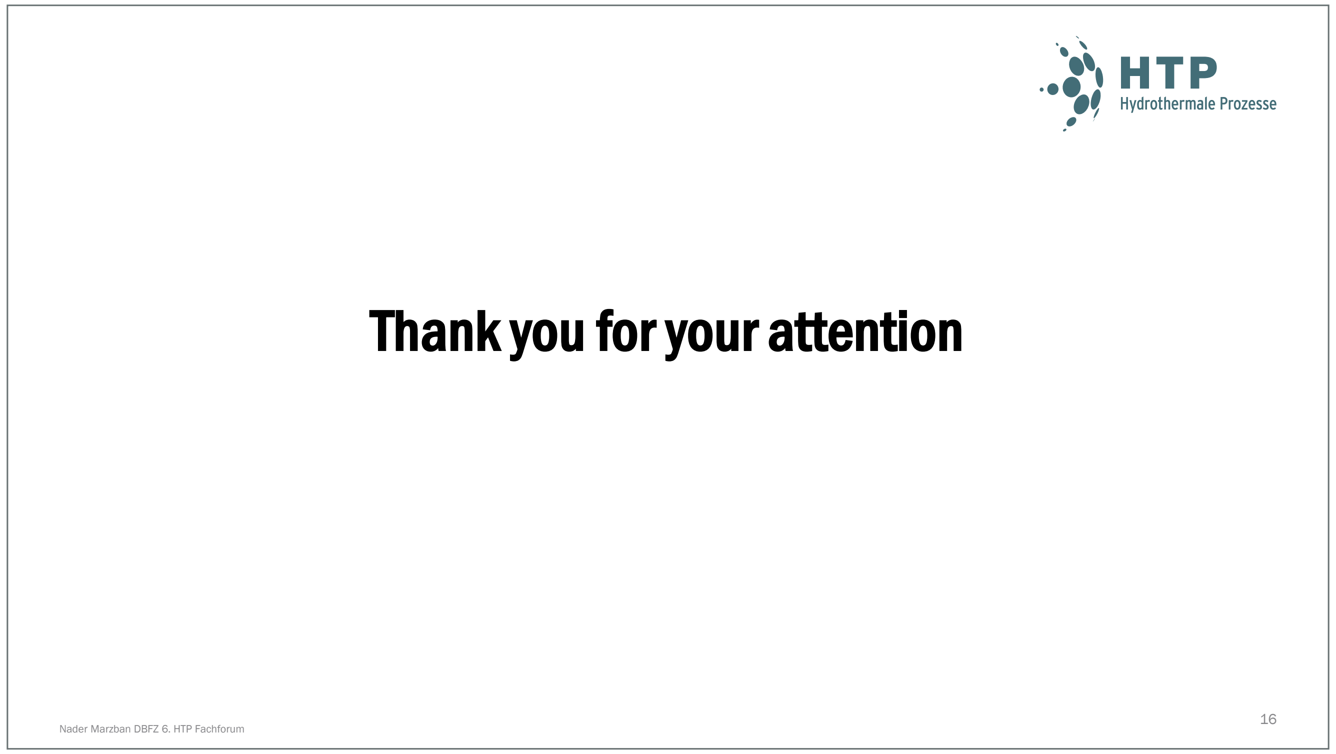
Need to perform HTC runs



Conclusion

HTP Hydrothermale Prozesse

- The correlations were derived based on different feedstocks, therefore, they can be used for a wide range of bio-wastes
- The experimenter can find information on the feedstock in the literature or by performing a simple analysis, such as elemental analysis or HHV measurement
- By combining the correlations, the HHV of hydrochar, solid yield and energy yield can be predicted without performing the HTC runs
- Using the correlations in this study gives an opportunity to find the best operating conditions for experimental plan



HTP Hydrothermale Prozesse

Thank you for your attention

6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

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Hydrothermale Carbonisierung von Klärschlamm – Ergebnisse einer szenariobasierten multi-kriteriellen Technologiebewertung

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Hydrothermalen Prozessen wird ein hohes Potential zur material- und energieeffizienten Verwertung wässriger Biomassen zugesprochen. Insbesondere die Verwertung von Klärschlamm bietet sich aufgrund aktueller rechtlicher Rahmenbedingungen an (u.a. Novellen der Klärschlamm- und Düngemittelverordnung), da etablierte Verwertungswege teils nicht mehr oder nur noch unter strengeren Auflagen möglich sind. Dieser Beitrag beschäftigt sich daher mit den techno-ökonomischen Potentialen der hydrothermalen Carbonisierung (HTC) von Klärschlamm im Vergleich zur klassischen thermischen Trocknung (Referenzfall) anhand eines fiktiven Fallbeispiels. Es werden drei Zukunftsszenarien einer industriellen Klärschlamm HTC und der Referenzfall mittels einer multi-kriteriellen Analyse vergleichend betrachtet. Anhand einer Sensitivitätsanalyse werden wichtige Parameter, wie beispielsweise Kosten pro behandelter Masseeinheit, auf deren Auswirkungen auf das Gesamtergebnis untersucht. Das Ergebnis zeigt, dass die Klärschlamm HTC nur unter spezifischen rechtlichen und technologischen Voraussetzungen konkurrenzfähig zum Referenzfall ist. Insbesondere die aktuell noch hohen Produktionskosten für das kohleähnliche Produkt aus der HTC sind ein wesentliches Hemmnis. Auch ist die rechtliche Unsicherheit aufgrund der aktuell noch geltenden „Abfalleigenschaft“ des Produkts wirkt hemmend für eine gezielte Vermarktung. Es ist daher empfehlenswert Kostenreduktions- und Vermarktungspotentiale künftig gezielt zu nutzen. Die Studie empfiehlt vor allem die Förderung systemintegrativer Konzepte und kosteneffizienter Lösungen für die Prozesswasserreinigung. Zudem ist es wesentlich, Kriterien bzw. eine Legaldefinition für das „Abfallende“ der Produkte aus der HTC festzulegen.

6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Welche Richtung sollen wir einschlagen?
Ergebnisse einer Bewertung szenario-basierter HTC Anwendungsfälle

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Helmholtz-Zentrum für Umweltforschung - UFZ

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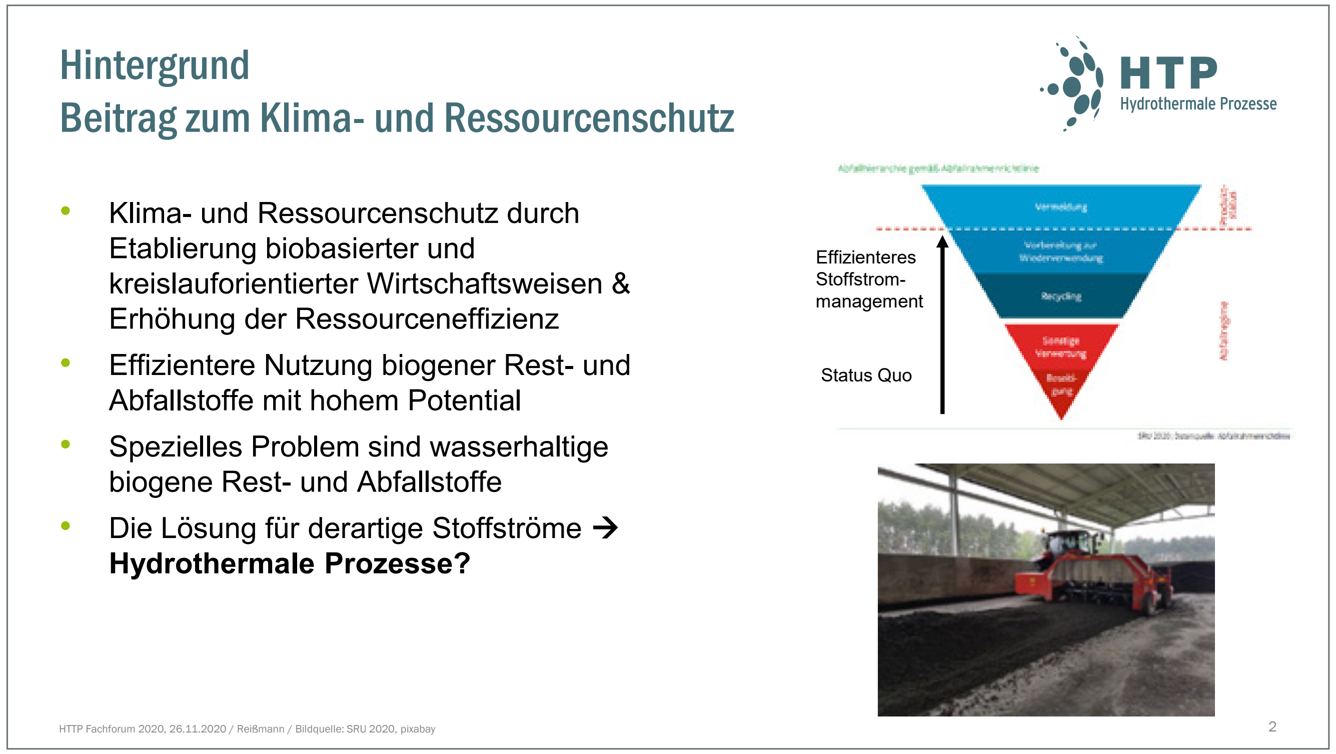

Hintergrund
Beitrag zum Klima- und Ressourcenschutz

- Klima- und Ressourcenschutz durch Etablierung biobasierter und kreislauforientierter Wirtschaftsweisen & Erhöhung der Ressourceneffizienz
- Effizientere Nutzung biogener Rest- und Abfallstoffe mit hohem Potential
- Spezielles Problem sind wasserhaltige biogene Rest- und Abfallstoffe
- Die Lösung für derartige Stoffströme → **Hydrothermale Prozesse?**

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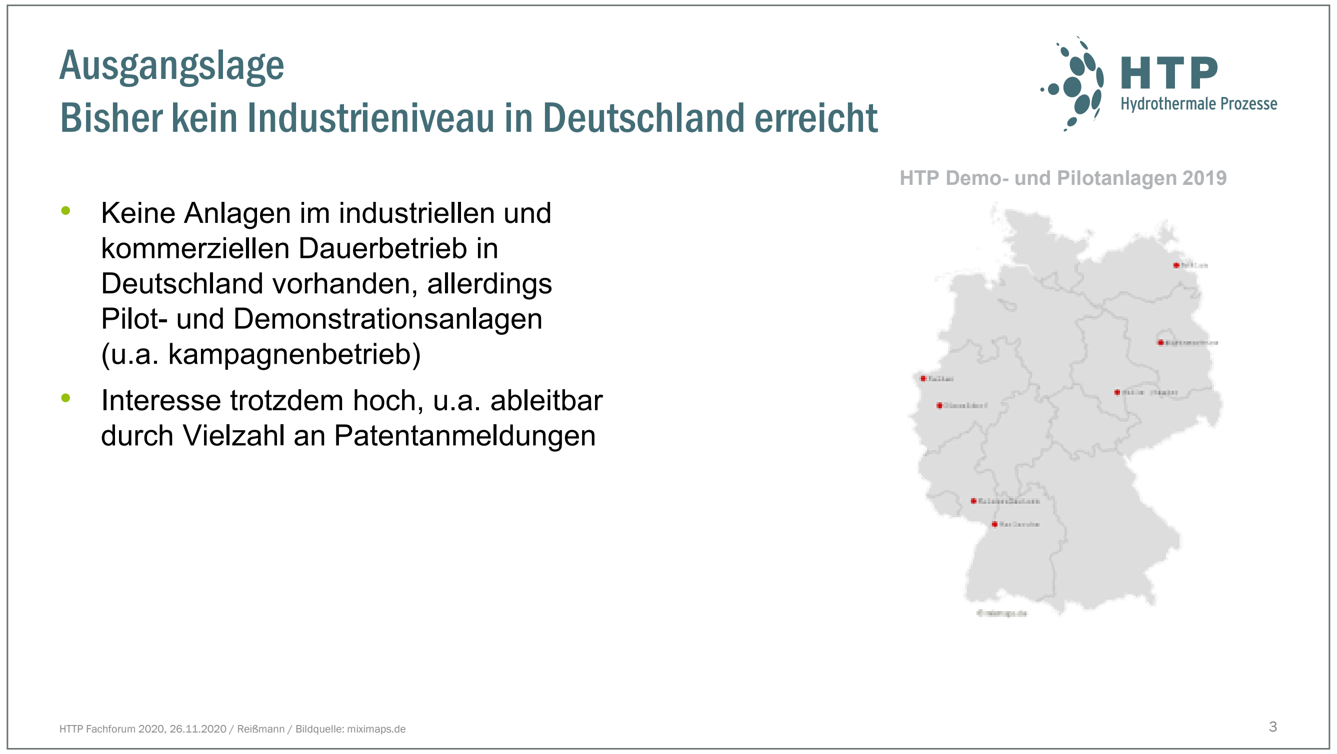

Ausgangslage
Bisher kein Industrieniveau in Deutschland erreicht

HTP Hydrothermale Prozesse

- Keine Anlagen im industriellen und kommerziellen Dauerbetrieb in Deutschland vorhanden, allerdings Pilot- und Demonstrationsanlagen (u.a. kampagnenbetrieb)
- Interesse trotzdem hoch, u.a. ableitbar durch Vielzahl an Patentanmeldungen

HTP Demo- und Pilotanlagen 2019

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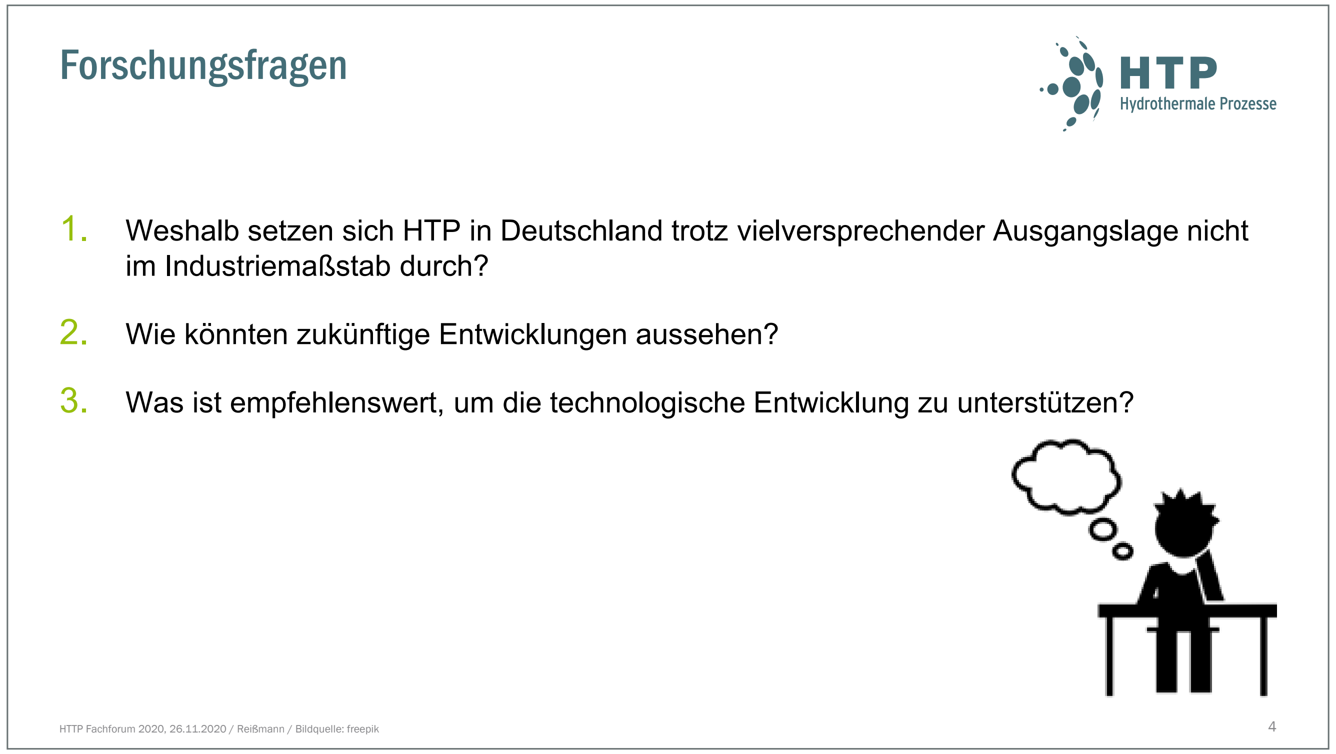

Forschungsfragen

HTP Hydrothermale Prozesse

1. Weshalb setzen sich HTP in Deutschland trotz vielversprechender Ausgangslage nicht im Industriemaßstab durch?
2. Wie könnten zukünftige Entwicklungen aussehen?
3. Was ist empfehlenswert, um die technologische Entwicklung zu unterstützen?

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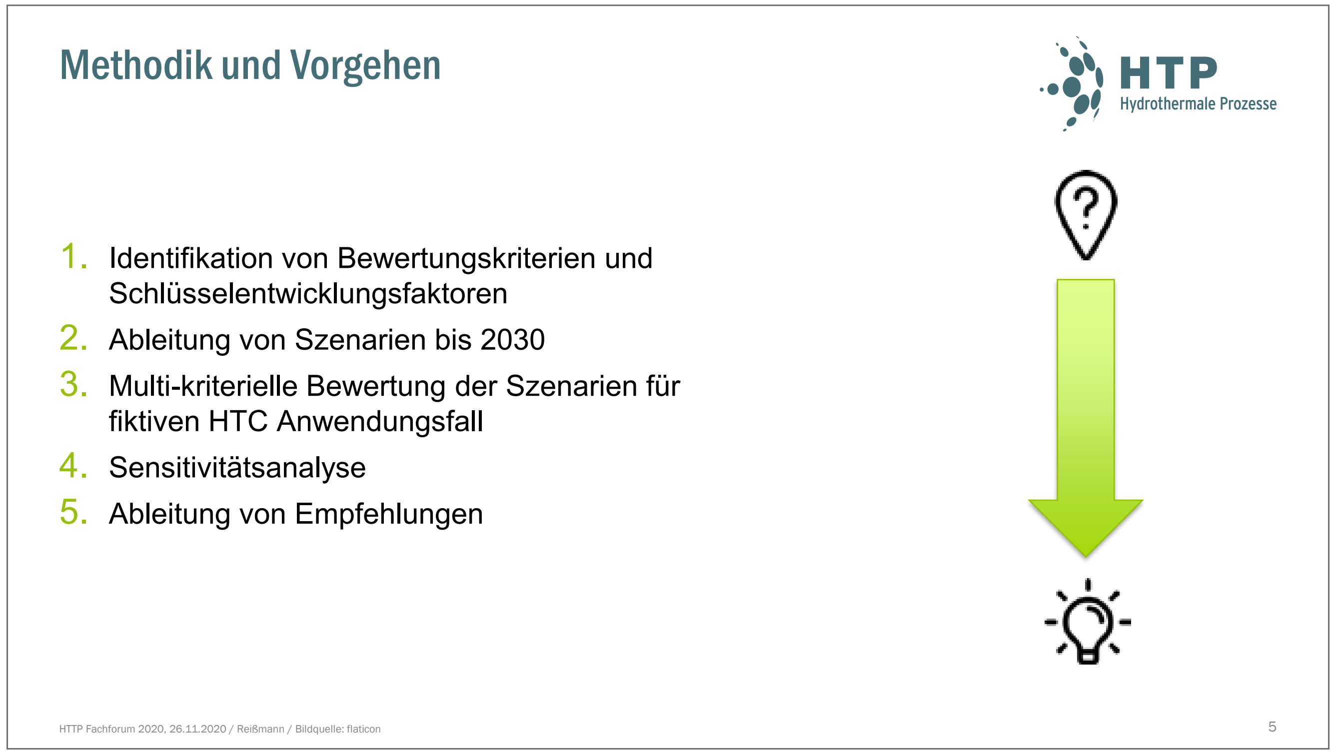

Methodik und Vorgehen

HTP Hydrothermale Prozesse

1. Identifikation von Bewertungskriterien und Schlüsselentwicklungsfaktoren
2. Ableitung von Szenarien bis 2030
3. Multi-kriterielle Bewertung der Szenarien für fiktiven HTC Anwendungsfall
4. Sensitivitätsanalyse
5. Ableitung von Empfehlungen

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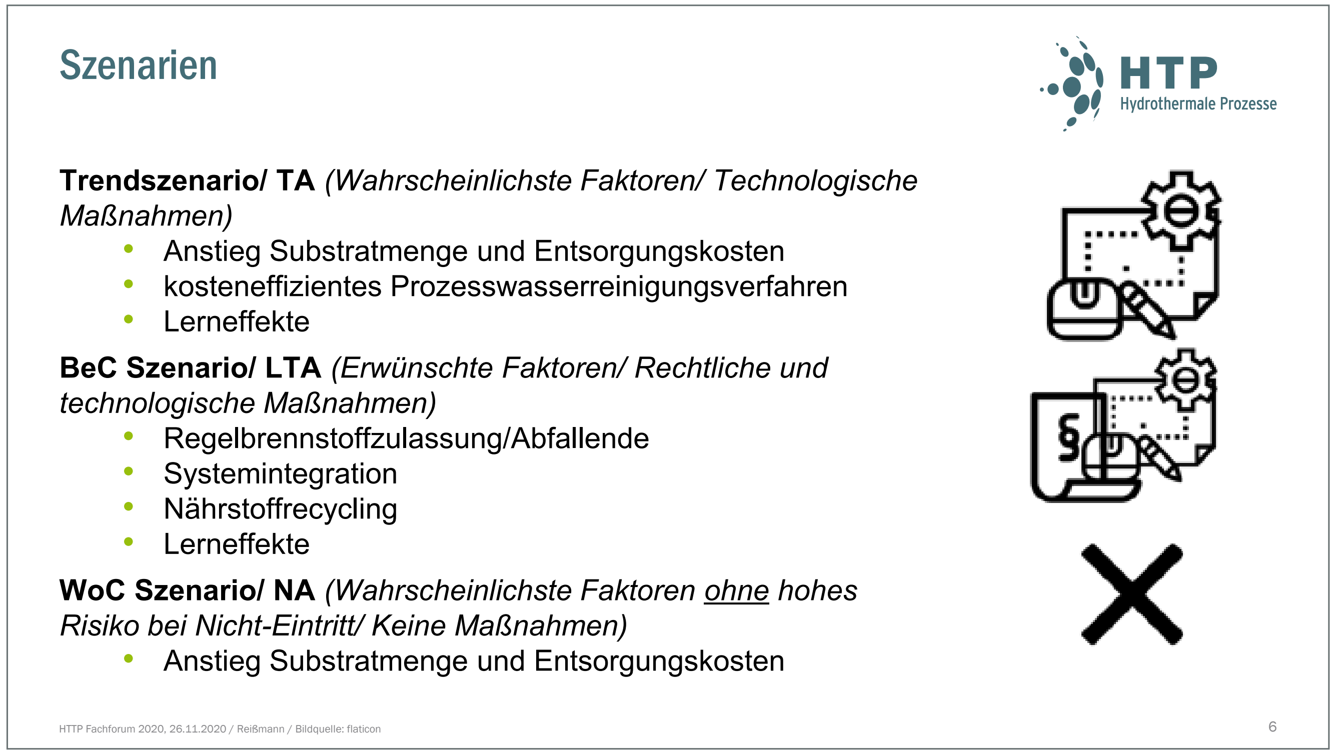

Szenarien

HTP Hydrothermale Prozesse

Trendszenario/ TA *(Wahrscheinlichste Faktoren/ Technologische Maßnahmen)*
- Anstieg Substratmenge und Entsorgungskosten
- kosteneffizientes Prozesswasserreinigungsverfahren
- Lerneffekte

BeC Szenario/ LTA *(Erwünschte Faktoren/ Rechtliche und technologische Maßnahmen)*
- Regelbrennstoffzulassung/Abfallende
- Systemintegration
- Nährstoffrecycling
- Lerneffekte

WoC Szenario/ NA *(Wahrscheinlichste Faktoren ohne hohes Risiko bei Nicht-Eintritt/ Keine Maßnahmen)*
- Anstieg Substratmenge und Entsorgungskosten

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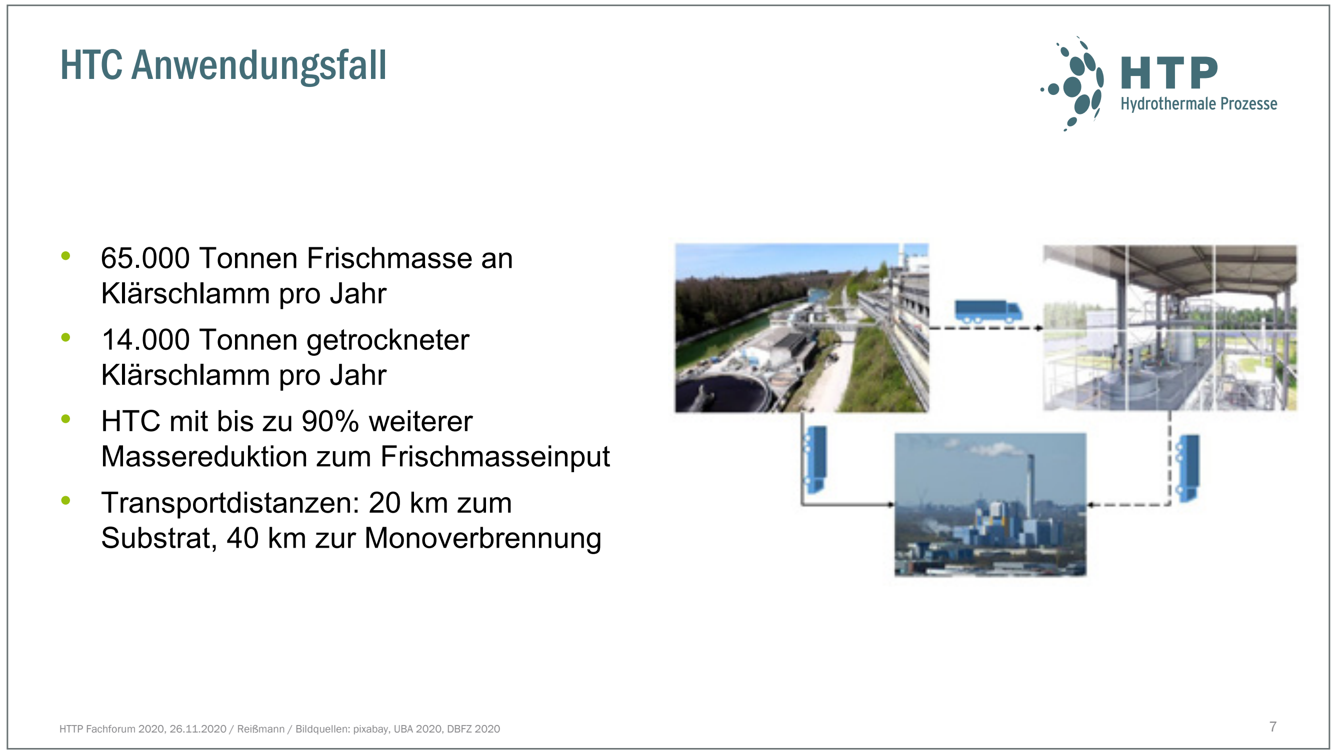

HTC Anwendungsfall

- 65.000 Tonnen Frischmasse an Klärschlamm pro Jahr
- 14.000 Tonnen getrockneter Klärschlamm pro Jahr
- HTC mit bis zu 90% weiterer Massereduktion zum Frischmasseinput
- Transportdistanzen: 20 km zum Substrat, 40 km zur Monoverbrennung

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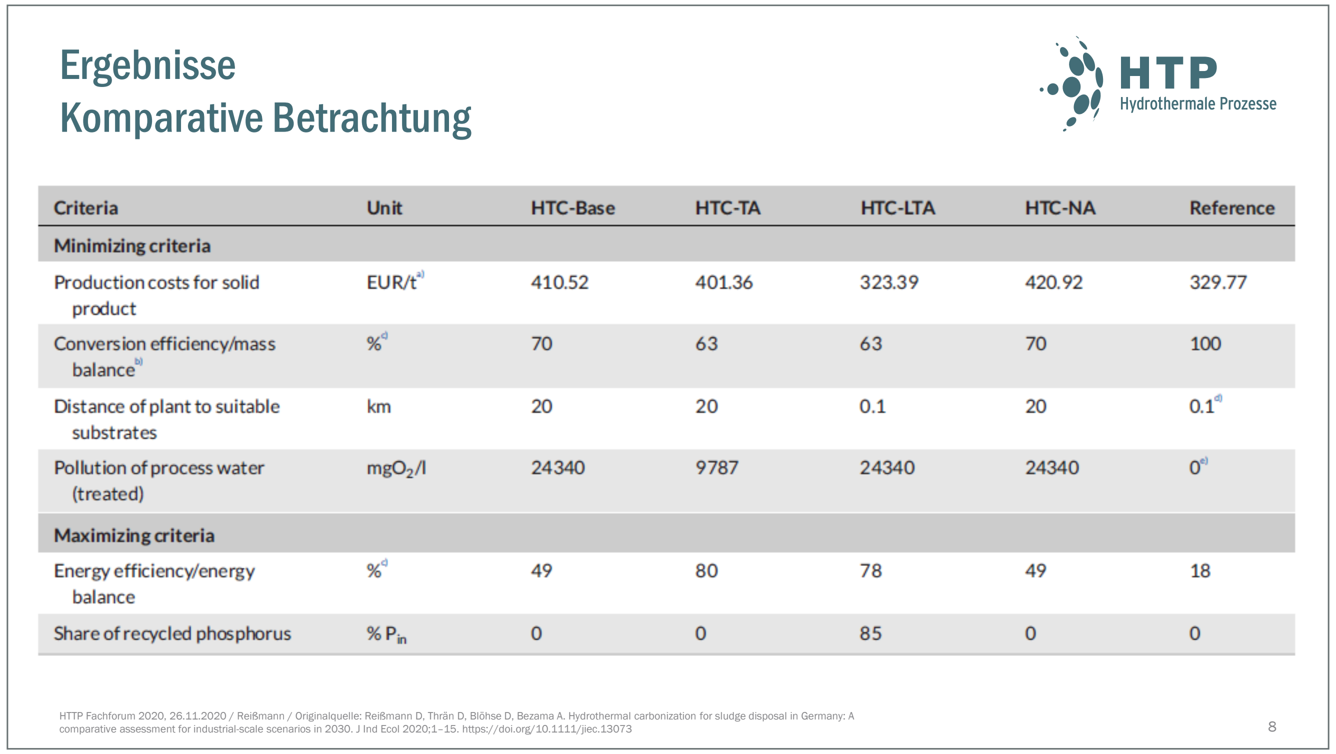
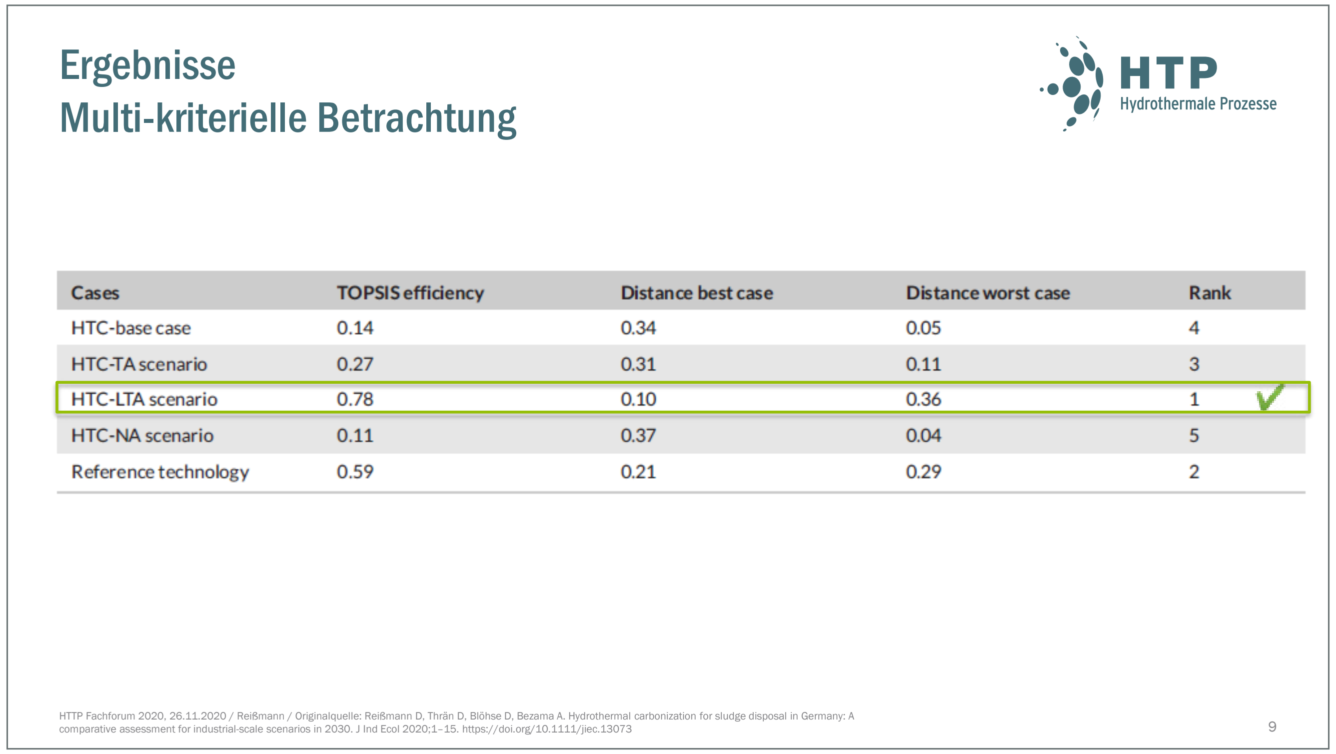


Ergebnisse
Komparative Betrachtung

Criteria	Unit	HTC-Base	HTC-TA	HTC-LTA	HTC-NA	Reference
Minimizing criteria						
Production costs for solid product	EUR/t[a)]	410.52	401.36	323.39	420.92	329.77
Conversion efficiency/mass balance[b)]	%[c)]	70	63	63	70	100
Distance of plant to suitable substrates	km	20	20	0.1	20	0.1[d)]
Pollution of process water (treated)	mgO_2/l	24340	9787	24340	24340	0[e)]
Maximizing criteria						
Energy efficiency/energy balance	%[c)]	49	80	78	49	18
Share of recycled phosphorus	% P_{in}	0	0	85	0	0

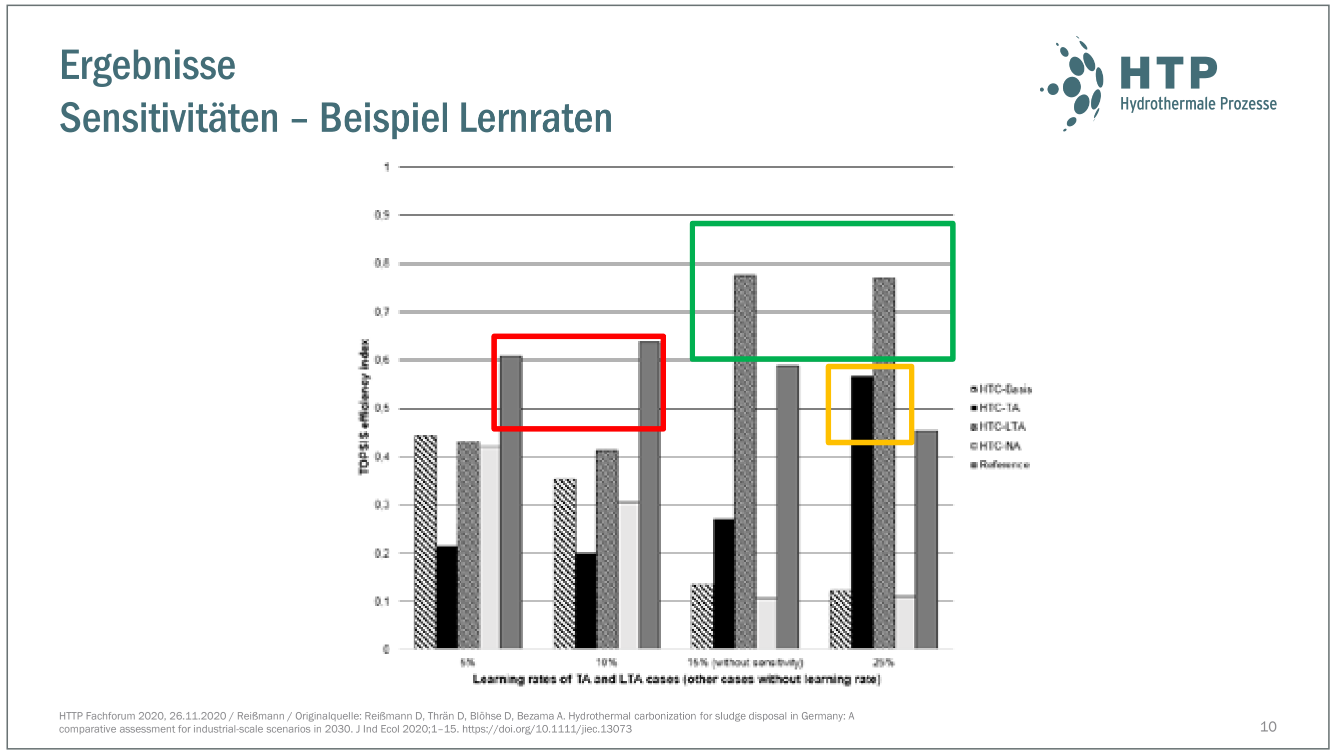
HTTP Fachforum 2020, 26.11.2020 / Reißmann / Originalquelle: Reißmann D, Thrän D, Blöhse D, Bezama A. Hydrothermal carbonization for sludge disposal in Germany: A comparative assessment for industrial-scale scenarios in 2030. J Ind Ecol 2020;1–15. https://doi.org/10.1111/jiec.13073



Ergebnisse
Multi-kriterielle Betrachtung

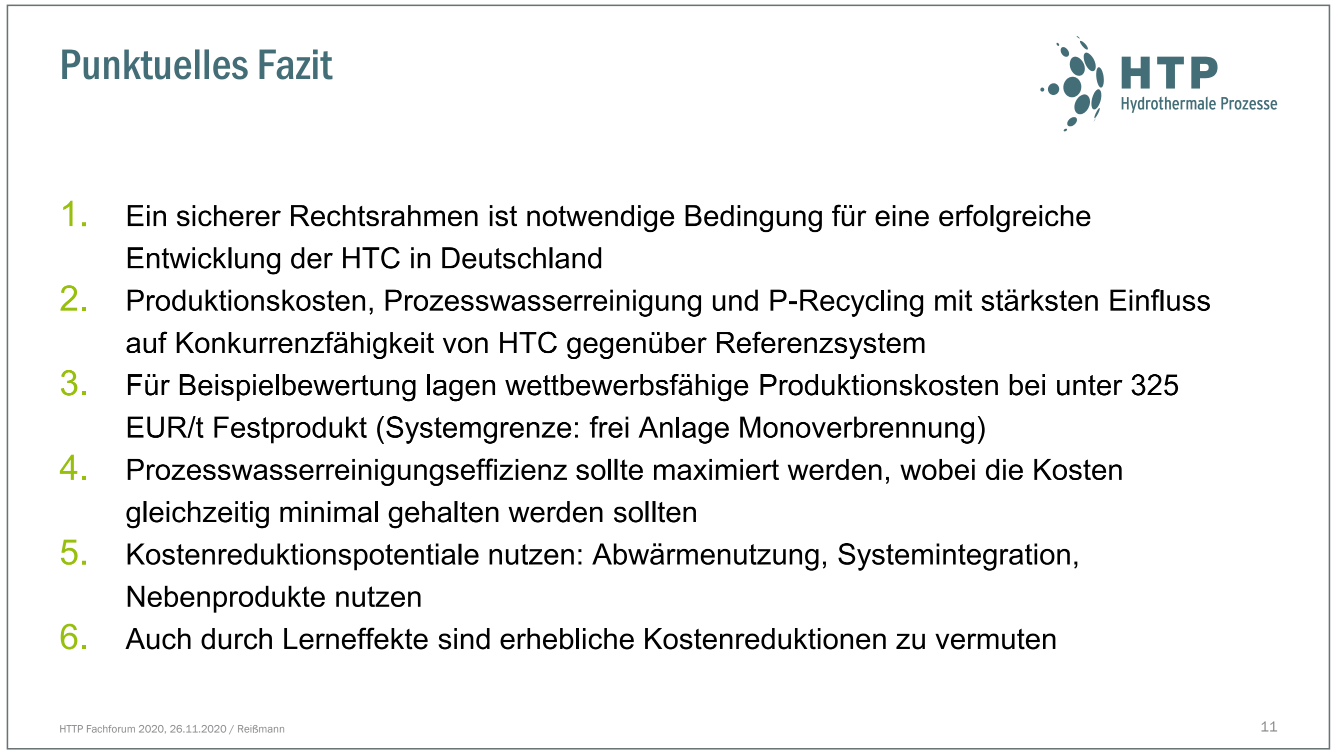
Cases	TOPSIS efficiency	Distance best case	Distance worst case	Rank
HTC-base case	0.14	0.34	0.05	4
HTC-TA scenario	0.27	0.31	0.11	3
HTC-LTA scenario	0.78	0.10	0.36	1 ✓
HTC-NA scenario	0.11	0.37	0.04	5
Reference technology	0.59	0.21	0.29	2

HTTP Fachforum 2020, 26.11.2020 / Reißmann / Originalquelle: Reißmann D, Thrän D, Blöhse D, Bezama A. Hydrothermal carbonization for sludge disposal in Germany: A comparative assessment for industrial-scale scenarios in 2030. J Ind Ecol 2020;1–15. https://doi.org/10.1111/jiec.13073



Ergebnisse
Sensitivitäten – Beispiel Lernraten

HTTP Fachforum 2020, 26.11.2020 / Reißmann / Originalquelle: Reißmann D, Thrän D, Blöhse D, Bezama A. Hydrothermal carbonization for sludge disposal in Germany: A comparative assessment for industrial-scale scenarios in 2030. J Ind Ecol 2020;1–15. https://doi.org/10.1111/jiec.13073



Punktuelles Fazit

HTP Hydrothermale Prozesse

1. Ein sicherer Rechtsrahmen ist notwendige Bedingung für eine erfolgreiche Entwicklung der HTC in Deutschland
2. Produktionskosten, Prozesswasserreinigung und P-Recycling mit stärksten Einfluss auf Konkurrenzfähigkeit von HTC gegenüber Referenzsystem
3. Für Beispielbewertung lagen wettbewerbsfähige Produktionskosten bei unter 325 EUR/t Festprodukt (Systemgrenze: frei Anlage Monoverbrennung)
4. Prozesswasserreinigungseffizienz sollte maximiert werden, wobei die Kosten gleichzeitig minimal gehalten werden sollten
5. Kostenreduktionspotentiale nutzen: Abwärmenutzung, Systemintegration, Nebenprodukte nutzen
6. Auch durch Lerneffekte sind erhebliche Kostenreduktionen zu vermuten

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6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

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Zur Lektüre:
Reißmann D, Thrän D, Blöhse D, Bezama A. Hydrothermal carbonization for sludge disposal in Germany: A comparative assessment for industrial-scale scenarios in 2030. J Ind Ecol 2020;1–15. https://doi.org/10.1111/jiec.13073 (Open Access)

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Dr. Geert Haarlemmer, Commissariat à l'Energie Atomique et aux Energies Alternatives

Predicting the fate CO_2-H_2S in supercritical water gasification of black liquor

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The Pulp&Fuel (http://pulpandfuel.eu/) project addresses the thermochemical conversion of industrial wastes produced at a pulp and paper mill into biofuels. We intend to make a significant contribution to the development of biofuels by taking advantage of the synergy between dry and supercritical water gasification. The project has chosen to demonstrate its applicability to the pulp industrythat has both dry and wet wastes available. The project works on bark for entrained flow and fixed bed gasification as well as black liquor in supercritical water gasification.

The aim to improve gasification performance for efficient downstream synthesis of motor fuel raw materials through dry gasification experiments for dry resource as bark (with fixed bed and entrained flow reactors), and supercritical water gasification for wet resource as black liquor. There will also be a focus on the fuel synthesis (gas cleaning technologies, catalysts, and scale-up). The process will be extrapolated to an industrial demonstration plant (energy integration, process integration in pulp mill, equipment upscaling). The project will show how liquids fuels can be produced on a pulp mill without negatively affecting traditional operations. This will be achieved by detailed process simulation and mass and energy integration.

Two different black liquors are considered in this project, Kraft and soda cooking black liquor. The supercritical water gasification of black liquor produces hydrogen and methane and, in the case of Kraft black liquor, also some hydrogen sulphide a very toxic gas. The challenge is to recover the sulphur after gasification. There are several issues to this. An important issue for the pulp mill is to conserve as much as sulphur as possible in the aqueous phase. It is also possible to recover the sulphur from the gas to reinject it into the process cycle, but this is more complex. The mixture carbon dioxide-hydrogen sulphide, present in the gas and the aqueous phase and in the presence of a strong base is a complex system that allows a certain freedom to be optimised.

In this presentation we will show how this system was simulated and optimised in Python using Cantera and Chempy. The model integrates the supercritical water conversion of the organic matter as well as the acid base reactions. This optimisation will be the basis of further design of the supercritical gasification unit.

This project has started in October 2018 (4 years project) and involves 10 partners: CEA, SINTEF, RISE ETC, EPFL, IVL, GRENOBLE INP, SOFRESID, TOPINDUSTRIE, FIBRE EXCELLENCE and ABSISKEY.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818011.


6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Predicting the fate CO_2-H_2S in supercritical water gasification of black liquor

Geert Haarlemmer, Giles Ratel, Guillaume Boissonnet, Hary Demey-Cedeno, Victor Vastra
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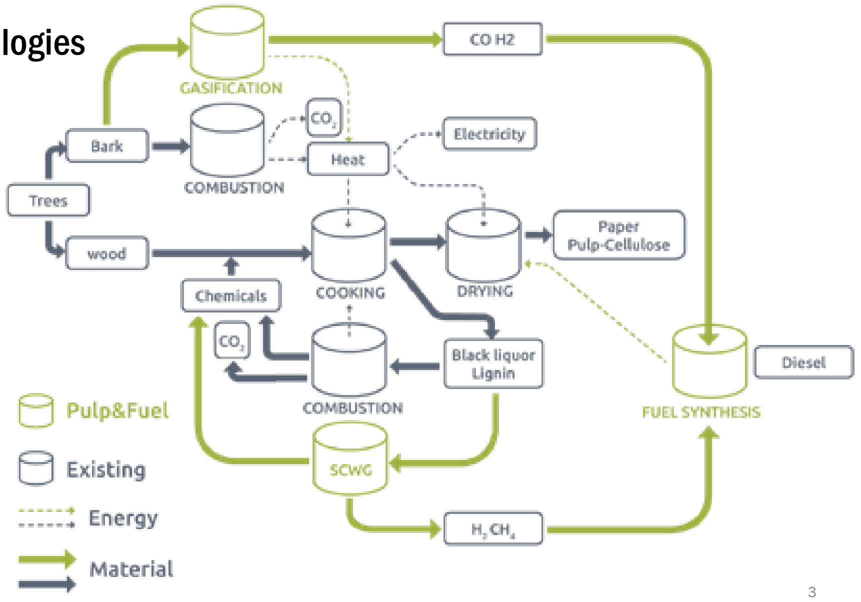
EU project Pulp&Fuel

Pulp Industry
- RES21 - Grant agreement No. 818011
- 435 man months, budget 4.9 M€
- 4 countries (F, N, S, CH)
- 10 Partners
- Coordinator CEA (G. Haarlemmer)
- http://pulpandfuel.eu/

EU project Pulp&Fuel - Concept

Integrate gasification technologies in the pulp industry



Kraft Black Liquor

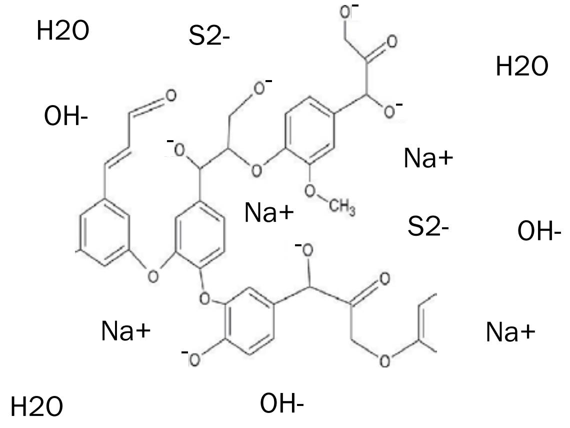
Organics = 8 %

Carbon = 60 g/L, 5 mol/L

Sodium = 1.7 mol/L

Sulphur = 0.3 mol/L

pH = 13.5



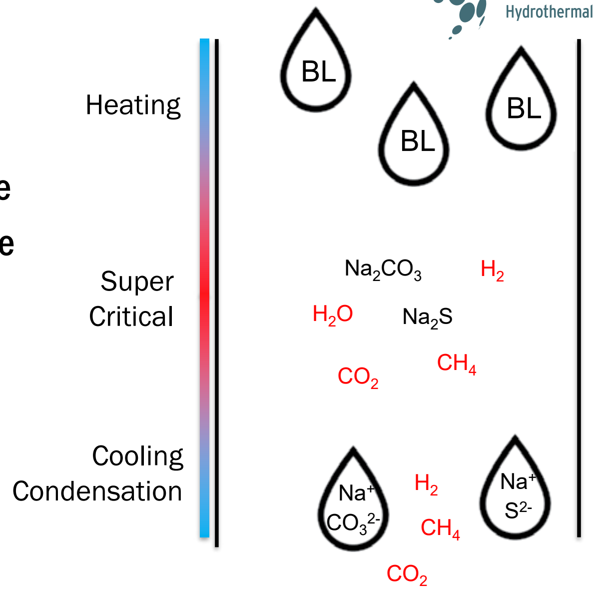
Expected behaviour

Conversion

- Decarbonation of the aqueous phase
- Cooking chemicals in aqueous phase

Products

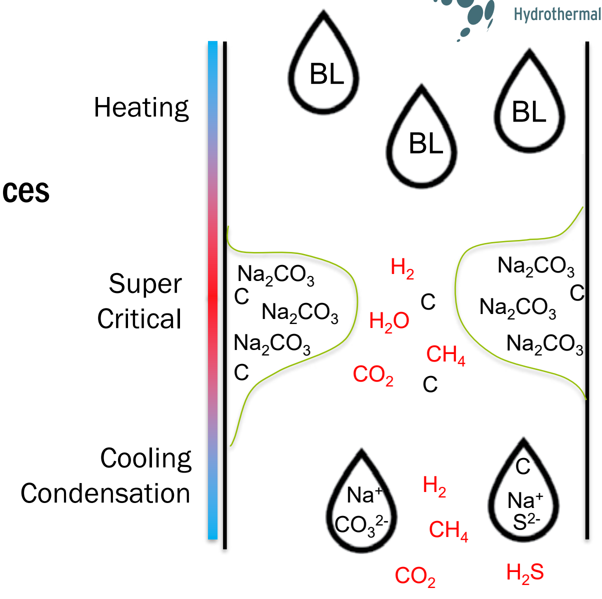
- H_2, CH_4, CO_2, H_2S
- Na_2CO_3, Na_2S

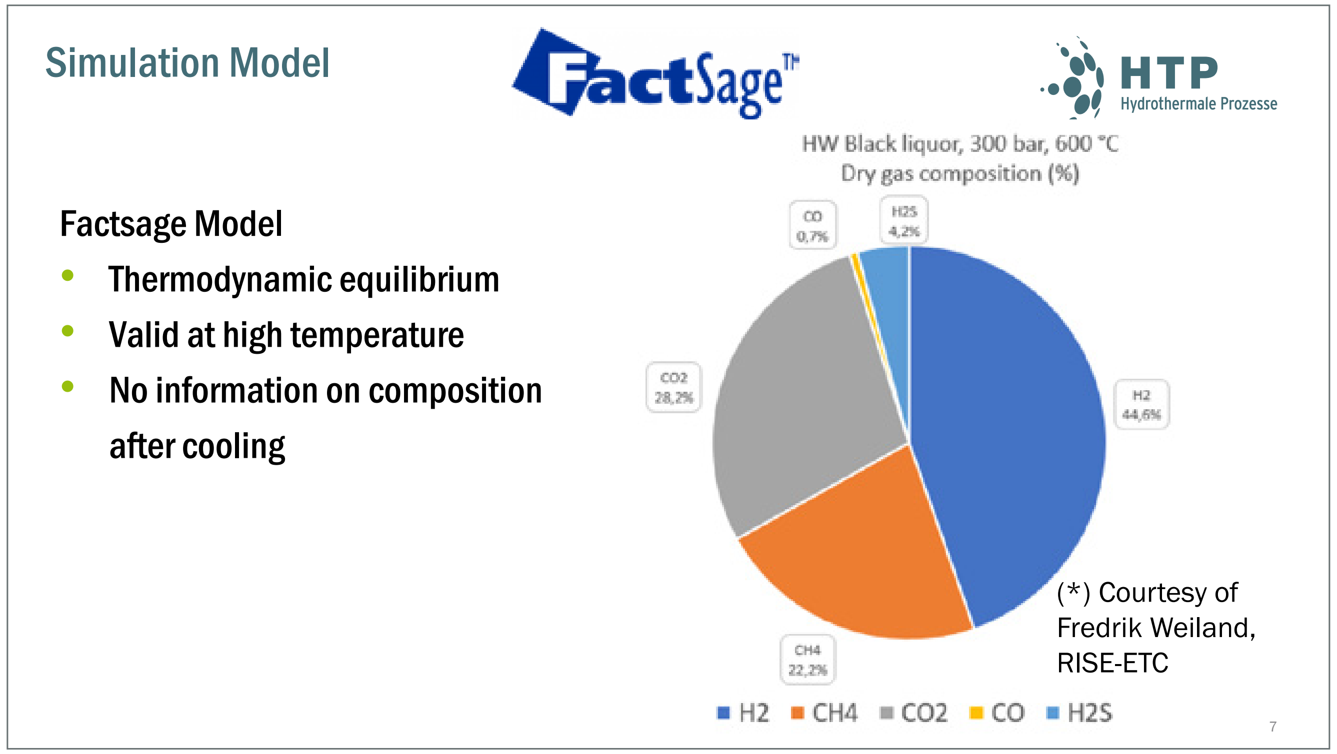


Difficulties in the experimentation

Reality

- Difficulties establishing mass balances
- Plugging
- Carbon conversion



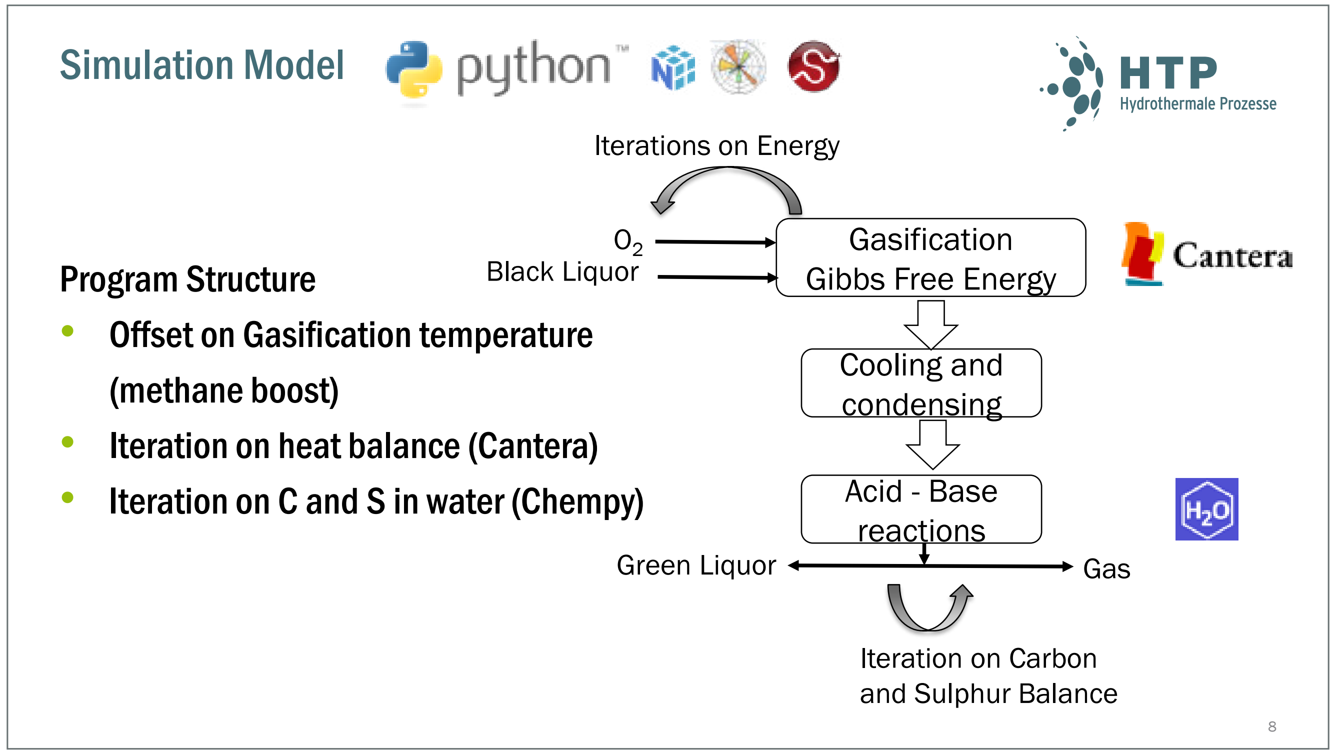


Simulation Model

Factsage Model

- Thermodynamic equilibrium
- Valid at high temperature
- No information on composition after cooling

(*) Courtesy of Fredrik Weiland, RISE-ETC



Simulation Model

Program Structure

- Offset on Gasification temperature (methane boost)
- Iteration on heat balance (Cantera)
- Iteration on C and S in water (Chempy)

Iterations on Energy

O_2

Black Liquor

Gasification Gibbs Free Energy

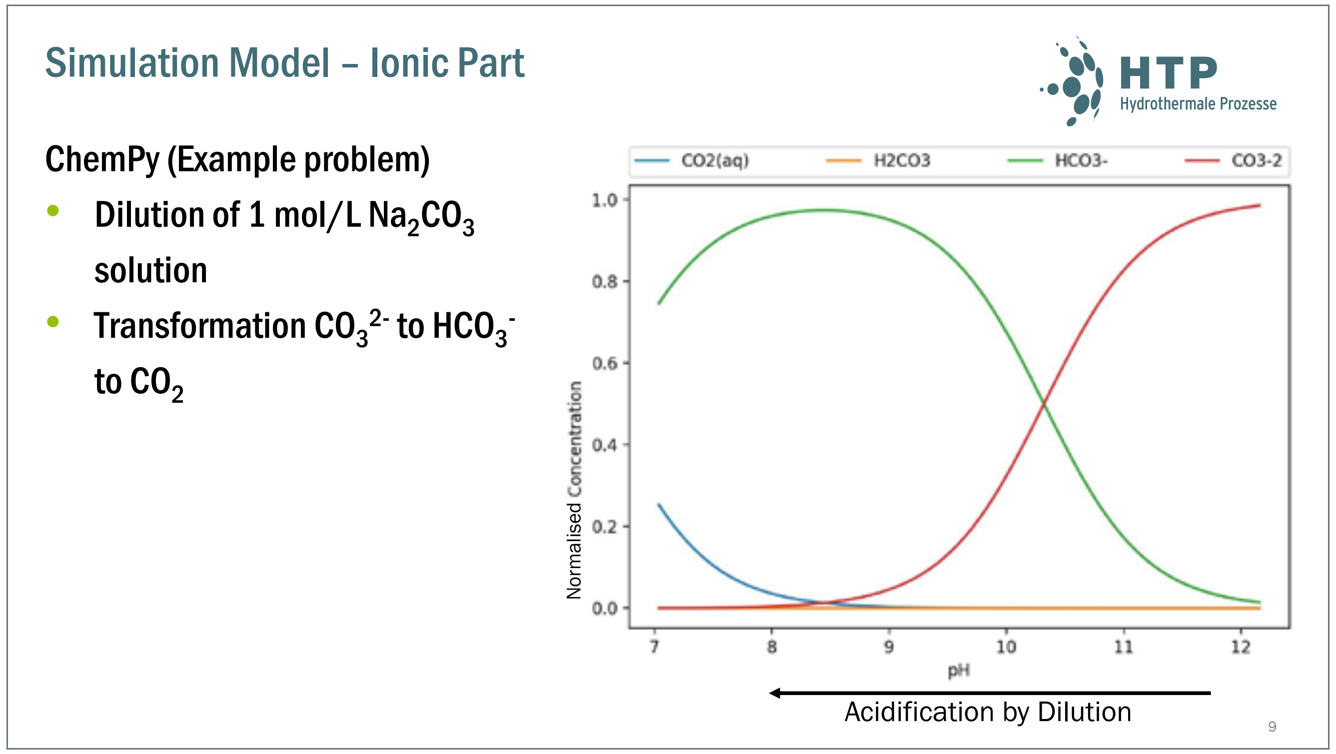
Cooling and condensing

Acid - Base reactions

Green Liquor

Gas

Iteration on Carbon and Sulphur Balance

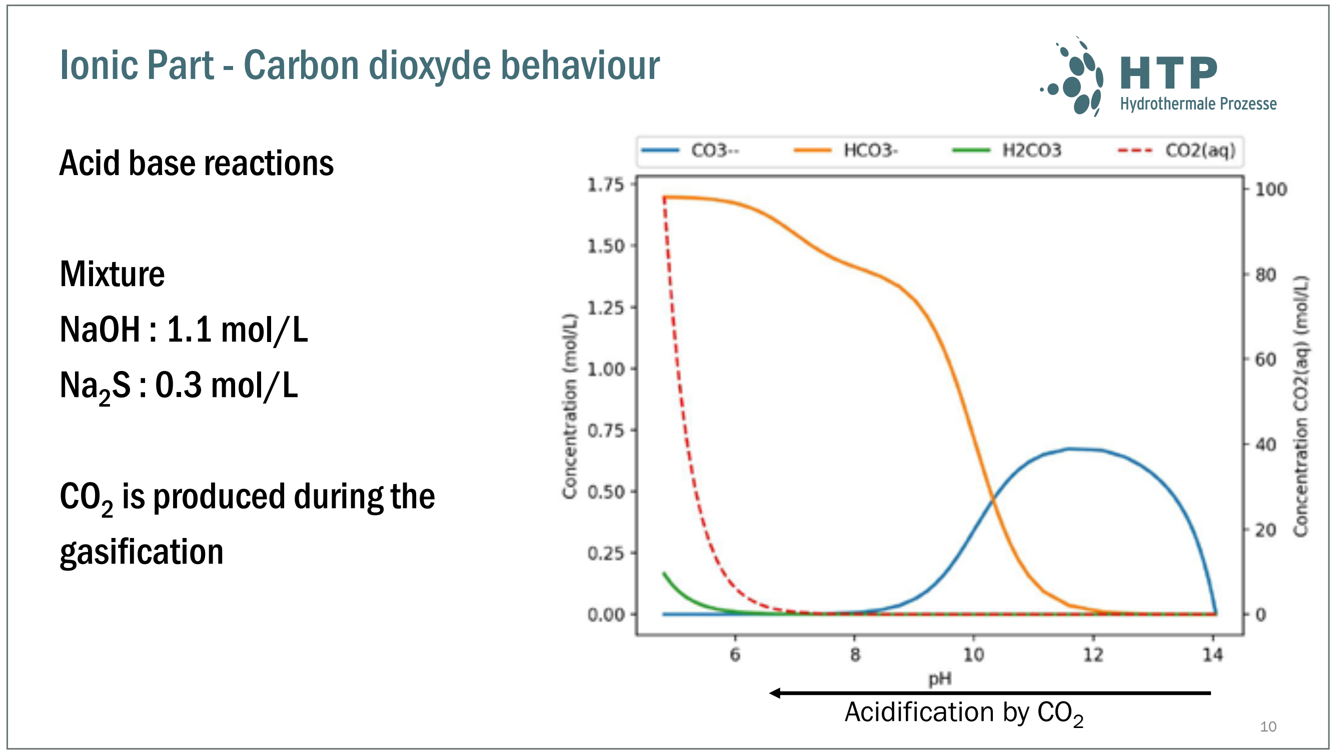


Simulation Model – Ionic Part

ChemPy (Example problem)

- Dilution of 1 mol/L Na_2CO_3 solution
- Transformation CO_3^{2-} to HCO_3^- to CO_2

Acidification by Dilution



Ionic Part - Carbon dioxyde behaviour

Acid base reactions

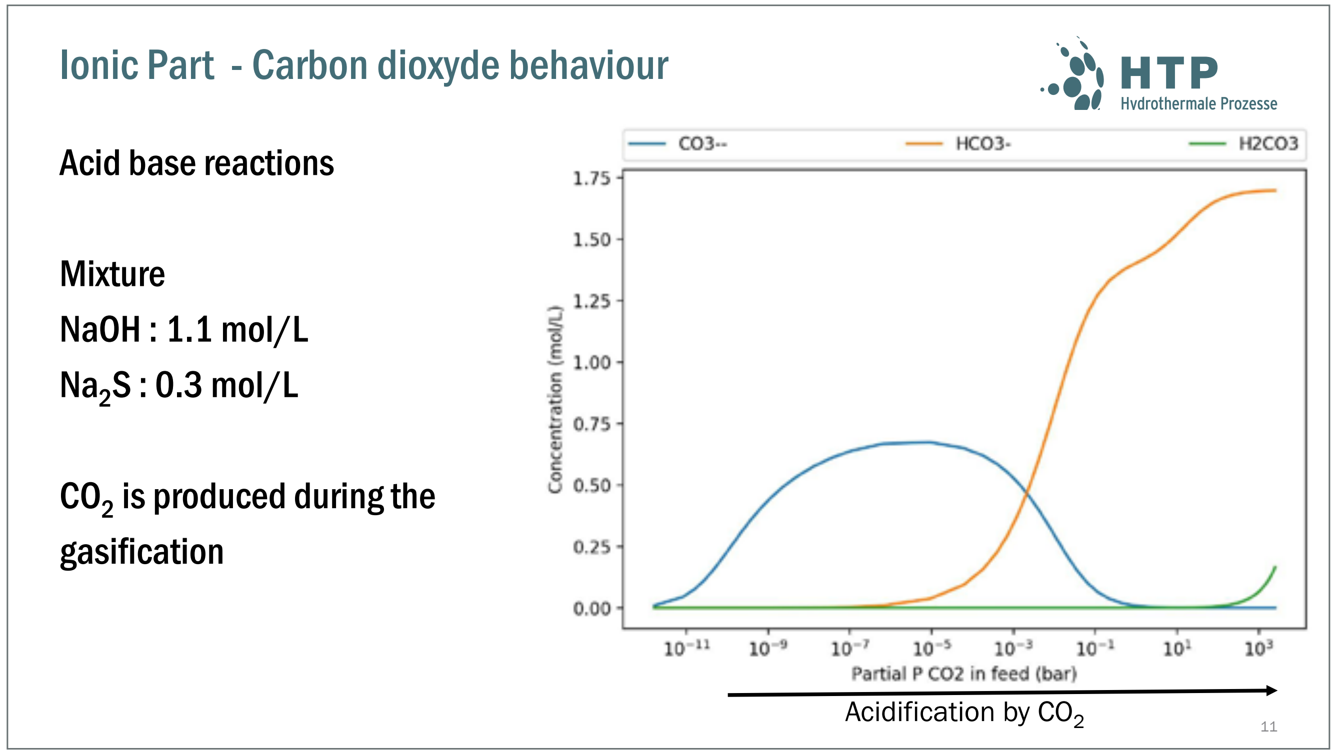
Mixture

NaOH : 1.1 mol/L

Na_2S : 0.3 mol/L

CO_2 is produced during the gasification

Acidification by CO_2

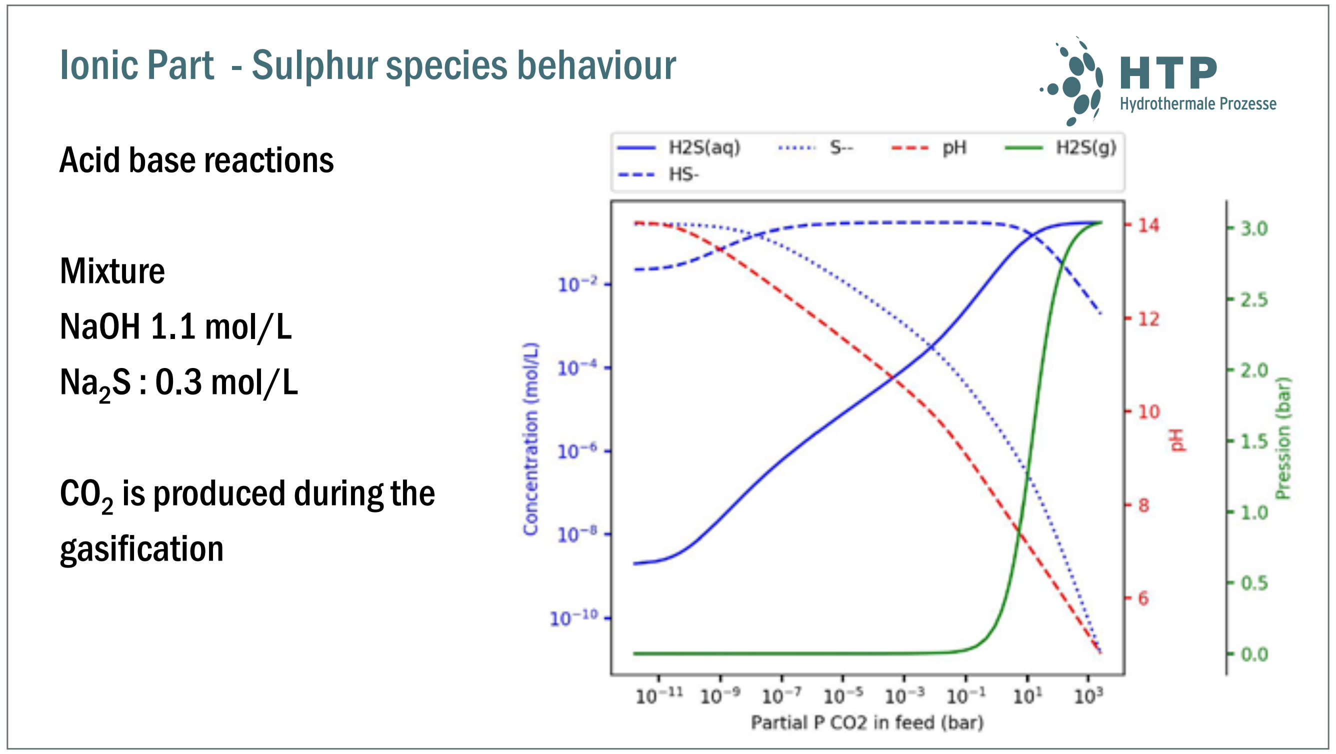


Ionic Part - Carbon dioxyde behaviour

Acid base reactions

Mixture
NaOH : 1.1 mol/L
Na_2S : 0.3 mol/L

CO_2 is produced during the gasification

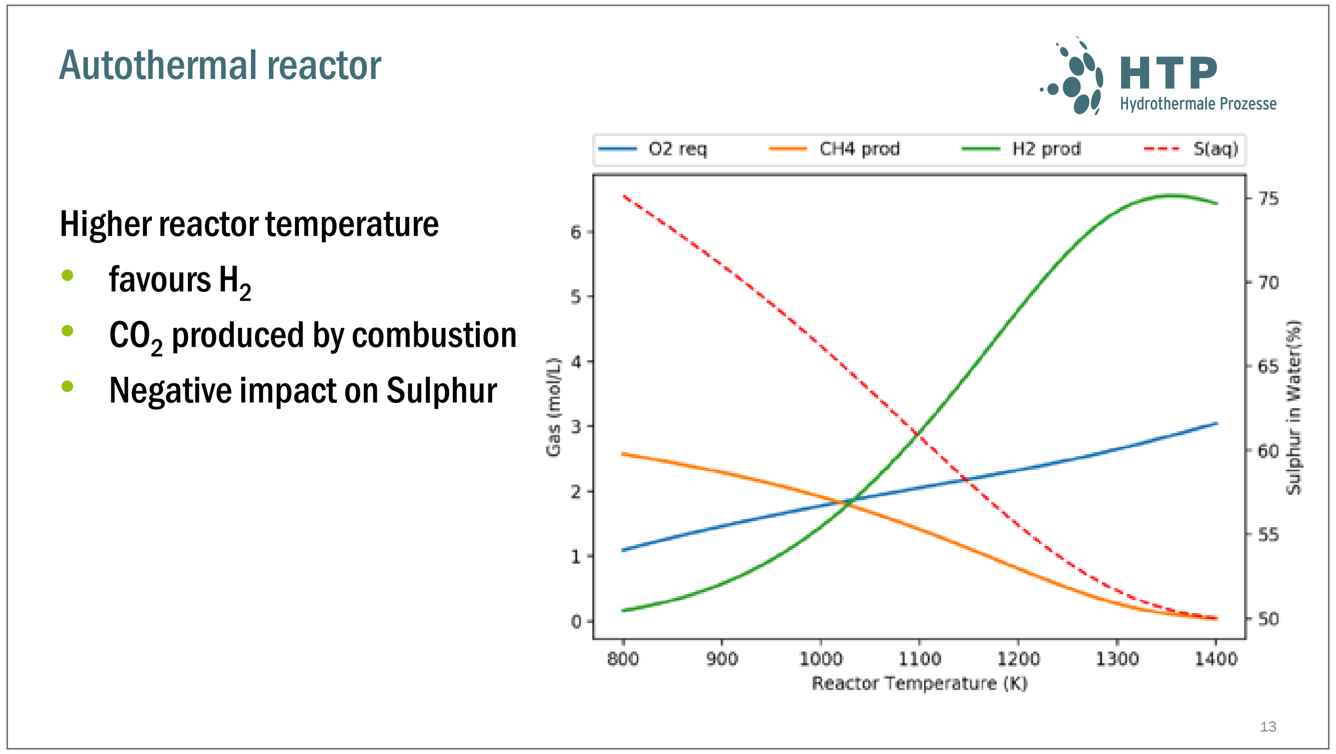


Ionic Part - Sulphur species behaviour

Acid base reactions

Mixture
NaOH 1.1 mol/L
Na_2S : 0.3 mol/L

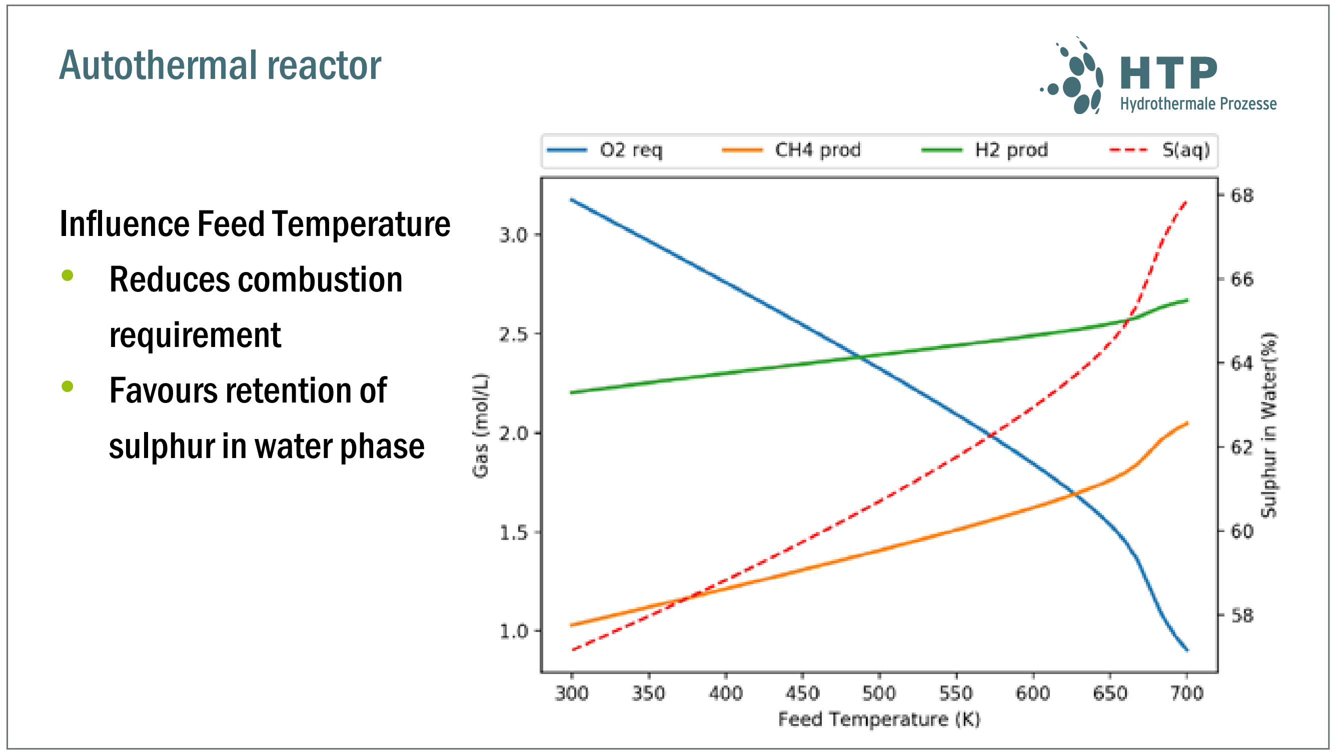
CO_2 is produced during the gasification



Autothermal reactor

Higher reactor temperature

- favours H_2
- CO_2 produced by combustion
- Negative impact on Sulphur



Autothermal reactor

Influence Feed Temperature

- Reduces combustion requirement
- Favours retention of sulphur in water phase

Conclusions

SCWG transforms Sulphur into H2S

Sulphur can be retained in the water phase

- Presence of CO_2 is not favourable
- Autothermal is not favourable

Powerful tool to find optimal conditions

Perspectives : Experimental validation !

6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818011

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Session II

Chemikalien und Nährstoffrückgewinnung

Jakob Köchermann, Deutsches Biomasseforschungszentrum

Hydrothermal reactive distillation of biomass and biomass hydrolysates for the production of furfural

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Population growth and climate change will lead to a shortage of agricultural land per capita. Therefore, agricultural products must be used as effectively as possible in the future. Against this backdrop, process development for the production of bio-based building blocks or chemicals from agricultural residues plays an important role. One chemical that has been widely discussed over the last decade is furfural. Furfural is a versatile precursor, e.g. for the production of resins, fuels, solvents or plastics and is therefore called a platform chemical. For the production, hemicellulose-rich biogenic residues such as oat hulls, bagasse or corn cobs are used. However, commercial plants have low furfural yields (< 11% based on the dry initial weight of the biomass) and require huge amounts of sulfuric acid, which afterwards leads to acidified waste water and contaminated, unconverted biomass (cellulose, lignin). From this point of view, more efficient and sustainable processes have to be developed.

In this contribution, hydrothermal reactive distillation (HRD) should be presented as such a process. During HRD a water biomass suspension is hydrothermally treated, whereby a continuous vapor stream exits the reactor. Due to the continuous steam exhausting, the reaction medium remains in a state of boiling. Since furfural is water vapor volatile, any formed furfural immediately goes over into the steam and exits the reactor. Through this approach, loss reactions of furfural such as self- and cross-polymerization are avoided.

This work aims to compare and evaluate the HRD process with regard to the direct use of biomass or the corresponding biomass hydrolysates, respectively. Beside spelt husks, birch wood shavings were used as starting material. The corresponding spelt husk hydrolysate was produced by a hydrothermal pretreatment step, whereas birch wood hydrolysate was provided by Fraunhofer CBP as organosolv hemicellulose fraction. Preliminary results show higher furfural yields based on the use of hydrolysates. However, total furfural yield, related to the used biomass, shows higher yields for direct HRD of biomass. Furthermore, all samples enriched with furfural showed high purities without the presence of any sugar residues or humins. Further investigations, such as the accumulation of by-products like formic or acetic acid, are still in progress and are part of the conference contribution.

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Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Hydrothermal reactive distillation of biomass and biomass hydrolysates for the production of furfural

Jakob Köchermann
DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH

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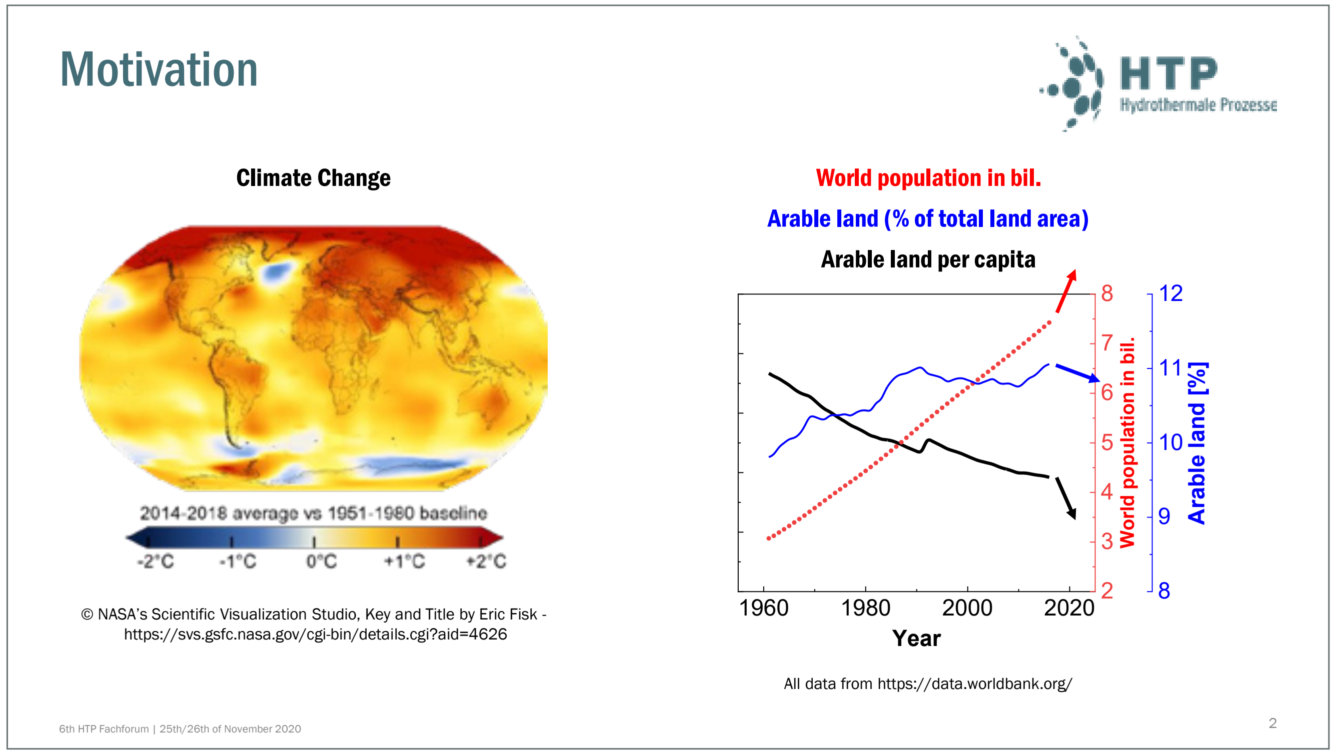

Motivation

Climate Change

© NASA's Scientific Visualization Studio, Key and Title by Eric Fisk - https://svs.gsfc.nasa.gov/cgi-bin/details.cgi?aid=4626

World population in bil.
Arable land (% of total land area)
Arable land per capita

All data from https://data.worldbank.org/

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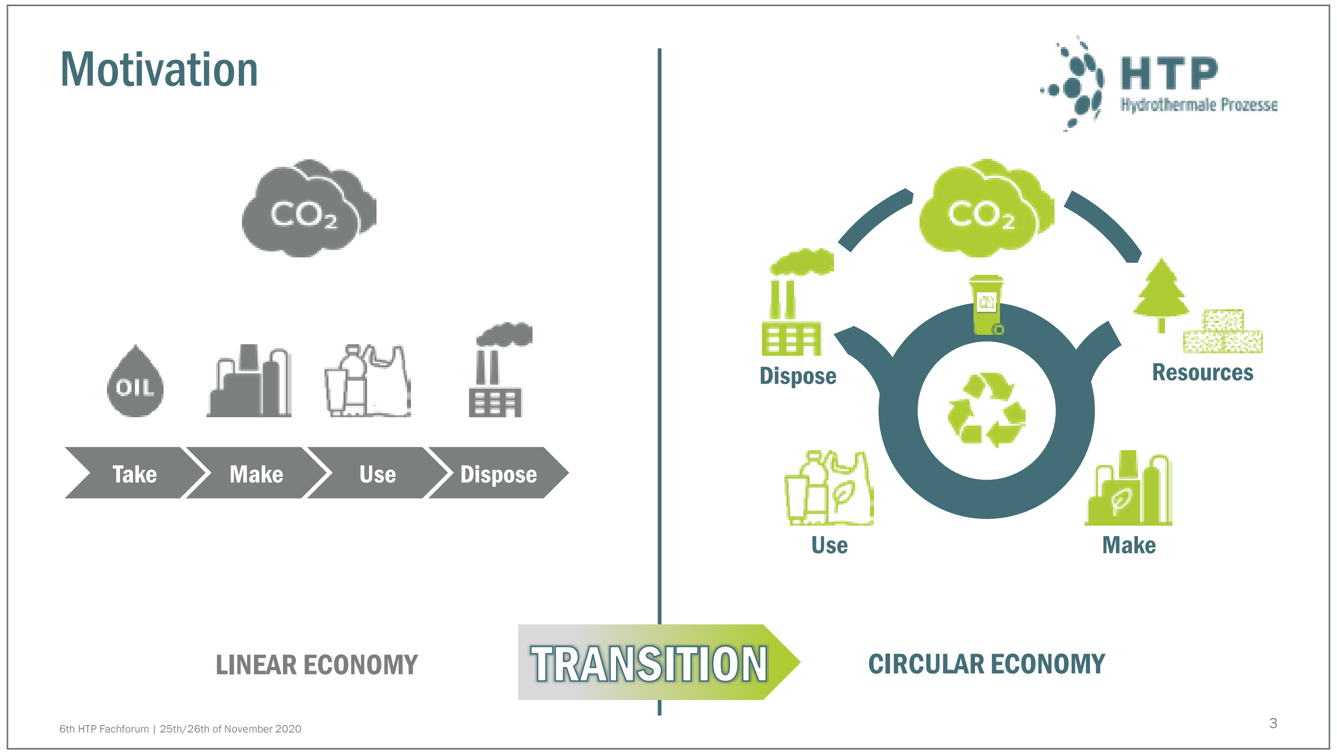

Motivation

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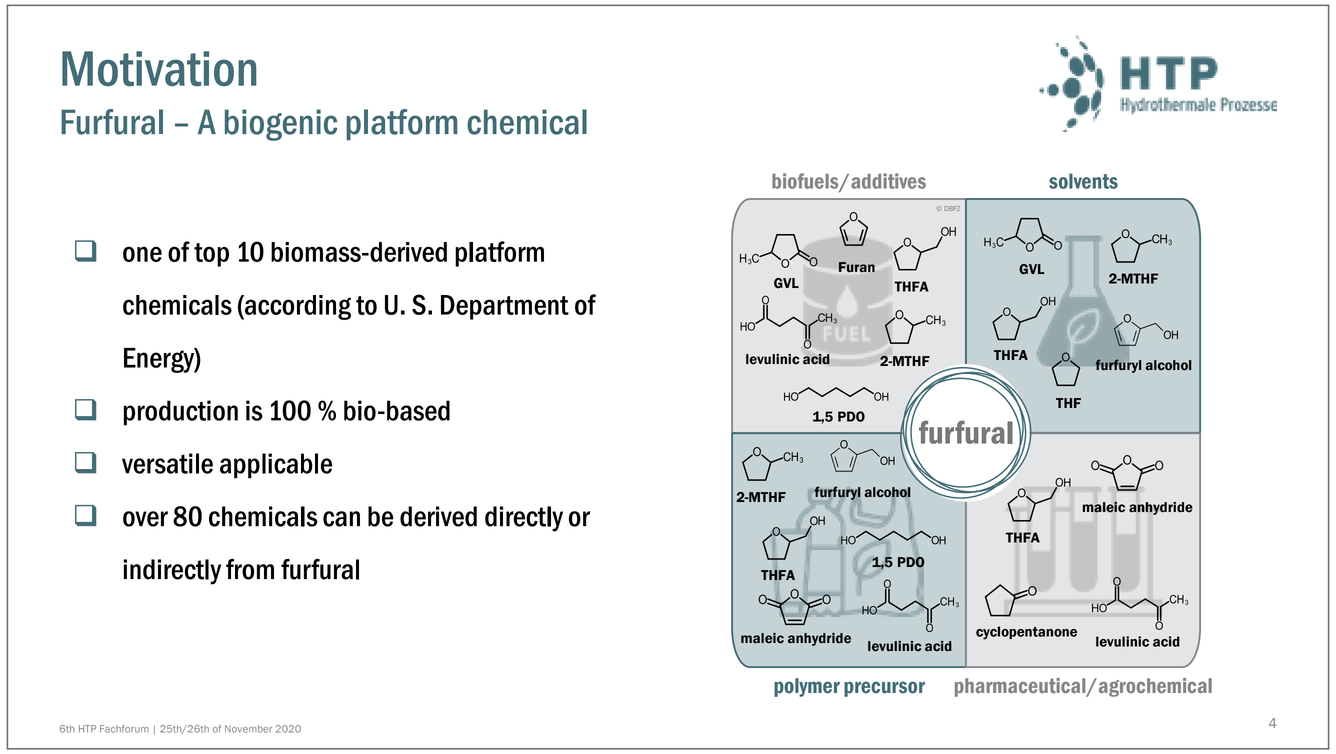

Motivation

Furfural – A biogenic platform chemical

- ❑ one of top 10 biomass-derived platform chemicals (according to U. S. Department of Energy)
- ❑ production is 100 % bio-based
- ❑ versatile applicable
- ❑ over 80 chemicals can be derived directly or indirectly from furfural

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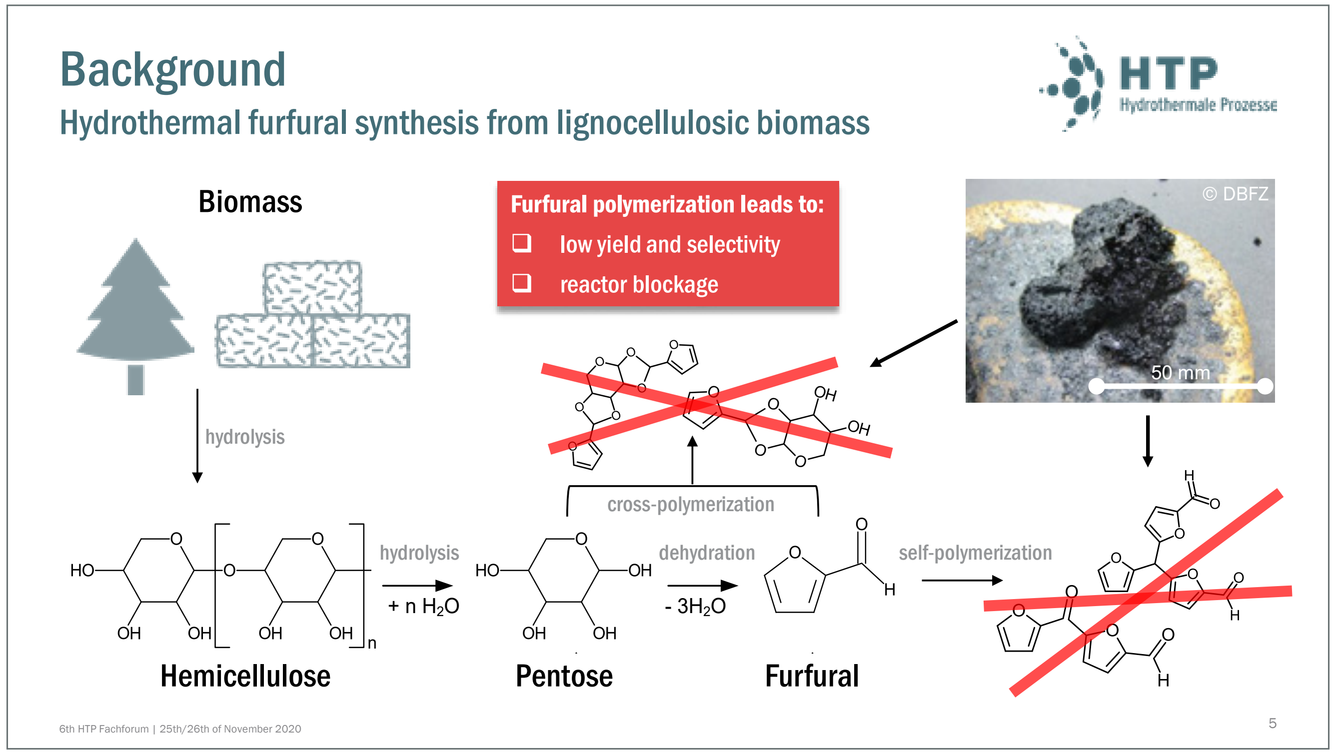

Background

Hydrothermal furfural synthesis from lignocellulosic biomass

Furfural polymerization leads to:

- ❑ low yield and selectivity
- ❑ reactor blockage

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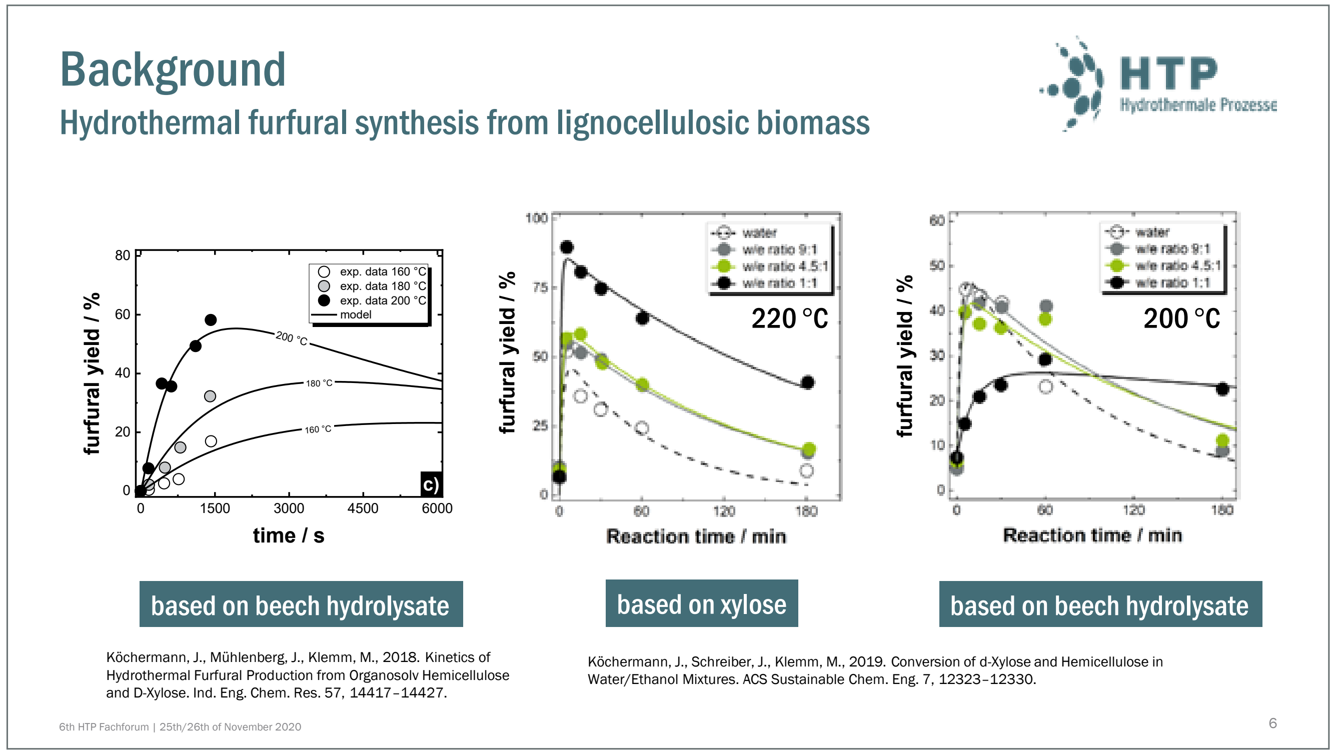

Background

Hydrothermal furfural synthesis from lignocellulosic biomass

based on beech hydrolysate

based on xylose

based on beech hydrolysate

Köchermann, J., Mühlenberg, J., Klemm, M., 2018. Kinetics of Hydrothermal Furfural Production from Organosolv Hemicellulose and D-Xylose. Ind. Eng. Chem. Res. 57, 14417–14427.

Köchermann, J., Schreiber, J., Klemm, M., 2019. Conversion of d-Xylose and Hemicellulose in Water/Ethanol Mixtures. ACS Sustainable Chem. Eng. 7, 12323–12330.

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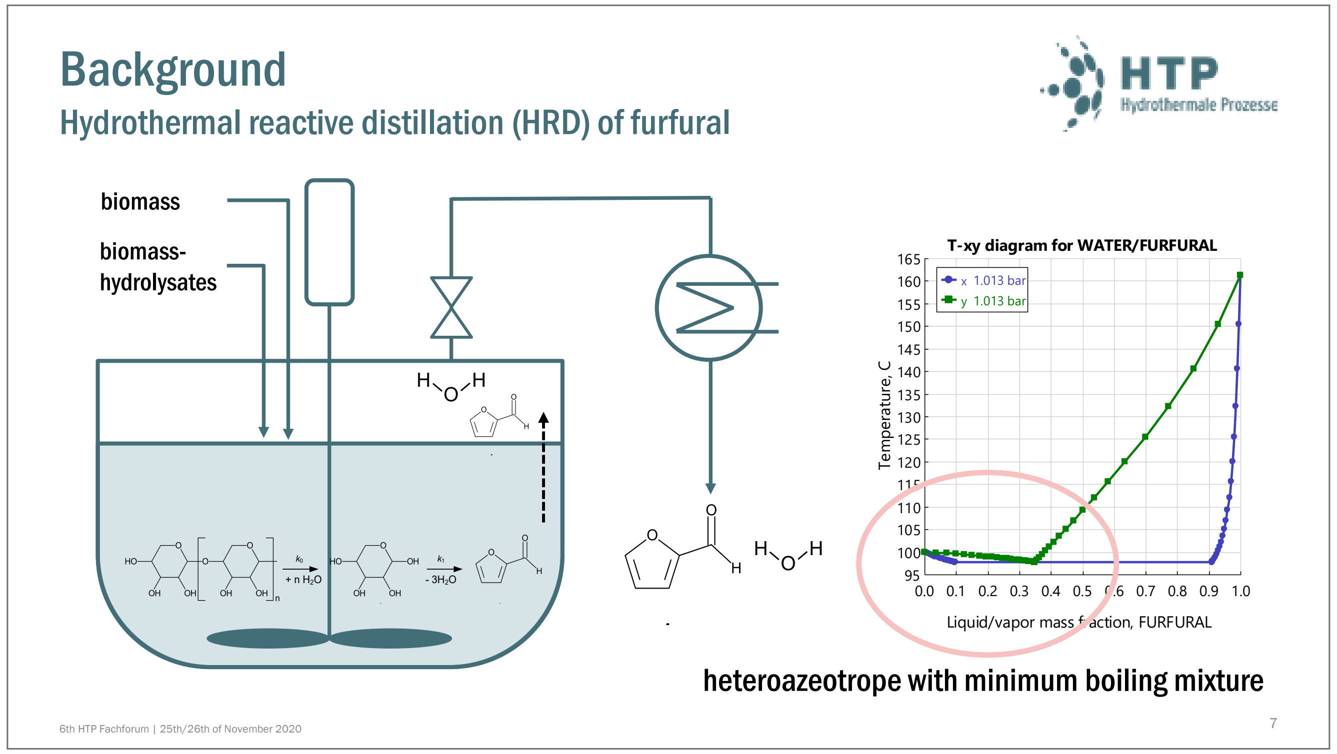

Background

Hydrothermal reactive distillation (HRD) of furfural

heteroazeotrope with minimum boiling mixture

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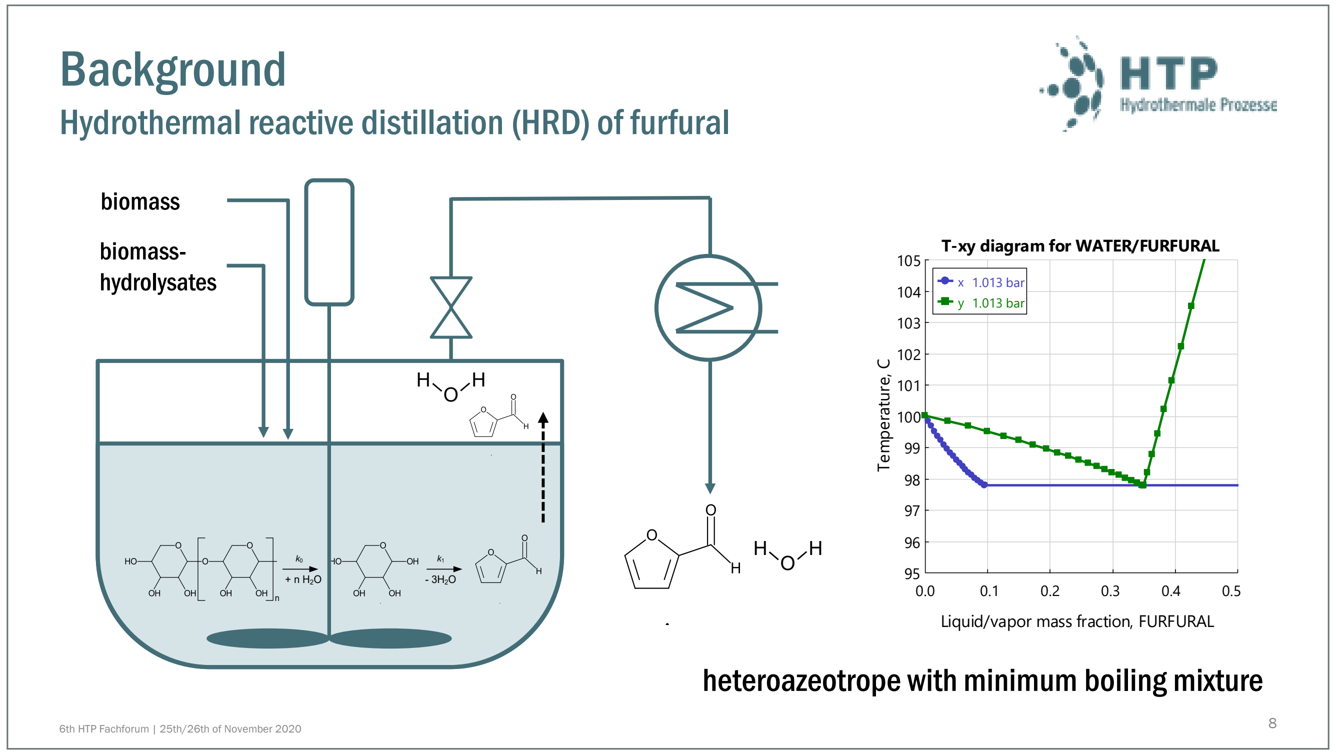

Background

Hydrothermal reactive distillation (HRD) of furfural

heteroazeotrope with minimum boiling mixture

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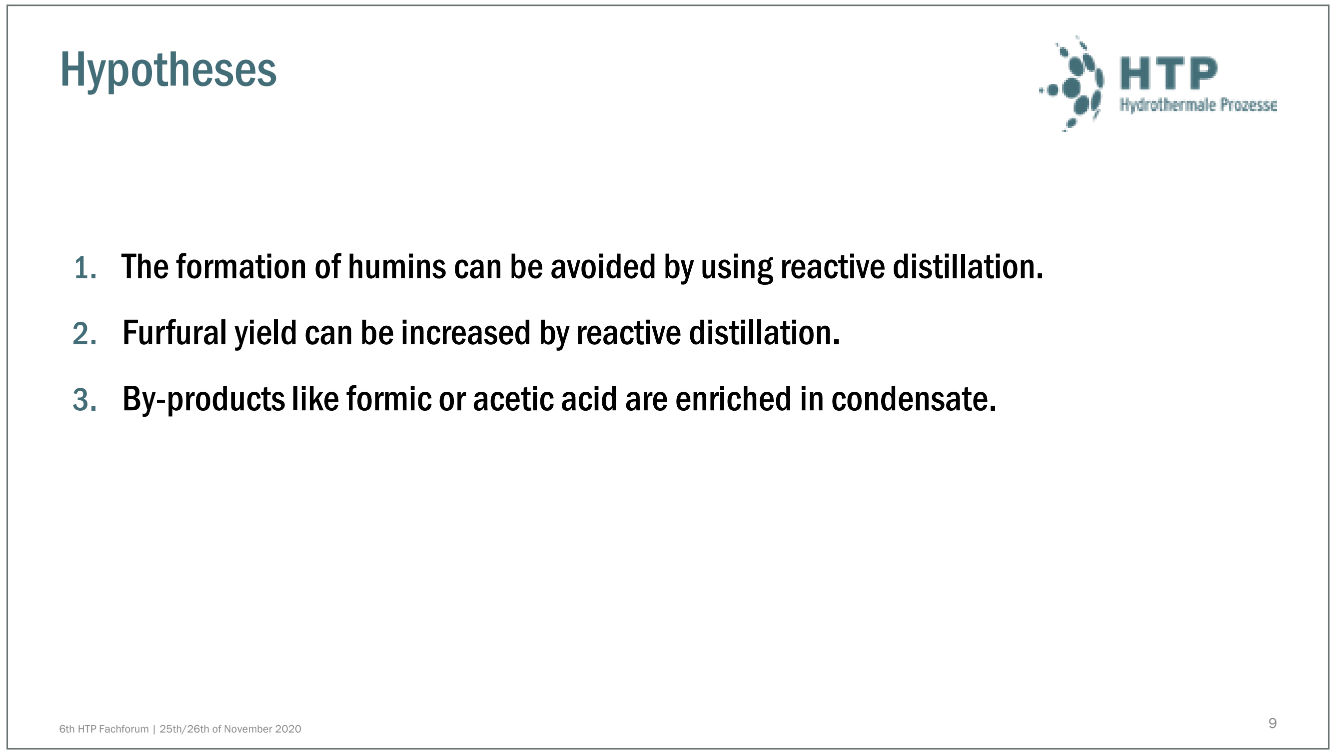

Hypotheses

1. The formation of humins can be avoided by using reactive distillation.
2. Furfural yield can be increased by reactive distillation.
3. By-products like formic or acetic acid are enriched in condensate.

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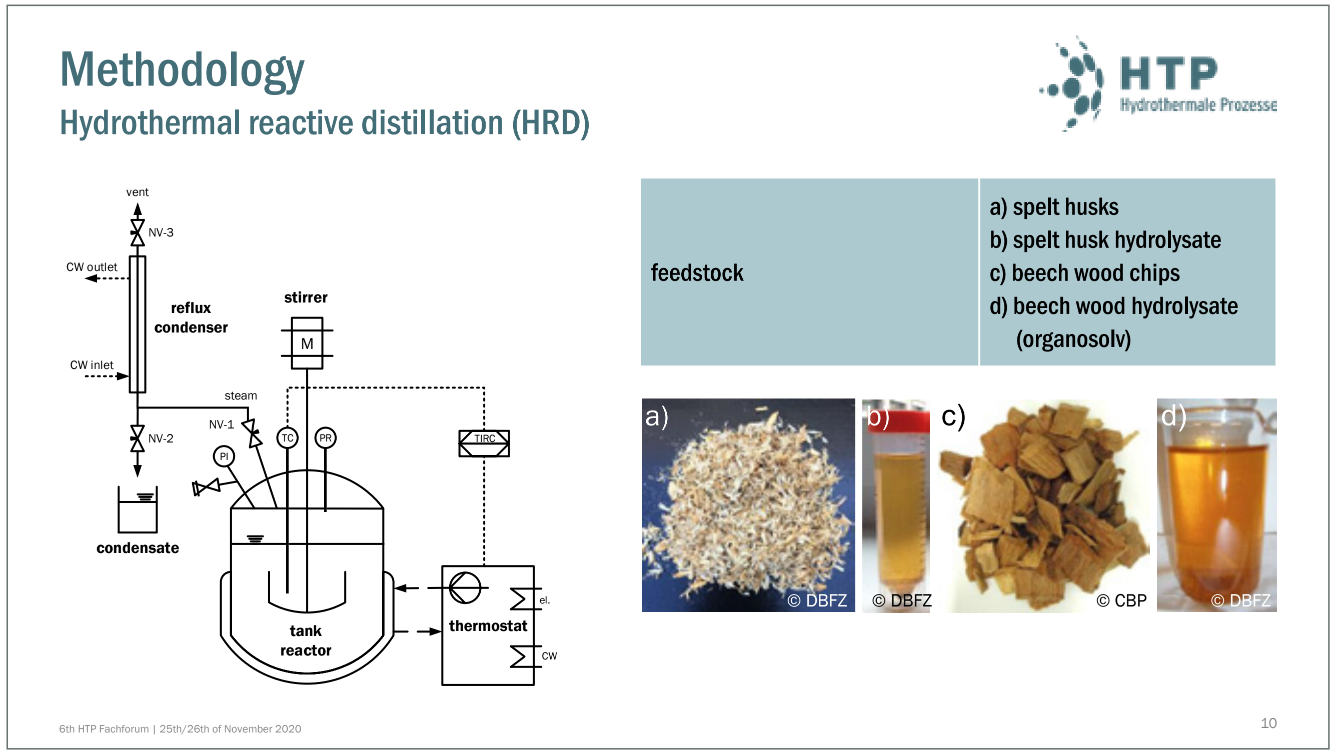

Methodology

Hydrothermal reactive distillation (HRD)

feedstock	a) spelt husks b) spelt husk hydrolysate c) beech wood chips d) beech wood hydrolysate (organosolv)

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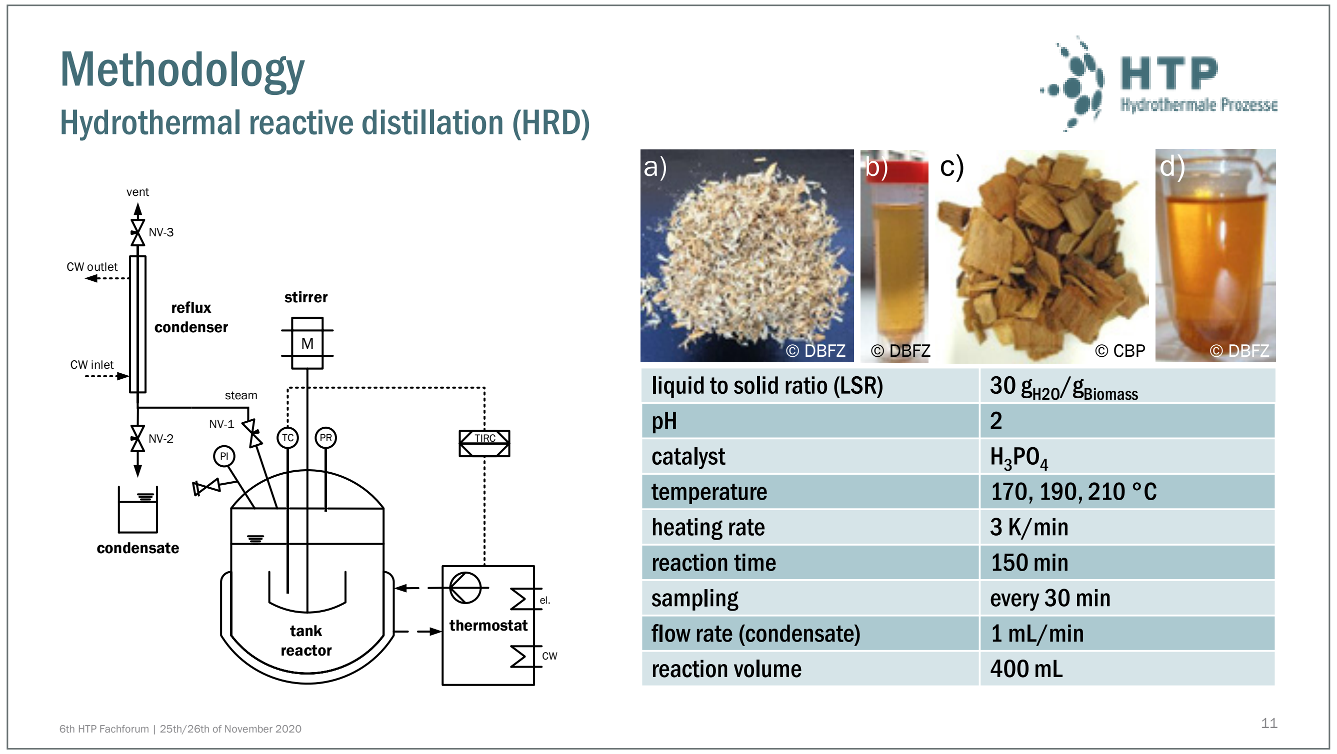

Methodology

Hydrothermal reactive distillation (HRD)

liquid to solid ratio (LSR)	30 $g_{H20}/g_{Biomass}$
pH	2
catalyst	H_3PO_4
temperature	170, 190, 210 °C
heating rate	3 K/min
reaction time	150 min
sampling	every 30 min
flow rate (condensate)	1 mL/min
reaction volume	400 mL

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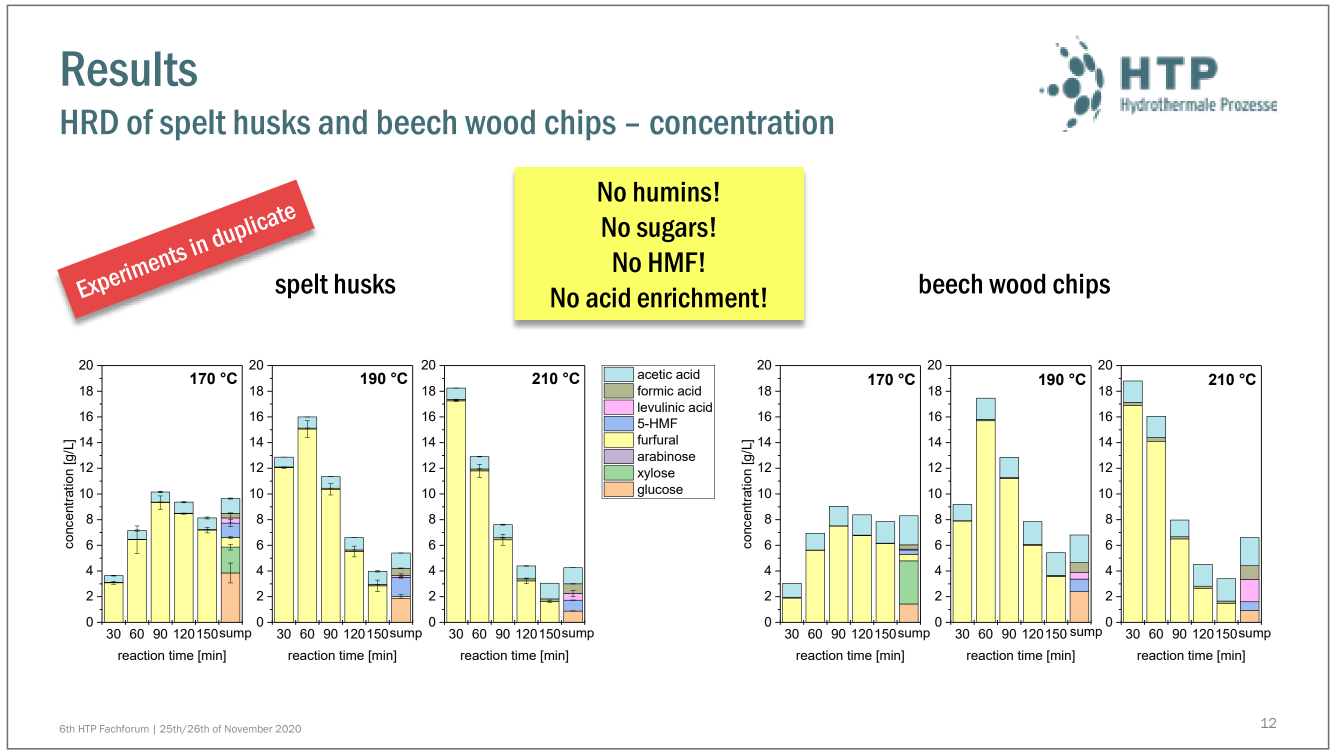

Results

HRD of spelt husks and beech wood chips – concentration

Experiments in duplicate

No humins!
No sugars!
No HMF!
No acid enrichment!

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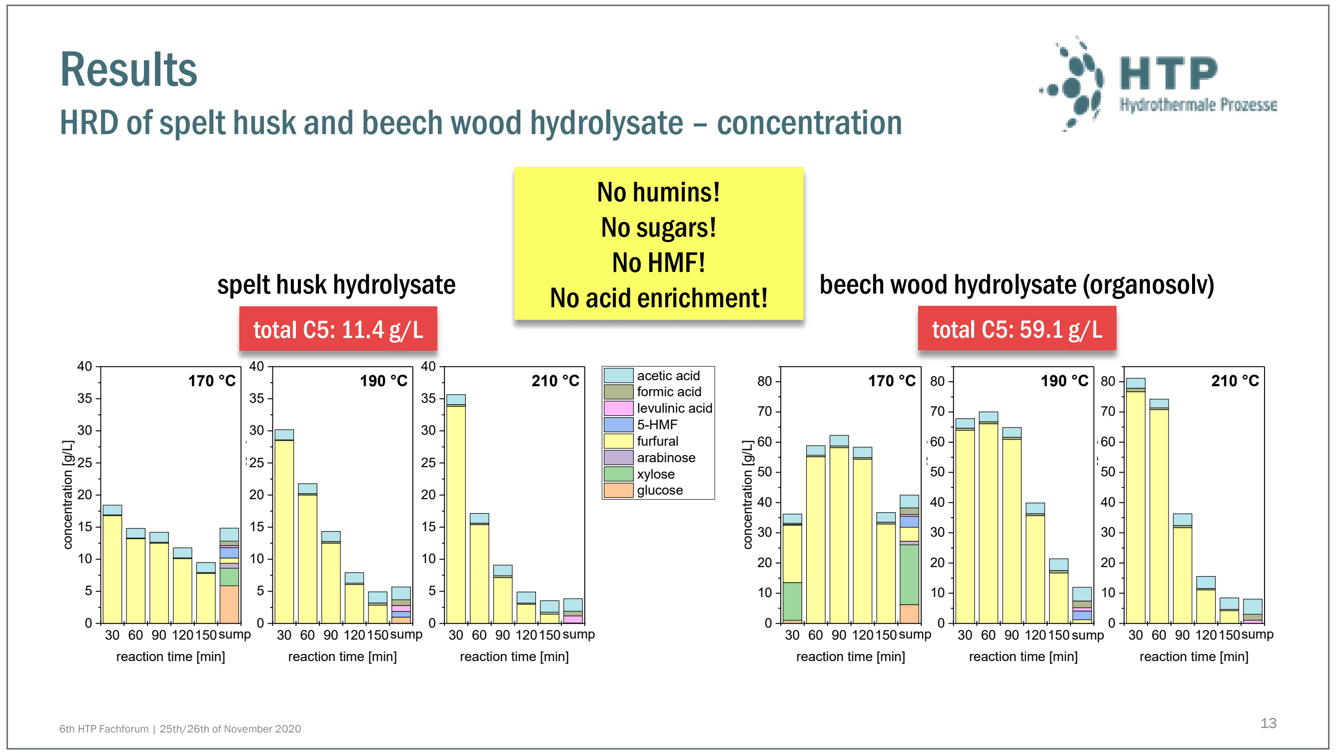

Results

HRD of spelt husk and beech wood hydrolysate – concentration

No humins!
No sugars!
No HMF!
No acid enrichment!

spelt husk hydrolysate

total C5: 11.4 g/L

beech wood hydrolysate (organosolv)

total C5: 59.1 g/L

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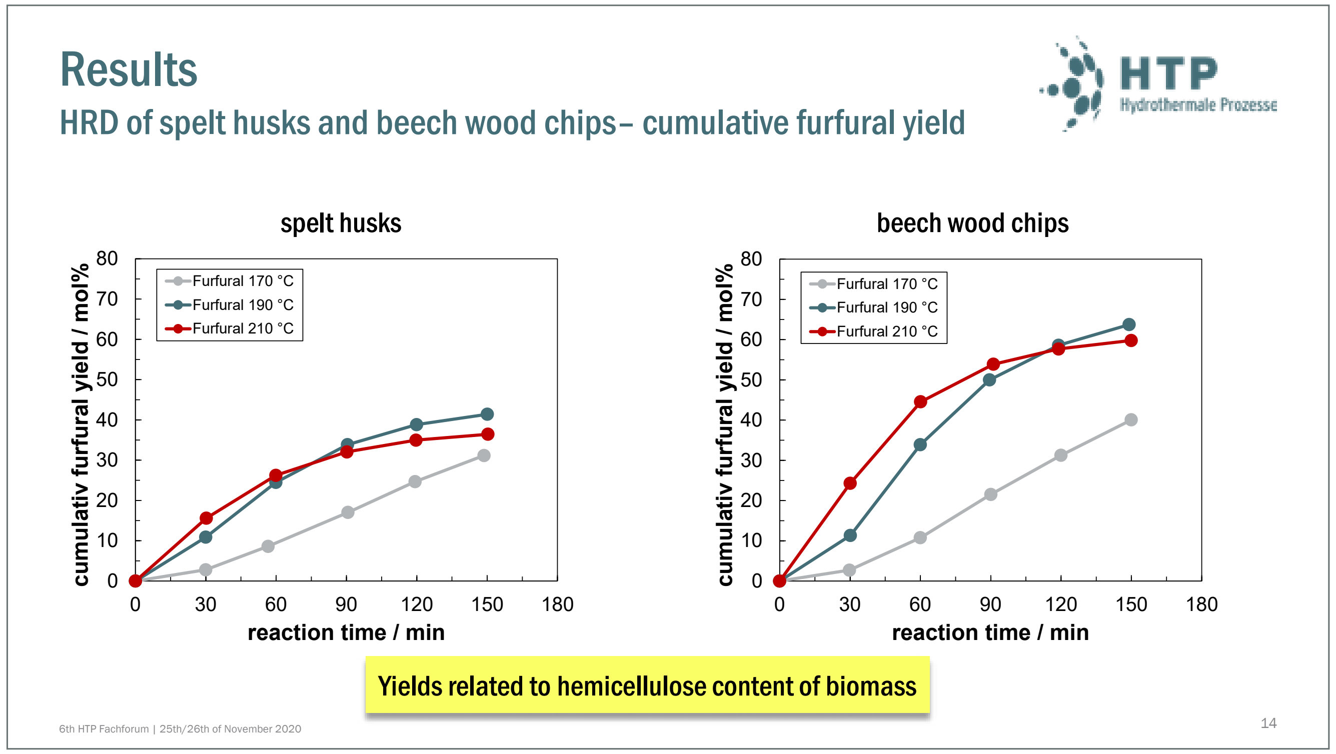

Results

HRD of spelt husks and beech wood chips– cumulative furfural yield

Yields related to hemicellulose content of biomass

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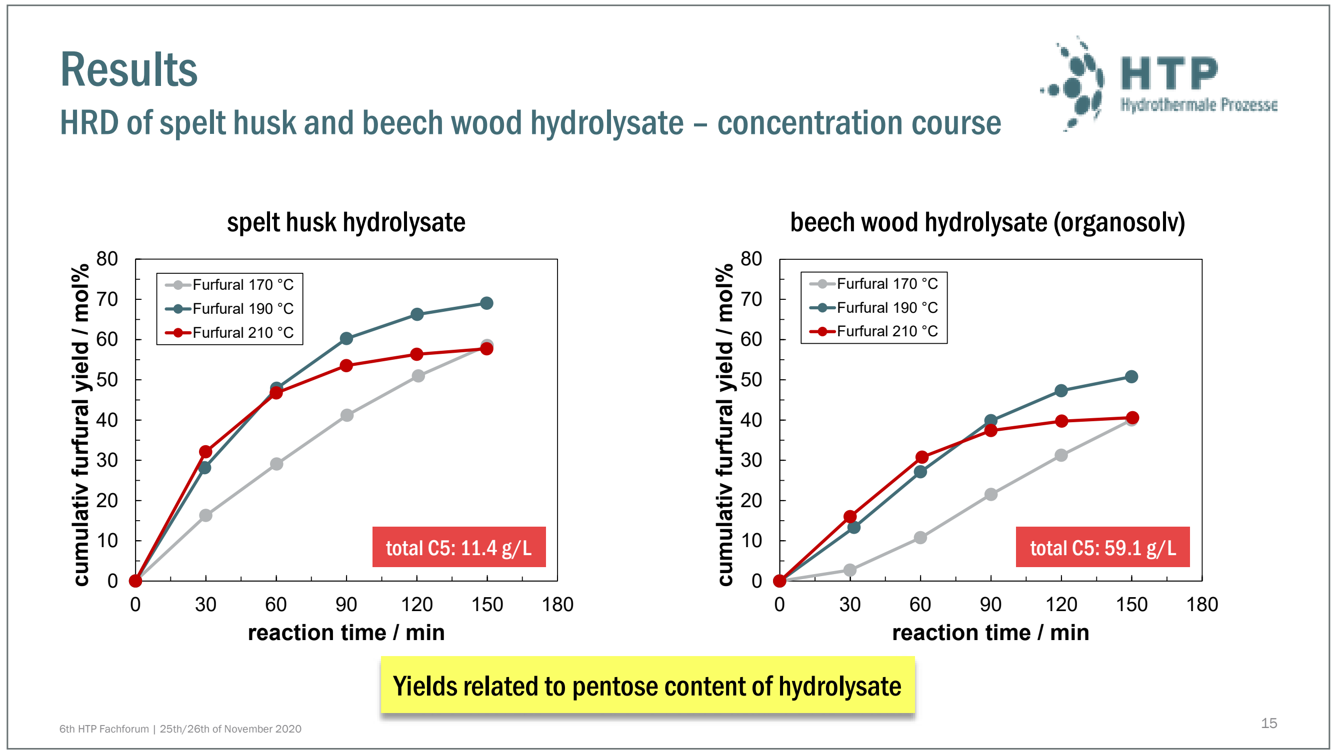

Results

HRD of spelt husk and beech wood hydrolysate – concentration course

spelt husk hydrolysate

beech wood hydrolysate (organosolv)

Yields related to pentose content of hydrolysate

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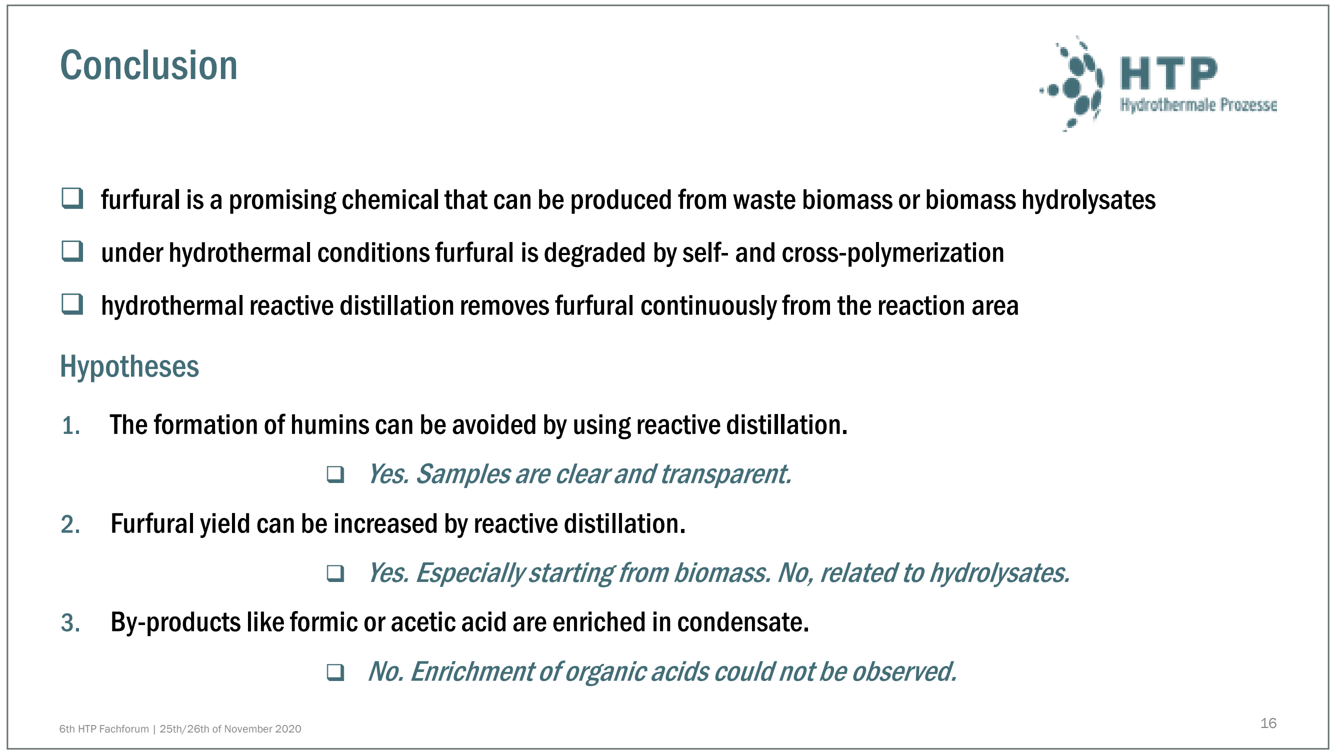

Conclusion

- ☐ furfural is a promising chemical that can be produced from waste biomass or biomass hydrolysates
- ☐ under hydrothermal conditions furfural is degraded by self- and cross-polymerization
- ☐ hydrothermal reactive distillation removes furfural continuously from the reaction area

Hypotheses

1. The formation of humins can be avoided by using reactive distillation.
   - ☐ *Yes. Samples are clear and transparent.*
2. Furfural yield can be increased by reactive distillation.
   - ☐ *Yes. Especially starting from biomass. No, related to hydrolysates.*
3. By-products like formic or acetic acid are enriched in condensate.
   - ☐ *No. Enrichment of organic acids could not be observed.*

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6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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Christian Klüpfel, Deutsches Biomasseforschungszentrum

Kinetic investigation of various Brønsted and Lewis acids for the production of levulinic acid from starch

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Limiting global warming requires sustainable solutions for global energy supply. Practical alternatives to fossil hydrocarbons are biogenic residues, such as agricultural and forestry wastes. In addition to their use for energy generation, material-wise utilization is also the subject of extensive research.

The U.S. Department of Energy lists levulinic acid among the 12 most promising bio-based basic chemicals, with potential secondary products ranging from plastics, biofuels, resins, solvents and paints. Levulinic acid can be produced by acid hydrolysis of starch. The reaction includes: (1) hydrolysis to glucose, (2) isomerization of glucose to fructose, (3) dehydration of fructose to 5-HMF, (4) hydrolysis of 5-HMF to levulinic acid. The dehydration/hydrolysis is catalyzed by Brønsted acids, the isomerization by Lewis acids. The applicability of a set of chlorine-free acids is to be investigated on a waste product of starch production. For this purpose, kinetic experiments are performed in a 500 ml batch reactor between 433 and 473 K. The effect of the catalysts and the temperature on the course of the reaction is examined on the basis of turnover and yield. The highest Levulinic acid yield achieved was 47.56 % with 0.04 M sulfuric acid at 473 K. The measurement data are then used to calculate the rate constants with a simplified model by numerical simulation. With these constants the activation energy and the pre-exponential factor of the partial reactions are calculated for phosphoric acid.

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Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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Kinetic investigation of various Brønsted and Lewis acids for the production of levulinic acid from starch

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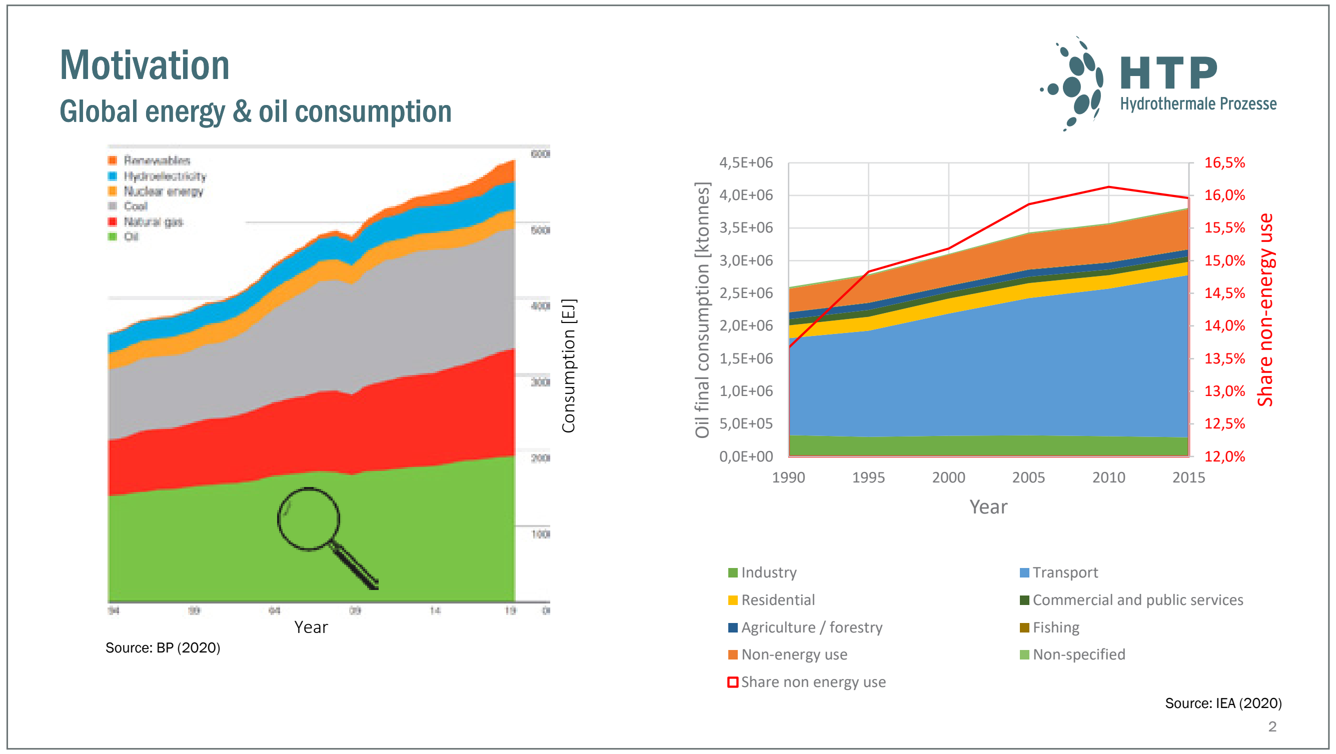

Motivation

Global energy & oil consumption

HTP
Hydrothermale Prozesse

Source: BP (2020)

Source: IEA (2020)

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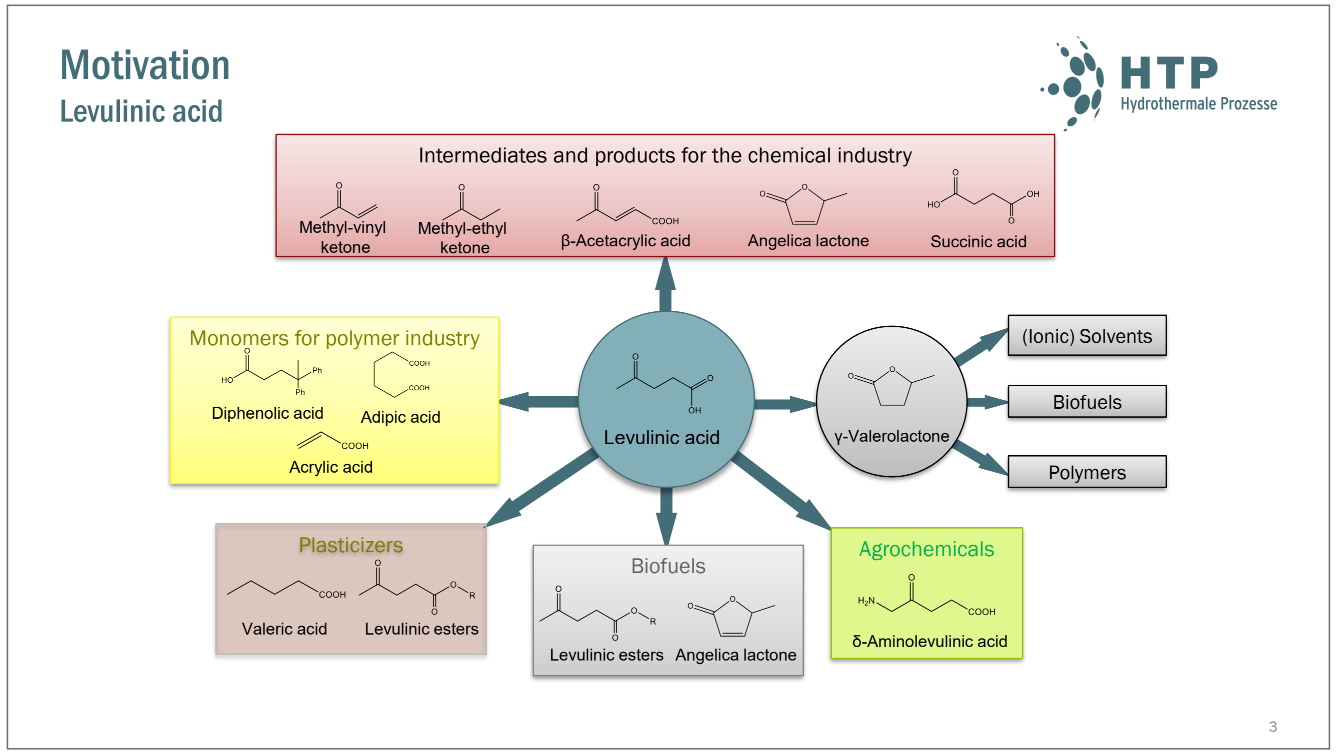


Motivation

Levulinic acid

Intermediates and products for the chemical industry

Methyl-vinyl ketone | Methyl-ethyl ketone | β-Acetacrylic acid | Angelica lactone | Succinic acid

Monomers for polymer industry

Diphenolic acid | Adipic acid | Acrylic acid

Levulinic acid

γ-Valerolactone

(Ionic) Solvents

Biofuels

Polymers

Plasticizers

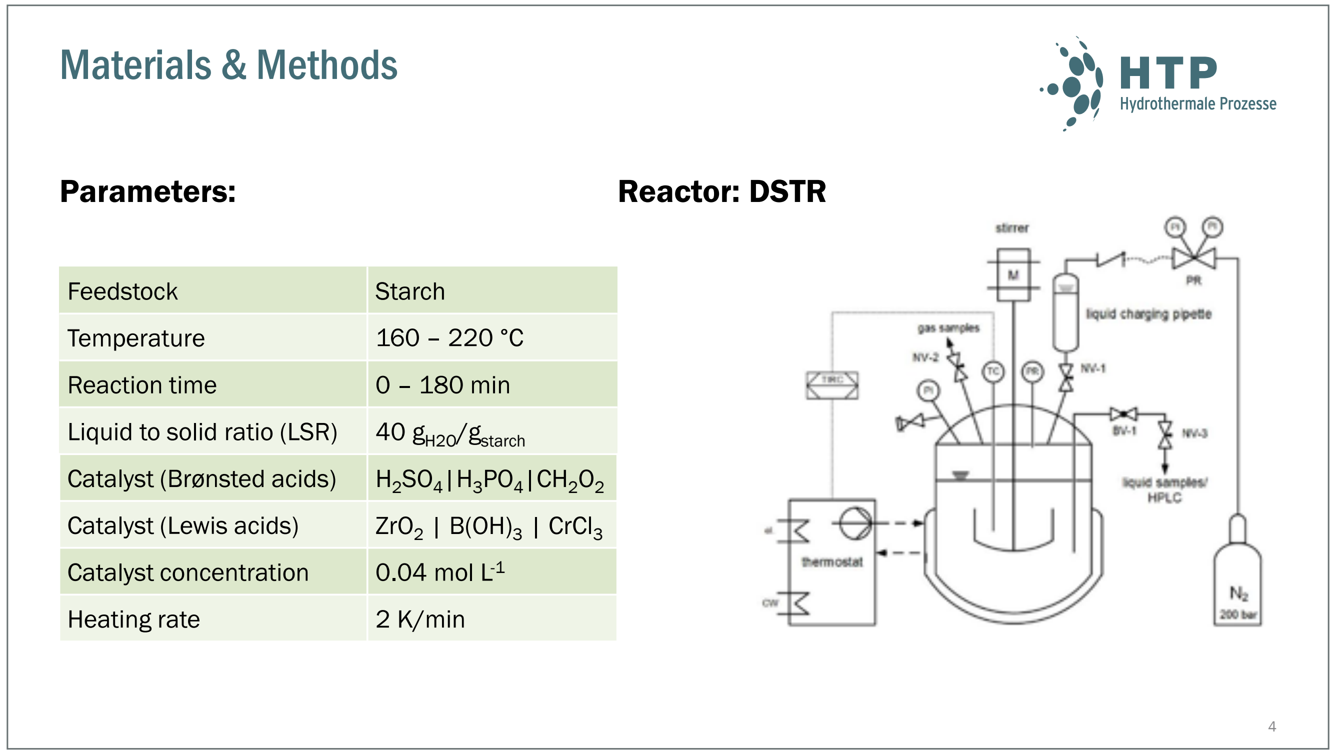
Valeric acid | Levulinic esters

Biofuels

Levulinic esters | Angelica lactone

Agrochemicals

δ-Aminolevulinic acid

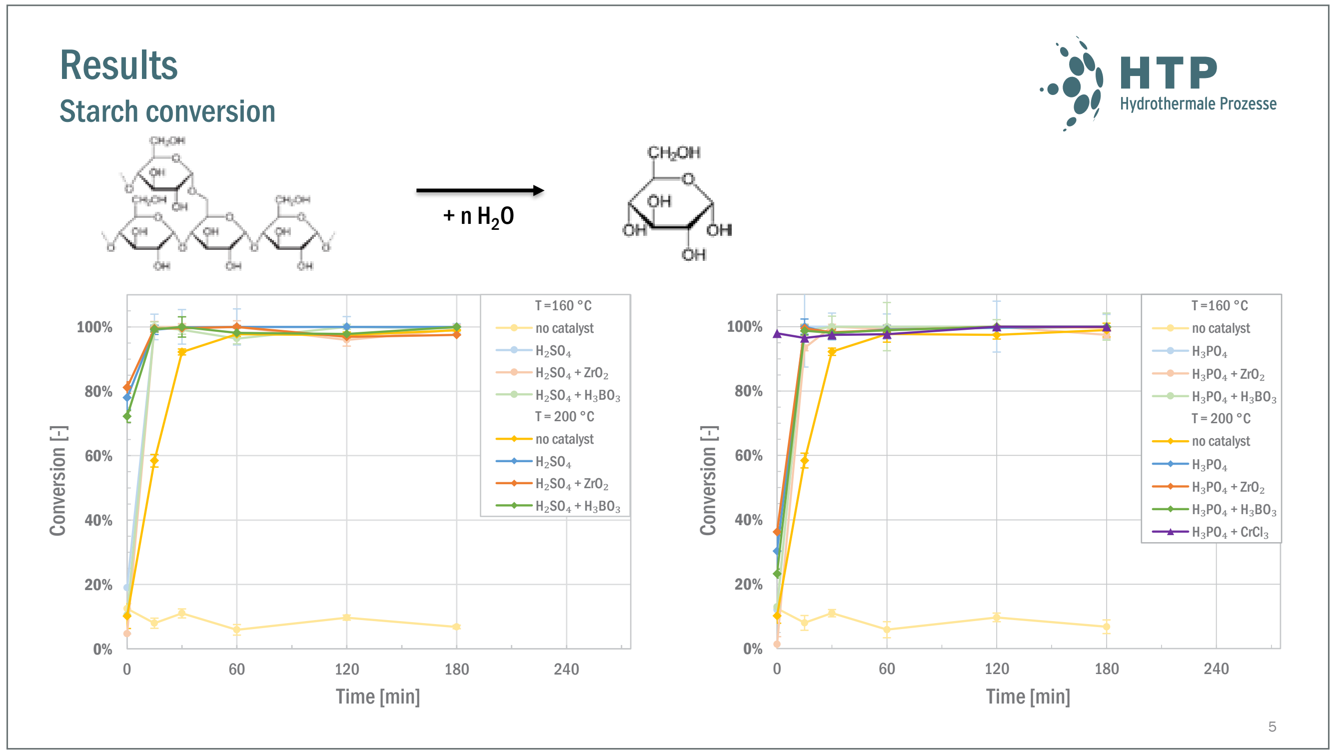


Materials & Methods

Parameters:

Feedstock	Starch
Temperature	160 – 220 °C
Reaction time	0 – 180 min
Liquid to solid ratio (LSR)	40 g_{H2O}/g_{starch}
Catalyst (Brønsted acids)	H_2SO_4 | H_3PO_4 | CH_2O_2
Catalyst (Lewis acids)	ZrO_2 | $B(OH)_3$ | $CrCl_3$
Catalyst concentration	0.04 mol L^{-1}
Heating rate	2 K/min

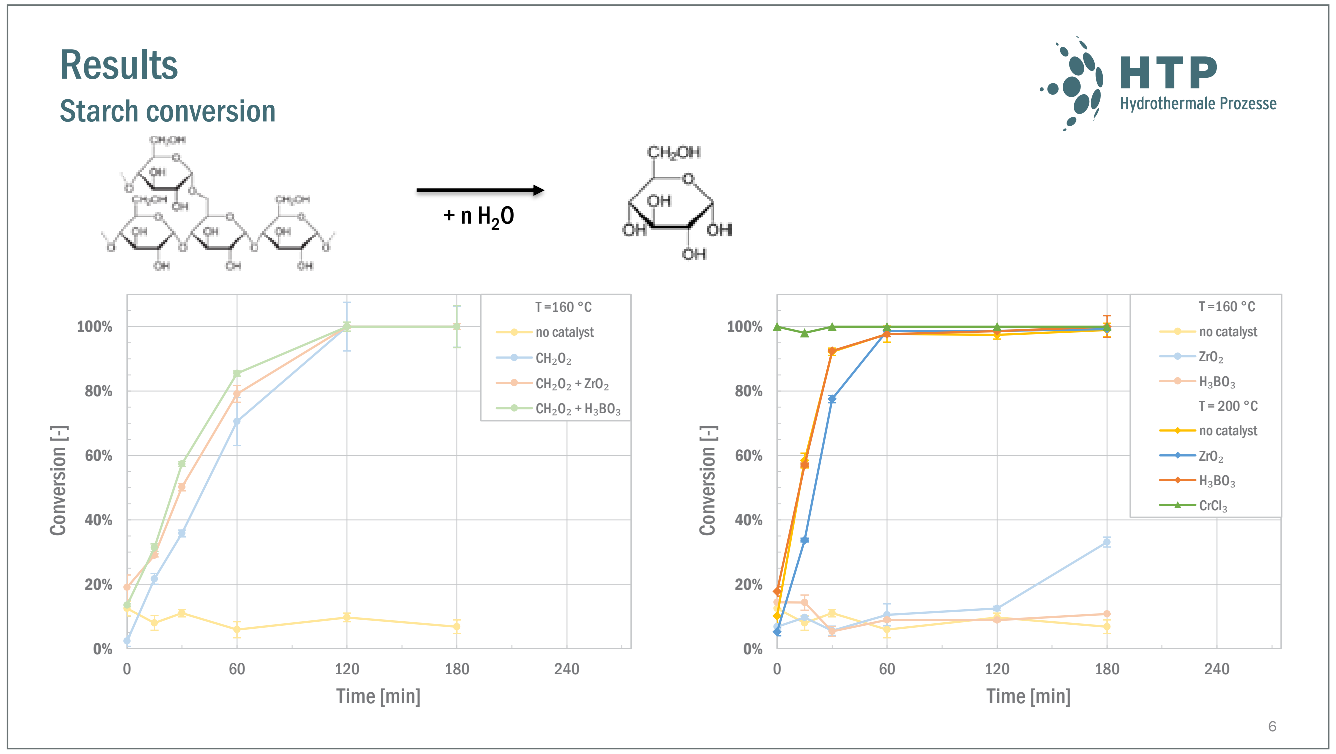
Reactor: DSTR



Results

Starch conversion

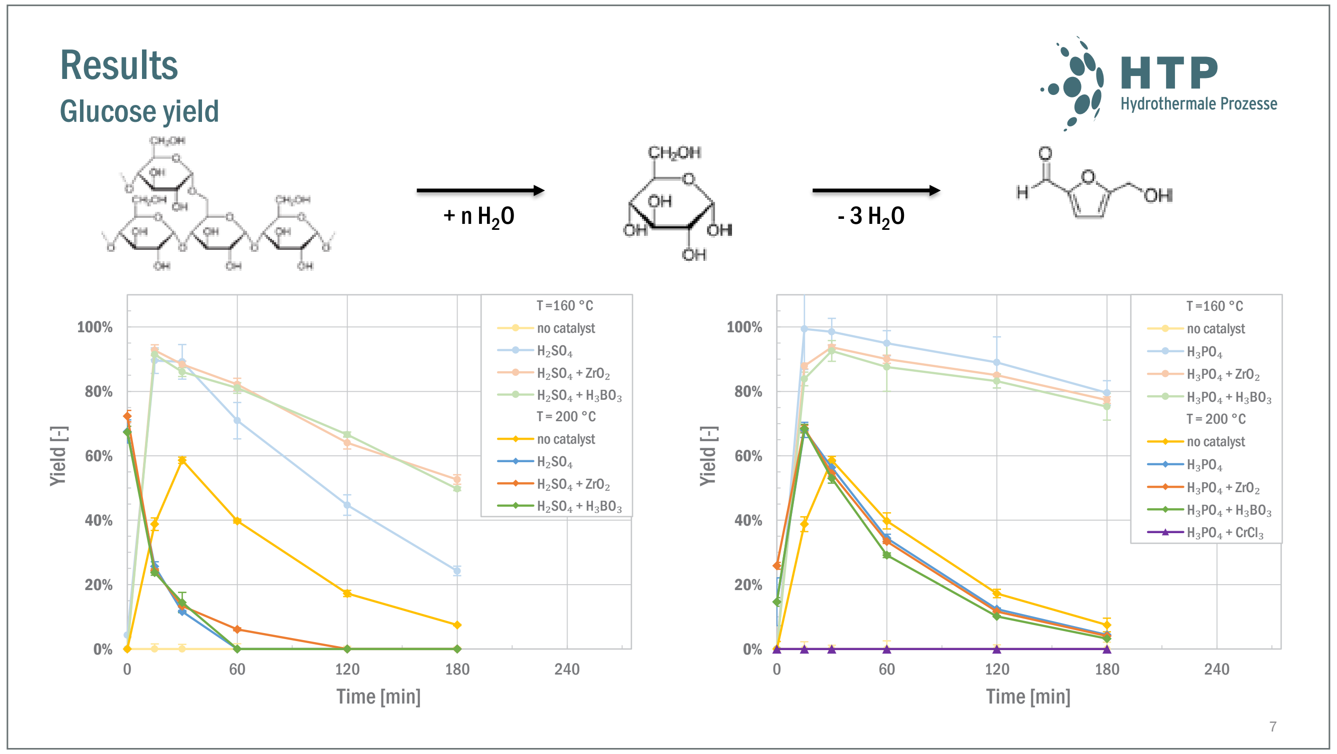
+ n H_2O



Results

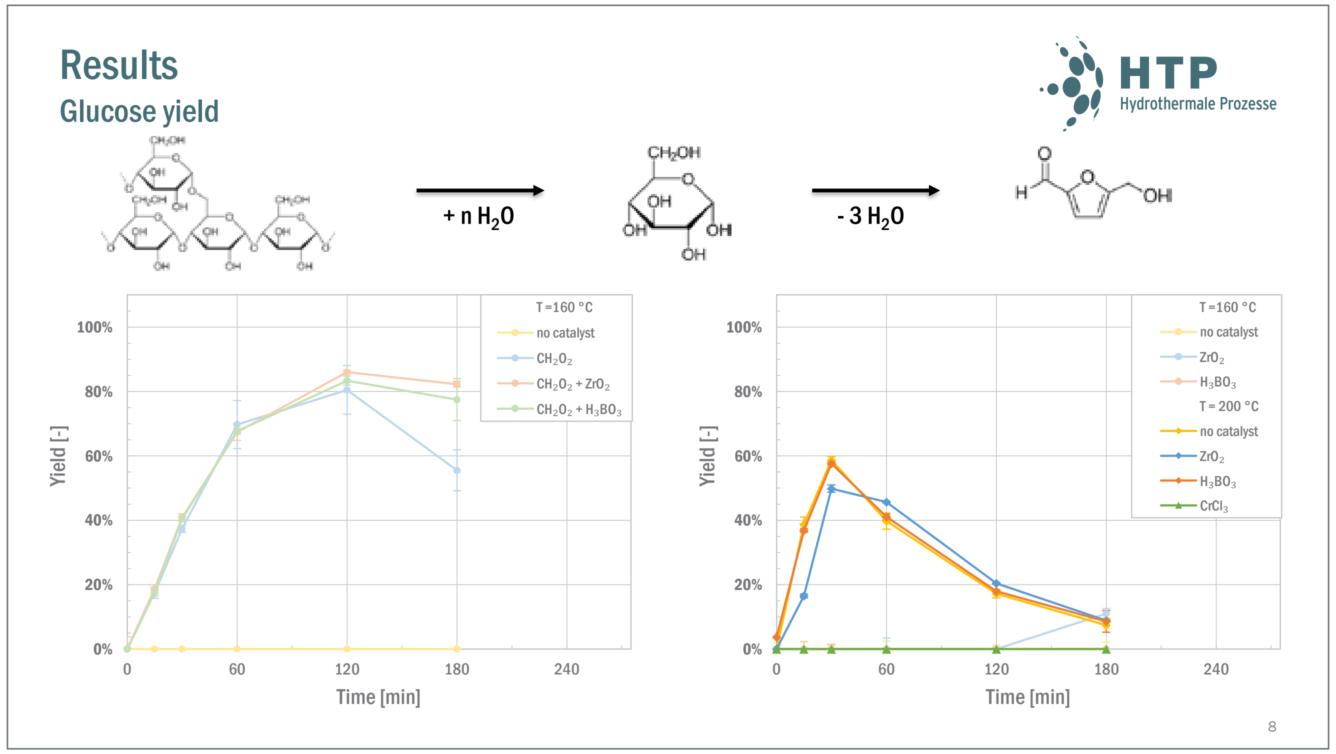
Starch conversion

+ n H_2O



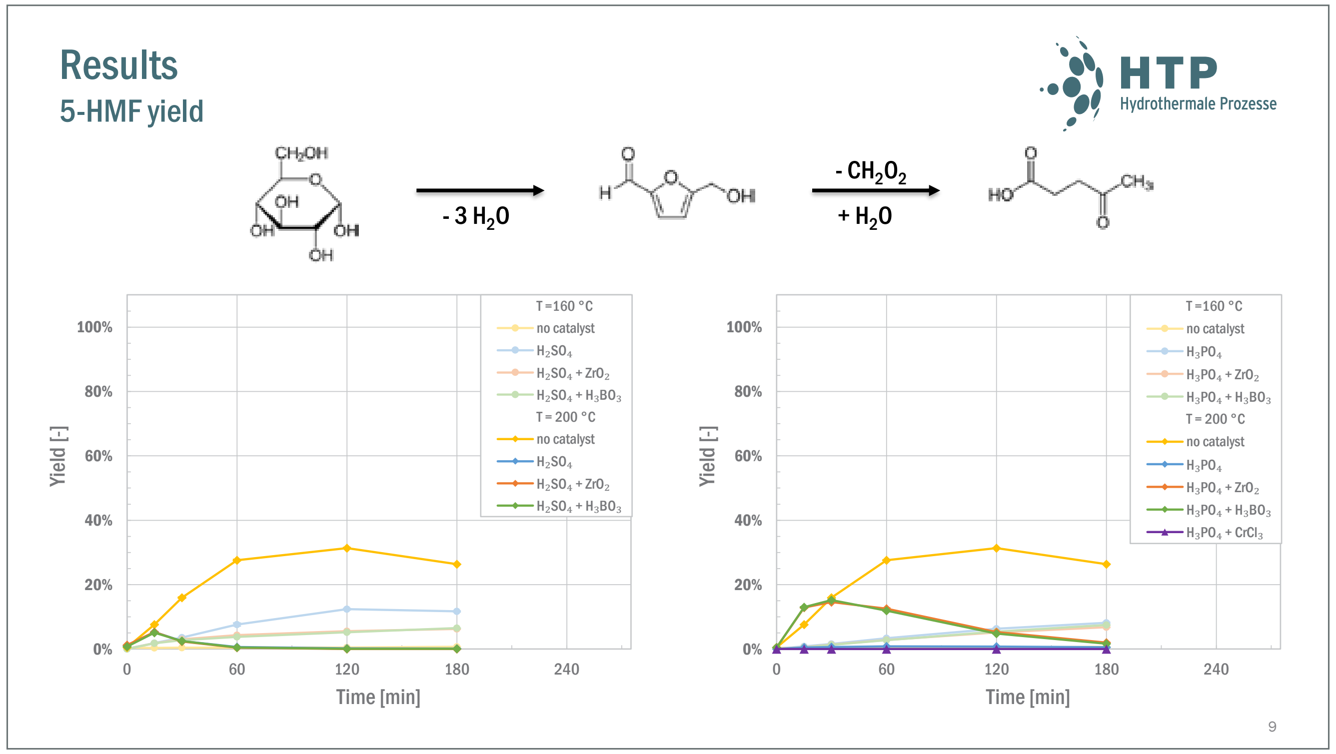
Results

Glucose yield



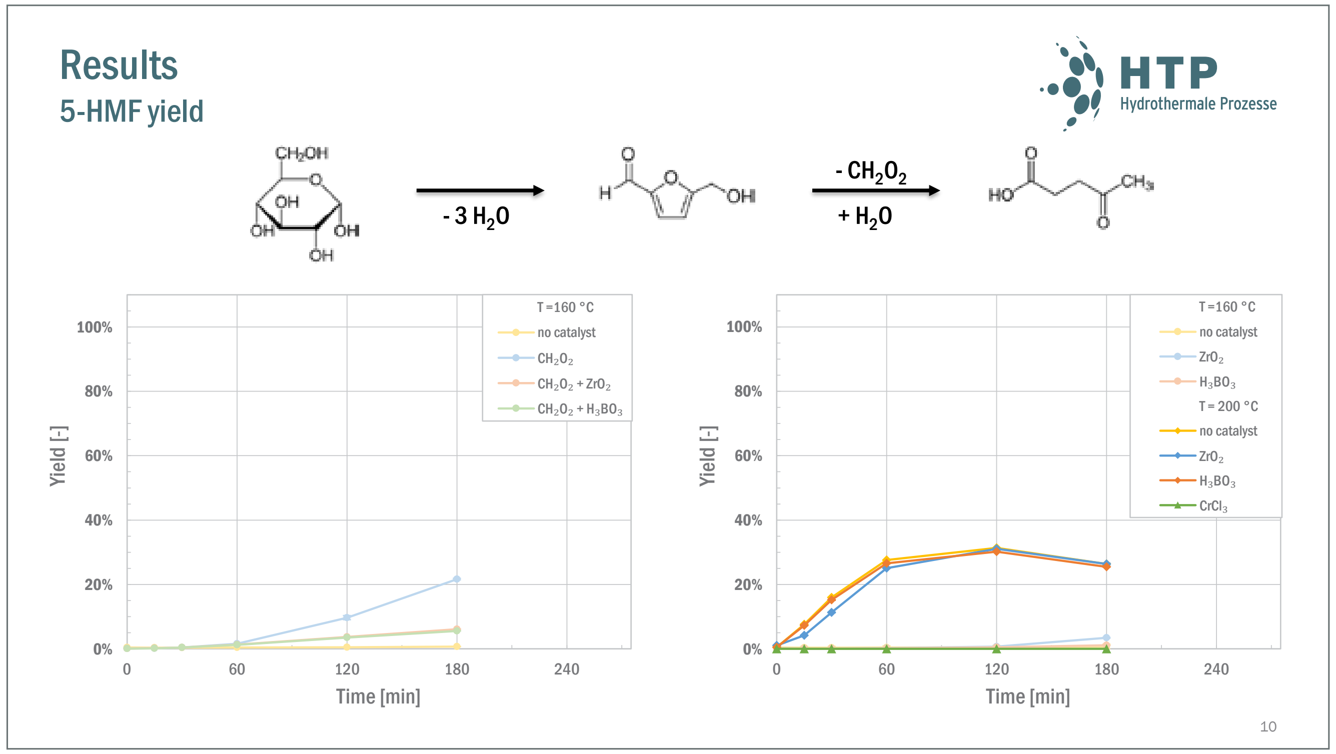
Results

Glucose yield



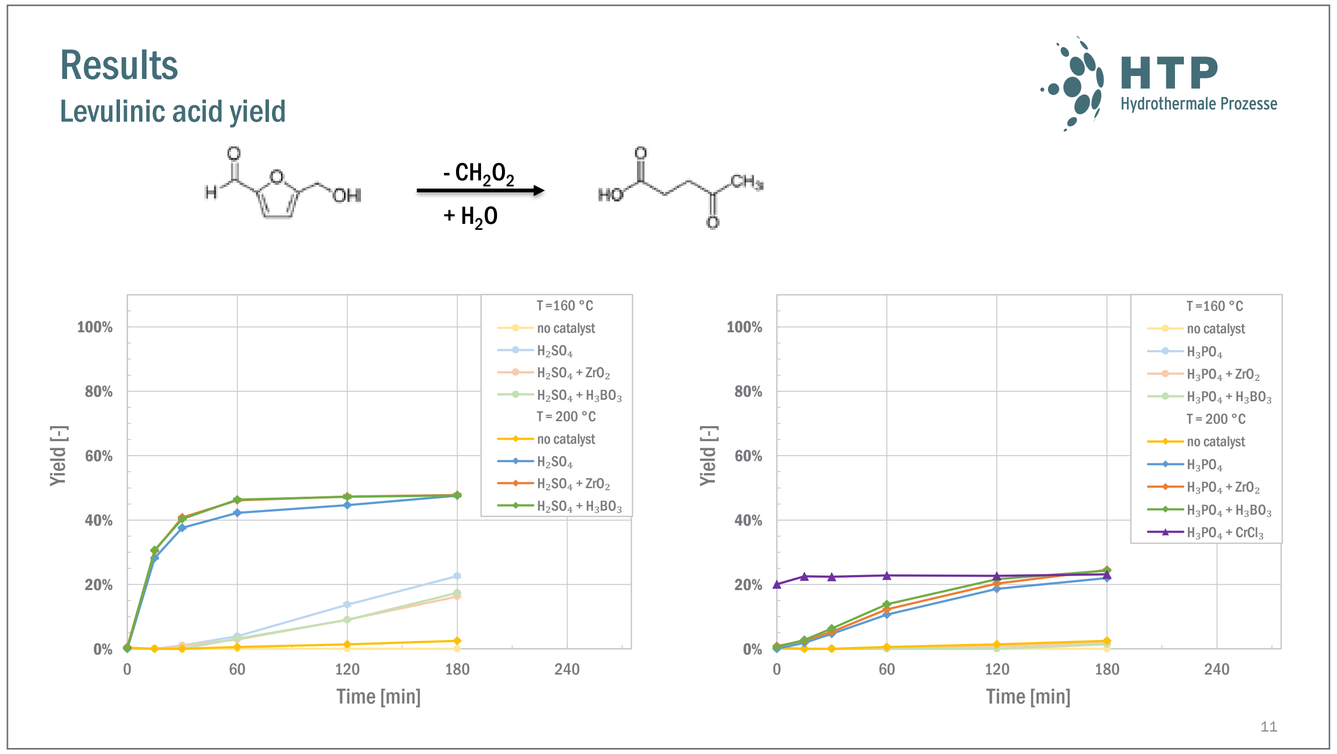
Results

5-HMF yield



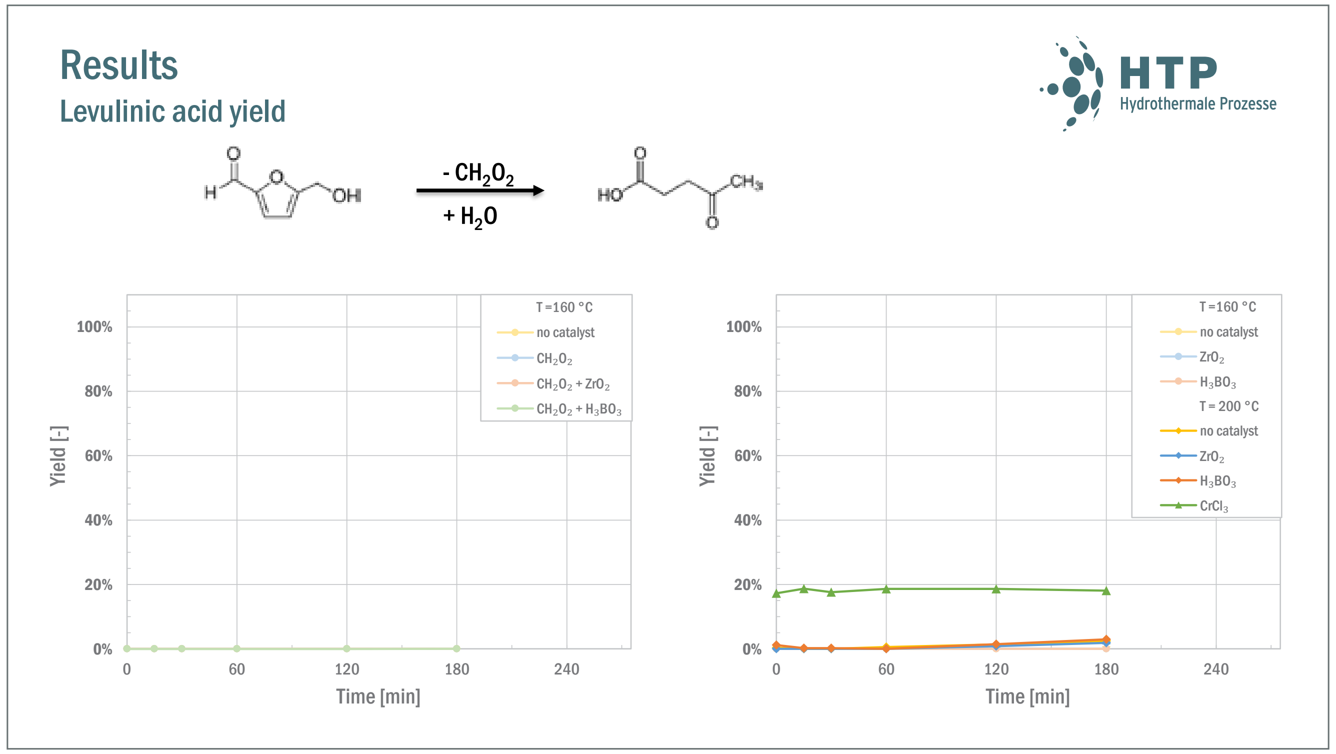
Results

5-HMF yield



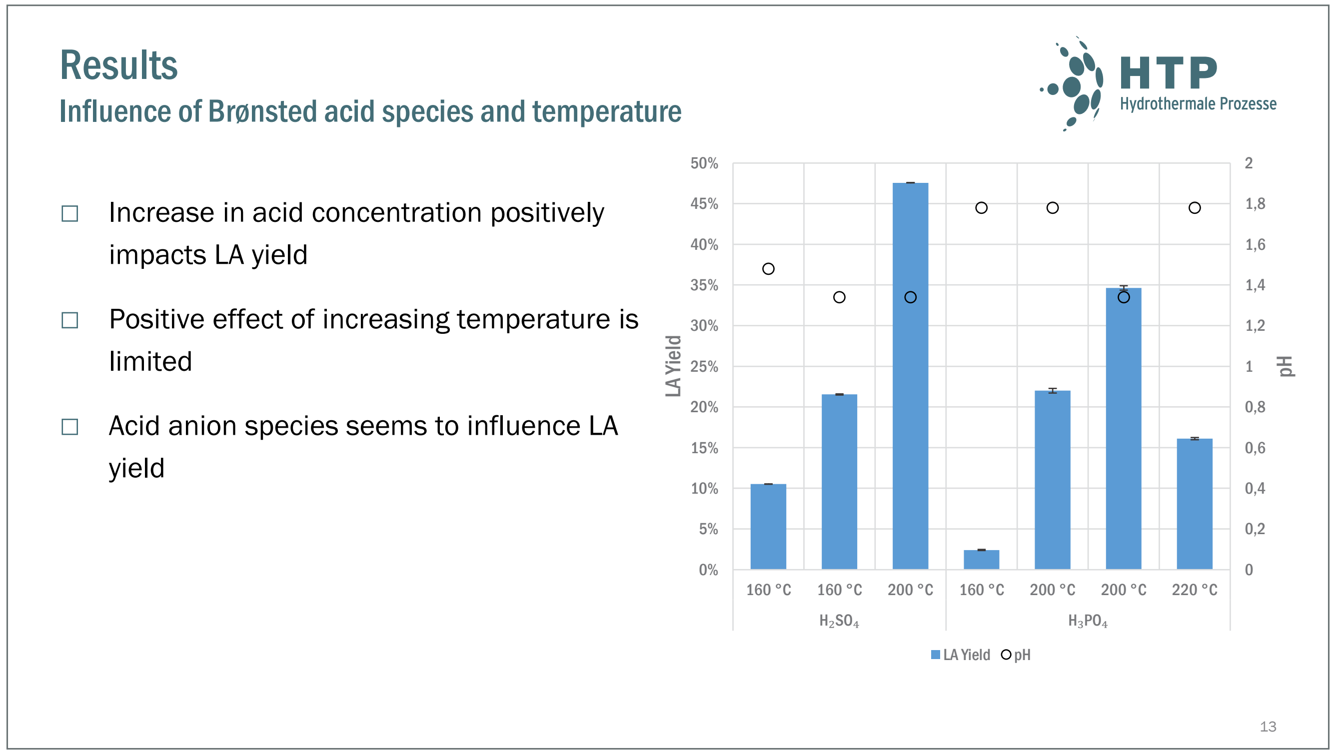
Results

Levulinic acid yield



Results

Levulinic acid yield



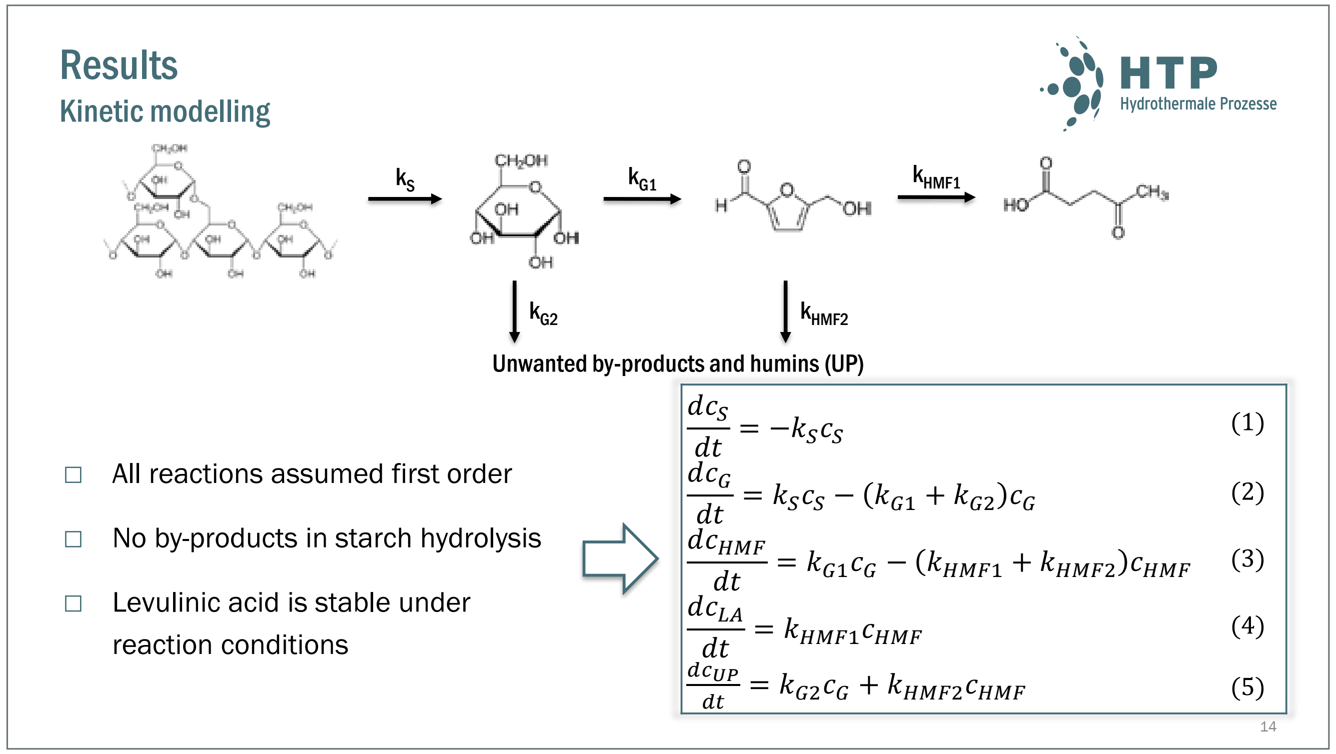
Results

Influence of Brønsted acid species and temperature

☐ Increase in acid concentration positively impacts LA yield

☐ Positive effect of increasing temperature is limited

☐ Acid anion species seems to influence LA yield



Results

Kinetic modelling

Unwanted by-products and humins (UP)

☐ All reactions assumed first order

☐ No by-products in starch hydrolysis

☐ Levulinic acid is stable under reaction conditions

$$\frac{dc_S}{dt} = -k_S c_S \tag{1}$$

$$\frac{dc_G}{dt} = k_S c_S - (k_{G1} + k_{G2}) c_G \tag{2}$$

$$\frac{dc_{HMF}}{dt} = k_{G1} c_G - (k_{HMF1} + k_{HMF2}) c_{HMF} \tag{3}$$

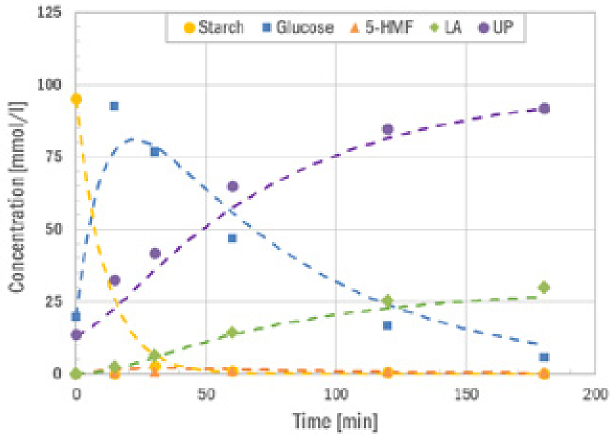
$$\frac{dc_{LA}}{dt} = k_{HMF1} c_{HMF} \tag{4}$$

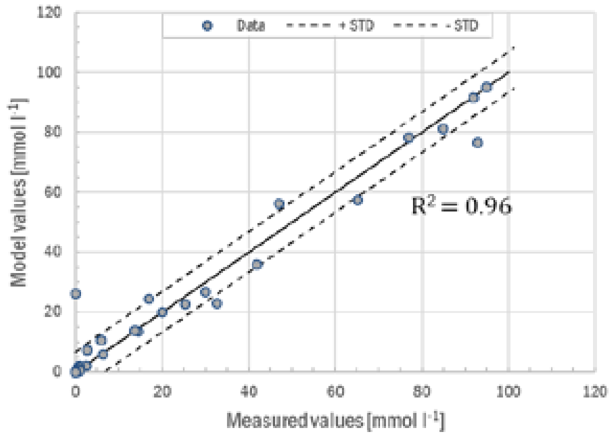
$$\frac{dc_{UP}}{dt} = k_{G2} c_G + k_{HMF2} c_{HMF} \tag{5}$$

Results

Numeric simulation

HTP Hydrothermale Prozesse

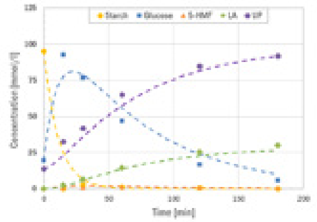


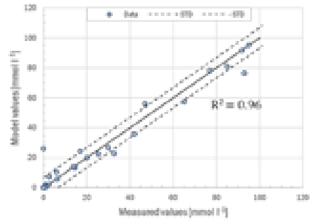


Results

Numeric simulation

HTP Hydrothermale Prozesse





Catalyst	T [K]	k_S [s^{-1}]	k_{G1}[s^{-1}]	k_{G2}[s^{-1}]	k_{HMF1}[s^{-1}]	k_{HMF2} [s^{-1}]	R^2
H_3PO_4	433.15	$1.56 \cdot 10^{-3}$	$1.52 \cdot 10^{-5}$	$2.07 \cdot 10^{-7}$	$2.89 \cdot 10^{-5}$	$1.35 \cdot 10^{-4}$	0.96
H_3PO_4	473.15	$1.45 \cdot 10^{-3}$	$6.10 \cdot 10^{-5}$	$1.78 \cdot 10^{-4}$	$2.45 \cdot 10^{-3}$	0.0	0.96
H_3PO_4	493.15	$8.19 \cdot 10^{-4}$	$6.68 \cdot 10^{-4}$	$2.84 \cdot 10^{-4}$	$3.66 \cdot 10^{-4}$	$9.73 \cdot 10^{-4}$	0.99

Results

Kinetic data

HTP Hydrothermale Prozesse

$$k(T) = A \cdot e^{-\frac{E_A}{RT}}$$

⬇

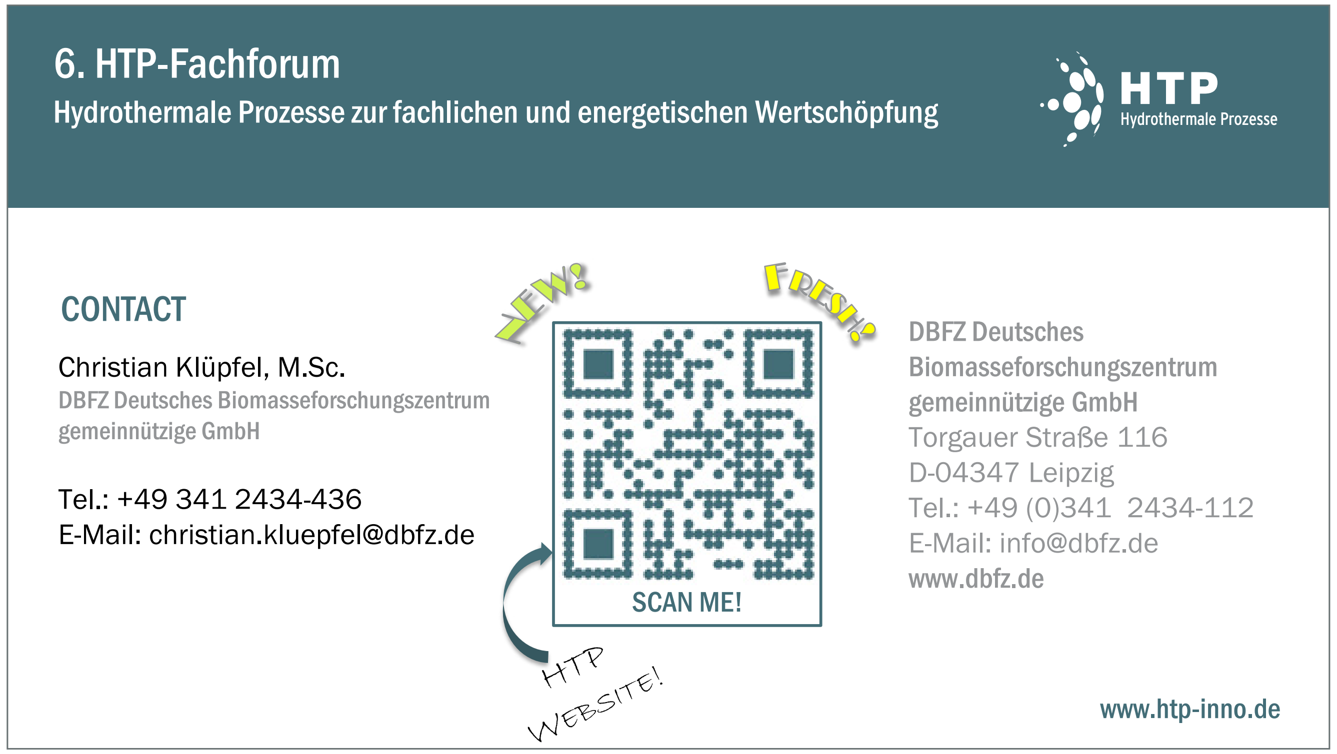
Reaction	A [s^{-1}]	E$_A$[kJ mol^{-1}]
$S \rightarrow G$	$1.7957 \cdot 10^{-5}$	-16.3468
$G \rightarrow UP$	$6.0895 \cdot 10^{20}$	226.5698
$G \rightarrow HMF$	$3.0443 \cdot 10^{7}$	102.8672
$HMF \rightarrow UP$	$1.5518 \cdot 10^{3}$	58.5587
$HMF \rightarrow LA$	$1.3160 \cdot 10^{7}$	94.8020

Conclusions and Outlook

HTP Hydrothermale Prozesse

☐ Starch hydrolysis requires strong acid catalyst
☐ ZrO_2 and H_3BO_3 have little to no influence
☐ Lower pH increases LA yield
☐ Higher temperature does not necessarily increase LA yield

☐ Continue the search for “mild“ Lewis acids
☐ Closer examination of side product formation
☐ Validation and refinement of the kinetic model



6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

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Dr. Hanan Atia, Leibniz-Institut für Katalyse e.V.

Catalytic conversion of Levulinic acid to GVL over mono and bimetallic supported metals using formic acid as a hydrogen donor

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Biomass, which is regarded as a renewable feedstock, has attracted much attention for the production of valuable chemicals and fuels [1]. Levulinic acid (LA) is one of the most important products from biomass. It is produced via the acidic hydrolysis of cellulosic feed stocks. LA can be converted to γ-valerolactone (GVL) which is used as a fuel additives or for the production of other useful chemicals as 1,4-pentandiol and acrylic polymers [2,3]. Both homogenous and heterogeneous catalysts are used for the hydrogenation of LA to GVL in the presence of formic acid (FA) as hydrogen donor. Among the heterogeneous catalysts supported nobel metals as Ru and Pd are efficient for the hydrogenation of LA but they are expensive, not stable and hydrogen gas is needed which limit their application. Therefore, it was interesting to study the hydrogenation of LA in the presence of FA as hydrogen donor.

In the present study several commercial and homemade supported catalysts were tested in the hydrogenation of LA to GVL. Furthermore, different acidic supports were examined. Before reaction the catalysts were reduced at 250 °C for 16 h. The catalytic tests were done in 300 ml Ti autoclave with 1 g catalyst. The molar ratio of LA to FA was 1:1.2. In all the catalytic tests water was used as solvent. The reaction temperature was varied between 180-230 °C and reaction time for 3,6 and 24 h.

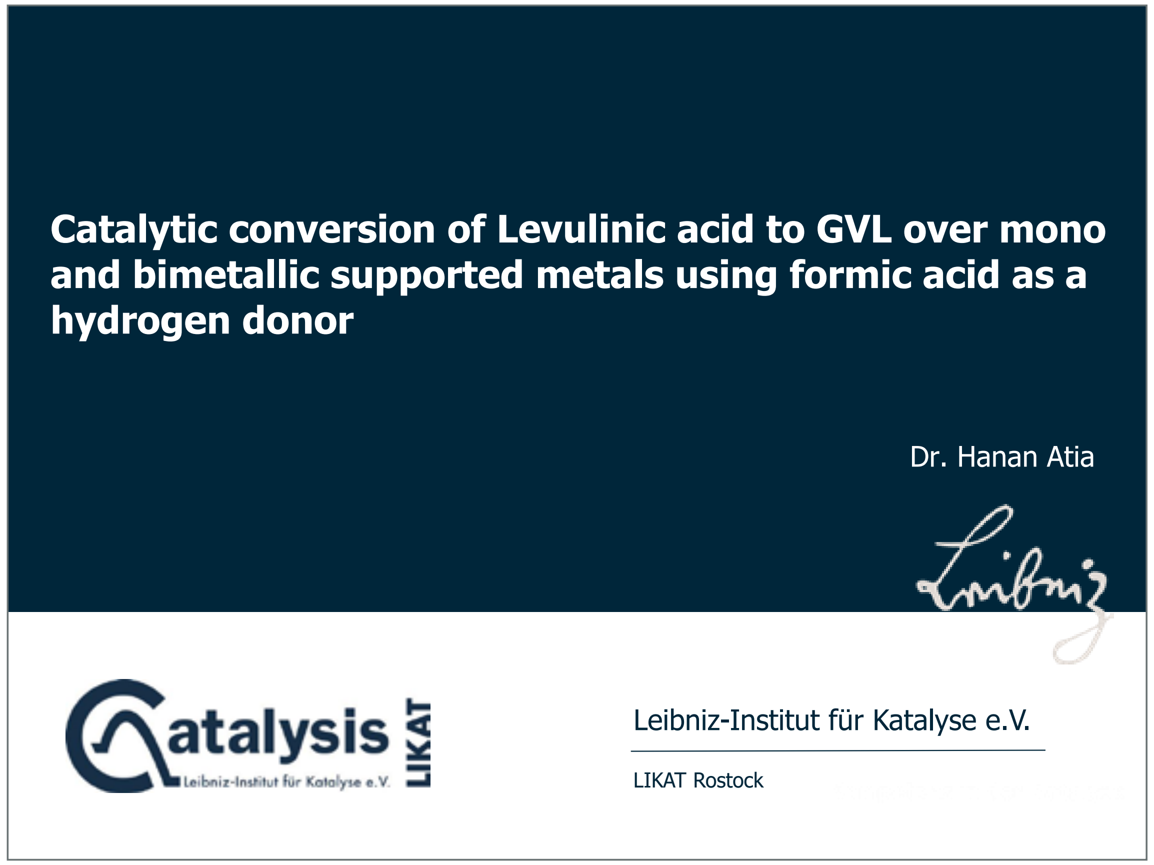
Among the commercial catalysts Ru/C showed 55 % LA conversion and 100 % GVL selectivity at 200 °C after 24h but with high formation of hydrogenation byproducts as methane. In comparison to commercial catalysts homemade prepared 50% Ni supported on Siral-40 (Al_2O_3:SiO_2 60:40) showed 96% LA conversion, 100 % GVL selectivity and with 6.1% methane selectivity at 200 °C and after 24 h. The effect of using different acidic supports as ZrO_2, TiO_2 was studied. The conversion of LA decreased as follows: Siral-40 > TiO_2 > ZrO_2 > SiO_2-ZrO_2. Optimization of the catalyst and the reaction conditions (reaction temperature, reaction time, catalyst reduction temperature) were studied. Also, both the fresh and spent catalysts were characterized using different methods as XRD, TPR, BET, XPS and ICP.

References:

[1] D. He, Q. He, P. Jiang, G. Zhou, R. Hu, W. Fu, Catal. Comm. 125 (2019) 82–86.

[2] E.I. Gürbüz, J.M.R. Gallo, D.M. Alonso, S.G. Wettstein, W.Y. Lim, J.A. Dumesic, Angew. Chem. Int. Ed. 52 (2013) 1270–1274.

[3] K. Yan, T. Lafleur, X. Wu, J. Chai, G. Wu, X. Xie, Chem. Commun. 51 (2015) 6984–6987.



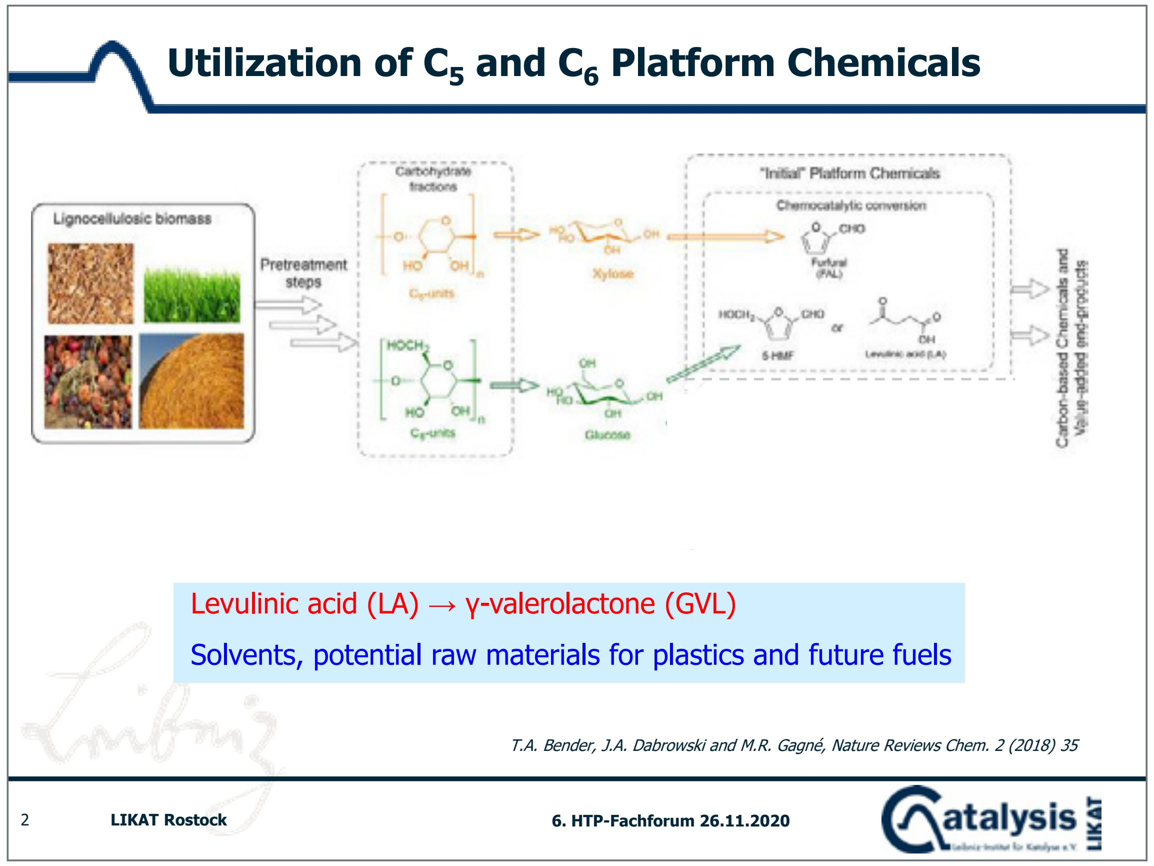
Catalytic conversion of Levulinic acid to GVL over mono and bimetallic supported metals using formic acid as a hydrogen donor

Dr. Hanan Atia

Catalysis LIKAT Leibniz-Institut für Katalyse e.V.

Leibniz-Institut für Katalyse e.V.

LIKAT Rostock



Utilization of C_5 and C_6 Platform Chemicals

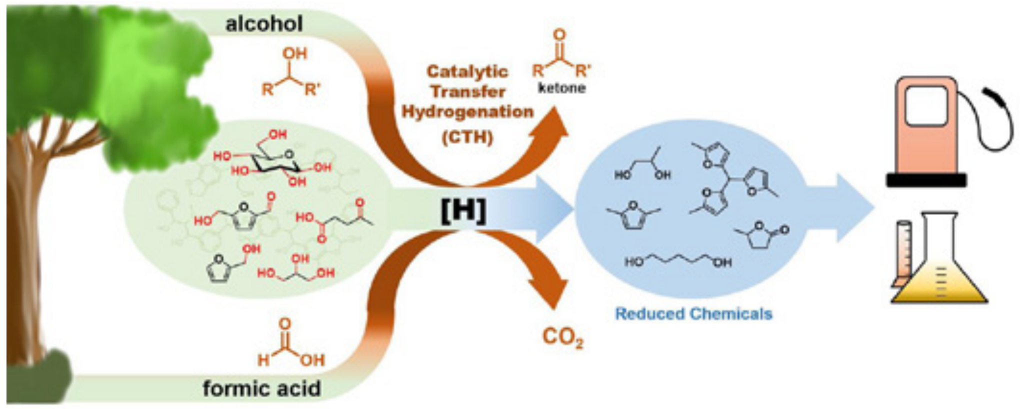
Levulinic acid (LA) → γ-valerolactone (GVL)

Solvents, potential raw materials for plastics and future fuels

T.A. Bender, J.A. Dabrowski and M.R. Gagné, Nature Reviews Chem. 2 (2018) 35

2 LIKAT Rostock 6. HTP-Fachforum 26.11.2020 Catalysis LIKAT

Catalytic Transfer Hydrogenation (CTH)



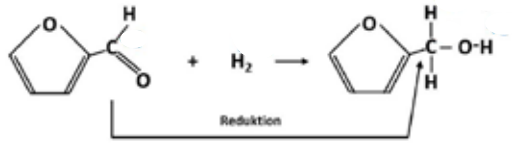
What is transfer hydrogenation ?

- Transfer of hydrogen (not H_2) between organic molecules
- Common hydrogen donors: formic acid (FA) or alcohol

M.J. Gilkey and B. Xu, ACS Catal. 6 (2016) 1420

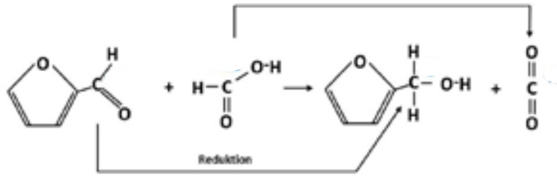
Advantages and disadvantages of CTH

Reaction with molecular H_2



furfural + H_2 → furfuryl alcohol

Transfer hydrogenation



furfural + formic acid → furfuryl alcohol + CO_2

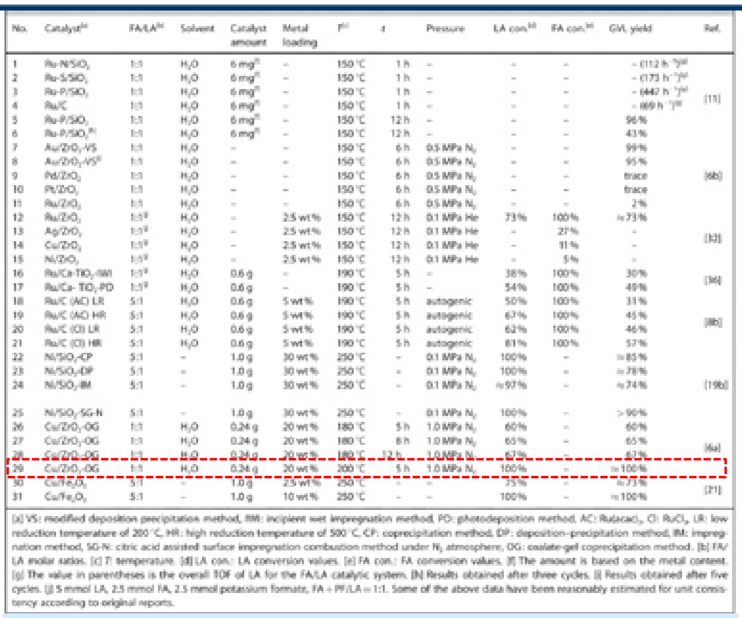
Advantage of using hydrogen donors

- Avoids usage of flammable hydrogen gas under high pressure
- Improves the selectivity towards hydrogenated products

Disadvantage

- Separation of unreacted hydrogen donor from the reaction mixture

Literature survey



No.	Catalyst[a]	FA/LA[b]	Solvent	Catalyst amount	Metal loading	T[c]	t	Pressure	LA con.[d]	FA con.[e]	GVL yield	Ref.
1	Ru-N/SiO_2	1:1	H_2O	6 mg[f]	–	150 °C	1 h	–	–	–	– (112 h^{-1})[g]	[11]
2	Ru-S/SiO_2	1:1	H_2O	6 mg[f]	–	150 °C	1 h	–	–	–	– (173 h^{-1})[g]	
3	Ru-P/SiO_2	1:1	H_2O	6 mg[f]	–	150 °C	1 h	–	–	–	– (447 h^{-1})[g]	
4	Ru/C	1:1	H_2O	6 mg[f]	–	150 °C	1 h	–	–	–	– (69 h^{-1})[g]	
5	Ru-P/SiO_2	1:1	H_2O	6 mg[f]	–	150 °C	12 h	–	–	–	96 %	
6	Ru-P/SiO_2[h]	1:1	H_2O	6 mg[f]	–	150 °C	12 h	–	–	–	43 %	
7	Au/ZrO_2-VS	1:1	H_2O	–	–	150 °C	6 h	0.5 MPa N_2	–	–	99 %	[6b]
8	Au/ZrO_2-VS[i]	1:1	H_2O	–	–	150 °C	6 h	0.5 MPa N_2	–	–	95 %	
9	Pd/ZrO_2	1:1	H_2O	–	–	150 °C	6 h	0.5 MPa N_2	–	–	trace	
10	Pt/ZrO_2	1:1	H_2O	–	–	150 °C	6 h	0.5 MPa N_2	–	–	trace	
11	Ru/ZrO_2	1:1	H_2O	–	–	150 °C	6 h	0.5 MPa N_2	–	–	2 %	
12	Ru/ZrO_2	1:1[j]	H_2O	–	2.5 wt %	150 °C	12 h	0.1 MPa He	73 %	100 %	≈73 %	[32]
13	Ag/ZrO_2	1:1[j]	H_2O	–	2.5 wt %	150 °C	12 h	0.1 MPa He	–	27 %	–	
14	Cu/ZrO_2	1:1[j]	H_2O	–	2.5 wt %	150 °C	12 h	0.1 MPa He	–	11 %	–	
15	Ni/ZrO_2	1:1[j]	H_2O	–	2.5 wt %	150 °C	12 h	0.1 MPa He	–	5 %	–	
16	Ru/Ca-TiO_2-IWI	1:1[j]	H_2O	0.6 g	–	190 °C	5 h	–	38 %	100 %	30 %	[36]
17	Ru/Ca- TiO_2-PD	1:1[j]	H_2O	0.6 g	–	190 °C	5 h	–	54 %	100 %	49 %	
18	Ru/C (AC) LR	5:1	H_2O	0.6 g	5 wt %	190 °C	5 h	autogenic	50 %	100 %	31 %	[8b]
19	Ru/C (AC) HR	5:1	H_2O	0.6 g	5 wt %	190 °C	5 h	autogenic	67 %	100 %	45 %	
20	Ru/C (Cl) LR	5:1	H_2O	0.6 g	5 wt %	190 °C	5 h	autogenic	62 %	100 %	46 %	
21	Ru/C (Cl) HR	5:1	H_2O	0.6 g	5 wt %	190 °C	5 h	autogenic	81 %	100 %	57 %	
22	Ni/SiO_2-CP	5:1	–	1.0 g	30 wt %	250 °C	–	0.1 MPa N_2	100 %	–	≈85 %	[19b]
23	Ni/SiO_2-DP	5:1	–	1.0 g	30 wt %	250 °C	–	0.1 MPa N_2	100 %	–	≈78 %	
24	Ni/SiO_2-IM	5:1	–	1.0 g	30 wt %	250 °C	–	0.1 MPa N_2	≈97 %	–	≈74 %	
25	Ni/SiO_2-SG-N	5:1	–	1.0 g	30 wt %	250 °C	–	0.1 MPa N_2	100 %	–	> 90 %	
26	Cu/ZrO_2-OG	1:1	H_2O	0.24 g	20 wt %	180 °C	5 h	1.0 MPa N_2	60 %	–	60 %	[6a]
27	Cu/ZrO_2-OG	1:1	H_2O	0.24 g	20 wt %	180 °C	8 h	1.0 MPa N_2	65 %	–	65 %	
28	Cu/ZrO_2-OG	1:1	H_2O	0.24 g	20 wt %	180 °C	12 h	1.0 MPa N_2	67 %	–	67 %	
29	Cu/ZrO_2-OG	1:1	H_2O	0.24 g	20 wt %	200 °C	5 h	1.0 MPa N_2	100 %	–	≈100 %	
30	Cu/Fe_2O_3	5:1	–	1.0 g	2.5 wt %	250 °C	–	–	75 %	–	≈73 %	[21]
31	Cu/Fe_2O_3	5:1	–	1.0 g	10 wt %	250 °C	–	–	100 %	–	≈100 %	

[a] VS: modified deposition precipitation method, IWI: incipient wet impregnation method, PD: photodeposition method, AC: $Ru(acac)_3$, Cl: $RuCl_3$, LR: low reduction temperature of 200 °C, HR: high reduction temperature of 500 °C, CP: coprecipitation method, DP: deposition–precipitation method, IM: impregnation method, SG-N: citric acid assisted surface impregnation combustion method under N_2 atmosphere, OG: oxalate-gel coprecipitation method. [b] FA/LA molar ratios. [c] T: temperature. [d] LA con.: LA conversion values. [e] FA con.: FA conversion values. [f] The amount is based on the metal content. [g] The value in parentheses is the overall TOF of LA for the FA/LA catalytic system. [h] Results obtained after three cycles. [i] Results obtained after five cycles. [j] 5 mmol LA, 2.5 mmol FA, 2.5 mmol potassium formate, FA + PF/LA = 1:1. Some of the above data have been reasonably estimated for unit consistency according to original reports.

Ru, Ag, Ni and Cu showed potential for the hydrogenation of LA

Z. Yu. et al., ChemSusChem, 13 (2020) 2916 – 2930

Aim of the work

- Preparation of inexpensive mono and bimetallic catalysts
- Screening of the prepared catalysts using water as solvent and formic acid as hydrogen source
- Optimization of the reaction condition
- Studying the stability of the best catalyst

Experimental

Catalyst preparation

- Metals: Ni, Cu, Co, Ru
- Support: Siral-40 (Al_2O_3:SiO_2 = 60:40)
- Loading of the metal: 50%
- Preparation method: Co-precipitation
- Calcination temperature: 400 °C
- Reduction temperature: 200-400 °C

Reaction condition

- Autoclave= 300 ml
- Reaction temperature = 200-220 °C
- Stirring speed = 650 rpm
- Reaction time = 3, 5, 8 and 24 h
- Catalyst mass = 1 g
- LA / FA = 3.0 g: 1.5 g = 1: 1.2 (mol)
- Solvent: water

Results – Screening

1 g catalyst, LA/FA = 1:1.2 in water, 200 °C, 24 h

Catalyst	X_{LA}%	X_{FA}%	S_{GVL}%*	S_{CH4}%**	S_{C2H6}%	S_{C3H8}%
5% Ru/Siral 40***	31.7	100.0	100.0	16.29	0.54	0.54
50% Cu/Siral 40	36.6	100.0	100.0	0.08	0.002	0.001
50% Ni/Siral 40	95.1	100.0	100.0	4.39	0.19	0.13
50% Ni/Siral 40****	95.2	100.0	100.0	5.78	0.23	0.14
50% Ni/Siral 40 (800 °C)	45.2	100.0	100.0	4.28	0.37	0.20

*Selectivity of GVL calculated based on levulinic acid (LA); **Selectivity of gaseous products based on HCOOH (FA);
***Siral 40: Al_2O_3/SiO_2 = 60:40, 500 m²/g; ****Experiment repeated with the same catalyst lot for reproduction

- Ni metal gave the highest LA conversion of 95%
- Results were reproducible
- Increasing support calcination temperature decreased LA conversion to the half, might be due to loss in surface area

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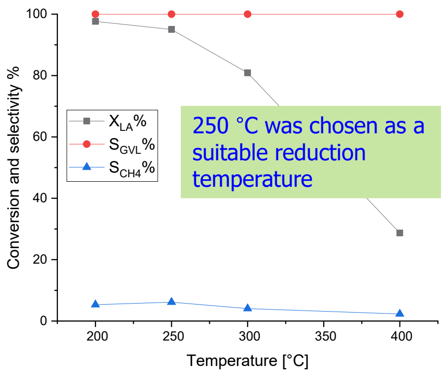
Catalyst optimization – reduction temperature

1 g 50% Ni/Siral-40, LA/FA = 1:1.2 in water, 200 °C, 24 h



Reduction temperature [°C]	Metal dispersion [%]	Surface area [m²/g]
250	1.6	214.0
400	2.6	216.0

- LA conversion decreases with increasing pre-reduction temperature
- Pre-reduction at 200 °C resulted in complete conversion but the catalyst is not stable
- Selectivity towards CH_4 is 5% at 200 °C and decreases on increasing reduction temperature

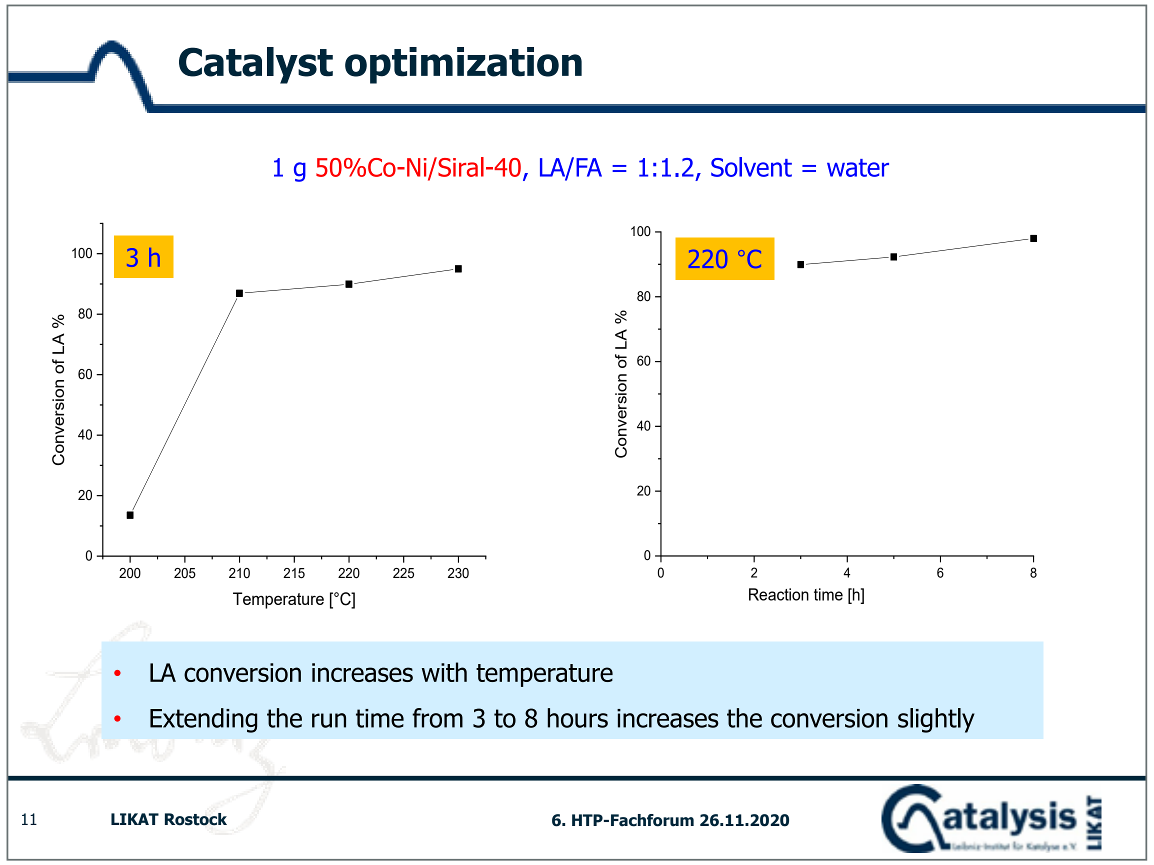
Catalyst optimization – bimetallic materials

1 g catalyst, LA/FA = 1:1.2 in water, 3 h, 220 °C

Catalyst	X_{LA}%	X_{FA}%	S_{GVL}%*	S_{CH4}%**	S_{C2H6}%	S_{C3H8}%
50%Ni/Siral-40 Co-precipitation	25.0	100.0	100.0	5.7	0.24	0.10
50%Cu+Ni/Siral-40 Co-precipitation	8.0	100.0	100.0	0.04	0.10	0.50
50%Co+Ni/Siral-40 Co-precipitation	89.9	100.0	100.0	4.1	0.66	0.43
50%Co+Ni/Siral-40 mechanical mixing	76.0	100.0	100.0	6.0	0.10	0.40

*Selectivity of GVL based on levulinic acid (LA), **Selectivity of gaseous products based on HCOOH (FA)

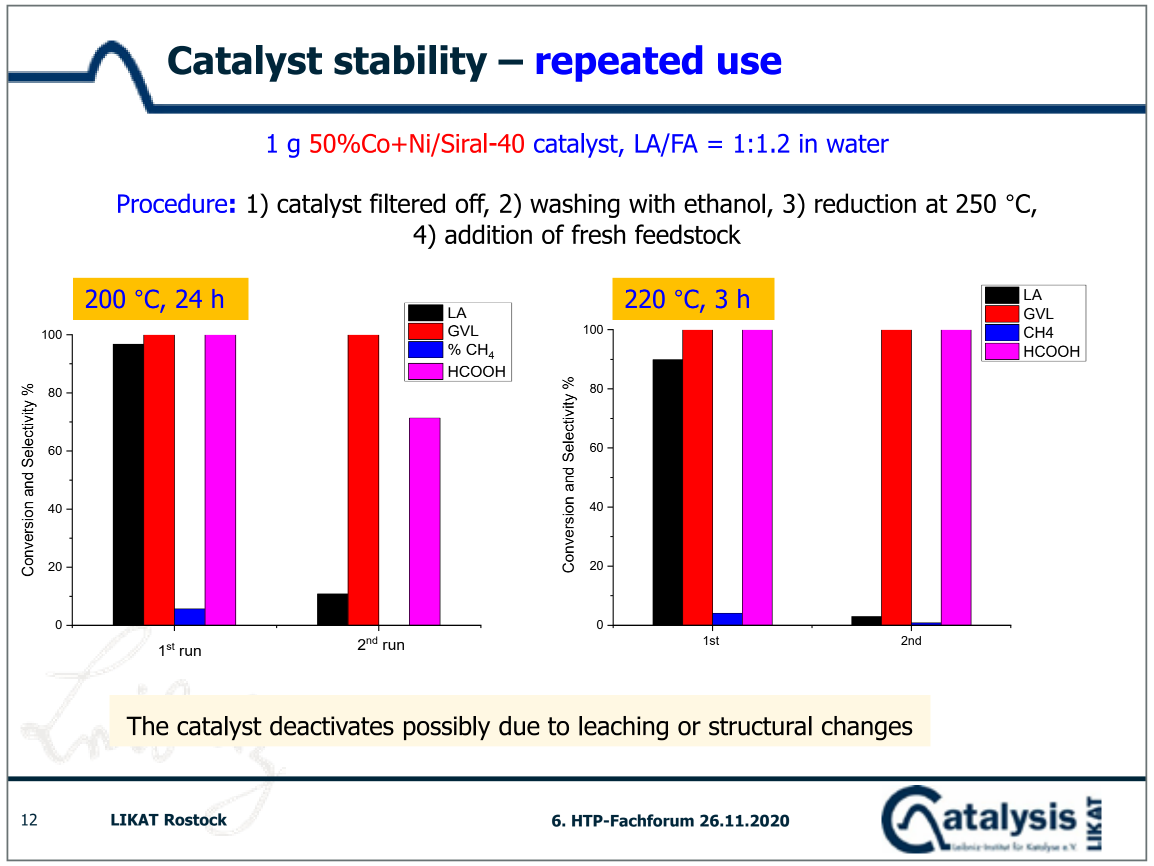
- Addition of Co to Ni increases LA conversion more than 3 times
- As a second metal, Cu is less active than Co
- Ni+Co catalyst prepared by mechanical mixing also achieved good results



Catalyst optimization

1 g 50%Co-Ni/Siral-40, LA/FA = 1:1.2, Solvent = water

- LA conversion increases with temperature
- Extending the run time from 3 to 8 hours increases the conversion slightly

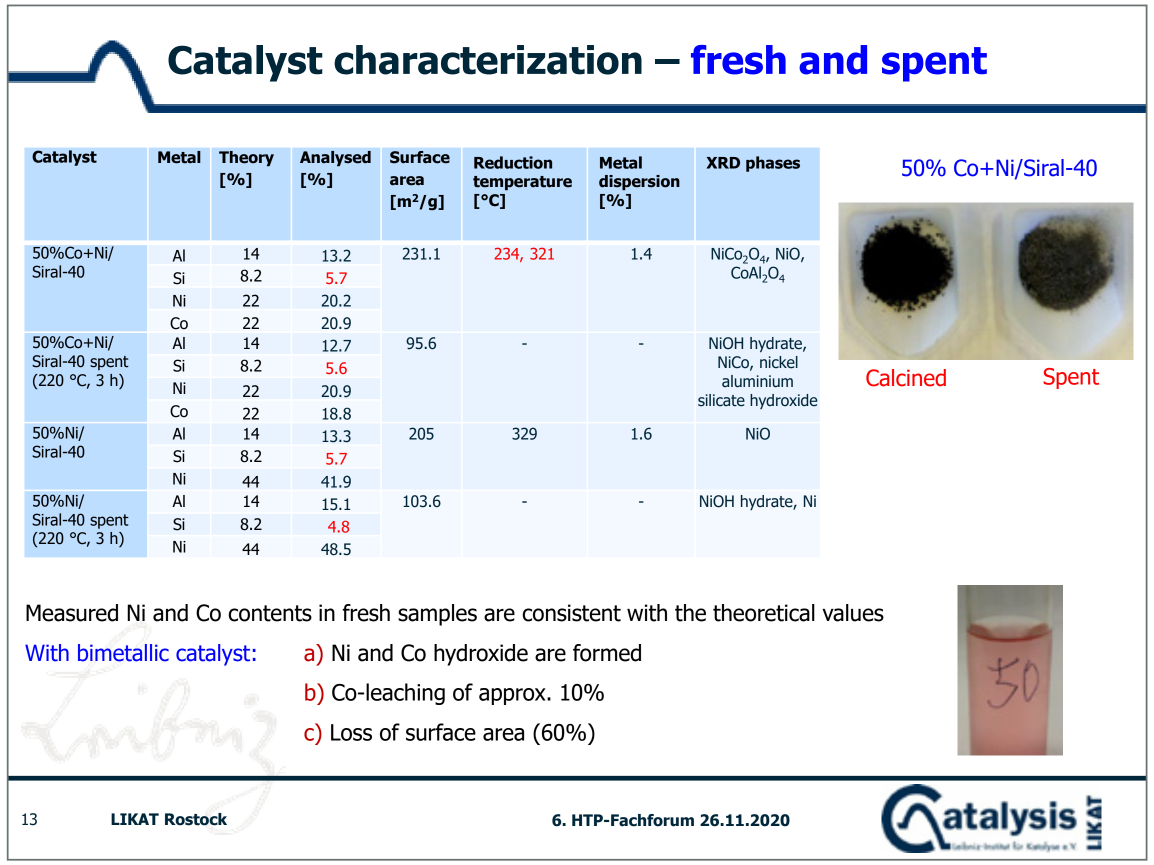


Catalyst stability – repeated use

1 g 50%Co+Ni/Siral-40 catalyst, LA/FA = 1:1.2 in water

Procedure: 1) catalyst filtered off, 2) washing with ethanol, 3) reduction at 250 °C, 4) addition of fresh feedstock

The catalyst deactivates possibly due to leaching or structural changes



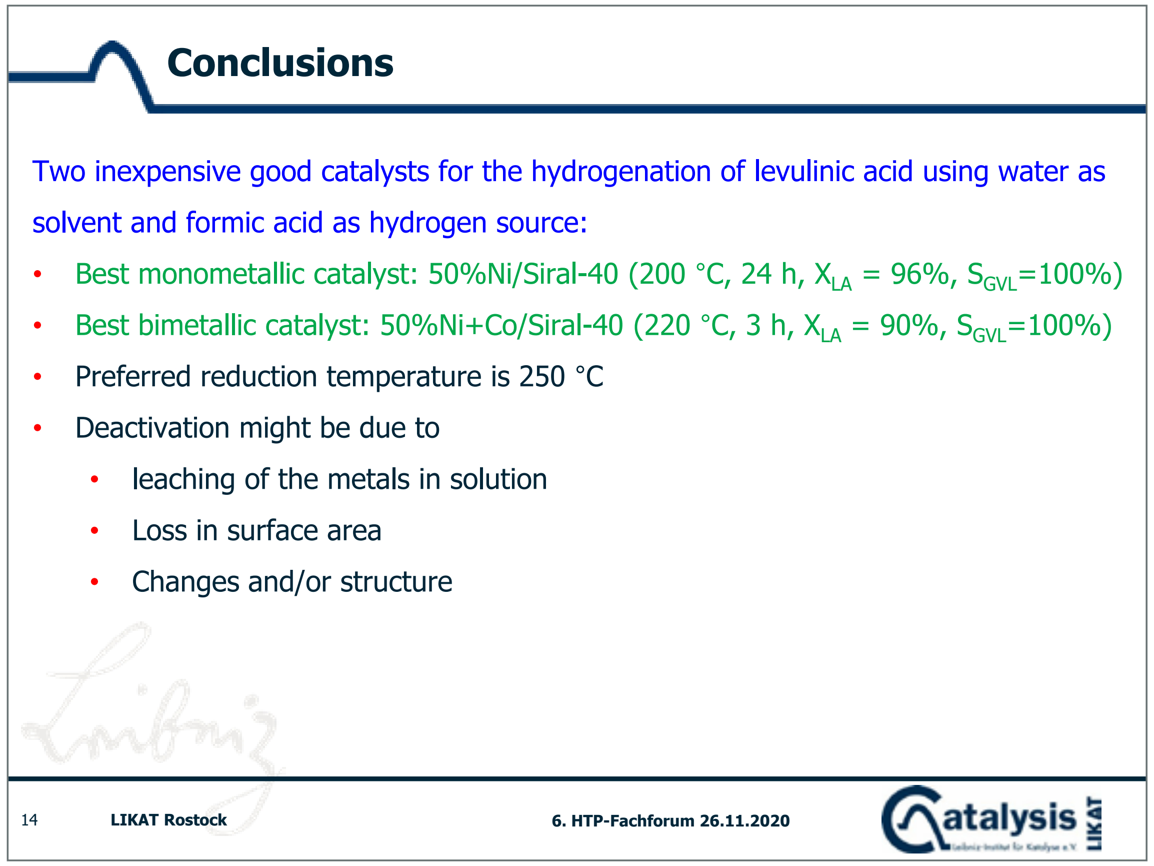
Catalyst characterization – fresh and spent

Catalyst	Metal	Theory [%]	Analysed [%]	Surface area [m²/g]	Reduction temperature [°C]	Metal dispersion [%]	XRD phases
50%Co+Ni/ Siral-40	Al	14	13.2	231.1	234, 321	1.4	$NiCo_2O_4$, NiO, $CoAl_2O_4$
	Si	8.2	5.7				
	Ni	22	20.2				
	Co	22	20.9				
50%Co+Ni/ Siral-40 spent (220 °C, 3 h)	Al	14	12.7	95.6	-	-	NiOH hydrate, NiCo, nickel aluminium silicate hydroxide
	Si	8.2	5.6				
	Ni	22	20.9				
	Co	22	18.8				
50%Ni/ Siral-40	Al	14	13.3	205	329	1.6	NiO
	Si	8.2	5.7				
	Ni	44	41.9				
50%Ni/ Siral-40 spent (220 °C, 3 h)	Al	14	15.1	103.6	-	-	NiOH hydrate, Ni
	Si	8.2	4.8				
	Ni	44	48.5				

50% Co+Ni/Siral-40

Measured Ni and Co contents in fresh samples are consistent with the theoretical values

With bimetallic catalyst:
a) Ni and Co hydroxide are formed
b) Co-leaching of approx. 10%
c) Loss of surface area (60%)



Conclusions

Two inexpensive good catalysts for the hydrogenation of levulinic acid using water as solvent and formic acid as hydrogen source:

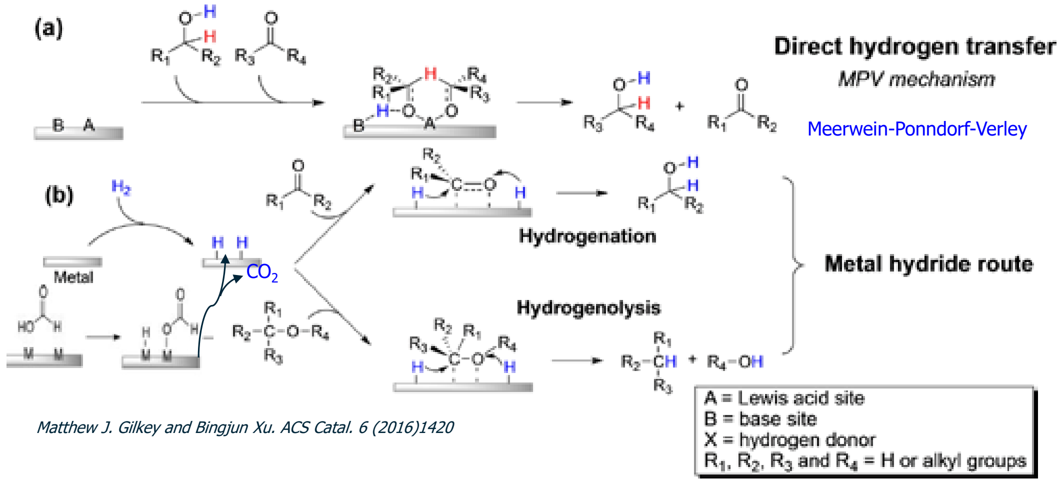
- Best monometallic catalyst: 50%Ni/Siral-40 (200 °C, 24 h, X_{LA} = 96%, S_{GVL}=100%)
- Best bimetallic catalyst: 50%Ni+Co/Siral-40 (220 °C, 3 h, X_{LA} = 90%, S_{GVL}=100%)
- Preferred reduction temperature is 250 °C
- Deactivation might be due to
  - leaching of the metals in solution
  - Loss in surface area
  - Changes and/or structure

Acknowledgments

Dr. Sebastian Wohlrab
Dr. Udo Armbruster
Herr Reinhard Eckelt
Frau Astrid Lehmann
Frau Anja Simmula

Thank you for your attention

CTH - mechanism using heterogeneous catalysts



A = Lewis acid site
B = base site
X = hydrogen donor
R_1, R_2, R_3 and R_4 = H or alkyl groups

Matthew J. Gilkey and Bingjun Xu. ACS Catal. 6 (2016)1420

- In direct hydrogen transfer, the α-hydrogen is transferred from the α-carbon of the alcohol or formic acid to the carbonyl carbon and a six-membered ring is formed.
- Via metal hydride route, dissociative adsorption of H_2 occurs through activation of the hydrogen donor

Ekaterina Ovsyannikova, Universität Hohenheim

Valorization of by-products from hydrothermal liquefaction-based biofuel production through nutrient recovery

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The technology readiness level of hydrothermal liquefaction (HTL) is rapidly increasing, enabling the processing of more difficult biomasses such as sewage sludge or animal manure to crude bio-oils, ready for upgrading. The first pilot plants generated valuable insights into continuous production and subsequent fuel refining. However, since the feedstock for HTL has an increased content of interesting nutrients such as nitrogen and phosphorous, an important question arises: how can we improve oil quality and save catalysts from heteroatoms without merely producing waste by-products, but recovering these nutrients in the form of a high-quality fertilizer?

This study addresses nutrient recovery from by-products that were generated along the biofuel production chain in the HyFlexFuel process. Sewage sludge and manure were converted into crude bio-oil at 350 °C and 220 bars in the HTL pilot plant system operated by Aarhus University. The analyses of the product streams of this conversion provided the distribution of most relevant nutrients between them and identified the initial strategy for nutrient recovery. Combining the liquid by-product and the leachate from solid by-product of HTL as sources of ammonium and phosphate was found to be efficient for simultaneous P and N recovery in the form of a ready-to-use slow-release fertilizer – Struvite ($MgNH_4PO_4 \cdot 6H_2O$). The examination of correlations between the quality of the obtained fertilizer product and crucial process parameters (e.g. the mixing ratio, type of stirring and content of foreign ions) at laboratory scale supplied basic data for the following upscaling. This study will therefore present the first experiences with the operation of a struvite crystallization reactor with HTL mass flows arising from the HyFlexFuel project.

HyFlexFuel

UNIVERSITY OF HOHENHEIM

26.11.2020

Valorization of by-products from hydrothermal liquefaction-based biofuel production through nutrient recovery

E. Ovsyannikova, G. C. Becker, A. Kruse

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

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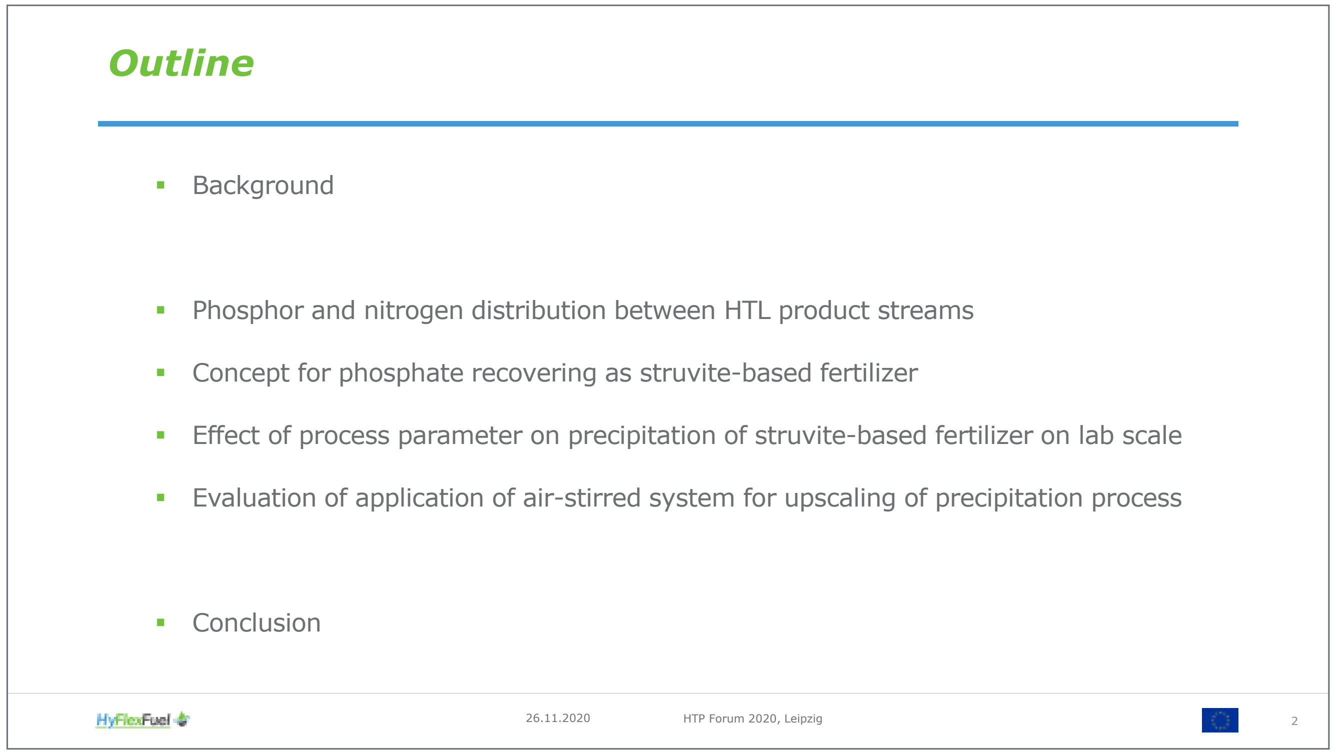

Outline

- Background
- Phosphor and nitrogen distribution between HTL product streams
- Concept for phosphate recovering as struvite-based fertilizer
- Effect of process parameter on precipitation of struvite-based fertilizer on lab scale
- Evaluation of application of air-stirred system for upscaling of precipitation process
- Conclusion

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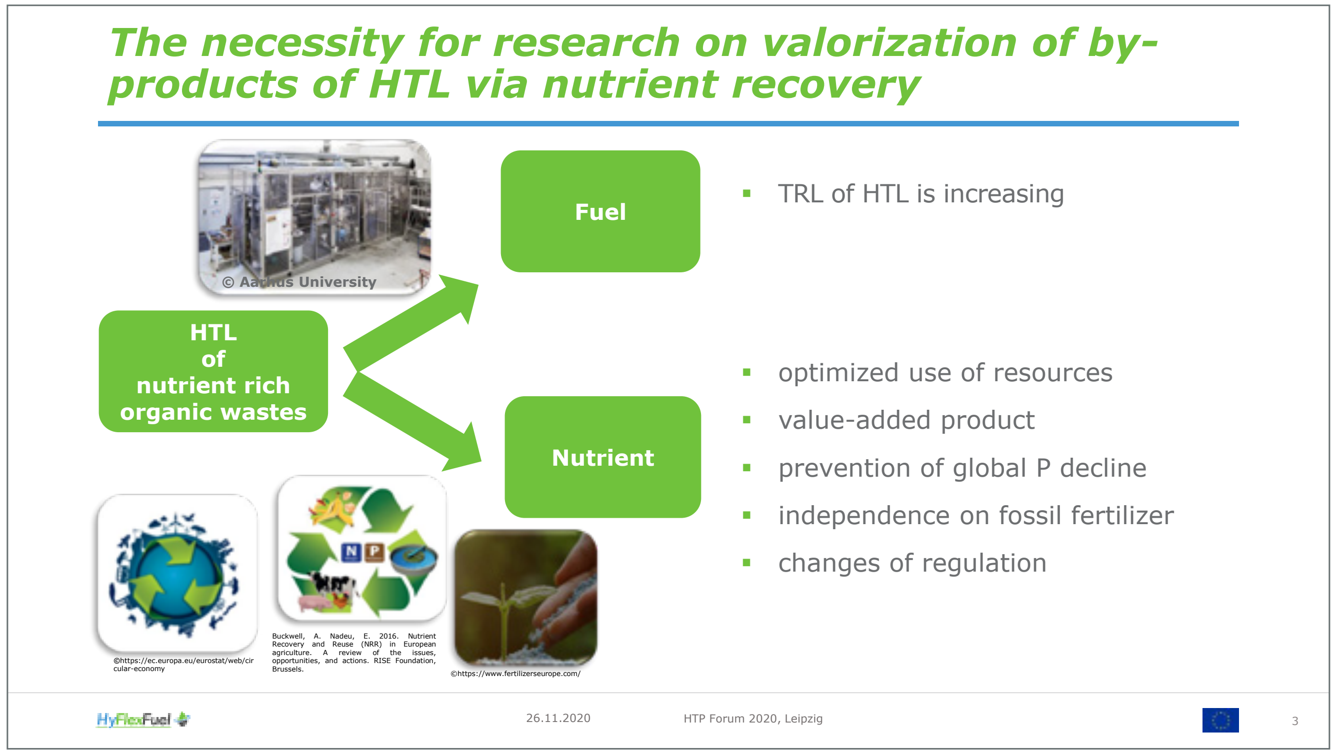

The necessity for research on valorization of by-products of HTL via nutrient recovery

- TRL of HTL is increasing

- optimized use of resources
- value-added product
- prevention of global P decline
- independence on fossil fertilizer
- changes of regulation

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Buckwell, A. Nadeu, E. 2016. Nutrient Recovery and Reuse (NRR) in European agriculture. A review of the issues, opportunities, and actions. RISE Foundation, Brussels.

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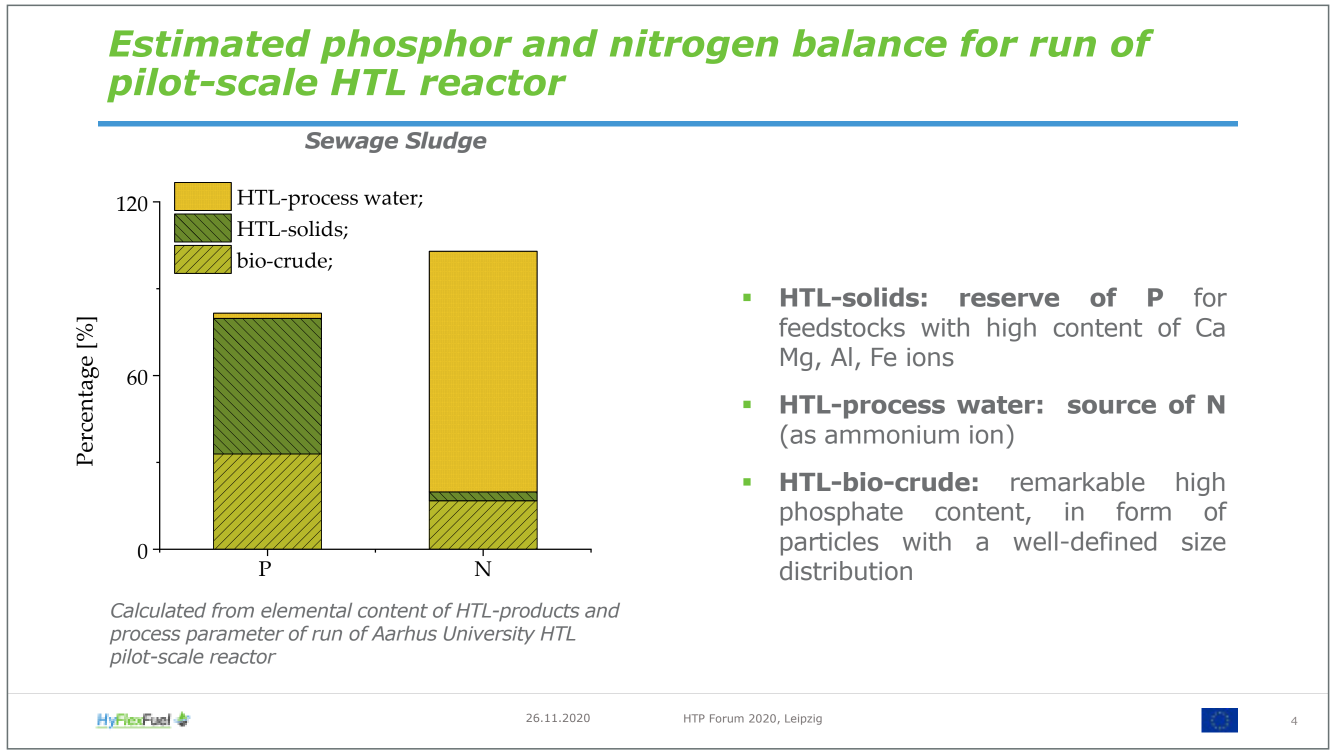

Estimated phosphor and nitrogen balance for run of pilot-scale HTL reactor

Sewage Sludge

Calculated from elemental content of HTL-products and process parameter of run of Aarhus University HTL pilot-scale reactor

- **HTL-solids: reserve of P** for feedstocks with high content of Ca Mg, Al, Fe ions
- **HTL-process water: source of N** (as ammonium ion)
- **HTL-bio-crude:** remarkable high phosphate content, in form of particles with a well-defined size distribution

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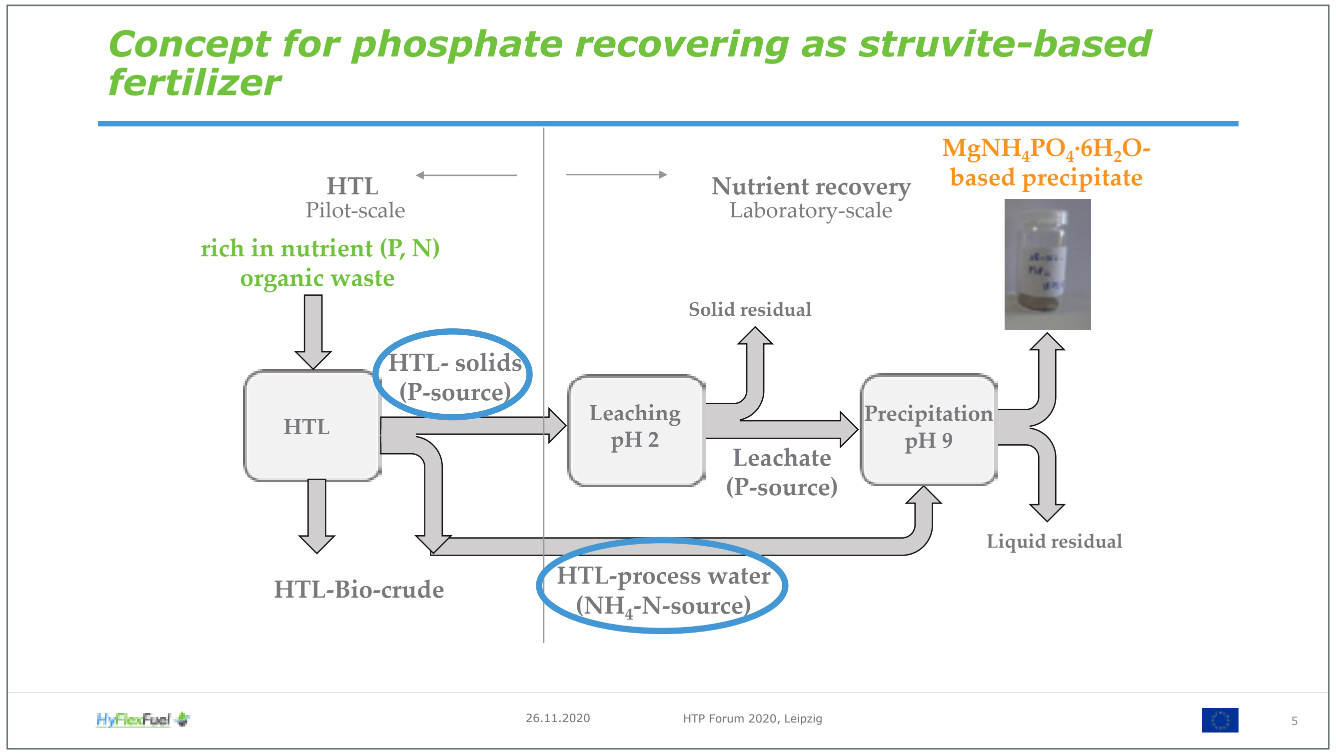

Concept for phosphate recovering as struvite-based fertilizer

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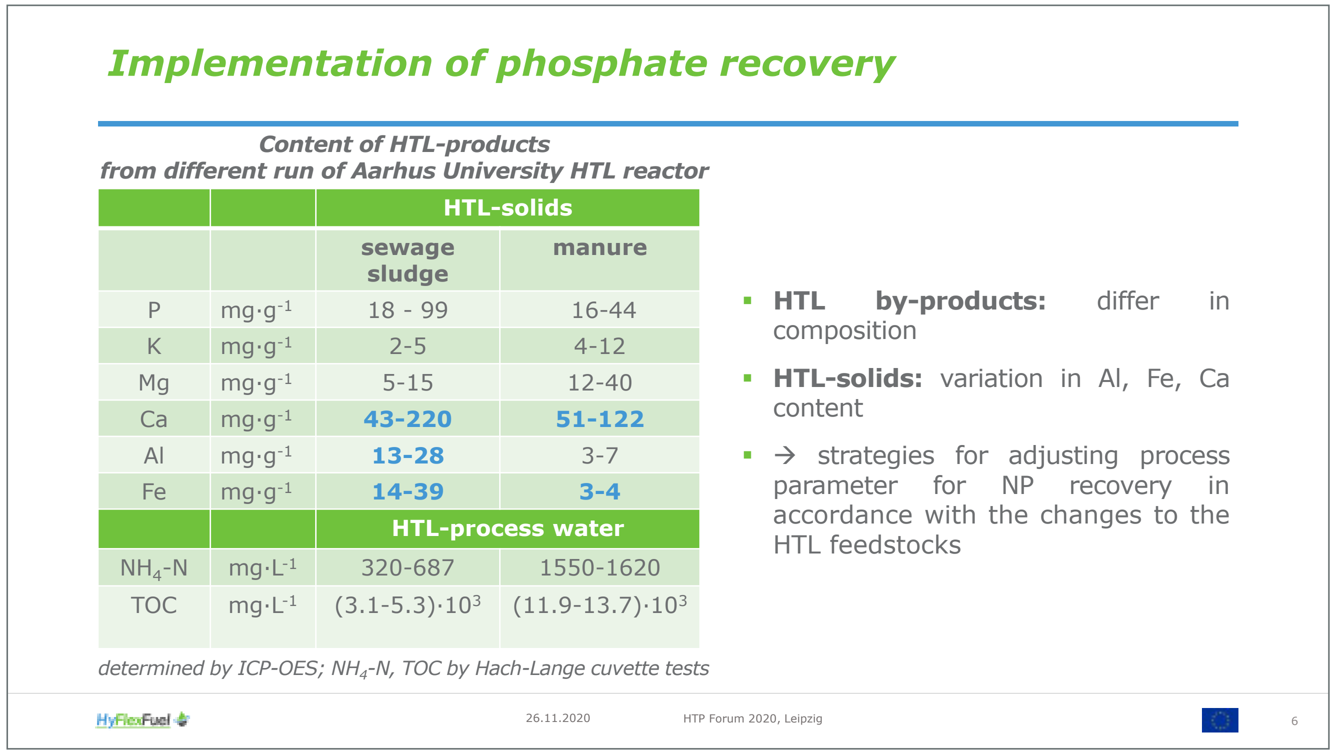

Implementation of phosphate recovery

Content of HTL-products from different run of Aarhus University HTL reactor

		HTL-solids	
		sewage sludge	**manure**
P	$mg{\cdot}g^{-1}$	18 - 99	16-44
K	$mg{\cdot}g^{-1}$	2-5	4-12
Mg	$mg{\cdot}g^{-1}$	5-15	12-40
Ca	$mg{\cdot}g^{-1}$	**43-220**	**51-122**
Al	$mg{\cdot}g^{-1}$	**13-28**	3-7
Fe	$mg{\cdot}g^{-1}$	**14-39**	**3-4**
		HTL-process water	
NH_4-N	$mg{\cdot}L^{-1}$	320-687	1550-1620
TOC	$mg{\cdot}L^{-1}$	$(3.1\text{-}5.3){\cdot}10^3$	$(11.9\text{-}13.7){\cdot}10^3$

determined by ICP-OES; NH_4-N, TOC by Hach-Lange cuvette tests

- **HTL by-products:** differ in composition
- **HTL-solids:** variation in Al, Fe, Ca content
- → strategies for adjusting process parameter for NP recovery in accordance with the changes to the HTL feedstocks

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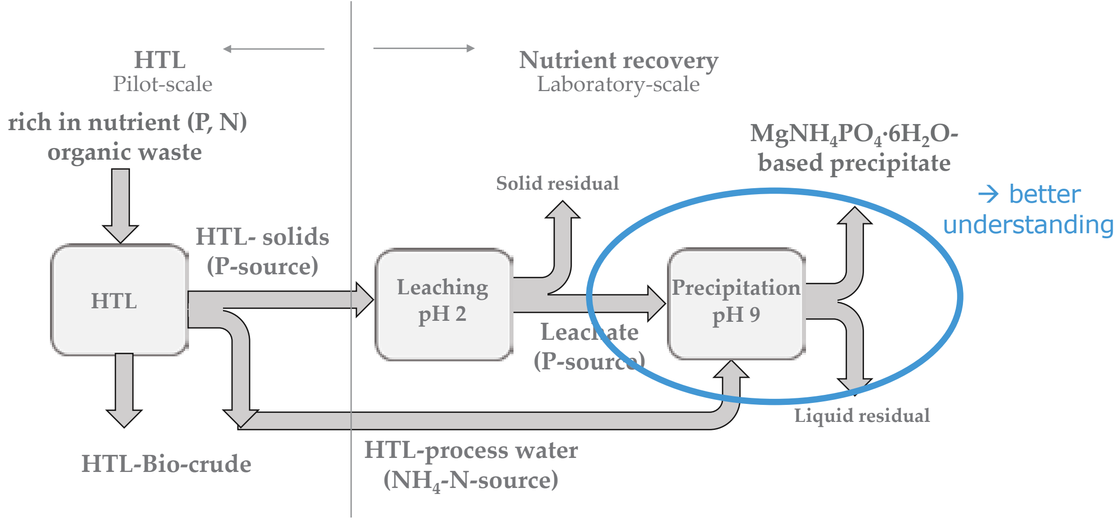
Implementation of phosphate recovery



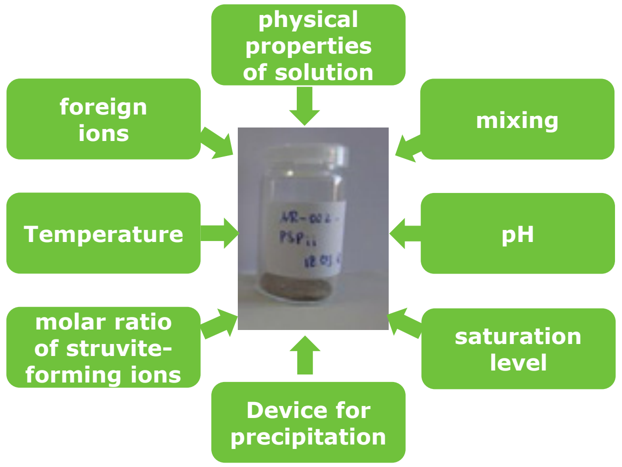
Composition of HTL-process water and leachate from HTL-solids

	Sewage sludge		Manure	
	Leachate	**HTL-process water**	**Leachate**	**HTL-process water**
	[mg·L^{-1}]			
P	**3089**	1	**4455**	0.4
Mg	669	1	**2277**	18
Ca	661	102	619	177
Fe	**3065**	<0.3	**322**	<0.3
Al	**1600**	<1.5	**260**	<1.5
NH$_4$-N	NA	**454**	NA	**1550**

Leachate: mixing the HTL-solids with 1M sulfuric acid in 1-to-10 ratio over night; elemental content determined by ICP-OES

- **P content:** in same order of magnitude
- **(Al+Fe+Ca)/P:** sewage sludge 1.3 and manure 0.2 mol·mol^{-1}
- **NH$_4$-N content**: 3 times higher for manure HTL-process water

Effect of process parameter on precipitation of struvite-based fertilizer



- **Composition of precipitate** → fit to the Fertilizer Product Regulation
- **Morphology of particle** → the rheological properties of suspension, filtration efficiency, formation of granules
- **Size of particle** → fertilizer effectiveness, further processing, environmental aspects
- Efficiency of precipitation, P-recovery

Precipitation experiments on lab scale (Titrator, SI-Analytics TitroLine 7000)

- **Molar ratio of struvite-forming ions**
  - Mix ratio of process water and leachate (NH$_4$-N : P)
  - Dosage of MgCl·6H$_2$O (Mg : P)
- **Presence of foreign ions**
- **Changes of pH**

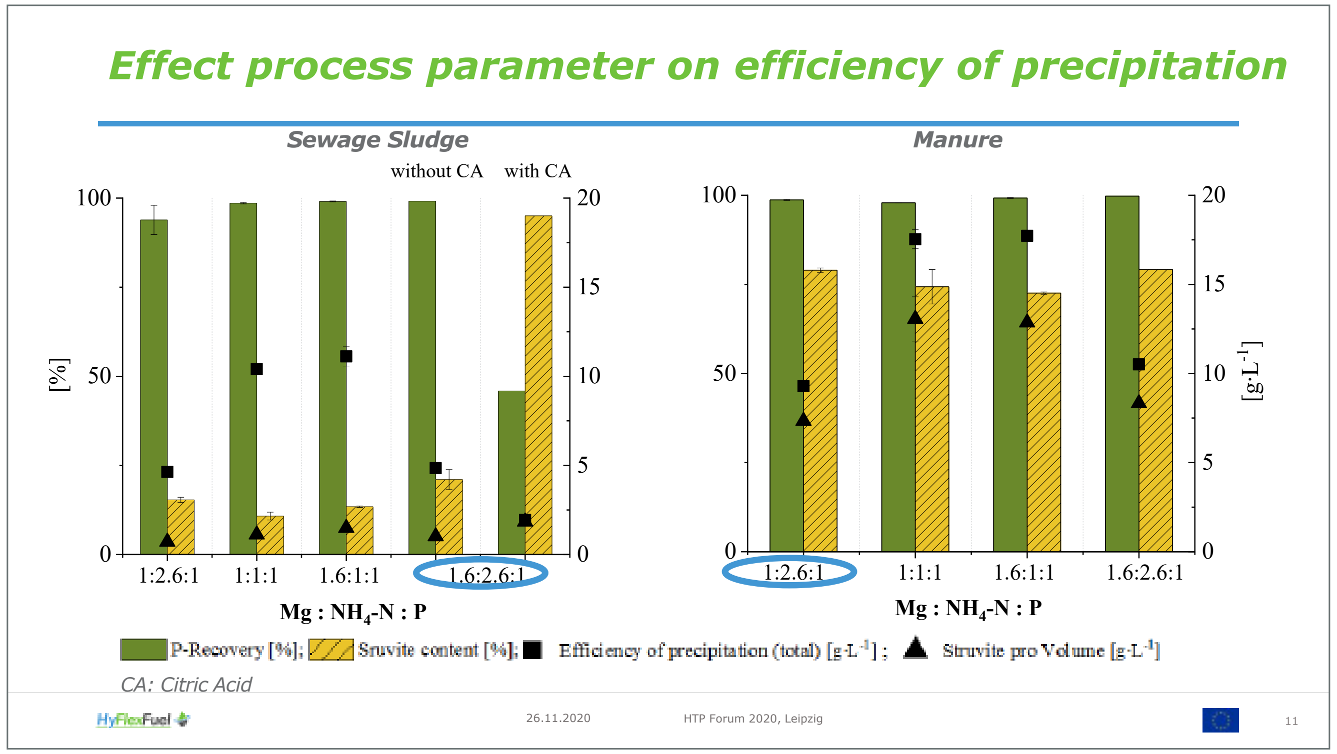
$$\text{P recovery} = \frac{m_{\text{Pin}} - m_{\text{Pout}}}{m_{\text{Pin}}} 100\% \ [\%]$$

$$\text{Stuvite content} = \frac{n_{\text{N in Precipitate}} \cdot M_{\text{struvite}}}{m_{\text{precipitate}}} 100 \ [\%]$$

$$\text{Efficiency of precipitation} = \frac{m_{\text{precipitate}}}{V_L + V_{PW}} \ [gL^{-1}]$$

$$\text{Struvite pro Volume} = \frac{m_{\text{struvite}}}{V_L + V_{PW}} \ [gL^{-1}]$$

Elemental composition



Effect process parameter on efficiency of precipitation

CA: Citric Acid

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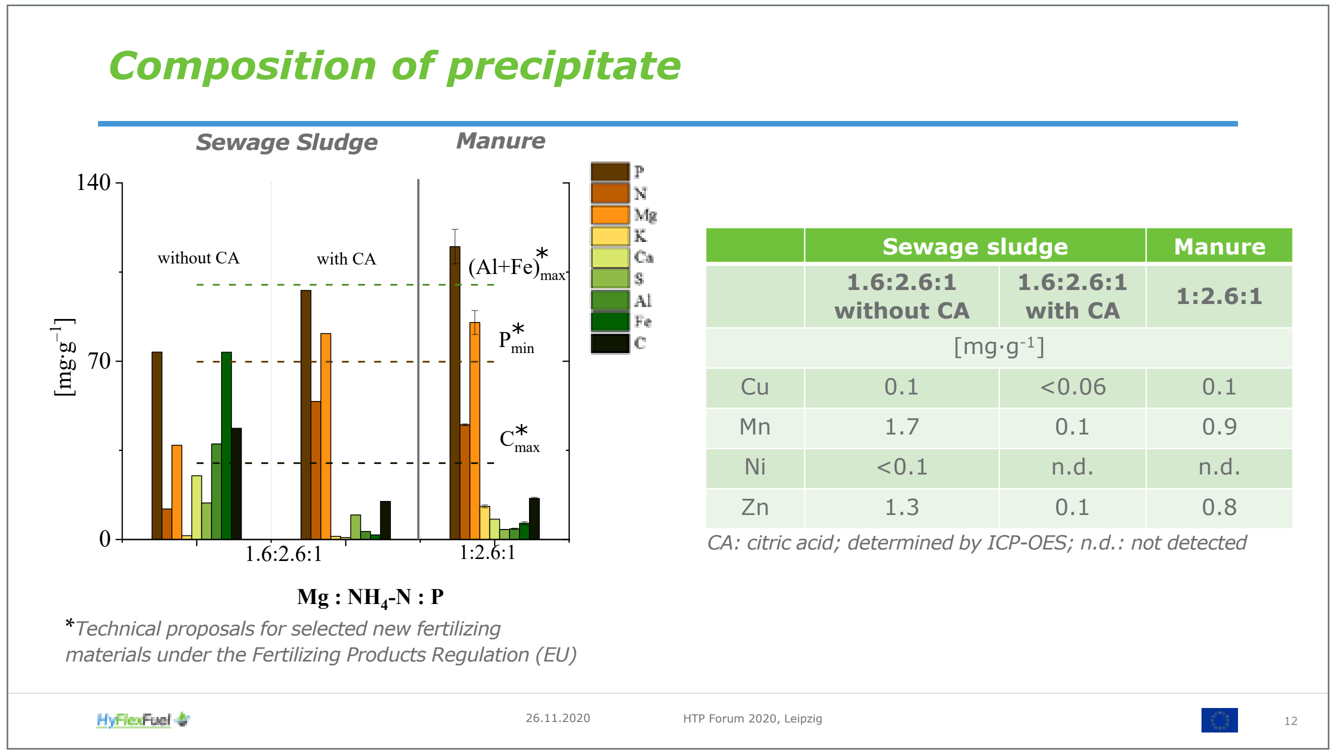

Composition of precipitate

	Sewage sludge		Manure
	1.6:2.6:1 without CA	**1.6:2.6:1 with CA**	**1:2.6:1**
	[mg·g^{-1}]		
Cu	0.1	<0.06	0.1
Mn	1.7	0.1	0.9
Ni	<0.1	n.d.	n.d.
Zn	1.3	0.1	0.8

CA: citric acid; determined by ICP-OES; n.d.: not detected

**Technical proposals for selected new fertilizing materials under the Fertilizing Products Regulation (EU)*

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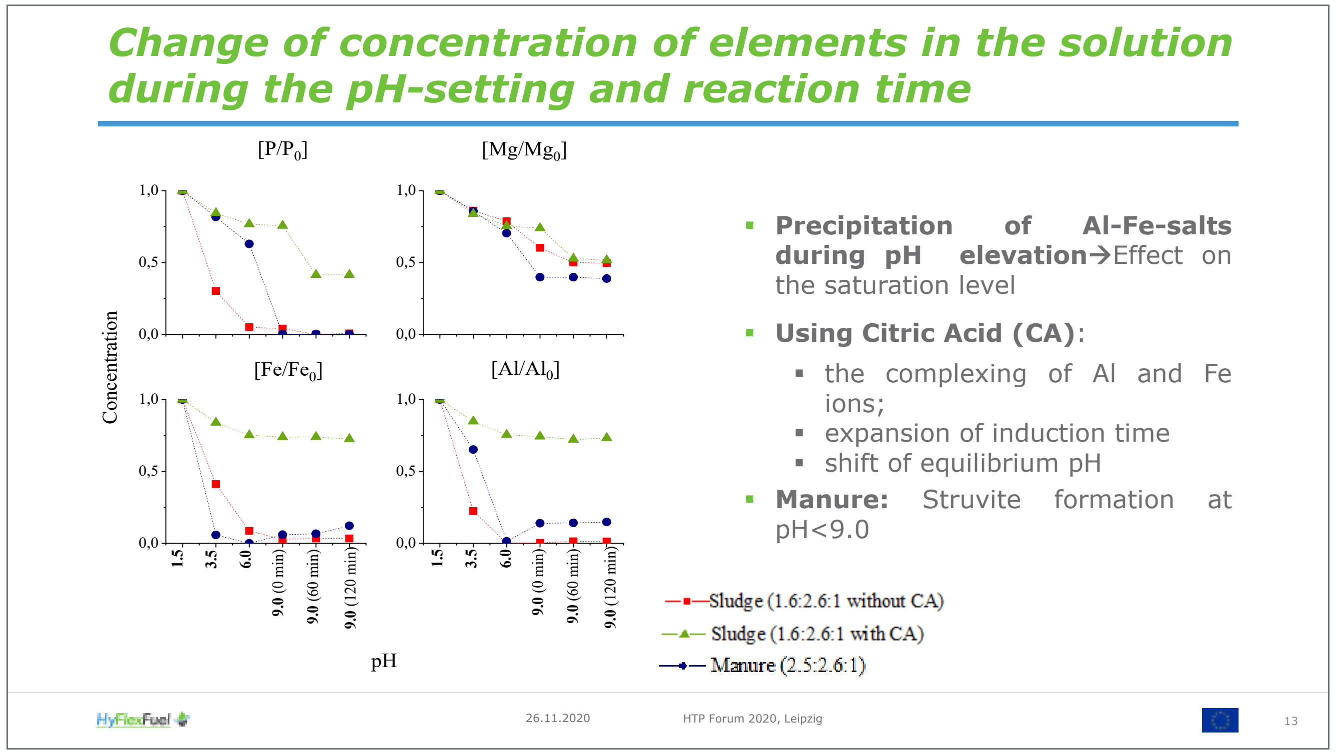

Change of concentration of elements in the solution during the pH-setting and reaction time

- **Precipitation of Al-Fe-salts during pH elevation**→Effect on the saturation level
- **Using Citric Acid (CA)**:
    - the complexing of Al and Fe ions;
    - expansion of induction time
    - shift of equilibrium pH
- **Manure:** Struvite formation at pH<9.0

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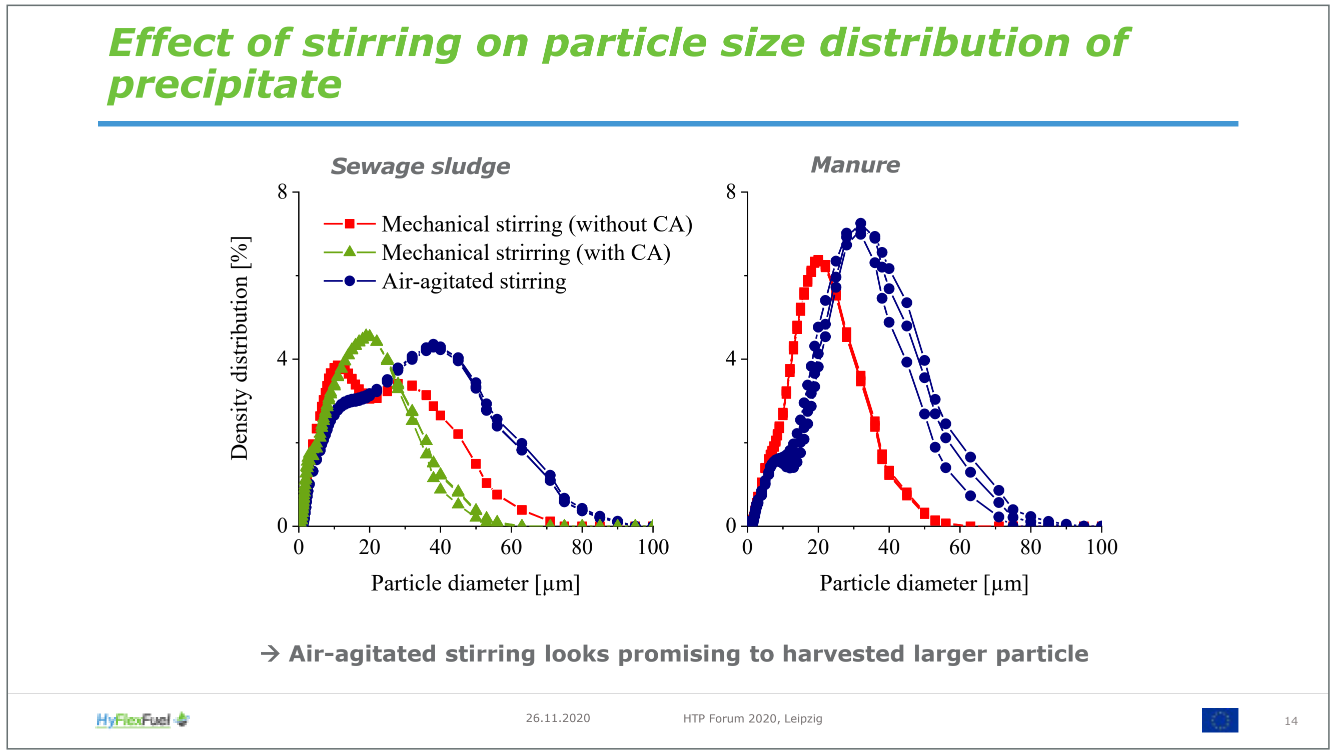

Effect of stirring on particle size distribution of precipitate

→ **Air-agitated stirring looks promising to harvested larger particle**

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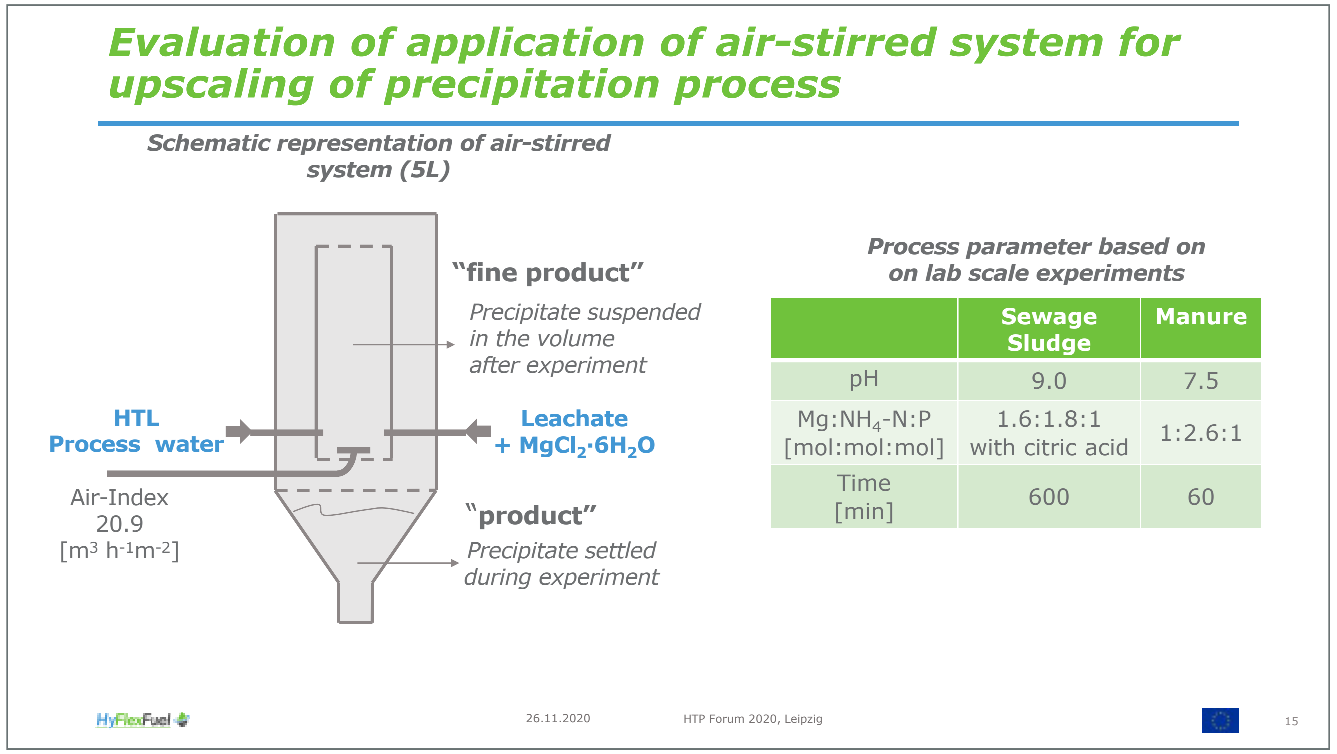

Evaluation of application of air-stirred system for upscaling of precipitation process

Schematic representation of air-stirred system (5L)

Process parameter based on on lab scale experiments

	Sewage Sludge	Manure
pH	9.0	7.5
Mg:NH_4-N:P [mol:mol:mol]	1.6:1.8:1 with citric acid	1:2.6:1
Time [min]	600	60

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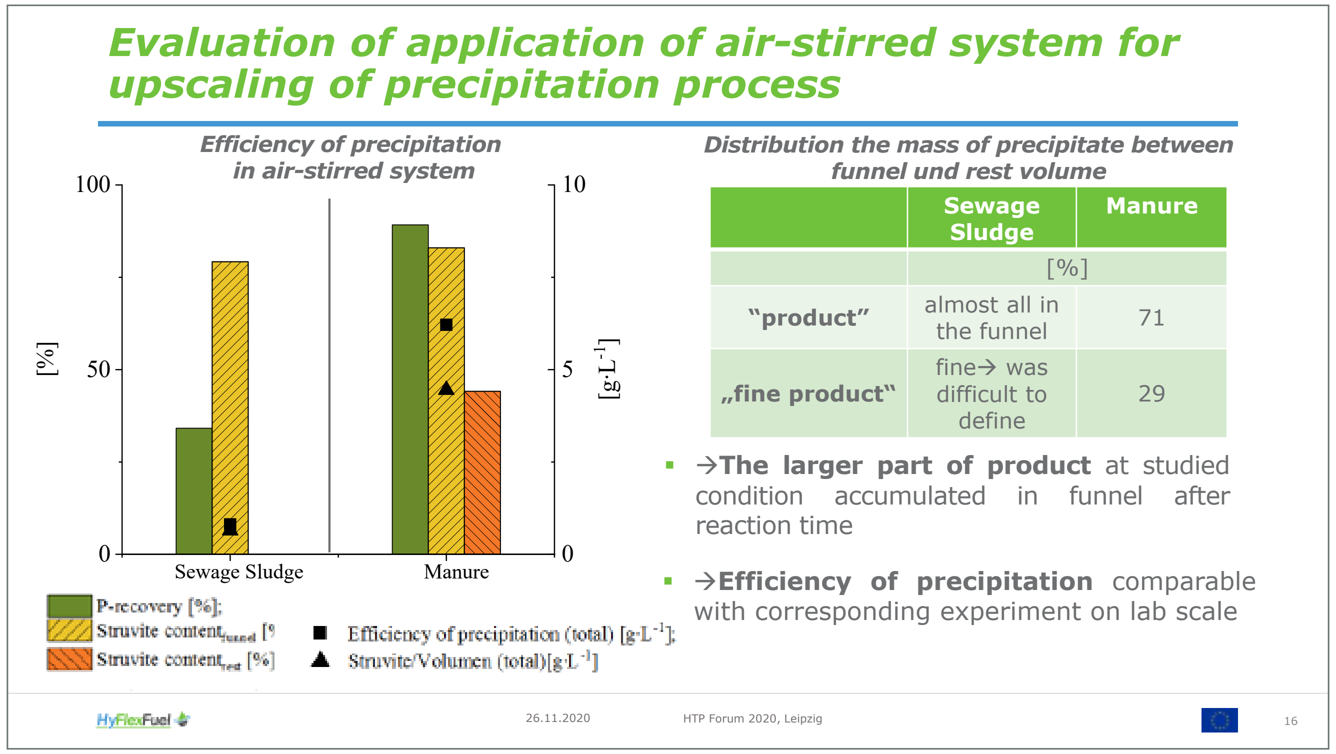

Evaluation of application of air-stirred system for upscaling of precipitation process

Efficiency of precipitation in air-stirred system

Distribution the mass of precipitate between funnel und rest volume

	Sewage Sludge	Manure
	[%]	
"product"	almost all in the funnel	71
„fine product"	fine→ was difficult to define	29

- **→The larger part of product** at studied condition accumulated in funnel after reaction time
- **→Efficiency of precipitation** comparable with corresponding experiment on lab scale

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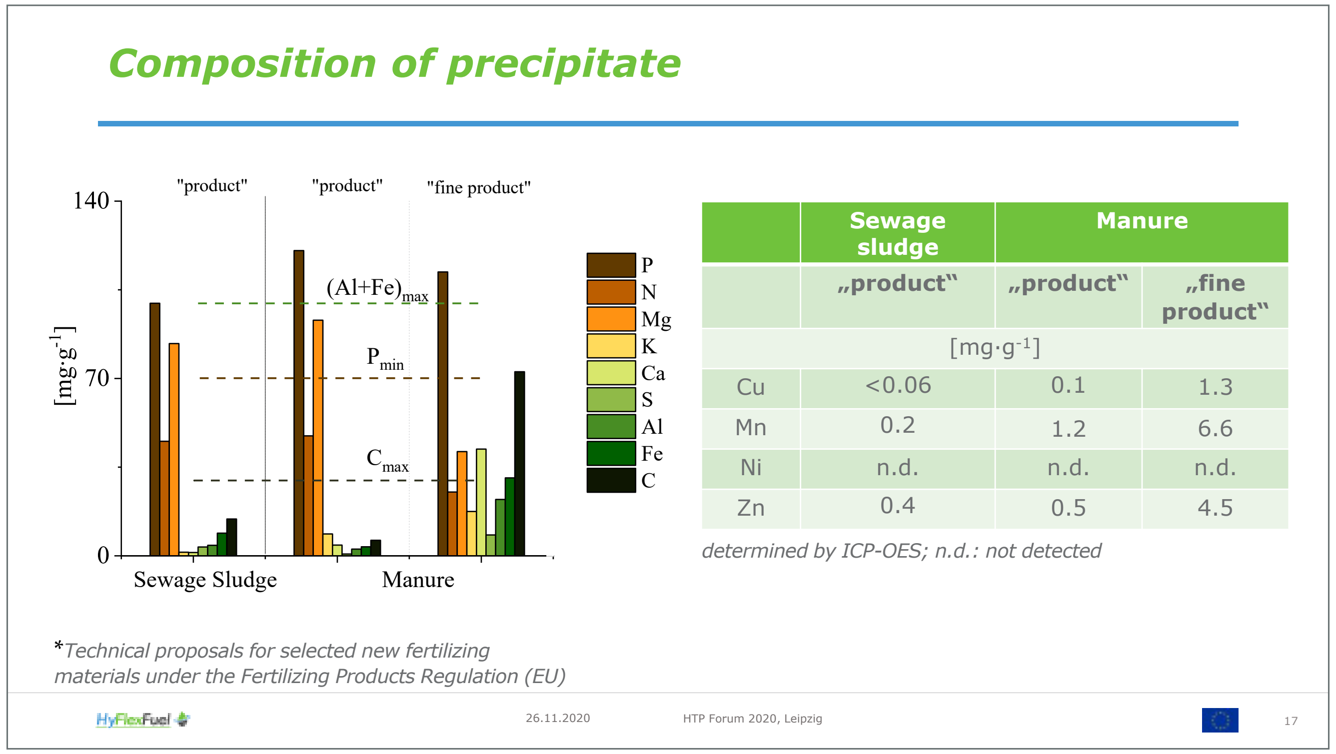

Composition of precipitate

	Sewage sludge	Manure	
	„product"	**„product"**	**„fine product"**
	[mg·g⁻¹]		
Cu	<0.06	0.1	1.3
Mn	0.2	1.2	6.6
Ni	n.d.	n.d.	n.d.
Zn	0.4	0.5	4.5

determined by ICP-OES; n.d.: not detected

**Technical proposals for selected new fertilizing materials under the Fertilizing Products Regulation (EU)*

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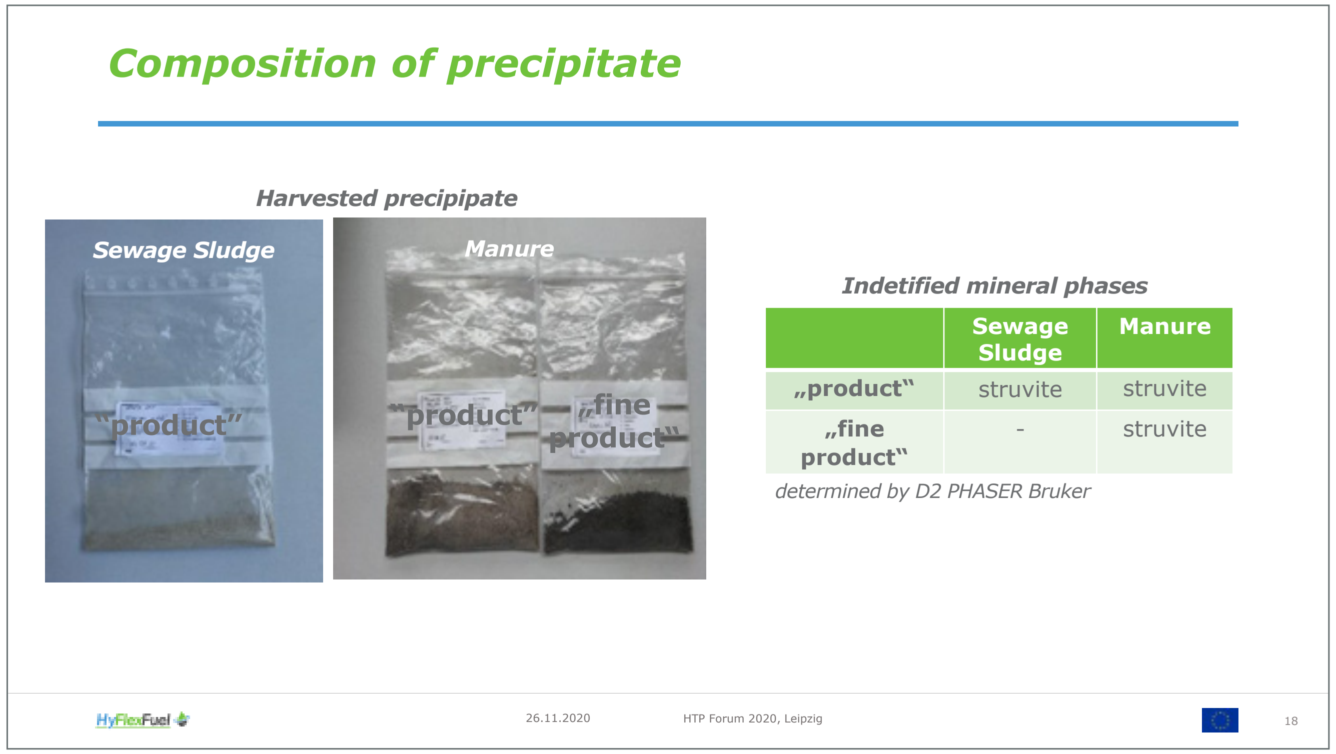

Composition of precipitate

Harvested precipipate

Indetified mineral phases

	Sewage Sludge	Manure
„product"	struvite	struvite
„fine product"	-	struvite

determined by D2 PHASER Bruker

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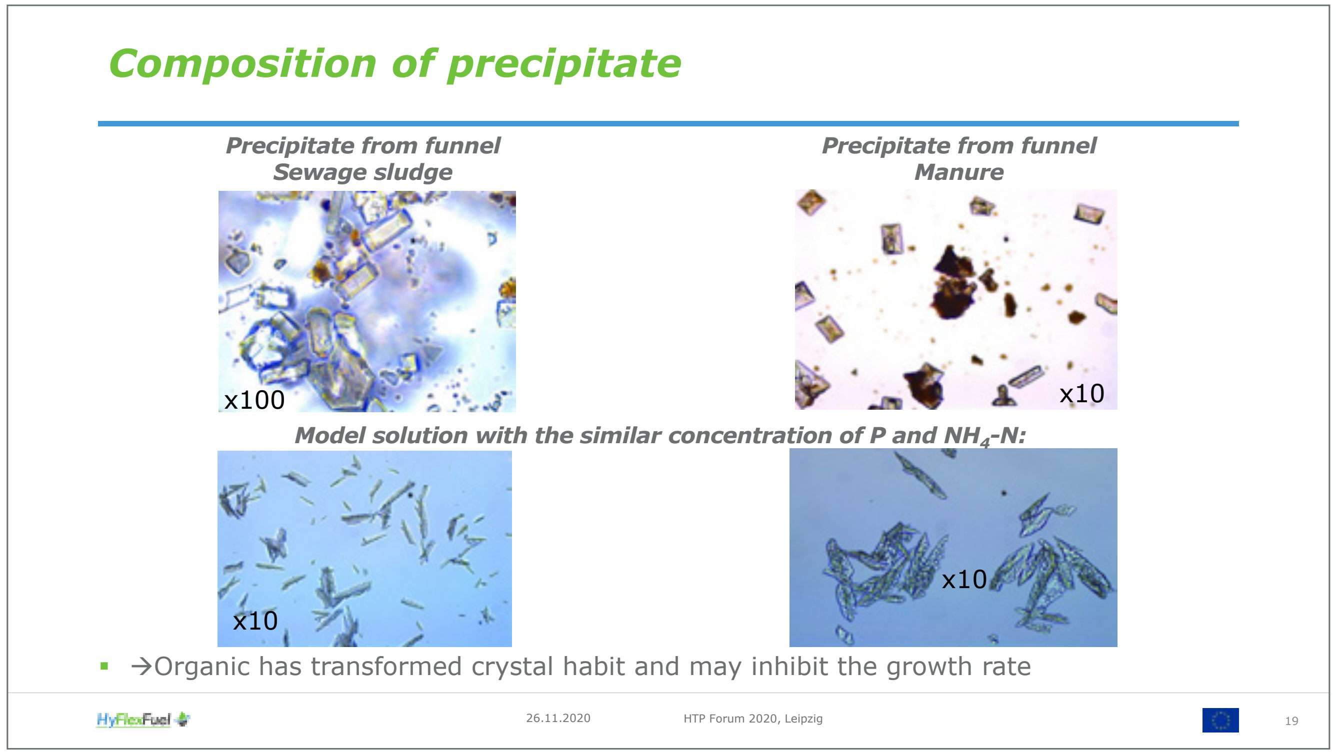


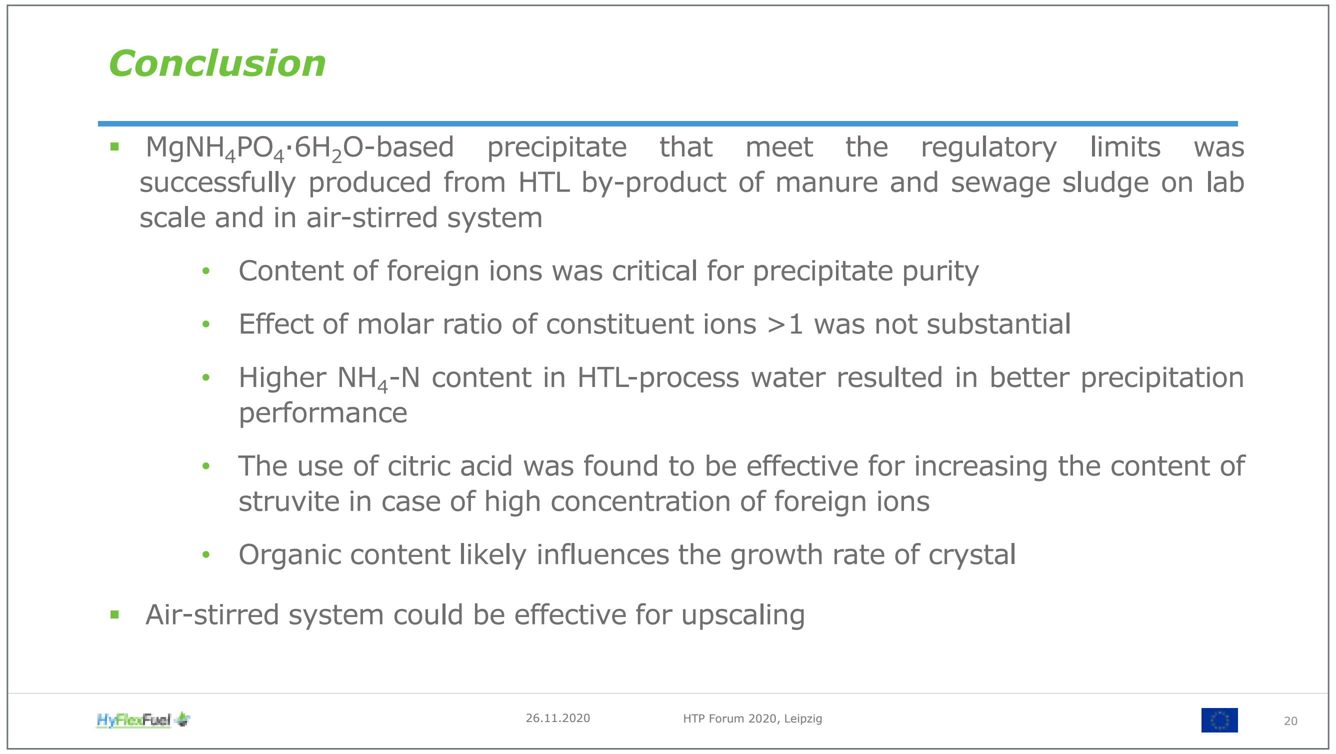
Composition of precipitate

Precipitate from funnel
Sewage sludge

Precipitate from funnel
Manure

Model solution with the similar concentration of P and NH_4-N:

- →Organic has transformed crystal habit and may inhibit the growth rate



Conclusion

- $MgNH_4PO_4 \cdot 6H_2O$-based precipitate that meet the regulatory limits was successfully produced from HTL by-product of manure and sewage sludge on lab scale and in air-stirred system
  - Content of foreign ions was critical for precipitate purity
  - Effect of molar ratio of constituent ions >1 was not substantial
  - Higher NH_4-N content in HTL-process water resulted in better precipitation performance
  - The use of citric acid was found to be effective for increasing the content of struvite in case of high concentration of foreign ions
  - Organic content likely influences the growth rate of crystal
- Air-stirred system could be effective for upscaling

HyFlexFuel

UNIVERSITY OF HOHENHEIM

Thank you!

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Dr. Paul Körner, Deutsches Biomasseforschungszentrum

Hydrothermal Carbonisation of Nitrogen Rich Substrates

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Hydrothermal carbonisation (HTC) is a promising technology for an improved exploitation of biogenic residues. Biomass consisting mainly of carbon, hydrogen and oxygen, such a lignocellulosic biomass, shows a characteristic reaction pattern during HTC that mainly involves dehydration reactions. In the consequence, hydrogen and oxygen are released in the form of water while carbon is retained in a solid product possessing thus relatively low O/C and H/C ratios. Nitrogen however makes up a fourth sphere, as its reaction behaviour is more variable with regard to release and retention. The correlation between elemental composition and process parameters is therefore more complex in the HTC of nitrogen rich substrates and rarely studied to date. In this work, the HTC of four different substrates: residues from insect rearing, Hermetia illucens larvae and two sewage sludges, that were performed in different contexts are reviewed. In the case of the larvae even the amino acid profiles prior and post HTC were available allowing an insight into the individual degradation pathways of single amino acids under hydrothermal conditions. It can be demonstrated that each substrate undergoes a specific hydrothermal conversion with respect to the changes of the elemental composition as well as concerning the correlation with different process parameters. Reviewing the rather sparse literature on hydrothermal amino acid degradation opens up a manifold research field offering a bundle of unanswered research questions and numerous perspectives to the production of protein derived chemicals.

Overall, this study provides novel insights into the complexities of hydrothermal nitrogen chemistry.

6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Hydrothermal Carbonisation of Nitrogen Rich Substrates

Dr. Paul Körner
DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH

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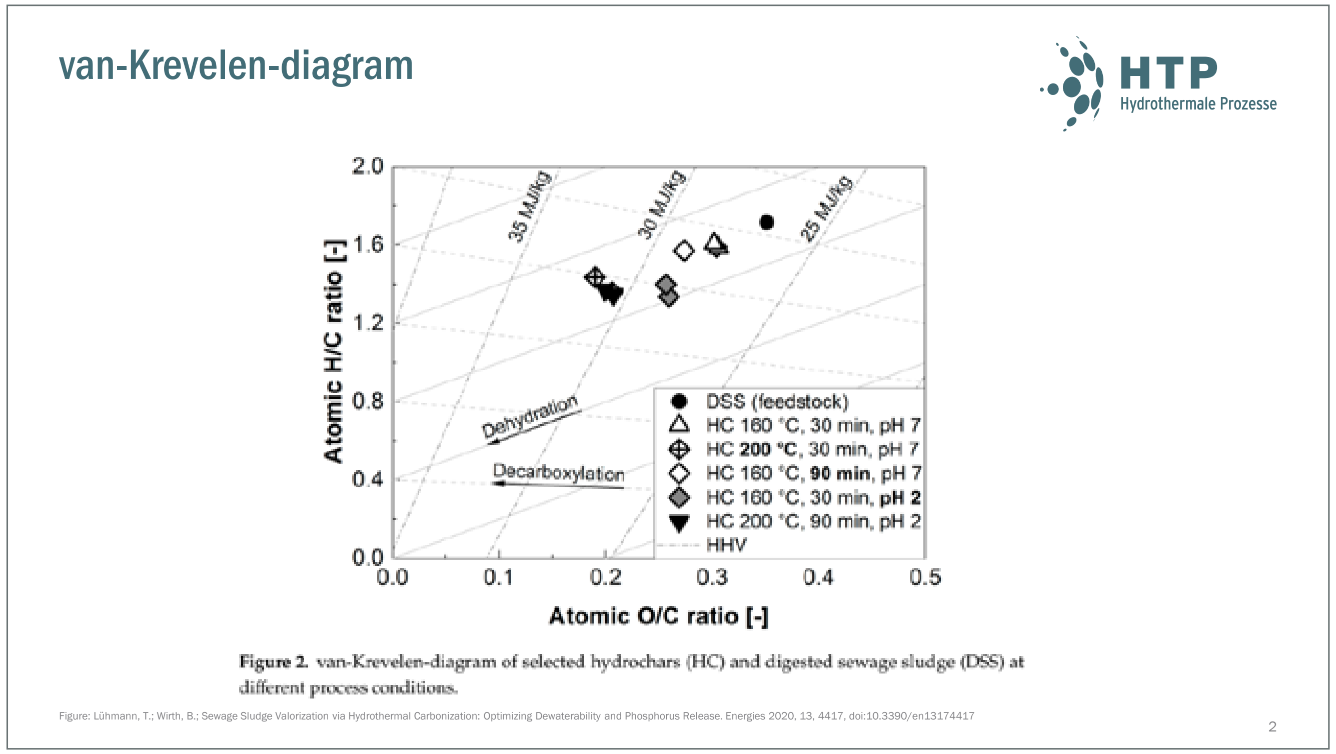

van-Krevelen-diagram

Figure 2. van-Krevelen-diagram of selected hydrochars (HC) and digested sewage sludge (DSS) at different process conditions.

Figure: Lühmann, T.; Wirth, B.; Sewage Sludge Valorization via Hydrothermal Carbonization: Optimizing Dewaterability and Phosphorus Release. Energies 2020, 13, 4417, doi:10.3390/en13174417

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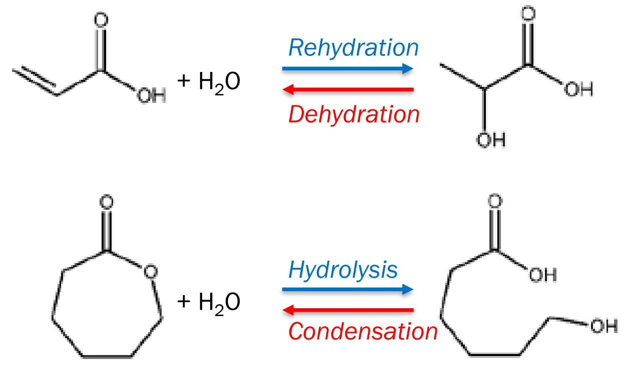
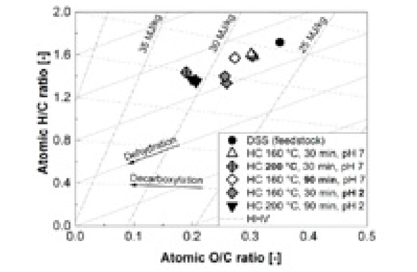
van-Krevelen-diagram





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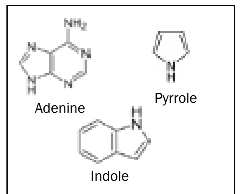
Nitrogen species

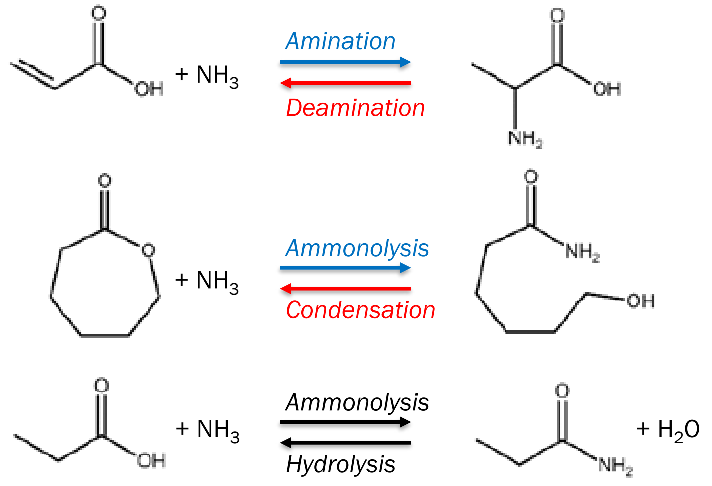
Inorganic nitrogen species

NH_3/NH_4^+	NO_2^-	NO_3^-
Ammonia/ ammonium	Nitrite	Nitrate

Organic nitrogen species

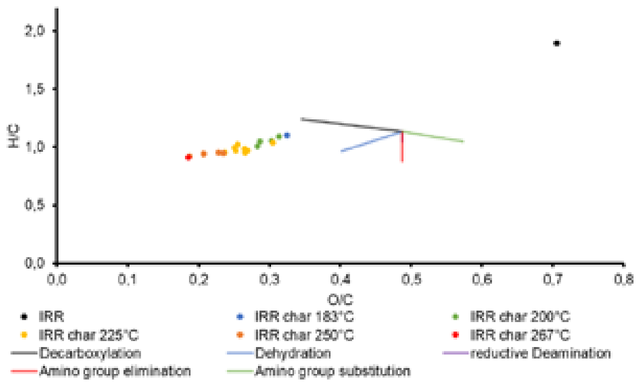
$R\text{-}NH_2$	$R\text{-}NO_2$	
Amines	Nitro-compounds	 N-Heterocycles

Nitrogen species

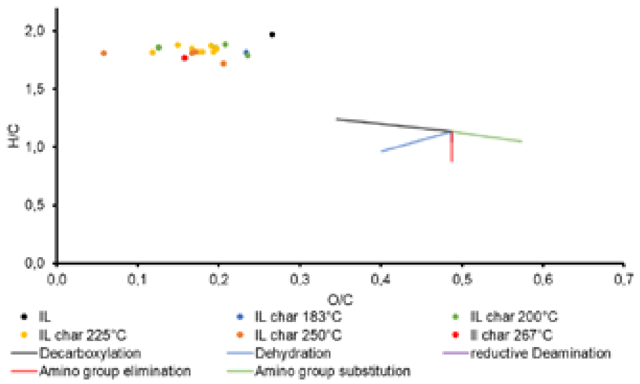


Reactions involving nitrogen

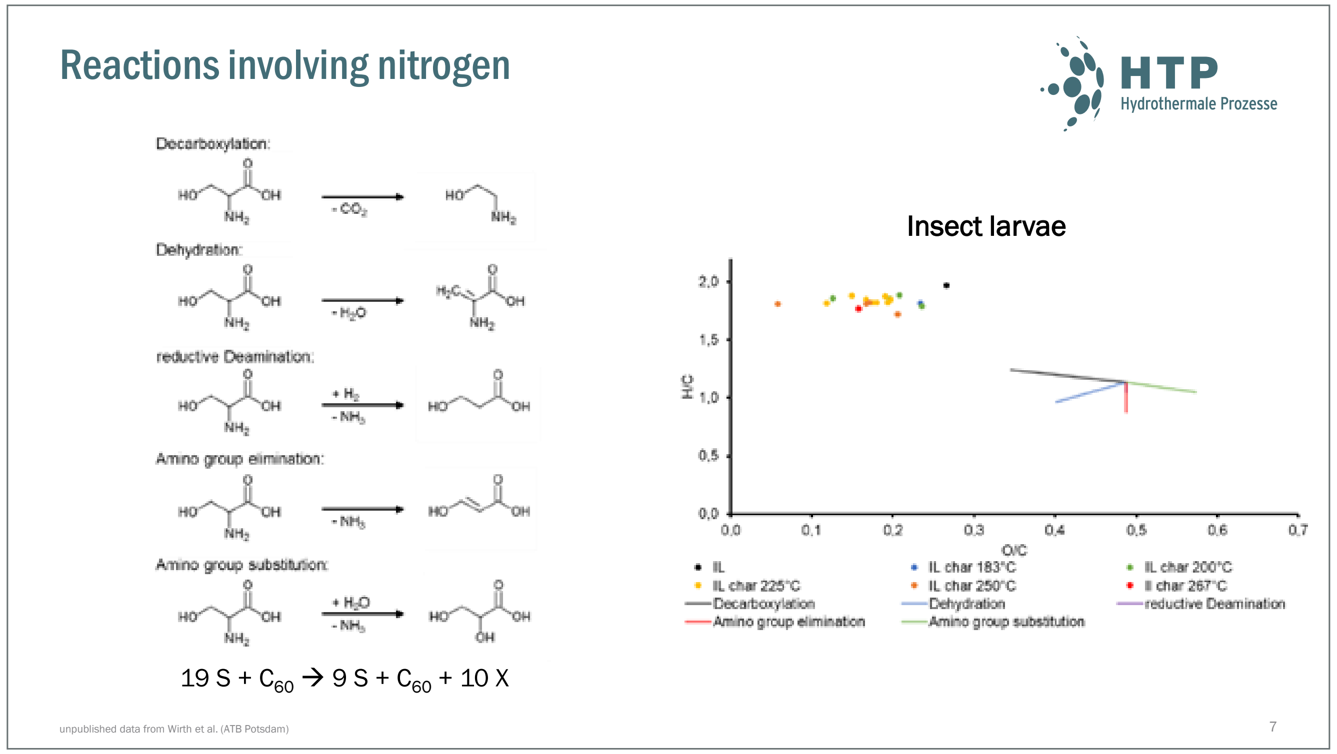
Insect rearing residues



Insect larvae



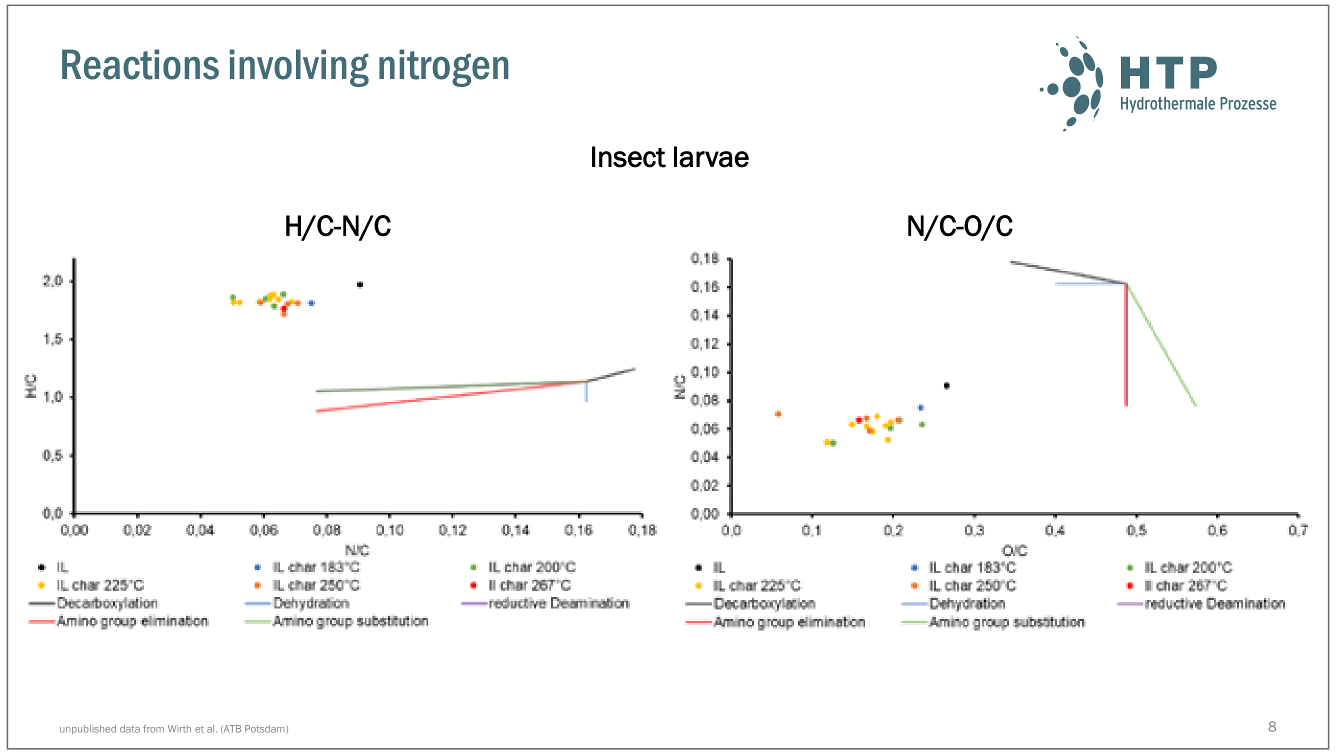
unpublished data from Wirth et al. (ATB Potsdam)



Reactions involving nitrogen

$19 S + C_{60} \rightarrow 9 S + C_{60} + 10 X$

unpublished data from Wirth et al. (ATB Potsdam)



Reactions involving nitrogen

Insect larvae

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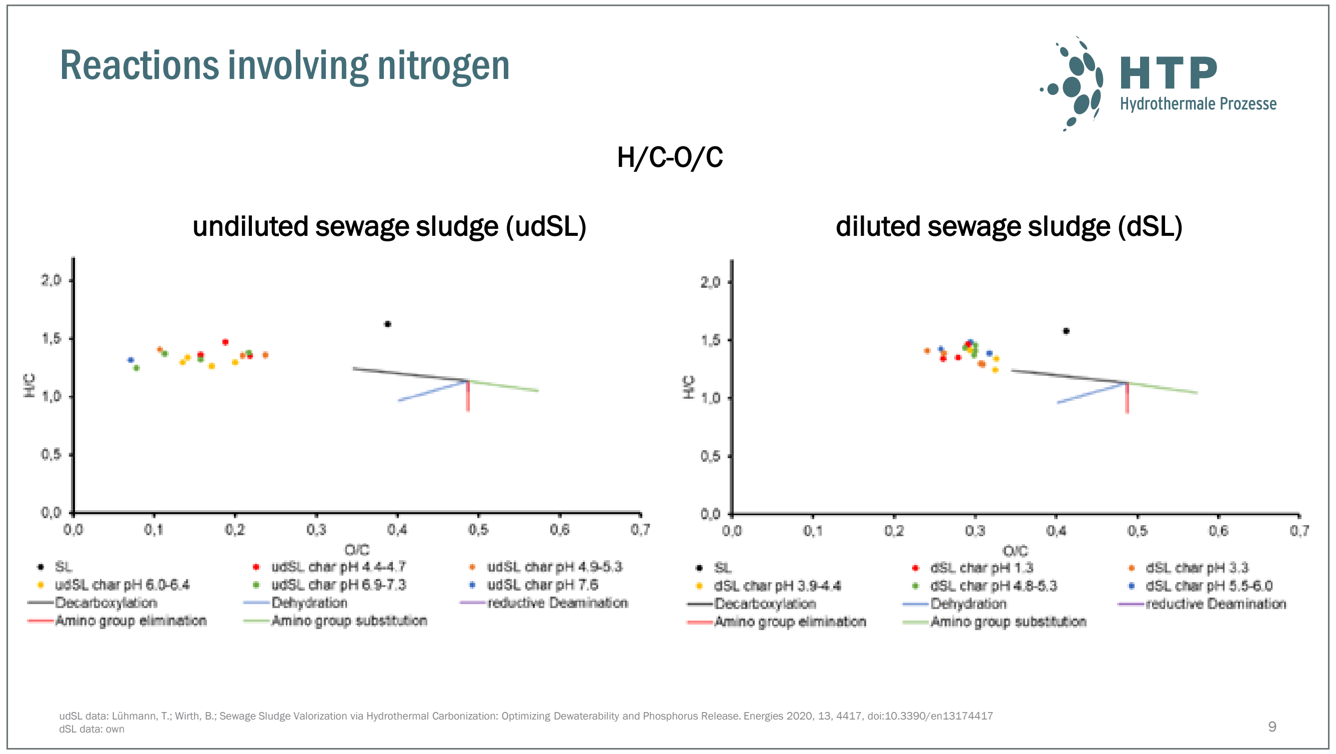
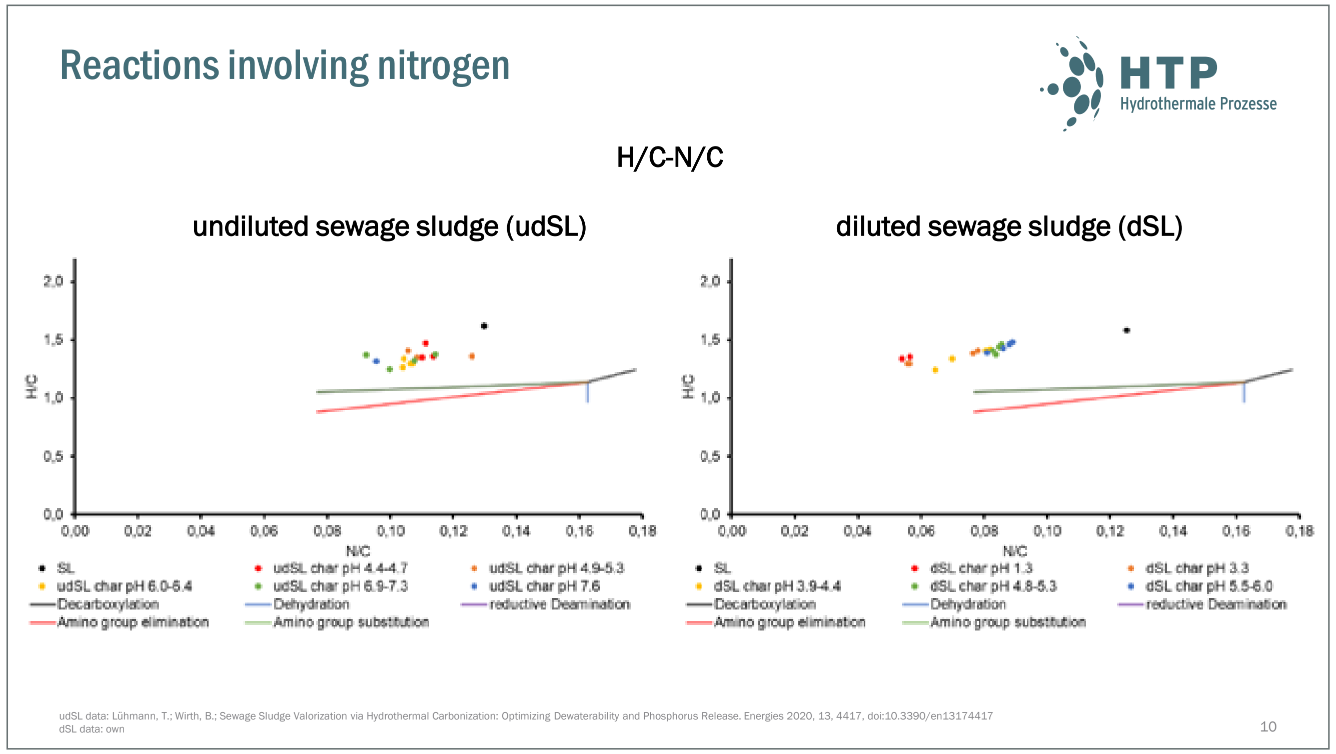


Reactions involving nitrogen

H/C-O/C

udSL data: Lühmann, T.; Wirth, B.; Sewage Sludge Valorization via Hydrothermal Carbonization: Optimizing Dewaterability and Phosphorus Release. Energies 2020, 13, 4417, doi:10.3390/en13174417
dSL data: own



Reactions involving nitrogen

H/C-N/C

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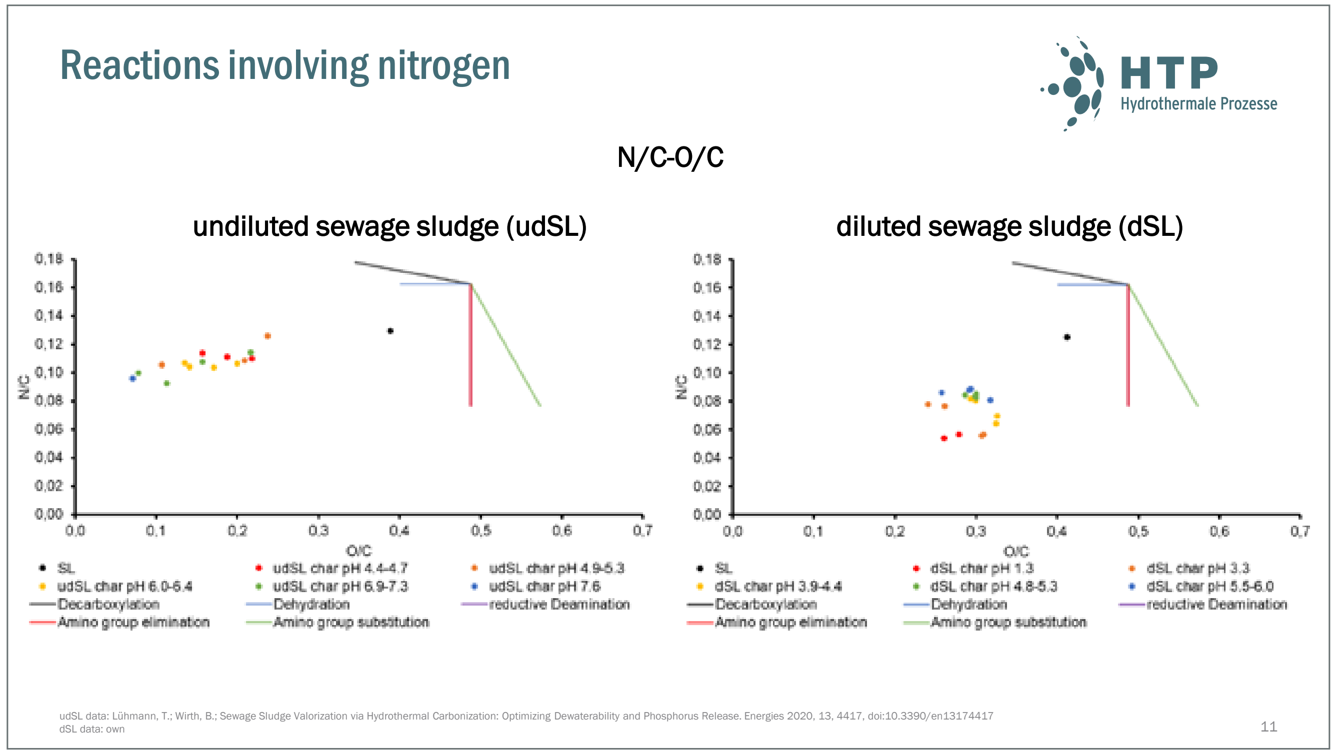

Reactions involving nitrogen

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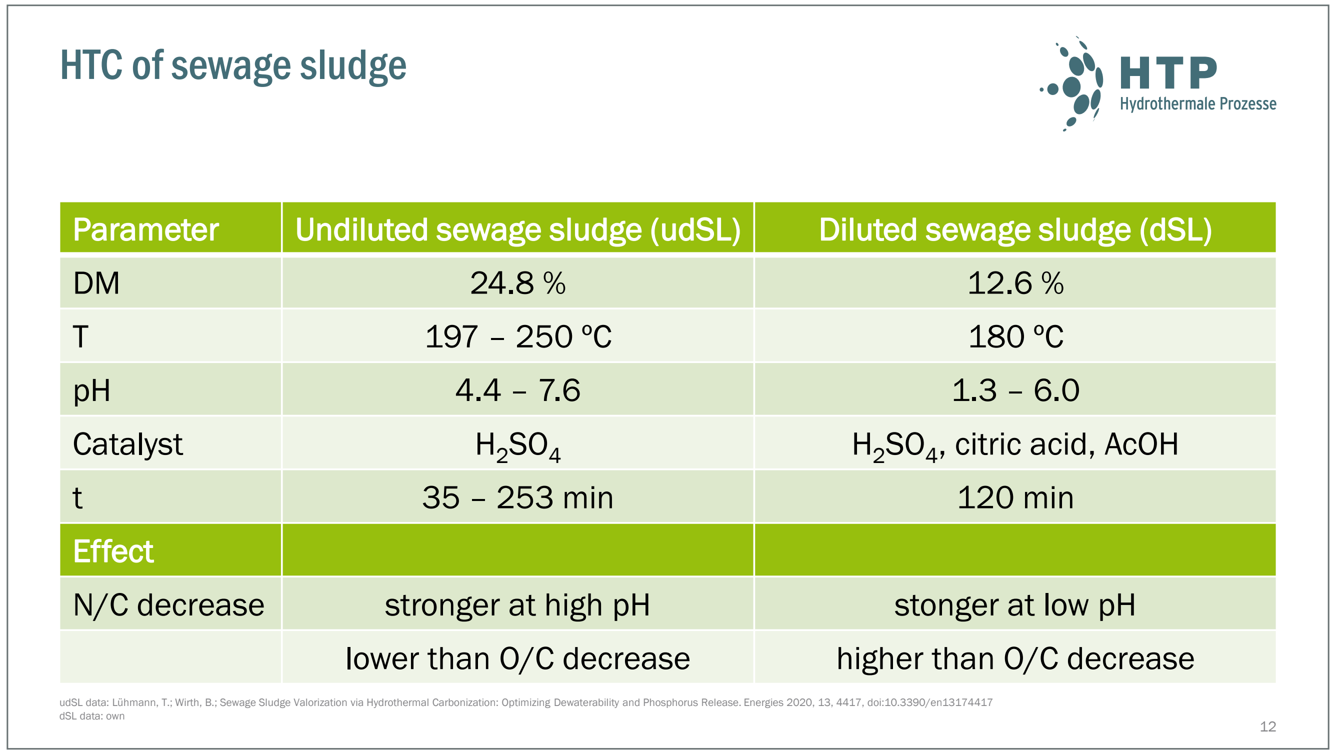
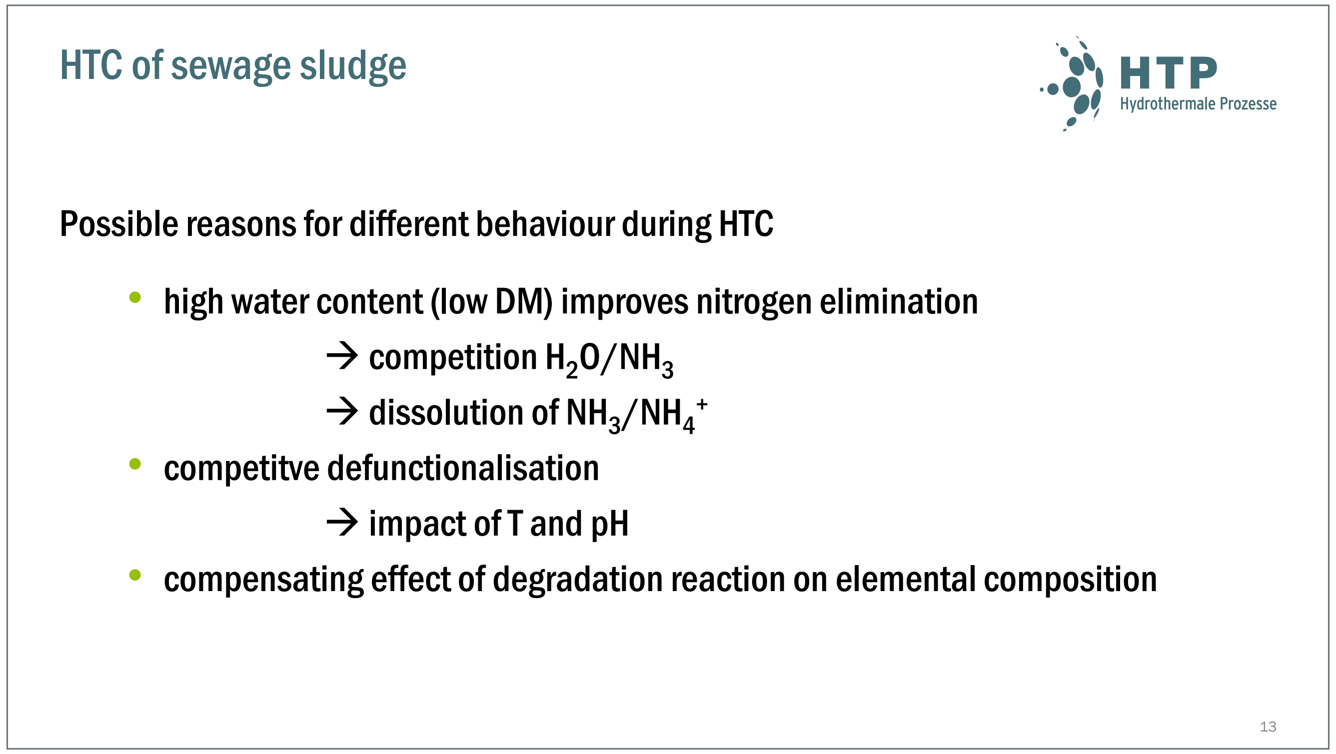


HTC of sewage sludge

Parameter	Undiluted sewage sludge (udSL)	Diluted sewage sludge (dSL)
DM	24.8 %	12.6 %
T	197 – 250 °C	180 °C
pH	4.4 – 7.6	1.3 – 6.0
Catalyst	H_2SO_4	H_2SO_4, citric acid, AcOH
t	35 – 253 min	120 min
Effect		
N/C decrease	stronger at high pH	stonger at low pH
	lower than O/C decrease	higher than O/C decrease

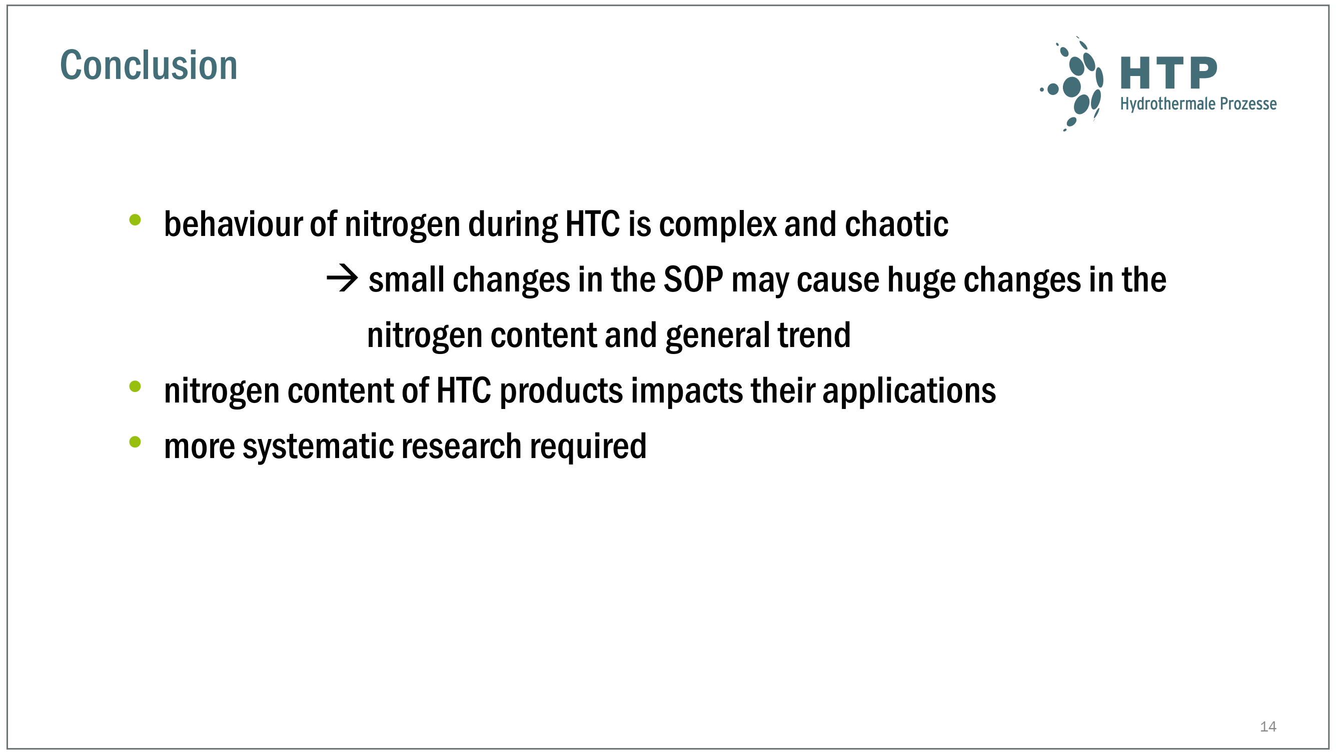
udSL data: Lühmann, T.; Wirth, B.; Sewage Sludge Valorization via Hydrothermal Carbonization: Optimizing Dewaterability and Phosphorus Release. Energies 2020, 13, 4417, doi:10.3390/en13174417
dSL data: own



HTC of sewage sludge

Possible reasons for different behaviour during HTC

- high water content (low DM) improves nitrogen elimination
  → competition H_2O/NH_3
  → dissolution of NH_3/NH_4^+
- competitve defunctionalisation
  → impact of T and pH
- compensating effect of degradation reaction on elemental composition



Conclusion

- behaviour of nitrogen during HTC is complex and chaotic
  → small changes in the SOP may cause huge changes in the nitrogen content and general trend
- nitrogen content of HTC products impacts their applications
- more systematic research required

6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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Can vapor thermal carbonization (VTC) play a role in the production of fuel and nutrient recovery from agricultural feedstocks?

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In the search for sustainable uses for agricultural feedstocks, hydrothermal carbonization treatment has often been studied as a refining step to improve their heating value and/or increase their stability for use as a soil amendment. Inorganics (heavy metals, nutrients, minerals, and chloride) play an important but contrasting role in the assessment of the fuel or fertilizer quality of the chars produced in these processes. The dependence of their fate on the operating conditions during the hydrothermal process is not yet fully understood. Process operation with the feedstock submerged in liquid water (HTC) has been shown to improve the heating value of biomasses by increasing the carbon content, and heating value and reducing ash content. Vapor thermal operation, in which the feedstock is contacted by water vapor only (VTC), has also been shown to increase the carbon content and heating value without as much loss of solids, but also with little to no reduction in ash content. This would imply that the VTC operation mode is not suited for improving feedstock for use as a fuel. However, for the recovery of nutrients, the reduction of operational complexity and the decrease of process water production, the VTC process is very attractive. Therefore, in this study, the partitioning behaviour of inorganics in a hydrothermal reactor system operating under two different modes, HTC and VTC, was compared for a fast growing grass as feedstock at two different temperatures (190 °C and 220 °C). The effects of the operation mode on energy recovery and the heating value, as well as the distribution of nutrients, salts and heavy metals were studied to understand how the partitioning of the water in the reactor system influenced the distribution of the elements between the solid and liquid phases (char or process water). Additionally, a second goal was to identify if the produced chars could meet different quality standards for fuels (e.g. DIN EN 15359 and RAL-GZ 724 for Solid Recovered Fuels), specifically regarding the inorganic composition.

In the presentation the appropriate uses of the two operating modes will be discussed. The initial results show that both the HTC and VTC operating mode at 220 °C were able to increase the lower heating values from class 3 for the feedstock to class 2 (DIN EN 15359). However, only HTC improved the feedstock enough to meet a higher Cl quality standard, moving the char up from class 4 to class 1, while the VTC char stayed as class 4. However, when the two operating modes are assessed for producing chars to be used as soil amendments, the results reverse. The inorganic partitioning into the liquid phase when the grass was submitted to an HTC process removes nutrients, and the NPK value of the feedstock decreases in the HTC char. On average, the weight content of nutrients decreased sharply in HTC chars (-24% N,-81% P, -83% K), while the values increased for the VTC chars (on average, +7% N, +6% P, +12% K).

Session III

Fragen zur Demonstration und Anwendung

Andreas Leichner, MURA Europe GmbH

Chemical Recycling with Cat-HTR™: Using supercritical water for the depolymerization of waste plastic

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Mura's proprietary technology, Cat-HTR™ (Catalytic Hydrothermal Reactor) is a chemical recycling process able to convert end-of-life plastics back into the chemical and oils from which they were made, for use in the petrochemical industry in the production of new plastic and other materials. This broadens the scope of recyclable plastic materials, and helps to create a circular economy for plastic.

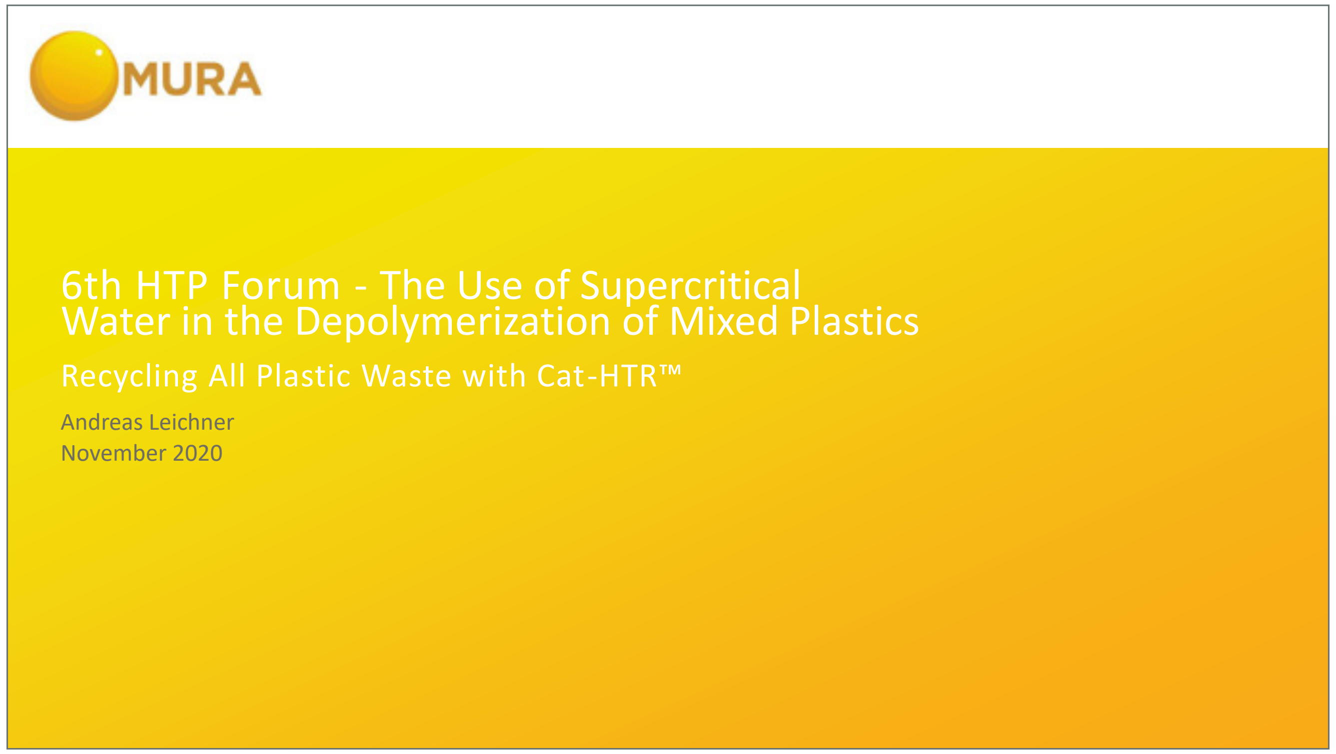
Cat-HTR™ uses supercritical water, heat and pressure via hydrothermal liquefaction to break long-chain hydrocarbons, donating hydrogen to produce shorter-chain, stable hydrocarbon products, which can be stored and shipped.

A key benefit of the Cat-HTR™ technology is its ability to recycle multi-layer, flexible plastic materials such as films, pots, tubs and trays, considered unrecyclable through traditional mechanical recycling, and are instead sent to landfill or incineration, leading to environmental pollution and loss of this flexible, hard-working and valuable resource.

Vitally, new materials made using Cat-HTR™ recycled feedstock are suitable for use in food-contact packaging material, a problem area for mechanical recycling systems whose products do not meet European Food Standard Agency requirements. Cat-HTR™ also offers a beneficial technology to help increase the recycled content of packaging and provide a recycling solution for plastic packaging materials.

Alongside diverting plastic away from polluting the environment, chemical recycling represents significant overall environmental benefit, including a reduction of CO_2 emissions by 1.5 tonnes for every tonne of plastic waste processed when compared to incineration (CE Delft). In addition, alongside increasing the scope of recyclable plastic materials, Cat-HTR™ also contributes to a reduction in fossil feedstock for the manufacture of new plastics, and as it is not a combustion process, does not produce toxic by-products, such as dioxins.

The technology demonstrates a complementary solution to sit alongside traditional mechanical recycling to create a circular economy and goes hand in hand with efforts to reduce single-use plastic and create a plastic-neutral society.

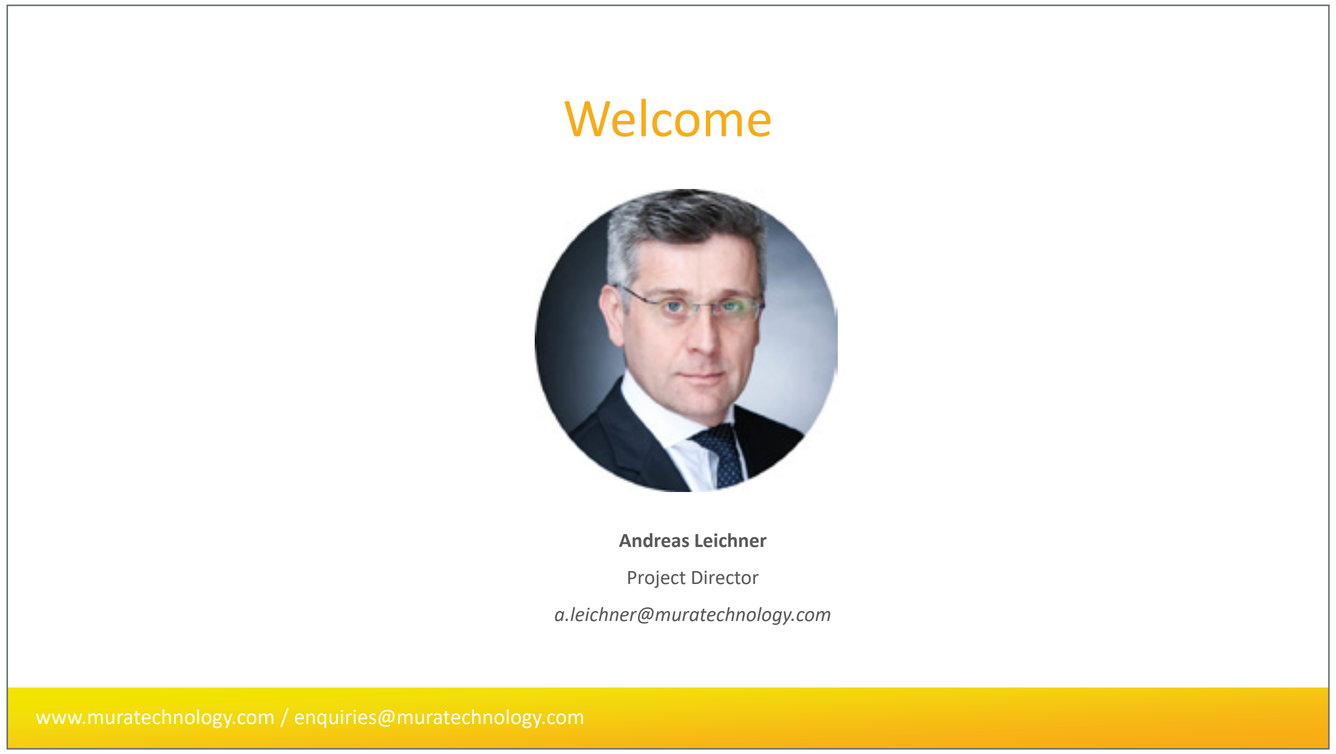


MURA

6th HTP Forum - The Use of Supercritical Water in the Depolymerization of Mixed Plastics

Recycling All Plastic Waste with Cat-HTR™

Andreas Leichner
November 2020



Welcome

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1. Chemical Recycling

Chemical recycling (sometimes called Advanced Recycling) is currently not defined in any EU Regulation.

According to Chemical Recycling Europe (CRE), Chemical Recycling is defined as:

- ***any reprocessing technology that directly affects either the formulation of the polymeric waste or the polymer itself; and,***
- ***converts them into chemical substances and/or products whether for the original or other purposes, excluding energy recovery.***

Critically:

- Process changes the polymer formulation or polymer
- Wide potential for use in a range of products
- End-product is 'a recyclate' – ***not*** used as a ***fuel.***
- *Conversion to fuel / energy is termed **'recovery'***

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2. Chemical Recycling Processes

Chemical Recycling (or Advanced Recycling) of plastics covers many different technologies, using many different processes and giving different outputs/products, for example;

- Depolymerization
- Pyrolysis/thermal cracking
- Gasification
- Hydrothermal liquefaction (HTL)
- Dissolution

Some technologies are aimed at specific polymer types (e.g. depolymerization of PET) whereas others (pyrolysis, HTL) can take in mixed plastic types and produce outputs which are used to make new materials, these processes are also sometimes referred to as 'feedstock recycling'.

Cat-HTR™

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3. Chemical Recycling with Cat-HTR™

Cat-HTR™ is a HydroThermal Liquefaction (or Upgrading) technology, using supercritical water to convert plastics into shorter-chain, stable hydrocarbons, for re-use in feedstocks for the manufacture of new plastic and other materials.

The use of supercritical water provides:

- An organic solvent
- A source of hydrogen to complete the broken chemical chains – no external hydrogen is required
- A means of rapid heating that avoids excessive temperatures that would lead to excessive cracking
- The ability to scale the process

Typically, up to 85% of the mass of plastic is converted to liquid hydrocarbons that could be used to make new plastics or other products.

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4. The Cat-HTR™ Process

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5. Feedstock (German Market)

- DSD Specification 323/350/352
- End of life post-consumer plastics (films and rigids)
- Material which cannot be mechanically recycled
- Able to process mixed plastic streams (films and rigids) without the need for segregation
- Able to process contaminated materials (organics & paper etc)
- No need to pre-dry feedstock
- Able to process multi-layered, complex plastic materials

The current option for these streams is incineration or landfill.

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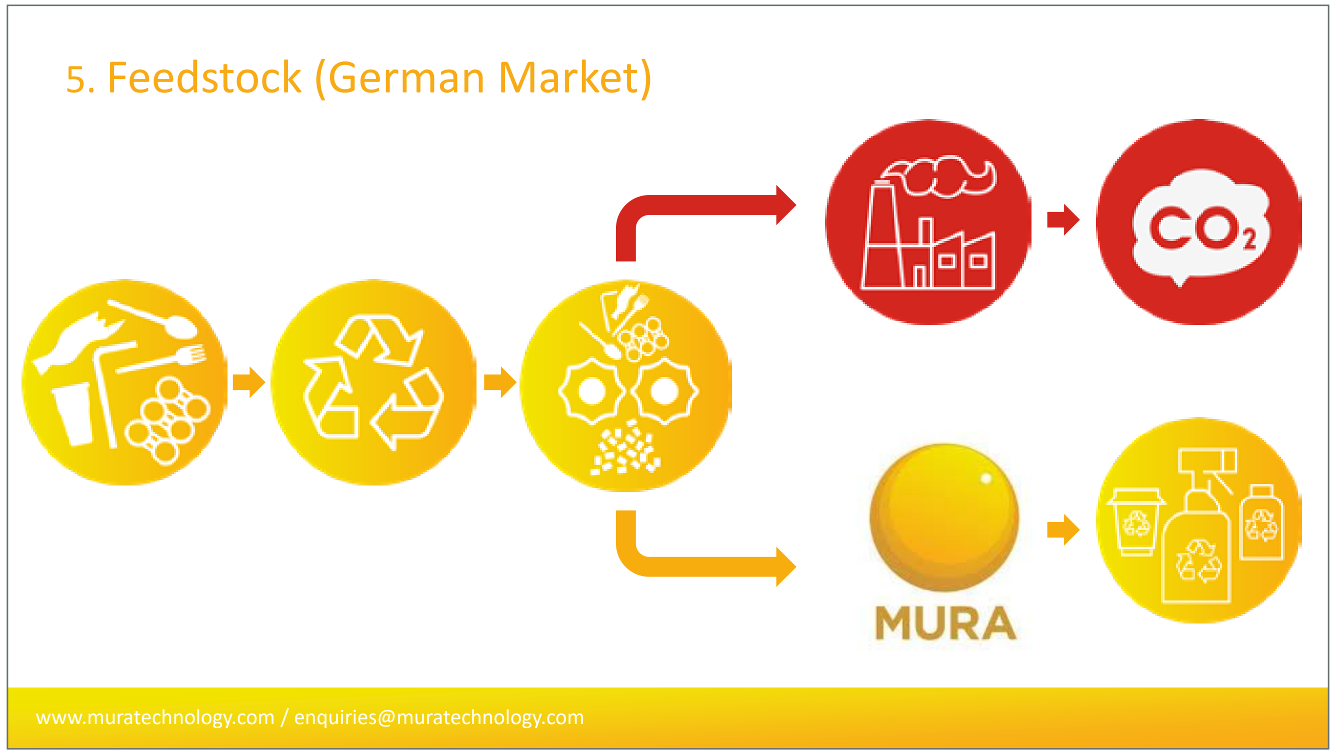

5. Feedstock (German Market)

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6. Technology Benefits

A key benefit of the Cat-HTR™ technology is its ability to recycle multi-layer, flexible plastic materials such as films, and pots, tubs and trays, without need for segregation.

There are no limits to the number of times that plastic can be recycled using Cat-HTR™.

New materials made from Mura's recycled feedstocks are suitable for food-contact packaging materials.

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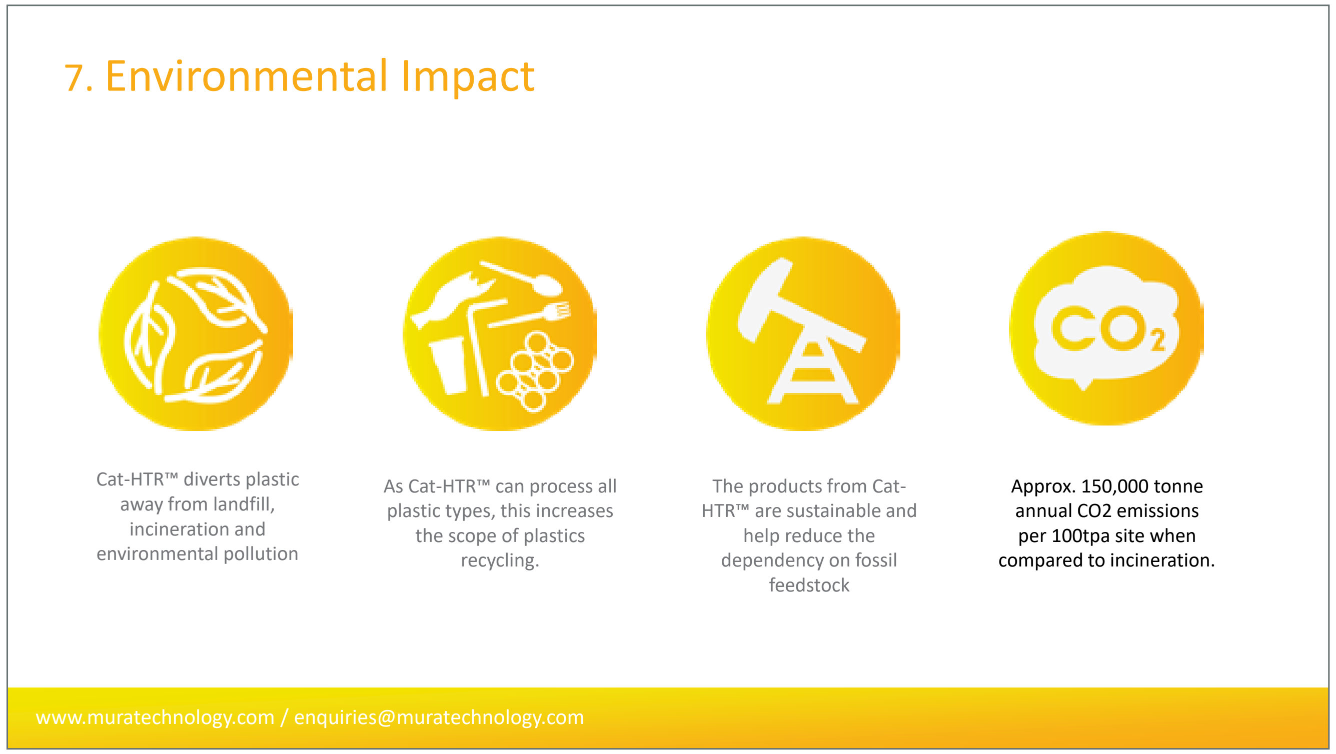

7. Environmental Impact

Cat-HTR™ diverts plastic away from landfill, incineration and environmental pollution

As Cat-HTR™ can process all plastic types, this increases the scope of plastics recycling.

The products from Cat-HTR™ are sustainable and help reduce the dependency on fossil feedstock

Approx. 150,000 tonne annual CO2 emissions per 100tpa site when compared to incineration.

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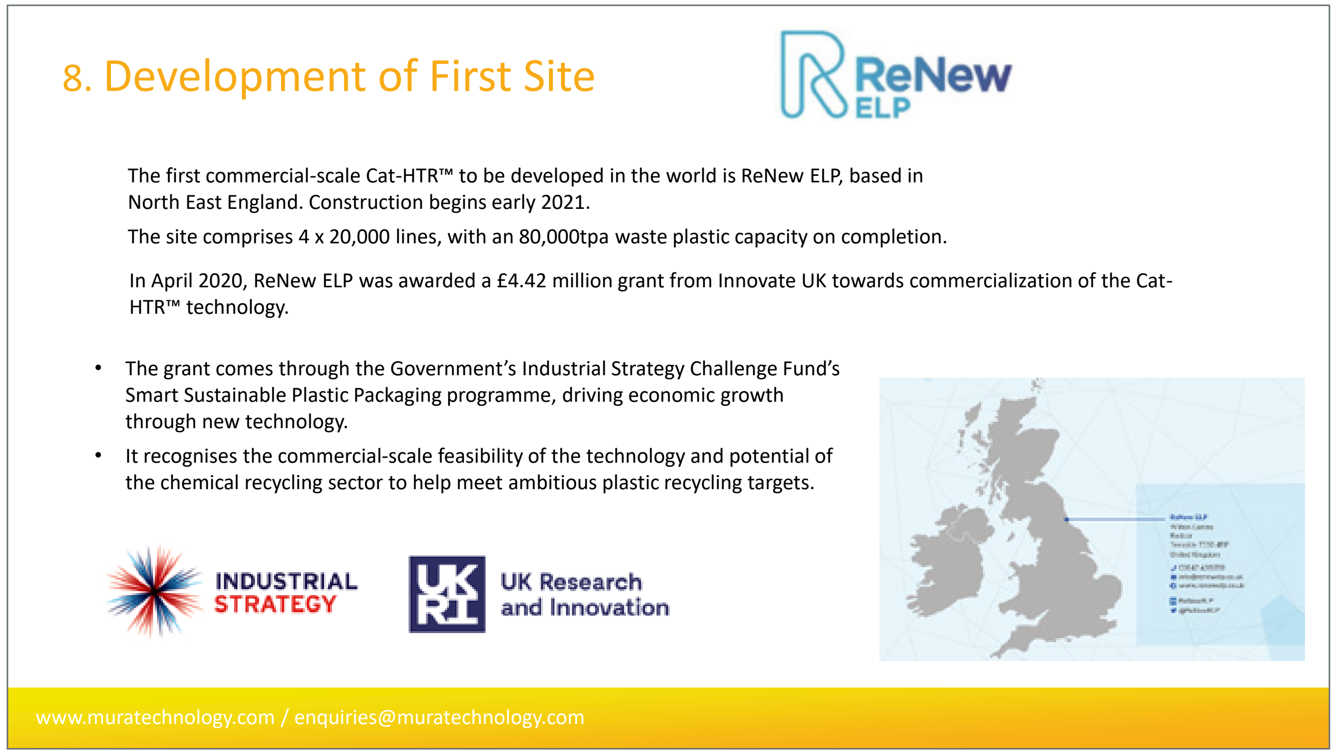

8. Development of First Site

The first commercial-scale Cat-HTR™ to be developed in the world is ReNew ELP, based in North East England. Construction begins early 2021.

The site comprises 4 x 20,000 lines, with an 80,000tpa waste plastic capacity on completion.

In April 2020, ReNew ELP was awarded a £4.42 million grant from Innovate UK towards commercialization of the Cat-HTR™ technology.

- The grant comes through the Government's Industrial Strategy Challenge Fund's Smart Sustainable Plastic Packaging programme, driving economic growth through new technology.
- It recognises the commercial-scale feasibility of the technology and potential of the chemical recycling sector to help meet ambitious plastic recycling targets.

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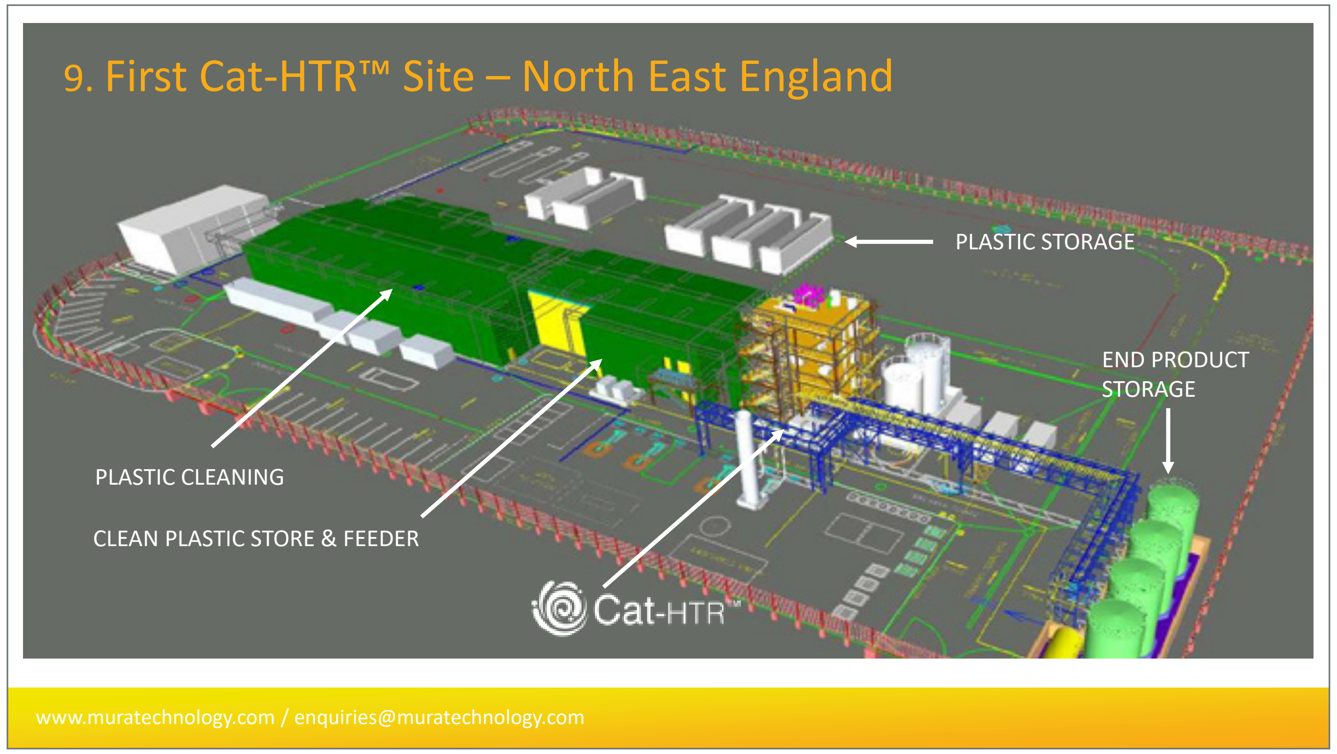

9. First Cat-HTR™ Site – North East England

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10. Global Roll Out

- Alongside ReNew ELP, Mura Technology are developing a global portfolio of Cat-HTR™ sites, including the USA, Germany and Asia, with sites ranging in scale up to 200,000 tonnes per annum.
- Each of the identified markets offer a level of waste collection infrastructure, alongside developed chemical and science parks and utilities to support a Cat-HTR™ site.
- Mura are aiming **towards 1,000,000** tpa global capacity in development by 2025

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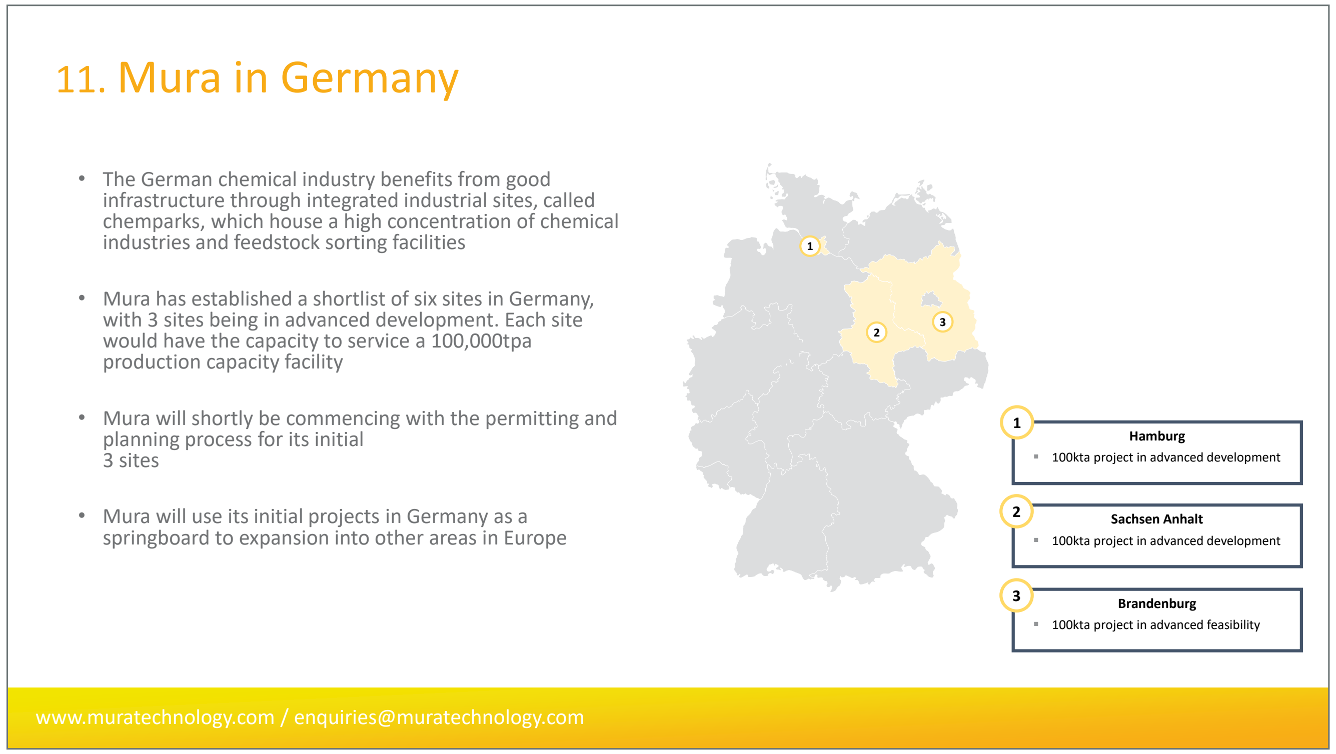

11. Mura in Germany

- The German chemical industry benefits from good infrastructure through integrated industrial sites, called chemparks, which house a high concentration of chemical industries and feedstock sorting facilities
- Mura has established a shortlist of six sites in Germany, with 3 sites being in advanced development. Each site would have the capacity to service a 100,000tpa production capacity facility
- Mura will shortly be commencing with the permitting and planning process for its initial 3 sites
- Mura will use its initial projects in Germany as a springboard to expansion into other areas in Europe

① **Hamburg**
- 100kta project in advanced development

② **Sachsen Anhalt**
- 100kta project in advanced development

③ **Brandenburg**
- 100kta project in advanced feasibility

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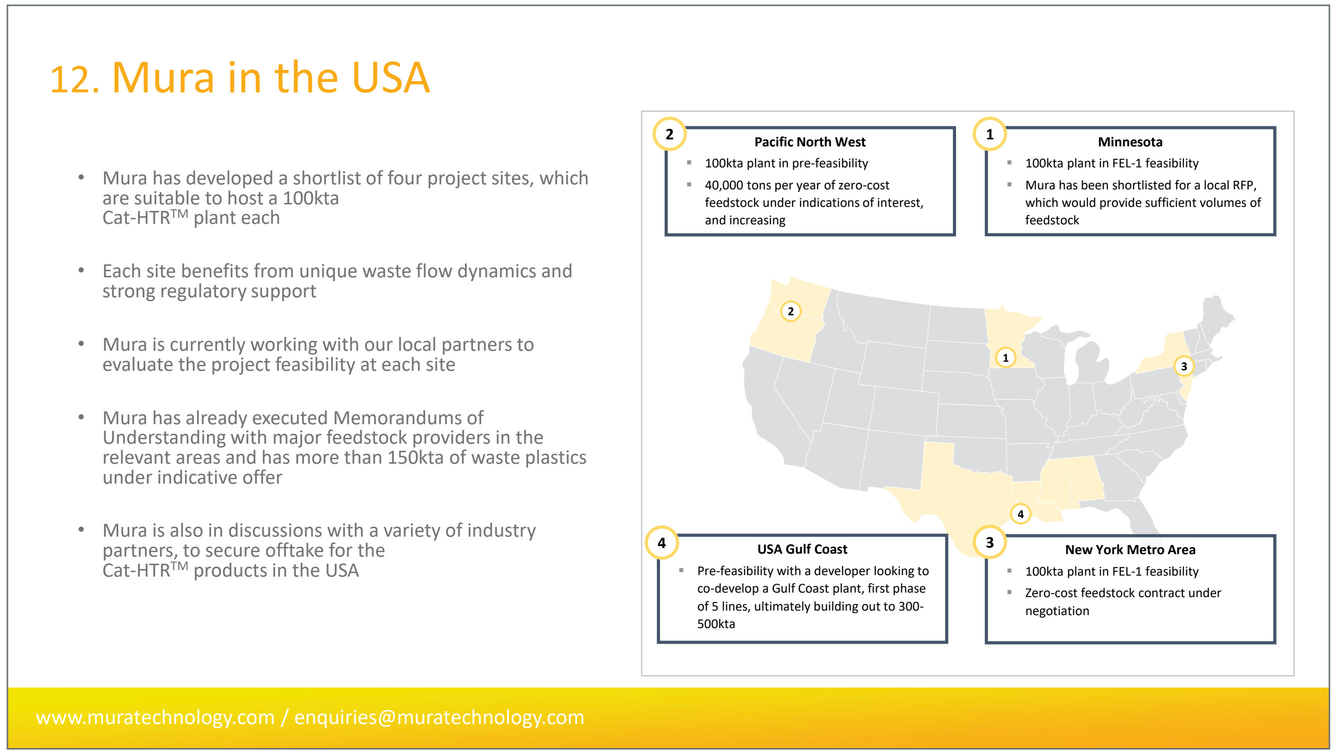

12. Mura in the USA

- Mura has developed a shortlist of four project sites, which are suitable to host a 100kta Cat-HTR™ plant each
- Each site benefits from unique waste flow dynamics and strong regulatory support
- Mura is currently working with our local partners to evaluate the project feasibility at each site
- Mura has already executed Memorandums of Understanding with major feedstock providers in the relevant areas and has more than 150kta of waste plastics under indicative offer
- Mura is also in discussions with a variety of industry partners, to secure offtake for the Cat-HTR™ products in the USA

② **Pacific North West**
- 100kta plant in pre-feasibility
- 40,000 tons per year of zero-cost feedstock under indications of interest, and increasing

① **Minnesota**
- 100kta plant in FEL-1 feasibility
- Mura has been shortlisted for a local RFP, which would provide sufficient volumes of feedstock

④ **USA Gulf Coast**
- Pre-feasibility with a developer looking to co-develop a Gulf Coast plant, first phase of 5 lines, ultimately building out to 300-500kta

③ **New York Metro Area**
- 100kta plant in FEL-1 feasibility
- Zero-cost feedstock contract under negotiation

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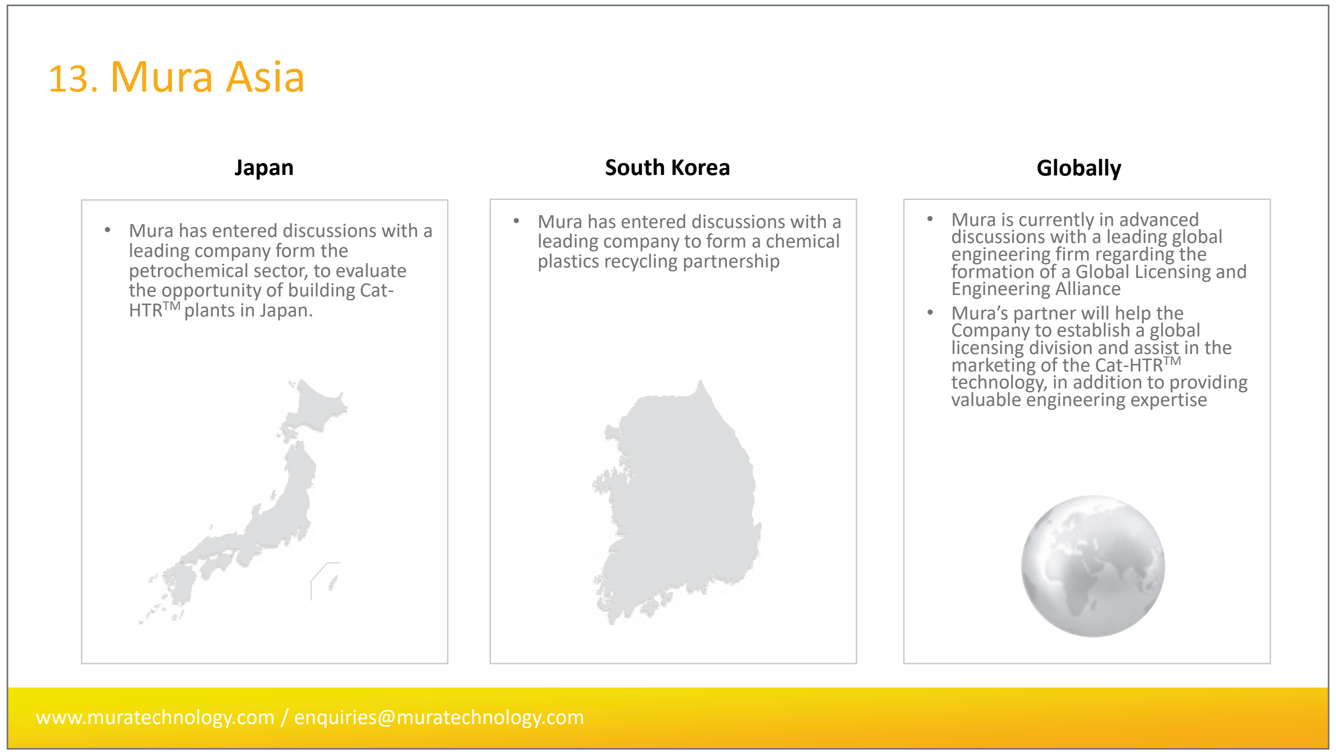

13. Mura Asia

Japan
- Mura has entered discussions with a leading company form the petrochemical sector, to evaluate the opportunity of building Cat-HTR™ plants in Japan.

South Korea
- Mura has entered discussions with a leading company to form a chemical plastics recycling partnership

Globally
- Mura is currently in advanced discussions with a leading global engineering firm regarding the formation of a Global Licensing and Engineering Alliance
- Mura's partner will help the Company to establish a global licensing division and assist in the marketing of the Cat-HTR™ technology, in addition to providing valuable engineering expertise

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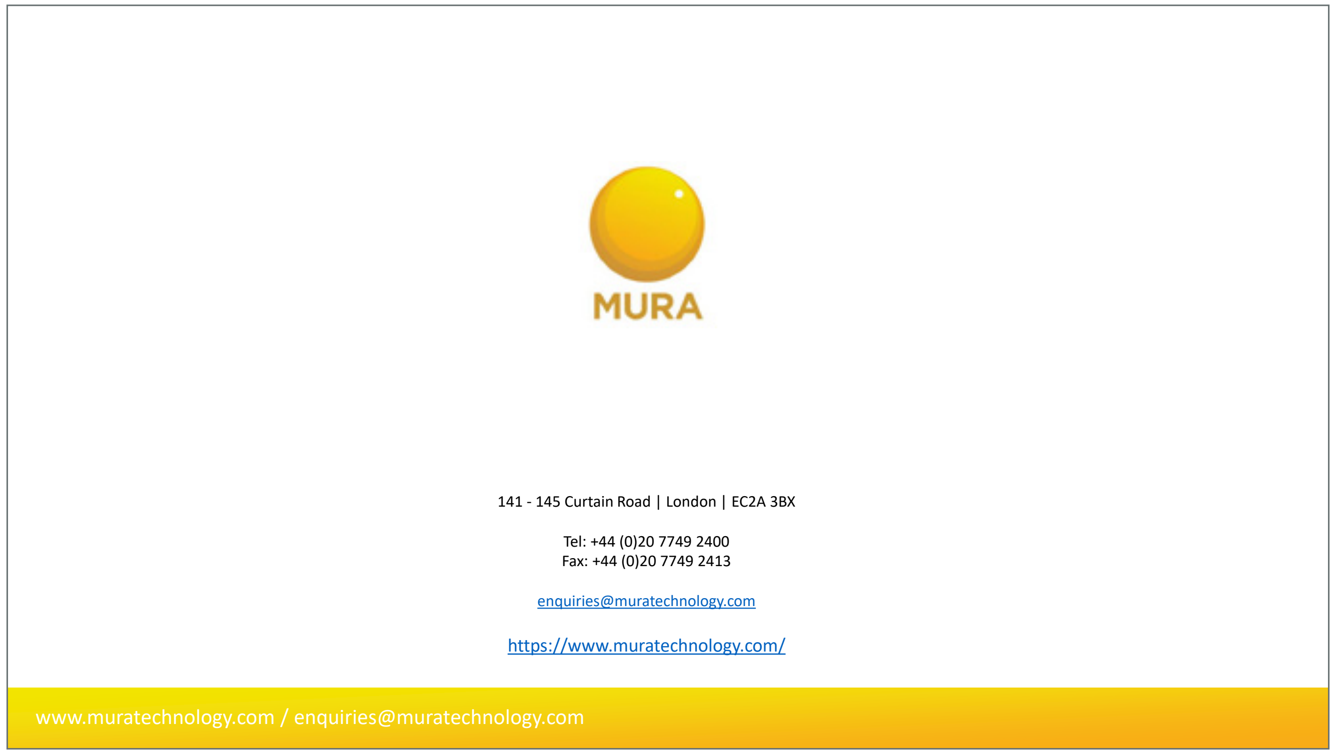

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Erkan Yalcin, TerraNova Energy GmbH

TerraNova® Ultra project Mexico City: Upcycling of Organic Fraction for Municipal Solid Waste in industrial scale

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The city council of Mexico City has started an initiative to upcycle the city's Organic Fraction of Municipal Solid Wastes (OFMSW) by means of Hydrothermal arbonisation (HTC) into a renewable biochar as a substitute for fossil coal for power generation or as a soil conditioner.

Currently the municipal waste is disposed on a vast landfill site and manually separated from valuable materials by waste-pickers. The current situation represents a serious impact on the environment through release of CO_2, nitrous oxide, methane and leachate among 2 others. The HTC-conditions on the other hand lead to a sterilized HTC-coal that is rich in nutrients like Nitrogen and Phosphorous. The project is executed in three consecutive stages:
Stage 1: input up to 72 t/d of OFMSW
Stage 2: input 350 t/d of OFMSW
Stage 3: input > 1.000 t/d of OFMSW

For the implementation of the project the TerraNova Ultra® technology was selected. TerraNova Energy GmbH was the first company to build a commercial, industrial size HTC plant in Jining/China in 2016. The plant runs in continuous operateration ever since with a treatment capacity of 14.000 t input per year indicating a TRL level 9.

In the TerraNova Ultra® process OFMSW is converted under pressure and temperature within a few hours into a regenerative coal (TR 65 %). Compared to conventional drying processes, a significant increase in energy efficiency and a reduction in the disposal mass and thus greenhouse gas emissions is achieved. The process runs in continuous mode and can deal with any feedstocks with dry matter content > 20%.Process overview
1. Input: Waste Biomass, 20-30% dry matter
2. Carbonisation to coal slurry
3. Separation of coal and liquid fraction
4. Downstream treatment of liquid fraction
5. Valorization of biocoal (incineration, soil conditioner)

In the lecture an overview of the project basics and the current project status is presented. The mechanical pretreatment steps required for the use of OFMSW - in contrast to the processing of sewage sludge – are explained. The material data of OFMSW relevant for carbonisation are discussed.

6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP
Hydrothermale Prozesse

Dipl. Ing. Erkan Yalcin
TerraNova Energy GmbH

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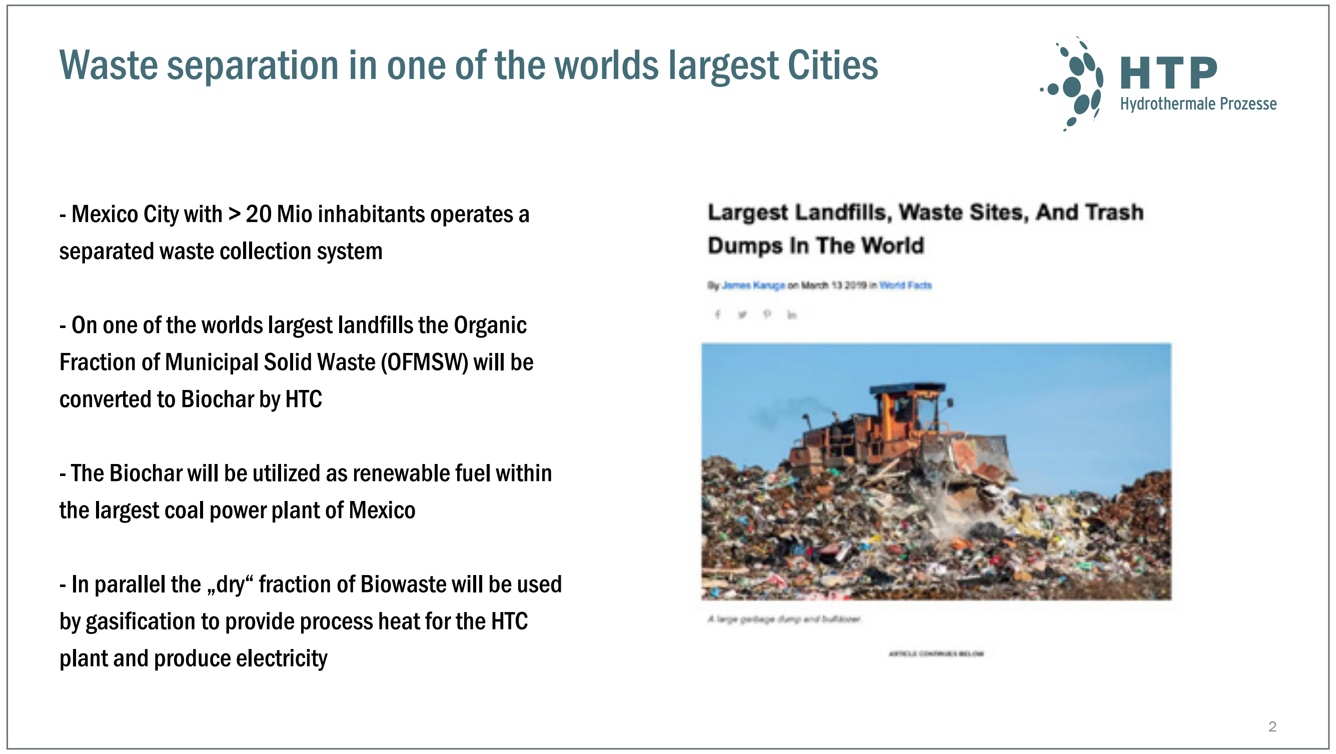


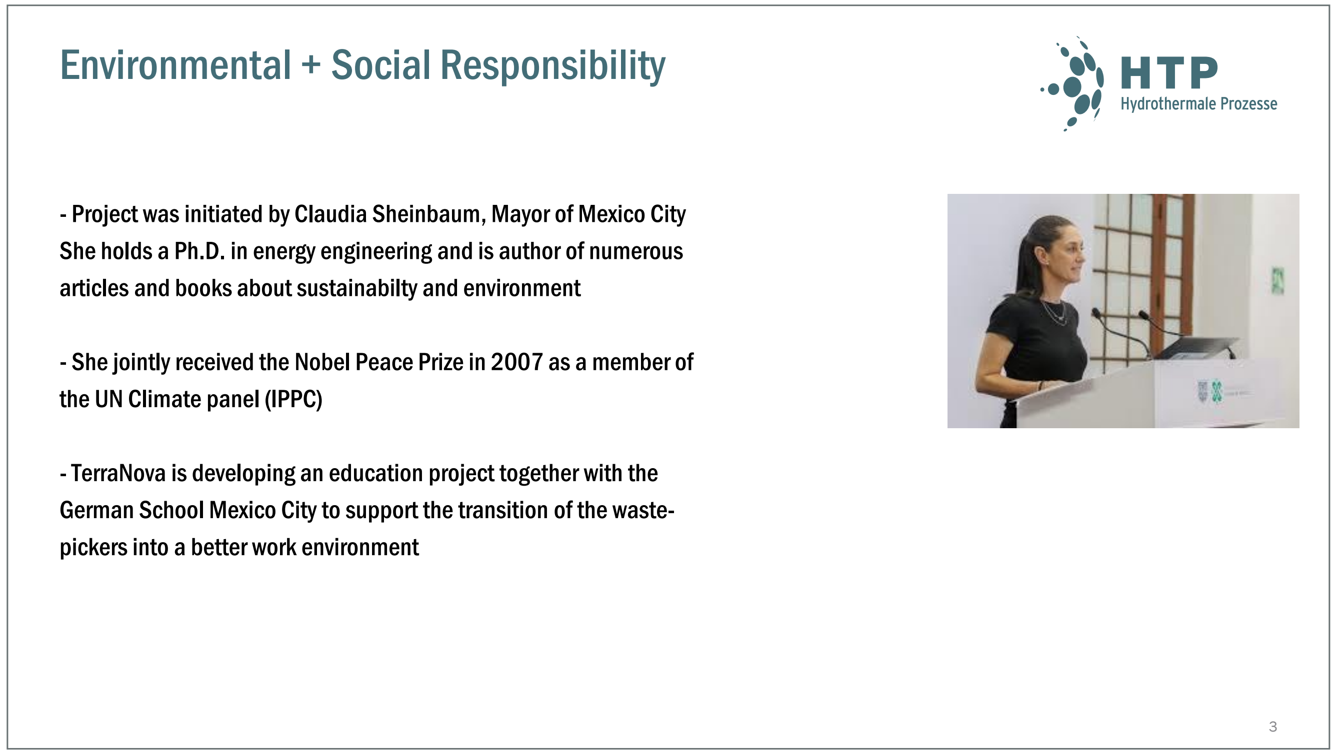
Waste separation in one of the worlds largest Cities

HTP
Hydrothermale Prozesse

- Mexico City with > 20 Mio inhabitants operates a separated waste collection system
- On one of the worlds largest landfills the Organic Fraction of Municipal Solid Waste (OFMSW) will be converted to Biochar by HTC
- The Biochar will be utilized as renewable fuel within the largest coal power plant of Mexico
- In parallel the „dry“ fraction of Biowaste will be used by gasification to provide process heat for the HTC plant and produce electricity

Largest Landfills, Waste Sites, And Trash Dumps In The World

By James Karuga on March 13 2019 in World Facts

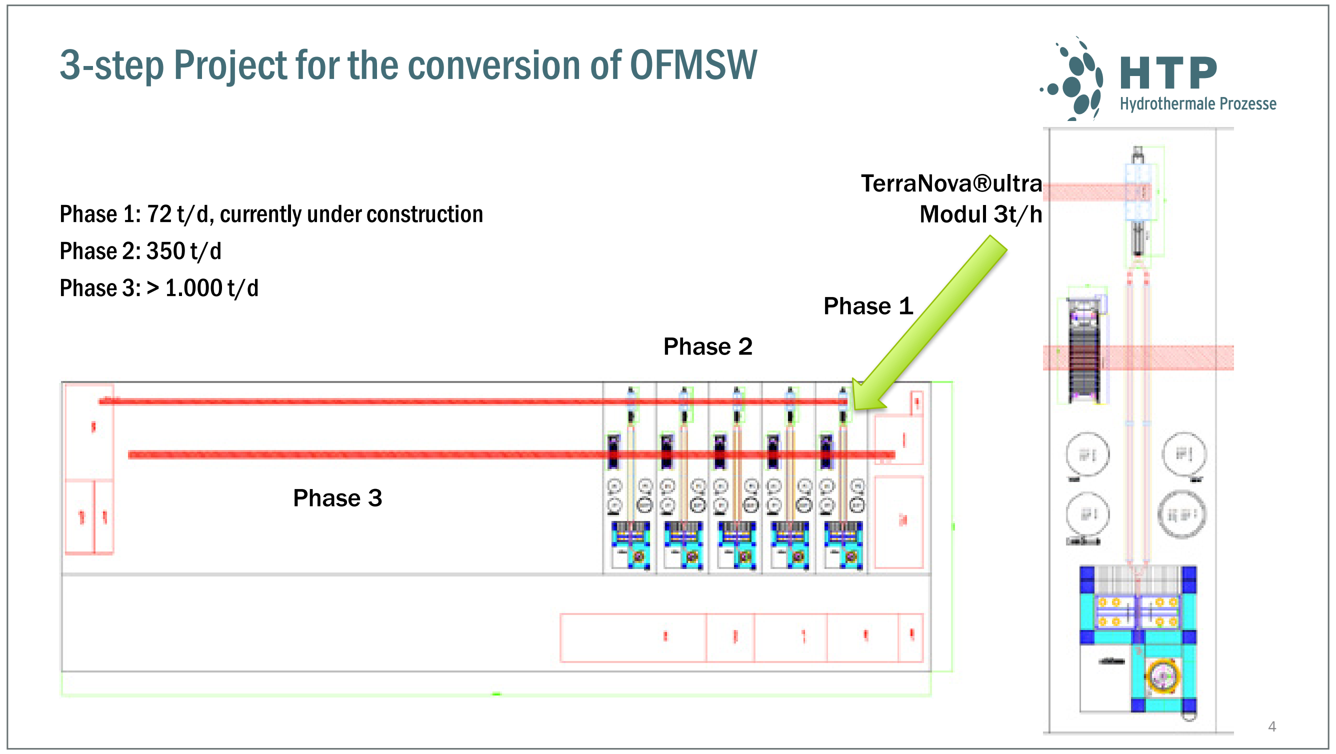


Environmental + Social Responsibility

- Project was initiated by Claudia Sheinbaum, Mayor of Mexico City She holds a Ph.D. in energy engineering and is author of numerous articles and books about sustainabilty and environment

- She jointly received the Nobel Peace Prize in 2007 as a member of the UN Climate panel (IPPC)

- TerraNova is developing an education project together with the German School Mexico City to support the transition of the waste-pickers into a better work environment



3-step Project for the conversion of OFMSW

Phase 1: 72 t/d, currently under construction
Phase 2: 350 t/d
Phase 3: > 1.000 t/d

Current situation on landfill site

Organic waste as delivered by truck

Typial composition of organic waste

Process Flow

- 3-step pretreatment of input material
- Adjustable feed rate into the TerraNova®ultra plant
- Adjustable return rate of HTC process water
- Adjustable treatment time, temperature and pH level
- Fully continuous HTC process with low energy demand
- Integrated separation of larger non-organic particles
- Coal dewatering in membrane filter press
- Exhaust air free final drying step with supply of low grade waste heat 90° C
- Thermal coupling with gasification step

La productora de composta de Bordo Poniente será reconvertida en una generadora de hidrocarbón.

Producirá la CDMX, de la basura, carbón

CIUDAD

Official press release of HTC project

6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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Alfons Kuhles, GRENOL GmbH

Biomassekonversion und Wasserstoffproduktion

Alfons Kuhles, H. Kohler, Dr. G. Dericks
GRENOL GmbH

Derzeit wird molekularer „grüner“ Wasserstoff (H_2) in Deutschland zum größten Teil aus Elektrolyse von Wasser gewonnen, wobei für die Elektrolyse ausschließlich Strom aus erneuerbaren Energien zum Einsatz kommen sollte. Nur „grüner“ Wasserstoff ist klimafreundlich, denn nur „grüner“ Wasserstoff ist ohne fossile Rohstoffe produzierbar. Alle andere Verfahren zur Herstellung von molekularem Wasserstoff benötigen fossile Einsatzmaterialen und hohe Energiekosten oder verursachen vermehrte Emissionen an Methan (CH_4) oder Kohlendioxid (CO_2) bei der Herstellung.

Mit der hydrothermalen und vaporthermalen Karbonisationsprozessen und der anschließenden Vergasung ist es nun möglich, auch aus derzeit ungenutzten Abfallbiomassen „grünen“ Wasserstoff herzustellen. Der gewonnene „grüne“ Wasserstoff kann zur direkten Verwendung in Brennstoffzellen, Verbrennungsmotoren und als Rohgas genutzt werden.

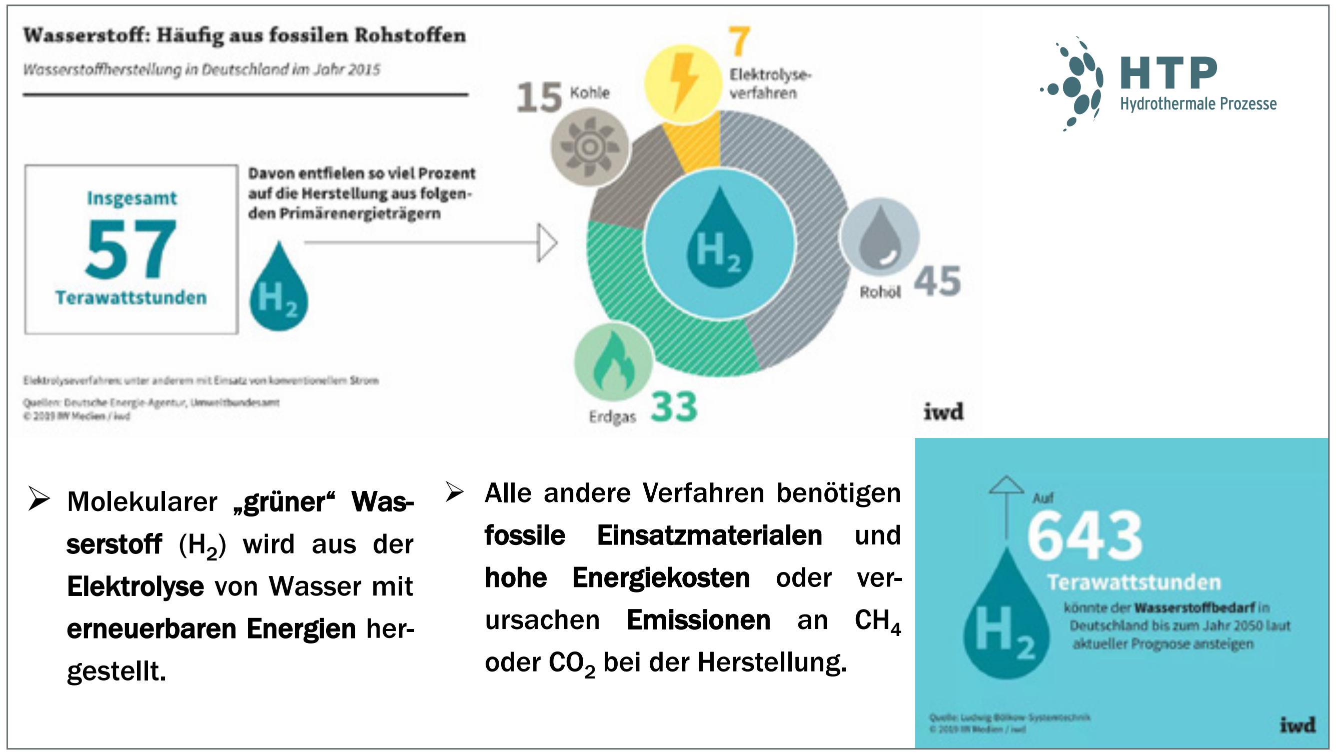
Da die derzeitigen Quellen aus erneuerbaren Strom nicht im Ansatz ausreichen, die benötigten Mengen an Wasserstoff zu produzieren, ist die hydrothermale Karbonisierung die ideale Technik, die Energie-wende im Allgemeinen und die „grüne“ Wasserstoffproduktion im Besonderen zu gewährleisten.

6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Biomassekonversion und Wasserstoffproduktion

Referent: Alfons Kuhles
Institut: GRENOL GmbH

www.htp-inno.de



- Molekularer **„grüner“ Wasserstoff** (H_2) wird aus der **Elektrolyse** von Wasser mit **erneuerbaren Energien** hergestellt.
- Alle andere Verfahren benötigen **fossile Einsatzmaterialen** und **hohe Energiekosten** oder verursachen **Emissionen** an CH_4 oder CO_2 bei der Herstellung.

Der Weg des Wasserstoffs

HTP Hydrothermale Prozesse

1. PRODUKTION

GRÜNE STROMERZEUGUNG

WASSER

GRÜNER STROM

ELEKTROLYSE

GRÜNER WASSERSTOFF

H H

2. TRANSPORT

3. NUTZUNG

STROM UND WÄRME

Grüner Strom, Wärme, Brennstoffzellen-Antriebe

SYNTHETISCHE KRAFTSTOFFE

Kerosin, Diesel-Ersatz

ROH- UND BRENNSTOFFE IN DER INDUSTRIE

Chemikalien, Kunststoffe, Stahl

© BMBF | Projektträger Jülich

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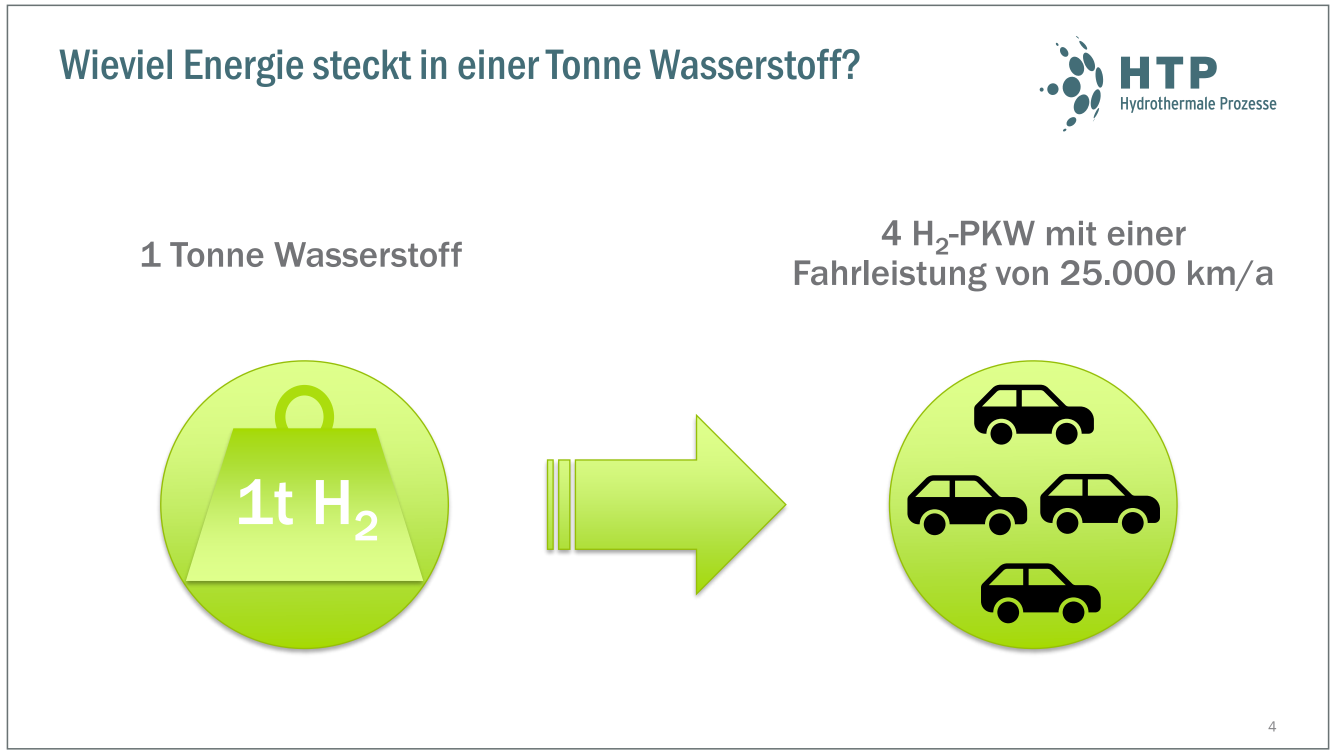


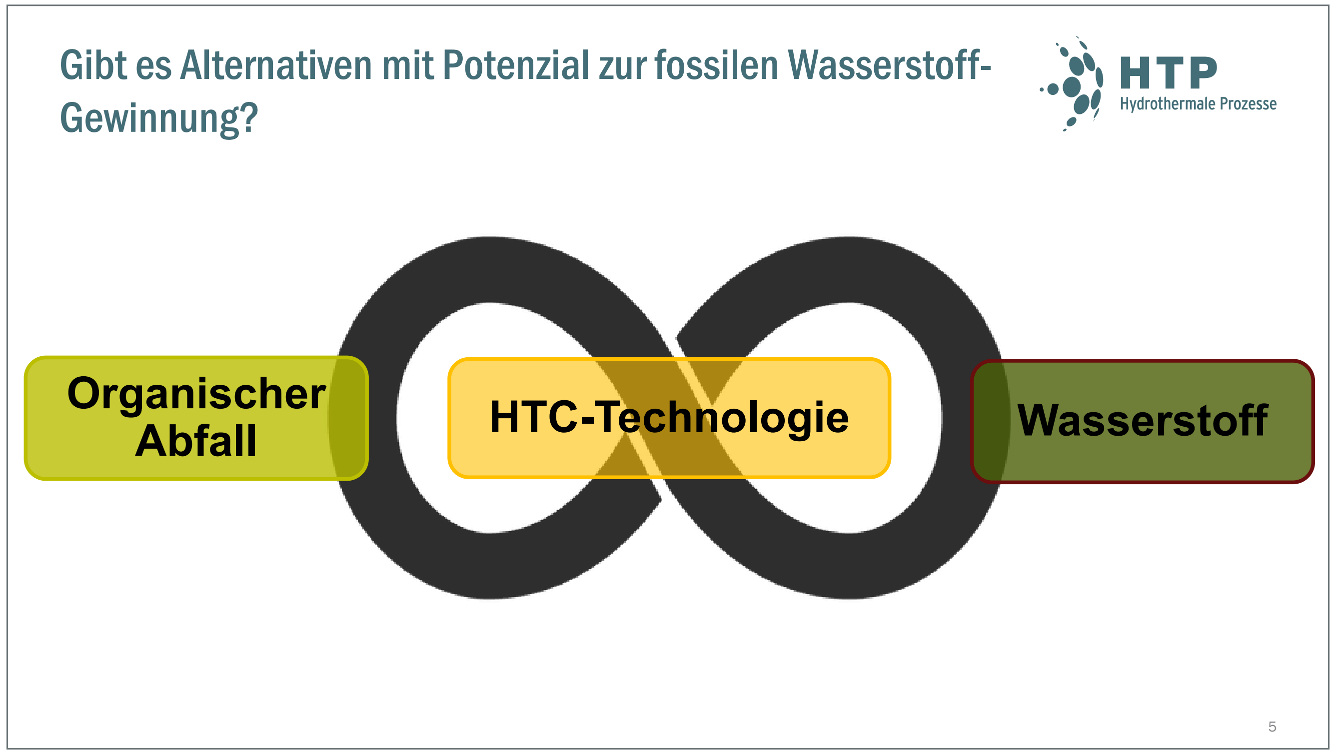
Wieviel Energie steckt in einer Tonne Wasserstoff?

HTP Hydrothermale Prozesse

1 Tonne Wasserstoff

4 H_2-PKW mit einer Fahrleistung von 25.000 km/a

4



Gibt es Alternativen mit Potenzial zur fossilen Wasserstoff-Gewinnung?

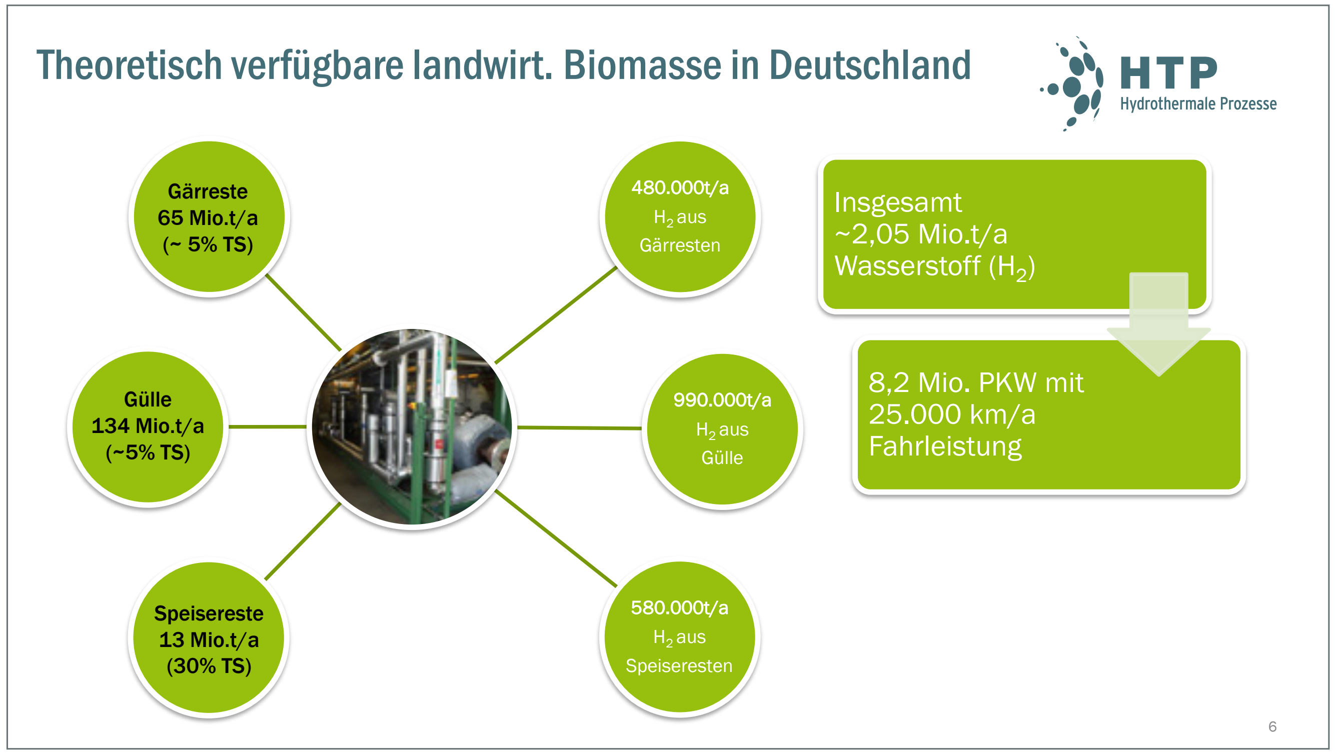
HTP Hydrothermale Prozesse

Organischer Abfall

HTC-Technologie

Wasserstoff

5



Theoretisch verfügbare landwirt. Biomasse in Deutschland

HTP Hydrothermale Prozesse

Gärreste 65 Mio.t/a (~ 5% TS)

Gülle 134 Mio.t/a (~5% TS)

Speisereste 13 Mio.t/a (30% TS)

480.000t/a H_2 aus Gärresten

990.000t/a H_2 aus Gülle

580.000t/a H_2 aus Speiseresten

Insgesamt ~2,05 Mio.t/a Wasserstoff (H_2)

8,2 Mio. PKW mit 25.000 km/a Fahrleistung

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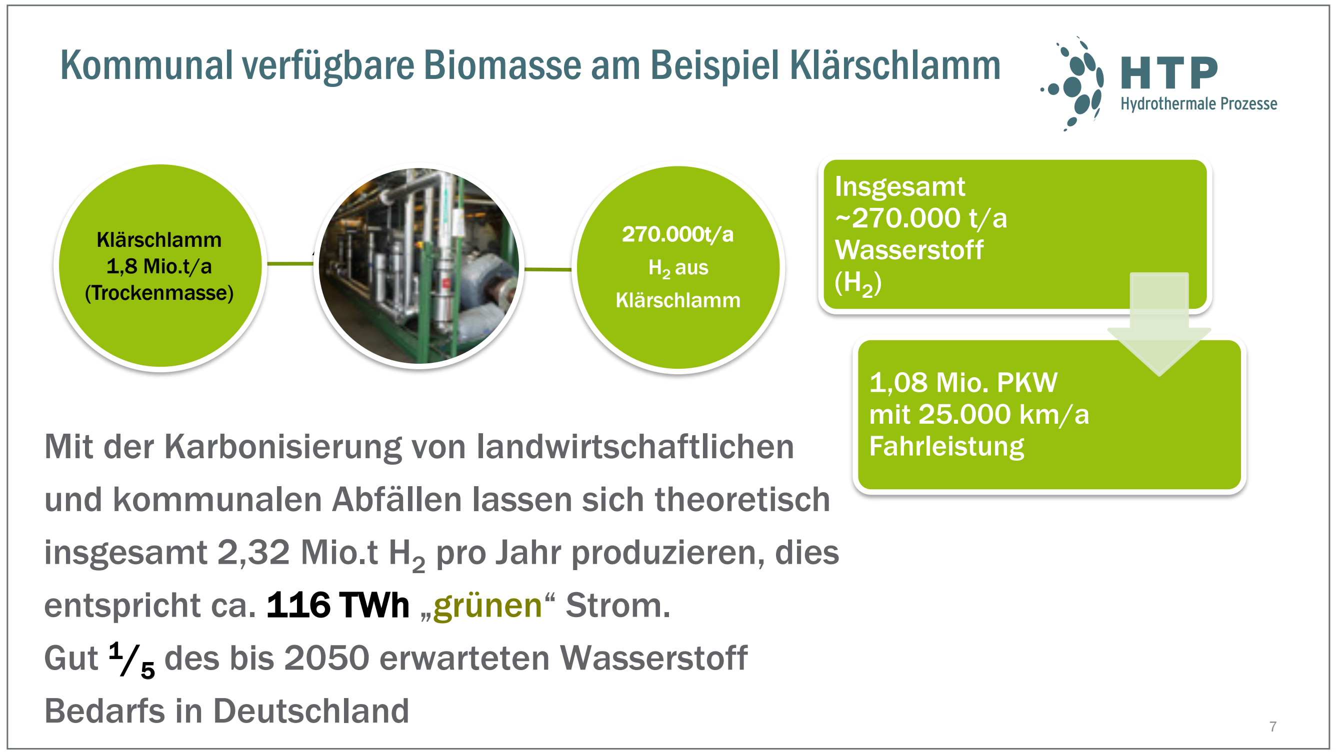


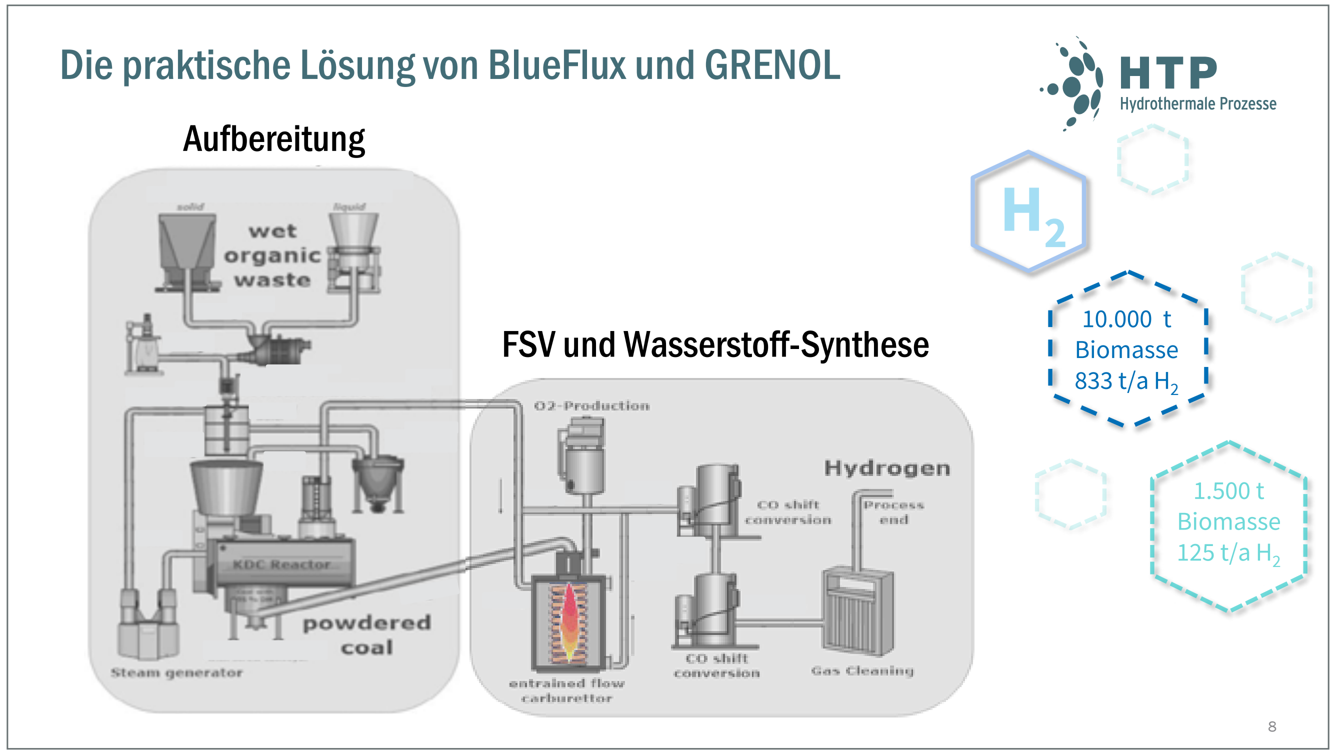
Kommunal verfügbare Biomasse am Beispiel Klärschlamm

Insgesamt ~270.000 t/a Wasserstoff (H_2)

1,08 Mio. PKW mit 25.000 km/a Fahrleistung

Mit der Karbonisierung von landwirtschaftlichen und kommunalen Abfällen lassen sich theoretisch insgesamt 2,32 Mio.t H_2 pro Jahr produzieren, dies entspricht ca. **116 TWh** „grünen“ Strom.

Gut $^1/_5$ des bis 2050 erwarteten Wasserstoff Bedarfs in Deutschland



Die praktische Lösung von BlueFlux und GRENOL

10.000 t Biomasse 833 t/a H_2

1.500 t Biomasse 125 t/a H_2

6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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Philipp Knötig, Deutsches Biomasseforschungszentrum

Entwicklung eines hydrothermalen Mehrzweckreaktors innerhalb eines Pilotanlagenkonzepts zur Gewinnung von Kraftstoffen aus biogenen Reststoffen

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Die Nutzung biogener Abfall- und Reststoffe ist essenziell auf dem Weg zu fortschrittlichen und klimafreundlichen Kraftstoffen. Die nicht erschlossenen Biogaspotenziale innerhalb Europas werden auf eine Energiemenge von 470 - 890 PJ geschätzt. Bisher ungenutzte städtische und landwirtschaftliche Potenziale finden sich bei Klärschlamm, biogenen kommunalen Abfällen, Grünschnitt, Stroh und tierischen Exkrementen.

Im Rahmen eines durch das BMVI geförderten Forschungsprojektes wird untersucht, wie hydrothermale Prozesse in einem Anlagenkonzept mit zentraler anaerober Vergärung zur Gesamteffizienzsteigerung beitragen und welche Vorteile sie aus energetischer, stofflicher und anlagentechnischer Sicht generieren.

Einen Untersuchungsschwerpunkt bildet die Substratvorbehandlung durch Thermodruckhydrolyse. Im Detail beinhaltet dies die Betrachtung der Effekte auf den Gesamt-Methanertrag sowie die Reaktionsgeschwindigkeit des nachgeschalteten Fermentationsprozesses nach Aufschluss lignocellulosehaltiger Materialien wie Stroh und Grünschnitt. Der mögliche stoffliche und energetische Zugewinn sowie die Durchsatzsteigerung machen das Verfahren besonders attraktiv.
Ein weiterer wesentlicher Bestandteil des Vorhabens ist die Nutzbarmachung des Gärrestes bestimmter Substrate mithilfe der hydrothermalen Carbonisierung (HTC). Hier ergeben sich einerseits Vorzüge hinsichtlich der Abfallminimierung durch eine bessere Entwässerbarkeit des Gärrestes und der Produktion einer energetisch vorteilhaften HTC-Kohle sowie andererseits in der stofflichen Nutzung dieses Feststoffs und der beim Verfahren entstehenden Flüssigphase. Eine geschickte Kombination aus Prozessführung und nachgeschalteten Downstreamprozessen ermöglicht die Rückgewinnung der dem Substrat inhärenten Nährstoffe und damit die Schließung von Wertstoffkreisläufen.

Neben der hieraus angedeuteten Variabilität in den Aufgabenfeldern, erfordern besonders die diversen physikalischen Eigenschaften der Reststoffe ein flexibles und robustes Reaktordesign. Schwerpunkte bilden hierbei der Substratein- und Produktaustrag sowie die effiziente Durchmischung zur Herstellung konstanter Reaktionsbedingungen. Unter Berücksichtigung dieser Anforderungen wurde innerhalb des Projektvorhabens ein Reaktor entwickelt, welcher sowohl einen flexiblen als auch logistisch effizienten Einsatz innerhalb des Pilotanlagenkonzepts ermöglicht und ein hohes Maß an Automatisierung aufweist.

6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

Development of a hydrothermal multi-purpose reactor within a pilot-scale biorefinery concept for fuel production from biogenic residues

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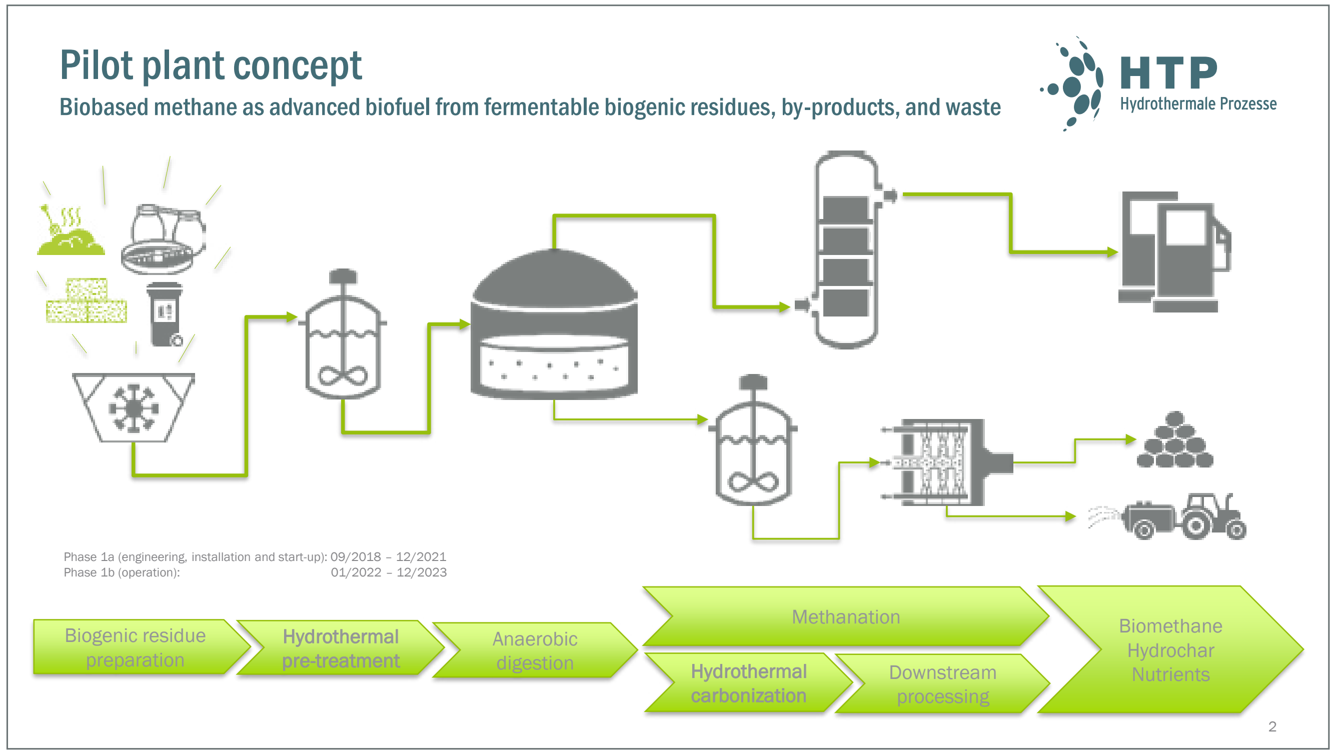
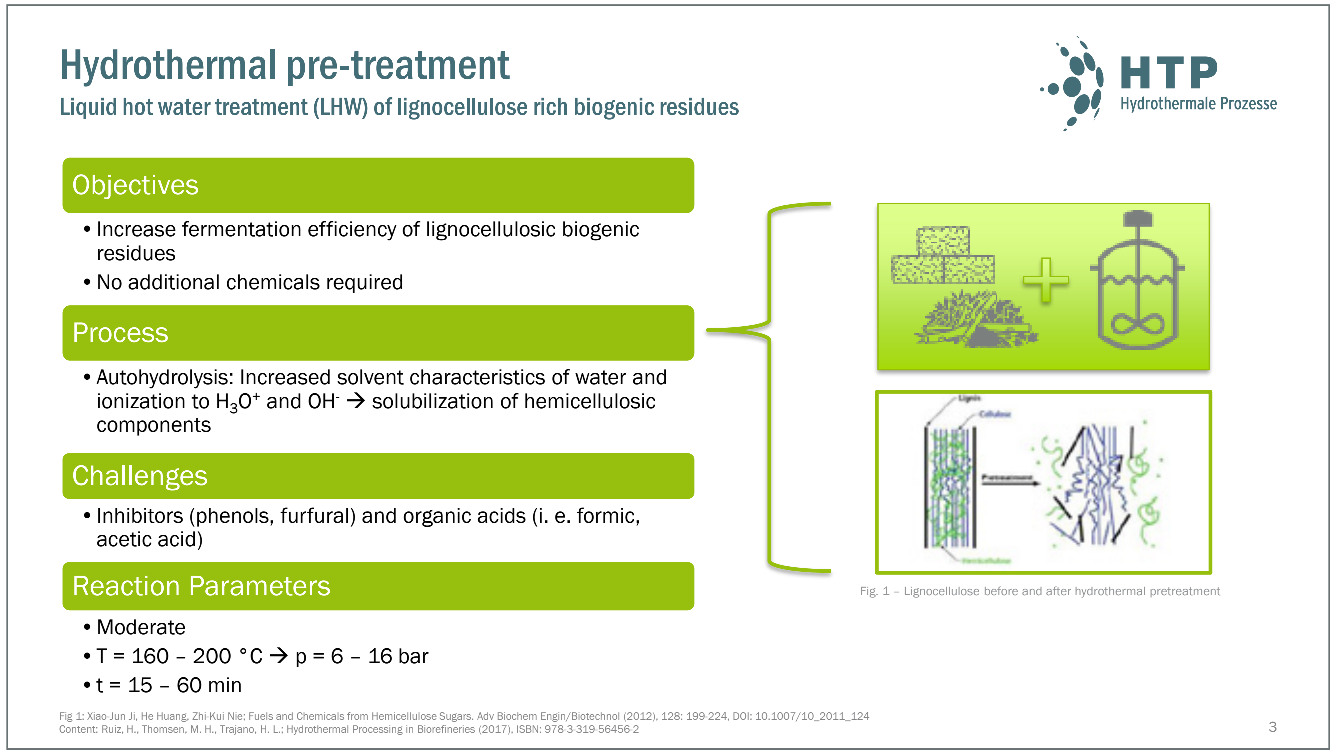


Pilot plant concept

Biobased methane as advanced biofuel from fermentable biogenic residues, by-products, and waste

Phase 1a (engineering, installation and start-up): 09/2018 – 12/2021
Phase 1b (operation): 01/2022 – 12/2023



Hydrothermal pre-treatment

Liquid hot water treatment (LHW) of lignocellulose rich biogenic residues

Objectives

- Increase fermentation efficiency of lignocellulosic biogenic residues
- No additional chemicals required

Process

- Autohydrolysis: Increased solvent characteristics of water and ionization to H_3O^+ and OH^- → solubilization of hemicellulosic components

Challenges

- Inhibitors (phenols, furfural) and organic acids (i. e. formic, acetic acid)

Reaction Parameters

- Moderate
- T = 160 – 200 °C → p = 6 – 16 bar
- t = 15 – 60 min

Fig. 1 – Lignocellulose before and after hydrothermal pretreatment

Fig 1: Xiao-Jun Ji, He Huang, Zhi-Kui Nie; Fuels and Chemicals from Hemicellulose Sugars. Adv Biochem Engin/Biotechnol (2012), 128: 199-224, DOI: 10.1007/10_2011_124
Content: Ruiz, H., Thomsen, M. H., Trajano, H. L.; Hydrothermal Processing in Biorefineries (2017), ISBN: 978-3-319-56456-2

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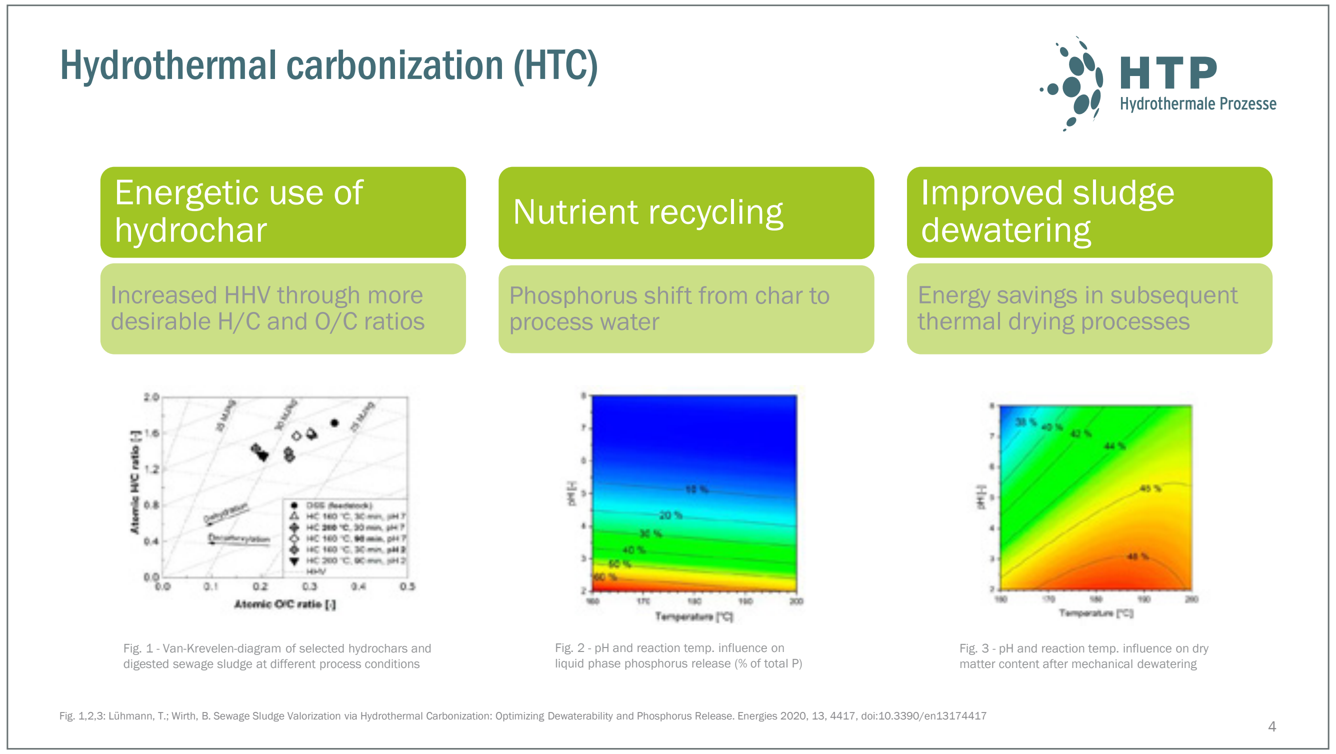

Hydrothermal carbonization (HTC)

Energetic use of hydrochar	Nutrient recycling	Improved sludge dewatering
Increased HHV through more desirable H/C and O/C ratios	Phosphorus shift from char to process water	Energy savings in subsequent thermal drying processes

Fig. 1 - Van-Krevelen-diagram of selected hydrochars and digested sewage sludge at different process conditions

Fig. 2 - pH and reaction temp. influence on liquid phase phosphorus release (% of total P)

Fig. 3 - pH and reaction temp. influence on dry matter content after mechanical dewatering

Fig. 1,2,3: Lühmann, T.; Wirth, B. Sewage Sludge Valorization via Hydrothermal Carbonization: Optimizing Dewaterability and Phosphorus Release. Energies 2020, 13, 4417, doi:10.3390/en13174417

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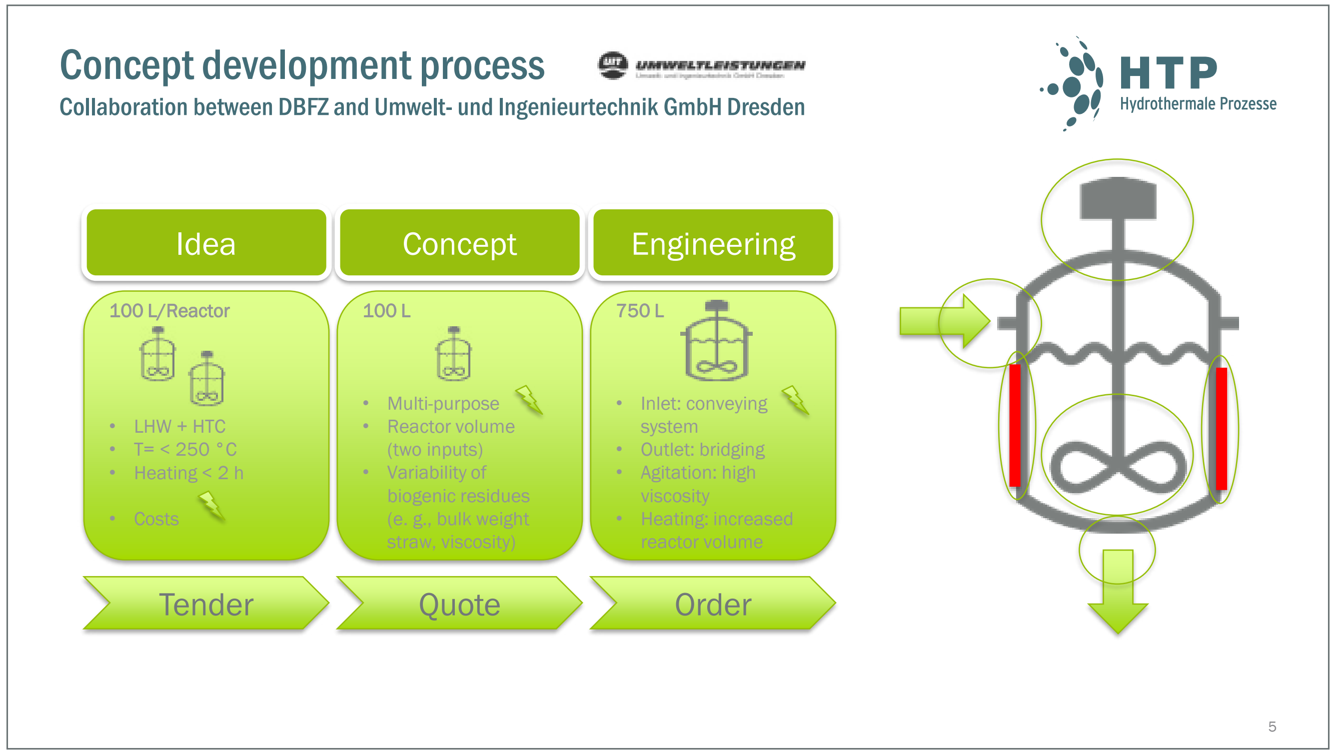
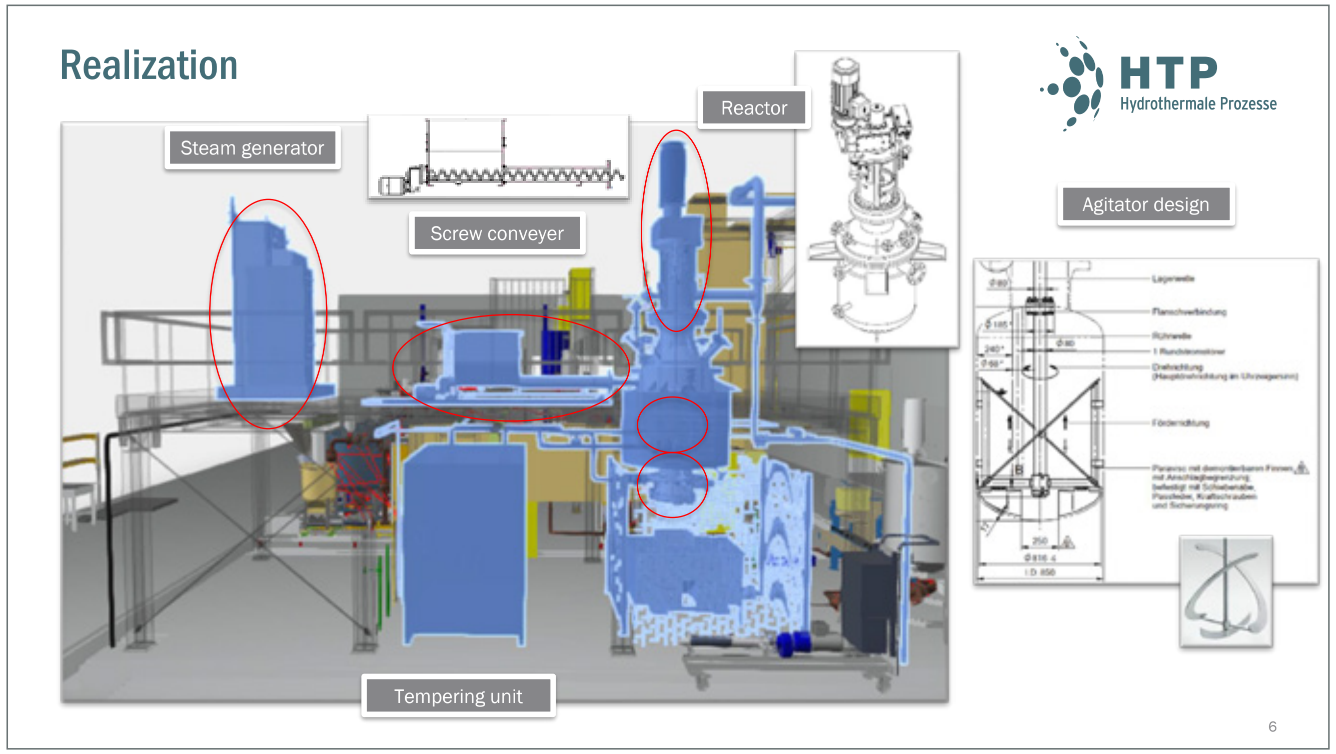


Concept development process

Collaboration between DBFZ and Umwelt- und Ingenieurtechnik GmbH Dresden

Idea	Concept	Engineering
100 L/Reactor	100 L	750 L
• LHW + HTC • T= < 250 °C • Heating < 2 h • Costs	• Multi-purpose • Reactor volume (two inputs) • Variability of biogenic residues (e. g., bulk weight straw, viscosity)	• Inlet: conveying system • Outlet: bridging • Agitation: high viscosity • Heating: increased reactor volume
Tender	Quote	Order

5



Realization

Steam generator

Screw conveyer

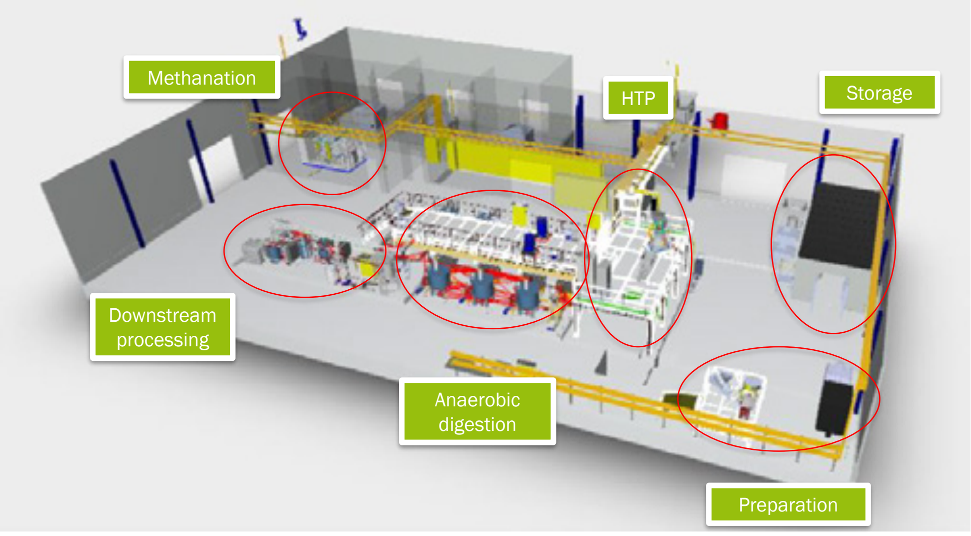
Reactor

Agitator design

Tempering unit

6

Implementation in pilot plant



6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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Session IV

Technologiebewertung hydrothermaler Verfahren

Lisa Röver, Deutsches Biomasseforschungszentrum

Heißentwässerung von hydrothermal behandelten Klärschlämmen

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Klärschlamm wird aktuell mittels mechanischer Entwässerungsverfahren auf ca. 20-30 % Trockenmasse entwässert. Der hohe Wassergehalt führt zu hohen Logistik- und Entsorgungskosten. Die hydrothermale Carbonisierung (HTC) erfolgt bei hohen Temperaturen und Drücken, sodass gebundenes Wasser (Zellinnenwasser, Zwischenraumwasser und Oberflächenwasser) nach der Behandlung verfügbar ist und durch eine anschließende mechanische Entwässerung leichter zu entfernen ist (Kopp, 2001). Während der HTC kommt es zu einer Abnahme von funktionellen Sauerstoffgruppen, wodurch die Anzahl der in den mono- und multimolekularen Schicht sorbierten Wassermoleküle, die nicht durch Druck abgepresst werden können, sinkt (Quicker and Weber, 2016). Die Heißentwässerung ist adaptiert von der Entwässerung von Braunkohle aufgrund der chemischen Ähnlichkeit zu HTC-Kohlen (Berger, 2002). Diese erfolgt bei einer Temperatur von 140 °C. Höhere Temperaturen führen zu einer Veränderung der physikalischen Eigenschaften des Wassers. wie die Abnahme der Oberflächenspannung, der Viskosität und der Dichte (Stemann, 2013). Damit können mit geringerem energetischen Aufwand Trockenmassegehalte von über 60 % erreicht werden. Eine Kopplung der Heißentwässerung an den Prozess der HTC ermöglicht, dass ein Teil der Wärme und des Drucks direkt für die Entwässerung genutzt werden können.

Am DBFZ wurde eine Heißentwässerungsanlage entwickelt und für unterschiedliche Biomassen untersucht. Im Rahmen von abonoCARE wurde systematisch untersucht, welchen Einfluss die HTC Parameter auf die Heißentwässerung haben. Unterschiedliche Filtermaterialien werden ebenfalls betrachtet. Die Erkenntnisse der werden anschließend auf eine Technikumsanlage übertragen, bei der die Heißentwässerung an einen HTC-Reaktor anschließt. Die Heißentwässerung ist eine vielversprechende Methode für die Trocknung hydrothermal behandelter Klärschlammkohlen.

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Kopp, Julia Beate. Wasseranteile in Klärschlammsuspensionen. Messmethode und Praxisrelevanz; Dissertation; Technische Universität Braunschweig, 2001.
Quicker, P., Weber, K., Eds.: Biokohle: Herstellung, Eigenschaften und Verwendung von Biomassekarbonisaten; Springer Vieweg: Wiesbaden, 2016.
Stemann, Jan. Hydrothermale Carbonisierung: Stoffliche und energetische Kreislaufführung; Dissertation; Technische Universität Berlin, 2013.

6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

High temperature dewatering of hydrothermally treated sewage sludge

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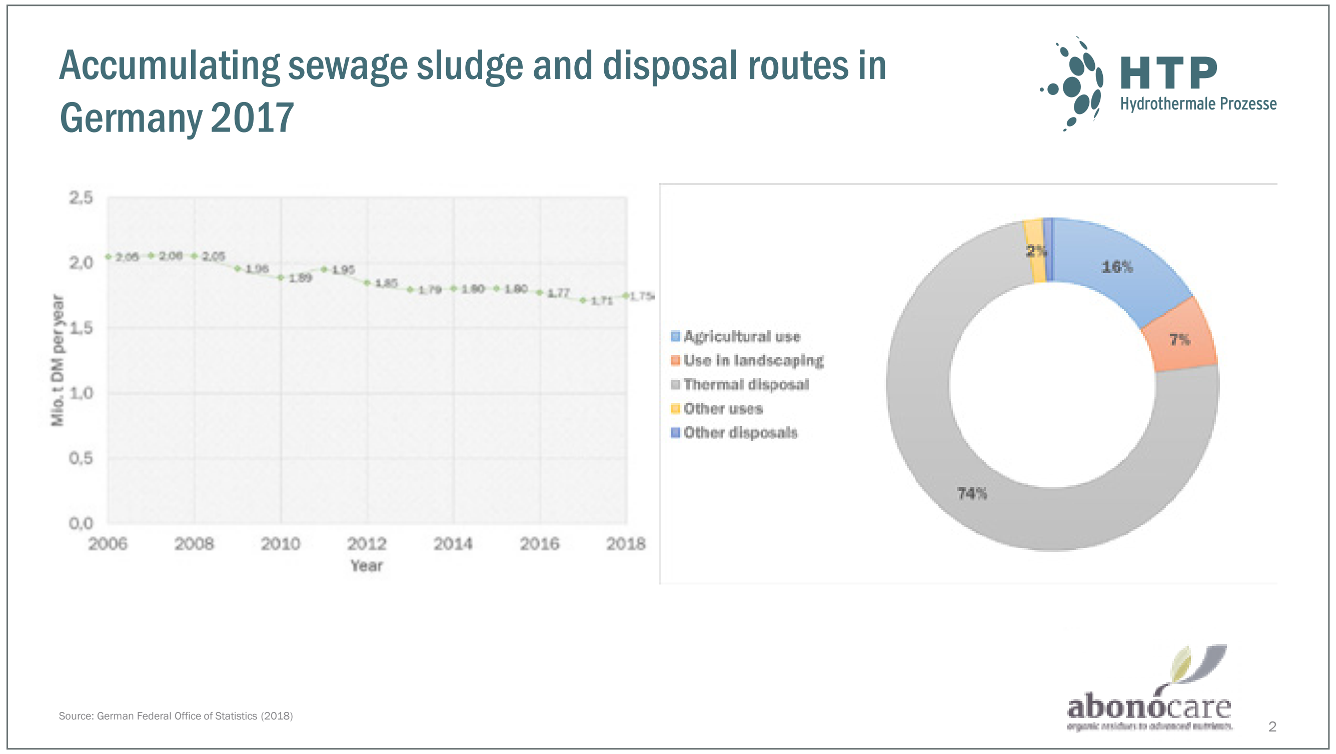


Accumulating sewage sludge and disposal routes in Germany 2017

Source: German Federal Office of Statistics (2018)

Disposal problem of sewage sludge

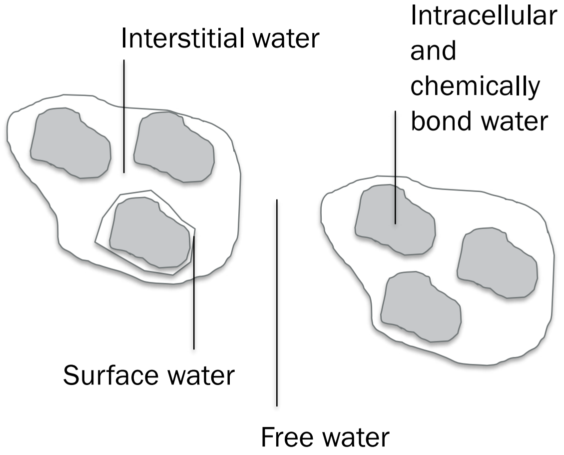
Amendment of the law (AbfKlärV) in 2017

- **Concept of phosphorus recovery in 2023**
- Mono combustion with following ash deposit or treatment is the „easiest“ solution
- **End of agricultural use of sewage sludge in 2029 | 2032**
- **Mandatory P-recovery in 2029 | 2032**

- **Aim: Elimination of contaminants from the circulation, preservation of nutrients**

Properties of sewage sludge

- **Dry matter (DM) of 25-35 % (w/w)[1]**
- **Lower heating value LHV 10 - 12 MJ/kg (at 85 % DM w/w)[2]**
- **Hydrothermal treatment favors a higher heating value**
- **Better dewaterability results in lower costs for transport**



Adapted from: Chen, Guohua; Lock Yue, Po; Mujumdar, Arun S. (2002): Dewatering and Drying. In: Drying Technology (20:4-Sludge5), S. 883–916.

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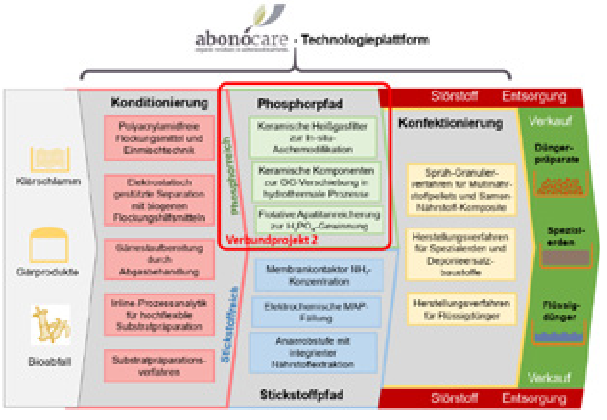
[1] DWA 387 report (2012)
[2] Umweltbundesamt Germany: Klärschlammentsorgung in der Bundesrepublik Deutschland, 2018

Project abonoCARE

Tasks at DBFZ:

- **Phosphorus recovery**
- **High temperature dewatering in combination with hydrothermal carbonization**
- **Previous project: HEPT high temperature dewatering press**
- **Project partners: Wartung und Instandhaltung GmbH und Lufttechnik Crimmitschau GmbH**

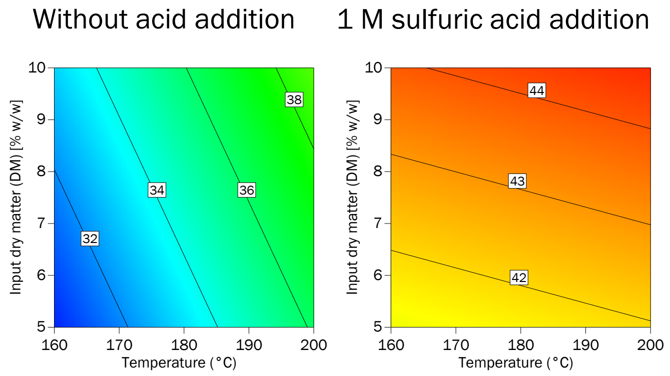


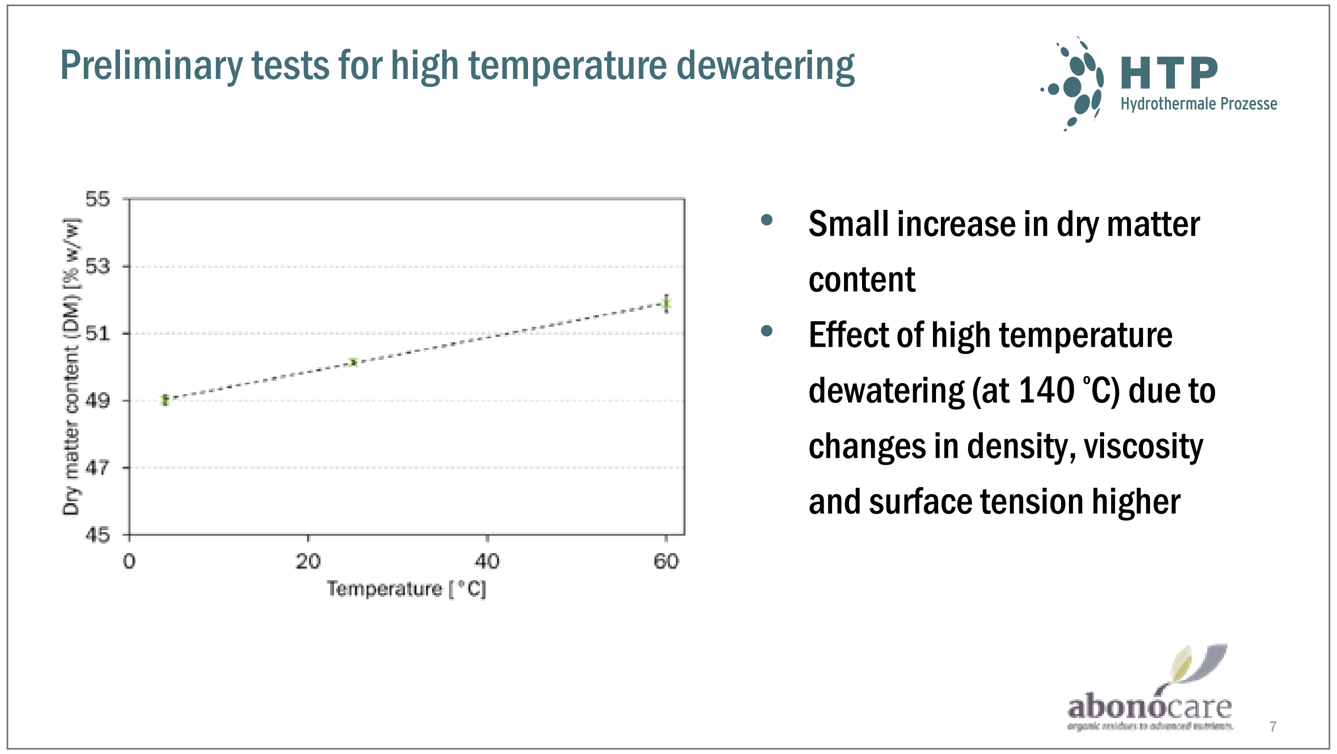
Abonocare.de

Process parameter variation for the dewatering process

Design of experiment: Face-centered central composite design (FCCD)

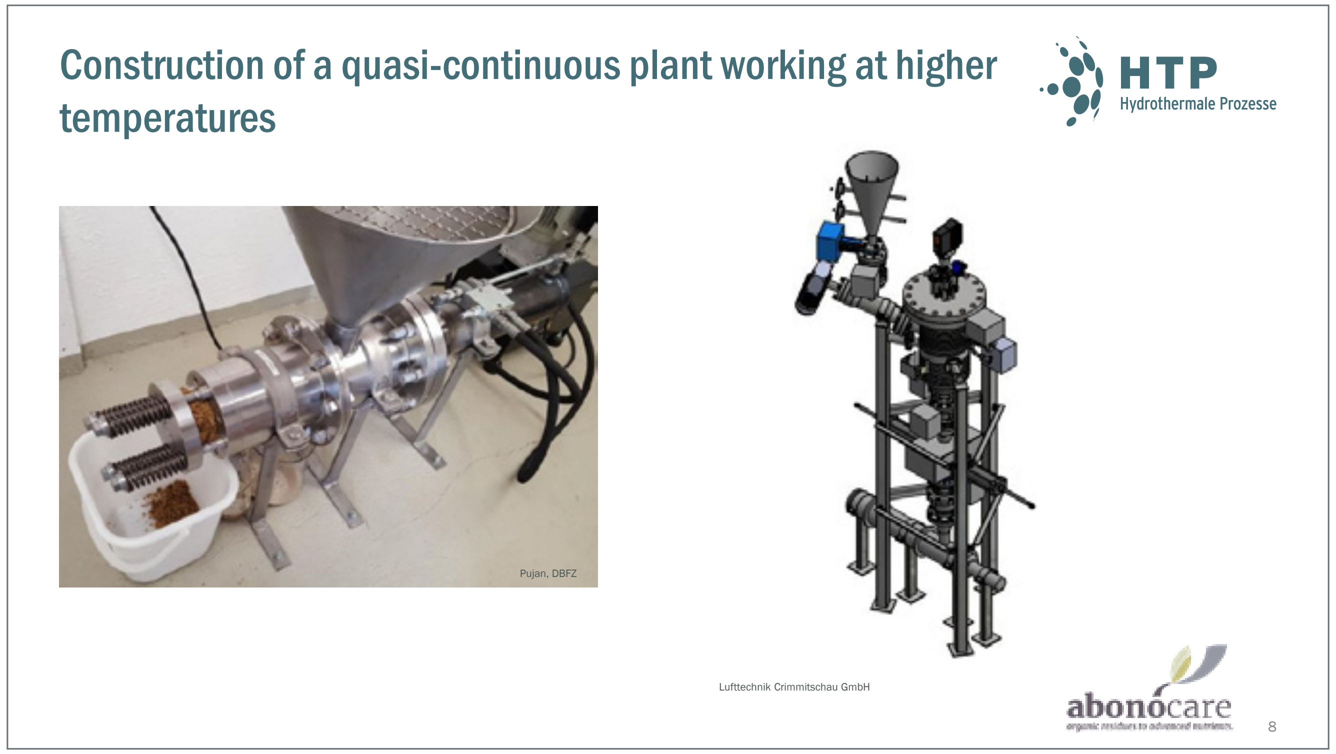
- **Temperature 160 – 200 °C**
- **Initial dry matter content 5 – 10 %**
- **In presence or absence of 1 M sulfuric acid in a 1:1 ratio (w/w) with sewage sludge**





Preliminary tests for high temperature dewatering

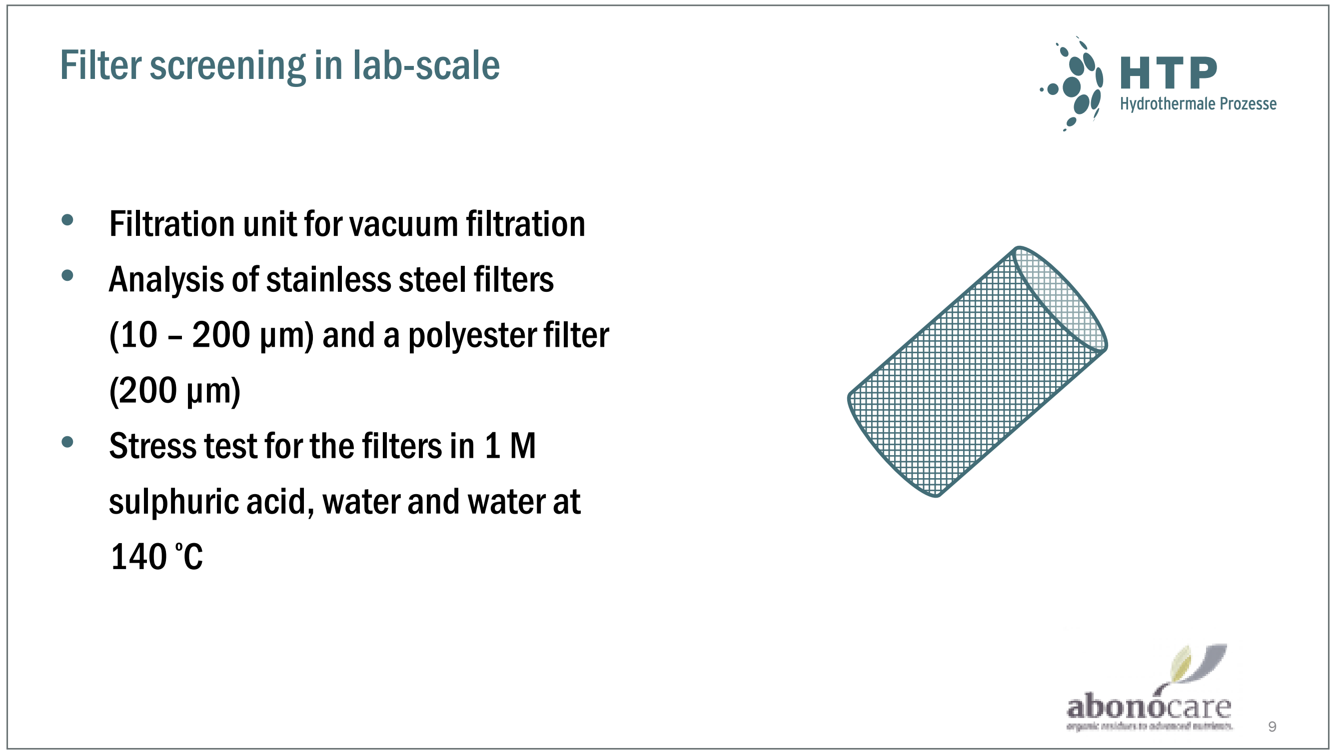
- Small increase in dry matter content
- Effect of high temperature dewatering (at 140 °C) due to changes in density, viscosity and surface tension higher



Construction of a quasi-continuous plant working at higher temperatures

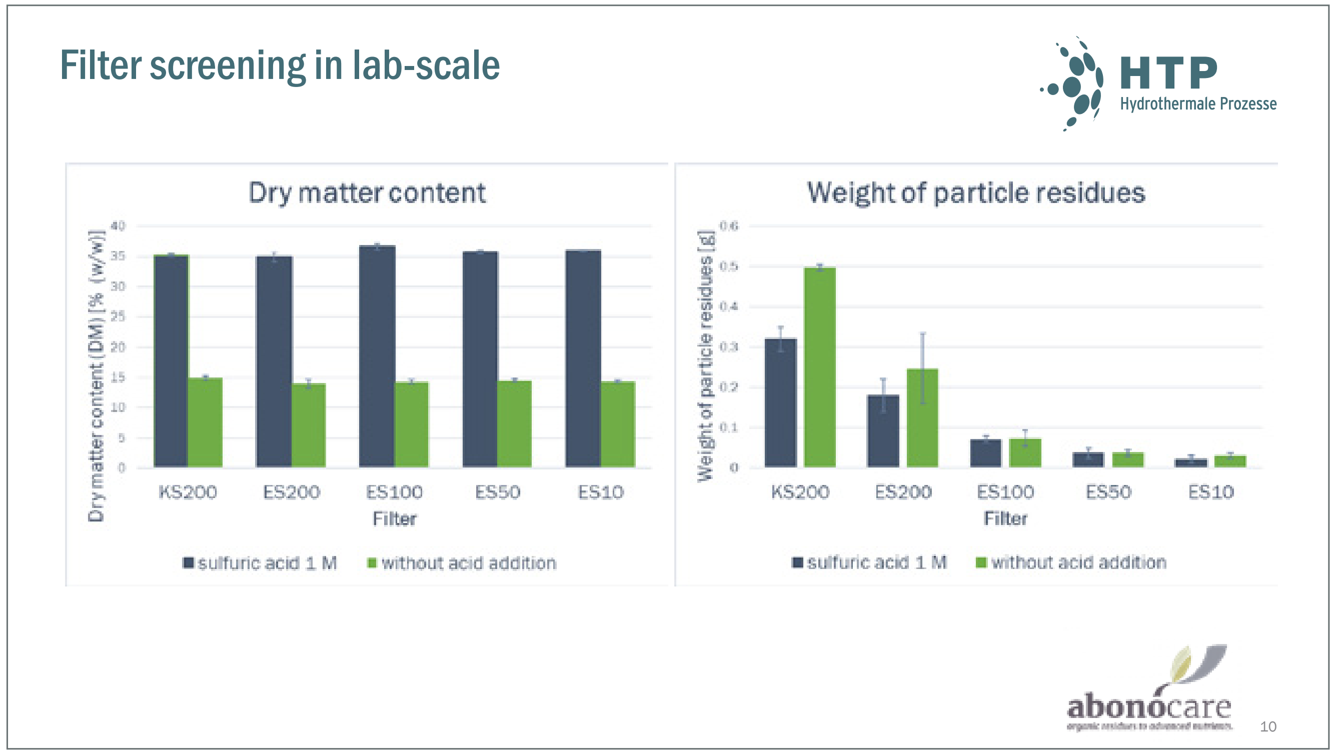
Pujan, DBFZ

Lufttechnik Crimmitschau GmbH



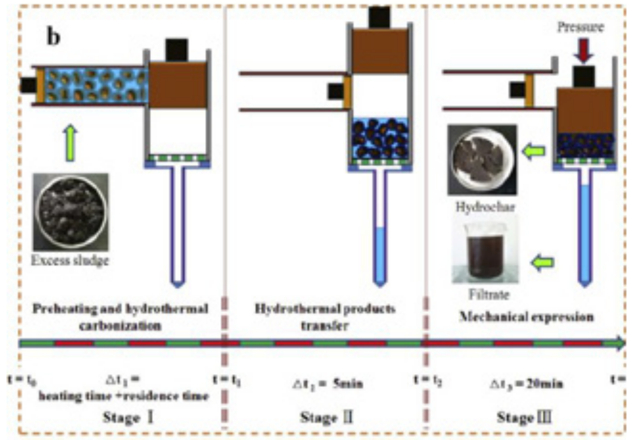
Filter screening in lab-scale

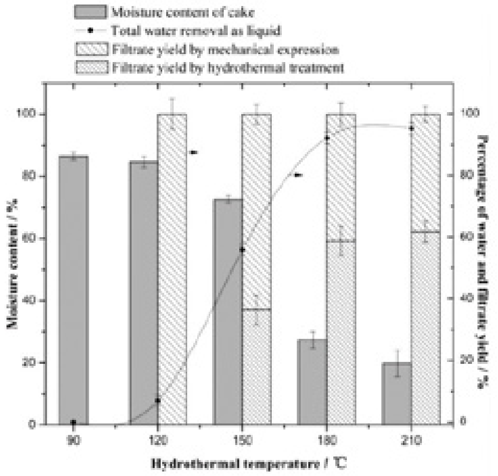
- Filtration unit for vacuum filtration
- Analysis of stainless steel filters (10 – 200 µm) and a polyester filter (200 µm)
- Stress test for the filters in 1 M sulphuric acid, water and water at 140 °C



Filter screening in lab-scale

High temperature dewatering in literature





Wang, L.; Zhang, L.; Li, A. (2014). "Hydrothermal treatment coupled with mechanical expression at increased temperature for excess sludge dewatering. Influence of operating conditions and the process energetics". Water Research 65, S. 85–97.

6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

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HTC von Klärschlamm – Eine Auswertung ökonomischer Daten

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Die hydrothermale Carbonisierung steht als Technologie aktuell vor einer Phase der Markteinführung. Bisher werden bis auf wenige Ausnahmen nur Kleinanlagen oder Pilotanlagen zu Forschungszwecken gebaut. In dieser Phase der Technologieentwicklung ist besonders das Zusammenspiel von potenziellen Investoren, Industriepartnern und der Wissenschaft für eine erfolgreiche Umsetzung von Industrieanlagen wichtig. Neben erlangten Forschungsergebnissen zu den Prozessen, möglichen Ausbeuten und der generellen Machbarkeit, spielt zunehmend die ökonomische Umsetzbarkeit eine wichtige Rolle.

Gerade bei neuen Technologien ist diese ökonomische Bewertung aufgrund vieler Unsicherheiten stark auf Erfahrungen, Experteneinschätzungen und Literaturangaben gestützt. Über ein Review verschiedener Veröffentlichungen soll in dieser Ausarbeitung ein möglicher Business Case dargestellt und mögliche Hürden sowie Chancen beleuchtet werden. Gerade ökonomische Kennzahlen sind in der Wirtschaft Informationen, die selten freiwillig geteilt werden, da es sich hierbei oft um interne Expertise handelt.

Durch die Zusammenfassung und Diskussion bereits öffentlicher Daten sollen die getroffenen Annahmen genauer und somit die Ergebnisse einer ökonomischen Bewertung belastbarer werden. So kann gezielt an möglichen Schwachstellen geforscht werden, um mit fortschreitender Technologieentwicklung auch die Barrieren für eine Markteinführung aus ökonomischer Sicht zu minimieren.

6. HTP-Fachforum | 25./26. November 2020
Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTC von Klärschlamm -
eine Auswertung ökonomischer Daten

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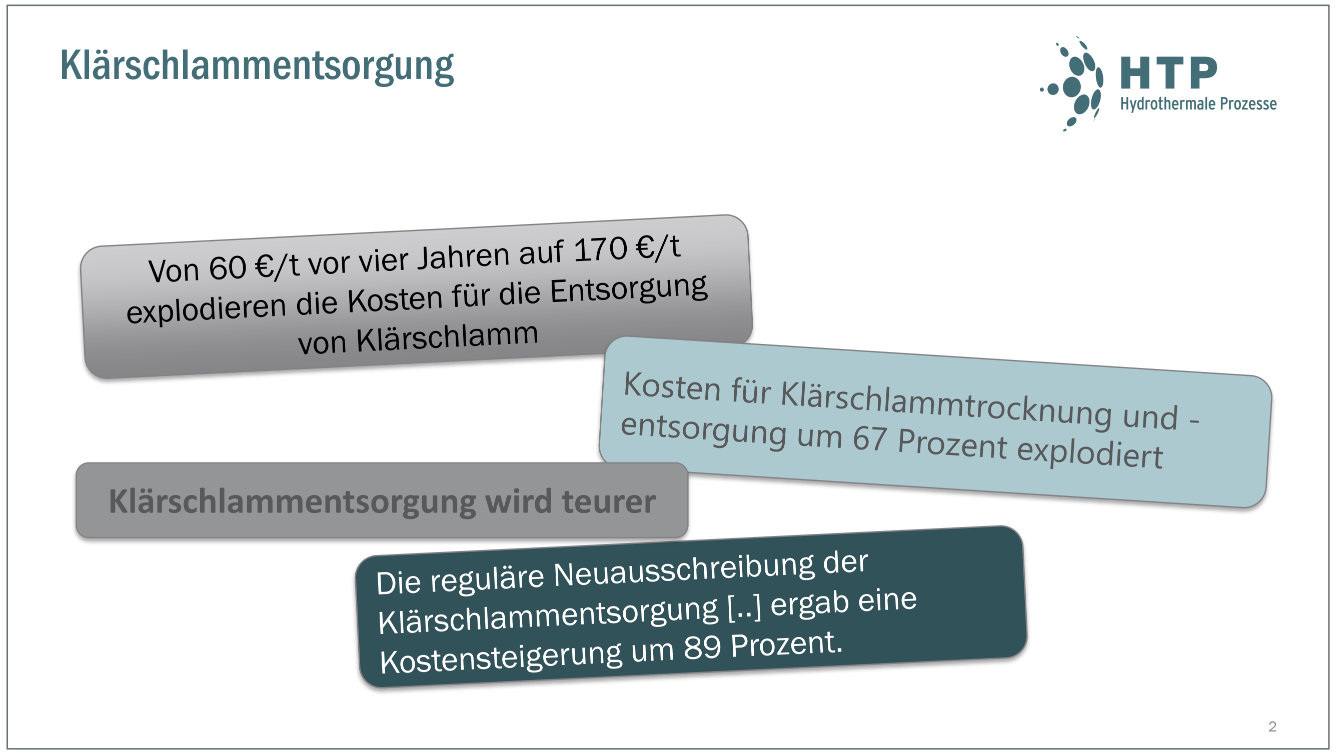


Klärschlammentsorgung

Von 60 €/t vor vier Jahren auf 170 €/t explodieren die Kosten für die Entsorgung von Klärschlamm

Kosten für Klärschlammtrocknung und -entsorgung um 67 Prozent explodiert

Klärschlammentsorgung wird teurer

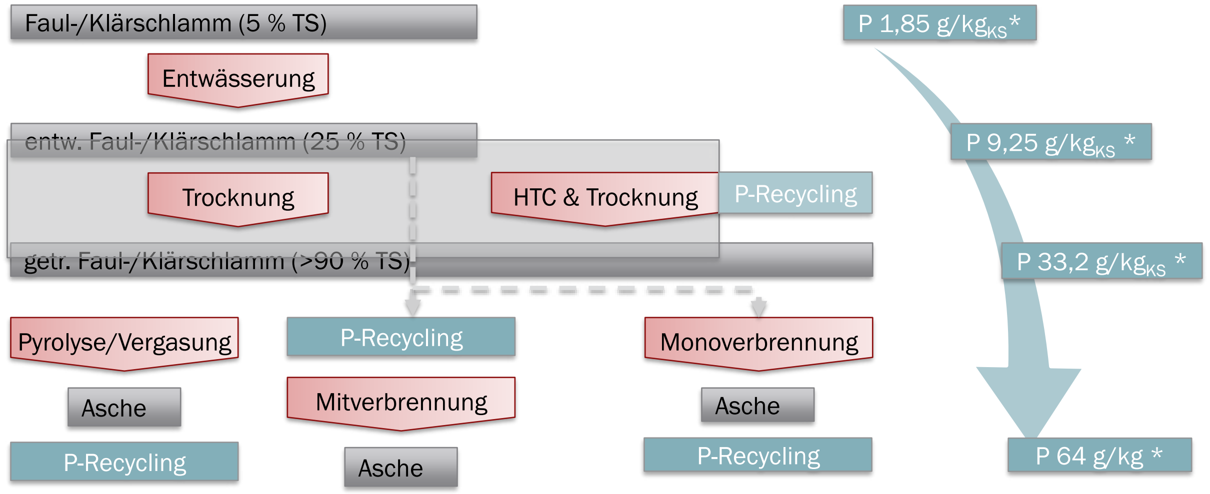
Die reguläre Neuausschreibung der Klärschlammentsorgung [..] ergab eine Kostensteigerung um 89 Prozent.

Klärschlamm ein Rest-/Rohstoff

Koalitionsvertrag Union/SPD	„Wir werden die Klärschlammausbringung zu Düngezwecken beenden und Phosphor und andere Nährstoffe zurückgewinnen“
AbfKlärV 1992	schadstoffseitige Anforderungen an die Verwertung von Klärschlämmen zu Düngezwecken auf landwirtschaftlich genutzten Böden
AbfKlärV 2017	stärkerer nachhaltiger Umwelt- und Ressourcenschutz
→	ab 2029 keine bodenbezogene Verwertung von Klärschlamm sowie Pflicht zum Phosphorrecycling (ab 20 g P/kg_{TS})

Theor. Potenzial ca. 60.000 t/a Phosphor aus Klärschlämmen in D
mit 80 % Recycling können 60 % der Importe gedeckt werden
Phosphordünger (DAP) ca. 350 €/t (zuletzt stark schwankend, Quelle: agrarheute)

Aktuelle Lösungsansätze



Faul-/Klärschlamm (5 % TS)

Entwässerung

entw. Faul-/Klärschlamm (25 % TS)

Trocknung

HTC & Trocknung

P-Recycling

getr. Faul-/Klärschlamm (>90 % TS)

Pyrolyse/Vergasung

Asche

P-Recycling

P-Recycling

Mitverbrennung

Asche

Monoverbrennung

Asche

P-Recycling

P 1,85 g/kg_{KS}*

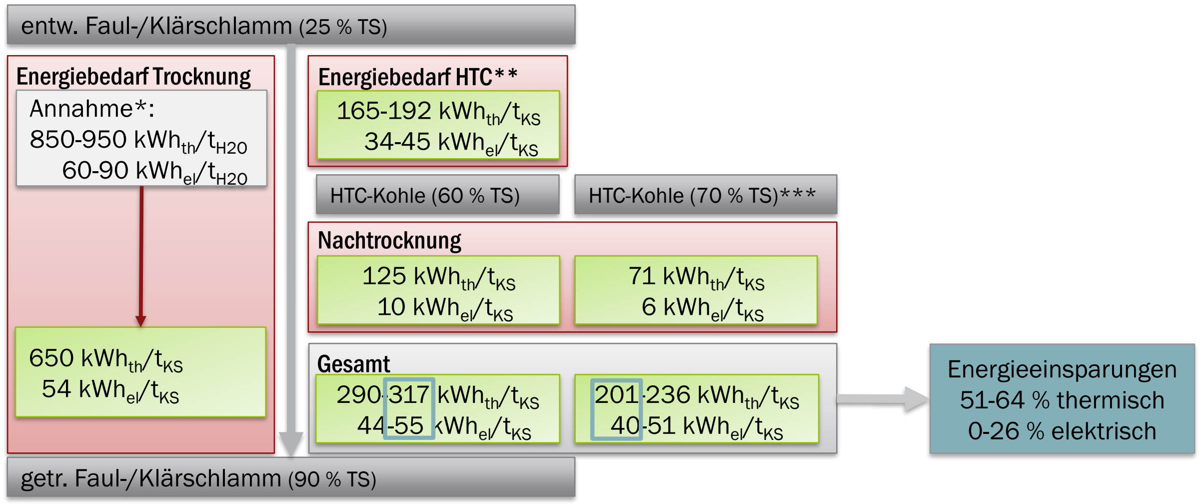
P 9,25 g/kg_{KS} *

P 33,2 g/kg_{KS} *

P 64 g/kg *

Quelle: *Montag; David Markus (2008): Phosphorrückgewinnung bei der Abwasserreinigung. Phosphorrückgewinnung bei der Abwasserreinigung - Entwicklung eines Verfahrens zur Integration in kommunalen Kläranlagen. Aachen.

Energieverbrauch KS Trocknung / HTC+Trocknung



entw. Faul-/Klärschlamm (25 % TS)

Energiebedarf Trocknung
Annahme*:
850-950 kWh_{th}/t_{H20}
60-90 kWh_{el}/t_{H20}

650 kWh_{th}/t_{KS}
54 kWh_{el}/t_{KS}

Energiebedarf HTC**
165-192 kWh_{th}/t_{KS}
34-45 kWh_{el}/t_{KS}

HTC-Kohle (60 % TS)

HTC-Kohle (70 % TS)***

Nachtrocknung
125 kWh_{th}/t_{KS}
10 kWh_{el}/t_{KS}

71 kWh_{th}/t_{KS}
6 kWh_{el}/t_{KS}

Gesamt
290-317 kWh_{th}/t_{KS}
44-55 kWh_{el}/t_{KS}

201-236 kWh_{th}/t_{KS}
40-51 kWh_{el}/t_{KS}

Energieeinsparungen
51-64 % thermisch
0-26 % elektrisch

getr. Faul-/Klärschlamm (90 % TS)

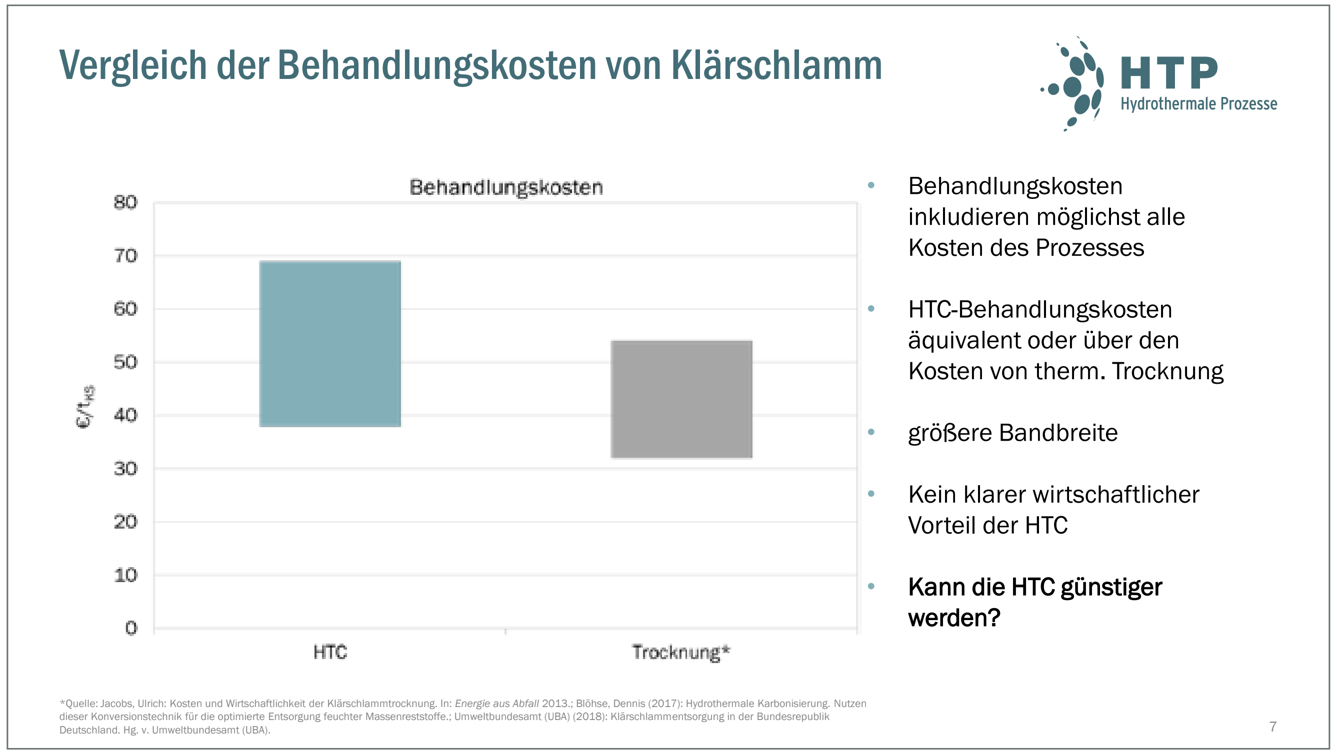
* Quellen: Geyer, Jürgen (2013): Klärschlammtrocknung in Deutschland. Stand und Perspektiven. In: Energie aus Abfall.; Blöhse, Dennis (2017): Hydrothermale Karbonisierung. Nutzen dieser Konversionstechnik für die optimierte Entsorgung feuchter Massenreststoffe.
** Quellen:Buttmann, M. (2011): Klimafreundliche Kohle durch Hydrothermale Karbonisierung von Biomasse. Blöhse, Dennis (2017): Hydrothermale Karbonisierung. Nutzen dieser Konversionstechnik für die optimierte Entsorgung feuchter Massenreststoffe.
*** Escala, M.; Zumbühl, T.; Koller, Ch.; Junge, R.; Krebs, Rolf (2012): Hydrothermal Carbonization as an Energy-Efficient Alternative to Established Drying Technologies for Sewage Sludge

Spezifische Kosten der Energieverbräuche

		Trocknung	HTC_{Worst}	HTC_{Best}
Strom	€/t_{KS}	5,4	5,5	4,0
Wärme	€/t_{KS}	26,0	12,7	9,4
Gesamt	€/t_{KS}	31,4	18,2	13,4

- **entspricht einer Kostenersparnis von 42-57 %**
- **energetischer Vorteil auch wirtschaftlich relevant (abhängig von Energiekosten)**
- **aber Gesamtkosten der Prozesse müssen verglichen werden**

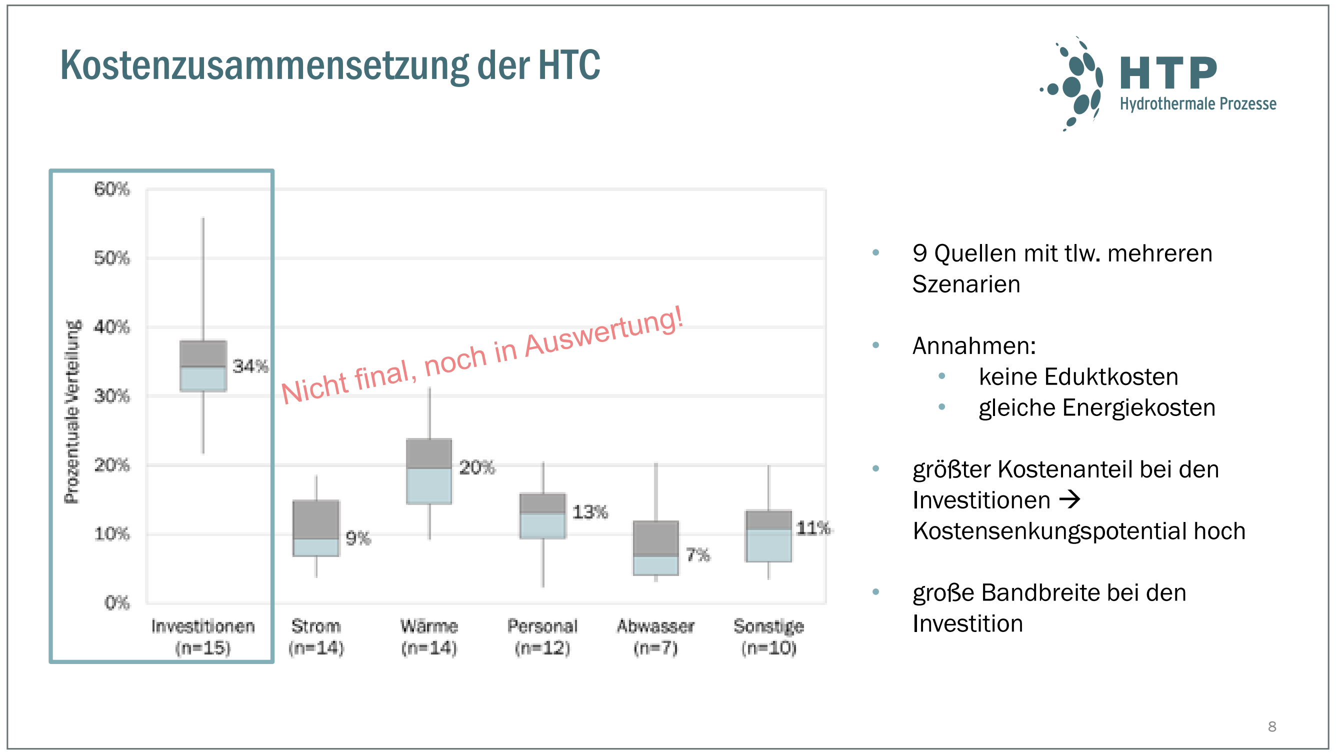
Annahme: Wärme 0,04 €/kWh; Strom 0,1 €/kWh



Vergleich der Behandlungskosten von Klärschlamm

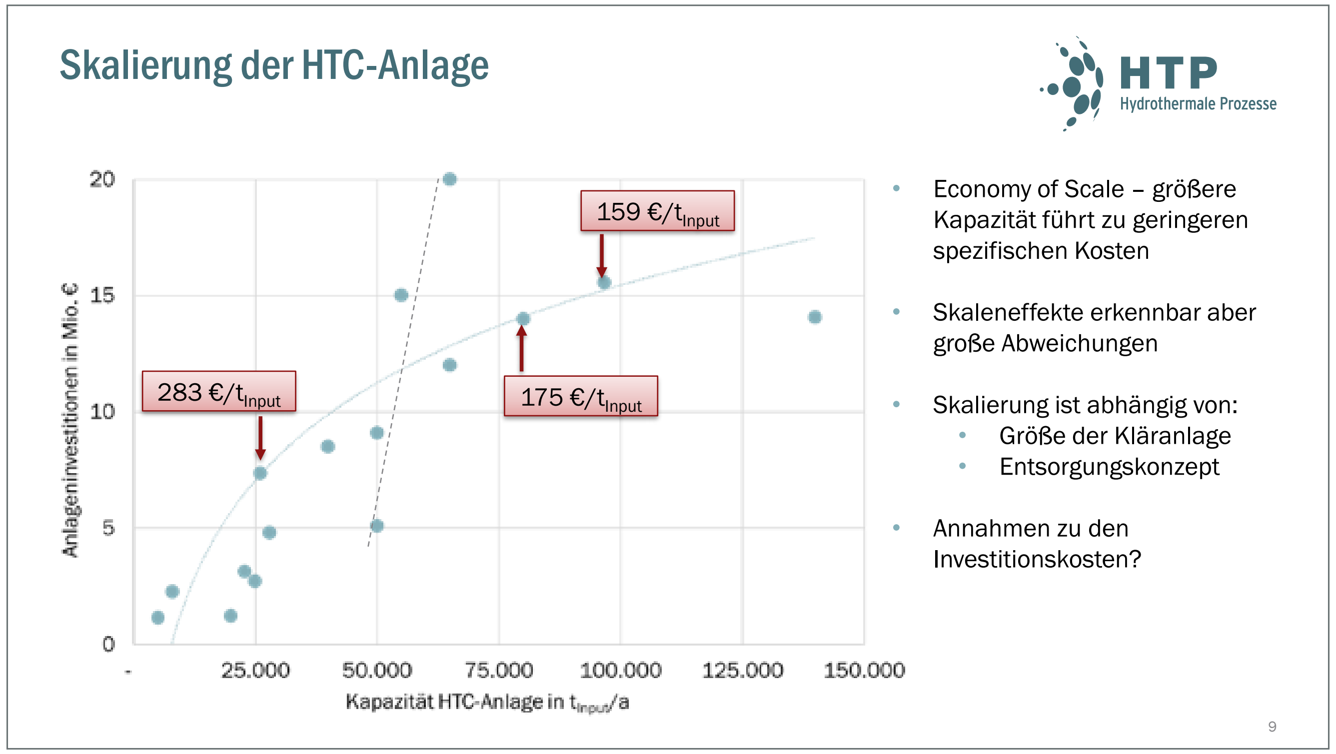
- Behandlungskosten inkludieren möglichst alle Kosten des Prozesses
- HTC-Behandlungskosten äquivalent oder über den Kosten von therm. Trocknung
- größere Bandbreite
- Kein klarer wirtschaftlicher Vorteil der HTC
- **Kann die HTC günstiger werden?**

*Quelle: Jacobs, Ulrich: Kosten und Wirtschaftlichkeit der Klärschlammtrocknung. In: *Energie aus Abfall* 2013.; Blöhse, Dennis (2017): Hydrothermale Karbonisierung. Nutzen dieser Konversionstechnik für die optimierte Entsorgung feuchter Massenreststoffe.; Umweltbundesamt (UBA) (2018): Klärschlammentsorgung in der Bundesrepublik Deutschland. Hg. v. Umweltbundesamt (UBA).



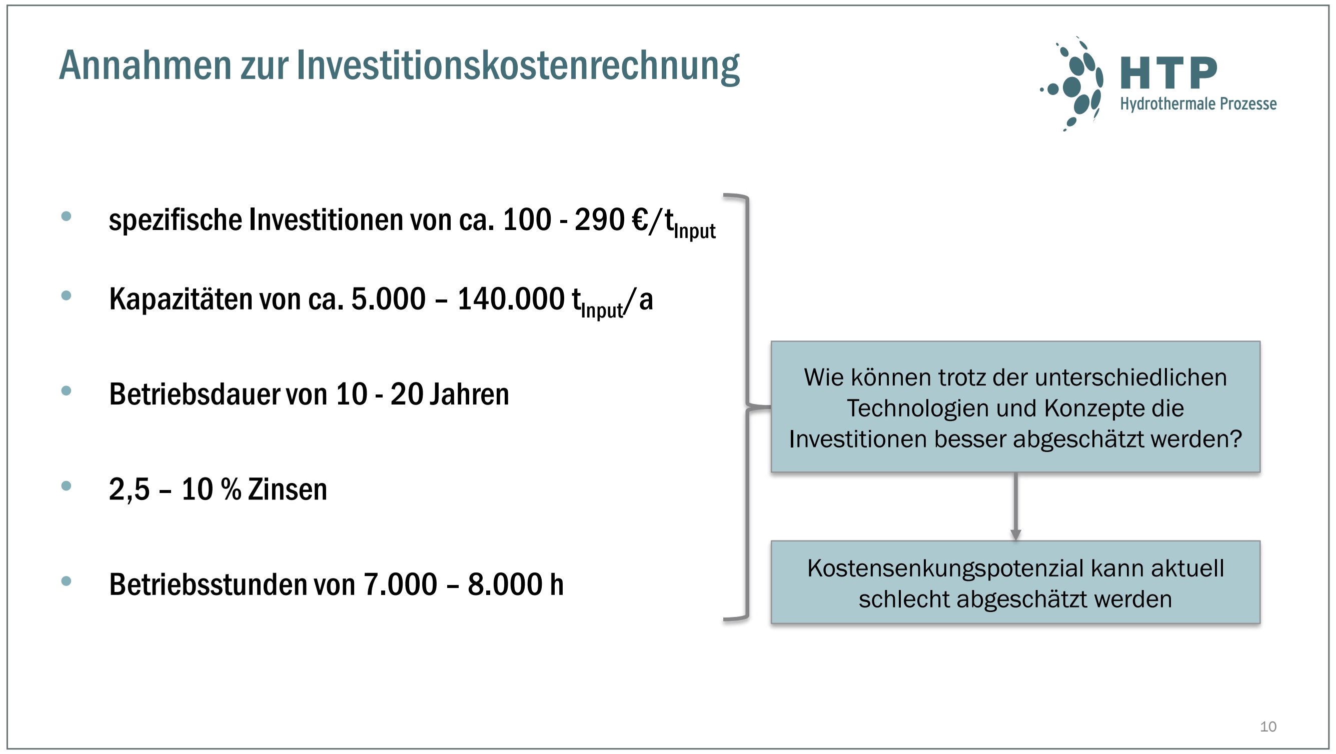
Kostenzusammensetzung der HTC

- 9 Quellen mit tlw. mehreren Szenarien
- Annahmen:
  - keine Eduktkosten
  - gleiche Energiekosten
- größter Kostenanteil bei den Investitionen → Kostensenkungspotential hoch
- große Bandbreite bei den Investition



Skalierung der HTC-Anlage

- Economy of Scale – größere Kapazität führt zu geringeren spezifischen Kosten
- Skaleneffekte erkennbar aber große Abweichungen
- Skalierung ist abhängig von:
  - Größe der Kläranlage
  - Entsorgungskonzept
- Annahmen zu den Investitionskosten?



Annahmen zur Investitionskostenrechnung

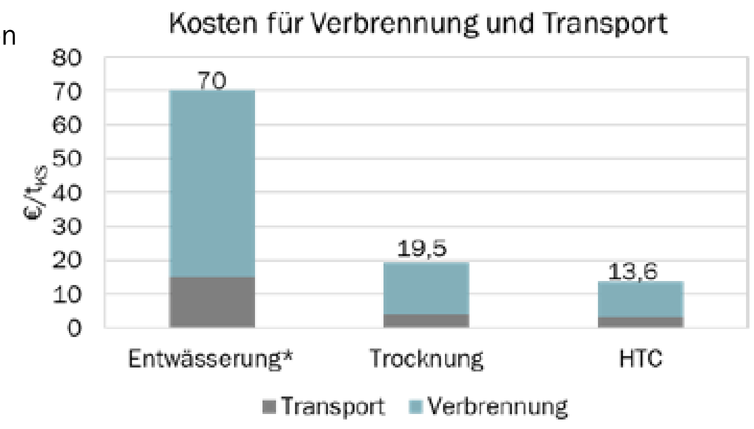
- **spezifische Investitionen von ca. 100 - 290 €/t_{Input}**
- **Kapazitäten von ca. 5.000 – 140.000 t_{Input}/a**
- **Betriebsdauer von 10 - 20 Jahren**
- **2,5 – 10 % Zinsen**
- **Betriebsstunden von 7.000 – 8.000 h**

Wie können trotz der unterschiedlichen Technologien und Konzepte die Investitionen besser abgeschätzt werden?

Kostensenkungspotenzial kann aktuell schlecht abgeschätzt werden

Wie wird die HTC von Klärschlamm wirtschaftlicher?

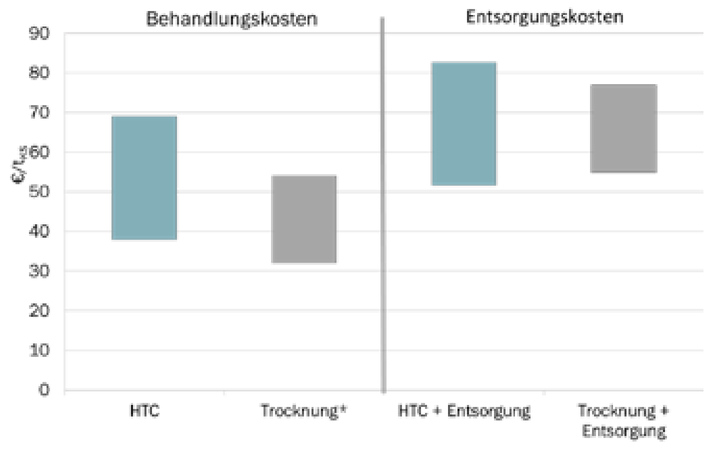
- **Zusätzlichen wirtschaftlichen Nutzen durch HTC:**
  - ca. 30 % Feststoffreduktion durch HTC
  - ca. 30 % weniger Entsorgungskosten ggü. Trocknung



* Quelle: Jacobs, Ulrich: Kosten und Wirtschaftlichkeit der Klärschlammtrocknung. In: *Energie aus Abfall* 2013.; Umweltbundesamt (UBA) (2018): Klärschlammentsorgung in der Bundesrepublik Deutschland. Hg. v. Umweltbundesamt (UBA).

Wie wird die HTC von Klärschlamm wirtschaftlicher?

- **Zusätzlichen wirtschaftlichen Nutzen durch HTC:**
  - HTC - Entsorgungskosten 52 – 83 €/t_{KS}
  - Trocknungs-Entsorgungskosten 55 – 77 €/t_{KS}
  - Ersparnis gegenüber Trocknung steigt mit Verbrennungskosten



Wie wird die HTC von Klärschlamm wirtschaftlicher?

- **Zusätzlichen wirtschaftlichen Nutzen durch HTC:**
  - Steigerung des Brennwerts (5-10 MJ/kg_{OS}) monetarisieren
  - Nährstoffrecycling von z.B. Phosphor
    - Kostenvergleich gegenüber Phosphorrückgewinnung aus Asche
    - Mitverbrennung wieder möglich → günstiger als die Monoverbrennung
  - Kombination mit Heißentwässerung
    - Energieeinsparung durch geringere Nachtrocknung

Zusammenfassung

- **HTC als reine Entwässerungstechnologie kein klaren ökon. Vorteil gegenüber reiner Trocknung**
- **Datenlage zu (Investitions-)Kosten von HTC-Anlagen inhomogen → Informationslücke**
- **Notwendigkeit einen wirtschaftlichen Mehrwert aus den Vorteilen der HTC zu ziehen**
- **Mehrere Möglichkeiten zur Kostenoptimierung sind vorhanden, müssen aber noch validiert und quantifiziert werden**

6. HTP-Fachforum

Hydrothermale Prozesse zur fachlichen und energetischen Wertschöpfung

HTP Hydrothermale Prozesse

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Unser Auftrag

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

Kommende Veranstaltungen

4. FEBRUAR 2021

Online-Veranstaltung

12. Fachgespräch „Partikelabscheider in häuslichen Feuerungen“

FRÜHJAHR 2022

DBFZ Jahrestagung 2022

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