BIOENERGY
DOC2021
4TH DOCTORAL
COLLOQUIUM BIOENERGY

4TH DOCTORAL COLLOQUIUM BIOENERGY

13TH / 14TH SEPTEMBER, 2021

FORTBILDUNGSZENTRUM TECHNIK UND UMWELT (FTU),
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4thDOCTORAL COLLOQUIUM BIOENERGY
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4TH DOCTORAL COLLOQUIUM BIOENERGY

13TH / 14TH SEPTEMBER, 2021

FORTBILDUNGSZENTRUM TECHNIK UND UMWELT (FTU), KIT CAMPUS NORD

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Greetings from the organizers Prof. Dr.-Ing. Jörg Sauer/ Prof. Dr. Nicolaus Dahmen

Prof. Dr.-Ing. Jörg Sauer, Prof. Dr. Nicolaus Dahmen
Institute of Catalysis Research and Technology

Thank you very much for your participation in this year‘s Bioenergy Doctoral Colloquium DOC 2021. We can look back at two successful days of interesting presentations, networking and exchange of information. With your participation and contributions, you have provided significantly to the success of the event. This year‘s DOC 2021 was held under the motto „Integration of Bioenergy into Bioeconomy" and addressed various topics and research approaches from all areas of bioenergy and bioeconomy in six partly parallel oral sessions and three poster sessions in physical meeting after a long time for most of us.

Bioenergy and Bioeconomy both are essential elements of future sustainable economy to supply energy in form of heat, power and fuels as well as to provide chemical intermediates and life science products based on agricultural, forestry or waste biomass. In a bioeconomy, where biomass is increasingly used as a feedstock to produce chemicals, materials, and fuels also the energy required to obtain these products needs to be renewable in order to achieve significant greenhouse gas reductions. In both areas, Bioenergy and Bioeconomy, excellent multi- and interdisciplinary research is carried out in Europe across natural, engineering, economic, social and other sciences and we were glad to host a choice of excellent presentations from this areas provided by the participants originating from more than 20 different countries at the DOC 2021.

The 4th DOC 2021 Doctoral Colloquium Bioenergy was held at the Karlsruhe Institute of Technology (KIT), which is “The Research University in the Helmholtz Association” As one of the biggest science institutions in Europe, KIT combines a long university tradition with program-oriented top-level research as member of the Helmholtz Association (HGF). Together with the DBFZ (Deutsches Biomasseforschungszentrum gmbH) in Leipzig and supported by the members of the Program Committee we were able to set up an attractive and interesting program from the 50 submitted contributions organized in parallel oral sessions and active poster sessions. There were technical sessions on thermochemical and biochemical biomass conversion, on biorefineries and biofuels as well as sessions related to feedstock supply and systems analysis to evaluate bioconversion pathways and biorefinery scenarios.

The Colloquium was held in cooperation with the BBW-ForWerts Graduate School, which was created within the Bioeconomy Research Program in Baden-Württemberg. The Bioeconomy Research Program Baden-Württemberg was designed to support research and networking in bioeconomy. Thus, the DOC2021 was held in a multidisciplinary environment of bioenergy and bioeconomy research of.

In this conference reader we present the abstracts of the oral and poster presentations along with the slides of the visual presentations for you to read.

We thank you for your participation and remain with best regards.

We are looking forward to meet again on another DOC or any other occasion

Prof. Dr.-Ing. Jörg Sauer, Prof. Dr. Nicolaus Dahmen

Greetings from the patron Prof. Dr.-Ing. Daniela Thrän

Prof. Dr.-Ing. Daniela Thrän
UFZ / DBFZ / University of Leipzig

As a follow-up to our successful event, I am pleased to present the conference reader of the 4th Doctoral Colloquium BIOENERGY to you all. This year‘s event was particularly remarkable. Not only because it was finally a live event again. But we were able to welcome a total of 70 participants from 14 countries (including Greece, Canada, Brazil, Iran, China and many others). It clearly shows that our efforts to internationalise the promotion of young researchers have now paid off. It represents a very good foundation on which we can build in the future.

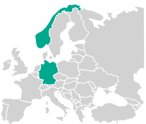
More than fifty young researchers covered a variety of topics, ranging from „Potentials of agricultural residues and current problems of the biogas industry in China“ to „Bioenergy villages in Germany - funding programmes and obstacles“ and „Catalytic hydrothermal gasification of glycerine“. Numerous other aspects and presentations made for an extremely exciting and thematically multi-layered event. In addition, there were a large number of live discussions and networking activities. For this, I would like to expressly thank all the participants of the colloquium on behalf of the entire programme committee. You have made a valuable contribution and presented the broad topic area of bioenergy and bioeconomy in an excellent way. Of course, the Doctoral Colloquium BIOENERGY will not only grow in terms of participants. A cooperation with EERA Bioenergy and an expansion of the event to EU level are also planned. Future events therefore promise to be exciting at this level as well.

This year, the two-day conference programme was rounded off by a poster session in addition to a plant tour and a get-together. The 1st prize for the best scientific poster went to Josha Zimmermann from Karlsruhe Institute of Technology (KIT) for his topic on „Fractional extraction and physiochemical characterisation of Biocrude from Hydrothermal liquefaction of sewage sludge“. Other prizes were awarded to Kathazyna Swiatek (University of Hohenheim) for her topic on „Production of platform chemicals in on-farm biorefinery“ (2nd place) and the (3rd place) went to Katharina Chan (University of Leipzig/UFZ) for her poster „How changing diets could reduce climate burdens in the German society“. Congratulations to all the winners and thank you all for your contribution!

In this conference reader you will find all the abstracts, presentation slides and posters. We wish you an informative read and hope to see you all again next year at the DOC2022!

Prof. Dr.-Ing. Daniela Thrän
UFZ / DBFZ / University of Leipzig

The recent history of Doctoral Colloquium Bioenergy

1st Doctoral Colloquium BIOENERGY **2018**	**2nd Doctoral Colloquium BIOENERGY** **2019**	**3rd Doctoral Colloquium BIOENERGY** **2020**	**4th Doctoral Colloquium BIOENERGY** **2021**
Initiator and host: **DBFZ, Leipzig**	**Host:** **FAU, Nuremberg**	**Host:** **DBFZ, Leipzig**	**Host:** **KIT, Karlsruhe**
71 **Participants**	**51** **Participants**	**185** **Participants**	**70** **Participants**
 **Participants from Germany**	 **Participants from Germany and Norway**	**Participants from Algeria, Austria, Brazil, France, Germany, India, Indonesia, Ireland, Mexico, Netherlands, Nigeria, Norway, Poland, Sweden, Switzerland, Turkey and USA**	**Participants from Austria, Brazil, Canada, China, Germany, Ghana, Greece, Iran, Nigeria, Poland, Russia, Syria, Thailand and Zambia**
Scientific Advisory Board **9** **Members representing** **11** **Institutions**	**Scientific Advisory Board** **34** **Members representing** **27** **Institutions**	**Scientific Advisory Board** **46** **Members representing** **37** **Institutions**	**Scientific Advisory Board** **46** **Members representing** **37** **Institutions**

Keynote lecture: How to get bioeconomy into practical life

Prof. Dr. Ralf Kindervater, CEO
BIOPRO Baden-Württemberg GmbH

Prof. Dr. Ralf Kindervater studied chemistry and obtained his PhD in biochemistry and biotechnology at the Gesellschaft für Biotechnologische Forschung mbH (GBF) in Braunschweig.

He then took on a managerial role at the Institute for Physical and Theoretical Chemistry of the University of Tübingen before moving on to another managerial role at the Fraunhofer Institute for Interfacial Engineering and Biotechnology (IGB) in Stuttgart.

After many years in marketing and sales with Eppendorf AG in Hamburg, he accepted the position as CEO of the Regionalansiedlungsgesellschaft Biostart mbH in Jena in 1997.

In 2001 and 2002, Prof. Dr. Kindervater held a number of seats on the advisory and management boards of several biotech companies.

In 2003 Prof. Dr. Kindervater became CEO of BIOPRO Baden-Württemberg GmbH, and in 2014 he was appointed honorary professor in the Department of Chemical and Process Engineering at the Karlsruhe Institute of Technology (KIT).

Since november 2020 he is appointed as a member of the German National Bioeconomy Council. He is also member of the Baden-Württemberg Council on sustainable Bioeconomy.

Impressions of the 4th Doctoral Colloquium Bioenergy

ORAL PRESENTATIONS

SESSION I

THERMOCHEMICAL PROCESSES I

Manuel Haas, Karlsruhe Institute of Technology (KIT)

Investigation of Burner Near Processes in Entrained Flow Gasification

Manuel Haas, Sabine Fleck, Thomas Kolb
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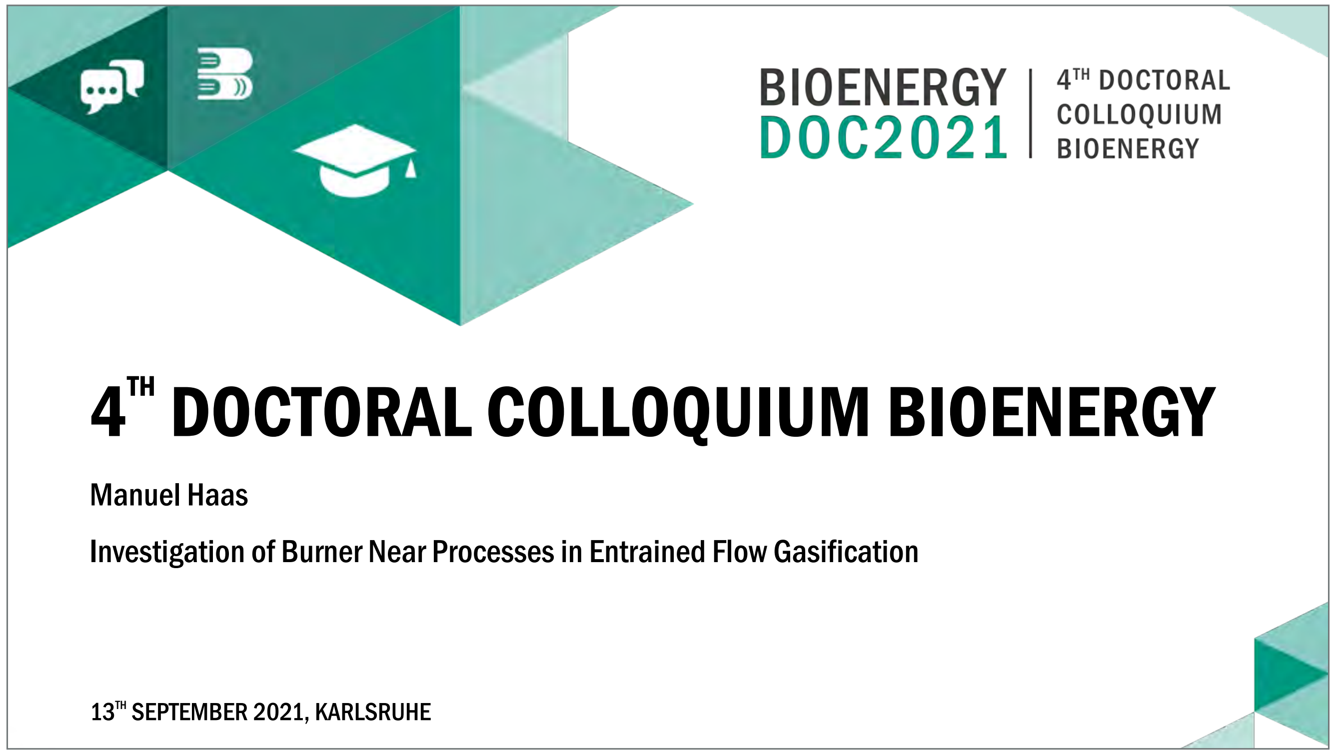
An increase in world wide energy demand paired with the need to establish a sustainable and CO_2-neutral energy system makes the use of biogenic and waste based fuels necessary. Entrained Flow Gasification is a process for the conversion of low grade organic fuels into the high quality chemical energy carrier syngas by partial oxidation. Due to its wide fuel range (municipal and agricultural residues, plastic waste, sewage sludge) and the broad spectrum of applications of syngas (renewable fuels, chemicals, electric power), entrained flow gasification is a promising interface technology in a future circular economy.

For an efficient gasification process, a high fuel conversion and a minimum amount of by-products (soot, tars) in the syngas is desired. In former work, the physical and thermochemical sub-processes in the burner near region were identified to have an impact on formation and degredation of by-products and thus play a major role in achieving a high process efficiency. In order to determine optimal process conditions, the interaction between these sub-processes must be understood.

At the pilot-scale atmospheric Research Entrained flow GAsifier (REGA), a detailed experimental study on flow field, droplet evaporation and flame structure was performed. Optical access ports at the reactor, allowed detailed measurements by PDA/LDA and OH*-chemiluminescence. Different reaction zones, specifically a central spray zone, an oxidation zone and a gasification zone were identified. This work aims to provide a link between reaction zone structure and the fuel conversion in the gasifier.

Future work will be directed towards investigating the impact of different burner geometries and fuel specifications. Measurements with OH-LIF will give further insight into the structure of the reaction zones, whereas a method for fuel-tracer-LIF is adapted to the application at the gasifier in order to determine local liquid fuel conversion.



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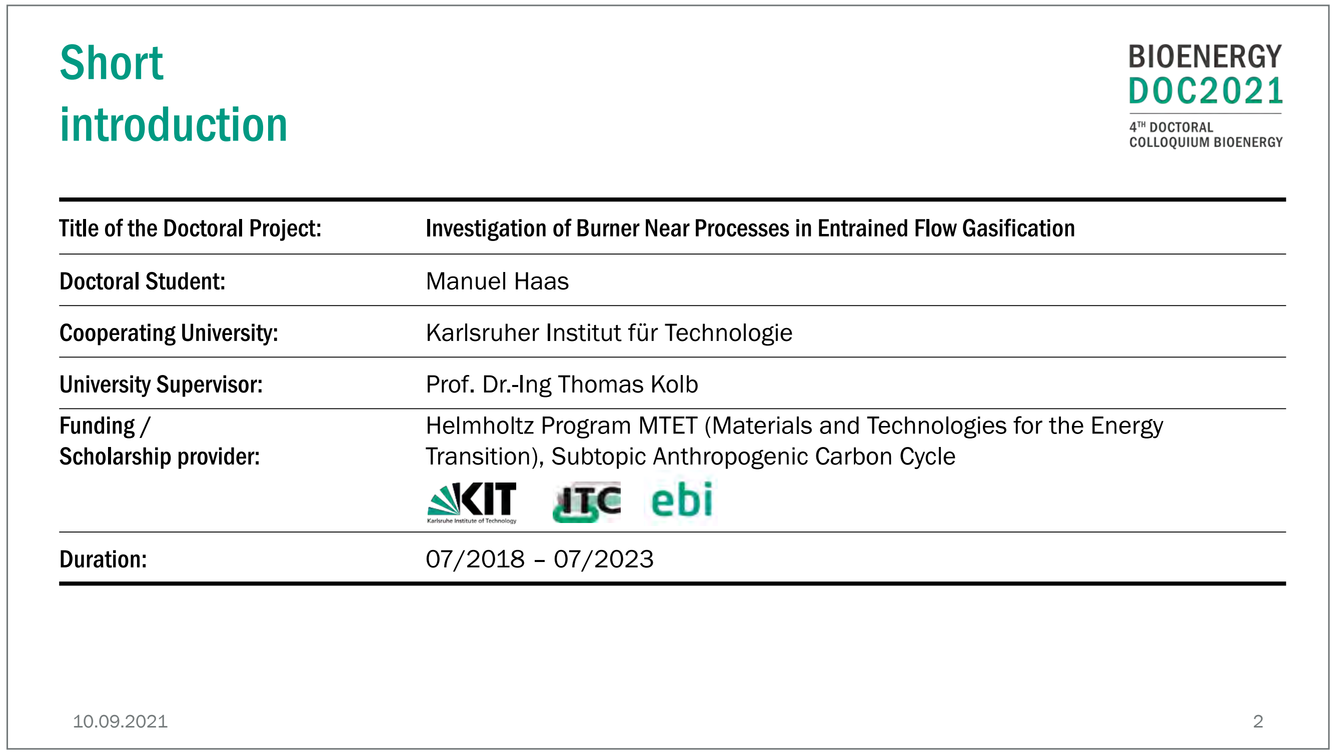
Manuel Haas

Investigation of Burner Near Processes in Entrained Flow Gasification

13TH SEPTEMBER 2021, KARLSRUHE



Short introduction

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Title of the Doctoral Project:	Investigation of Burner Near Processes in Entrained Flow Gasification
Doctoral Student:	Manuel Haas
Cooperating University:	Karlsruher Institut für Technologie
University Supervisor:	Prof. Dr.-Ing Thomas Kolb
Funding / Scholarship provider:	Helmholtz Program MTET (Materials and Technologies for the Energy Transition), Subtopic Anthropogenic Carbon Cycle
Duration:	07/2018 – 07/2023

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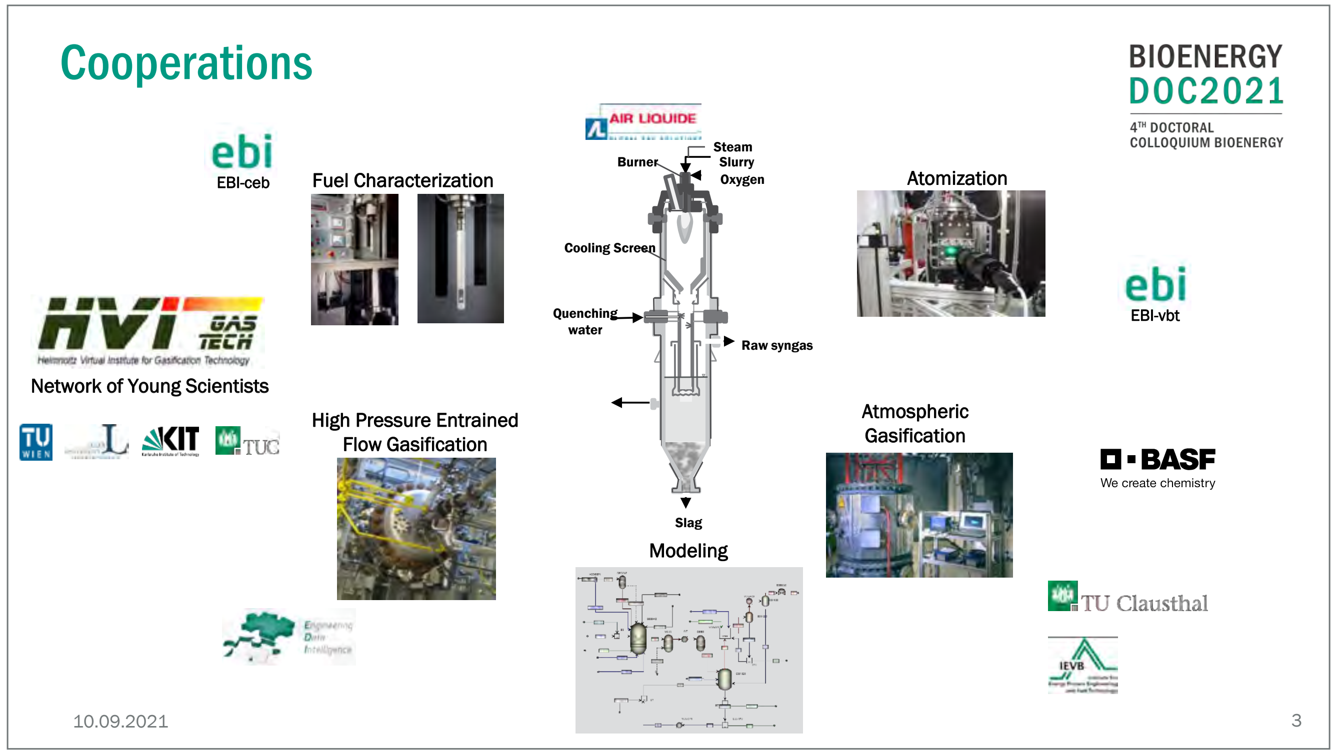

Cooperations

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EBI-ceb

Fuel Characterization

Atomization

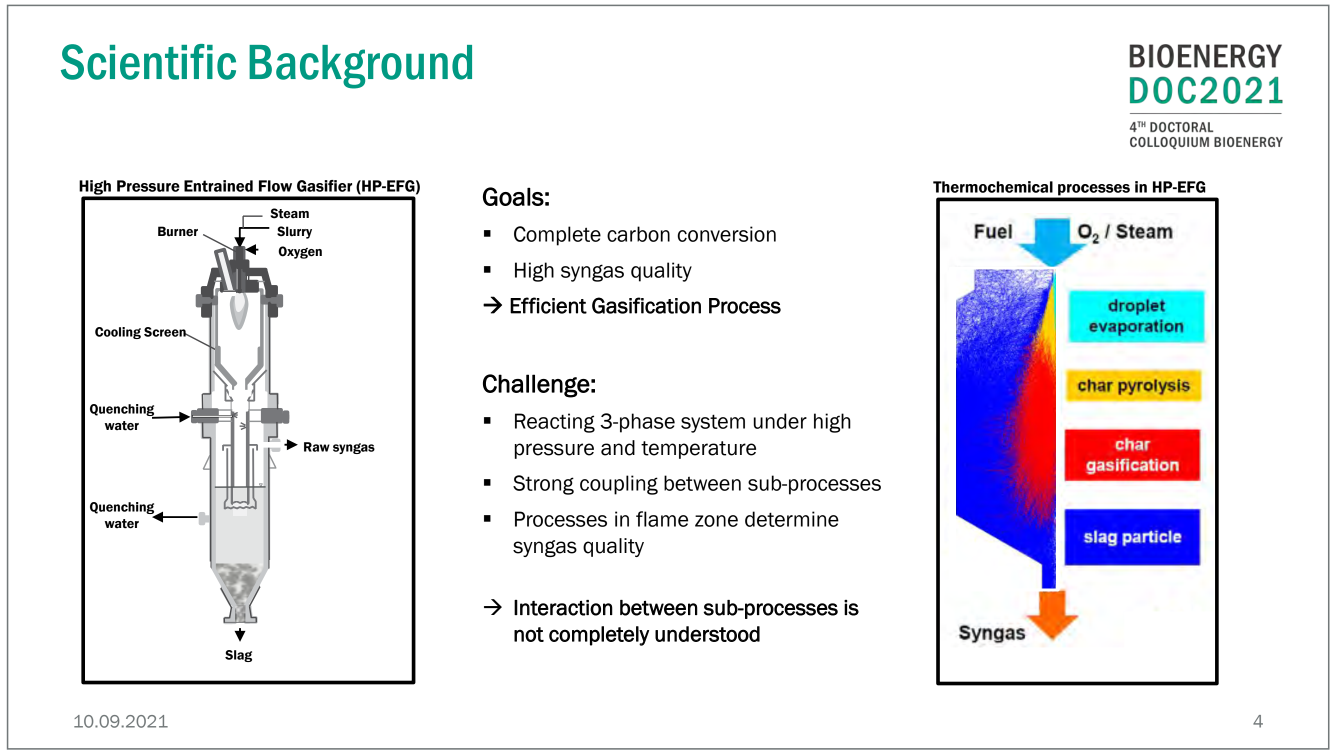
EBI-vbt

Network of Young Scientists

High Pressure Entrained Flow Gasification

Atmospheric Gasification

Modeling



Scientific Background

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High Pressure Entrained Flow Gasifier (HP-EFG)

Goals:

- Complete carbon conversion
- High syngas quality

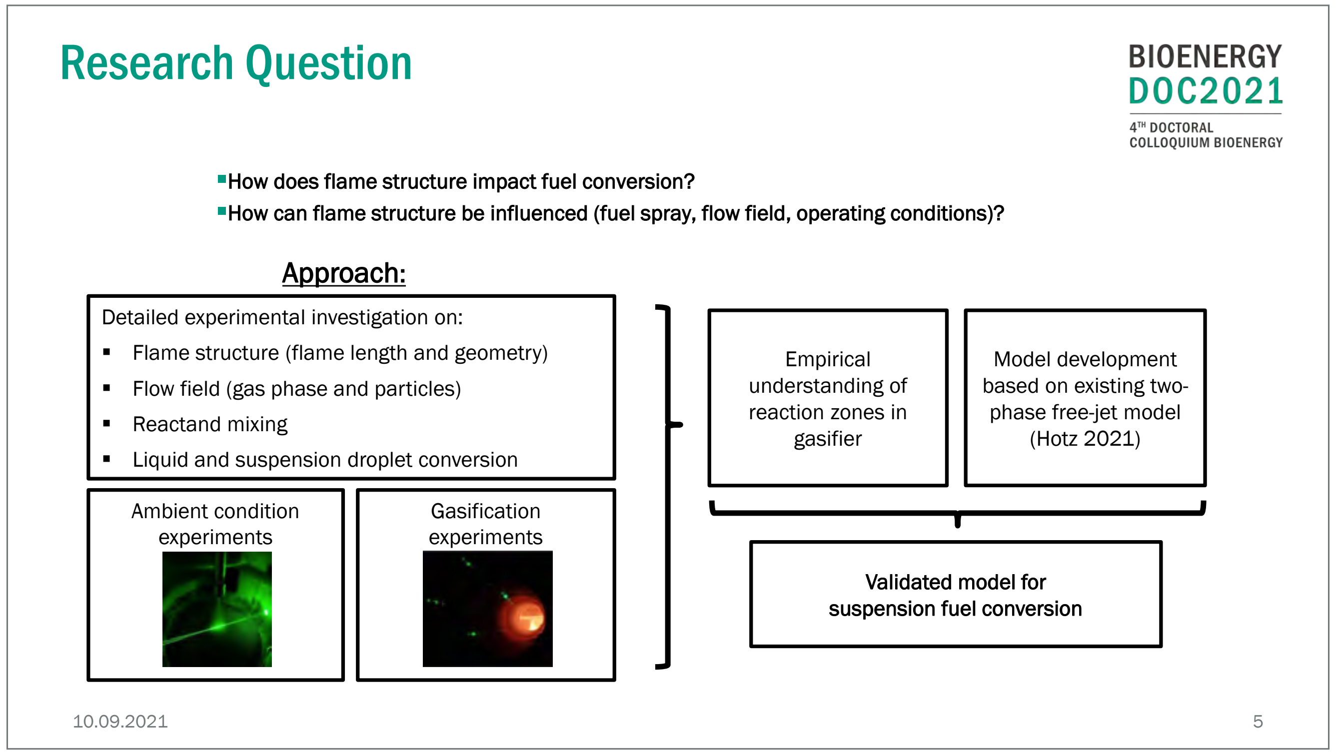
→ Efficient Gasification Process

Challenge:

- Reacting 3-phase system under high pressure and temperature
- Strong coupling between sub-processes
- Processes in flame zone determine syngas quality

→ Interaction between sub-processes is not completely understood

Thermochemical processes in HP-EFG



Research Question

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- How does flame structure impact fuel conversion?
- How can flame structure be influenced (fuel spray, flow field, operating conditions)?

Approach:

Detailed experimental investigation on:

- Flame structure (flame length and geometry)
- Flow field (gas phase and particles)
- Reactand mixing
- Liquid and suspension droplet conversion

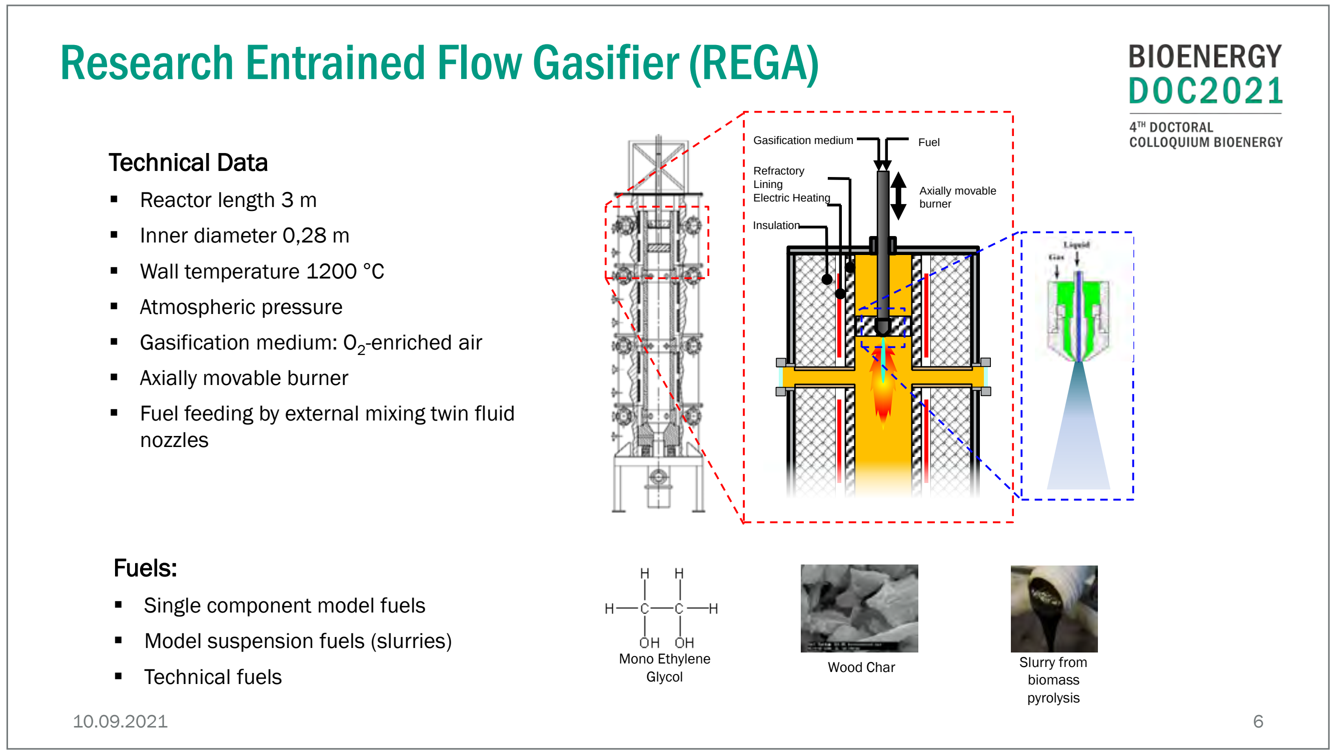
Ambient condition experiments

Gasification experiments

Empirical understanding of reaction zones in gasifier

Model development based on existing two-phase free-jet model (Hotz 2021)

Validated model for suspension fuel conversion



Research Entrained Flow Gasifier (REGA)

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Technical Data

- Reactor length 3 m
- Inner diameter 0,28 m
- Wall temperature 1200 °C
- Atmospheric pressure
- Gasification medium: O_2-enriched air
- Axially movable burner
- Fuel feeding by external mixing twin fluid nozzles

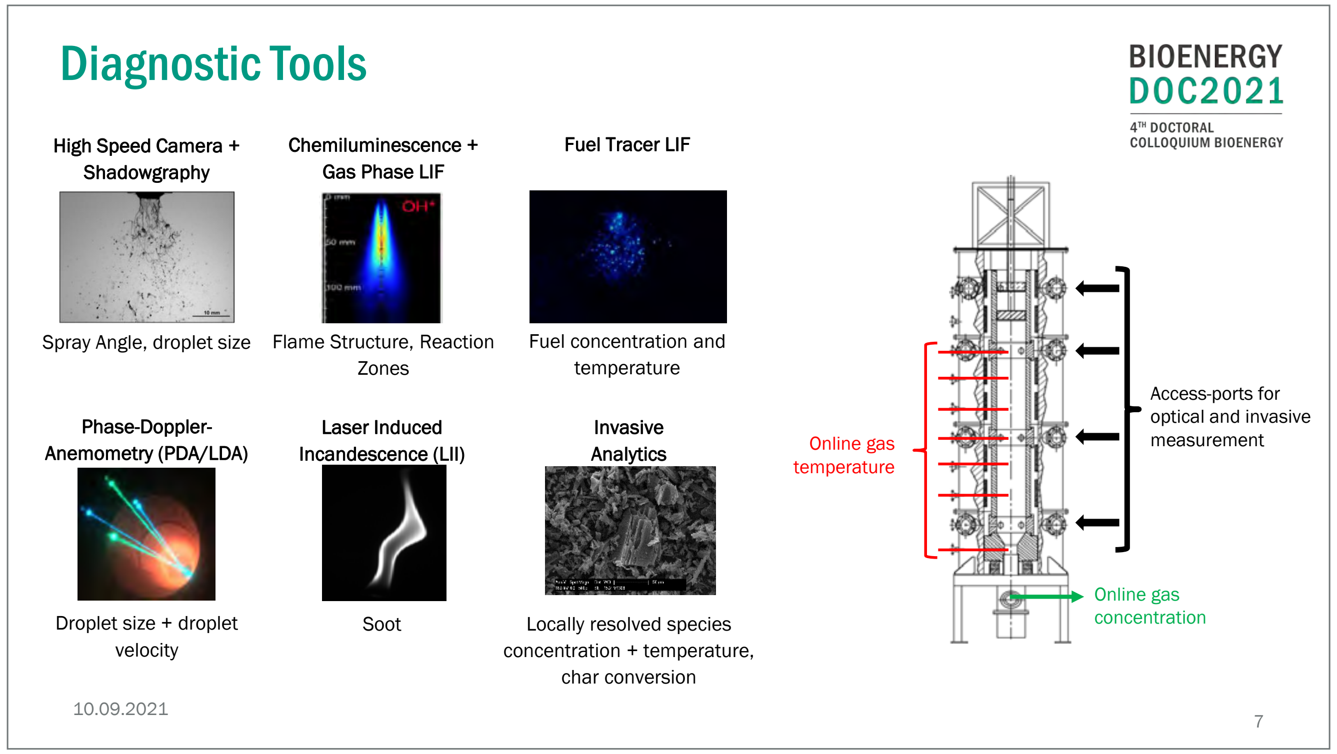
Fuels:

- Single component model fuels
- Model suspension fuels (slurries)
- Technical fuels

Mono Ethylene Glycol

Wood Char

Slurry from biomass pyrolysis



Diagnostic Tools

High Speed Camera + Shadowgraphy
Spray Angle, droplet size

Chemiluminescence + Gas Phase LIF
Flame Structure, Reaction Zones

Fuel Tracer LIF
Fuel concentration and temperature

Phase-Doppler-Anemometry (PDA/LDA)
Droplet size + droplet velocity

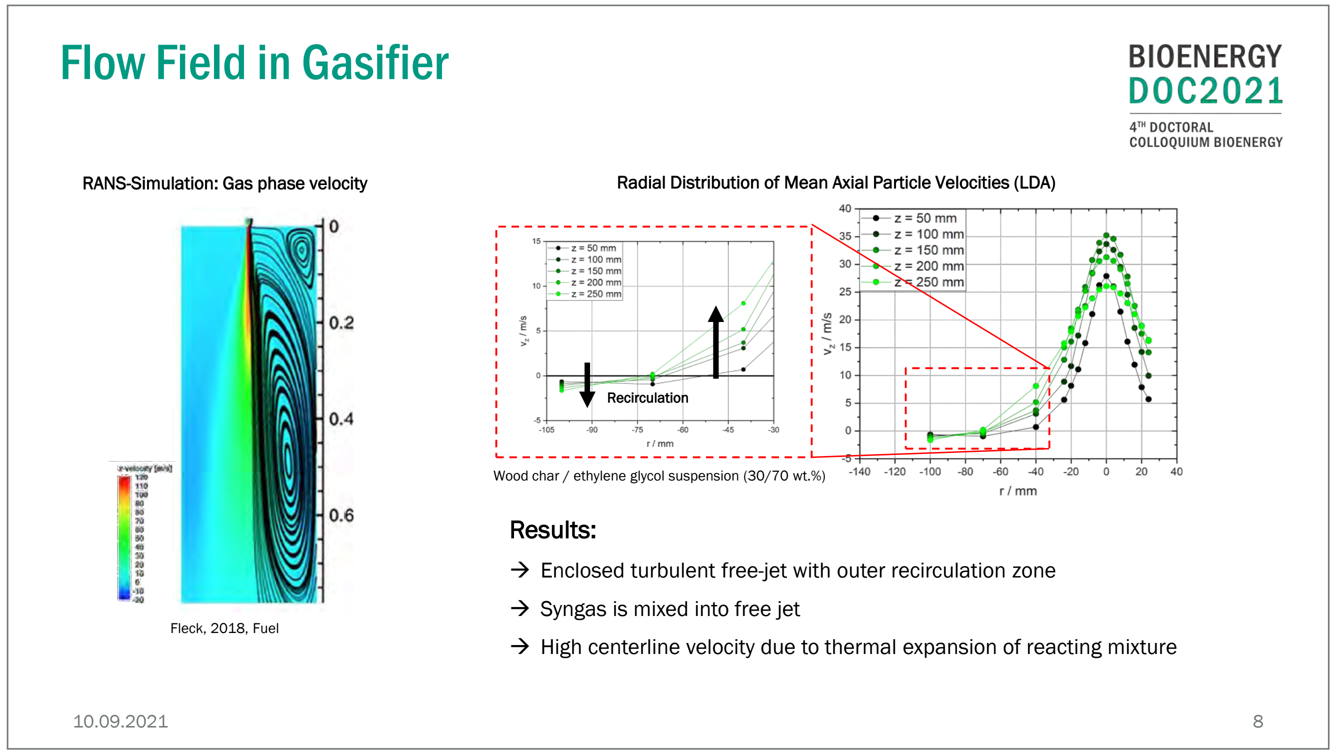
Laser Induced Incandescence (LII)
Soot

Invasive Analytics
Locally resolved species concentration + temperature, char conversion

Online gas temperature

Access-ports for optical and invasive measurement

Online gas concentration



Flow Field in Gasifier

RANS-Simulation: Gas phase velocity

Fleck, 2018, Fuel

Radial Distribution of Mean Axial Particle Velocities (LDA)

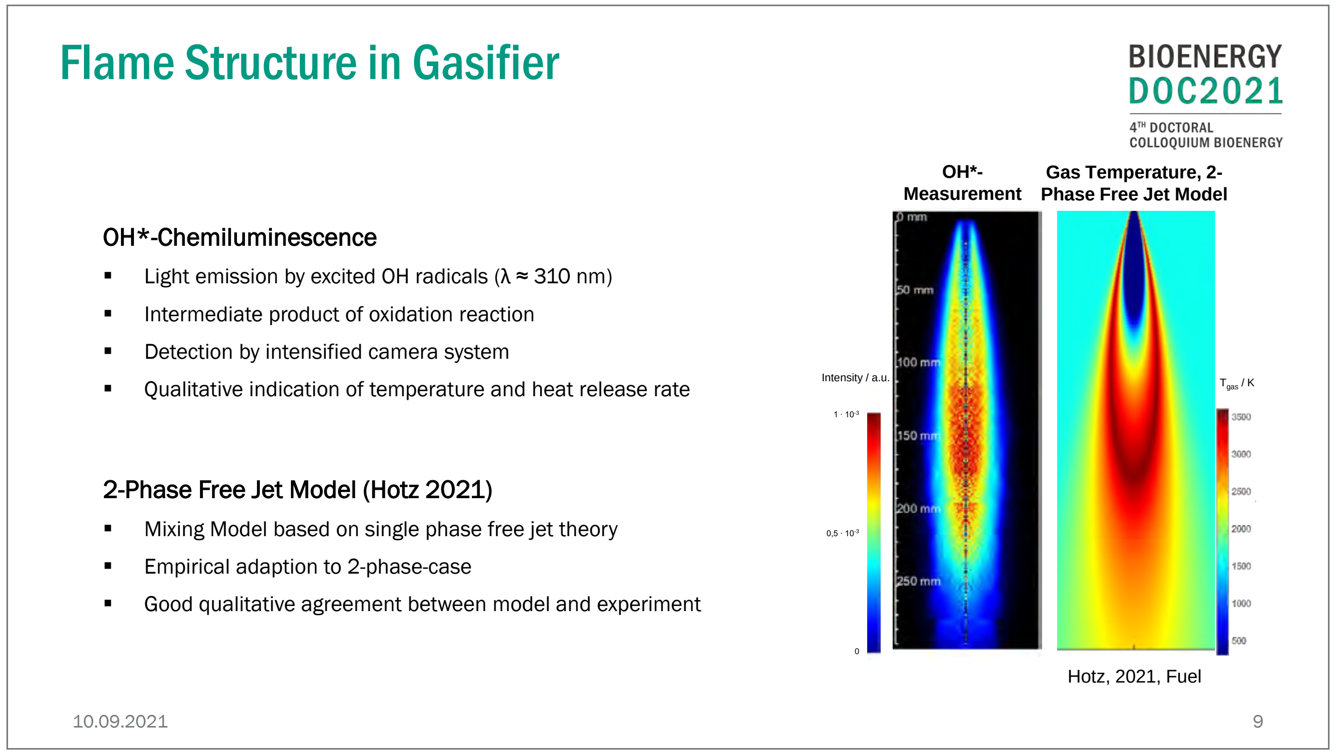
Wood char / ethylene glycol suspension (30/70 wt.%)

Results:

→ Enclosed turbulent free-jet with outer recirculation zone

→ Syngas is mixed into free jet

→ High centerline velocity due to thermal expansion of reacting mixture



Flame Structure in Gasifier

OH*-Chemiluminescence

- Light emission by excited OH radicals (λ ≈ 310 nm)
- Intermediate product of oxidation reaction
- Detection by intensified camera system
- Qualitative indication of temperature and heat release rate

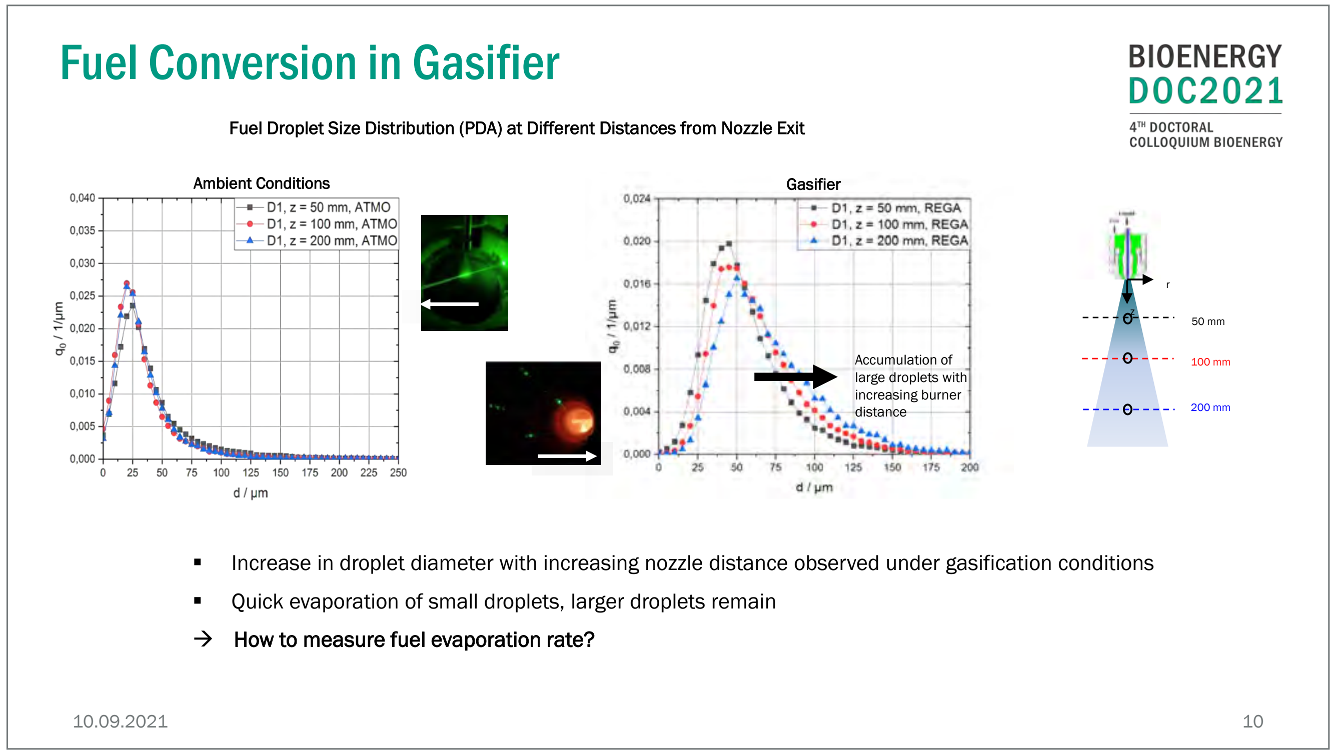
2-Phase Free Jet Model (Hotz 2021)

- Mixing Model based on single phase free jet theory
- Empirical adaption to 2-phase-case
- Good qualitative agreement between model and experiment

OH*-Measurement

Gas Temperature, 2-Phase Free Jet Model

Hotz, 2021, Fuel

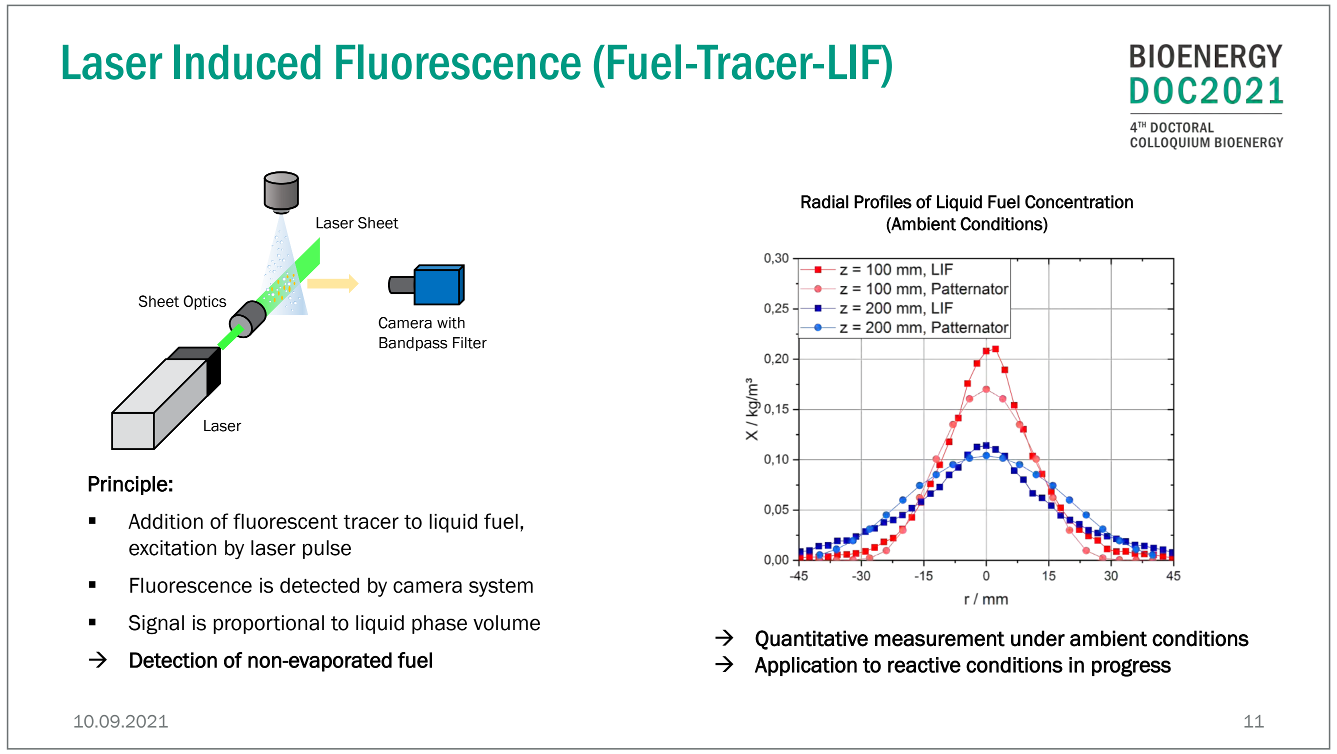


Fuel Conversion in Gasifier

Fuel Droplet Size Distribution (PDA) at Different Distances from Nozzle Exit

- Increase in droplet diameter with increasing nozzle distance observed under gasification conditions
- Quick evaporation of small droplets, larger droplets remain

→ **How to measure fuel evaporation rate?**



Laser Induced Fluorescence (Fuel-Tracer-LIF)

Principle:

- Addition of fluorescent tracer to liquid fuel, excitation by laser pulse
- Fluorescence is detected by camera system
- Signal is proportional to liquid phase volume

→ Detection of non-evaporated fuel

→ Quantitative measurement under ambient conditions

→ Application to reactive conditions in progress

Summary and Outlook

Goal

- Investigate relationship between burner concept, flame structure and fuel conversion in entrained flow gasification

Results

- 2-Phase Free Jet Model (Hotz 2021) validated for gasification of reference fuel ethylene glycol
- Fuel evaporation studied under gasification conditions: Increase in droplet size with increasing nozzle distance
- Fuel-Tracer-LIF adapted to gasification conditions, fuel concentration measurement validated in atmospheric experiment

Outlook

- Investigate influence of spray distribution and fuel specifications on flame structure
- Application of Fuel-Tracer-LIF to measure fuel evaporation in gasifier
- Describe conversion of liquid + suspension fuels with 2-Phase Free Jet Model

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Contact

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Steffen Leimbach, Friedrich-Alexander-University Erlangen/Nürnberg

Agglomeration and defluidization of stationary fluidized beds during gasification of biogenic fuels with low-melting ashes

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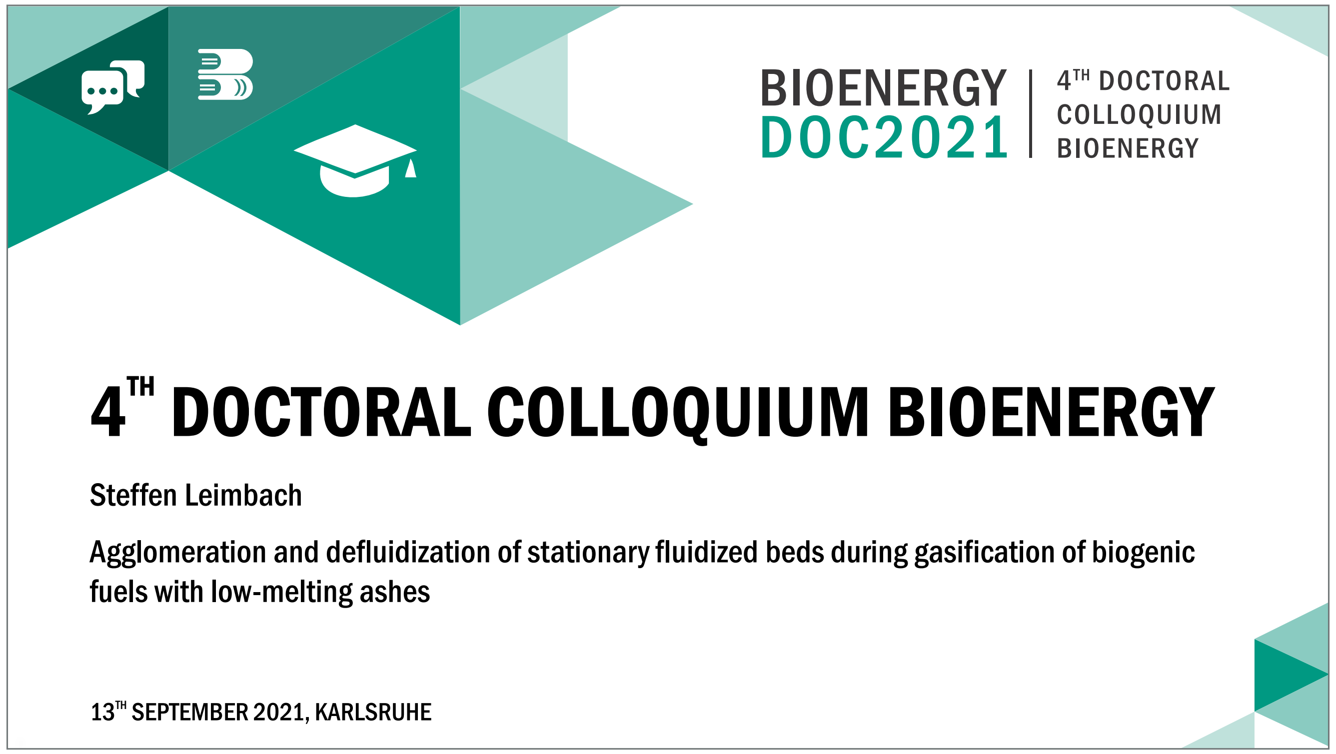
Agglomeration of bed material particles in bubbling and circulating fluidized bed combustion is a core problem in the operation of these boilers with biogenic fuels [1,2]. Especially the combustion of biogenic fuels with low-melting ashes leads to serious problems due to agglomeration of individual bed material particles. This leads to local defluidization of the fluidized bed and to the formation of agglomerates on the bed surface, at nozzle bottoms and in weakly fluidized areas. Controlled combustion of the biogenic fuels is then no longer guaranteed and costly plant shutdowns and damages will result [3]. In order to ensure a stable operation, the bed material of commercial boilers must be continuously regenerated by replacing a small percentage each day. However, the continuous regeneration of bed material is a cost factor [3].

The Chair for Energy Process Engineering at FAU Erlangen-Nürnberg investigates the understanding of the agglomeration mechanism to delay agglomeration and the defluidization. For a better understanding of the agglomeration mechanism, we carried out various experiments with synthetic ashes in a fluidized bed furnace as synthetic ashes ensure a comparability and traceable parametrization.

The focus of this work is the evaluation of agglomeration effects based on the measurement of pressure fluctuations. To get information about the bubble frequency in the fluidized bed, we performed a Fourier Transformation on the pressure fluctuations. From the obtained spectrum we determine the so called characteristic frequency.



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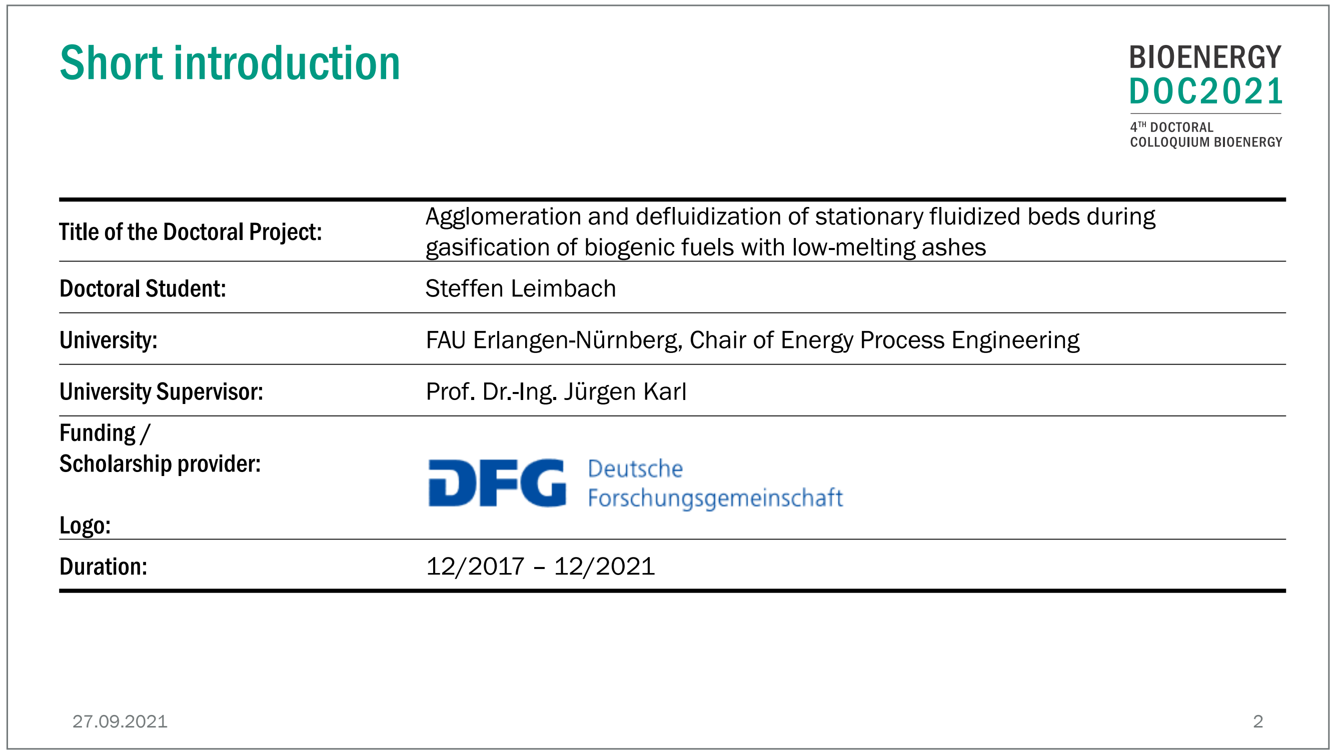
Steffen Leimbach

Agglomeration and defluidization of stationary fluidized beds during gasification of biogenic fuels with low-melting ashes

13TH SEPTEMBER 2021, KARLSRUHE



Short introduction

BIOENERGY DOC2021 4TH DOCTORAL COLLOQUIUM BIOENERGY

Title of the Doctoral Project:	Agglomeration and defluidization of stationary fluidized beds during gasification of biogenic fuels with low-melting ashes
Doctoral Student:	Steffen Leimbach
University:	FAU Erlangen-Nürnberg, Chair of Energy Process Engineering
University Supervisor:	Prof. Dr.-Ing. Jürgen Karl
Funding / Scholarship provider: **Logo:**	DFG Deutsche Forschungsgemeinschaft
Duration:	12/2017 – 12/2021

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Overview

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- **Introduction**
- **Methodology**
- **Experimental results**
- **Early detection of agglomeration**
- **Conclusion**

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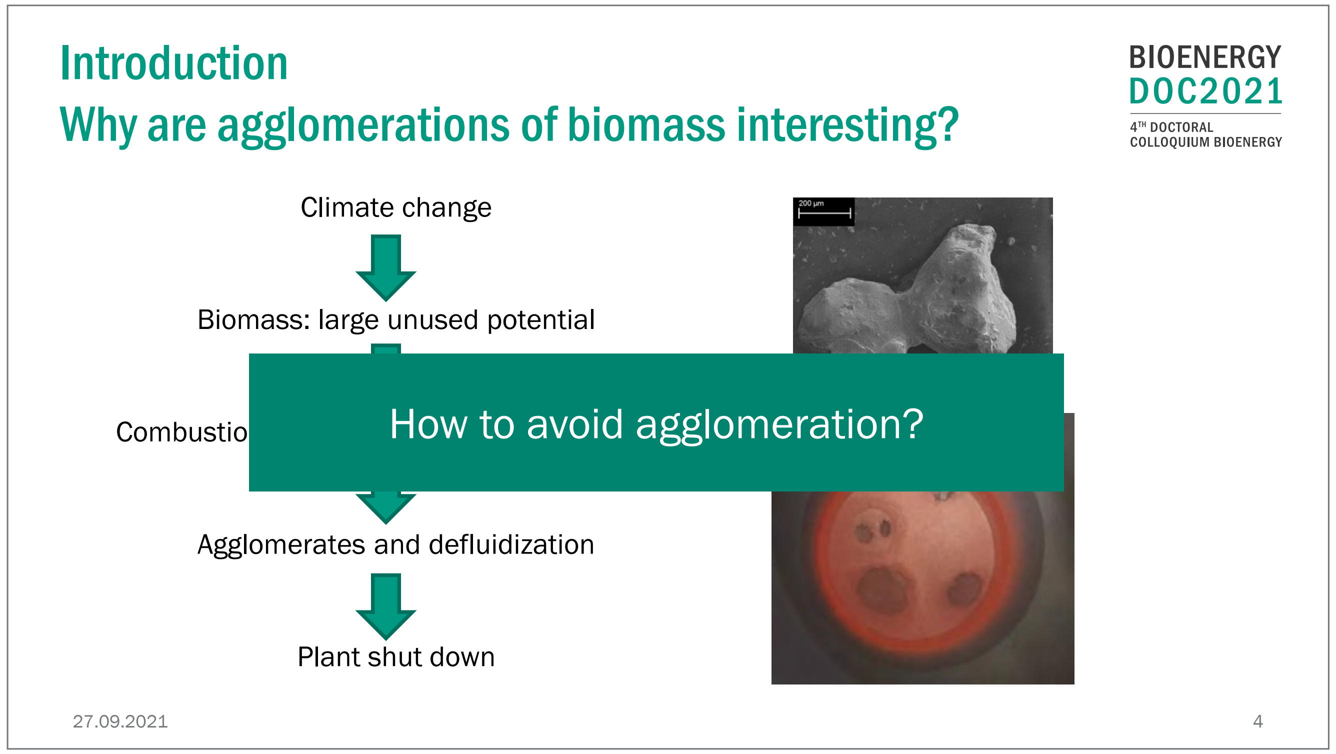

Introduction
Why are agglomerations of biomass interesting?

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Climate change

Biomass: large unused potential

Combustio

Agglomerates and defluidization

Plant shut down

How to avoid agglomeration?

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Introduction
What is the project about?

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- **DFG-project in cooperation with HIERN**

FAU FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG TECHNISCHE FAKULTÄT

HI ERN Helmholtz Institute Erlangen-Nürnberg

- **Our project aims:**
  - Understanding of the changed agglomeration behavior in fluidized beds during the gasification process compared to the combustion process
  - Development of a reliable method to early detect agglomeration based on high frequency analysis of pressure fluctuations

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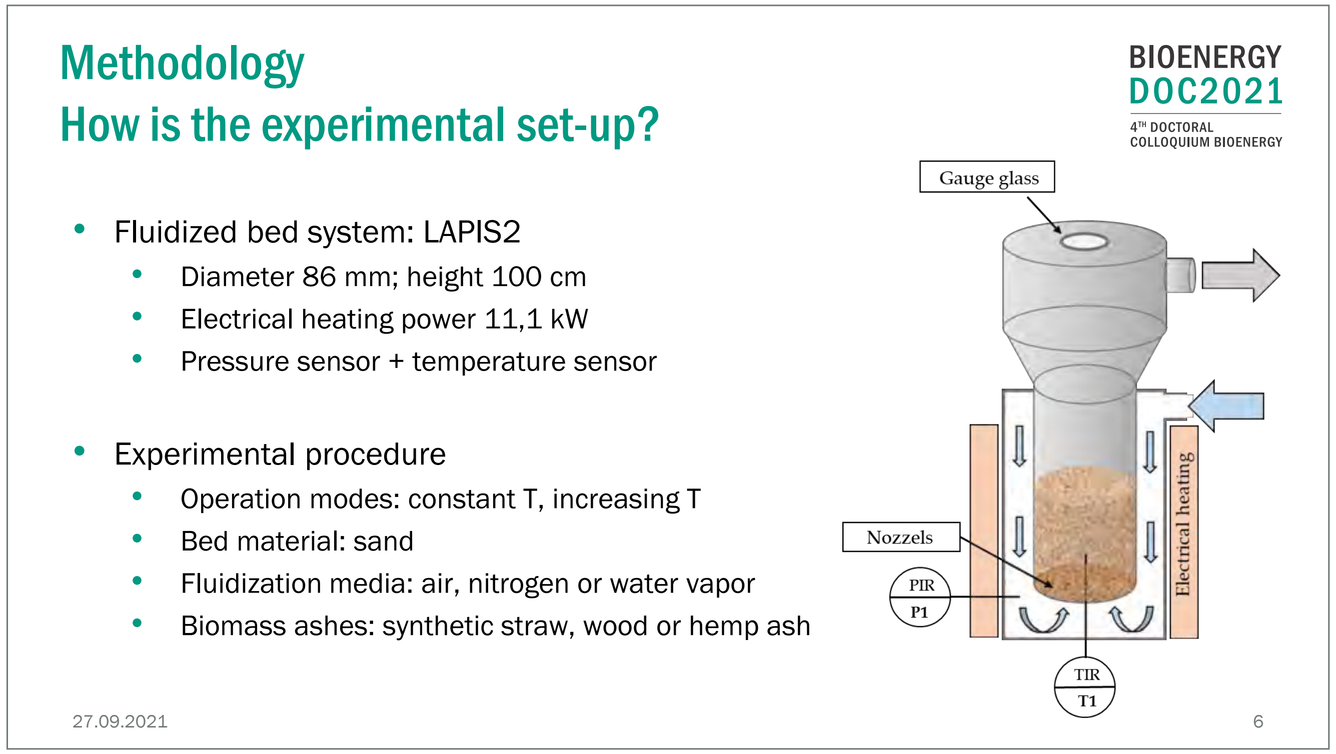

Methodology
How is the experimental set-up?

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- Fluidized bed system: LAPIS2
  - Diameter 86 mm; height 100 cm
  - Electrical heating power 11,1 kW
  - Pressure sensor + temperature sensor
- Experimental procedure
  - Operation modes: constant T, increasing T
  - Bed material: sand
  - Fluidization media: air, nitrogen or water vapor
  - Biomass ashes: synthetic straw, wood or hemp ash

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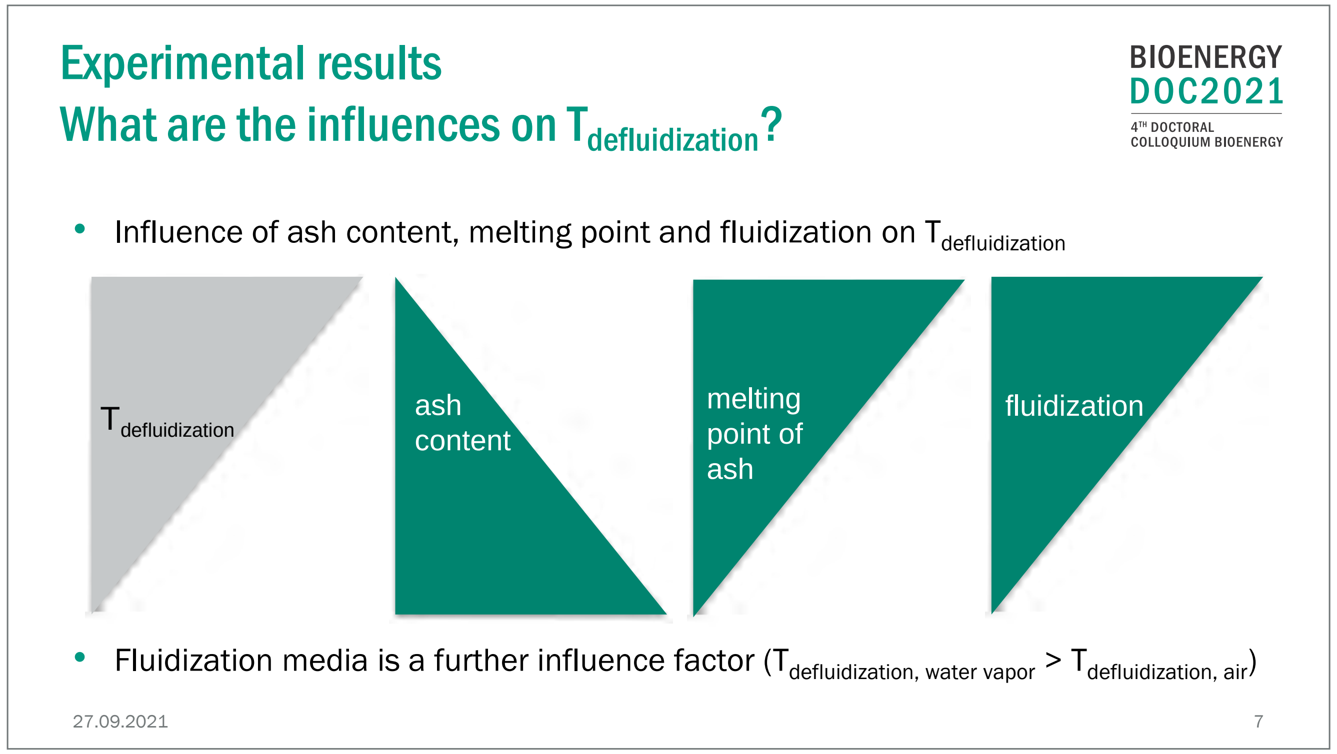

Experimental results
What are the influences on $T_{defluidization}$?

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- Influence of ash content, melting point and fluidization on $T_{defluidization}$

- Fluidization media is a further influence factor ($T_{defluidization,\ water\ vapor} > T_{defluidization,\ air}$)

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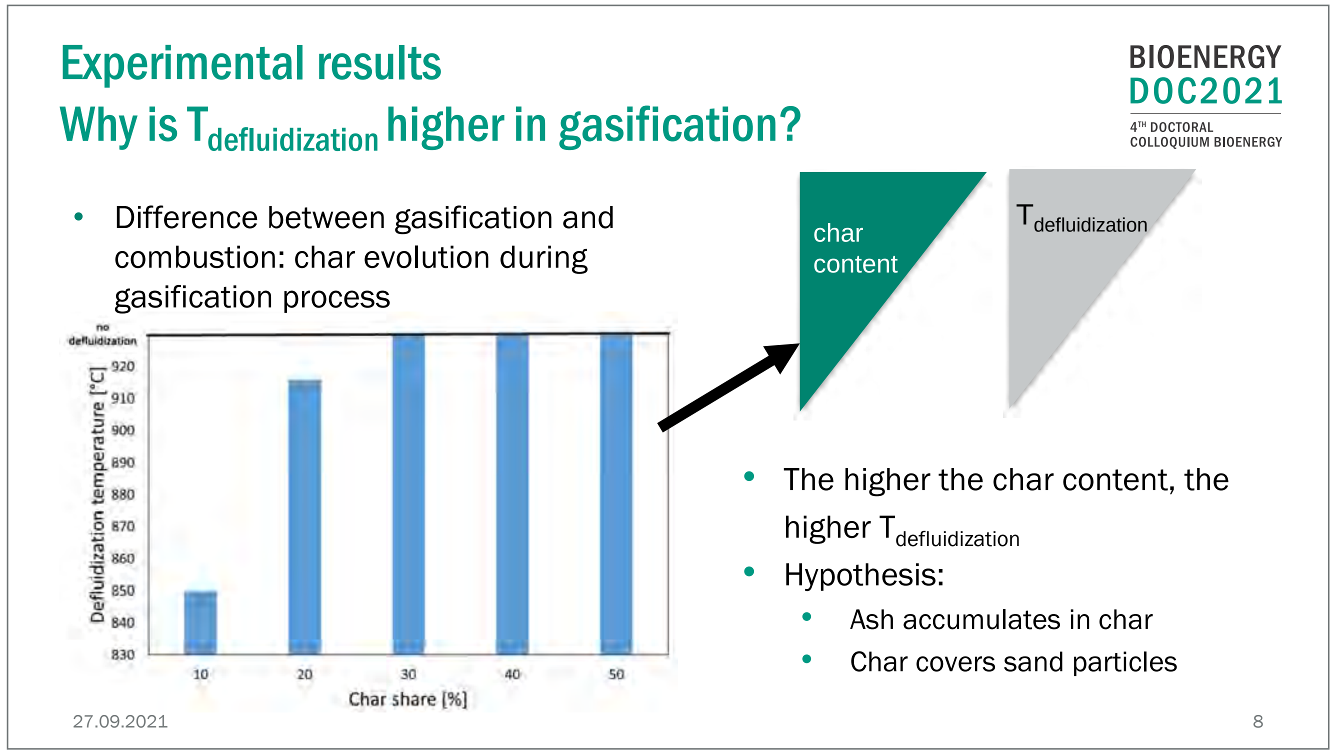

Experimental results
Why is $T_{defluidization}$ higher in gasification?

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- Difference between gasification and combustion: char evolution during gasification process

- The higher the char content, the higher $T_{defluidization}$
- Hypothesis:
  - Ash accumulates in char
  - Char covers sand particles

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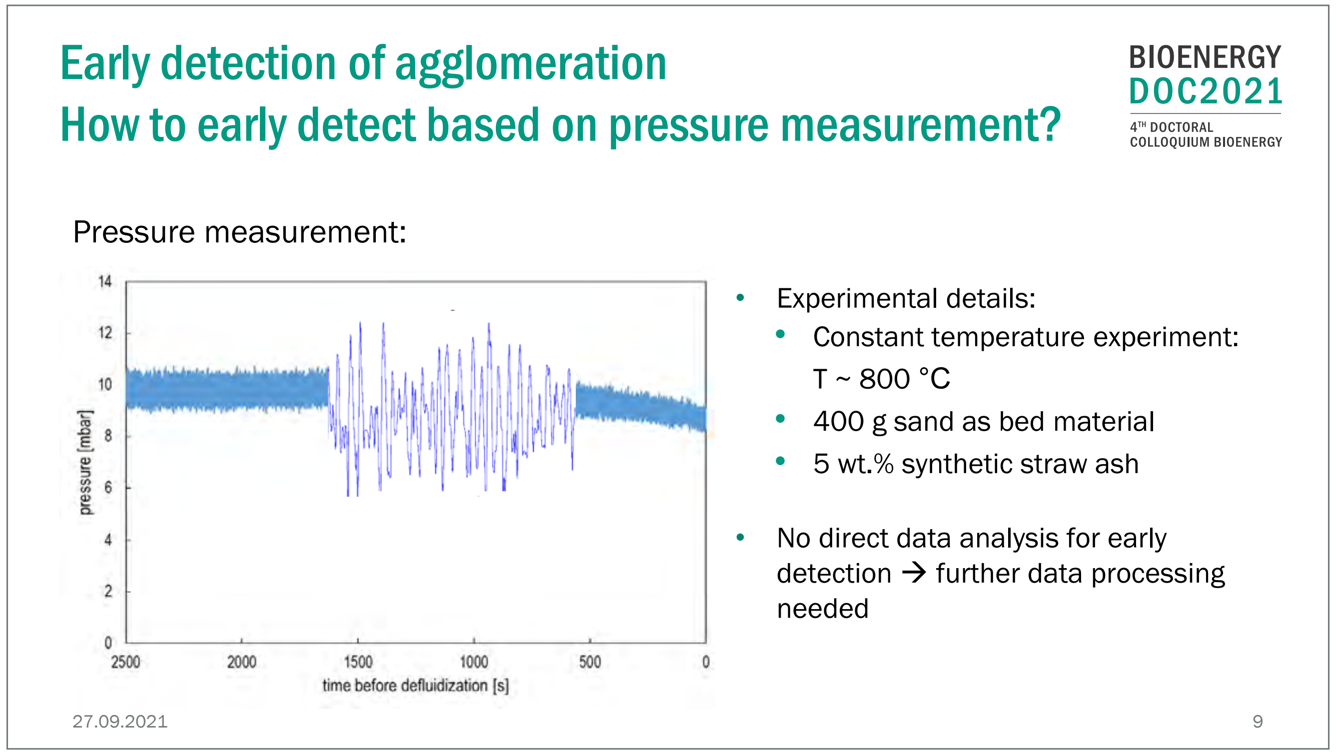

Early detection of agglomeration
How to early detect based on pressure measurement?

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Pressure measurement:

- Experimental details:
  - Constant temperature experiment: T ~ 800 °C
  - 400 g sand as bed material
  - 5 wt.% synthetic straw ash
- No direct data analysis for early detection → further data processing needed

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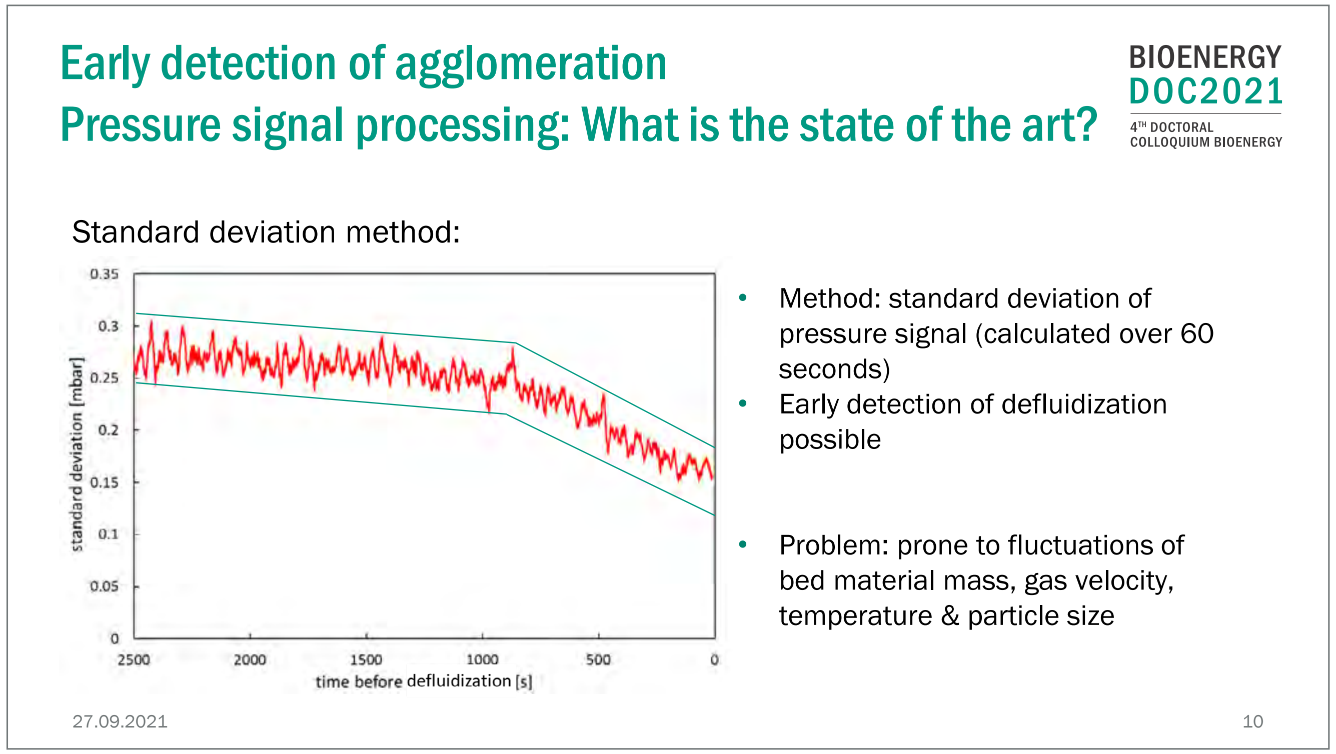

Early detection of agglomeration
Pressure signal processing: What is the state of the art?

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Standard deviation method:

- Method: standard deviation of pressure signal (calculated over 60 seconds)
- Early detection of defluidization possible
- Problem: prone to fluctuations of bed material mass, gas velocity, temperature & particle size

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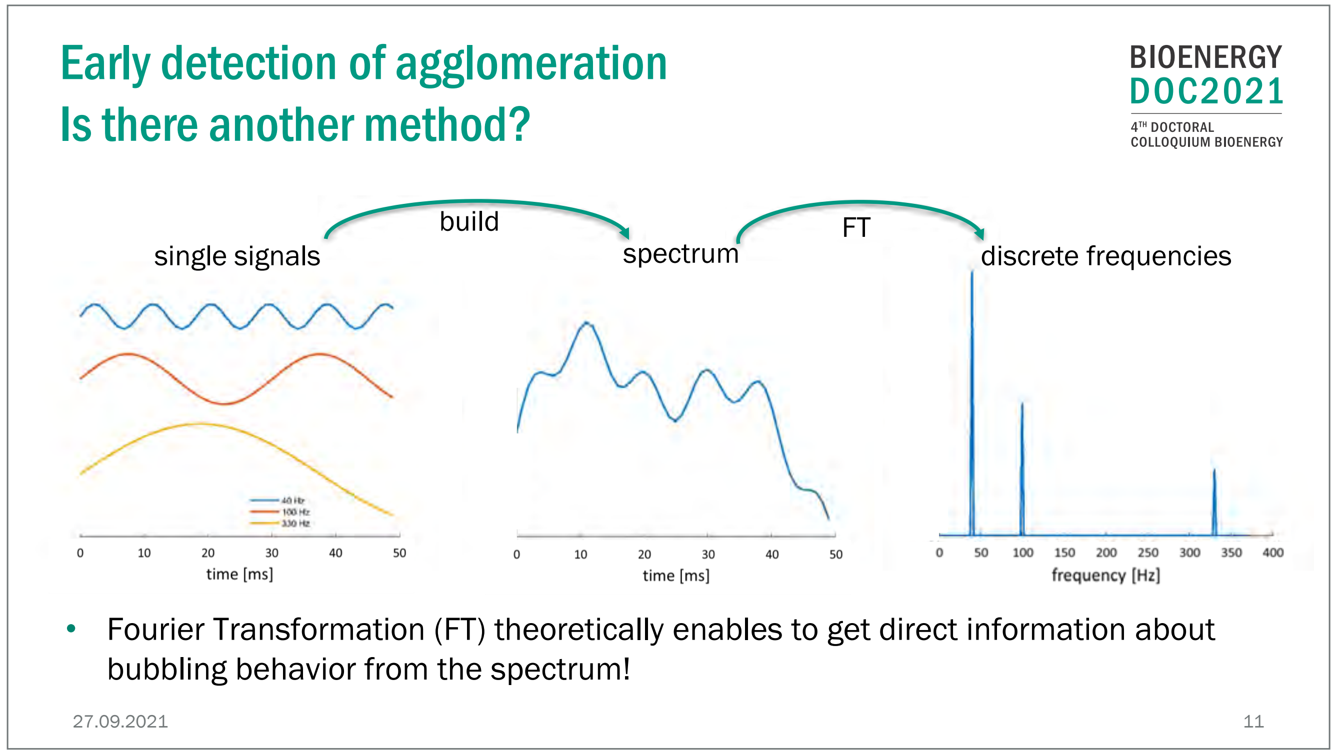

Early detection of agglomeration
Is there another method?

- Fourier Transformation (FT) theoretically enables to get direct information about bubbling behavior from the spectrum!

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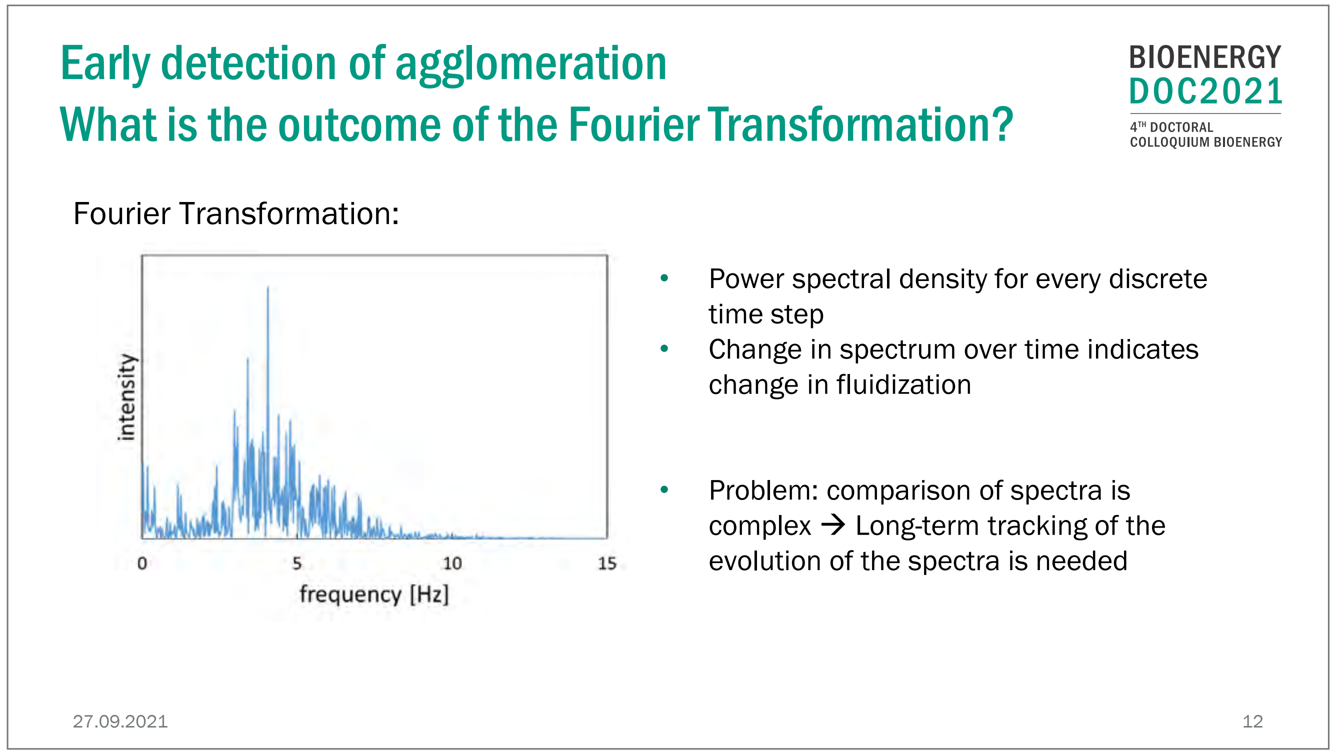

Early detection of agglomeration
What is the outcome of the Fourier Transformation?

Fourier Transformation:

- Power spectral density for every discrete time step
- Change in spectrum over time indicates change in fluidization
- Problem: comparison of spectra is complex → Long-term tracking of the evolution of the spectra is needed

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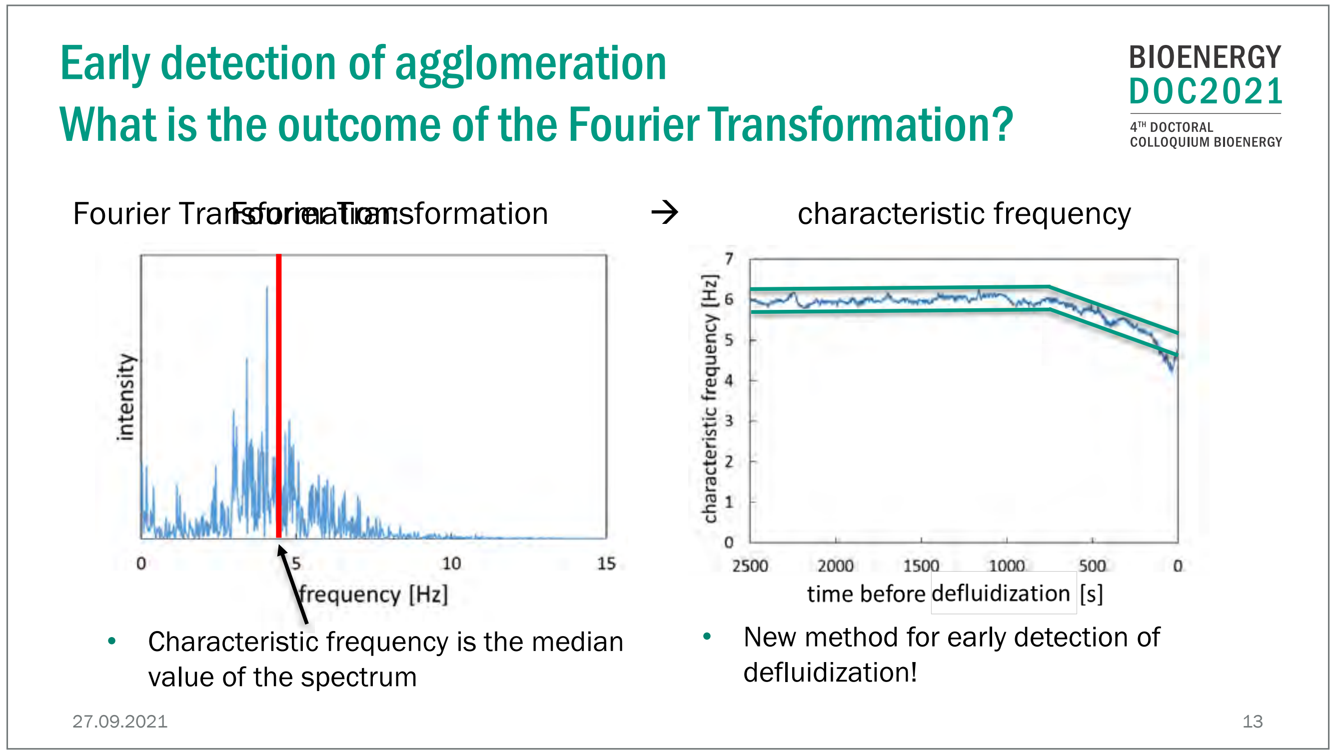

Early detection of agglomeration
What is the outcome of the Fourier Transformation?

Fourier Transformation → characteristic frequency

- Characteristic frequency is the median value of the spectrum
- New method for early detection of defluidization!

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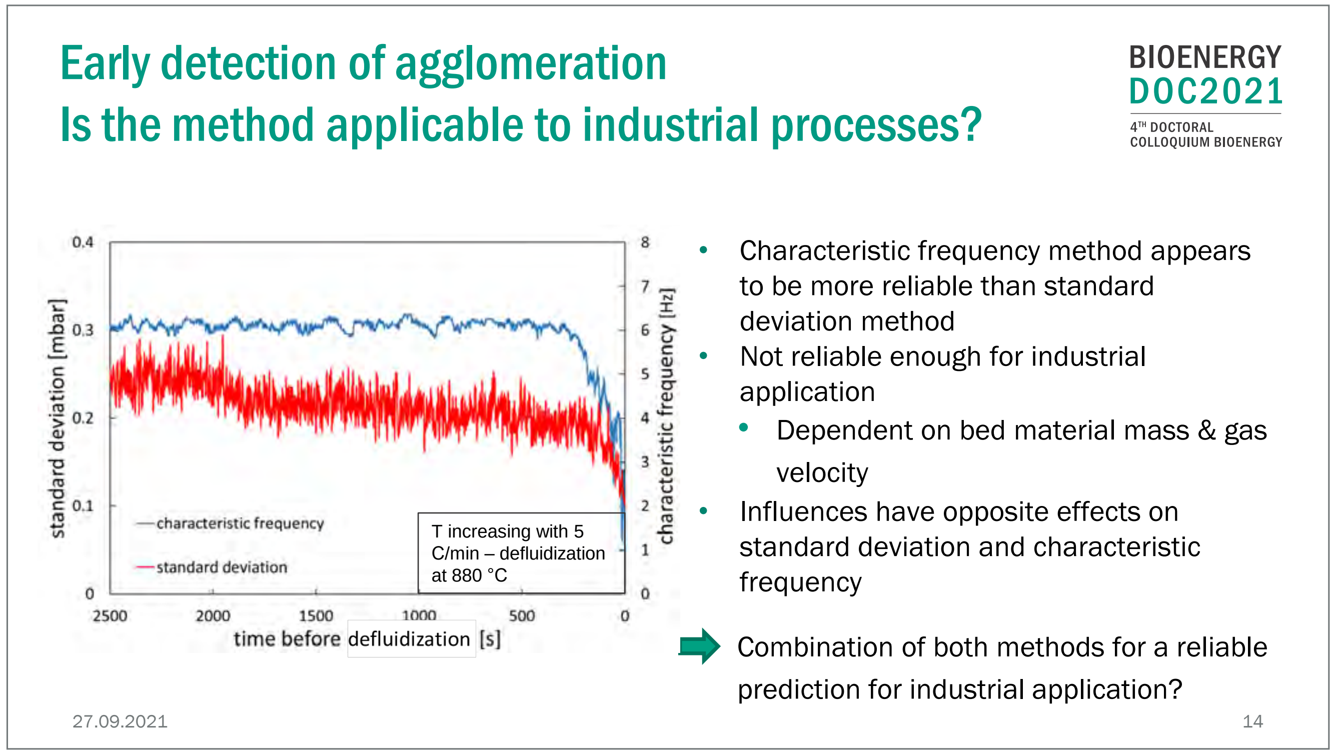

Early detection of agglomeration
Is the method applicable to industrial processes?

- Characteristic frequency method appears to be more reliable than standard deviation method
- Not reliable enough for industrial application
  - Dependent on bed material mass & gas velocity
- Influences have opposite effects on standard deviation and characteristic frequency

➡ Combination of both methods for a reliable prediction for industrial application?

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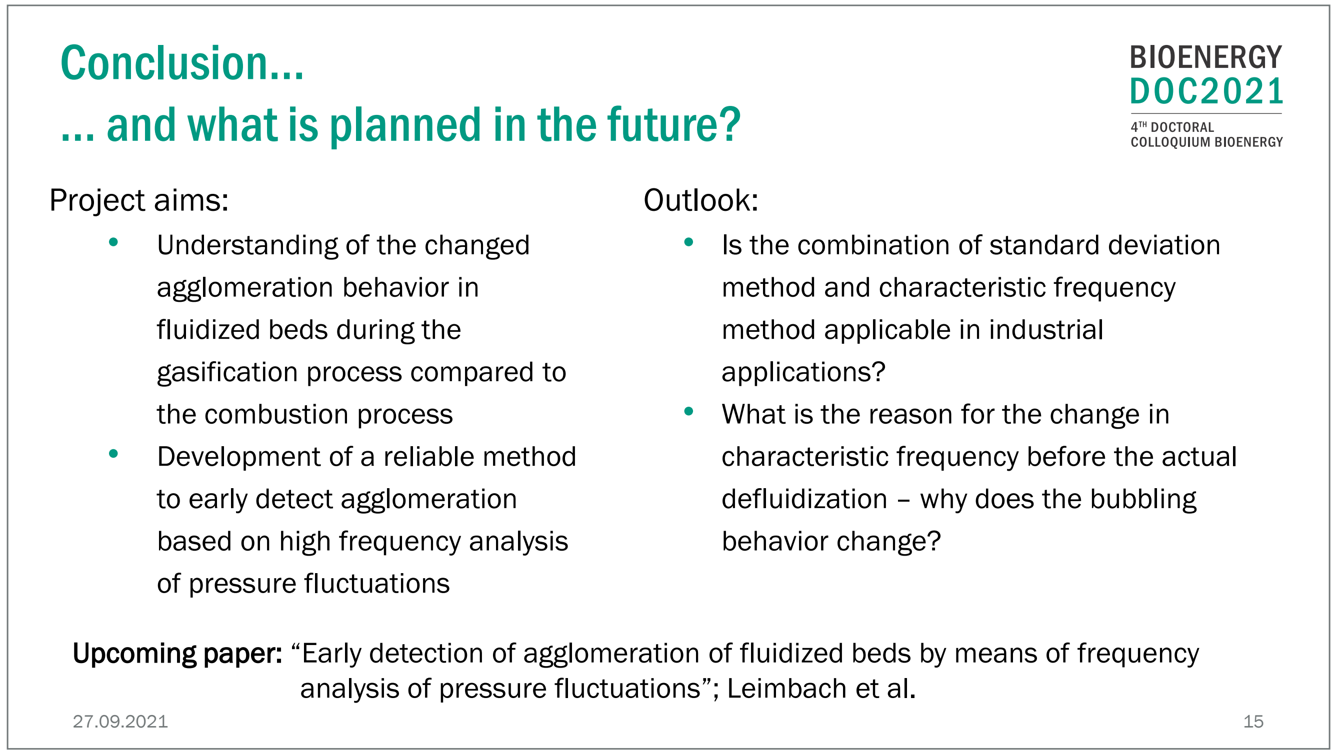

Conclusion…
… and what is planned in the future?

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Project aims:

- Understanding of the changed agglomeration behavior in fluidized beds during the gasification process compared to the combustion process
- Development of a reliable method to early detect agglomeration based on high frequency analysis of pressure fluctuations

Outlook:

- Is the combination of standard deviation method and characteristic frequency method applicable in industrial applications?
- What is the reason for the change in characteristic frequency before the actual defluidization – why does the bubbling behavior change?

Upcoming paper: “Early detection of agglomeration of fluidized beds by means of frequency analysis of pressure fluctuations”; Leimbach et al.

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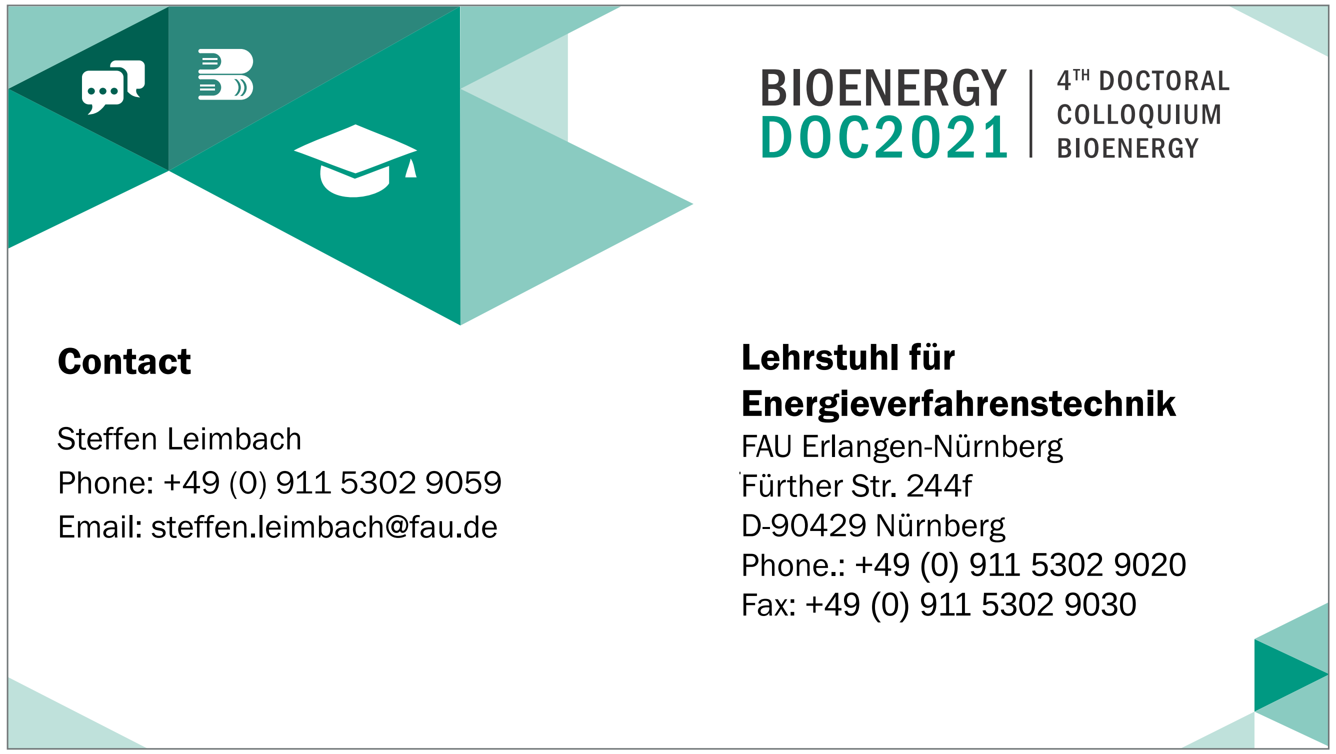

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Christian Wondra, Friedrich-Alexander-Universität Erlangen/Nürnberg

Determination of flammability limits and laminar flame velocity of biogenic synthesis gases

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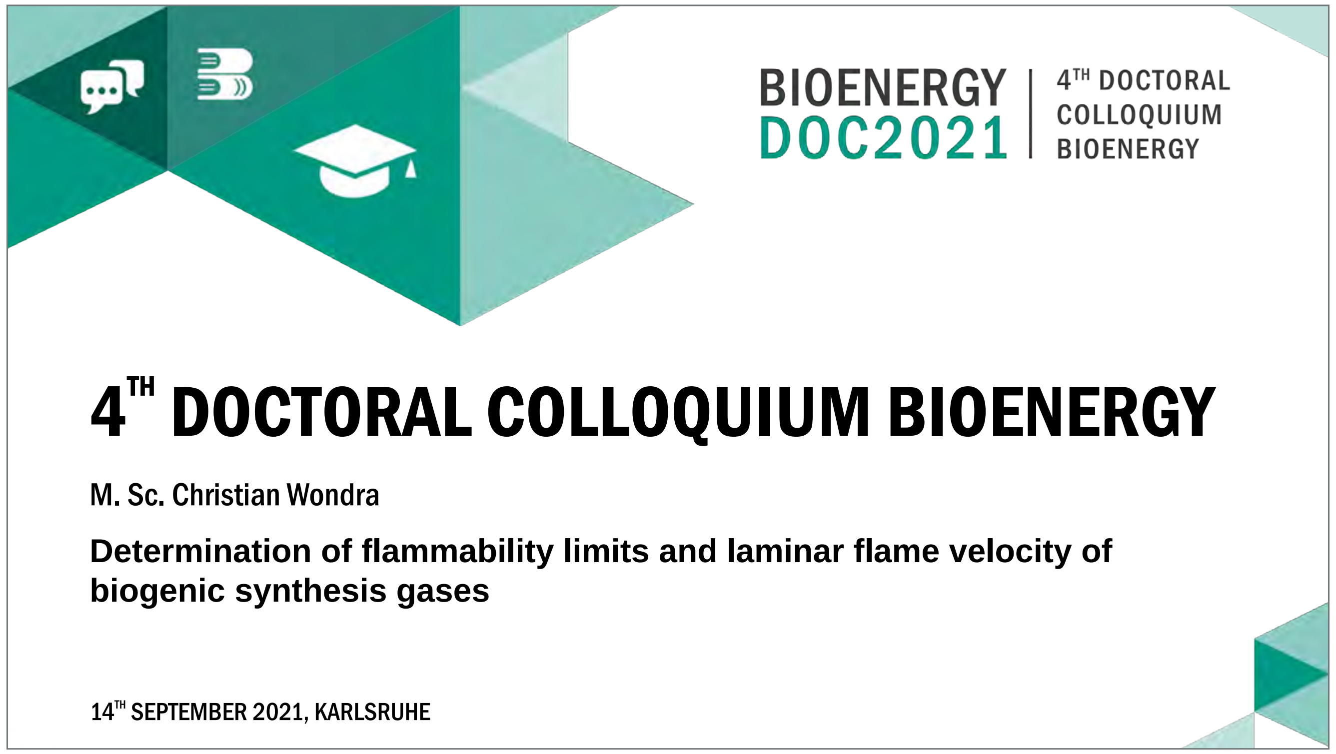
Industrial process heat, which accounts for 20 % of final energy consumption in Germany and is predominantly covered by natural gas, requires novel concepts to substitute fossil fuels and increase the share of renewable energies. In this context, biomass as a fuel has the advantage that it is utilized in a CO_2-neutral manner and thus leads to long-term climate-neutral process heat generation.

Direct combustion of biomass is usually out of the question for many melting, burning and other high-temperature processes, since the necessary adiabatic combustion temperatures cannot be achieved and the control of solid fuel firing systems cannot be implemented sufficiently quickly and flexibly, and fly ash can adversely affect the product. Processed biogenic synthesis gases from gasification, on the other hand, can be used with minor modifications in existing burners and furnaces. Ideal for such processes is the generation of Synthetic Natural Gas (SNG) from solid biomass. In this process, biomass is first thermo-chemically converted and the resulting syngas is then upgraded to current natural gas standards through complex gas purification and multi-stage catalytic methanation. For many industrial processes, however, it is not necessary to treat the synthesis gas produced during biomass gasification to natural gas quality. Instead, partial methanation and purification can already be used to individually adapt the gas quality to the needs of industrial processes and burners. A hot gas control section prevents the tars produced from condensing out, which increases the calorific value and eliminates the need for costly cold gas purification. This results in a significant technical and economic simplification of the process chain of gas processing and synthesis compared to the production of SNG that can be fed into the grid. For the direct utilization of partially conditioned biogenic synthesis gases in gas burners, the characterization of the combustion properties of the gases is very important. Heating value, Wobbe index as well as adiabatic combustion temperatures can be calculated via the exact gas composition, whereas the parameters laminar flame velocity and the flammability limits, which are decisive for the suitability as natural gas substitute, have to be determined experimentally. Due to the incomplete purification of the process gases, these values change strongly with higher hydrogen content, long-chain hydrocarbons and different CO_2 and nitrogen concentrations. Likewise, temperature and pressure influence the laminar flame speed and the flammability limits, which means that these parameters also have an influence on the design of the hot gas control system and the gas burner from a safety point of view. A test rig is being designed and set up at EVT to determine these parameters. The operation of the test rig as well as the first results of the characterization of the synthesis gases will be presented and discussed.



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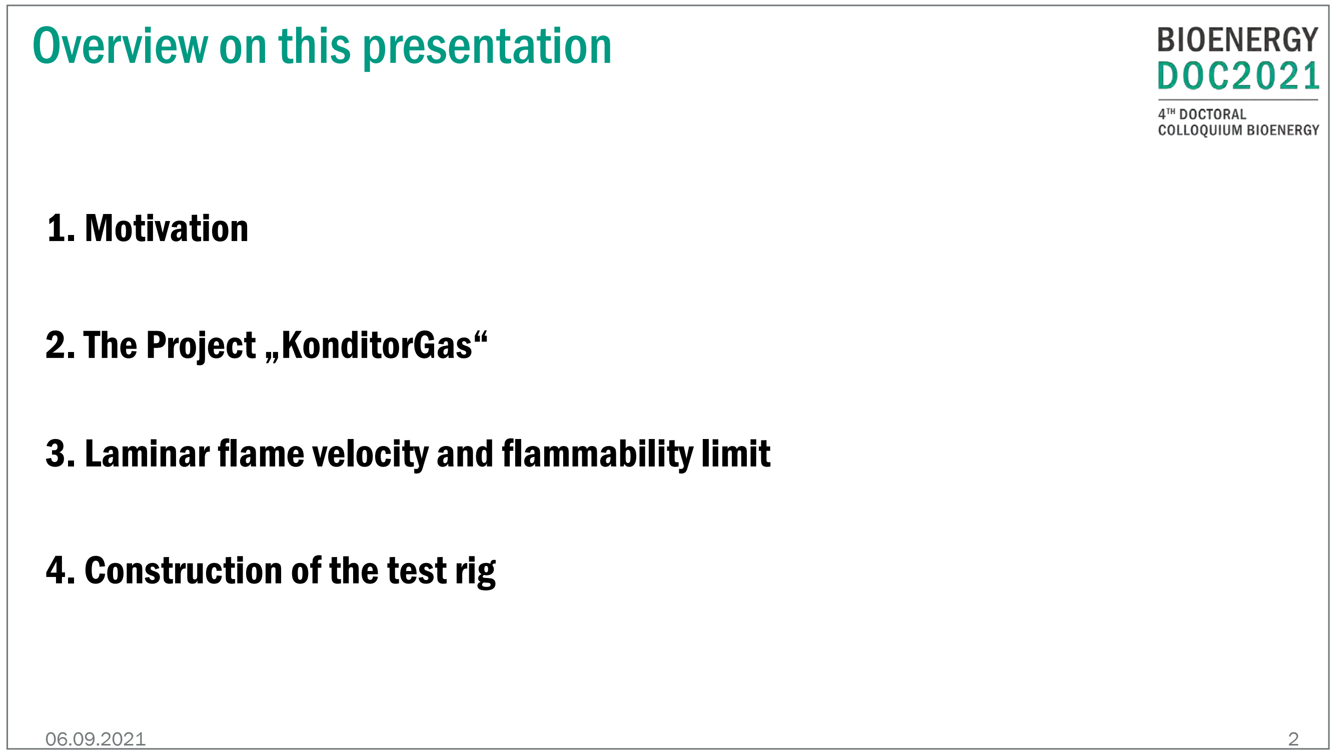
M. Sc. Christian Wondra

Determination of flammability limits and laminar flame velocity of biogenic synthesis gases

14TH SEPTEMBER 2021, KARLSRUHE



Overview on this presentation

BIOENERGY DOC2021 4TH DOCTORAL COLLOQUIUM BIOENERGY

1. **Motivation**
2. **The Project „KonditorGas“**
3. **Laminar flame velocity and flammability limit**
4. **Construction of the test rig**

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Project KonditorGas - Overview

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Title of the Doctoral Project:	„KonditorGas“
Doctoral Student:	Christian Wondra
Project Partners:	DBFZ Leipzig E-Flox GmbH TesTneT GmbH
University:	Friedrich-Alexander University Erlangen-Nürnberg
University Supervisor:	Prof. Dr.-Ing. Jürgen Karl
Funding :	BMWi, PTJ Bundesministerium für Wirtschaft und Energie Projektträger Jülich Forschungszentrum Jülich
Duration:	09/2020 – 08/2023

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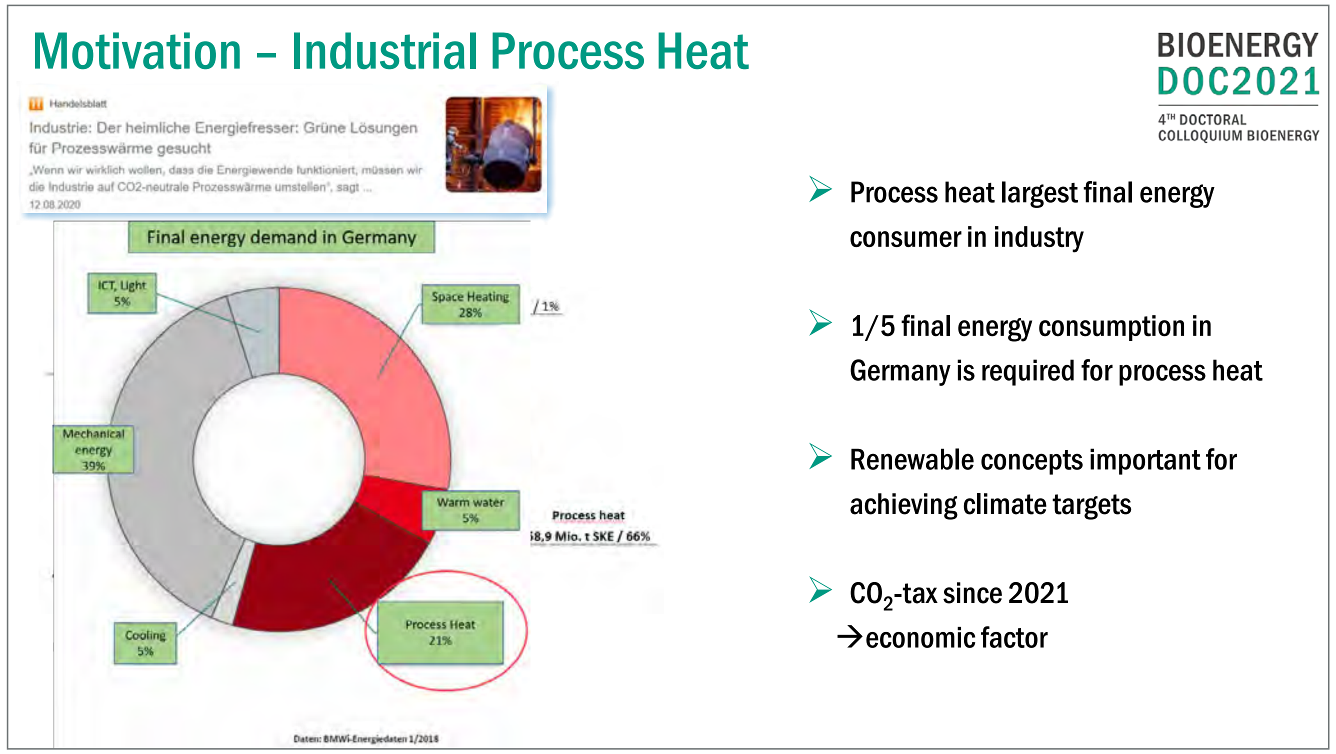

Motivation – Industrial Process Heat

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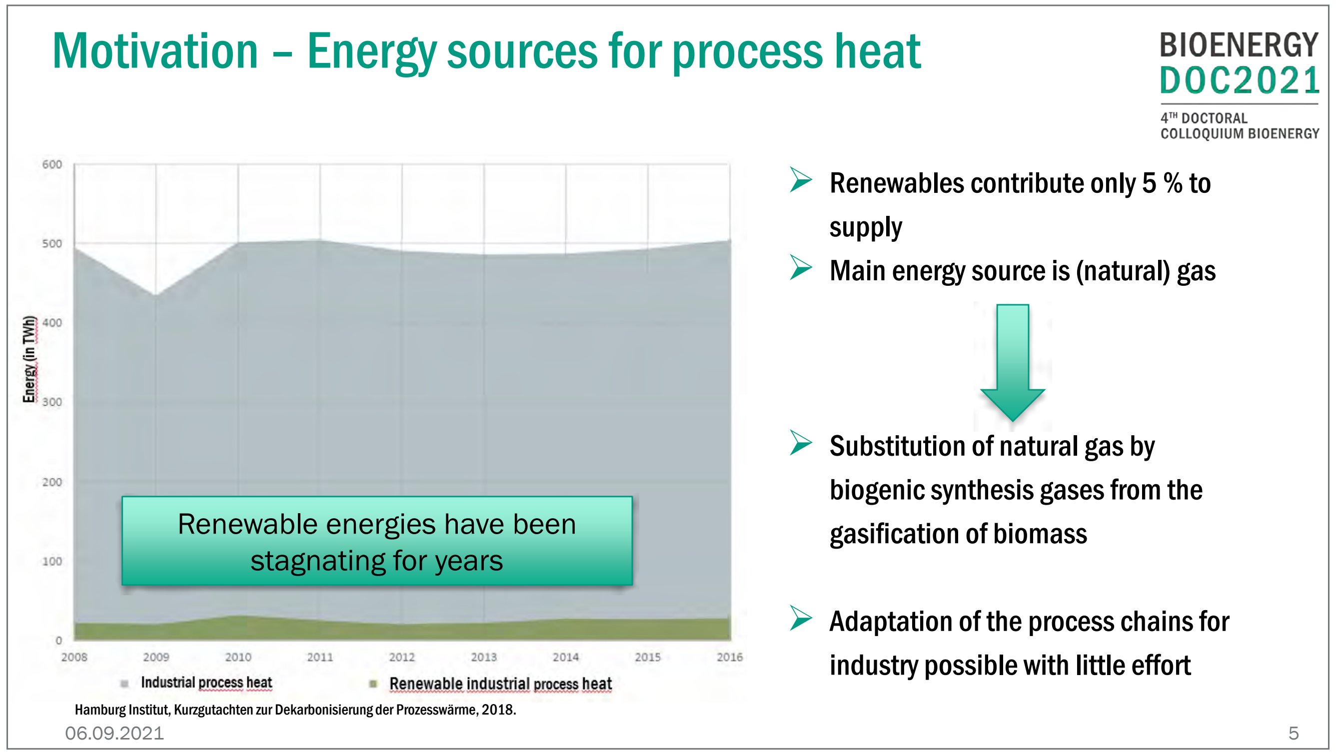
Handelsblatt
Industrie: Der heimliche Energiefresser: Grüne Lösungen für Prozesswärme gesucht
„Wenn wir wirklich wollen, dass die Energiewende funktioniert, müssen wir die Industrie auf CO2-neutrale Prozesswärme umstellen“, sagt ...
12.08.2020

Daten: BMWi-Energiedaten 1/2018

- Process heat largest final energy consumer in industry
- 1/5 final energy consumption in Germany is required for process heat
- Renewable concepts important for achieving climate targets
- CO_2-tax since 2021
  → economic factor



Motivation – Energy sources for process heat

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Hamburg Institut, Kurzgutachten zur Dekarbonisierung der Prozesswärme, 2018.

- Renewables contribute only 5 % to supply
- Main energy source is (natural) gas

- Substitution of natural gas by biogenic synthesis gases from the gasification of biomass
- Adaptation of the process chains for industry possible with little effort

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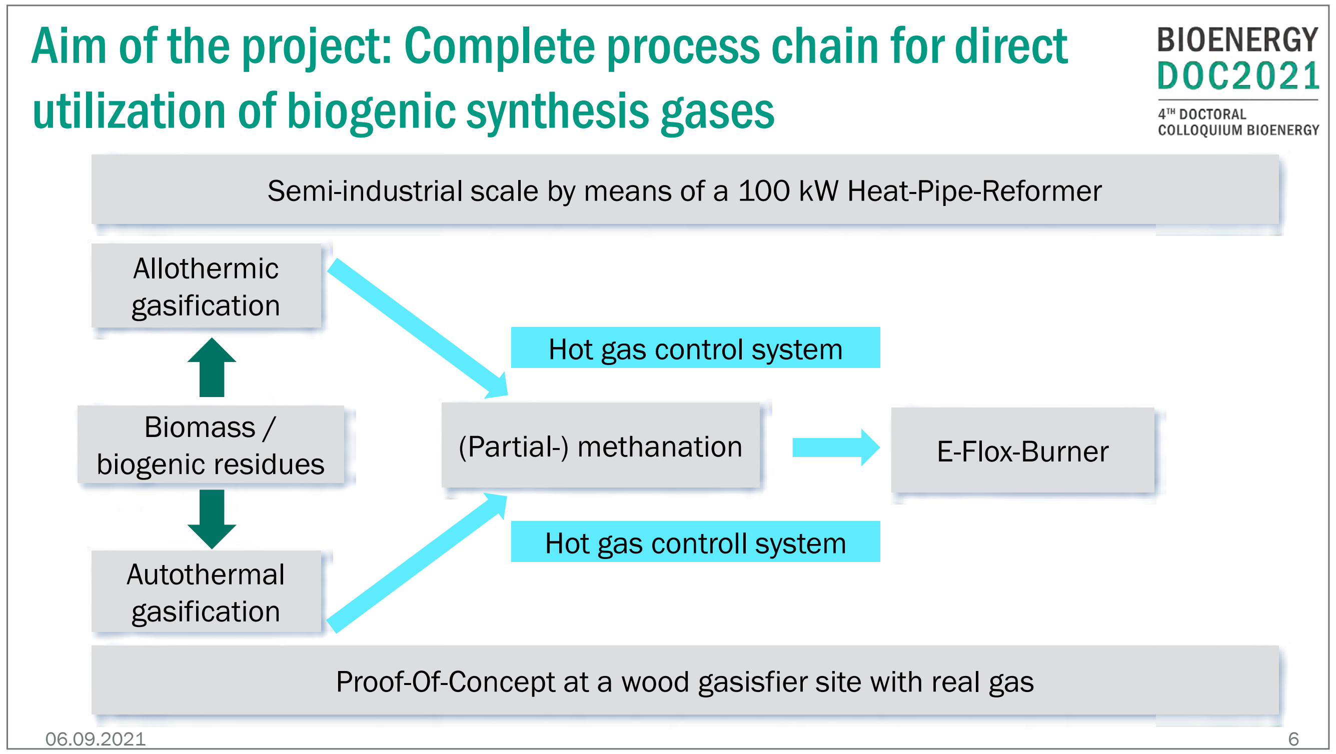

Aim of the project: Complete process chain for direct utilization of biogenic synthesis gases

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Semi-industrial scale by means of a 100 kW Heat-Pipe-Reformer

Proof-Of-Concept at a wood gasifier site with real gas

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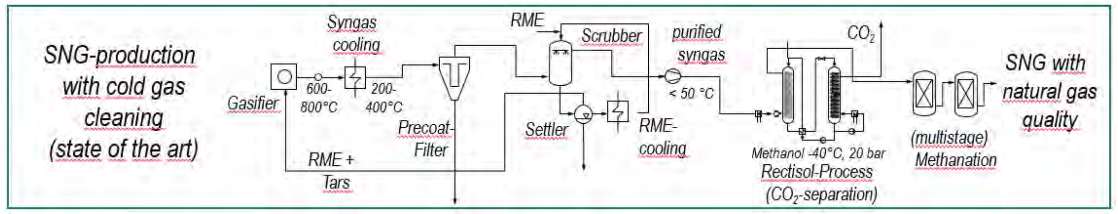
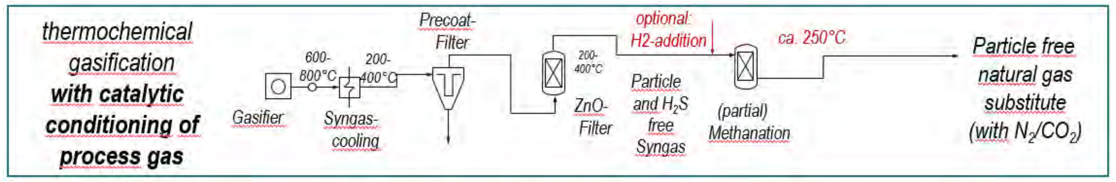
SNG production: State of the art vs. Catalytic conditioning

State of the art: SNG with natural gas quality



Aim of the project: Simplification of gas purification and methanation, resulting in technical and economic simplification of the process chain



Gasification: Different gas quality and inert gas content

Allothermal process chain:

- ➢ 5 kW fluidized bed gasifier
- ➢ Steam as gasification medium

H_2	CO	CO_2	CH_4	Tars
Vol %	Vol %	Vol %	Vol %	mg/m³
47,4	14,6	27,5	10,5	5000

Autothermal process chain:

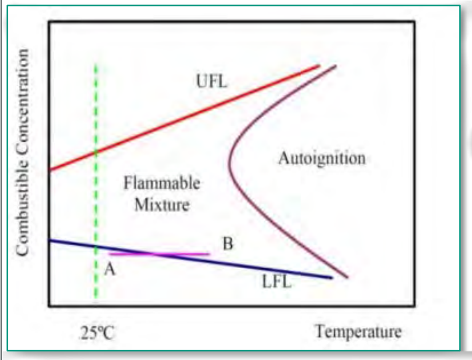
- ➢ 10 kW fixed bed gasifier (Spanner RE)
- ➢ Air as gasification medium

H_2	CO	CO_2	CH_4	N_2	Tars
Vol %	Vol %	Vol %	Vol %	Vol %	mg/m³
19,5	22,6	11,1	1,9	43,7	193

Due to the simplification of the process, the fuel gas contains higher concentrations of inert gases, which influence parameters such as flammability limits and flame velocities.

Theoretical background – Flammability limit of gas mixtures

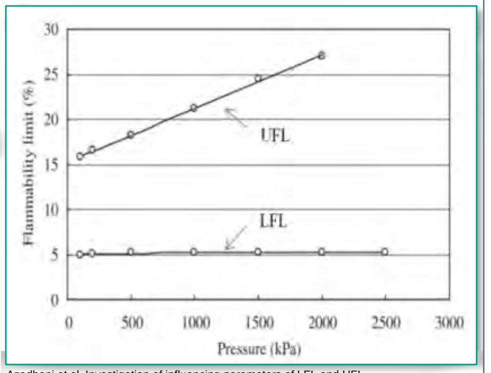
- ➢ Describes the flammability of a gas mixture in air
- ➢ Important safety characteristic
- ➢ Lower (LFL) and upper (UFL) flammability limit



Zabetakis, M.G, Flammability Characteristics of Combustible Gases and Vapors

Depends on:

- ➢ Temperature
- ➢ Pressure
- ➢ Inert gas content

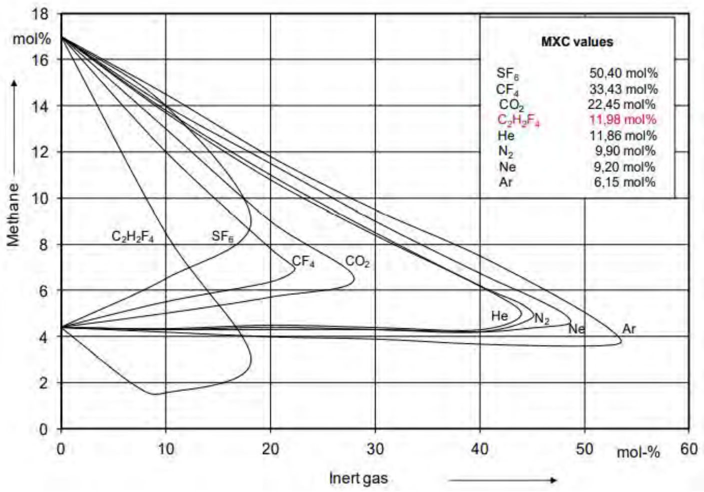


Azadboni et.al, Investigation of influencing parameters of LFL and UFL

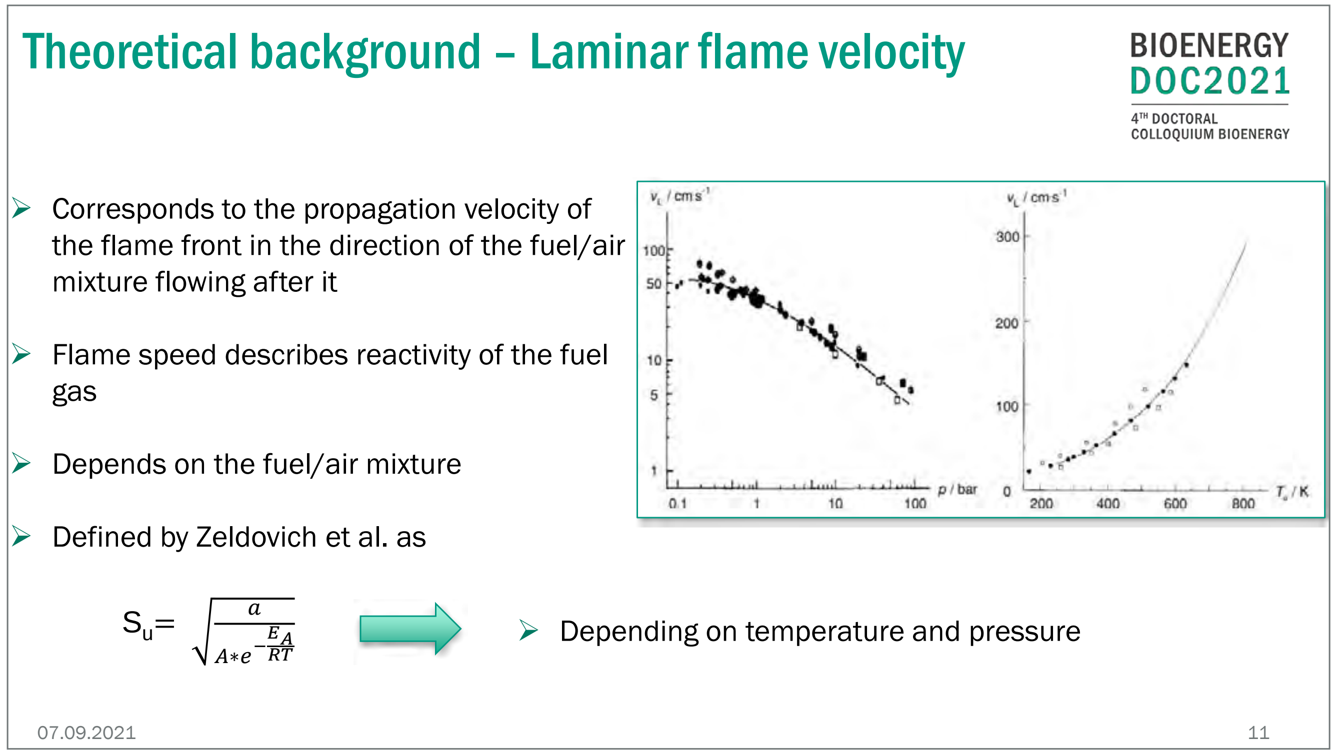
Flamability limit – Influence of inert/neutral gas

- ➢ Considerable effect on chemical reaction mechanism
- ➢ Dilution of the fuel gas mixture
- ➢ Inert gas with high thermal capacity reduce the flame temperature
- ➢ Also the thermal conductivity is a factor

With increasing inert gas content the range between LFL and UFL is reduced



CHEMSAFE®, Database of evaluated safety characteristics



Theoretical background – Laminar flame velocity

- Corresponds to the propagation velocity of the flame front in the direction of the fuel/air mixture flowing after it
- Flame speed describes reactivity of the fuel gas
- Depends on the fuel/air mixture
- Defined by Zeldovich et al. as

$$S_u = \sqrt{\frac{a}{A * e^{-\frac{E_A}{RT}}}}$$

- Depending on temperature and pressure

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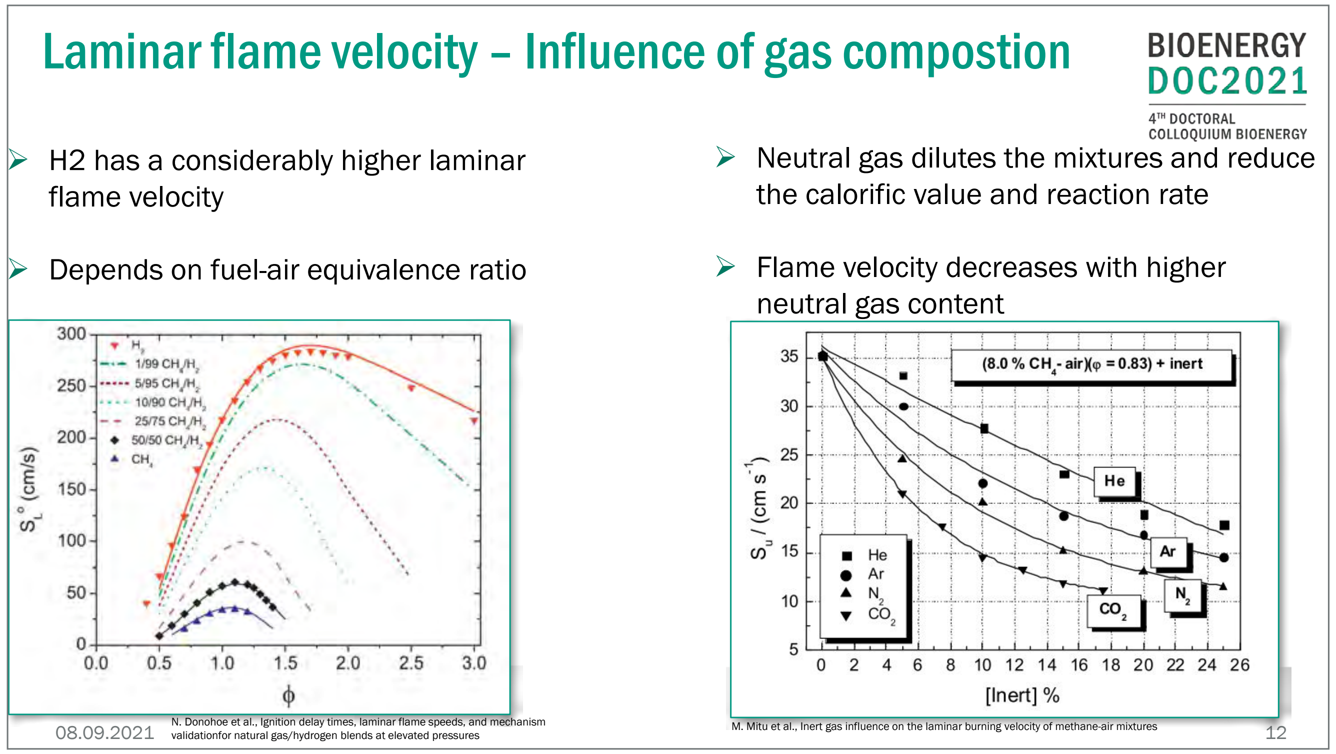

Laminar flame velocity – Influence of gas compostion

- H2 has a considerably higher laminar flame velocity
- Depends on fuel-air equivalence ratio

- Neutral gas dilutes the mixtures and reduce the calorific value and reaction rate
- Flame velocity decreases with higher neutral gas content

08.09.2021

N. Donohoe et al., Ignition delay times, laminar flame speeds, and mechanism validationfor natural gas/hydrogen blends at elevated pressures

M. Mitu et al., Inert gas influence on the laminar burning velocity of methane-air mixtures

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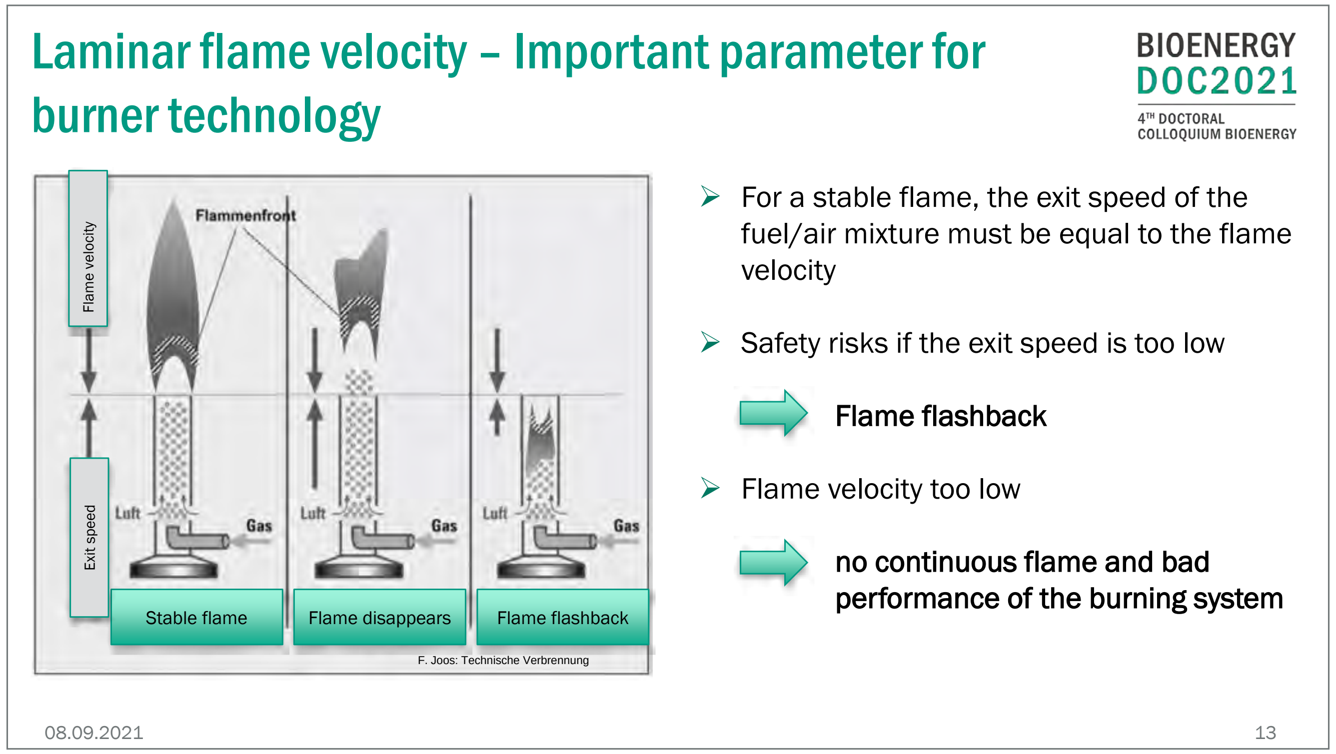

Laminar flame velocity – Important parameter for burner technology

F. Joos: Technische Verbrennung

- For a stable flame, the exit speed of the fuel/air mixture must be equal to the flame velocity
- Safety risks if the exit speed is too low

  Flame flashback
- Flame velocity too low

  no continuous flame and bad performance of the burning system

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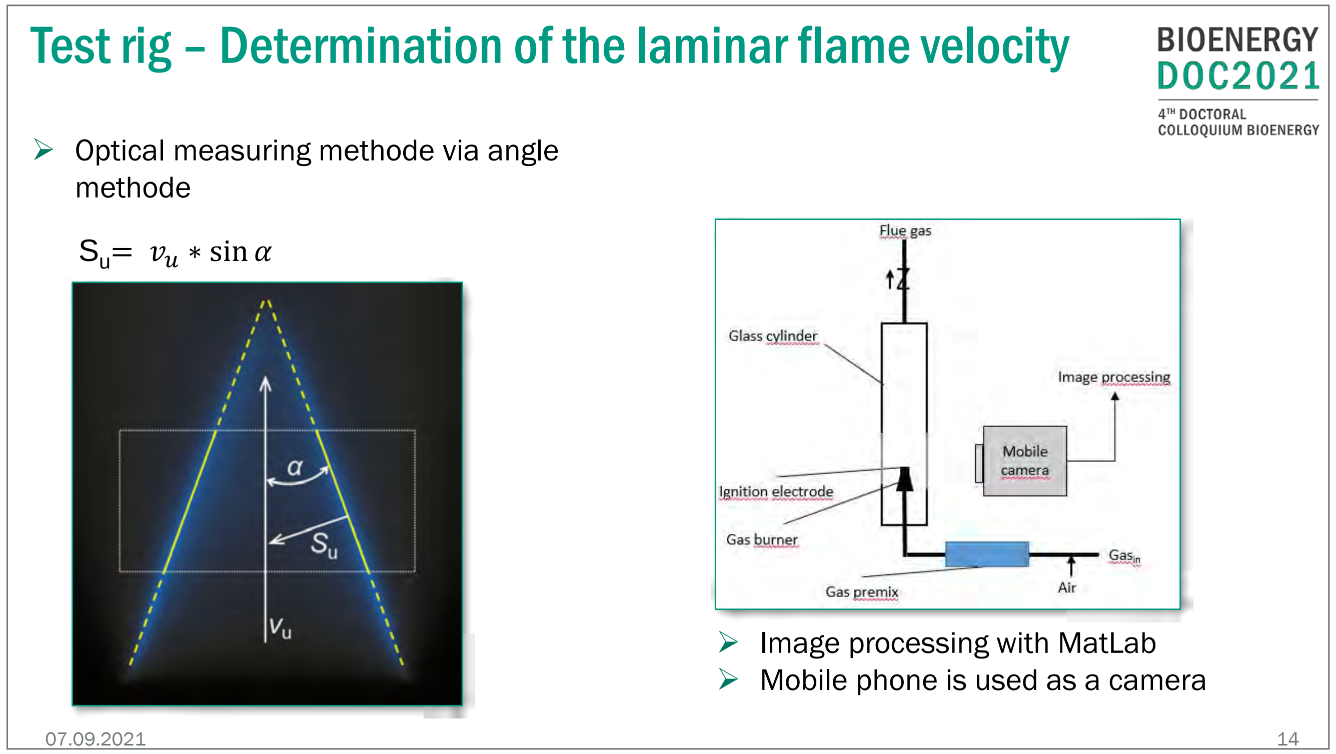

Test rig – Determination of the laminar flame velocity

- Optical measuring methode via angle methode

$$S_u = v_u * \sin\alpha$$

- Image processing with MatLab
- Mobile phone is used as a camera

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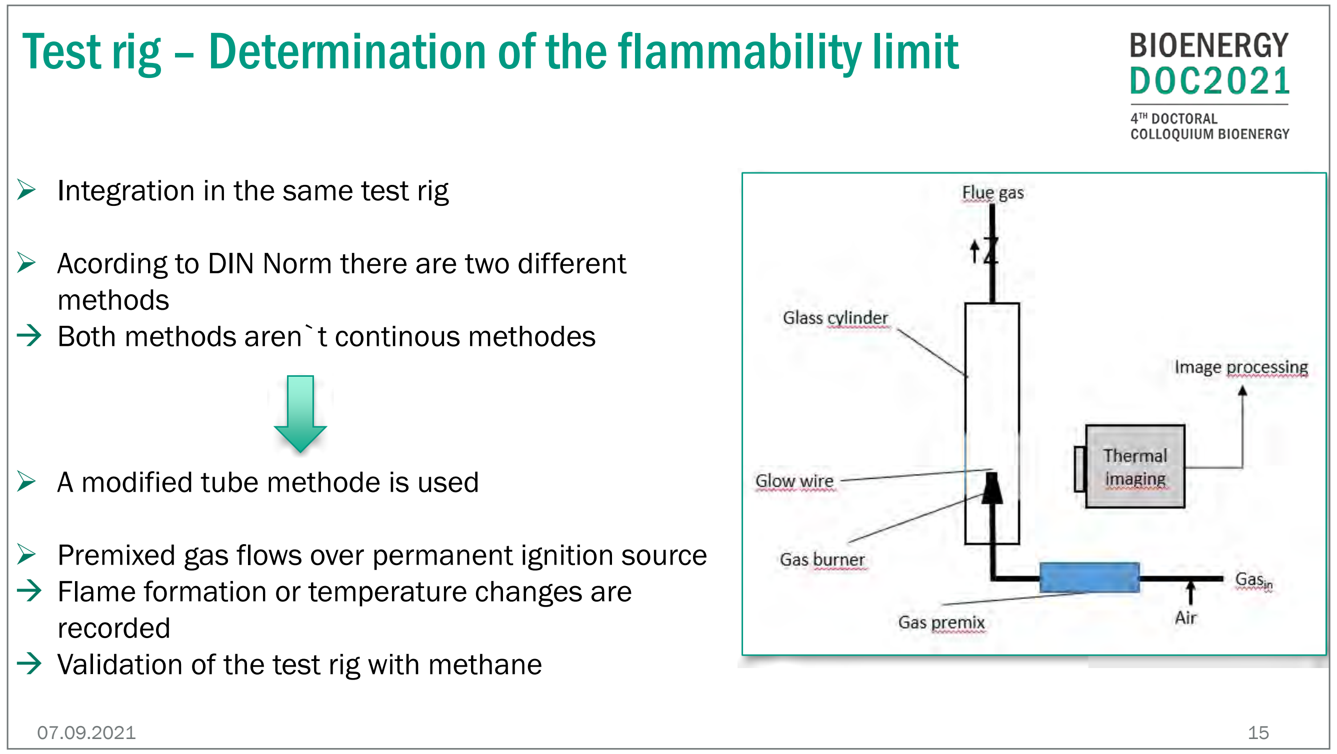
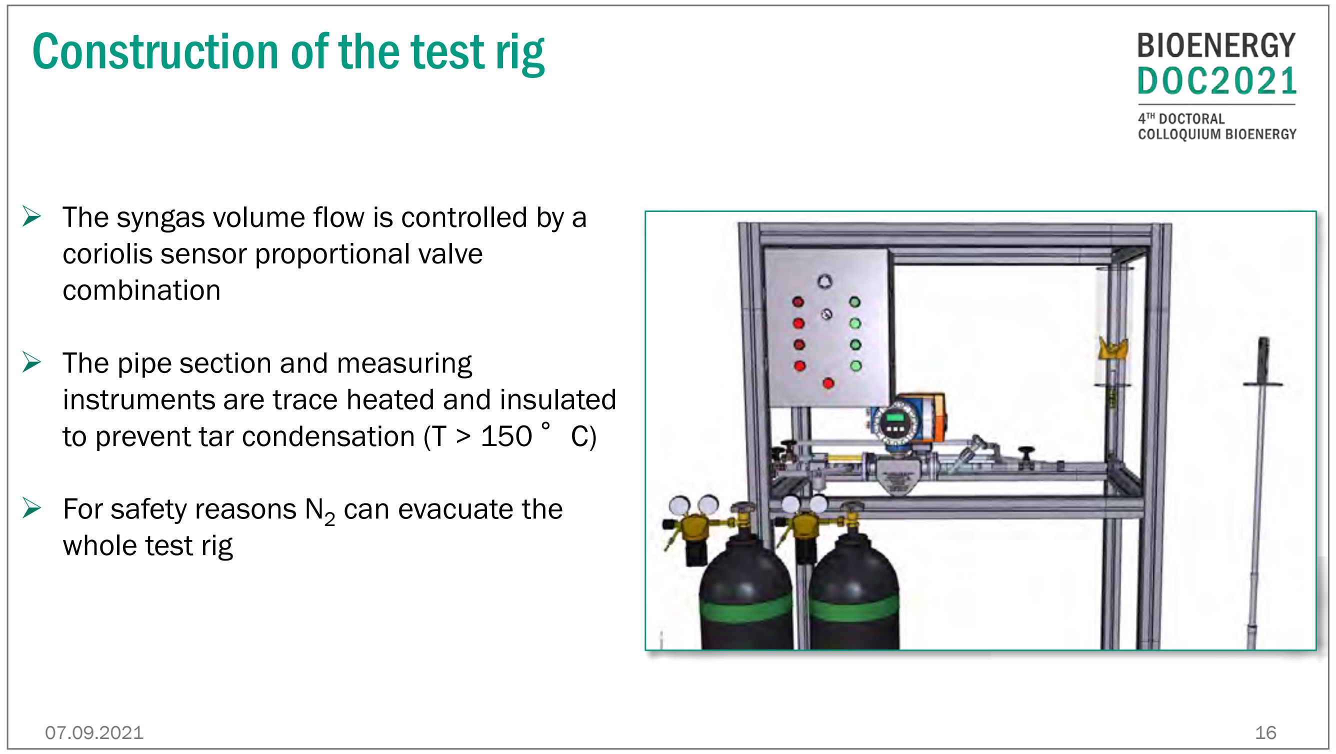


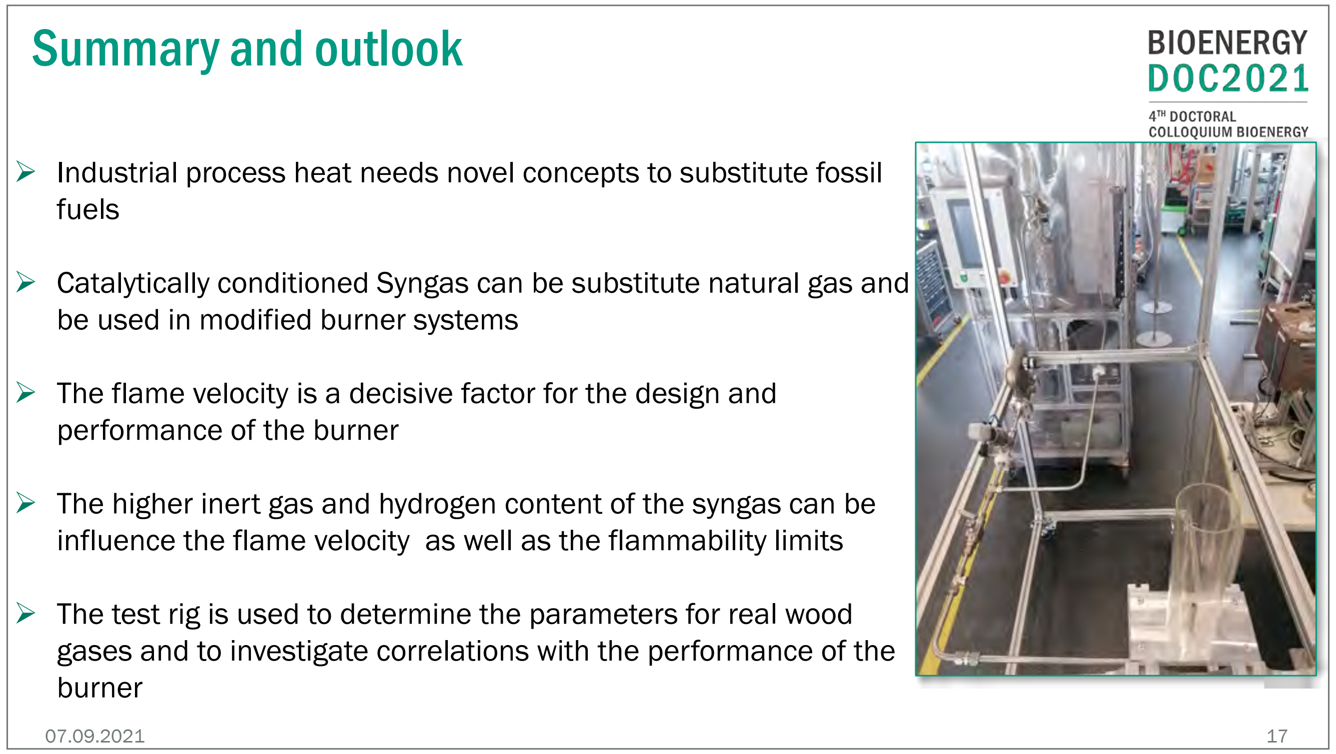
Test rig – Determination of the flammability limit

- Integration in the same test rig
- Acording to DIN Norm there are two different methods
- → Both methods aren`t continous methodes
- A modified tube methode is used
- Premixed gas flows over permanent ignition source
- → Flame formation or temperature changes are recorded
- → Validation of the test rig with methane



Construction of the test rig

- The syngas volume flow is controlled by a coriolis sensor proportional valve combination
- The pipe section and measuring instruments are trace heated and insulated to prevent tar condensation ($T > 150\,^{\circ}C$)
- For safety reasons N_2 can evacuate the whole test rig



Summary and outlook

- Industrial process heat needs novel concepts to substitute fossil fuels
- Catalytically conditioned Syngas can be substitute natural gas and be used in modified burner systems
- The flame velocity is a decisive factor for the design and performance of the burner
- The higher inert gas and hydrogen content of the syngas can be influence the flame velocity as well as the flammability limits
- The test rig is used to determine the parameters for real wood gases and to investigate correlations with the performance of the burner

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Hossein Beidaghy Dizaji, University of Leipzig/Deutsches Biomasseforschungszentrum

A comprehensive research study on the quality and behavior of silica-rich biomass ashes

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Increasing use of renewable energy is vital to reduce greenhouse gas emissions in short and mid-term perspective. Bioenergy production, in particular the exploitation of agricultural side products and biogenic residues, will play an important role to enable this sustainable development beside solar and wind energy. In this way, unique opportunities to combine energy generation, e.g. application of biomass in boilers, with the valorization of remaining ashes is of great importance. Consequently, innovative and integrated approaches producing biogenic silica based on the remaining ashes from the combustion of SiO_2-rich biomass such as rice straw and rice husk may contribute to this development. However, several measures have to be considered to fulfill the required properties for the technical application of the resulting rice straw (RS) and rice husk (RH) ashes, i.e. purity, amorphous structure, specific surface area, pore size, pore volume, and thus further increase its potential for new innovative material applications. For this development, however, slag formation is one of the main challenges as a barrier, especially for RS, and the ash melting behavior of silica-rich biomass fuels (i.e. slag formation, atomic structural and viscosity change) is linked to the ash quality (i.e. silica purity, porosity and crystallinity of the ash). Thus, the objective of the present work was to evaluate the slag formation tendency of original, chemically pre-treated and blended RS and RH fuels. In this regard, a comprehensive research was performed, and the ash transformation mechanism of silica-rich biomass fuels was investigated both experimentally and theoretically. Analysis was performed using different advanced spectroscopic and diffractometric techniques (i.e. SEM/EDX, XPS, ICP-OES, XRD followed by Rietveld refinement method) accompanied and supported by thermodynamic equilibrium calculations by FactSage 8.0 software, slag viscosity modeling toolbox, and chemical fractionation of the solid fuels. For example, Fig. 1 shows the link between crystallinity and BET specific surface area (BET SSA). Furthermore, a computer code was developed in Python to find the most relevant fuel indexes for the prediction of slag formation in silica-rich biomasses. These findings are highly relevant for future investigations in biomass boiler designs and production of biogenic silica for material applications.

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Quality and behavior of silica-rich ashes from biomass combustion

H. Beidaghy Dizaji [1–2], T. Zeng [1], D. Enke [2], H. Hölzig [3], and G. Klöß [3]

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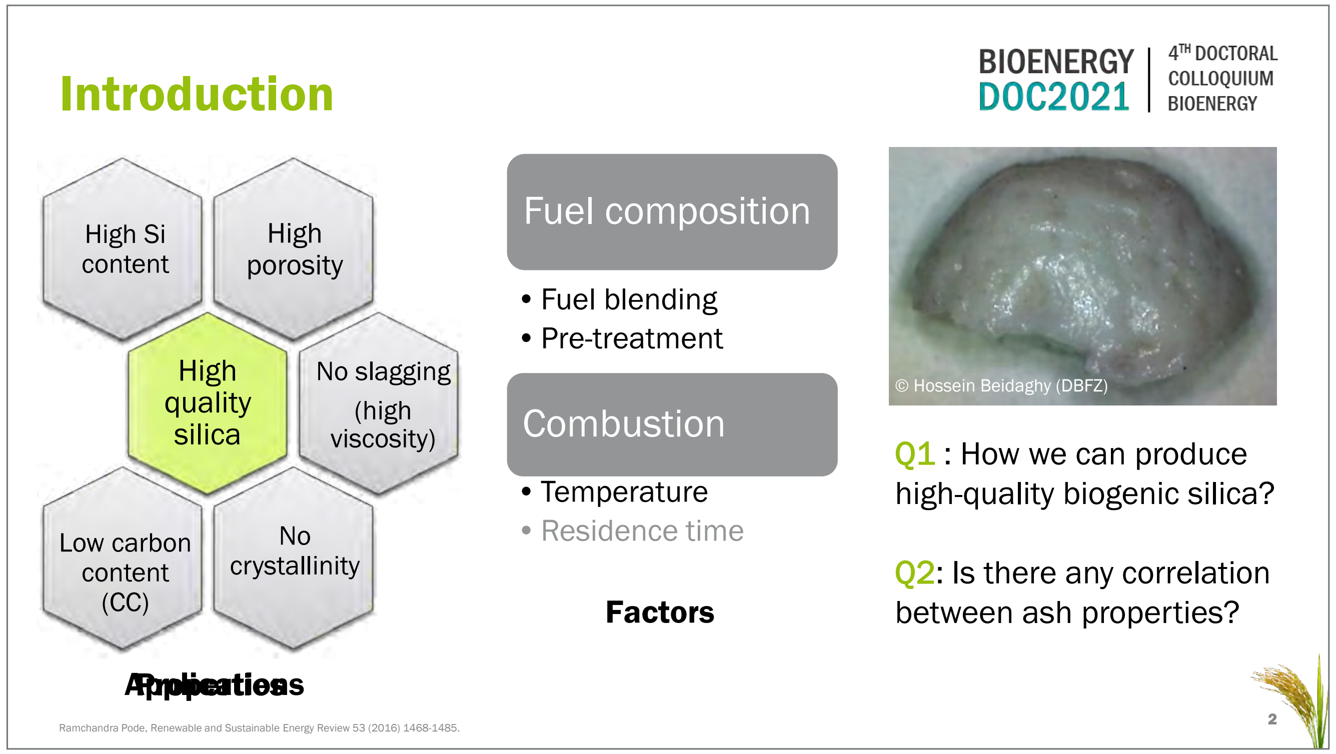
[2] Institute of Chemical Technology, Leipzig University, Linnéstr. 3, 04103 Leipzig, Germany
[3] Institute of Mineralogy, Crystallography and Materials Science, Leipzig University

4TH Doctoral Colloquium Bioenergy, KIT
Thermochemical processes I
13TH SEPTEMBER 2021, KIT



Introduction

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High Si content
High porosity
High quality silica
No slagging (high viscosity)
Low carbon content (CC)
No crystallinity

Applications
Properties

Fuel composition
- Fuel blending
- Pre-treatment

Combustion
- Temperature
- Residence time

Factors

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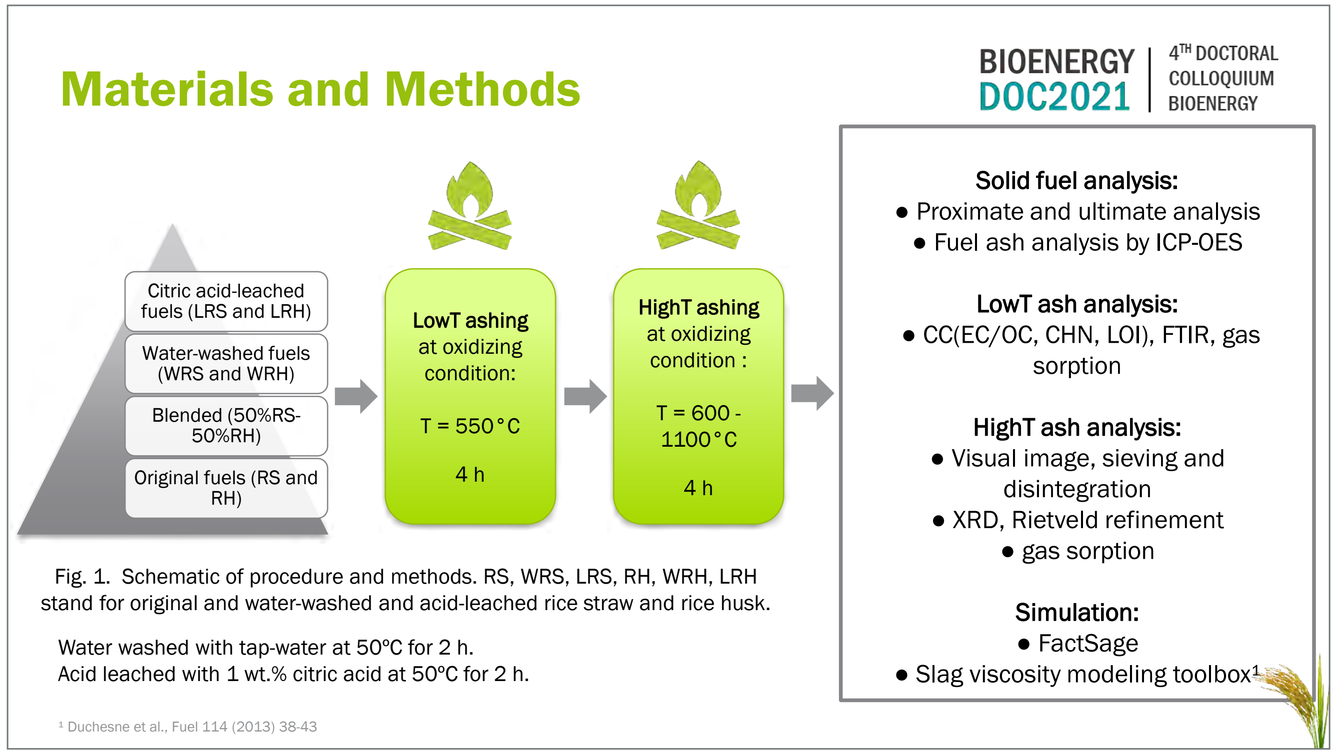
Q1 : How we can produce high-quality biogenic silica?

Q2: Is there any correlation between ash properties?

Ramchandra Pode, Renewable and Sustainable Energy Review 53 (2016) 1468-1485.



Materials and Methods

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Citric acid-leached fuels (LRS and LRH)
Water-washed fuels (WRS and WRH)
Blended (50%RS-50%RH)
Original fuels (RS and RH)

LowT ashing at oxidizing condition:
T = 550 °C
4 h

HighT ashing at oxidizing condition :
T = 600 - 1100 °C
4 h

Solid fuel analysis:
- Proximate and ultimate analysis
- Fuel ash analysis by ICP-OES

LowT ash analysis:
- CC(EC/OC, CHN, LOI), FTIR, gas sorption

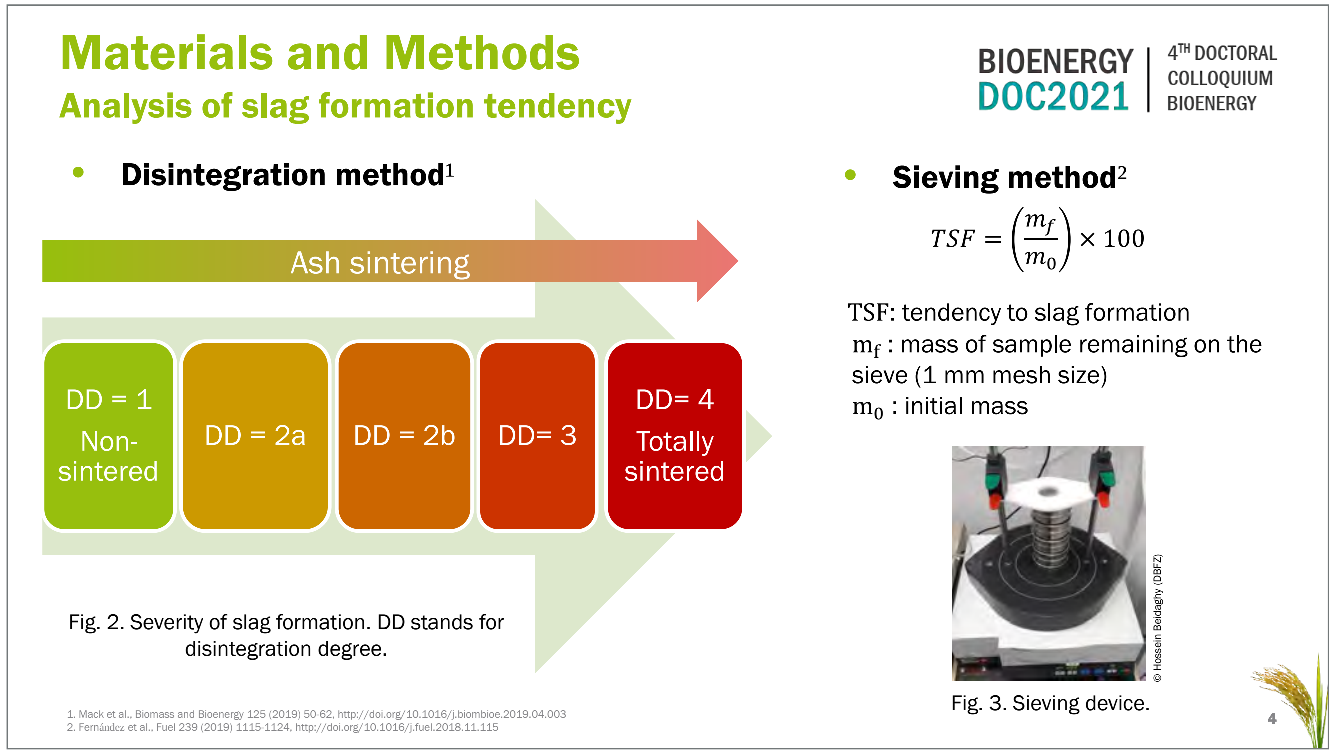
HighT ash analysis:
- Visual image, sieving and disintegration
- XRD, Rietveld refinement
- gas sorption

Simulation:
- FactSage
- Slag viscosity modeling toolbox[1]

Fig. 1. Schematic of procedure and methods. RS, WRS, LRS, RH, WRH, LRH stand for original and water-washed and acid-leached rice straw and rice husk.

Water washed with tap-water at 50°C for 2 h.
Acid leached with 1 wt.% citric acid at 50°C for 2 h.

[1] Duchesne et al., Fuel 114 (2013) 38-43



Materials and Methods

Analysis of slag formation tendency

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- **Disintegration method**[1]

Ash sintering

DD = 1 Non-sintered | DD = 2a | DD = 2b | DD= 3 | DD= 4 Totally sintered

Fig. 2. Severity of slag formation. DD stands for disintegration degree.

- **Sieving method**[2]

$$TSF = \left(\frac{m_f}{m_0}\right) \times 100$$

TSF: tendency to slag formation
m_f : mass of sample remaining on the sieve (1 mm mesh size)
m_0 : initial mass

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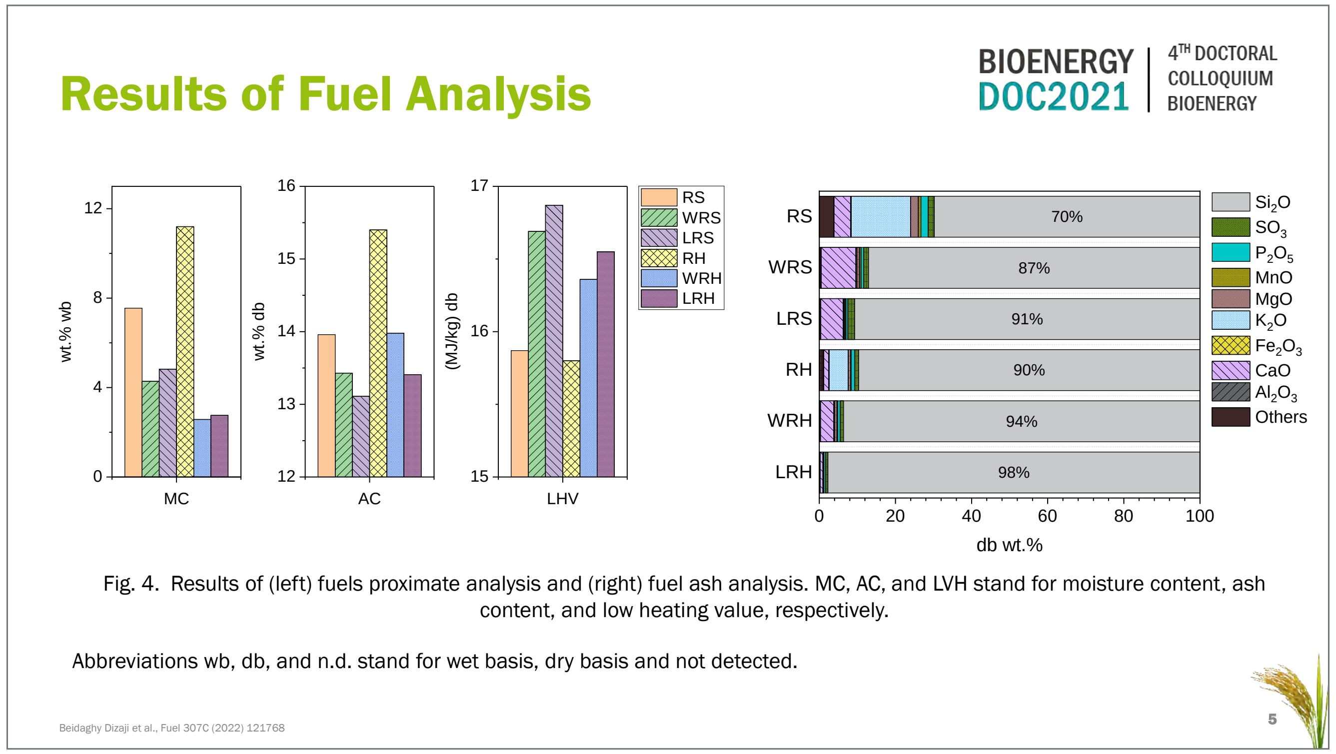
Fig. 3. Sieving device.

1. Mack et al., Biomass and Bioenergy 125 (2019) 50-62, http://doi.org/10.1016/j.biombioe.2019.04.003
2. Fernández et al., Fuel 239 (2019) 1115-1124, http://doi.org/10.1016/j.fuel.2018.11.115



Results of Fuel Analysis

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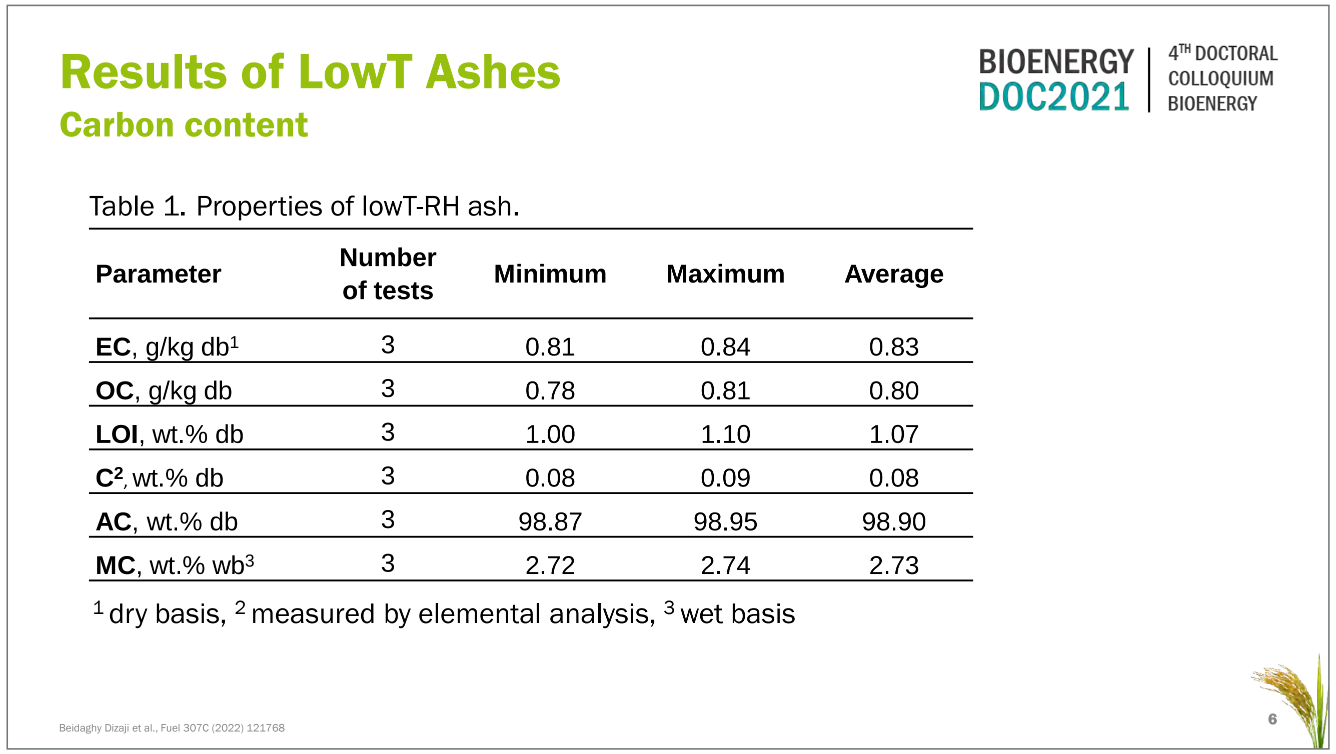
Fig. 4. Results of (left) fuels proximate analysis and (right) fuel ash analysis. MC, AC, and LVH stand for moisture content, ash content, and low heating value, respectively.

Abbreviations wb, db, and n.d. stand for wet basis, dry basis and not detected.

Beidaghy Dizaji et al., Fuel 307C (2022) 121768



Results of LowT Ashes

Carbon content

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Table 1. Properties of lowT-RH ash.

Parameter	Number of tests	Minimum	Maximum	Average
EC, g/kg db[1]	3	0.81	0.84	0.83
OC, g/kg db	3	0.78	0.81	0.80
LOI, wt.% db	3	1.00	1.10	1.07
C[2], wt.% db	3	0.08	0.09	0.08
AC, wt.% db	3	98.87	98.95	98.90
MC, wt.% wb[3]	3	2.72	2.74	2.73

[1] dry basis, [2] measured by elemental analysis, [3] wet basis

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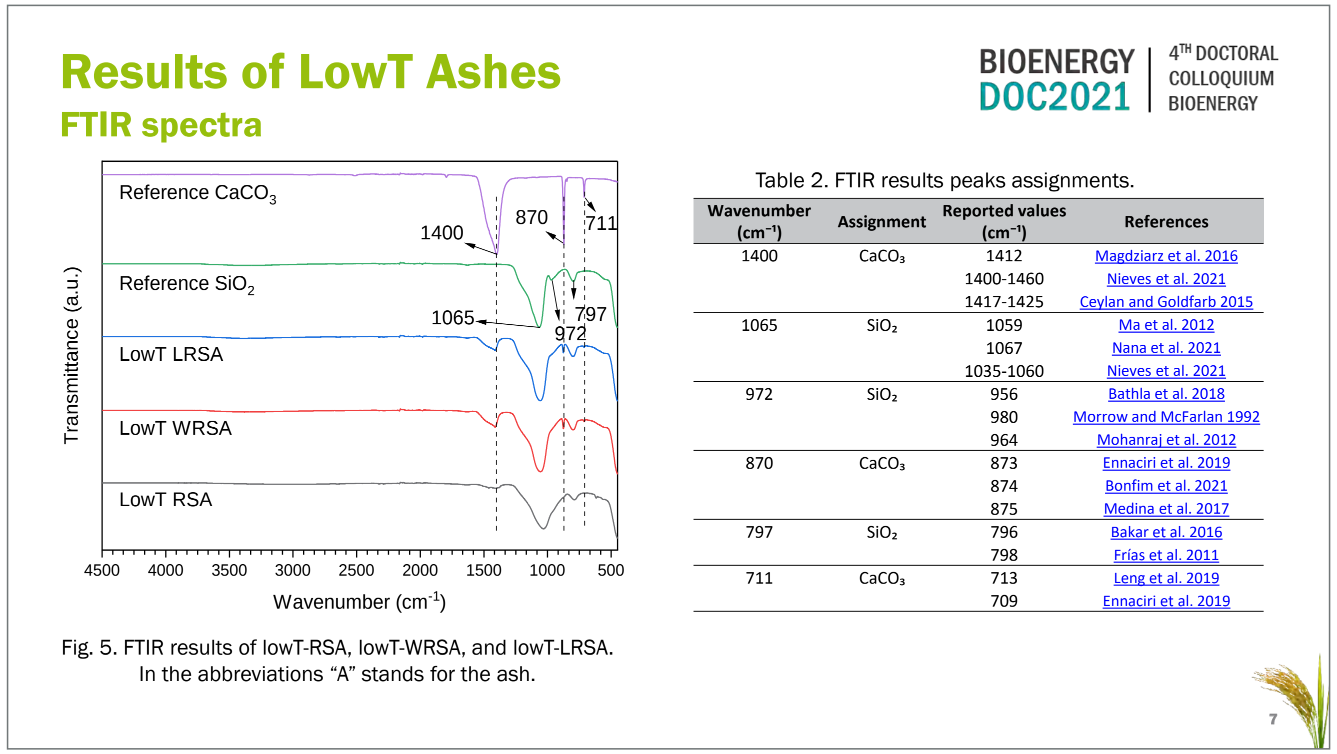


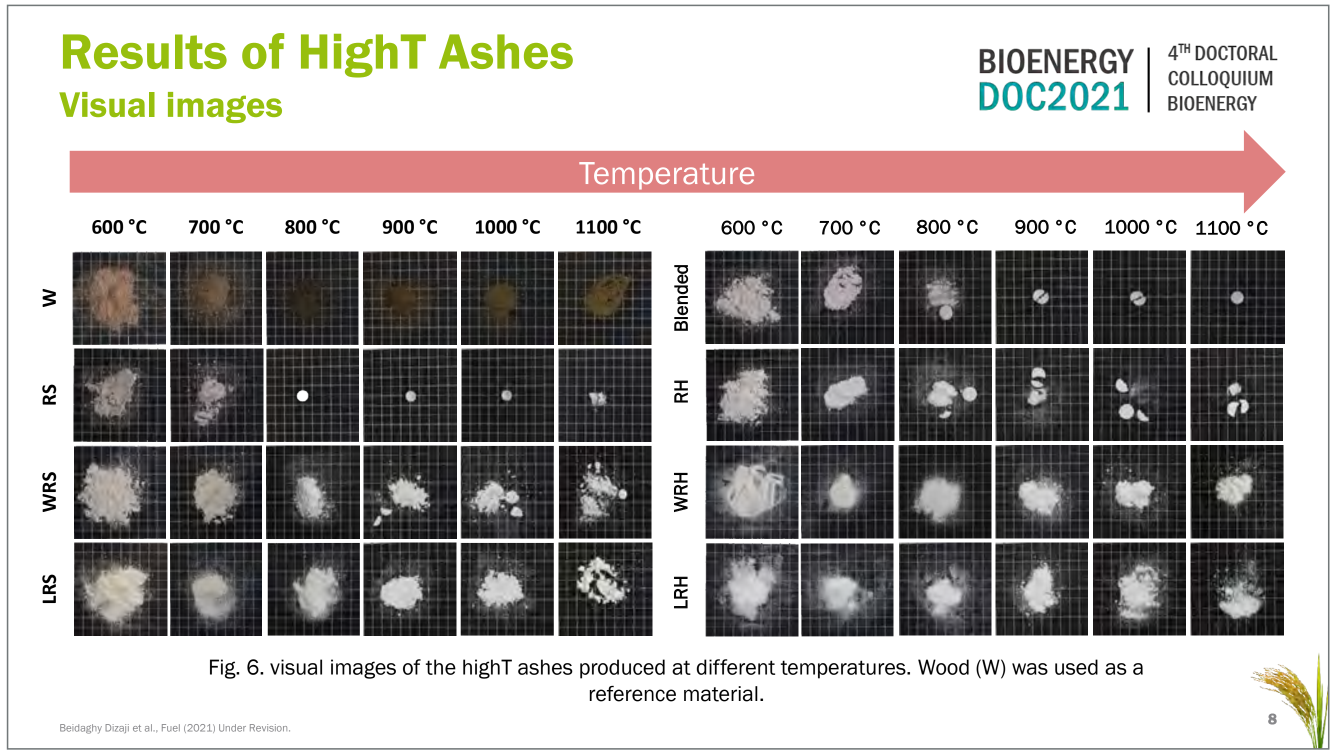
Results of LowT Ashes

FTIR spectra

Fig. 5. FTIR results of lowT-RSA, lowT-WRSA, and lowT-LRSA. In the abbreviations “A” stands for the ash.

Table 2. FTIR results peaks assignments.

Wavenumber (cm^{-1})	Assignment	Reported values (cm^{-1})	References
1400	$CaCO_3$	1412	Magdziarz et al. 2016
		1400-1460	Nieves et al. 2021
		1417-1425	Ceylan and Goldfarb 2015
1065	SiO_2	1059	Ma et al. 2012
		1067	Nana et al. 2021
		1035-1060	Nieves et al. 2021
972	SiO_2	956	Bathla et al. 2018
		980	Morrow and McFarlan 1992
		964	Mohanraj et al. 2012
870	$CaCO_3$	873	Ennaciri et al. 2019
		874	Bonfim et al. 2021
		875	Medina et al. 2017
797	SiO_2	796	Bakar et al. 2016
		798	Frías et al. 2011
711	$CaCO_3$	713	Leng et al. 2019
		709	Ennaciri et al. 2019

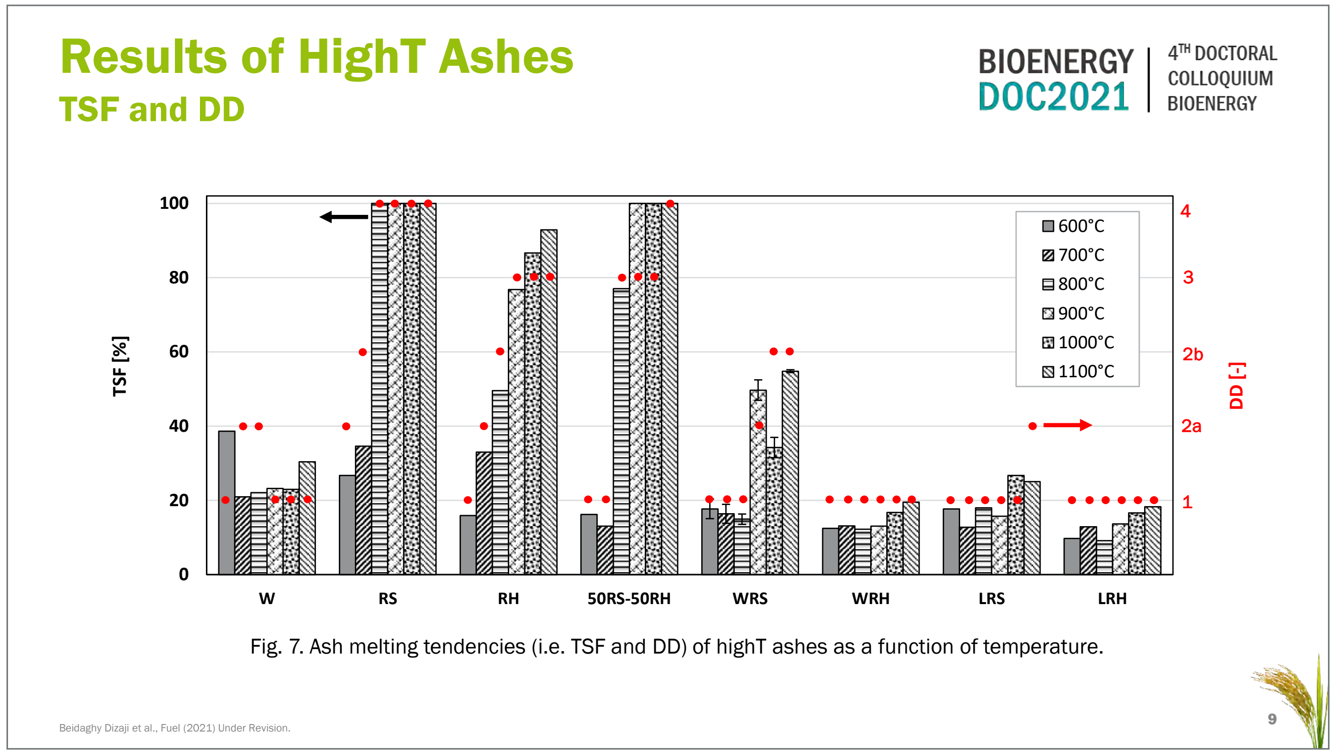


Results of HighT Ashes

Visual images

Fig. 6. visual images of the highT ashes produced at different temperatures. Wood (W) was used as a reference material.

Beidaghy Dizaji et al., Fuel (2021) Under Revision.

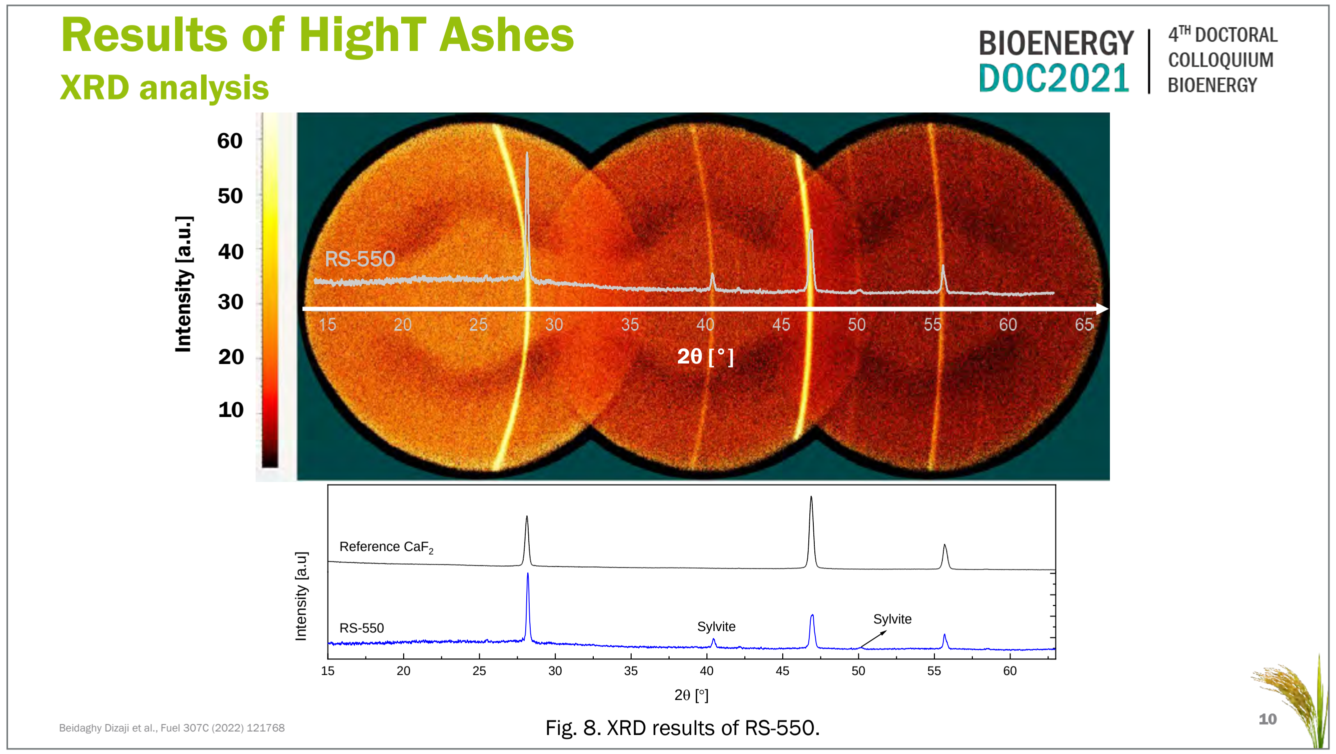


Results of HighT Ashes

TSF and DD

Fig. 7. Ash melting tendencies (i.e. TSF and DD) of highT ashes as a function of temperature.

Beidaghy Dizaji et al., Fuel (2021) Under Revision.



Results of HighT Ashes

XRD analysis

Beidaghy Dizaji et al., Fuel 307C (2022) 121768

Fig. 8. XRD results of RS-550.

Results of HighT Ashes

XRD analysis

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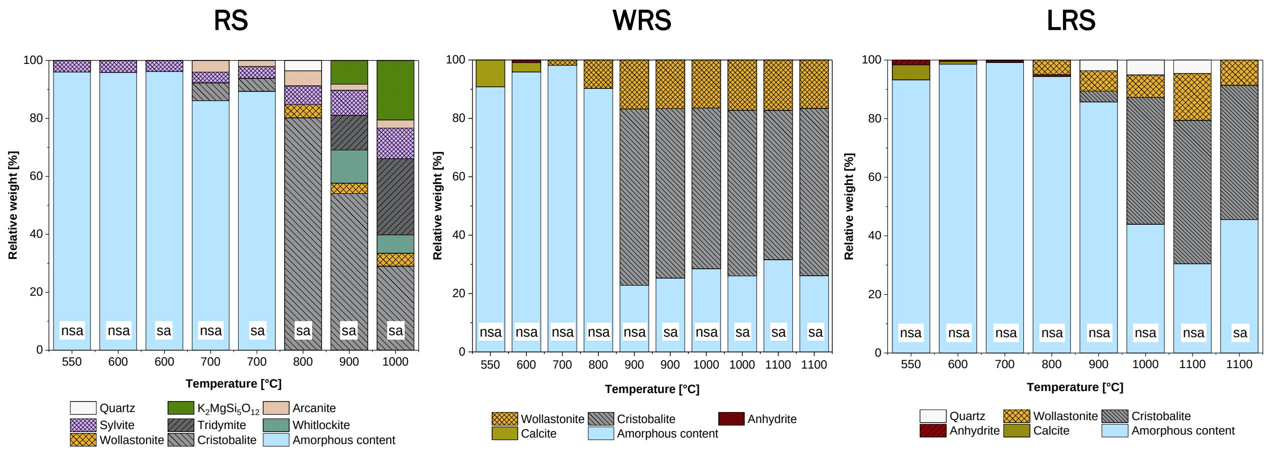

Fig. 9. Phase composition of RS (left) WRS (middle) and LRS (right) obtained from Rietveld refinement of XRD data. Slagged and non-slagged ashes are indicated as “sa” and “nsa, respectively.

Beidaghy Dizaji et al., Fuel 307C (2022) 121768

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Results of HighT Ashes

FactSage simulation

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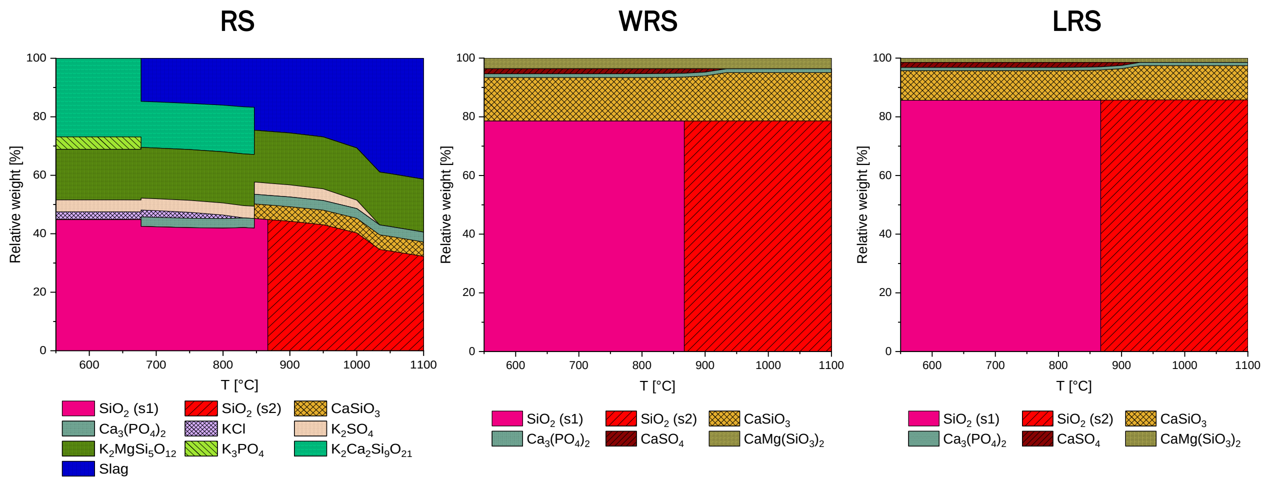

Fig. 10. Phase composition of RS (left) WRS (middle) and LRS (right) obtained from FactSage simulation.

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Results of HighT Ashes

Porosity evolution

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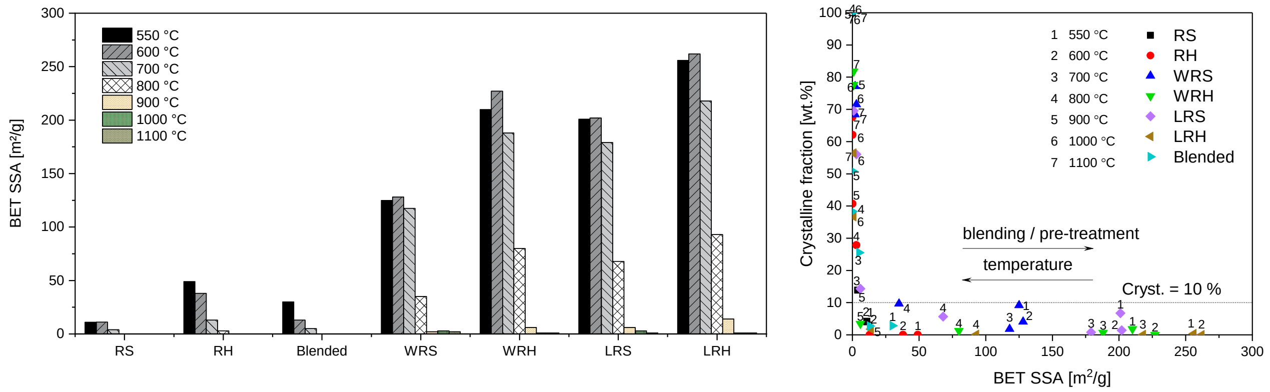

Fig. 11. BET specific surface area of the ashes (left) and crystallinity fraction as a function of BET SSA (right).

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Results of HighT Ashes

Viscosity changes

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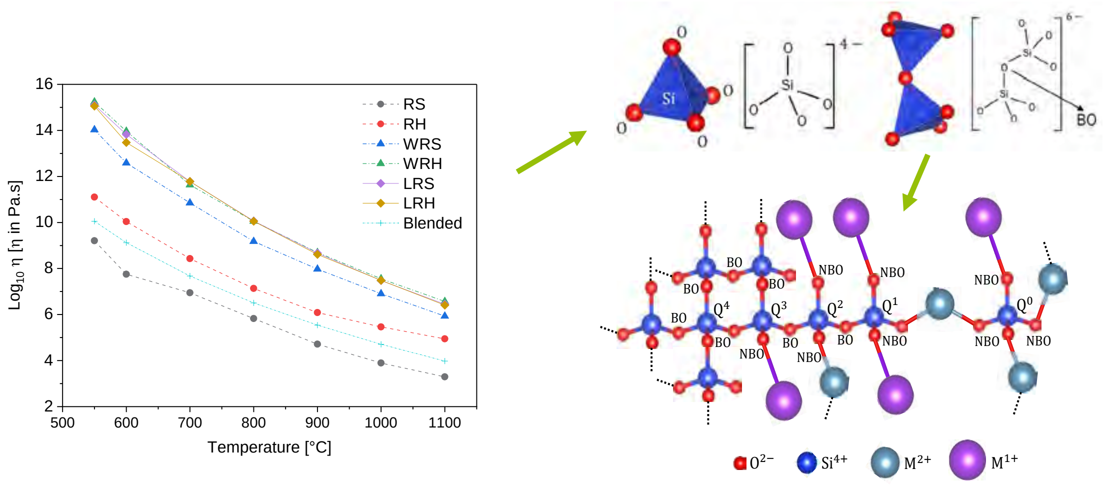

Fig. 12. viscosity of the ashes vs. temperature (left) and atomic structural model of silica-rich ashes (right).

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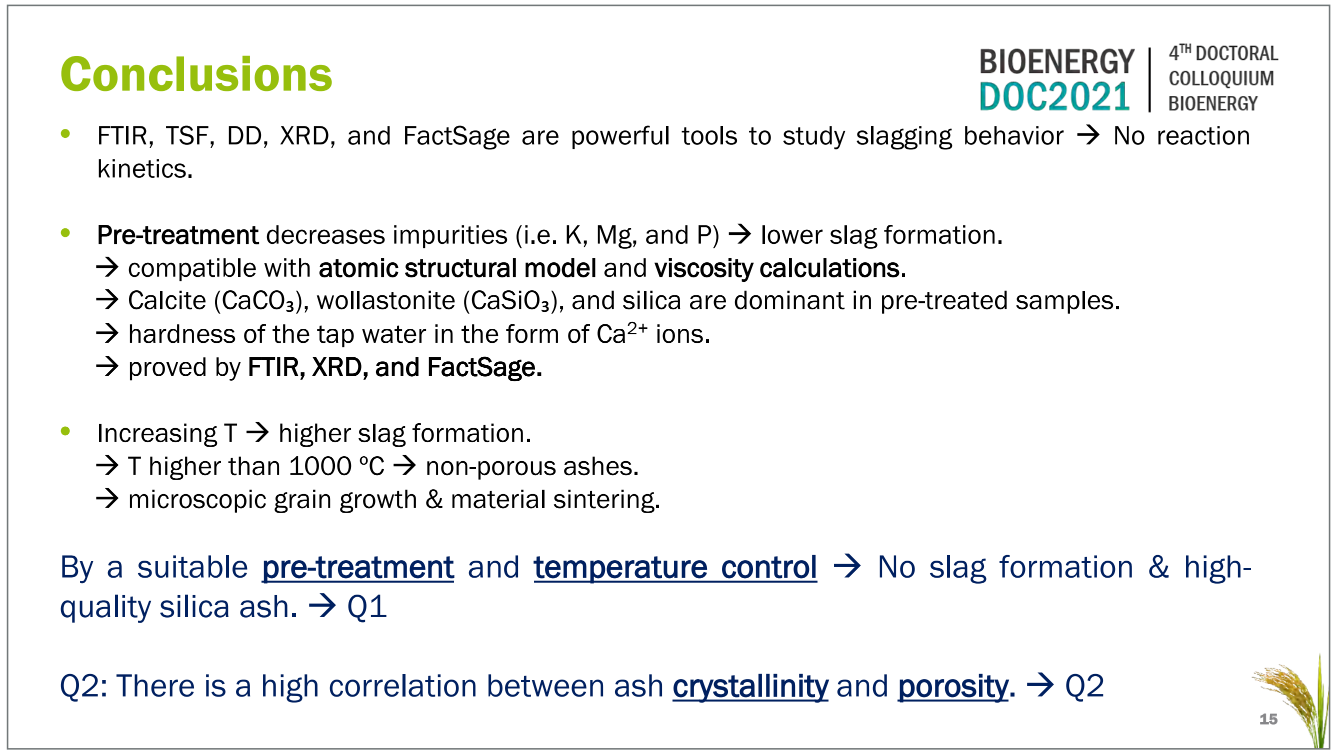

Conclusions

- FTIR, TSF, DD, XRD, and FactSage are powerful tools to study slagging behavior → No reaction kinetics.

- **Pre-treatment** decreases impurities (i.e. K, Mg, and P) → lower slag formation.
  → compatible with **atomic structural model** and **viscosity calculations.**
  → Calcite ($CaCO_3$), wollastonite ($CaSiO_3$), and silica are dominant in pre-treated samples.
  → hardness of the tap water in the form of Ca^{2+} ions.
  → proved by **FTIR, XRD, and FactSage.**

- Increasing T → higher slag formation.
  → T higher than 1000 °C → non-porous ashes.
  → microscopic grain growth & material sintering.

By a suitable pre-treatment and temperature control → No slag formation & high-quality silica ash. → Q1

Q2: There is a high correlation between ash crystallinity and porosity. → Q2

Thank you for your attention!

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https://www.pngkey.com/download/u2e6y3y3e6i1a9u2_rice-plant-transparent

ORAL PRESENTATIONS

SESSION II

BIOENERGY SYSTEM ANALYSIS

Sebastian Kolb, Friedrich-Alexander-University Erlangen/Nürnberg

Renewable Gases for the German Gas Market – A model-based Scenario Analysis

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Natural gas (NG) plays an essential role in Germany's heating and electricity sector. In light of rising concerns on upstream fugitive methane leakages during natural gas extraction, however, renewable substitutes for NG come to the fore. In this context, biomethane through the treatment of biogas, Substitute Natural Gas from thermo-chemical conversion, or Power-to-Methane and -Hydrogen offer the potential to defossilise the gas sector.

To promote the integration of those renewable gases in future energy systems, this contribution aims to analyse the effect of different market developments and funding strategies on the potential share of renewable gases in the German gas mix until 2050. For this purpose, we develop and implement the simulation-based optimisation model MIREG (Model for the Integration of Renewable Gases).
The simulation part of MIREG models each installed unit system dynamically, generating its values for productivity and prices based on volatile market conditions in hourly resolution. The optimisation steps model the market behaviour. This includes the optimisation of gas prices and storage operations under changing demand and supply structures. Additionally, it comprises the planning of the ideal yearly plant construction.

A scenario analysis applies MIREG to different market developments and funding strategies: The results imply that if renewable gases are to account for a significant share of gas consumed in the future, they need to be funded considerably or market conditions must change. The projected boundary conditions in the Business as Usual (BAU) do not lead to a noteworthy increase in renewable gas capacity. However, a stronger increase in CO_2 prices (up to 150 €/tCO_2 in 2050) than expected in the BAU can lead to 23 % of renewable gas in the 2050 gas mix (300 €/tCO_2 for 54 %). In contrast, investment subsidies as well as agricultural funding show little effect.

With MIREG it is possible to evaluate market developments under different boundary conditions. In particular, different governmental funding strategies may be compared regarding their costs and effectiveness in terms of their ability to promote renewable gases. This contribution will describe the technical approach of the model development and present simulation results of possible market developments under different governmental funding strategies.

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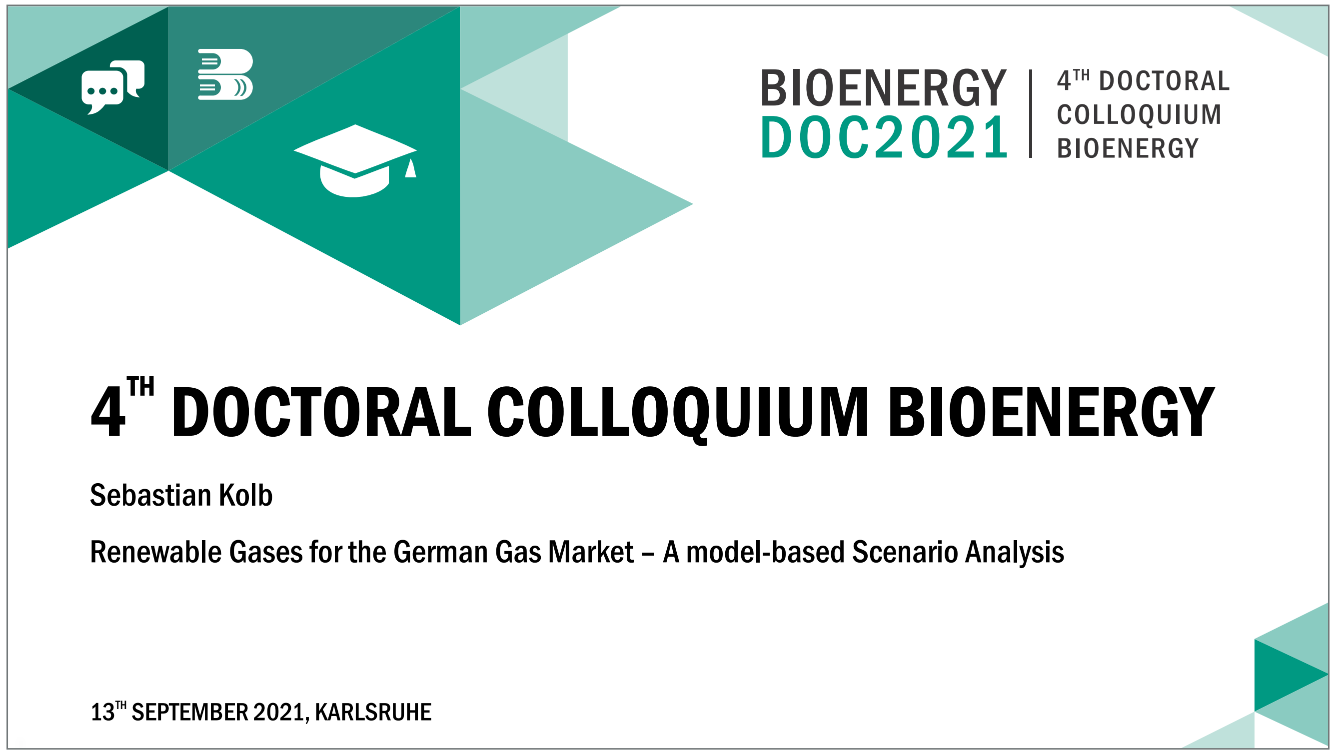
Kolb et al.: Scenario-based Analysis for the Integration of Renewable Gases into the German Gas Market. EUBCE 2019; p. 1863–8. doi:10.5071/27thEUBCE2019-5BV.3.32



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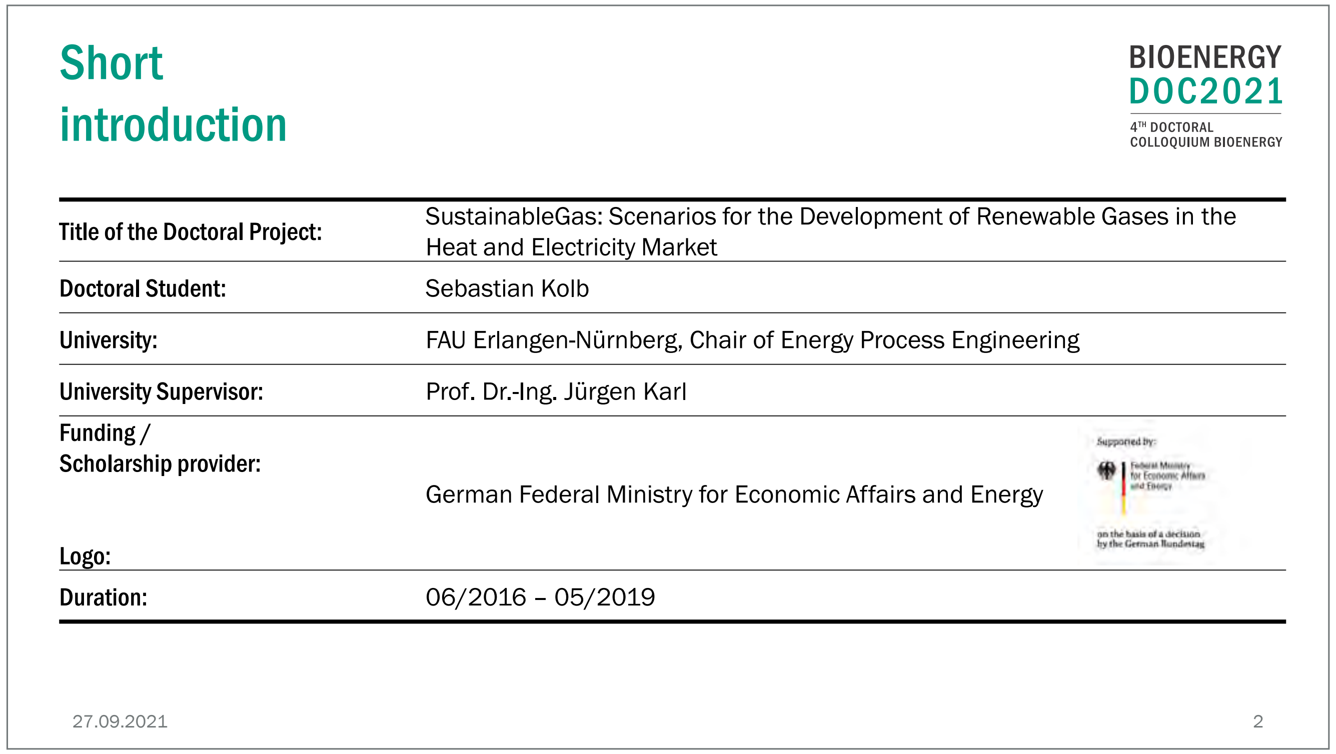
4TH DOCTORAL COLLOQUIUM BIOENERGY

Sebastian Kolb

Renewable Gases for the German Gas Market – A model-based Scenario Analysis

13TH SEPTEMBER 2021, KARLSRUHE



Short introduction

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Title of the Doctoral Project:	SustainableGas: Scenarios for the Development of Renewable Gases in the Heat and Electricity Market
Doctoral Student:	Sebastian Kolb
University:	FAU Erlangen-Nürnberg, Chair of Energy Process Engineering
University Supervisor:	Prof. Dr.-Ing. Jürgen Karl
Funding / Scholarship provider:	German Federal Ministry for Economic Affairs and Energy
Logo:	Supported by: Federal Ministry for Economic Affairs and Energy on the basis of a decision by the German Bundestag
Duration:	06/2016 – 05/2019

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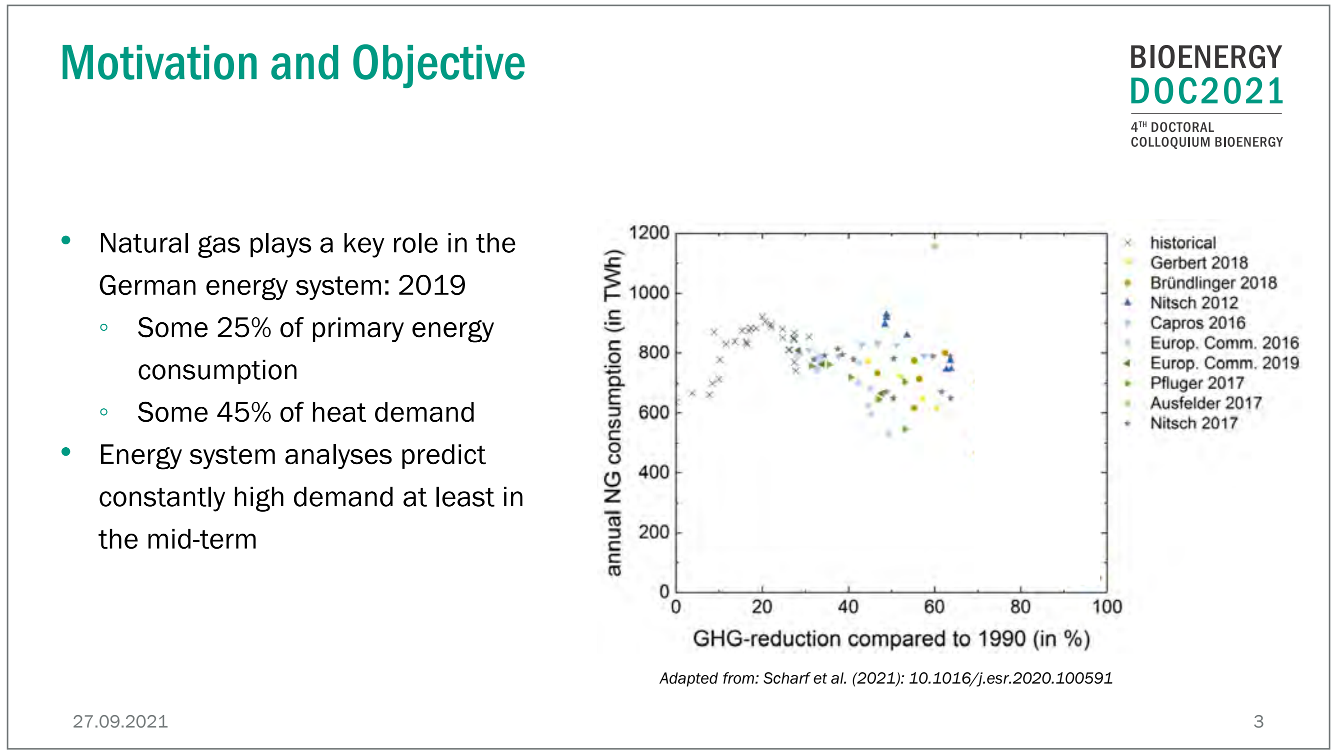

Motivation and Objective

- Natural gas plays a key role in the German energy system: 2019
  - Some 25% of primary energy consumption
  - Some 45% of heat demand
- Energy system analyses predict constantly high demand at least in the mid-term

Adapted from: Scharf et al. (2021): 10.1016/j.esr.2020.100591

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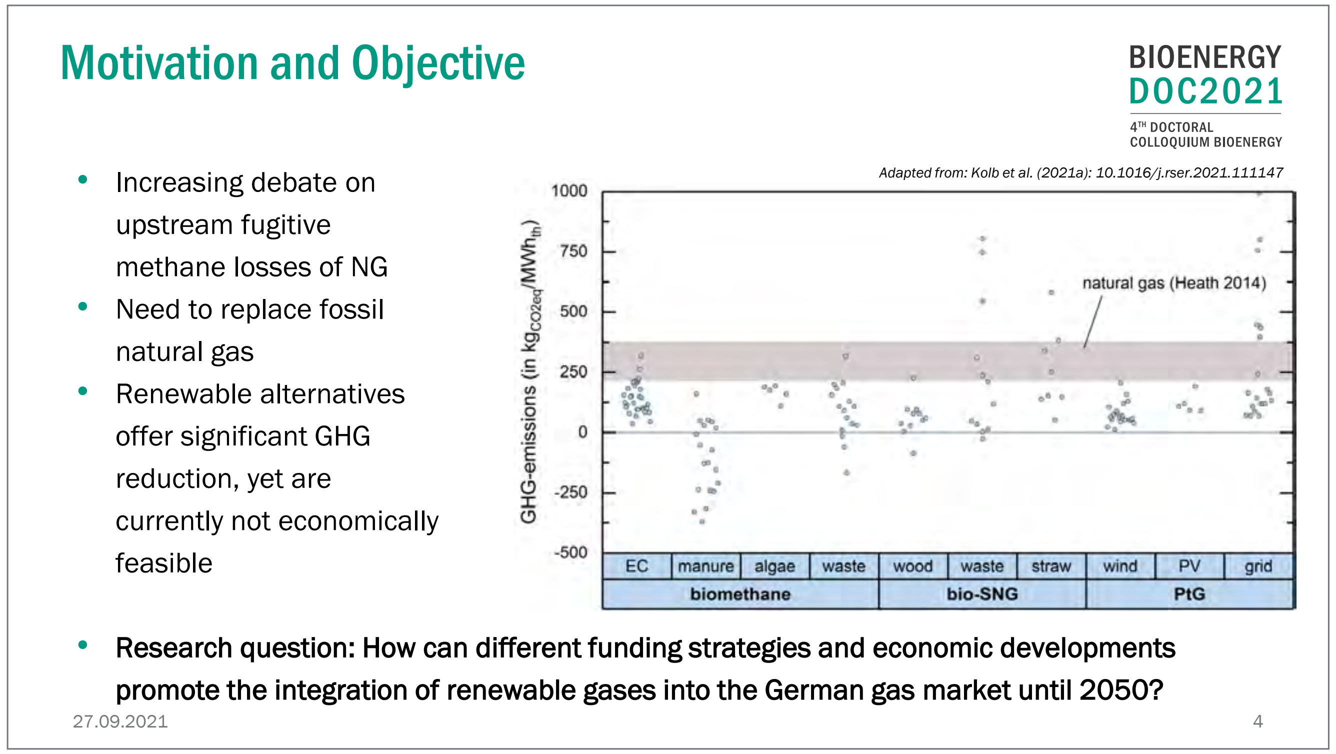

Motivation and Objective

Adapted from: Kolb et al. (2021a): 10.1016/j.rser.2021.111147

- Increasing debate on upstream fugitive methane losses of NG
- Need to replace fossil natural gas
- Renewable alternatives offer significant GHG reduction, yet are currently not economically feasible
- **Research question: How can different funding strategies and economic developments promote the integration of renewable gases into the German gas market until 2050?**

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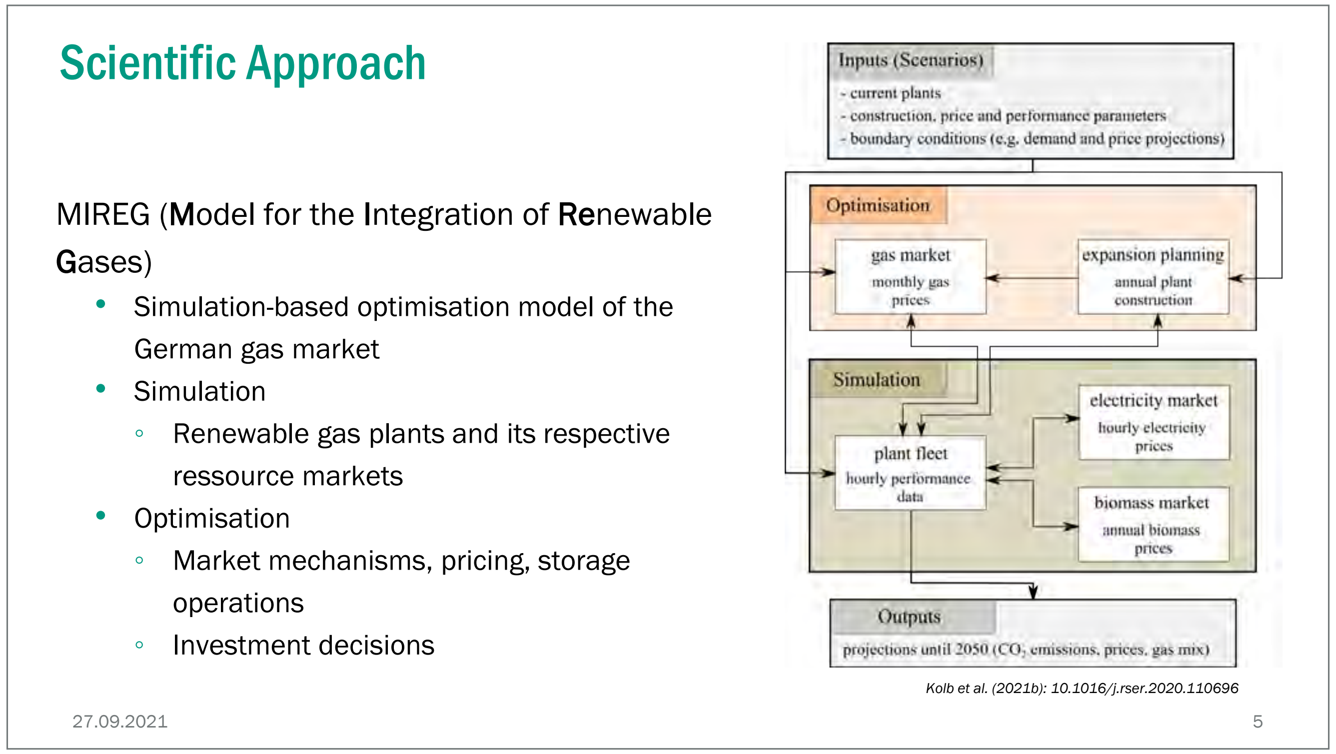

Scientific Approach

MIREG (**M**odel for the **I**ntegration of **Re**newable **G**ases)

- Simulation-based optimisation model of the German gas market
- Simulation
  - Renewable gas plants and its respective ressource markets
- Optimisation
  - Market mechanisms, pricing, storage operations
  - Investment decisions

Kolb et al. (2021b): 10.1016/j.rser.2020.110696

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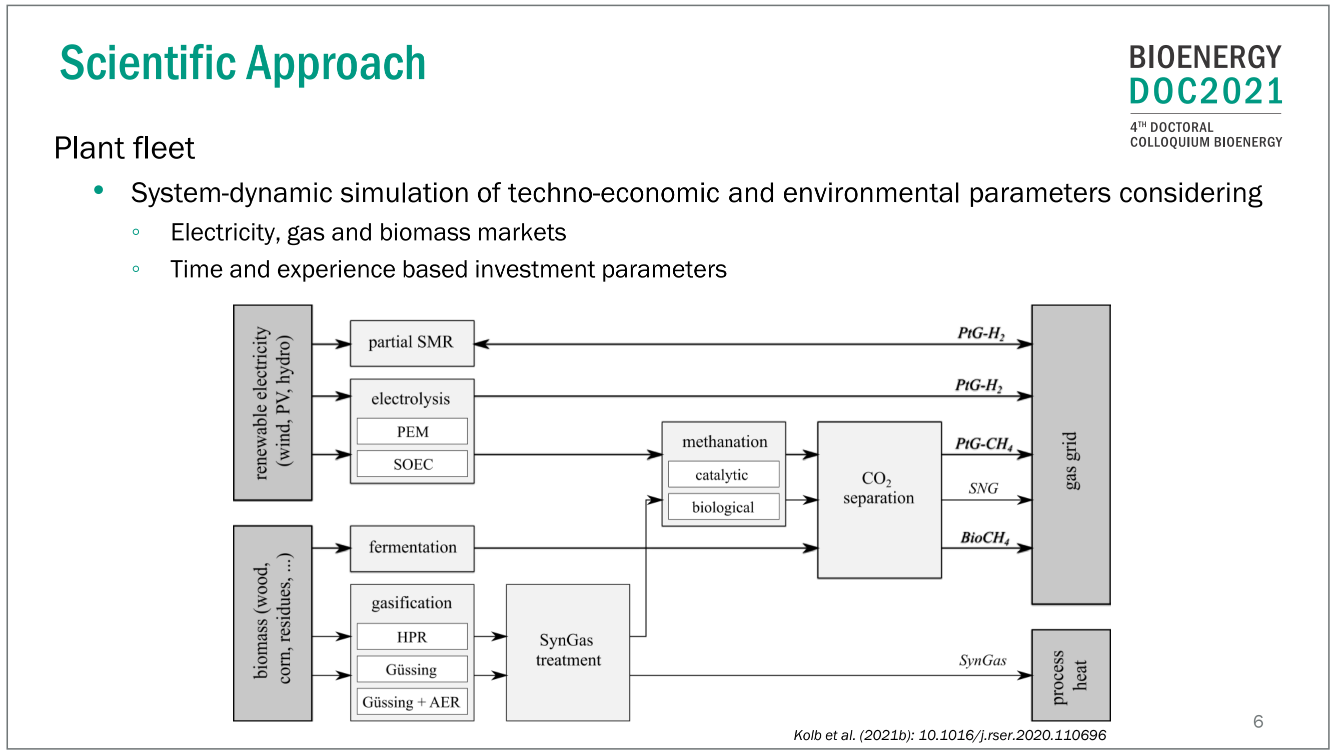

Scientific Approach

Plant fleet

- System-dynamic simulation of techno-economic and environmental parameters considering
  - Electricity, gas and biomass markets
  - Time and experience based investment parameters

Kolb et al. (2021b): 10.1016/j.rser.2020.110696

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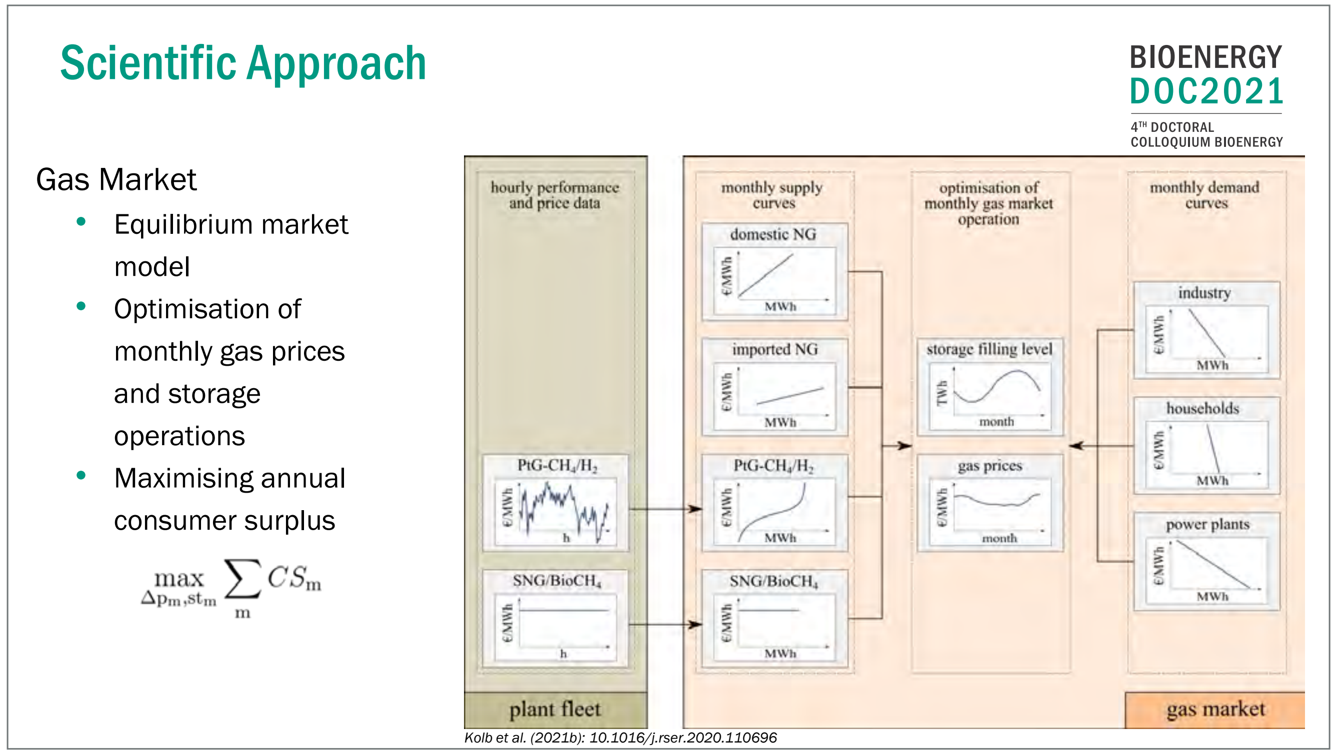

Scientific Approach

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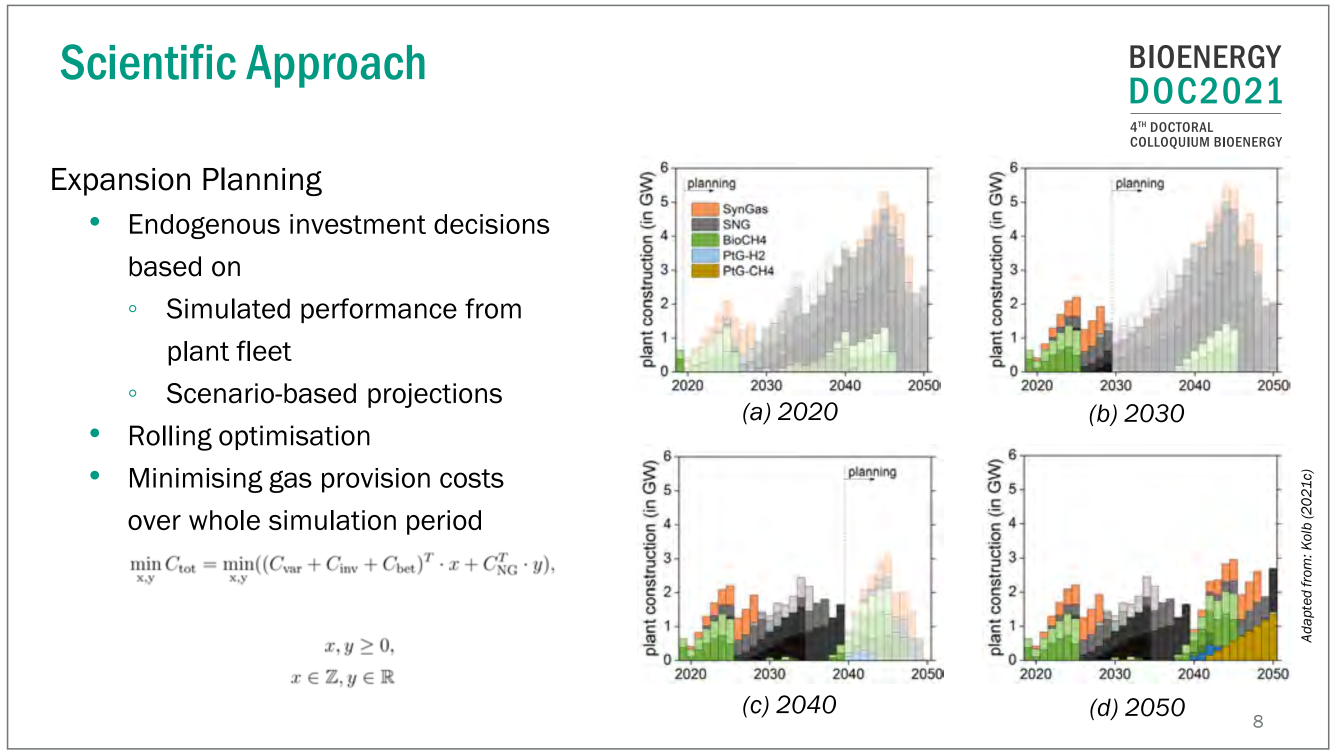
Gas Market

- Equilibrium market model
- Optimisation of monthly gas prices and storage operations
- Maximising annual consumer surplus

$$\max_{\Delta p_m, st_m} \sum_m CS_m$$

Kolb et al. (2021b): 10.1016/j.rser.2020.110696



Scientific Approach

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Expansion Planning

- Endogenous investment decisions based on
  - Simulated performance from plant fleet
  - Scenario-based projections
- Rolling optimisation
- Minimising gas provision costs over whole simulation period

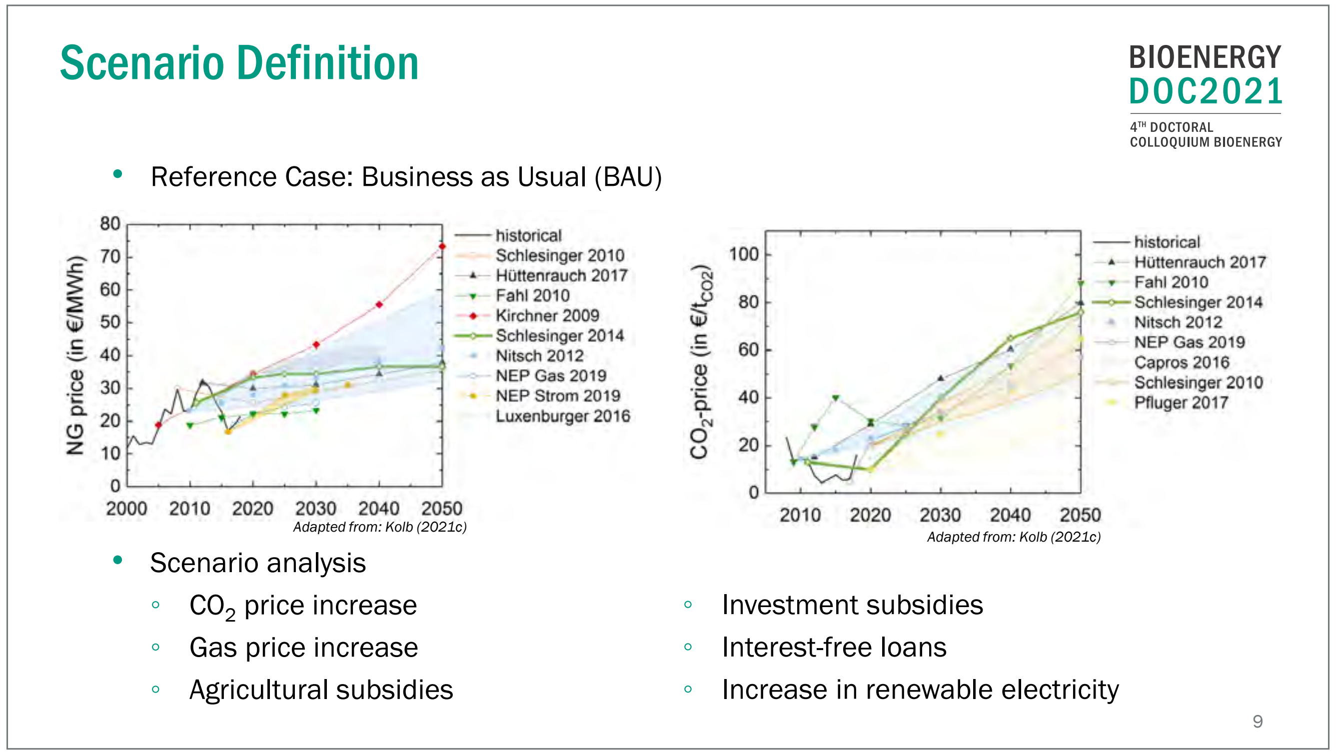
$$\min_{x,y} C_{\mathrm{tot}} = \min_{x,y}((C_{\mathrm{var}} + C_{\mathrm{inv}} + C_{\mathrm{bet}})^T \cdot x + C_{\mathrm{NG}}^T \cdot y),$$

$$x, y \geq 0,$$
$$x \in \mathbb{Z}, y \in \mathbb{R}$$

(a) 2020 (b) 2030

(c) 2040 (d) 2050

Adapted from: Kolb (2021c)



Scenario Definition

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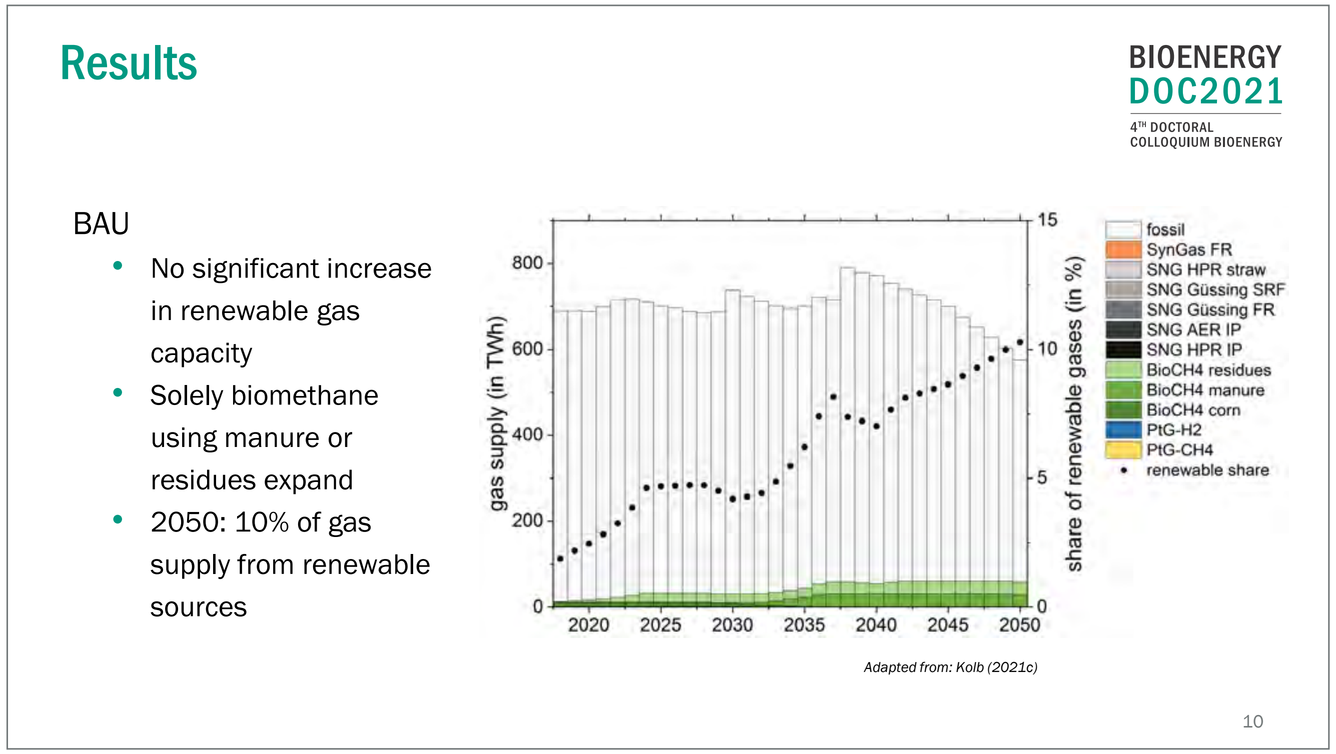
- Reference Case: Business as Usual (BAU)

Adapted from: Kolb (2021c)

Adapted from: Kolb (2021c)

- Scenario analysis
  - CO_2 price increase
  - Gas price increase
  - Agricultural subsidies
  - Investment subsidies
  - Interest-free loans
  - Increase in renewable electricity



Results

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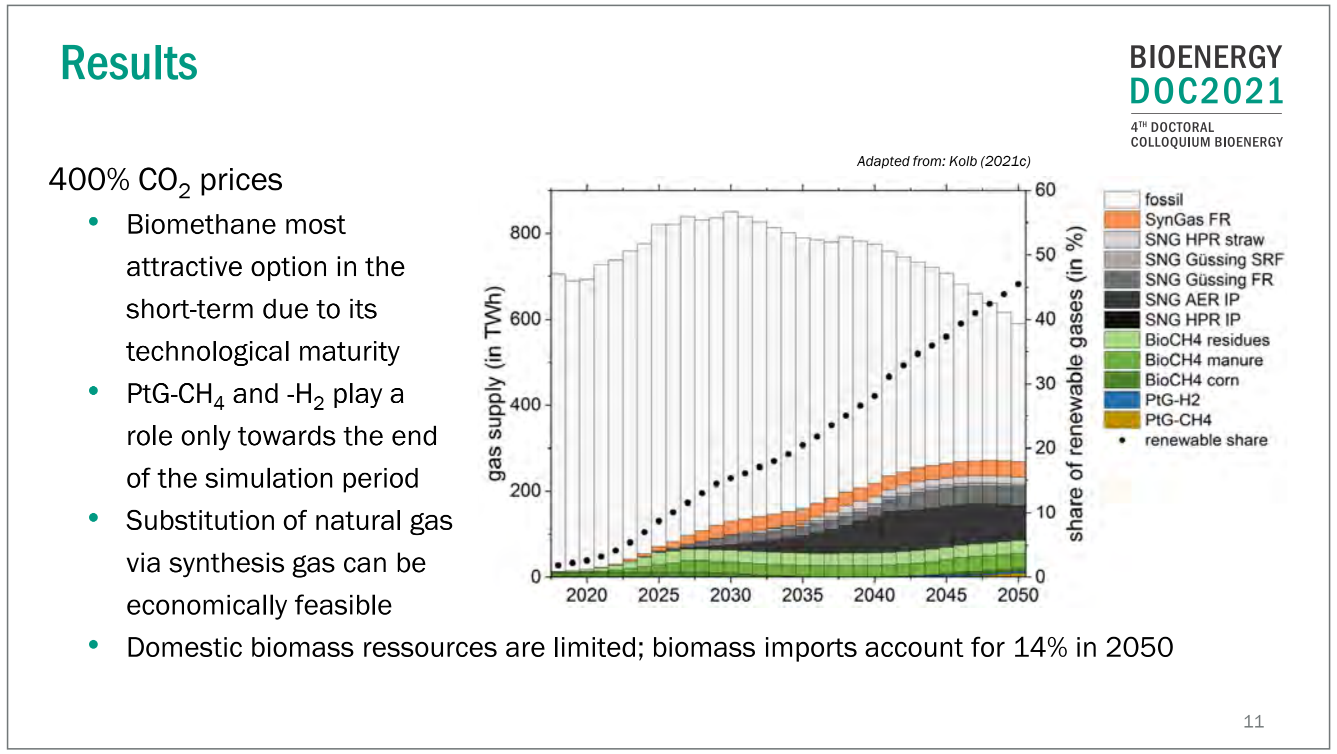
BAU

- No significant increase in renewable gas capacity
- Solely biomethane using manure or residues expand
- 2050: 10% of gas supply from renewable sources

Adapted from: Kolb (2021c)



Results

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400% CO_2 prices

- Biomethane most attractive option in the short-term due to its technological maturity
- PtG-CH_4 and -H_2 play a role only towards the end of the simulation period
- Substitution of natural gas via synthesis gas can be economically feasible
- Domestic biomass ressources are limited; biomass imports account for 14% in 2050

Adapted from: Kolb (2021c)

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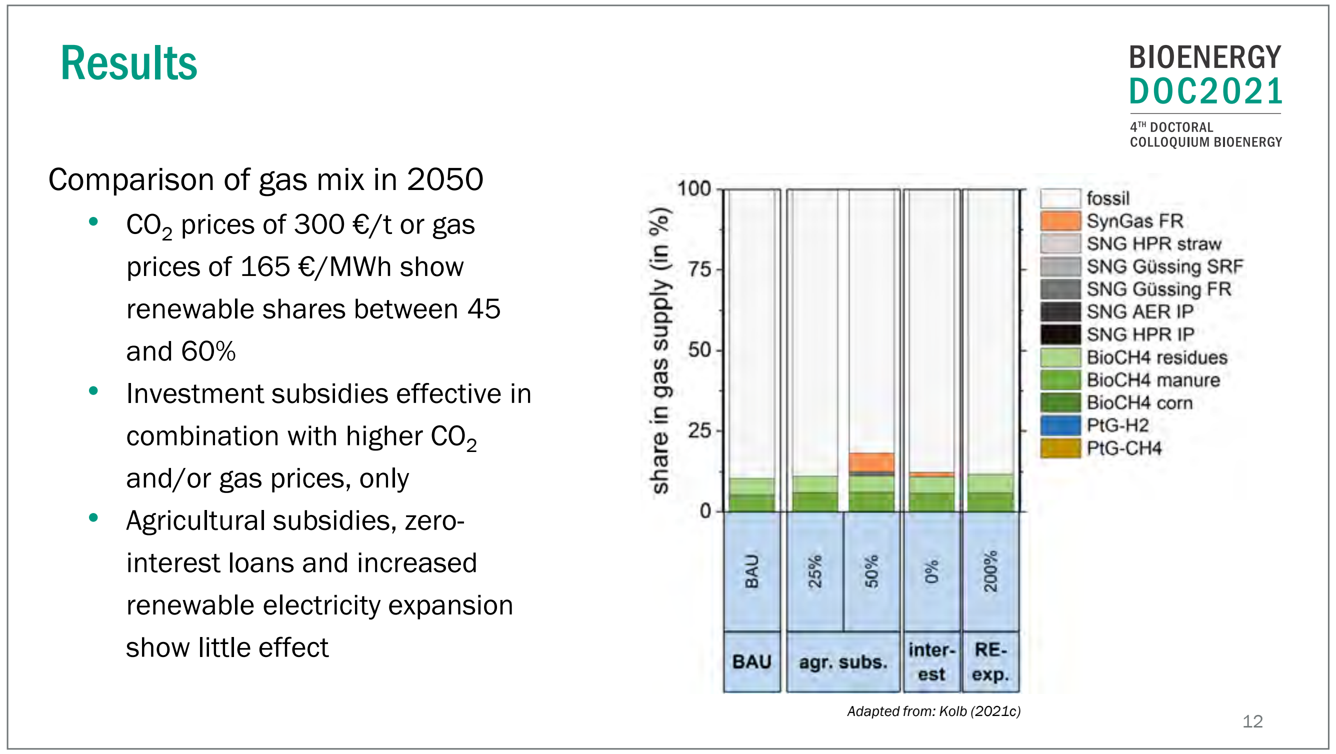

Results

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Comparison of gas mix in 2050

- CO_2 prices of 300 €/t or gas prices of 165 €/MWh show renewable shares between 45 and 60%
- Investment subsidies effective in combination with higher CO_2 and/or gas prices, only
- Agricultural subsidies, zero-interest loans and increased renewable electricity expansion show little effect

Adapted from: Kolb (2021c)

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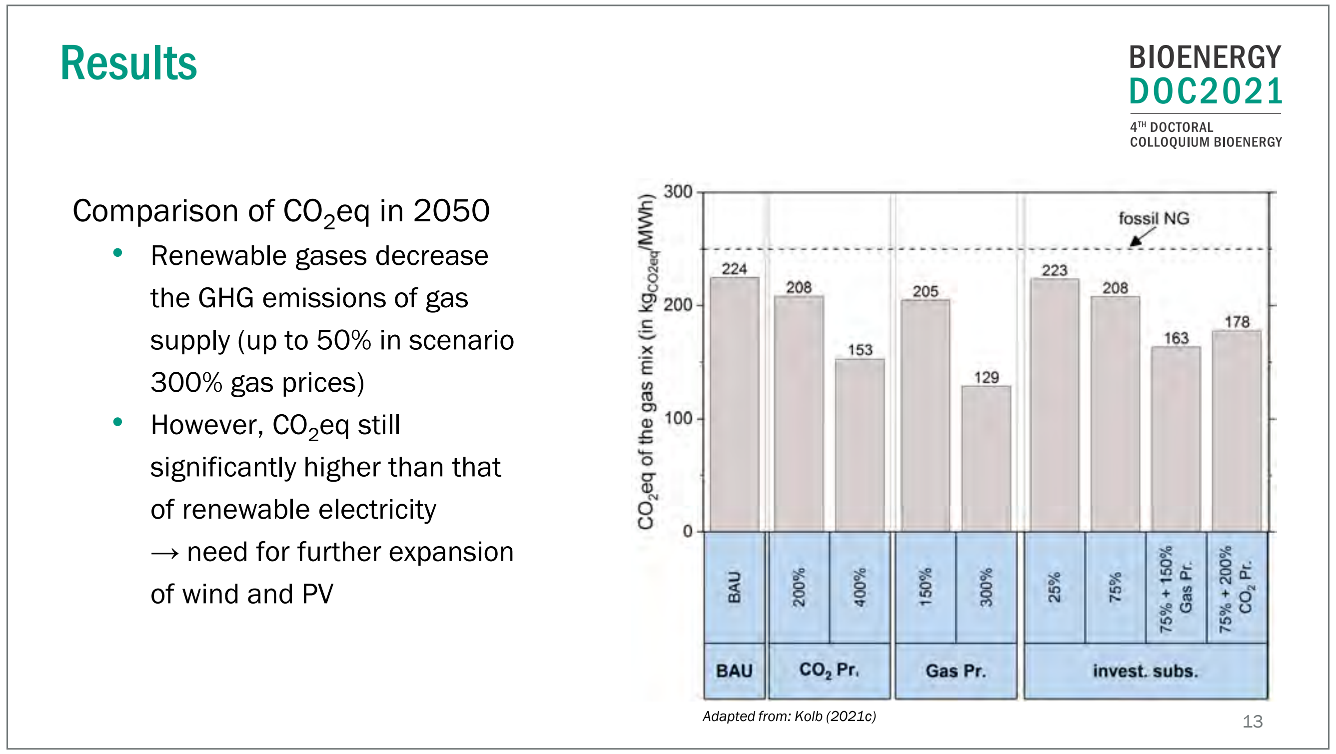

Results

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Comparison of CO_2eq in 2050

- Renewable gases decrease the GHG emissions of gas supply (up to 50% in scenario 300% gas prices)
- However, CO_2eq still significantly higher than that of renewable electricity
  → need for further expansion of wind and PV

Adapted from: Kolb (2021c)

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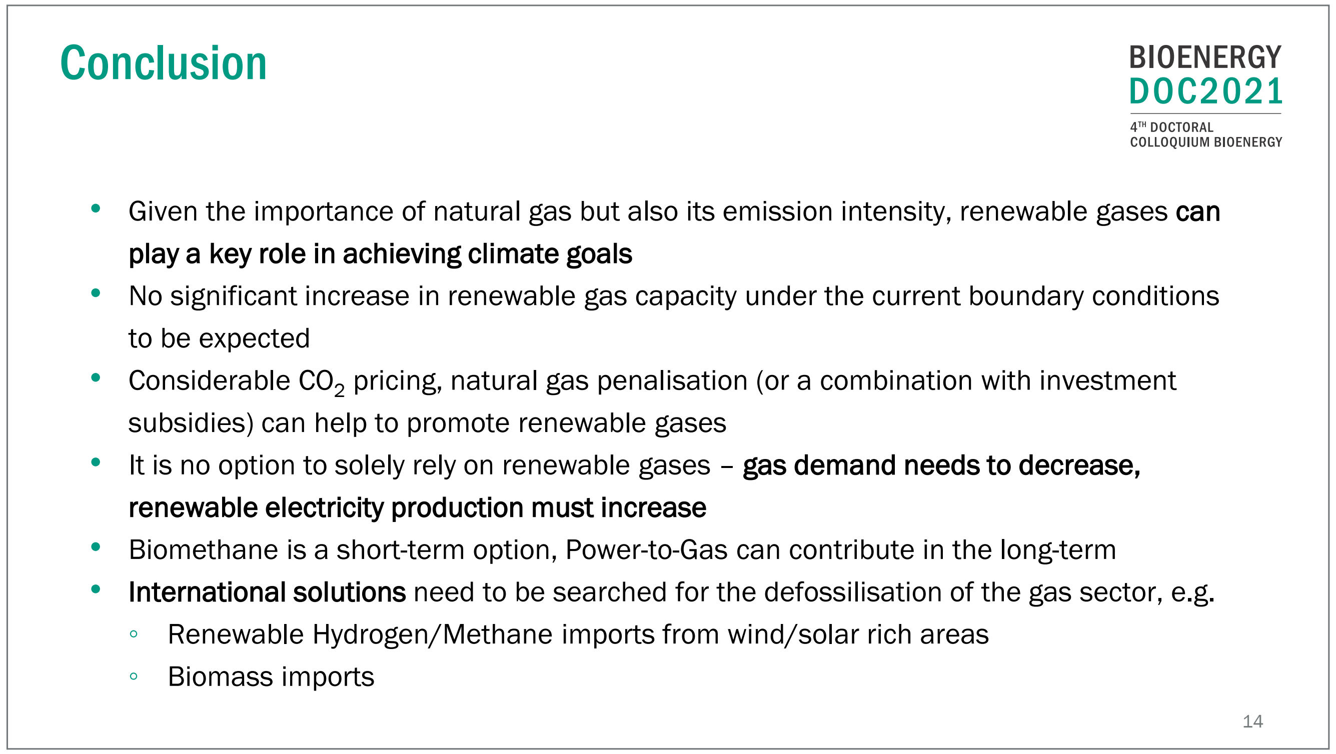

Conclusion

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- Given the importance of natural gas but also its emission intensity, renewable gases **can play a key role in achieving climate goals**
- No significant increase in renewable gas capacity under the current boundary conditions to be expected
- Considerable CO_2 pricing, natural gas penalisation (or a combination with investment subsidies) can help to promote renewable gases
- It is no option to solely rely on renewable gases – **gas demand needs to decrease, renewable electricity production must increase**
- Biomethane is a short-term option, Power-to-Gas can contribute in the long-term
- **International solutions** need to be searched for the defossilisation of the gas sector, e.g.
  - Renewable Hydrogen/Methane imports from wind/solar rich areas
  - Biomass imports

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References of Figures

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Keyu Bao, University of Leipzig/Stuttgart University of Applied Sciences (HTF)

Modelling and Assessment of Biomass Resource in Urban Energy Systems within the Framework of the Food-Energy-Water Nexus

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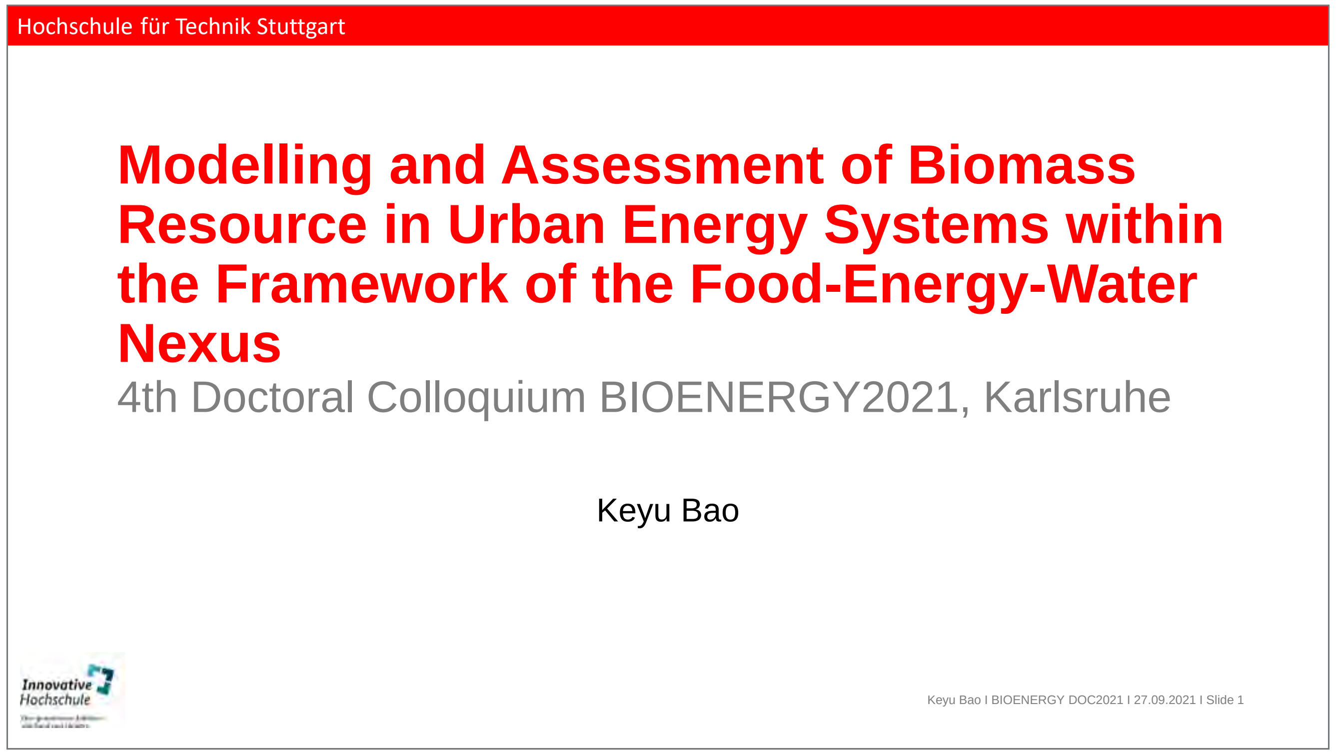
Biomass is can be used in various forms: it can be food, building material, energy carrier or key input to industries. Especially in and around urban areas, biomass can not only be derived from agricultural land or forests, but also from urban waste. Because of the limitations to local resources, i.e., land and water, and competition with other energy technologies, i.e., free land photovoltaic (PV), bioenergy should be modelled and assessed within the framework of the food-water-energy nexus. To the knowledge of the author, an assessment of biomass potentials along with other energetic potential and demand at regional level based on a consistent set of geographical input has not been performed yet. The research question of this work will be: What are the local biomass resource potentials, their dependency on other resources, mainly water, their conflicts with other usage, i.e., food, competition with other energetic technologies, i.e., wind and free land PV, and their contribution to renewable energy supply at the regional level?

In order to address this gap, work has been done to introduce a new workflow in SimStadt, the regional energy simulation platform developed at HFT Stuttgart. It evaluates the local biomass potential and irrigation demand on arable and forestry lands, and its transformation to different forms of secondary energy, i.e., solid fuels, biogas, or bioethanol, based on geographical inputs. Based on the intermediate results of the above-mentioned biomass workflow, vegetal and animal caloric food potentials of each land use fields are simulated.

Since urban areas are the main consumers of resources, urban food and water demand workflows were developed in SimStadt in relation to socio-economic factors, i.e., income, age, human development index and etc. While biomass in urban areas might not provide substantial amounts of bioenergy to local consumers, the example of green roof with PV modules is used to assess exemplarily the energetic impact and economic feasibility of urban biomass on the roof PV yield and heating demand, which are simulated by existing and well-validated workflows in SimStadt, using the same geoinformatics input data. The methods mentioned above are currently applied to two case studies and will be presented in two papers: (1) The island La Réunion is an ideal case study to assess bioenergy potentials in an isolated setting with tropic climate. Waste energy potentials are assessed in parallel to investigate whether energy autonomy can be achieved. Scenarios are tested to optimize electricity or fuel supply based on locally available resources. (2) Another case study is set in three German counties (Ludwigsburg, BW; Ilmkreis, TH; Dithmarschen, SH) to optimize the different uses of land and facilities, i.e., bioenergy from arable land, free land PV, wind power, food from arable land and green roofs, to best meet the energy and food demand considering the constrains of water resources and policies.



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Modelling and Assessment of Biomass Resource in Urban Energy Systems within the Framework of the Food-Energy-Water Nexus

4th Doctoral Colloquium BIOENERGY2021, Karlsruhe

Keyu Bao

Innovative Hochschule

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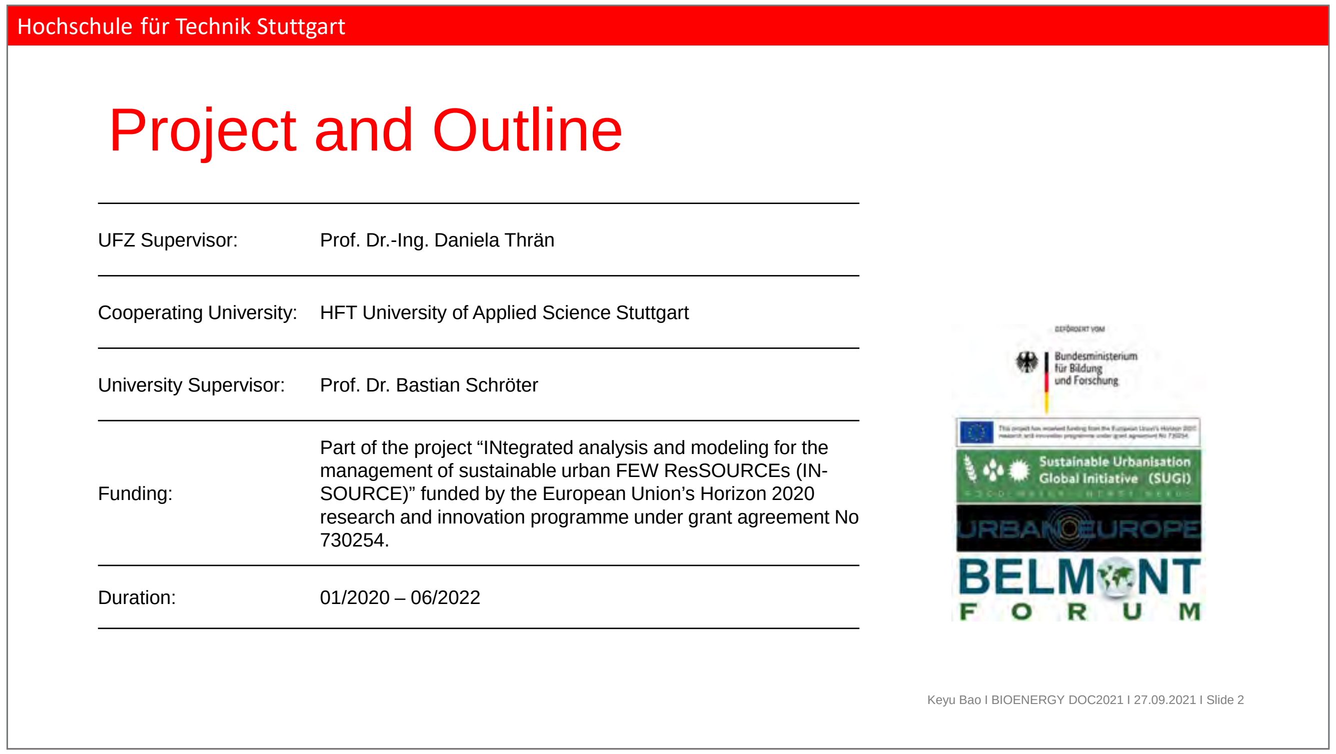

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Project and Outline

UFZ Supervisor:	Prof. Dr.-Ing. Daniela Thrän
Cooperating University:	HFT University of Applied Science Stuttgart
University Supervisor:	Prof. Dr. Bastian Schröter
Funding:	Part of the project "INtegrated analysis and modeling for the management of sustainable urban FEW ResSOURCEs (INSOURCE)" funded by the European Union's Horizon 2020 research and innovation programme under grant agreement No 730254.
Duration:	01/2020 – 06/2022

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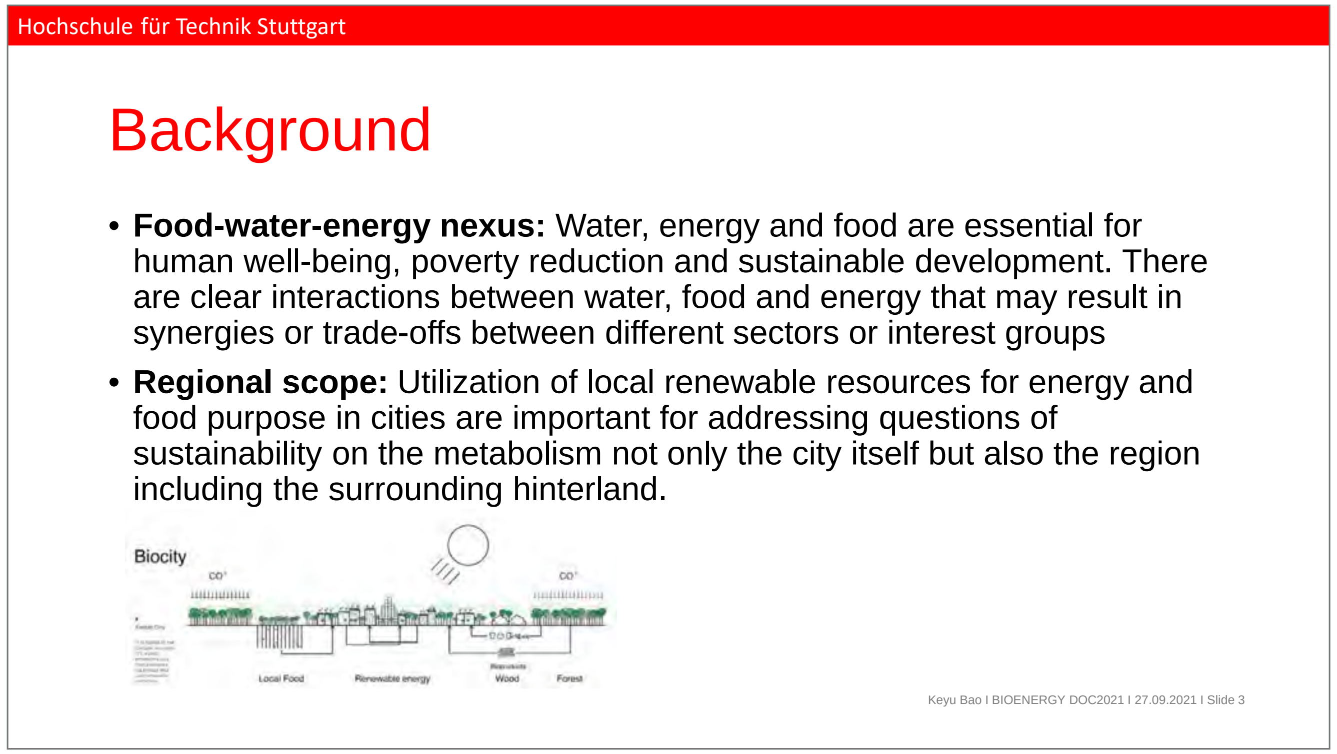

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Background

- **Food-water-energy nexus:** Water, energy and food are essential for human well-being, poverty reduction and sustainable development. There are clear interactions between water, food and energy that may result in synergies or trade-offs between different sectors or interest groups
- **Regional scope:** Utilization of local renewable resources for energy and food purpose in cities are important for addressing questions of sustainability on the metabolism not only the city itself but also the region including the surrounding hinterland.

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Research Gap

- **One comprehensive tool.** There are no standalone methods and tools for practicing and implementing the nexus approach, but rather combining multiple methods and tools.
- **Scalability and transferability.** Methods and tools can be replicated and/or adjusted at different sites and scales and/or new methods/tools can be constructed as specific case studies.
- **Single unified robust input**. Utilization of robust datasets from multiple sources is still lacking.
- **Trade-off between resources.** a focus on FWE resource security, i.e., availability, accessibility, quality of resources, was proposed. This can be addressed by interlinkages matrices as a tool to identify clear nexus synergies and tradeoffs in terms of the sustainability of the ecosystem and human system at different scales.

The goal of the dessertation
Develop a comprehensive tool and method to fill the above-mentioned gaps, especailly addressing the trade-off/synergy issues involving biomass in regional energy systems.

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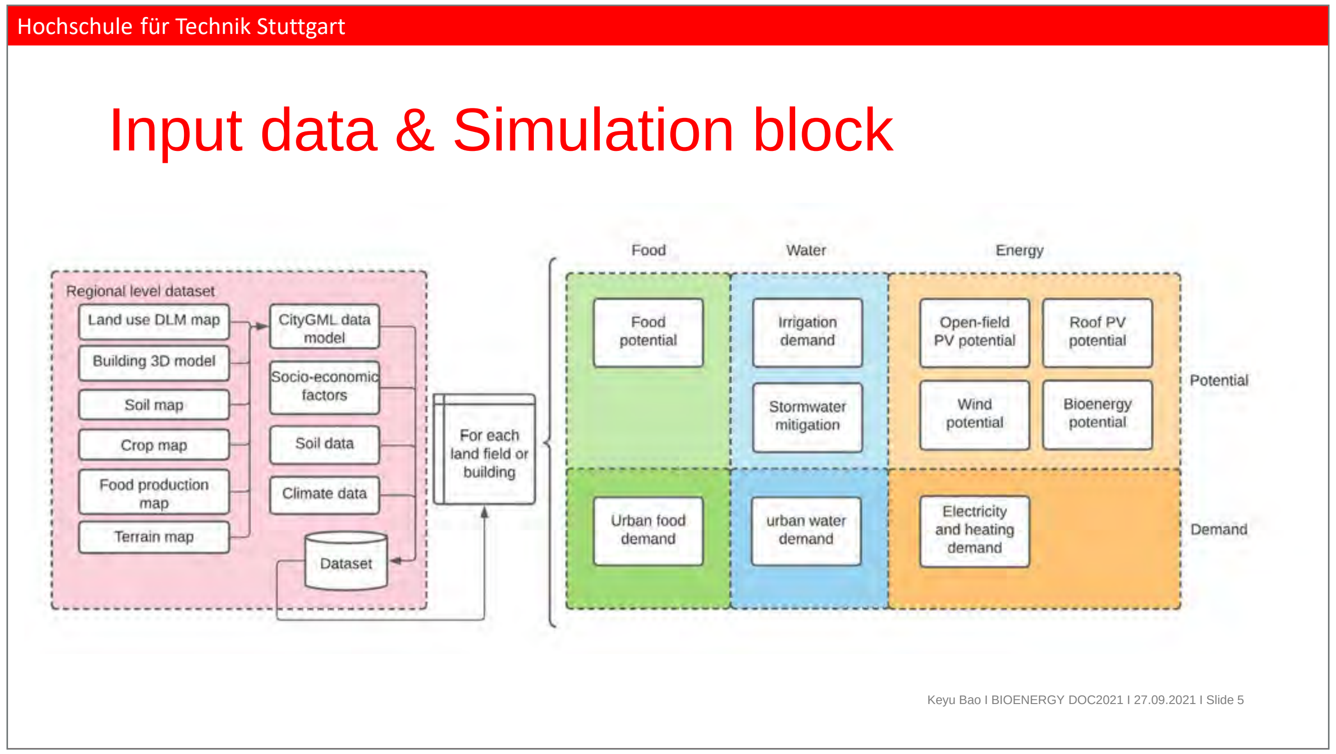

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Input data & Simulation block

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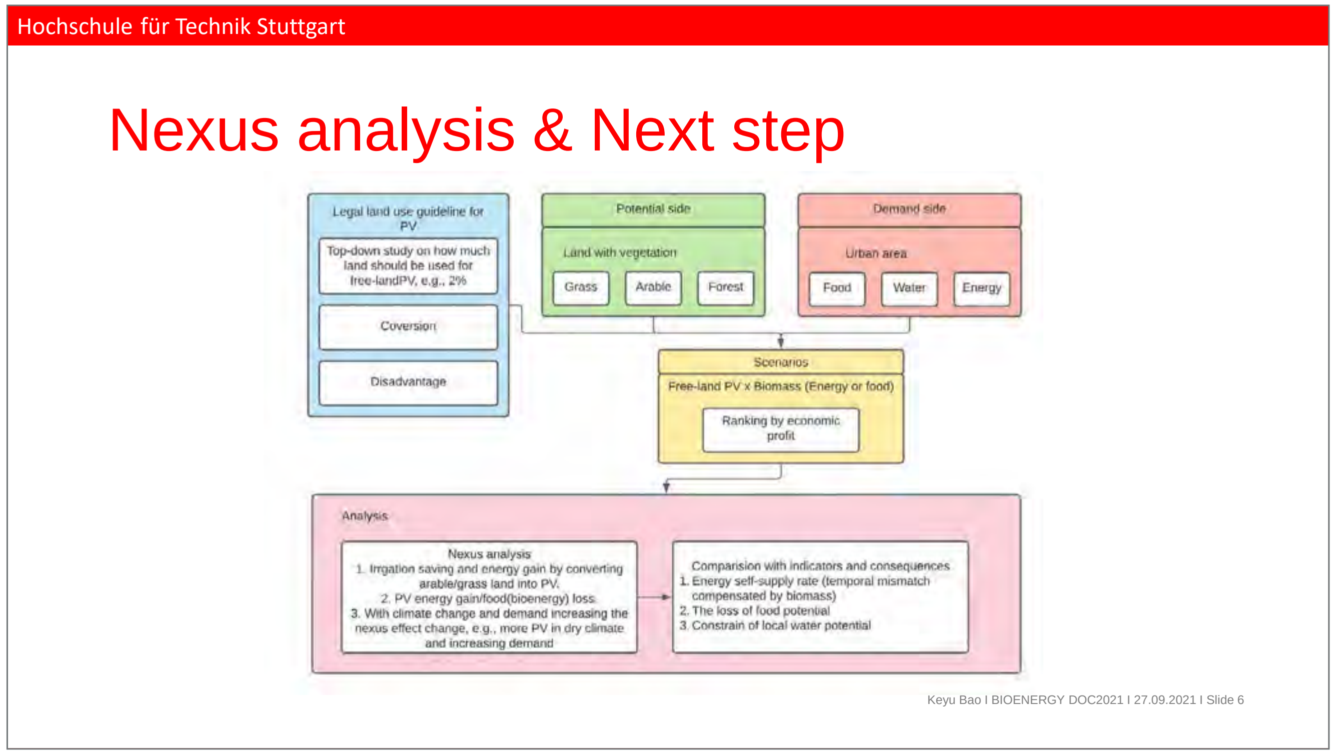

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Nexus analysis & Next step

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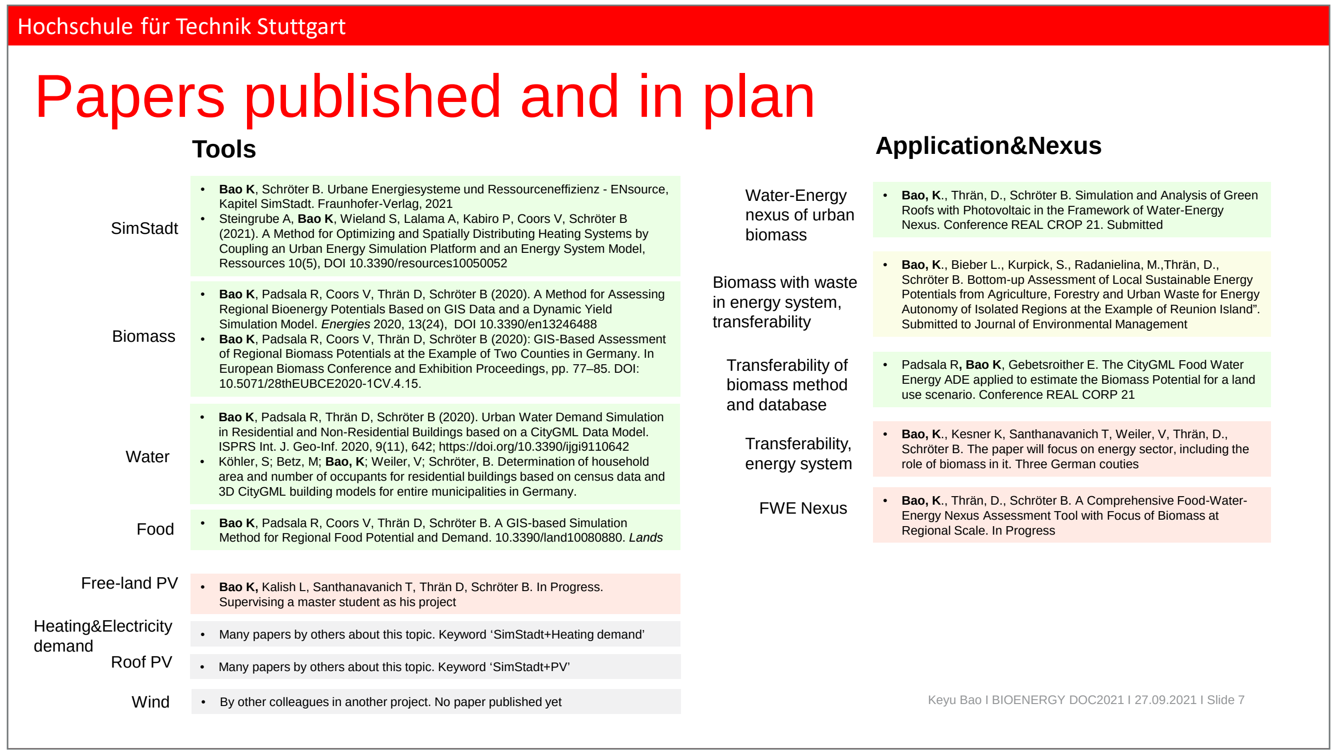

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Papers published and in plan

Tools

SimStadt	**Bao K**, Schröter B. Urbane Energiesysteme und Ressourceneffizienz - ENsource, Kapitel SimStadt. Fraunhofer-Verlag, 2021 Steingrube A, **Bao K**, Wieland S, Lalama A, Kabiro P, Coors V, Schröter B (2021). A Method for Optimizing and Spatially Distributing Heating Systems by Coupling an Urban Energy Simulation Platform and an Energy System Model, Ressources 10(5), DOI 10.3390/resources10050052
Biomass	**Bao K**, Padsala R, Coors V, Thrän D, Schröter B (2020). A Method for Assessing Regional Bioenergy Potentials Based on GIS Data and a Dynamic Yield Simulation Model. *Energies* 2020, 13(24), DOI 10.3390/en13246488 **Bao K**, Padsala R, Coors V, Thrän D, Schröter B (2020): GIS-Based Assessment of Regional Biomass Potentials at the Example of Two Counties in Germany. In European Biomass Conference and Exhibition Proceedings, pp. 77–85. DOI: 10.5071/28thEUBCE2020-1CV.4.15.
Water	**Bao K**, Padsala R, Thrän D, Schröter B (2020). Urban Water Demand Simulation in Residential and Non-Residential Buildings based on a CityGML Data Model. ISPRS Int. J. Geo-Inf. 2020, 9(11), 642; https://doi.org/10.3390/ijgi9110642 Köhler, S; Betz, M; **Bao, K**; Weiler, V; Schröter, B. Determination of household area and number of occupants for residential buildings based on census data and 3D CityGML building models for entire municipalities in Germany.
Food	**Bao K**, Padsala R, Coors V, Thrän D, Schröter B. A GIS-based Simulation Method for Regional Food Potential and Demand. 10.3390/land10080880. *Lands*
Free-land PV	**Bao K,** Kalish L, Santhanavanich T, Thrän D, Schröter B. In Progress. Supervising a master student as his project
Heating&Electricity demand	Many papers by others about this topic. Keyword ‘SimStadt+Heating demand’
Roof PV	Many papers by others about this topic. Keyword ‘SimStadt+PV’
Wind	By other colleagues in another project. No paper published yet

Application&Nexus

Water-Energy nexus of urban biomass	**Bao, K.**, Thrän, D., Schröter B. Simulation and Analysis of Green Roofs with Photovoltaic in the Framework of Water-Energy Nexus. Conference REAL CROP 21. Submitted
Biomass with waste in energy system, transferability	**Bao, K.**, Bieber L., Kurpick, S., Radanielina, M.,Thrän, D., Schröter B. Bottom-up Assessment of Local Sustainable Energy Potentials from Agriculture, Forestry and Urban Waste for Energy Autonomy of Isolated Regions at the Example of Reunion Island”. Submitted to Journal of Environmental Management
Transferability of biomass method and database	Padsala R**, Bao K**, Gebetsroither E. The CityGML Food Water Energy ADE applied to estimate the Biomass Potential for a land use scenario. Conference REAL CORP 21
Transferability, energy system	**Bao, K.**, Kesner K, Santhanavanich T, Weiler, V, Thrän, D., Schröter B. The paper will focus on energy sector, including the role of biomass in it. Three German couties
FWE Nexus	**Bao, K.**, Thrän, D., Schröter B. A Comprehensive Food-Water-Energy Nexus Assessment Tool with Focus of Biomass at Regional Scale. In Progress

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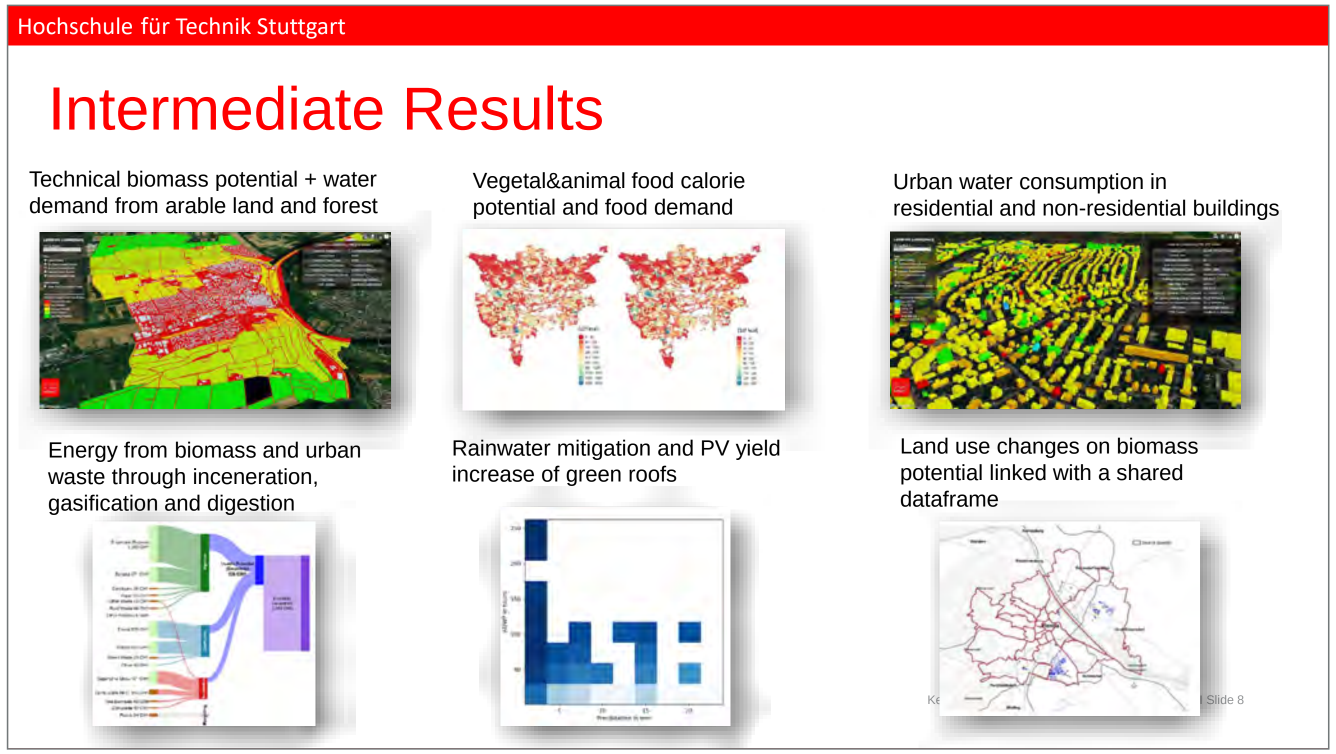

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Intermediate Results

Technical biomass potential + water demand from arable land and forest

Vegetal&animal food calorie potential and food demand

Urban water consumption in residential and non-residential buildings

Energy from biomass and urban waste through inceneration, gasification and digestion

Rainwater mitigation and PV yield increase of green roofs

Land use changes on biomass potential linked with a shared dataframe

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Thank you for your attention

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Piradee Jusakulvijit, Helmholtz Center for Environmental Research - UFZ/University of Leipzig

Integrated assessment of a potential decentralized bioethanol production system from agricultural residues in Thailand

Piradee Jusakulvijit, Alberto Bezama, Daniela Thrän
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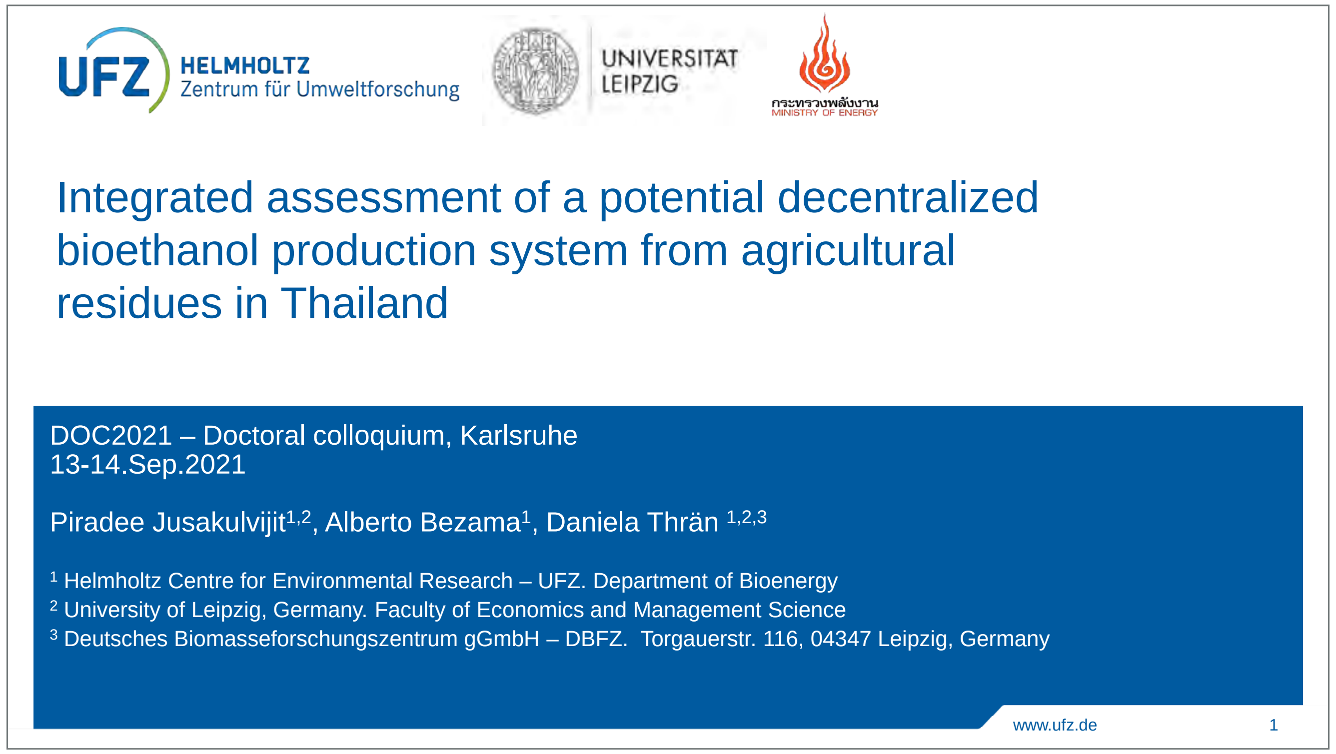
The current implementation of a centralized bioethanol production system from sugarcanes and cassavas in Thailand is prone to entail environmental impacts, such as land use expansion for massive feedstocks production. Concerning sustainable development, the study aims to verify the potential of decentralized ethanol production from regional agricultural residues with integrated assessment approaches. Previous steps of the PhD work focused on the determination of the regionalized biomass availability of major crops derived residues from sugarcanes, cassavas, rice, and palms. In these previous studies it was able to establish their distribution and potential for ethanol conversion.

As a further exploration, biomass allocation at 1x1 km^2 grid resolutions was identified through GIS-based spatial analysis on a whole area of Thailand. Biomass allocation was the key parameter in the supply chain analysis for biomass transportation from sources to production facilities. In this study, a comparative analysis was carried out on the alternatives of centralized and decentralized systems as scenarios. For the centralized system, collectable agricultural residues in different catchment areas were analyzed corresponding to the current operational units. Meanwhile, in decentralized system design, the suitability analysis on ArcGIS was conducted in order to indicate the candidate locations and suitable sizes for plant installation. The site-selection screening process was performed based on biomass statistical data and geographical factors, comprising the hotspots of biomass allocation, land use types, land elevation, and road networks. The decision on plant location, however, was carried out in a participatory manner. Due to the association of crossing dimensional datasets, multi-criteria prioritization obtained from the Delphi-AHP (Analytical Hierarchy Process method) finally determined the suitable location.

As a result of the expert participation events, it was highlighted the importance of economic feasibility from the main-criteria, while the highest-ranked criterion was the 'Final price per liter of ethanol'. This has become a crucial factor in exploring the optimal decentralized system, emphasizing to minimize the logistics cost while maximizing the residues utilization. For the interim results from the on-going process, the northeastern region could identify the candidate location for decentralized bioethanol facility in addition to the existing operational plants, proving competitiveness of bioethanol projection.

Following steps of the work are associated with the optimization of a number of small-scale production plants, feedstocks input, and plant capacities, which are expected to demonstrate the relative effects on the final price per liter of ethanol and energy balance in the bioethanol supply chain. Lastly, the candidate sites are planned to be compared with the existing facilities in terms of economic viability and technical feasibility.



Integrated assessment of a potential decentralized bioethanol production system from agricultural residues in Thailand

DOC2021 – Doctoral colloquium, Karlsruhe
13-14.Sep.2021

Piradee Jusakulvijit[1,2], Alberto Bezama[1], Daniela Thrän [1,2,3]

[1] Helmholtz Centre for Environmental Research – UFZ. Department of Bioenergy
[2] University of Leipzig, Germany. Faculty of Economics and Management Science
[3] Deutsches Biomasseforschungszentrum gGmbH – DBFZ. Torgauerstr. 116, 04347 Leipzig, Germany

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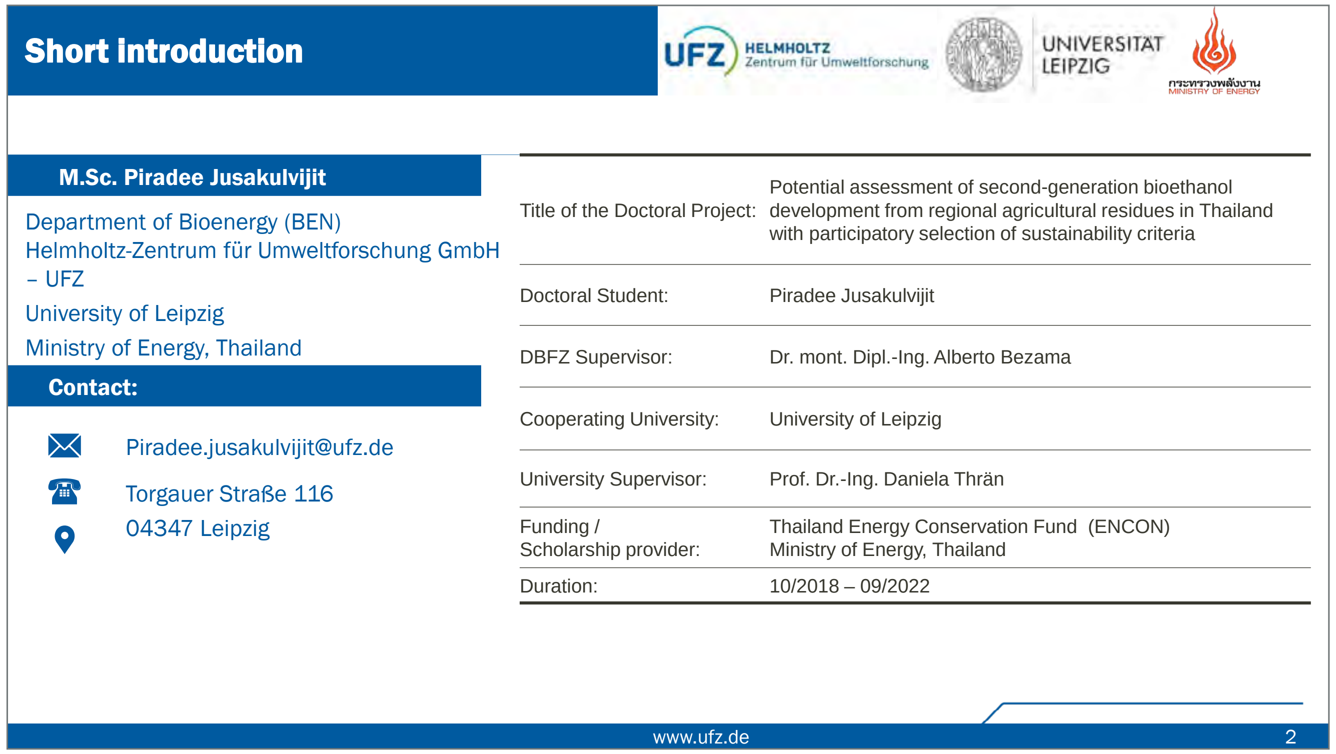

Short introduction

M.Sc. Piradee Jusakulvijit

Department of Bioenergy (BEN)
Helmholtz-Zentrum für Umweltforschung GmbH – UFZ
University of Leipzig
Ministry of Energy, Thailand

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✉ Piradee.jusakulvijit@ufz.de
☎ Torgauer Straße 116
04347 Leipzig

Title of the Doctoral Project:	Potential assessment of second-generation bioethanol development from regional agricultural residues in Thailand with participatory selection of sustainability criteria
Doctoral Student:	Piradee Jusakulvijit
DBFZ Supervisor:	Dr. mont. Dipl.-Ing. Alberto Bezama
Cooperating University:	University of Leipzig
University Supervisor:	Prof. Dr.-Ing. Daniela Thrän
Funding / Scholarship provider:	Thailand Energy Conservation Fund (ENCON) Ministry of Energy, Thailand
Duration:	10/2018 – 09/2022

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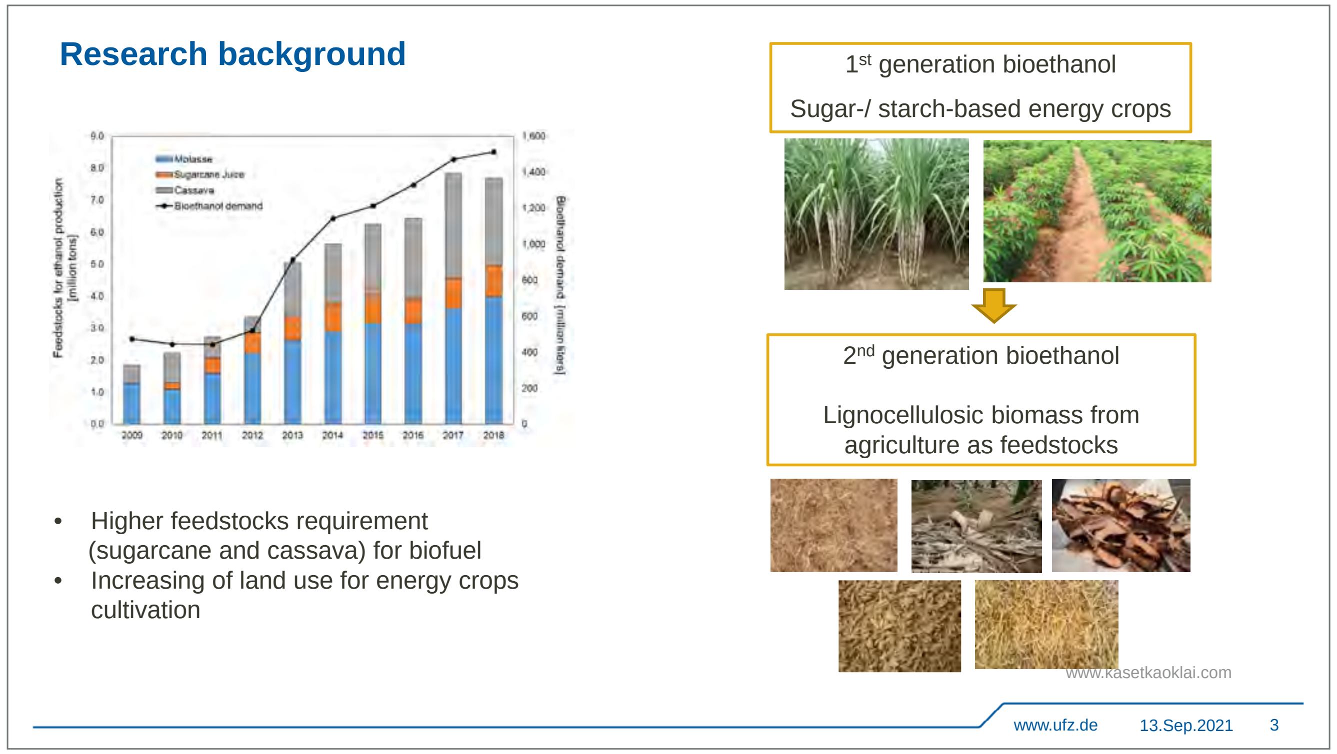


Research background

- Higher feedstocks requirement (sugarcane and cassava) for biofuel
- Increasing of land use for energy crops cultivation

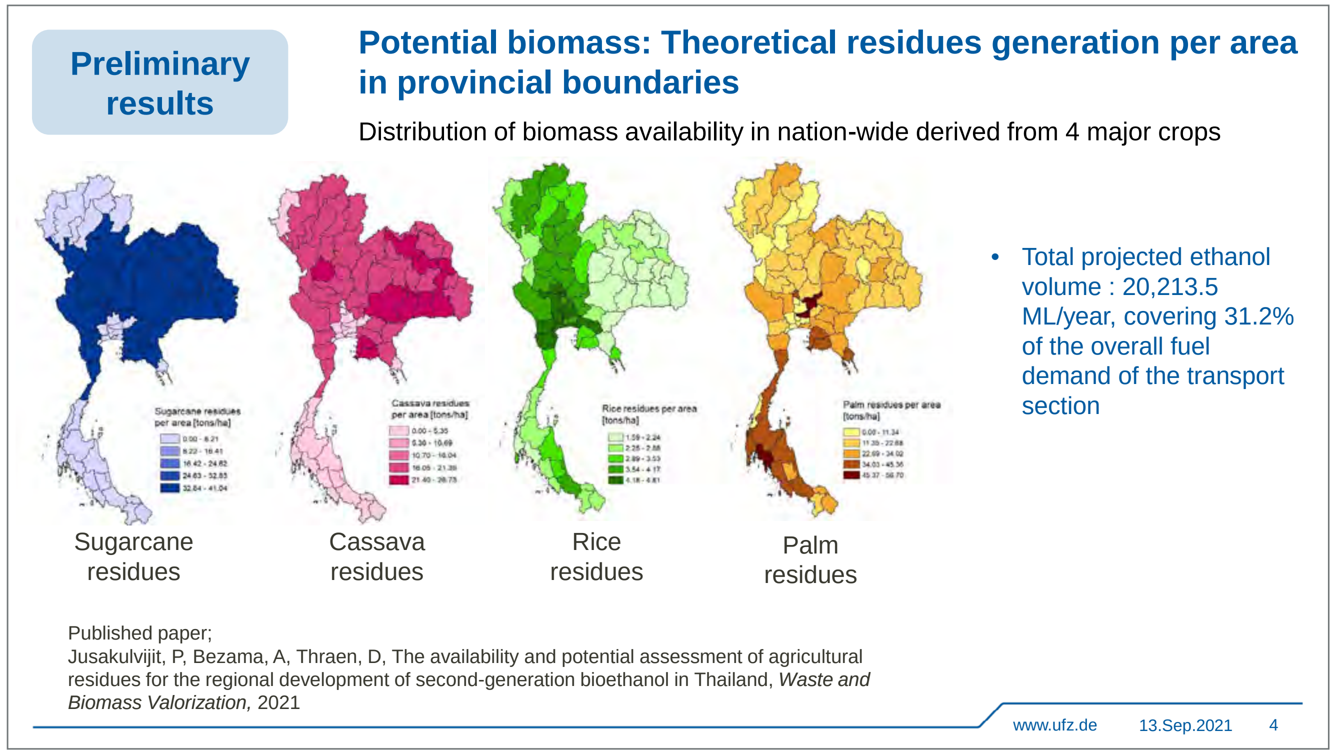
1st generation bioethanol

Sugar-/ starch-based energy crops

2nd generation bioethanol

Lignocellulosic biomass from agriculture as feedstocks

www.kasetkaoklai.com



Preliminary results

Potential biomass: Theoretical residues generation per area in provincial boundaries

Distribution of biomass availability in nation-wide derived from 4 major crops

Sugarcane residues

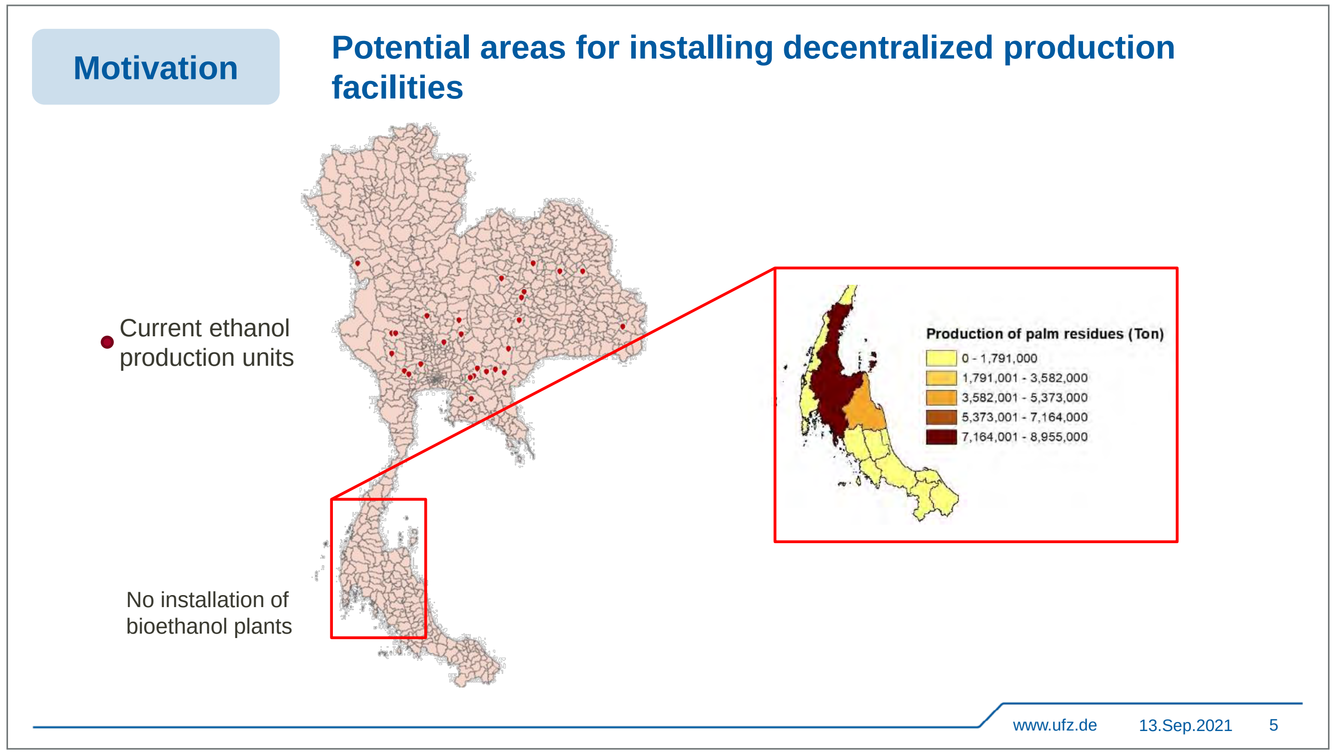
Cassava residues

Rice residues

Palm residues

- Total projected ethanol volume : 20,213.5 ML/year, covering 31.2% of the overall fuel demand of the transport section

Published paper;
Jusakulvijit, P, Bezama, A, Thraen, D, The availability and potential assessment of agricultural residues for the regional development of second-generation bioethanol in Thailand, *Waste and Biomass Valorization,* 2021



Motivation

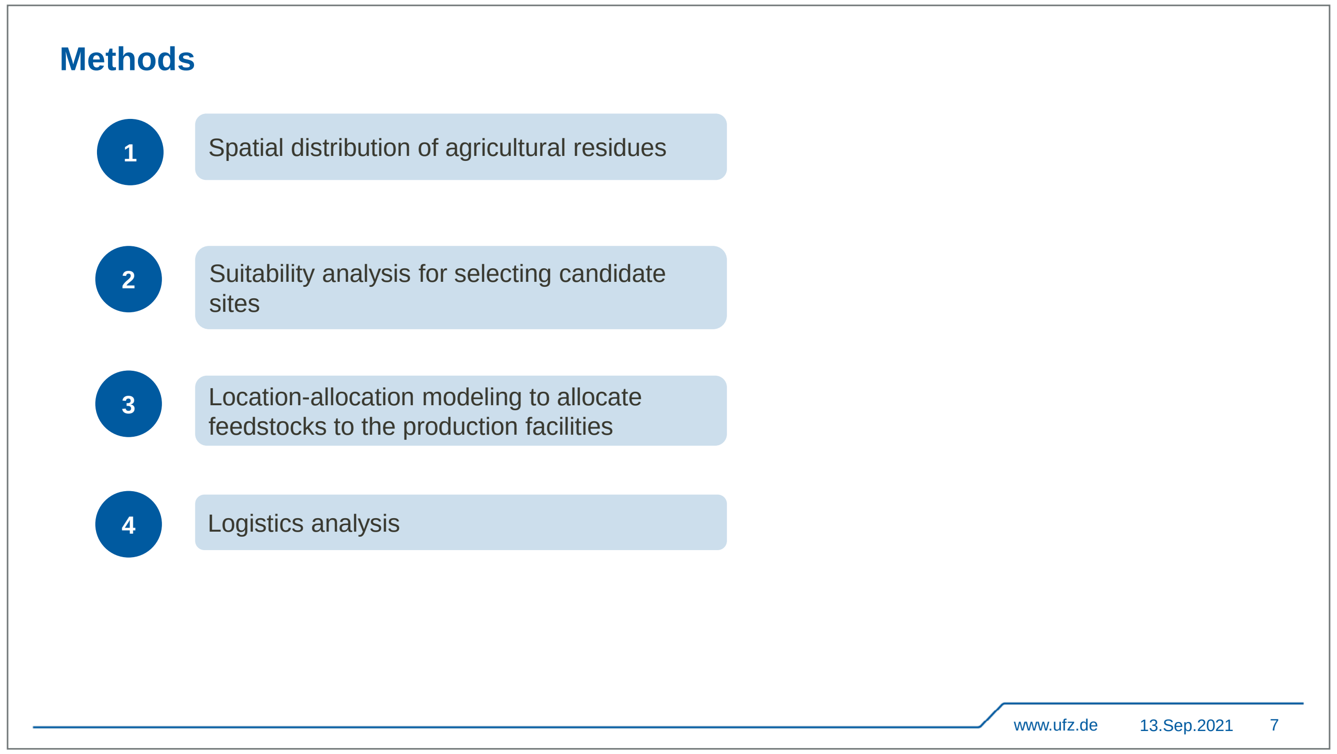
Potential areas for installing decentralized production facilities

● Current ethanol production units

No installation of bioethanol plants

Goal of the current study

- To determine the suitable locations based on results of important criteria evaluated by stakeholders (from previous study steps)
- To design the potential decentralized biorefinery system in order to maximize biomass utilization
- To propose the production capacities for decentralized bioethanol production based on residues catchment
- To verify the relation of number of installation units, production scales and transportation costs as part of techno-economic analysis to optimize the decentralized system



Methods

1. Spatial distribution of agricultural residues
2. Suitability analysis for selecting candidate sites
3. Location-allocation modeling to allocate feedstocks to the production facilities
4. Logistics analysis

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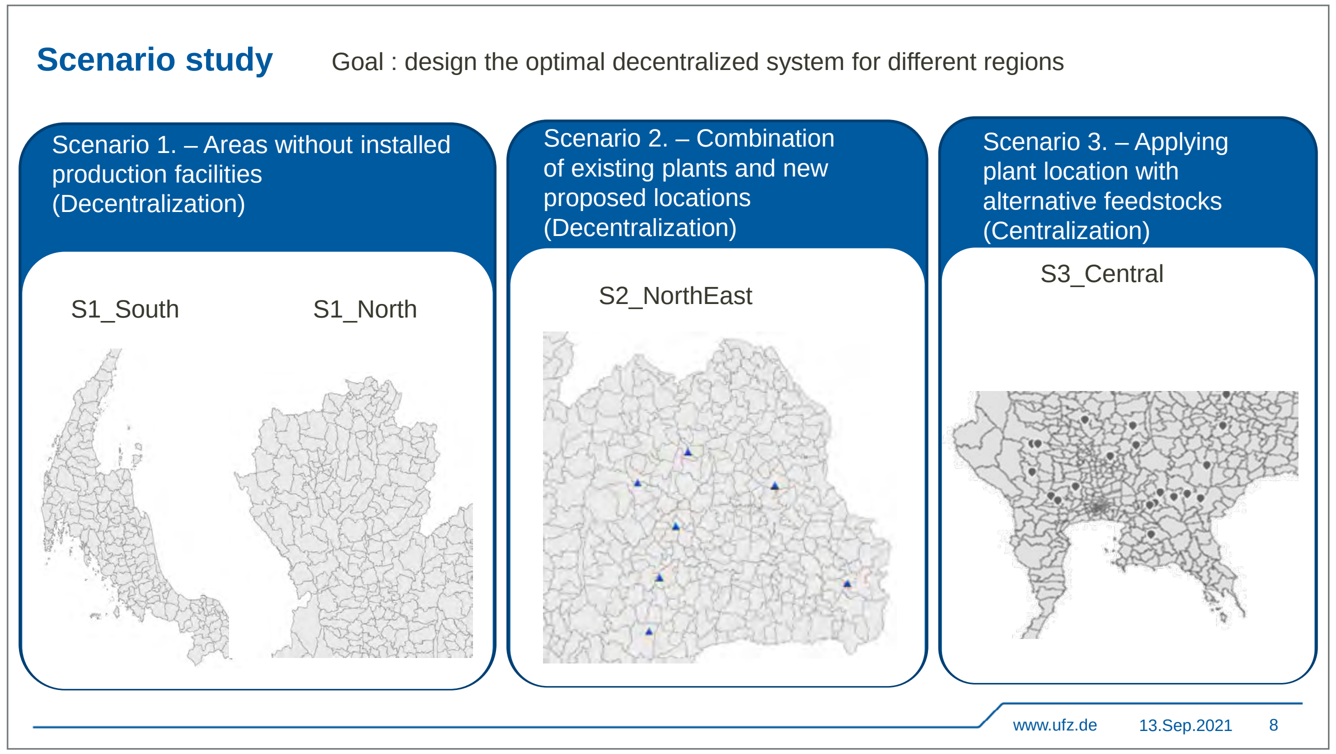

Scenario study

Goal : design the optimal decentralized system for different regions

Scenario 1. – Areas without installed production facilities (Decentralization)

S1_South S1_North

Scenario 2. – Combination of existing plants and new proposed locations (Decentralization)

S2_NorthEast

Scenario 3. – Applying plant location with alternative feedstocks (Centralization)

S3_Central

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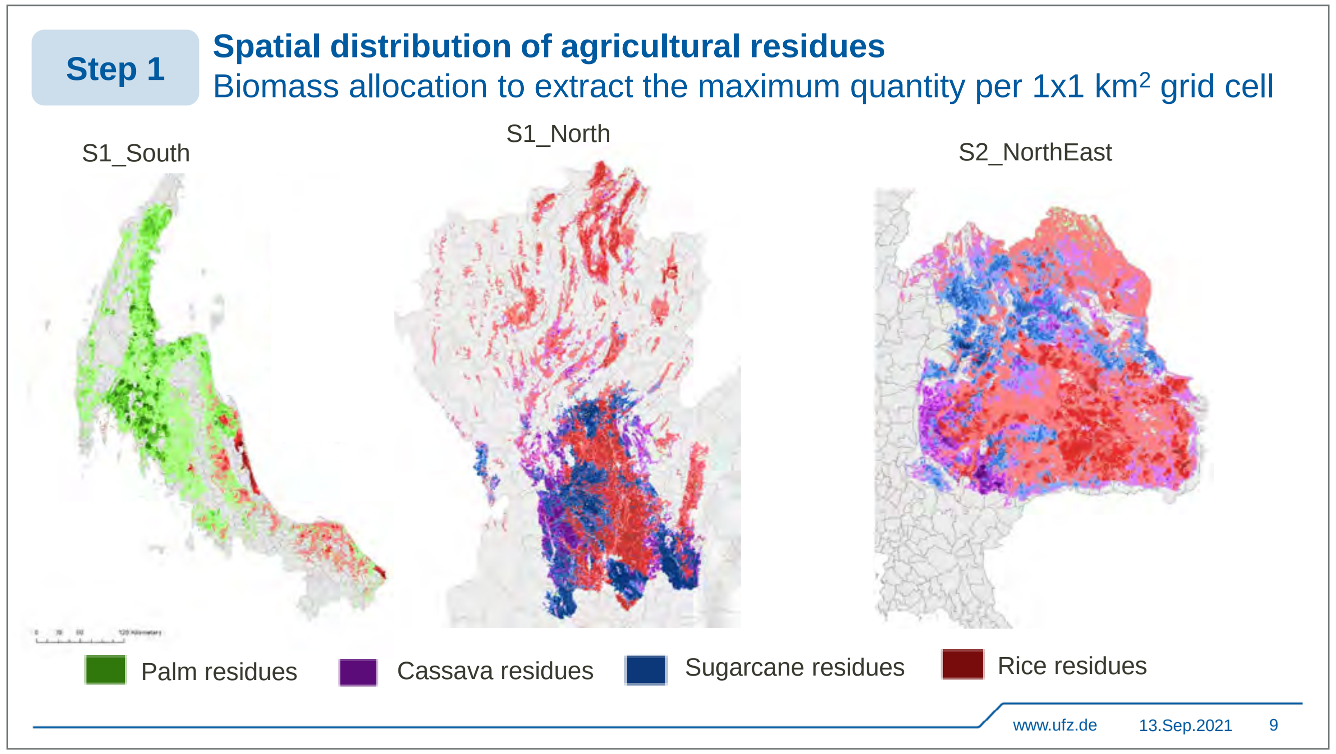

Step 1 Spatial distribution of agricultural residues

Biomass allocation to extract the maximum quantity per 1x1 km^2 grid cell

S1_South S1_North S2_NorthEast

🟩 Palm residues 🟪 Cassava residues 🟦 Sugarcane residues 🟥 Rice residues

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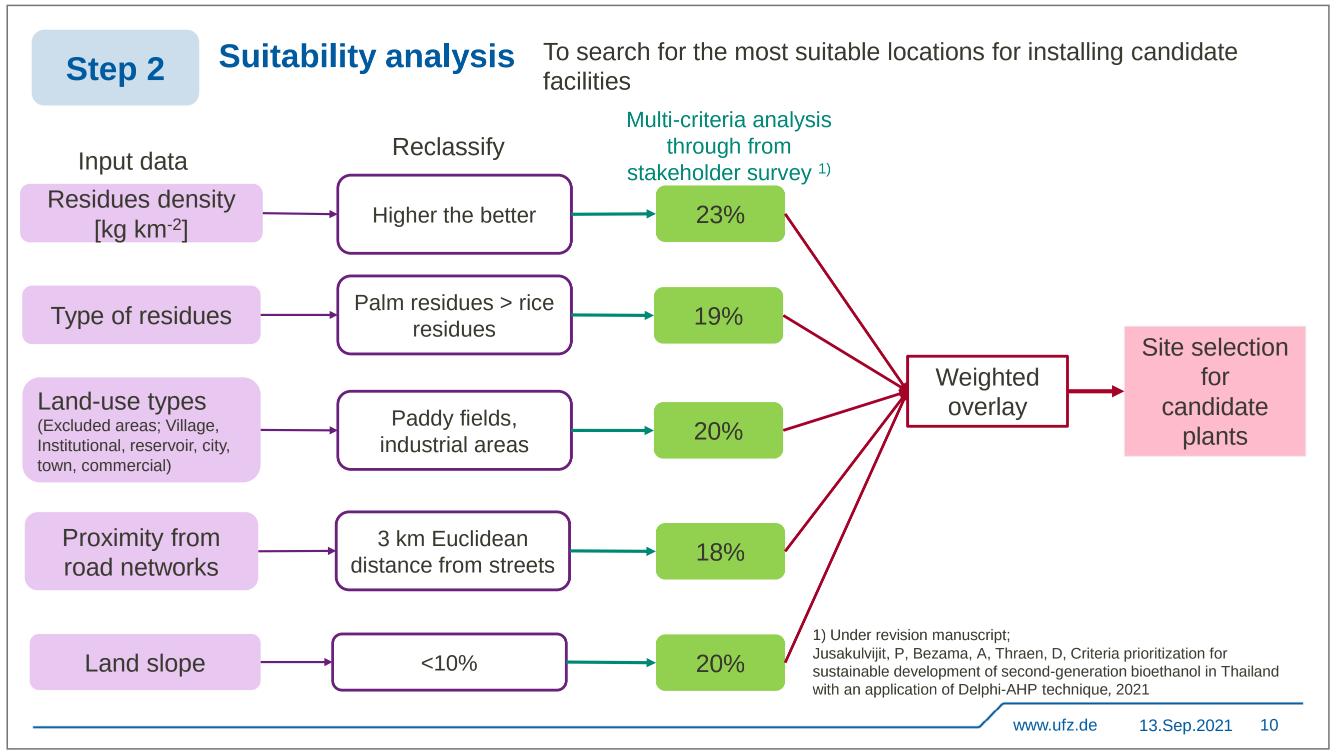

Step 2 Suitability analysis

To search for the most suitable locations for installing candidate facilities

Input data	Reclassify	Multi-criteria analysis through from stakeholder survey [1]
Residues density [kg km^{-2}]	Higher the better	23%
Type of residues	Palm residues > rice residues	19%
Land-use types (Excluded areas; Village, Institutional, reservoir, city, town, commercial)	Paddy fields, industrial areas	20%
Proximity from road networks	3 km Euclidean distance from streets	18%
Land slope	<10%	20%

Weighted overlay → Site selection for candidate plants

[1] Under revision manuscript; Jusakulvijit, P, Bezama, A, Thraen, D, Criteria prioritization for sustainable development of second-generation bioethanol in Thailand with an application of Delphi-AHP technique, 2021

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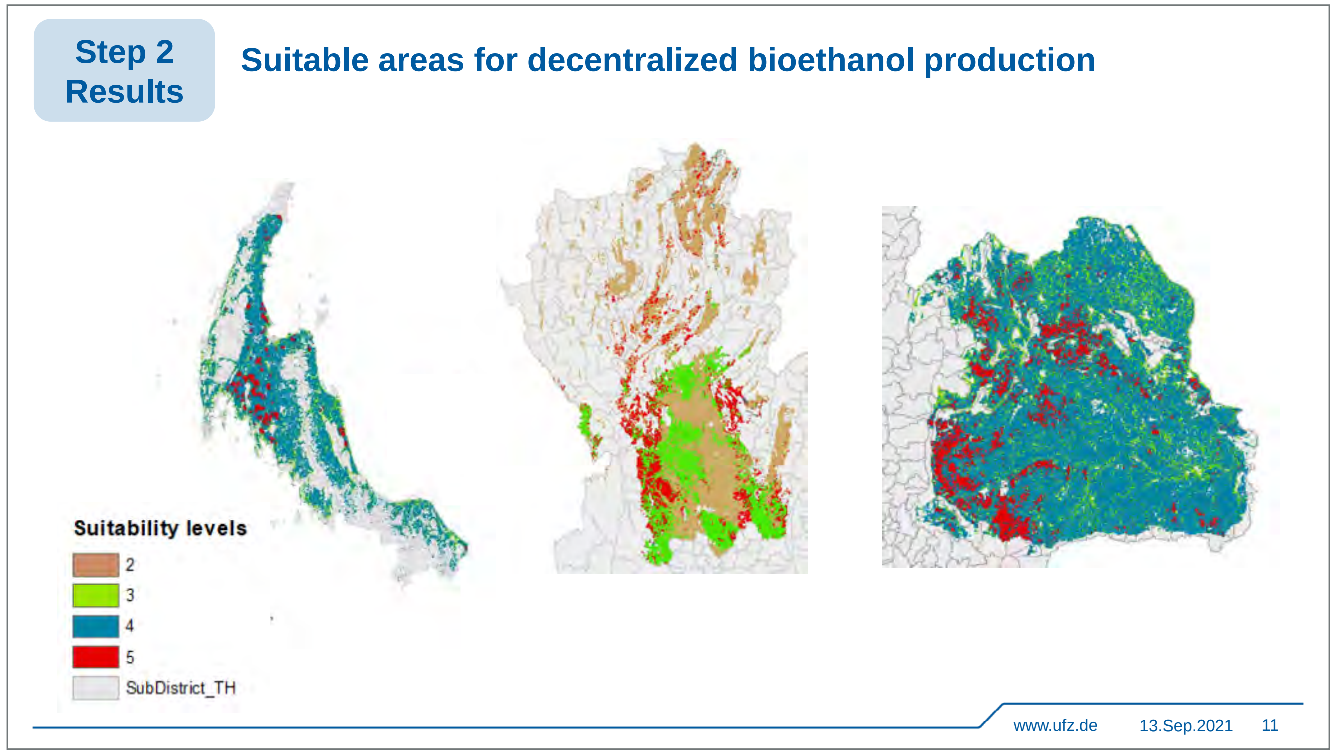
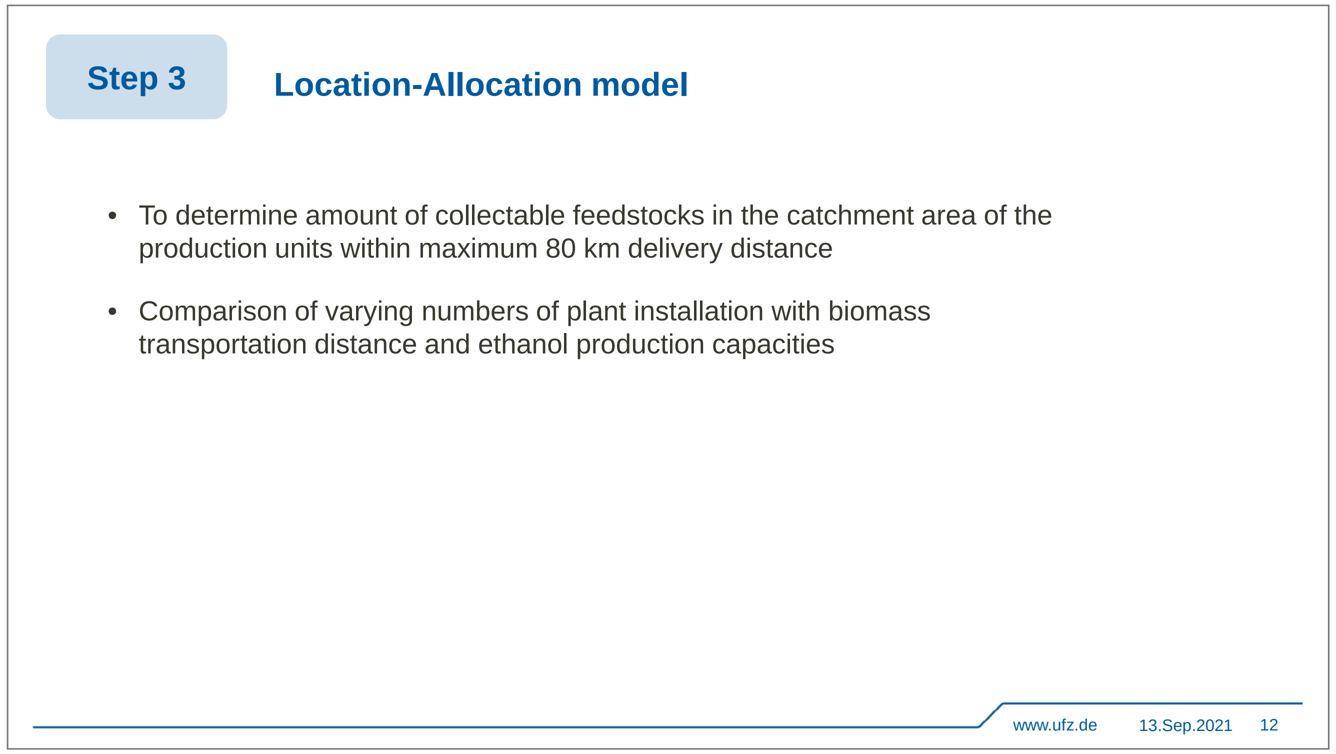


Step 2 Results

Suitable areas for decentralized bioethanol production

Suitability levels

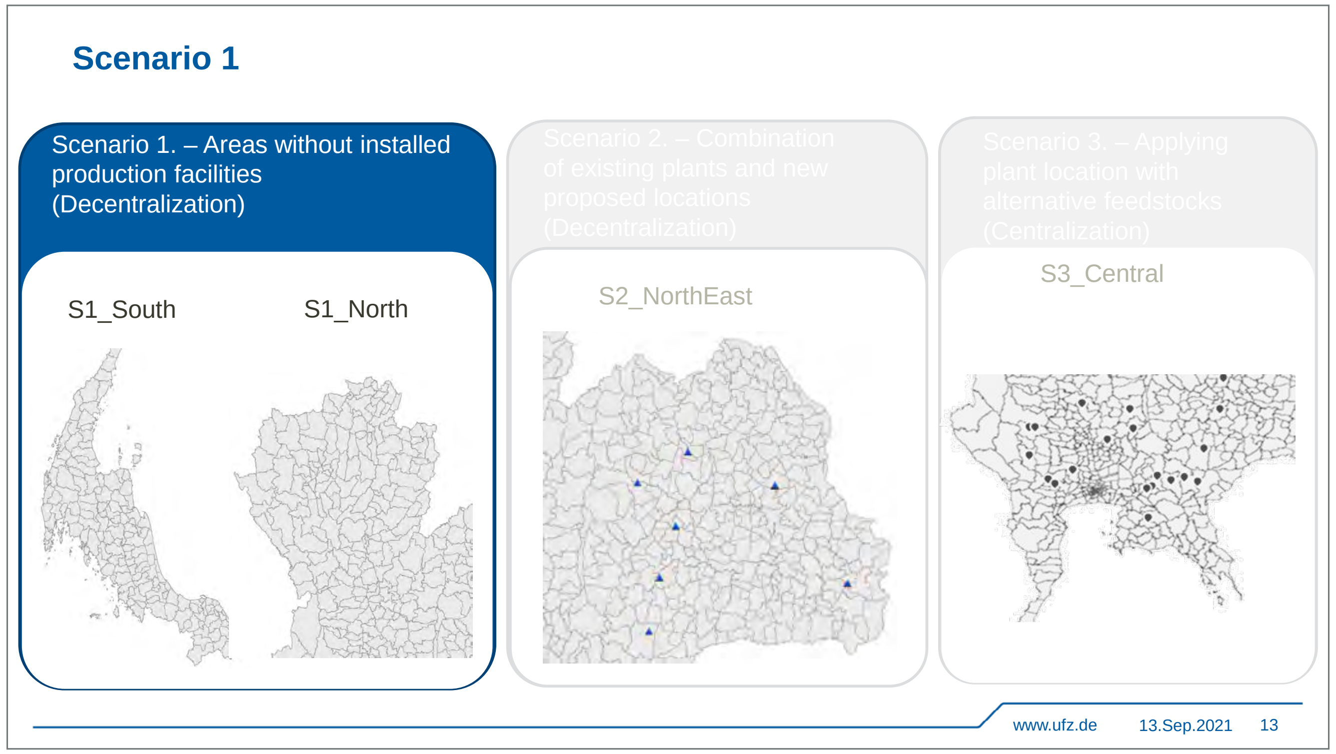
🟫 2
🟩 3
🟦 4
🟥 5
⬜ SubDistrict_TH



Step 3

Location-Allocation model

- To determine amount of collectable feedstocks in the catchment area of the production units within maximum 80 km delivery distance
- Comparison of varying numbers of plant installation with biomass transportation distance and ethanol production capacities



Scenario 1

Scenario 1. – Areas without installed production facilities (Decentralization)

S1_South

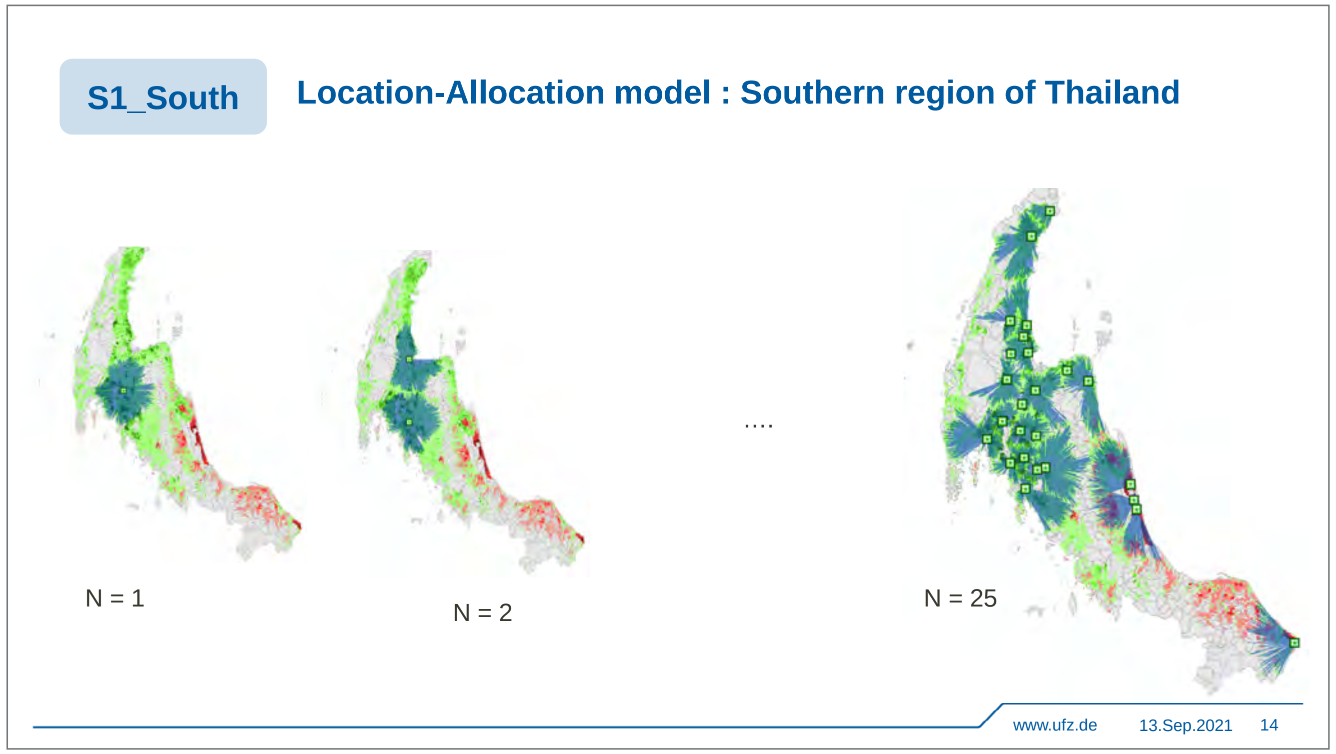
S1_North

Scenario 2. – Combination of existing plants and new proposed locations (Decentralization)

S2_NorthEast

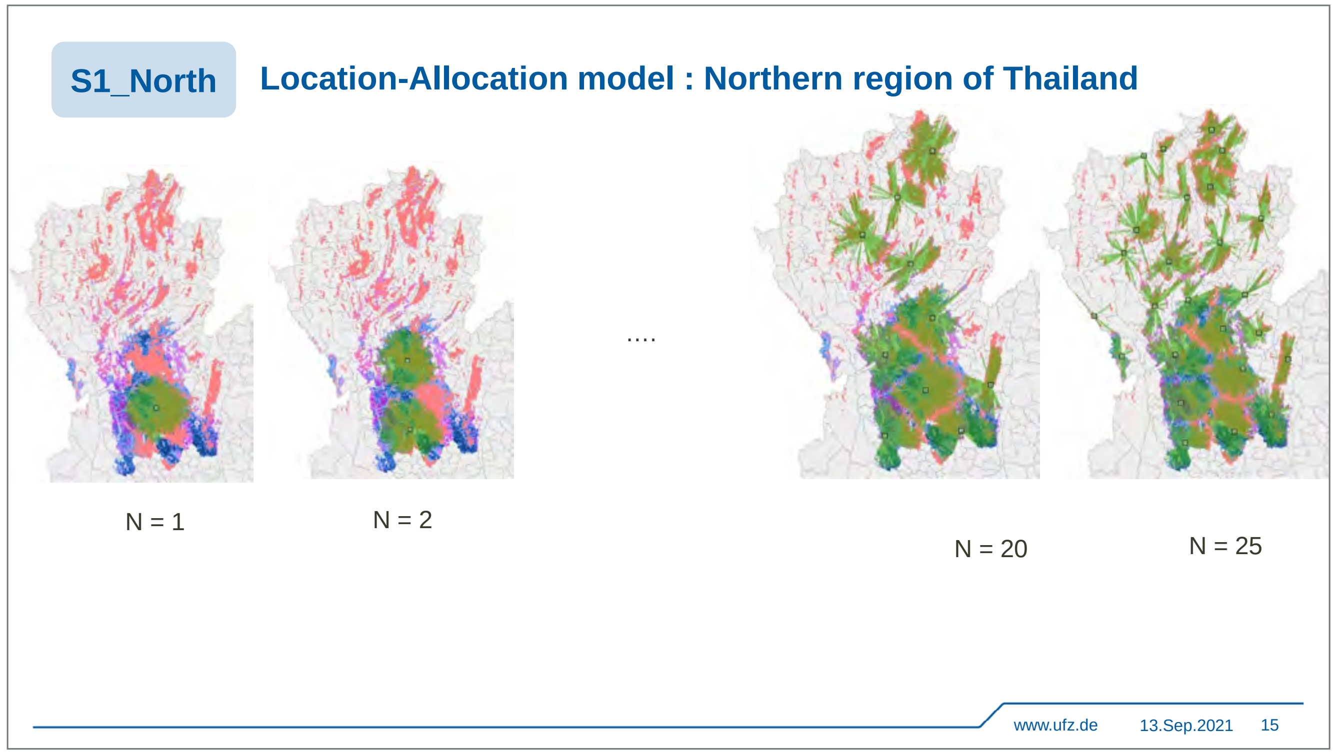
Scenario 3. – Applying plant location with alternative feedstocks (Centralization)

S3_Central



S1_South

Location-Allocation model : Southern region of Thailand



S1_North **Location-Allocation model : Northern region of Thailand**

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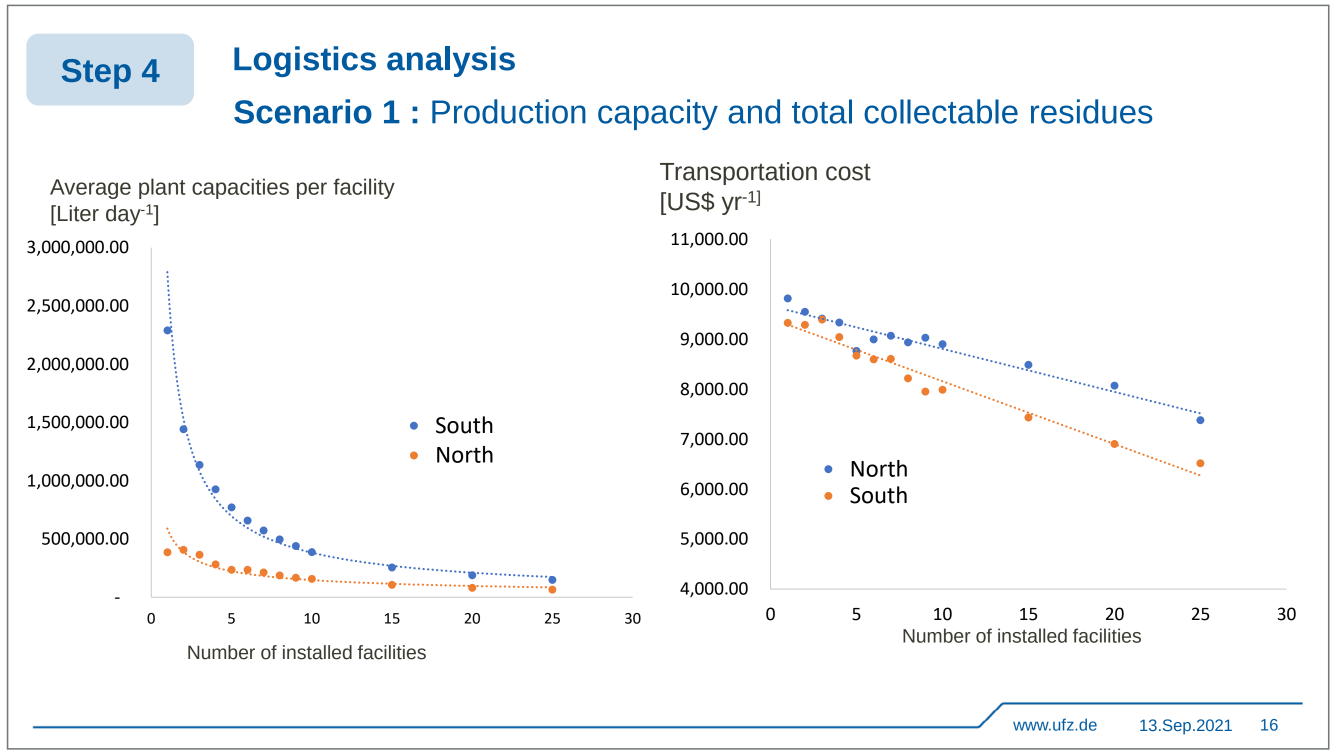

Step 4 **Logistics analysis**

Scenario 1 : Production capacity and total collectable residues

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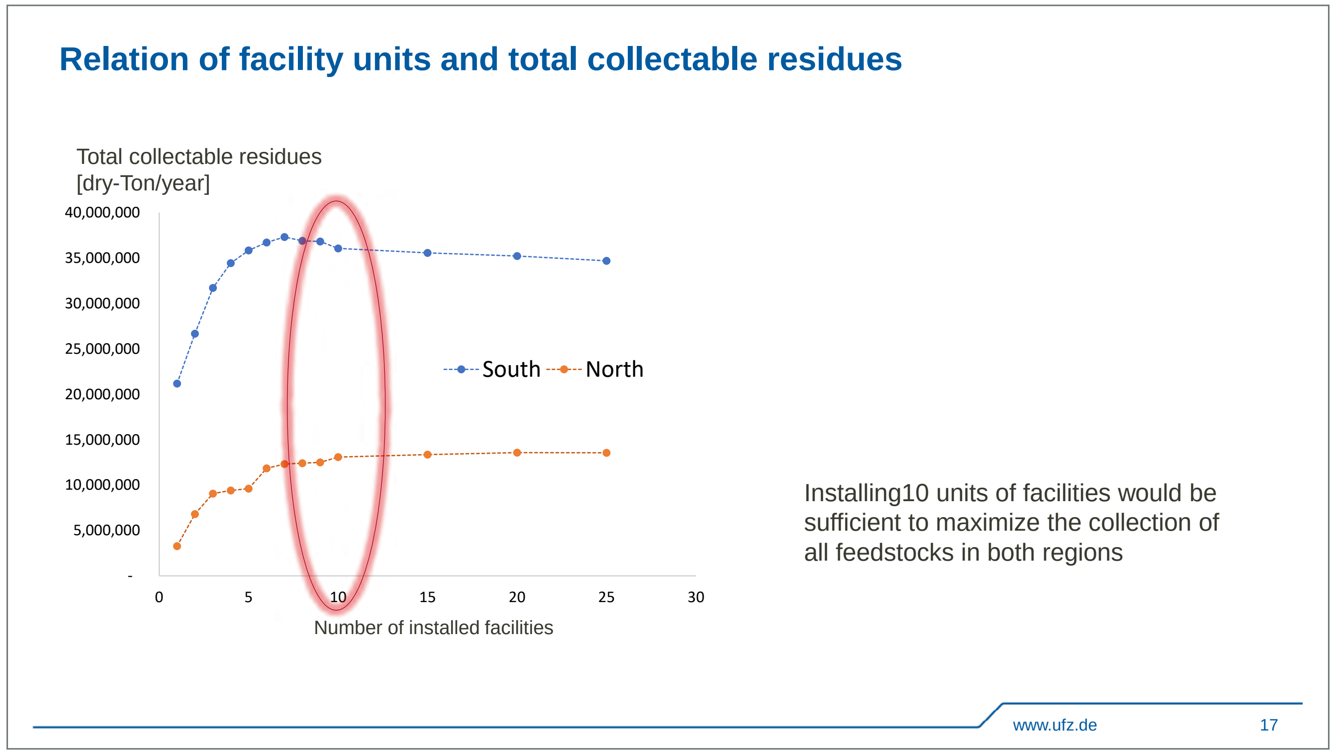

Relation of facility units and total collectable residues

Installing10 units of facilities would be sufficient to maximize the collection of all feedstocks in both regions

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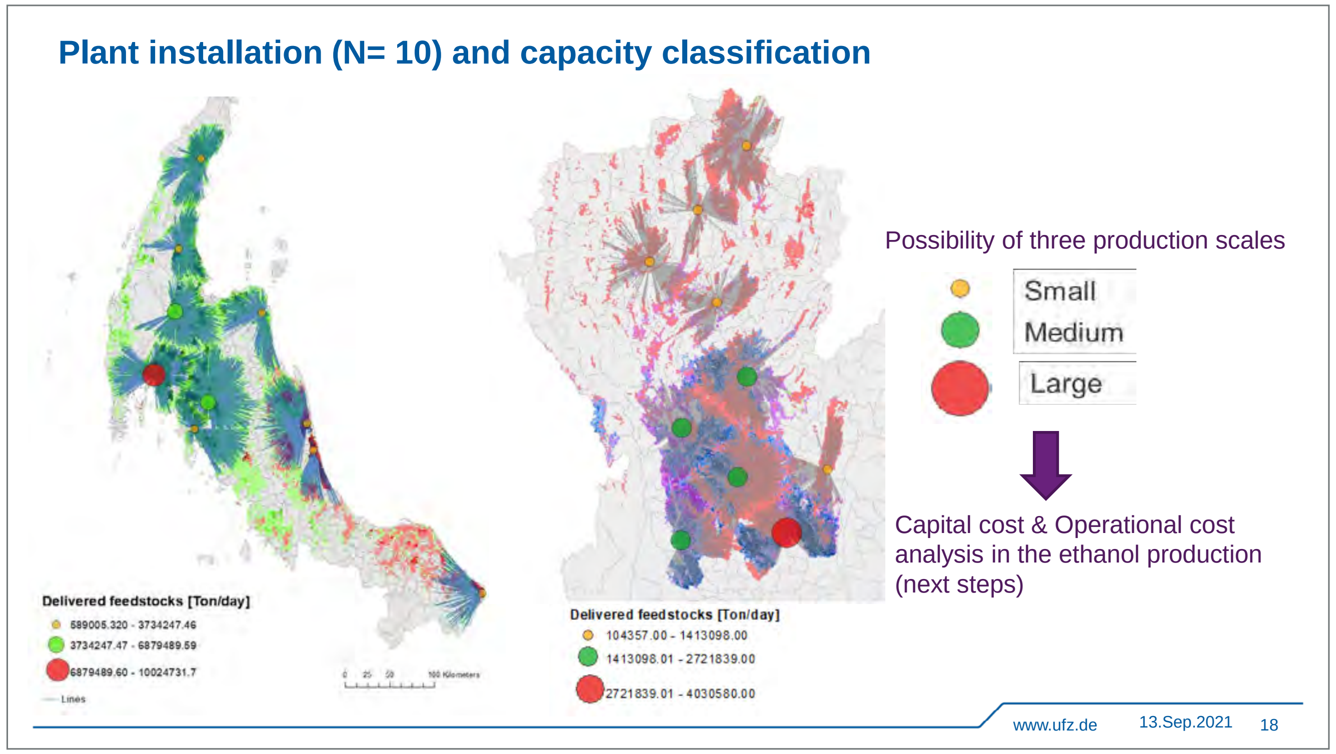

Plant installation (N= 10) and capacity classification

Possibility of three production scales

Small
Medium
Large

Capital cost & Operational cost analysis in the ethanol production (next steps)

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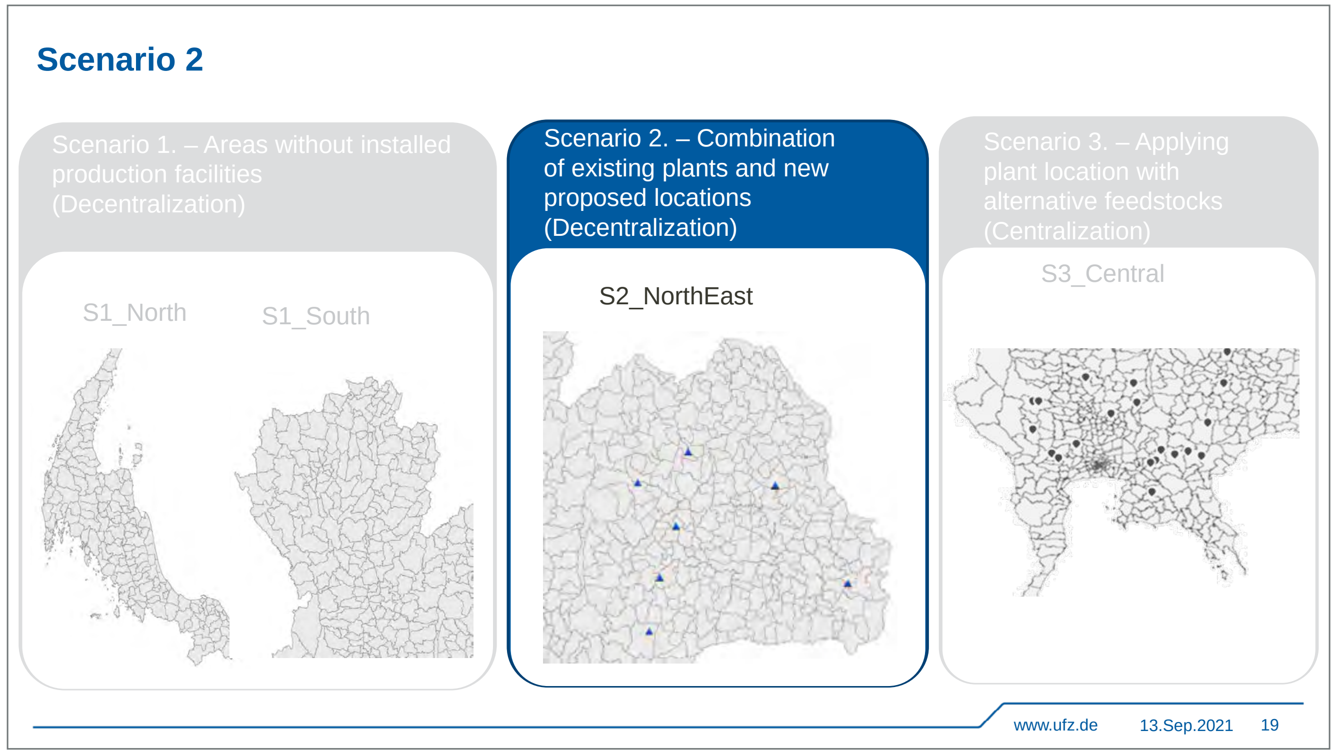

Scenario 2

Scenario 1. – Areas without installed production facilities (Decentralization)

Scenario 2. – Combination of existing plants and new proposed locations (Decentralization)

Scenario 3. – Applying plant location with alternative feedstocks (Centralization)

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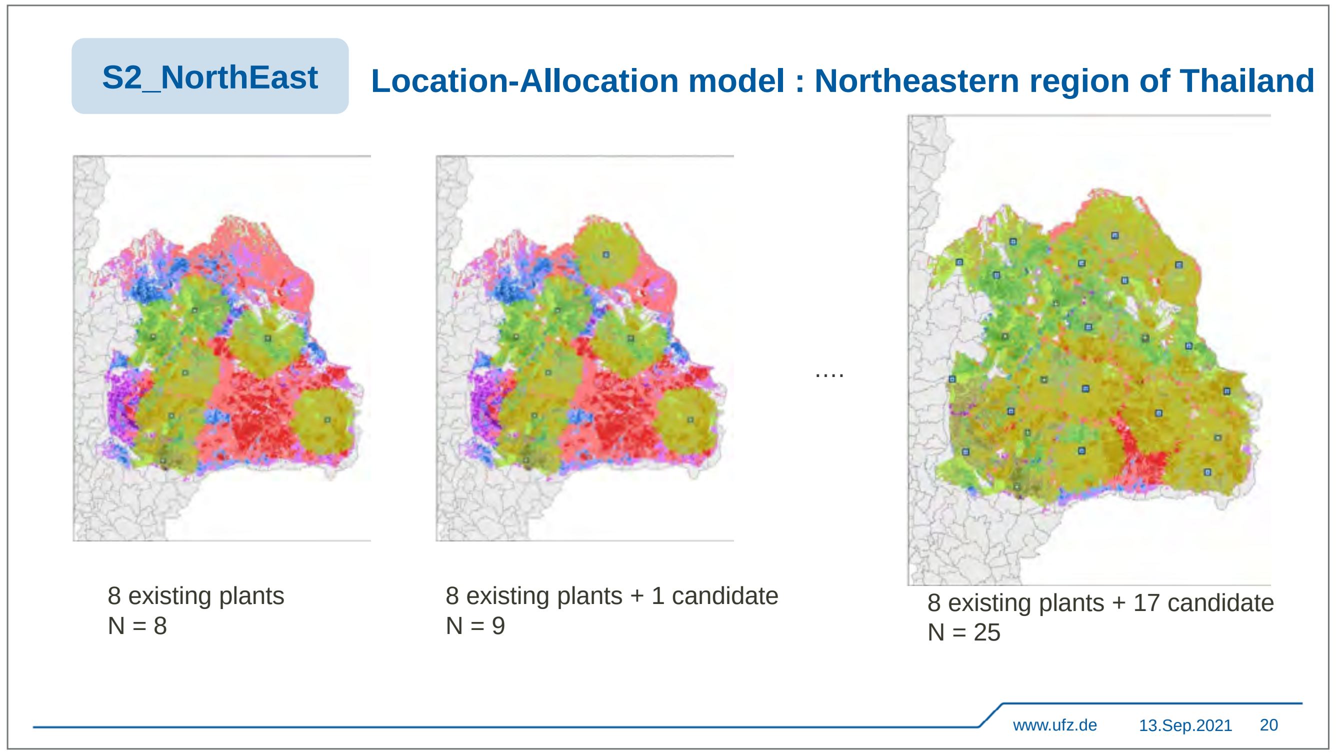

S2_NorthEast Location-Allocation model : Northeastern region of Thailand

8 existing plants
N = 8

8 existing plants + 1 candidate
N = 9

....

8 existing plants + 17 candidate
N = 25

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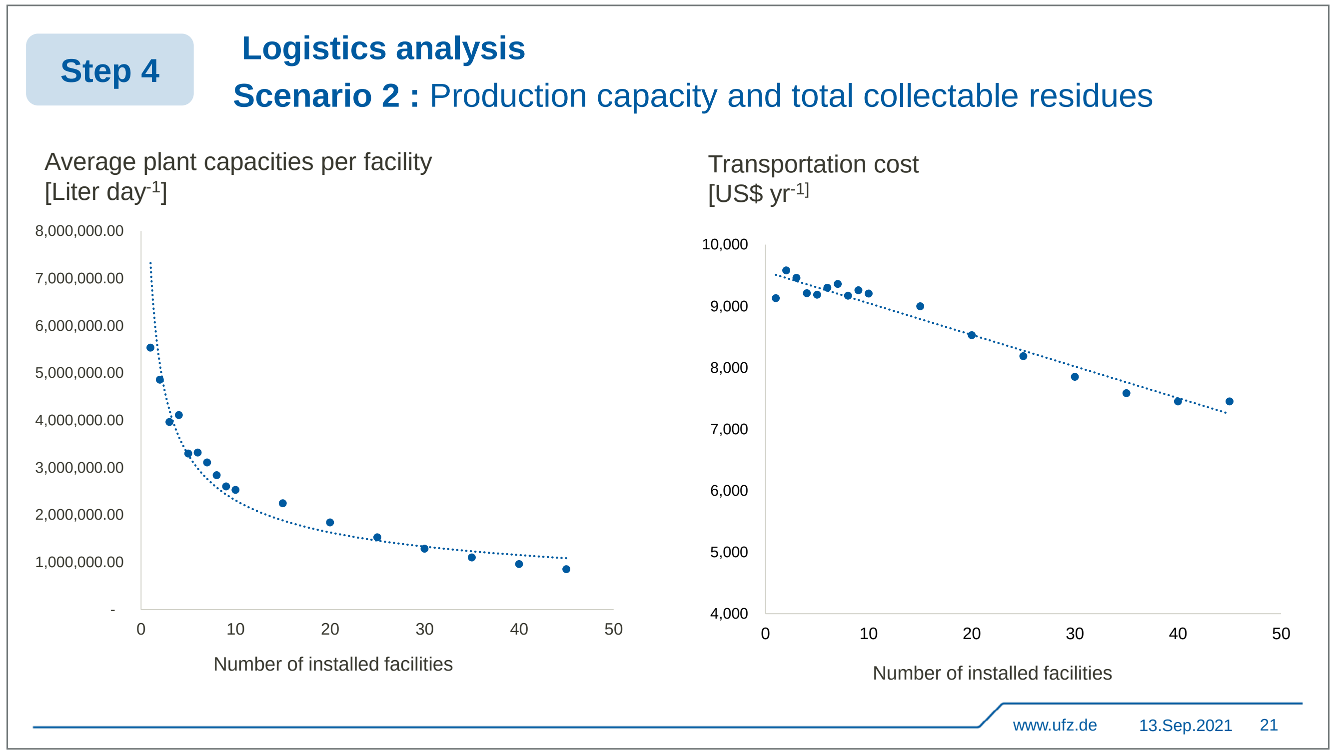

Step 4 Logistics analysis

Scenario 2 : Production capacity and total collectable residues

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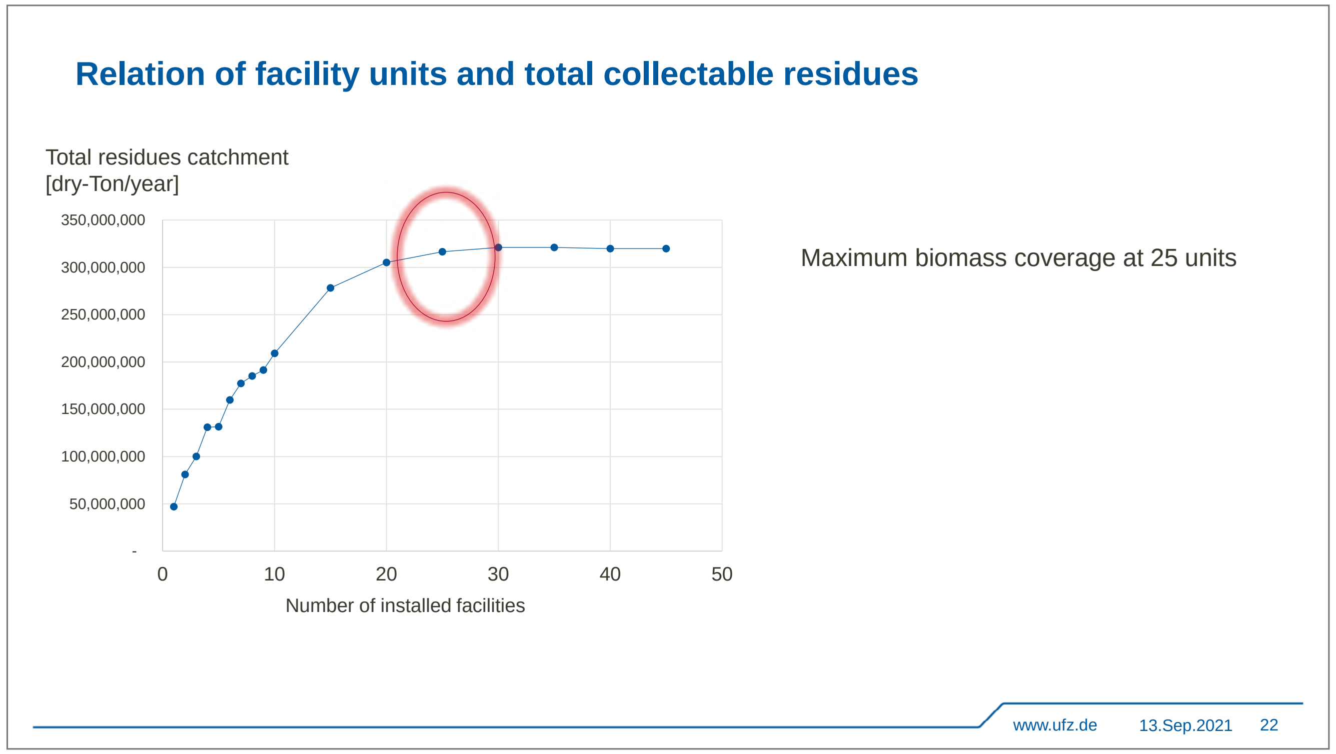

Relation of facility units and total collectable residues

Maximum biomass coverage at 25 units

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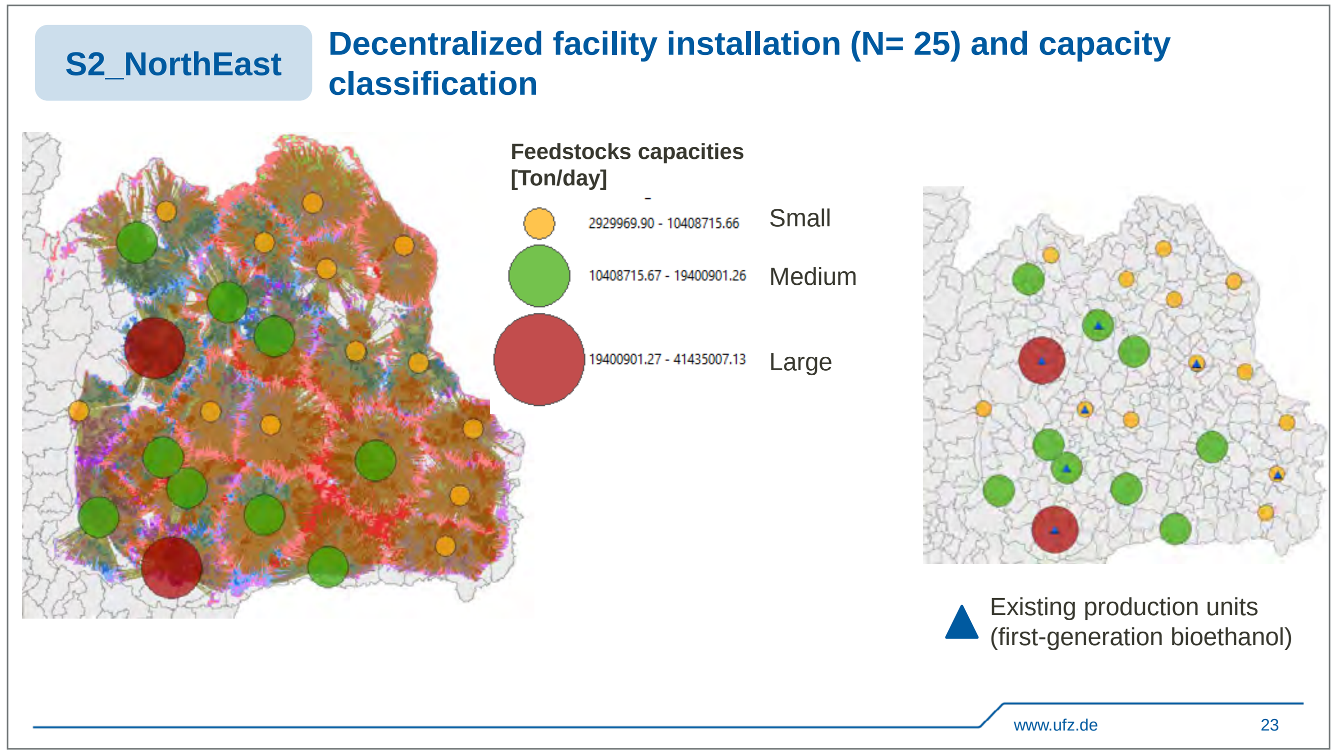
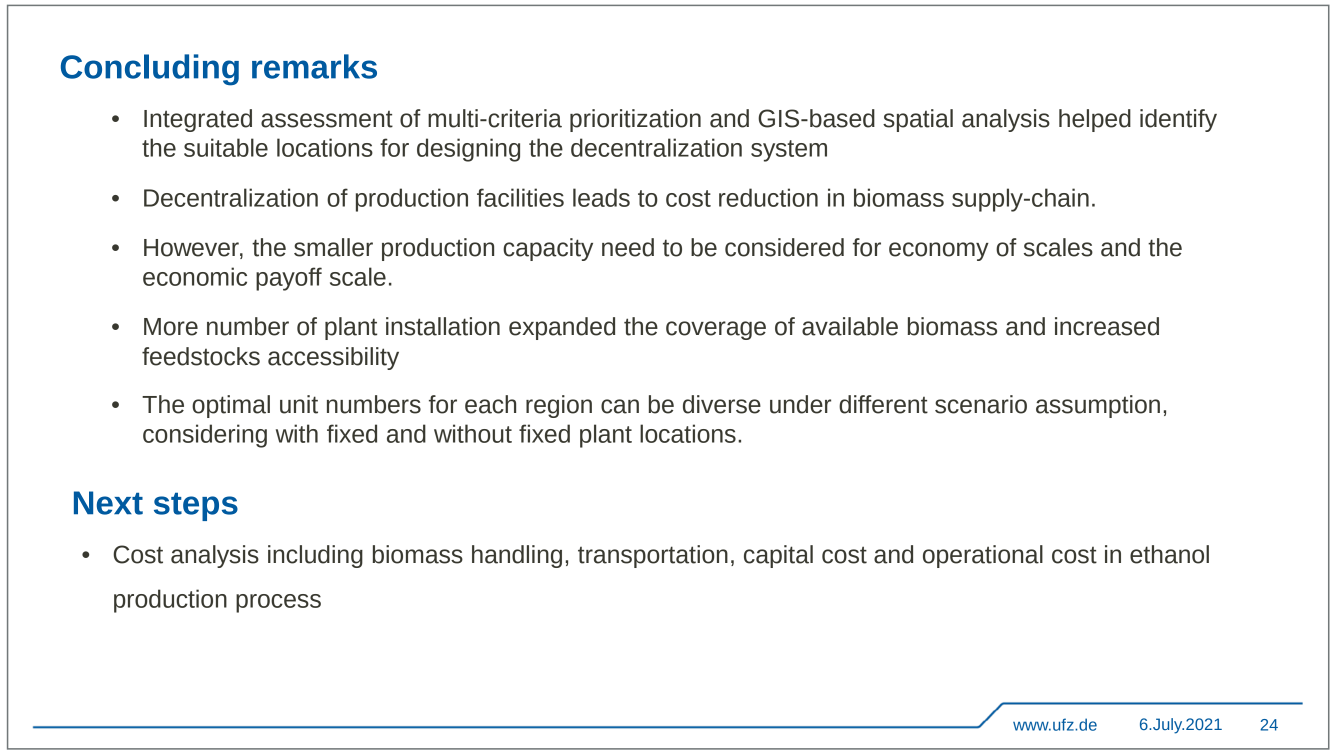


S2_NorthEast

Decentralized facility installation (N= 25) and capacity classification



Concluding remarks

- Integrated assessment of multi-criteria prioritization and GIS-based spatial analysis helped identify the suitable locations for designing the decentralization system
- Decentralization of production facilities leads to cost reduction in biomass supply-chain.
- However, the smaller production capacity need to be considered for economy of scales and the economic payoff scale.
- More number of plant installation expanded the coverage of available biomass and increased feedstocks accessibility
- The optimal unit numbers for each region can be diverse under different scenario assumption, considering with fixed and without fixed plant locations.

Next steps

- Cost analysis including biomass handling, transportation, capital cost and operational cost in ethanol production process

Frazer Musonda, Helmholtz Center for Environmental Research - UFZ

The potential for greenhouse abatement and the corresponding costs in the German chemicals sector

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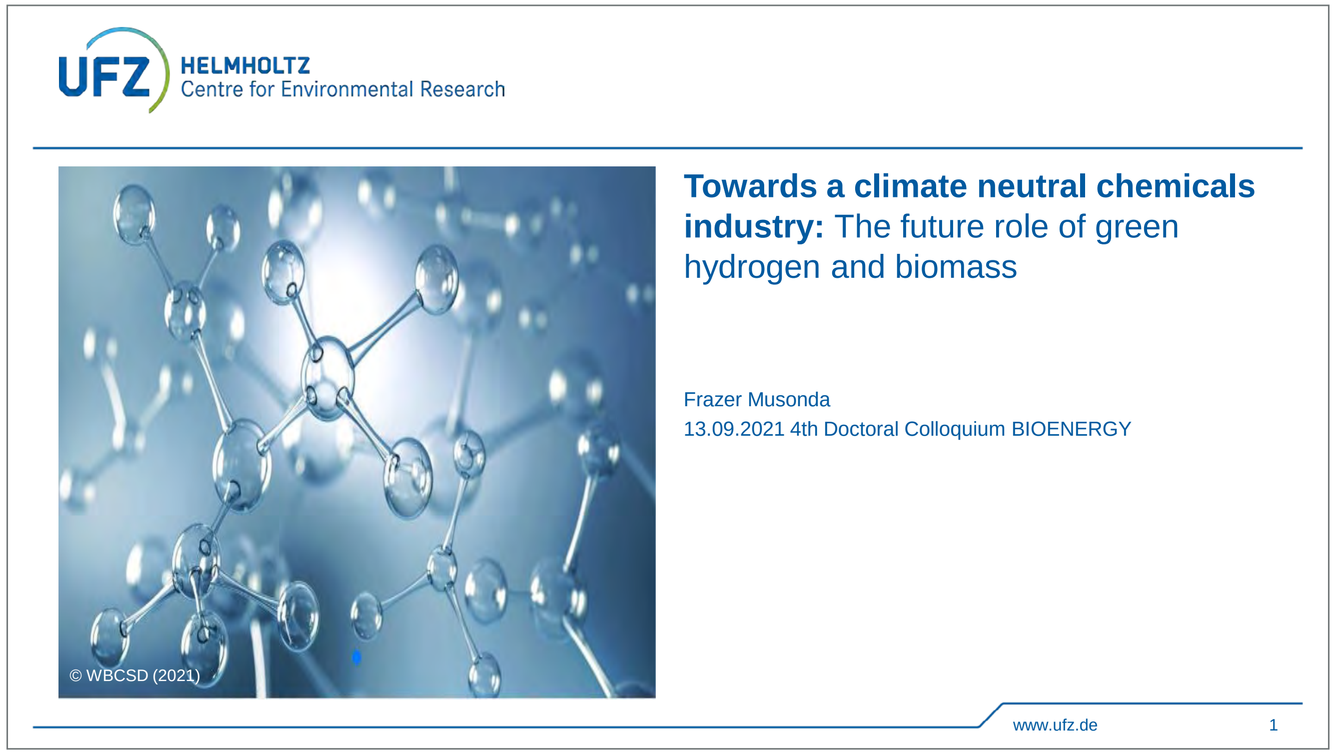
There is limited research focusing on the role of renewable chemicals' potential for greenhouse gas abatement and the corresponding costs in the German petrochemicals sector. Studies for the optimal allocation of limited biomass, and recently, green hydrogen from renewable electricity, have strongly focused on the power, heat and transport sectors. With German climate targets encompassing all sectors of the economy, the holistic tackling of climate change requires measures in all sectors in order to avoid problem shifting. In this work, from the point of view of limited yearly biomass and the renewable hydrogen potential resulting from excess electricity as a result of the deployment of solar and wind energy in Germany, we assess the potential that these two resources have in contributing to greenhouse abatement in the chemicals sector. This is done by the use of a bottom-up mathematical optimization model (BENOPT).

In BENOPT, technologies from the transport, power and heat sectors simultaneously compete with renewable chemicals for biomass and renewable hydrogen in order to minimize system costs or maximize greenhouse gas abatement. Results show that, with the resource potential and the competing uses from power, heat and transport sectors, a greenhouse gas abatement of 77 % for base chemicals is possible by 2050. The greenhouse gas abatement cost, represented by the marginal unit of greenhouse gas abatement was found to be 620 €/tCO_2eq from forest residues derived methanol. The result was found to be sensitive to the assumption of carbon dioxide sequestration into final products. It is therefore recommended that in addition to measures that support the market uptake of renewable chemicals, targeted measures should be implemented to ensure that carbon dioxide absorbed during the cultivation of biochemical feedstocks or uptake during the production of synthetic chemicals is never released at its end of life. This could be done by making plastic waste recycling an attractive business model, firstly by incentivizing the eco-design of the final products, which together with improved sorting at the disposal site, would reduce variability in the physical and chemical characteristics of plastic waste and ensure high-quality recyclates. Secondly, the incineration of plastic waste should be discouraged by taxing energy recovery from plastic waste.



UFZ HELMHOLTZ Centre for Environmental Research

Towards a climate neutral chemicals industry: The future role of green hydrogen and biomass

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Frazer Musonda
13.09.2021 4th Doctoral Colloquium BIOENERGY

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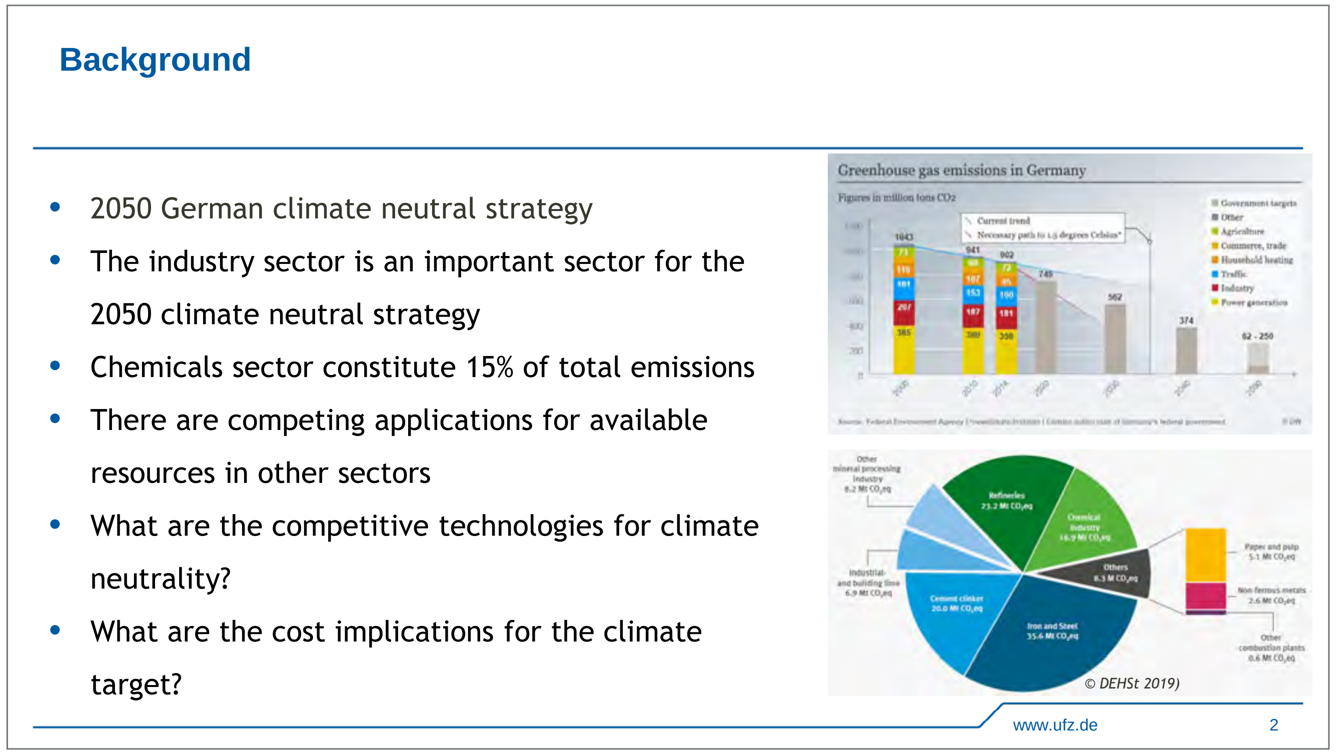

Background

- 2050 German climate neutral strategy
- The industry sector is an important sector for the 2050 climate neutral strategy
- Chemicals sector constitute 15% of total emissions
- There are competing applications for available resources in other sectors
- What are the competitive technologies for climate neutrality?
- What are the cost implications for the climate target?

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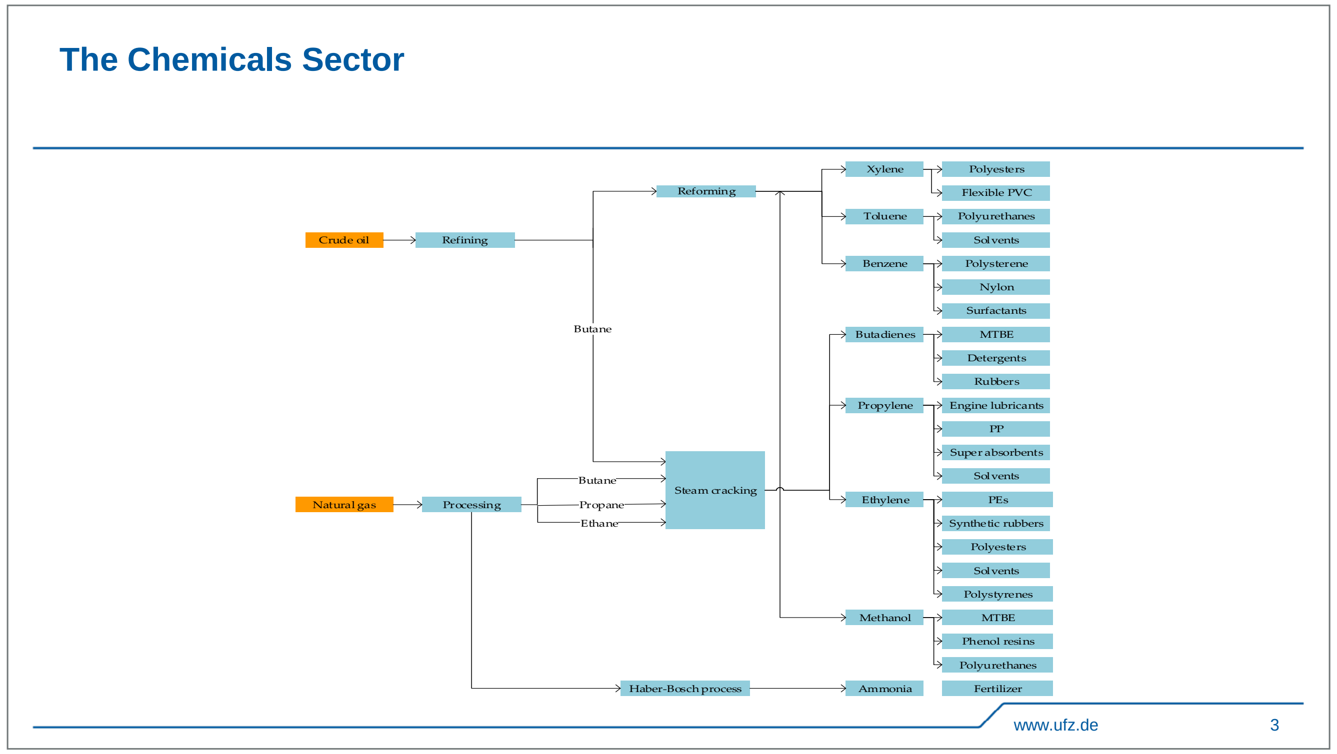

The Chemicals Sector

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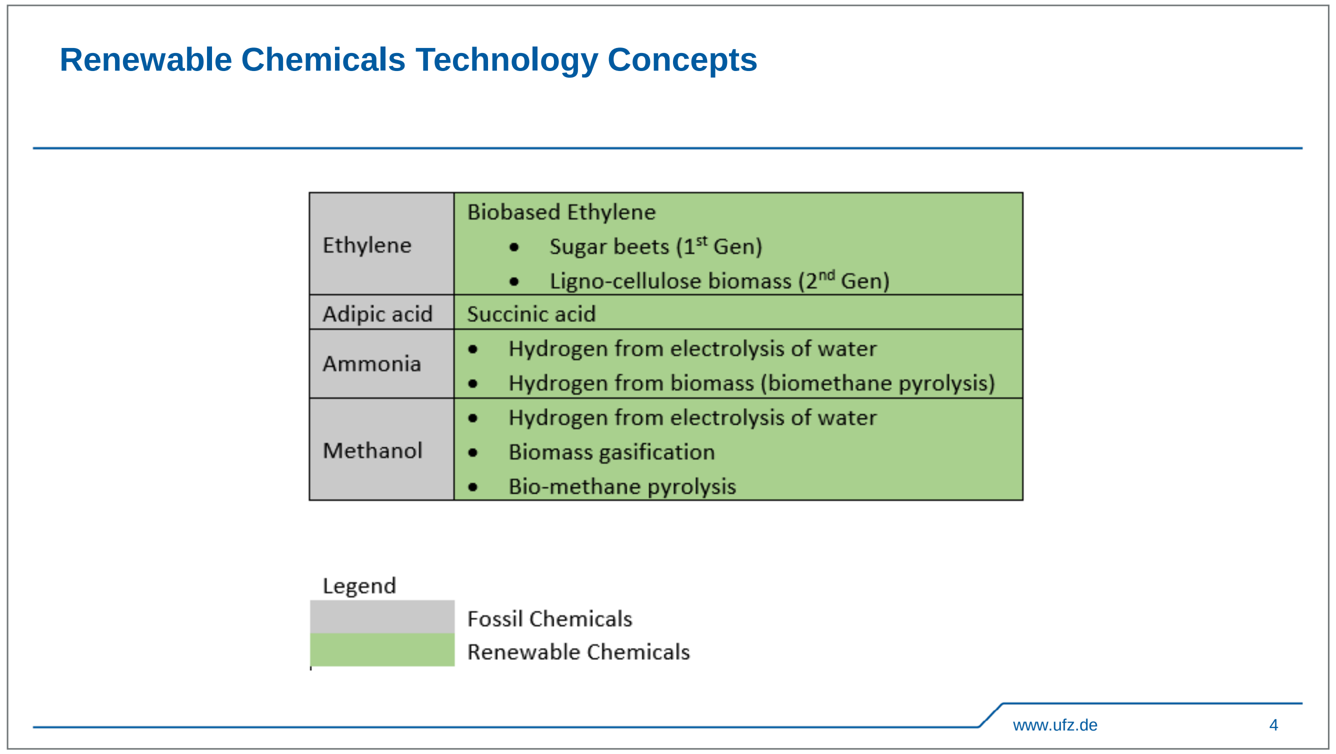

Renewable Chemicals Technology Concepts

Ethylene	Biobased Ethylene • Sugar beets (1st Gen) • Ligno-cellulose biomass (2nd Gen)
Adipic acid	Succinic acid
Ammonia	• Hydrogen from electrolysis of water • Hydrogen from biomass (biomethane pyrolysis)
Methanol	• Hydrogen from electrolysis of water • Biomass gasification • Bio-methane pyrolysis

Legend

▨ Fossil Chemicals

🟩 Renewable Chemicals

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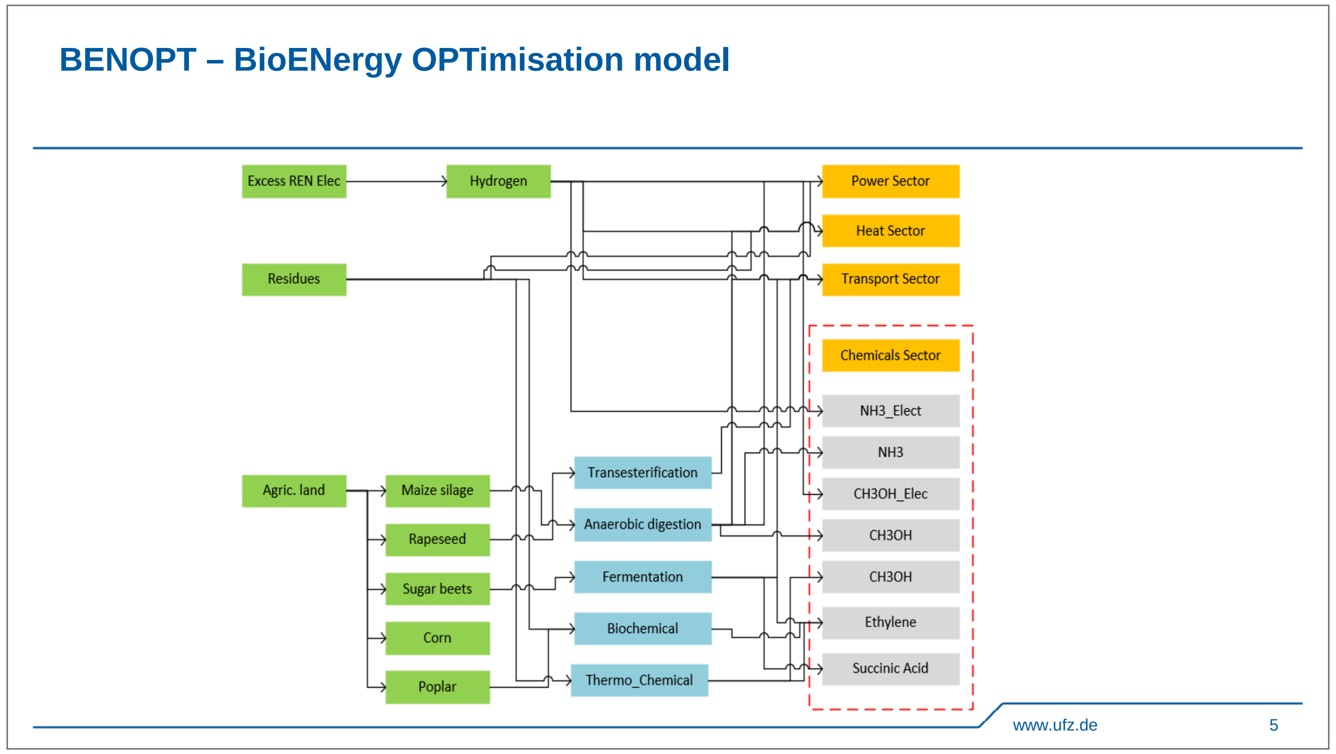

BENOPT – BioENergy OPTimisation model

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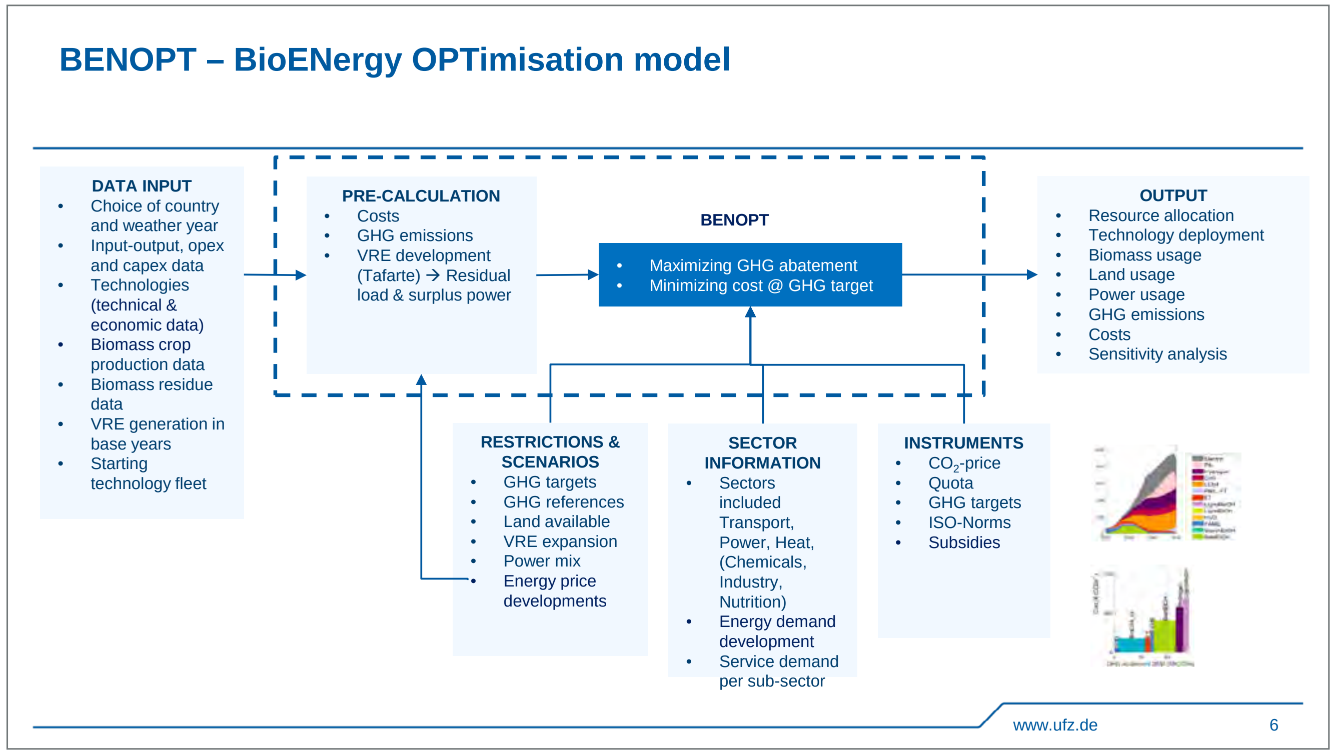

BENOPT – BioENergy OPTimisation model

DATA INPUT
- Choice of country and weather year
- Input-output, opex and capex data
- Technologies (technical & economic data)
- Biomass crop production data
- Biomass residue data
- VRE generation in base years
- Starting technology fleet

PRE-CALCULATION
- Costs
- GHG emissions
- VRE development (Tafarte) → Residual load & surplus power

BENOPT
- Maximizing GHG abatement
- Minimizing cost @ GHG target

OUTPUT
- Resource allocation
- Technology deployment
- Biomass usage
- Land usage
- Power usage
- GHG emissions
- Costs
- Sensitivity analysis

RESTRICTIONS & SCENARIOS
- GHG targets
- GHG references
- Land available
- VRE expansion
- Power mix
- Energy price developments

SECTOR INFORMATION
- Sectors included Transport, Power, Heat, (Chemicals, Industry, Nutrition)
- Energy demand development
- Service demand per sub-sector

INSTRUMENTS
- CO_2-price
- Quota
- GHG targets
- ISO-Norms
- Subsidies

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Scenarios and Sensitivity analysis

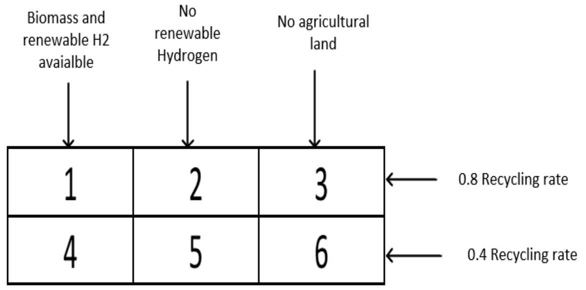
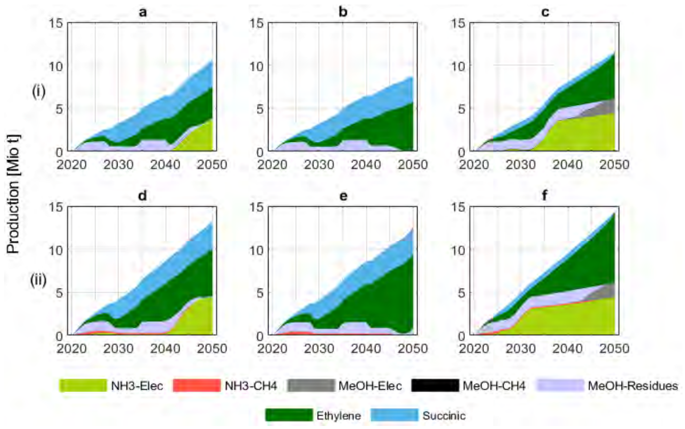


Table1. Global variations of the input parameters

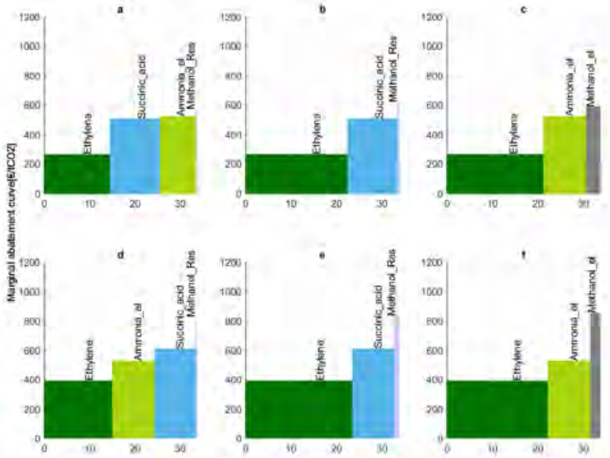
Parameters	Variation
Onshore wind power capacity (2050)	minus 30%
Offshore wind power capacity (2050)	minus 30%
Photovoltaic power capacity (2050)	minus 30%
Biomass residues potential (2050)	max-min
Land available (2050)	minus 50%
N2O emissions	max-min
Investment costs (2050)	max-min
Biomass feed price development factor	2-4%
Discount rate for investment costs	7-10%
Excess power price	± 20%
Power price	± 10%
Heat price	± 10%
CO2 sequestration level	minus 50%

Results



Renewable chemicals production in million tonnes in the considered scenarios. In the figure, a, b and c are scenarios in which, both biomass resources and H2 from excess electricity, no Hydrogen and no agricultural land are represented respectively. In all these scenarios, the rate of recycling of chemical products after their end of life is assumed to be 80%. Scenarios d, e and f represent the exact scenarios as a,b and c respectively but with a reduced recycling rate for of chemical products after their end of life.

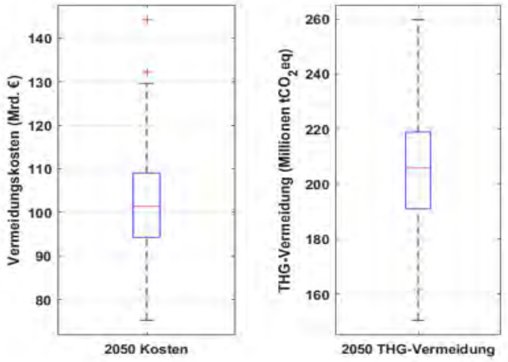
Results cont..

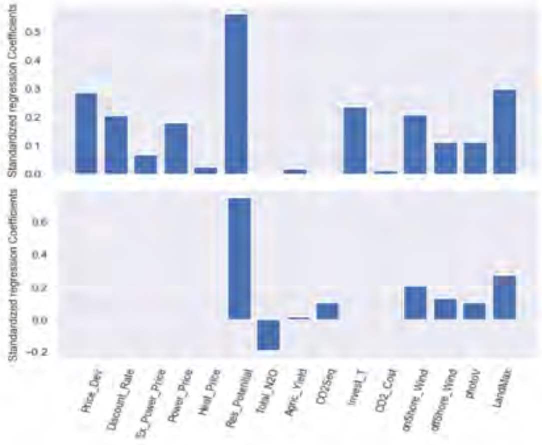


Marginal abatement cost curves for the year 2050 representing the costs and the potential GHG abatement for the considered renewable chemicals in the different scenarios

- Marginal unit for GHG abatement in all scenarios with 0.8 recycling rate has an abatement cost of around 600 €/tCO_2_eq
- A carbon dioxide tax of 600 €/tCO_2_eq has to be levied on fossil counterparts
- Bioethylene showed the lowest GHG abatement cost in all scenarios considered.

Sensitivity analysis





Objective function variability over input uncertainty

Parameter influence on the objective function variation

Key messages

- A carbon-neutral "baseline" chemical sector is possible with available resources by 2050
- Biomass residues could be an important feedstock to achieve this goal, especially considering the criticism that first generation feedstocks have regarding competition with food.
- Green hydrogen from biomass (i.e. biomethane pyrolysis and biomass residues gasification) have been found not to be cost competitive for meeting climate neutrality in the chemicals sector.
  - Biomethane preferable option for the marine and freight subsectors of the transport sector, and for power production predominantly in Combined Cycle Gas Turbine Power Plants
- The CO_2 price to support renewable chemicals represented by the marginal unit of GHG abatement is too high compared to current CO_2 price in Europe.
- The uncertainty of biomass residue supply has the greatest impact on GHG abatement and abatement costs for 2050.

Key messages cont…

- As acreage declines, renewable hydrogen (from electricity rather than biomass) plays an important role.
- Parameter development in future subject to uncertainty and whose uncertainty could be eliminated are investment costs, the corresponding interest rate, nitrous oxide emissions during feedstocks cultivation ad CO_2 sequestration into final products.
- Closed-loop material flows will be important for climate neutrality and reduction of primary production.

Thank you!

POSTER SESSIONS

SESSION I

SUPPLY MANAGEMENT AND SYSTEM EVALUATION

Christoph Siol, University of Leipzig/Deutsches Biomasseforschungszentrum

Assessing new technologies for the circular bioeconomy with combined environmental and economic

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The utilization of biogenic residues and by-products has become a major topic in the current scientific and political discourse about the bio-economy (BE), since it has great potential encountering multiple sustainability issues of the BE, e.g. food competitions and land use changes, while increasing the resource potential and letting bio-based value-chains become more efficient. Especially the utilization of straw, animal manures and residual forest wood has been highlighted by several authors for the ability of producing various types of bio-fuels, bio-products and bioenergy.

However, removing and utilizing residual biomasses from agriculture and forestry decreases the soil organic carbon and nutrition content, which consequently may has to be compensated by either fertilization, compost incorporation or an adaption of crop rotations. Current life-cycle assessments (LCA) largely fail to consider the various implications on the performance of agriculture and forestry, resulting from the utilization of residual biomasses. The aim of this thesis is to fill this gap by elaborating an assessment framework with appropriate indicators assessing the environmental and economic effects of different technological pathways for the utilization of agricultural and forestry residues and by-products, especially focusing on their cascading use and feedback effects when secondary by-products, e.g. digestate or biochar, return on the cultivation area for soil improvement.

For this purpose, the first publication will identify possible technological pathways for the utilization of European crop residues, animal manures and residual forest wood, followed by a systematic literature review on life-cycle assessments assessing utilization technologies for the biomasses mentioned above. Therefore, the 'Web of Science' database is used by searching for distinct keywords related to LCA in the combination with the mentioned biomasses. Subsequently, the synthesis of the considered literature will reveal, whether or how current life-cycle assessments deal with changes in soil organic carbon and nutrition contents and the implications on agricultural and forestry performance, e.g. adaption of crop rotations, fertilizer compensation, withdrawal rates and yields. Additionally, the quantitative results of the considered LCA-studies are summarized for different indicators and impact categories.

This first publication forms the basis for the further studies within this thesis, where an assessment framework for environmental and economic sustainability assessment is elaborated and subsequently applied for regional case studies and different technological pathways. The main added value of this thesis is to investigate the limits and trade-offs of a sustainable utilization of crop residues, animal manures and residual forest wood, also supporting resource potential monitoring programs in term of the sustainably mobilizable potential of these biomasses.

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13TH/14TH SEPTEMBER 2021, KARLSRUHE

Assessing new technologies for the circular bio-economy with combined environmental and economic LCSA

Christoph Siol, German Biomass Research Centre (DBFZ) gGmbH [1], Leipzig

Exposé → 1. Paper: Literature review → 2. Paper: Assessment framework → 3. Paper: Application and validation

SHORT ABSTRACT

Removing biogenic residues from agriculture and forestry can cause various sustainability issues, e.g. decreasing soil organic carbon and nutrition contents, increasing soil erosion and crop yield losses due to an decline of organic matter. On the other hand, utilizing the these resource potentials to produce bioenergy or bio-products could play an important role in climate change mitigation and some technologies even cause positive feedback effects on soil fertility when by-products are reincorporated into the soil.
Therefore, it is necessary to assess new utilization technologies regarding to their effects on sustainable agriculture and forestry and to identify possible benefits, limitations and trade-offs. This thesis aims to develop an assessment framework with appropriate indicators assessing the environmental and economic effects of different technological utilization pathways in the context of a circular bio-economy.

FOCUSSED BIOMASSES

Crop residues | Forest residues | Animal manure

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Figure 2: Focussed feedstocks for the technology assessment

MAIN RESEARCH QUESTION

Which technologies utilizing agricultural and forestry residues contribute to a sustainable development without compromising soil functions and fertility?

GOALS

- Development of an assessment framework for technologies of the circular bio-economy
- Giving recommendations about which utilization pathways are most beneficial in terms of environmental and economic sustainability
- Optimizing technological pathways through the identification of problematic processes
- Identifying the benefits, trade-offs and limitations of an increased or extended utilization of residues from agriculture and forestry
- And to assess how the circular bioeconomy contributes to the German energy transition and the SDG's

1st publication
- Systematic review of current LCA studies
- Identification of technologies and system boundaries

2nd publication
- Identification of methods and indicators
- Development of an assessment framework

3rd publication
- Data collection
- Application of the assessment framework

Figure 3: Structure of the thesis

Take a picture and stay informed

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[1] German Biomass Research Center (DBFZ) gGmbH, bioenergy systems, applied sustainability assessment, Leipzig

Jonas Miederer, Friedrich-Alexander-University Erlangen/Nürnberg

Enhancement of catalytic direct methanation for application in wastewater treatment plants

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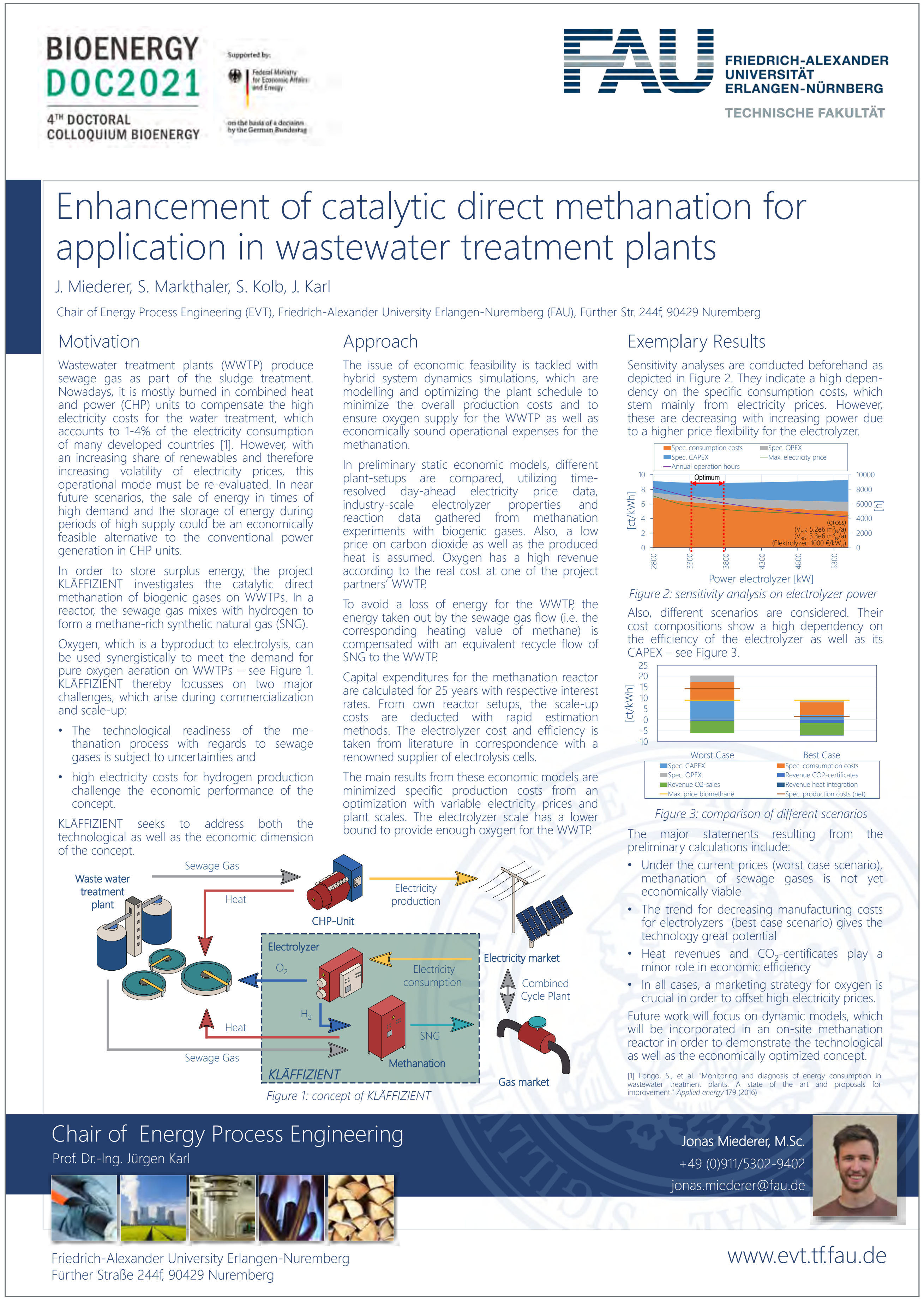
Sewage gas consists of approx. 2/3 methane. With its composition, it cannot be fed into the natural gas grid of the Federal Republic of Germany. As a measure for sector coupling, the BMWi-funded project KLÄFFIZIENT therefore investigates the catalytic direct methanation of sewage gas and hydrogen from electrolysis of volatile renewable electricity. The reaction product can be injected into the gas grid as synthetic natural gas (SNG). Besides, the concept offers numerous synergies such as the potential on-site consumption of the oxygen produced during electrolysis or the elimination of a CO_2 capture prior to methanation. However, major challenges arise regarding both, the economic and technological feasibility. Specifically,

- the technological readiness of the methanation reactor with regards to sewage gases is subject to uncertainties,
- and high electricity costs for hydrogen production challenge the economic performance.

KLÄFFIZIENT seeks to address the technological and economic dimension. For this purpose, investigations on the technical implementation help to understand load variation behavior of the reaction and also to address potential catalyst degradations. Direct methanation is utilized here to benefit from enhanced reaction control due to high inert gas content in the reactant. Further, the project tackles the economic feasibility of the concept, particularly taking into account load-optimized hydrogen production strategies. Here, using hybrid system dynamics simulations and optimizations as well as predictive control strategies for the plant allows economically sound operations. Considering technical and site-specific parameters as well as time-resolved market-data, this helps to rapidly figure the best point of operation.

In preliminary economic models, relevant parameters such as the maximum electricity price and the plant scale were investigated and optimized using historical energy price data, literature and experimental results. The results imply that direct methanation at wastewater treatment plants can be a reasonable technology for future scenarios in order to meet peak loads in an increasingly volatile electricity market. In the next steps, these results will be validated in a dynamic model and extended with e.g. gas storage facilities to investigate costs and to figure out viable operation strategies. Nevertheless, additional research is required to establish direct methanation on wastewater treatment plants.

Therefore, upcoming work will investigate characteristic impurities of sewage gases on their effect on catalyst degradation with regard to substances like siloxanes and sulfur components. Furthermore, the economic considerations will be incorporated into a predictive control system, which will be set up at a demonstration reactor on a sewage treatment plant with a capacity of 1.4 million residents. Long-term field-test series will demonstrate both, the intelligent control strategy and the resilience of direct methanation.



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FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

Enhancement of catalytic direct methanation for application in wastewater treatment plants

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Motivation

Wastewater treatment plants (WWTP) produce sewage gas as part of the sludge treatment. Nowadays, it is mostly burned in combined heat and power (CHP) units to compensate the high electricity costs for the water treatment, which accounts to 1-4% of the electricity consumption of many developed countries [1]. However, with an increasing share of renewables and therefore increasing volatility of electricity prices, this operational mode must be re-evaluated. In near future scenarios, the sale of energy in times of high demand and the storage of energy during periods of high supply could be an economically feasible alternative to the conventional power generation in CHP units.

In order to store surplus energy, the project KLÄFFIZIENT investigates the catalytic direct methanation of biogenic gases on WWTPs. In a reactor, the sewage gas mixes with hydrogen to form a methane-rich synthetic natural gas (SNG).

Oxygen, which is a byproduct to electrolysis, can be used synergistically to meet the demand for pure oxygen aeration on WWTPs – see Figure 1. KLÄFFIZIENT thereby focusses on two major challenges, which arise during commercialization and scale-up:

- The technological readiness of the methanation process with regards to sewage gases is subject to uncertainties and
- high electricity costs for hydrogen production challenge the economic performance of the concept.

KLÄFFIZIENT seeks to address both the technological as well as the economic dimension of the concept.

Figure 1: concept of KLÄFFIZIENT

Approach

The issue of economic feasibility is tackled with hybrid system dynamics simulations, which are modelling and optimizing the plant schedule to minimize the overall production costs and to ensure oxygen supply for the WWTP as well as economically sound operational expenses for the methanation.

In preliminary static economic models, different plant-setups are compared, utilizing time-resolved day-ahead electricity price data, industry-scale electrolyzer properties and reaction data gathered from methanation experiments with biogenic gases. Also, a low price on carbon dioxide as well as the produced heat is assumed. Oxygen has a high revenue according to the real cost at one of the project partners' WWTP.

To avoid a loss of energy for the WWTP, the energy taken out by the sewage gas flow (i.e. the corresponding heating value of methane) is compensated with an equivalent recycle flow of SNG to the WWTP.

Capital expenditures for the methanation reactor are calculated for 25 years with respective interest rates. From own reactor setups, the scale-up costs are deducted with rapid estimation methods. The electrolyzer cost and efficiency is taken from literature in correspondence with a renowned supplier of electrolysis cells.

The main results from these economic models are minimized specific production costs from an optimization with variable electricity prices and plant scales. The electrolyzer scale has a lower bound to provide enough oxygen for the WWTP.

Exemplary Results

Sensitivity analyses are conducted beforehand as depicted in Figure 2. They indicate a high dependency on the specific consumption costs, which stem mainly from electricity prices. However, these are decreasing with increasing power due to a higher price flexibility for the electrolyzer.

Figure 2: sensitivity analysis on electrolyzer power

Also, different scenarios are considered. Their cost compositions show a high dependency on the efficiency of the electrolyzer as well as its CAPEX – see Figure 3.

Figure 3: comparison of different scenarios

The major statements resulting from the preliminary calculations include:

- Under the current prices (worst case scenario), methanation of sewage gases is not yet economically viable
- The trend for decreasing manufacturing costs for electrolyzers (best case scenario) gives the technology great potential
- Heat revenues and CO_2-certificates play a minor role in economic efficiency
- In all cases, a marketing strategy for oxygen is crucial in order to offset high electricity prices.

Future work will focus on dynamic models, which will be incorporated in an on-site methanation reactor in order to demonstrate the technological as well as the economically optimized concept.

[1] Longo, S., et al. "Monitoring and diagnosis of energy consumption in wastewater treatment plants. A state of the art and proposals for improvement." *Applied energy* 179 (2016)

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Lilli Sophia Röder, Ruhr University of Bochum

Systematic analysis of the theoretical demand side management potential in biorefineries

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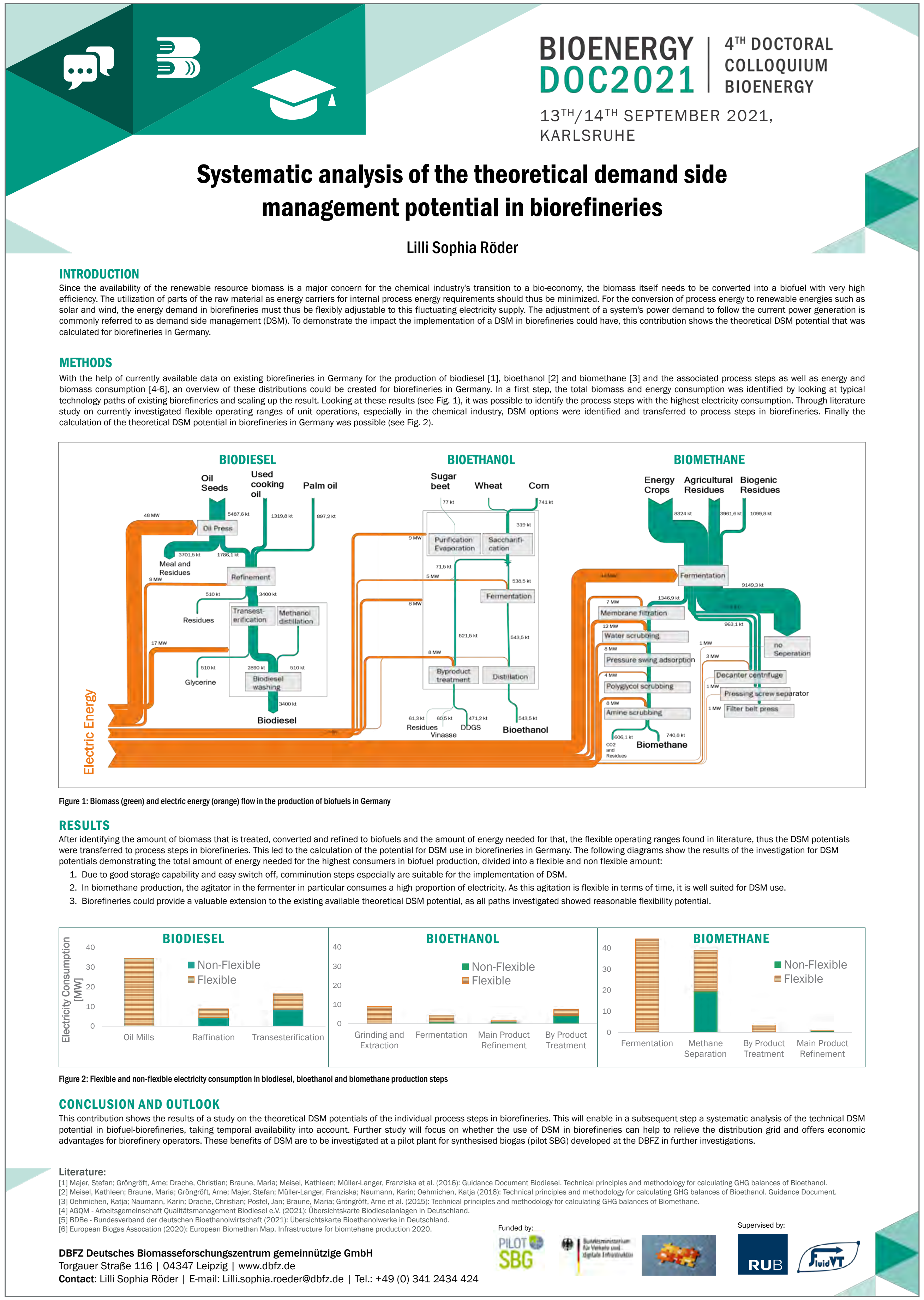
Strategies such as the European Green Deal aim to transform the economy into a resource-efficient system. Part of the solutions required for this is the conversion of economic sectors dependent on fossil fuels to renewable energy (RE) sources. Since the availability of the renewable resource biomass is a major concern for the chemical industry‘s transition to a bio-economy, the biomass itself is to be converted with very high efficiency. The utilization of parts of the raw material as energy carriers for internal process energy requirements should thus be minimized. For the conversion of process energy to RE such as solar and wind, the energy demand of biomass processing must flexibly be adjustable to the fluctuating electricity supply from volatile RE. The adjustment of a system‘s power demand to follow the current power generation is commonly referred to as demand side management (DSM).

This contribution shows the results of a recent DSM study on the implementation of a DSM in biofuel biorefineries. The first step was to identify possible flexibility potentials of the individual process steps in biorefineries. Using currently available data on flexibility options, especially in the chemical industry, DSM options were identified and transferred to process steps in biorefineries. These findings allow an assessment of the potential for different process units of biorefinery systems concerning the quantitative adaptability of the electricity load. This enables a systematic analysis of the theoretical DSM potential in biofuel-biorefineries. Further investigations will focus on whether the use of DSM in this area relieves the distribution grid and offers economic advantages for biorefinery operators. Furthermore, it is important to investigate whether the greenhouse gas balance of the entire plant can be improved without significant losses in product quality or quantity.



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Systematic analysis of the theoretical demand side management potential in biorefineries

Lilli Sophia Röder

INTRODUCTION

Since the availability of the renewable resource biomass is a major concern for the chemical industry's transition to a bio-economy, the biomass itself needs to be converted into a biofuel with very high efficiency. The utilization of parts of the raw material as energy carriers for internal process energy requirements should thus be minimized. For the conversion of process energy to renewable energies such as solar and wind, the energy demand in biorefineries must thus be flexibly adjustable to this fluctuating electricity supply. The adjustment of a system's power demand to follow the current power generation is commonly referred to as demand side management (DSM). To demonstrate the impact the implementation of a DSM in biorefineries could have, this contribution shows the theoretical DSM potential that was calculated for biorefineries in Germany.

METHODS

With the help of currently available data on existing biorefineries in Germany for the production of biodiesel [1], bioethanol [2] and biomethane [3] and the associated process steps as well as energy and biomass consumption [4-6], an overview of these distributions could be created for biorefineries in Germany. In a first step, the total biomass and energy consumption was identified by looking at typical technology paths of existing biorefineries and scaling up the result. Looking at these results (see Fig. 1), it was possible to identify the process steps with the highest electricity consumption. Through literature study on currently investigated flexible operating ranges of unit operations, especially in the chemical industry, DSM options were identified and transferred to process steps in biorefineries. Finally the calculation of the theoretical DSM potential in biorefineries in Germany was possible (see Fig. 2).

Figure 1: Biomass (green) and electric energy (orange) flow in the production of biofuels in Germany

RESULTS

After identifying the amount of biomass that is treated, converted and refined to biofuels and the amount of energy needed for that, the flexible operating ranges found in literature, thus the DSM potentials were transferred to process steps in biorefineries. This led to the calculation of the potential for DSM use in biorefineries in Germany. The following diagrams show the results of the investigation for DSM potentials demonstrating the total amount of energy needed for the highest consumers in biofuel production, divided into a flexible and non flexible amount:

1. Due to good storage capability and easy switch off, comminution steps especially are suitable for the implementation of DSM.
2. In biomethane production, the agitator in the fermenter in particular consumes a high proportion of electricity. As this agitation is flexible in terms of time, it is well suited for DSM use.
3. Biorefineries could provide a valuable extension to the existing available theoretical DSM potential, as all paths investigated showed reasonable flexibility potential.

Figure 2: Flexible and non-flexible electricity consumption in biodiesel, bioethanol and biomethane production steps

CONCLUSION AND OUTLOOK

This contribution shows the results of a study on the theoretical DSM potentials of the individual process steps in biorefineries. This will enable in a subsequent step a systematic analysis of the technical DSM potential in biofuel-biorefineries, taking temporal availability into account. Further study will focus on whether the use of DSM in biorefineries can help to relieve the distribution grid and offers economic advantages for biorefinery operators. These benefits of DSM are to be investigated at a pilot plant for synthesised biogas (pilot SBG) developed at the DBFZ in further investigations.

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Tom Karras, University of Leipzig/Deutsches Biomasseforschungszentrum

Supply costs of biogenic residues – Development of a regionalized supply cost model for Germany

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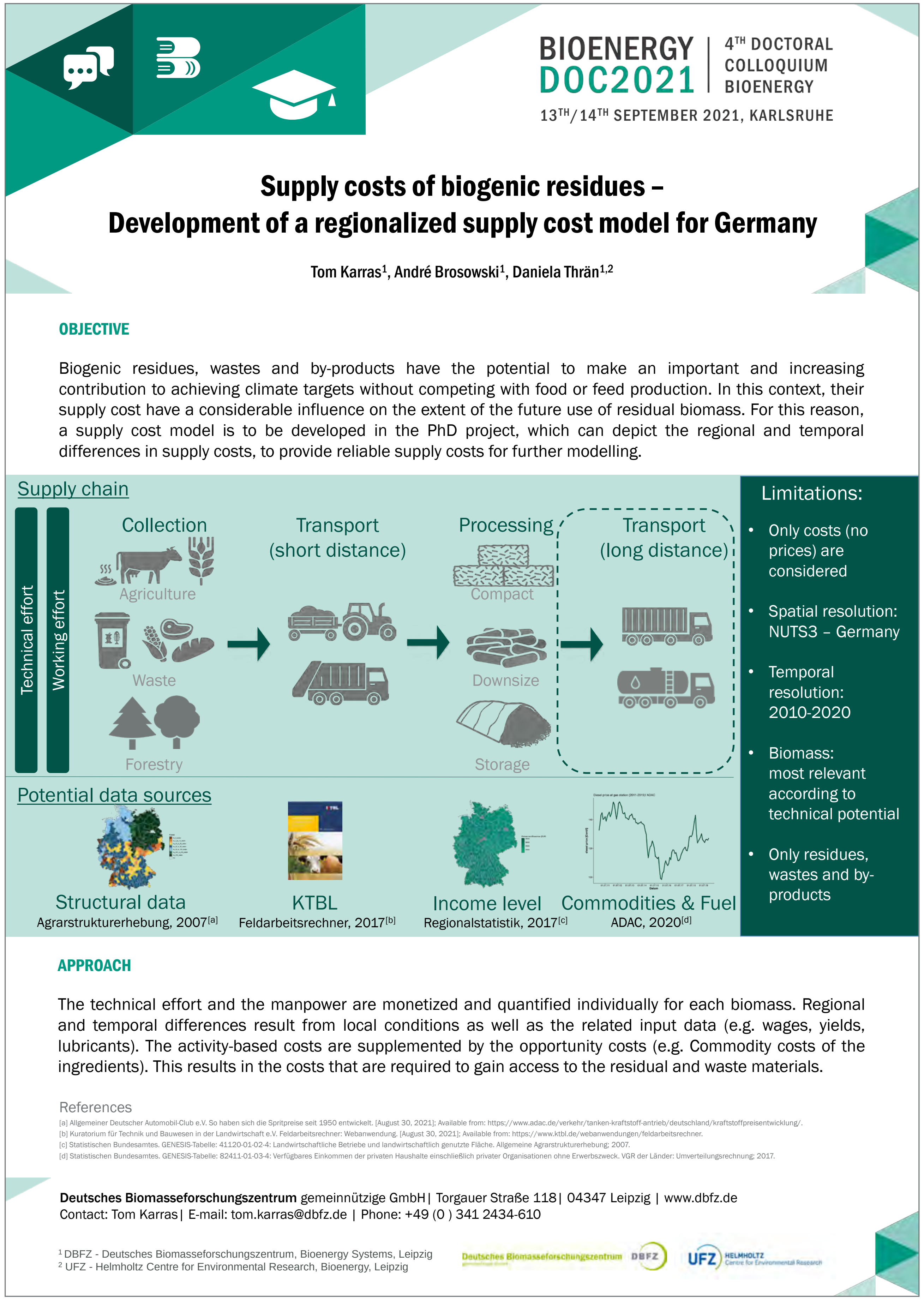
Biogenic residues, wastes and by-products have the potential to make an important and increasing contribution to achieving climate targets without competing with food or feed production. In this context, the supply cost have a considerable influence on the extent of the future use of residual biomass. In the first step of the PhD project, the costs and prices used in techno-economic models, for biomass supply were assessed on European level in a review. It showed that the costs or prices are not always available in a satisfactory quality. For this reason, the second step of the PhD project aims at determining the supply costs for different biogenic residues on a regional level with a supply cost model, the design of which will be presented during the PhD colloquium 2021. The model should help to answer the research question: "What regional differences can be observed for the supply costs of biogenic residues in Germany?" The spatial context is the NUTS3-level in Germany. The model will focus on the road-side supply costs for the most relevant biogenic residues, wastes and by-products. The supply costs will be calculated individually for each regarded biomass in the model. For this purpose, the residual specific supply chains must be investigated and defined. The approach of "Activity Based Costing" will be used, to monetize the efforts of biomass supply. Therefore, the individual processes along the supply chain are translated into work and technical effort and needs to be quantified. The model output will be visualized in maps that represent the regional distribution of supply cost.

The basic modeling approaches will be presented during the doctoral colloquium. Therefore, the material flows and supply chains of the considered biogenic residues will be illustrated. Furthermore, the data sets used to quantify and monetize the supply efforts will be specified. These preliminary ideas on the supply cost model can be used to discuss the model design during the doctoral colloquium.



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Supply costs of biogenic residues – Development of a regionalized supply cost model for Germany

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OBJECTIVE

Biogenic residues, wastes and by-products have the potential to make an important and increasing contribution to achieving climate targets without competing with food or feed production. In this context, their supply cost have a considerable influence on the extent of the future use of residual biomass. For this reason, a supply cost model is to be developed in the PhD project, which can depict the regional and temporal differences in supply costs, to provide reliable supply costs for further modelling.

Supply chain

Potential data sources

Structural data
Agrarstrukturerhebung, 2007[a]

KTBL
Feldarbeitsrechner, 2017[b]

Income level
Regionalstatistik, 2017[c]

Commodities & Fuel
ADAC, 2020[d]

Limitations:

- Only costs (no prices) are considered
- Spatial resolution: NUTS3 – Germany
- Temporal resolution: 2010-2020
- Biomass: most relevant according to technical potential
- Only residues, wastes and by-products

APPROACH

The technical effort and the manpower are monetized and quantified individually for each biomass. Regional and temporal differences result from local conditions as well as the related input data (e.g. wages, yields, lubricants). The activity-based costs are supplemented by the opportunity costs (e.g. Commodity costs of the ingredients). This results in the costs that are required to gain access to the residual and waste materials.

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Sebastian Foth, University of Rostock

Resource and energy recovery of water care material from the maintenance of water bodies

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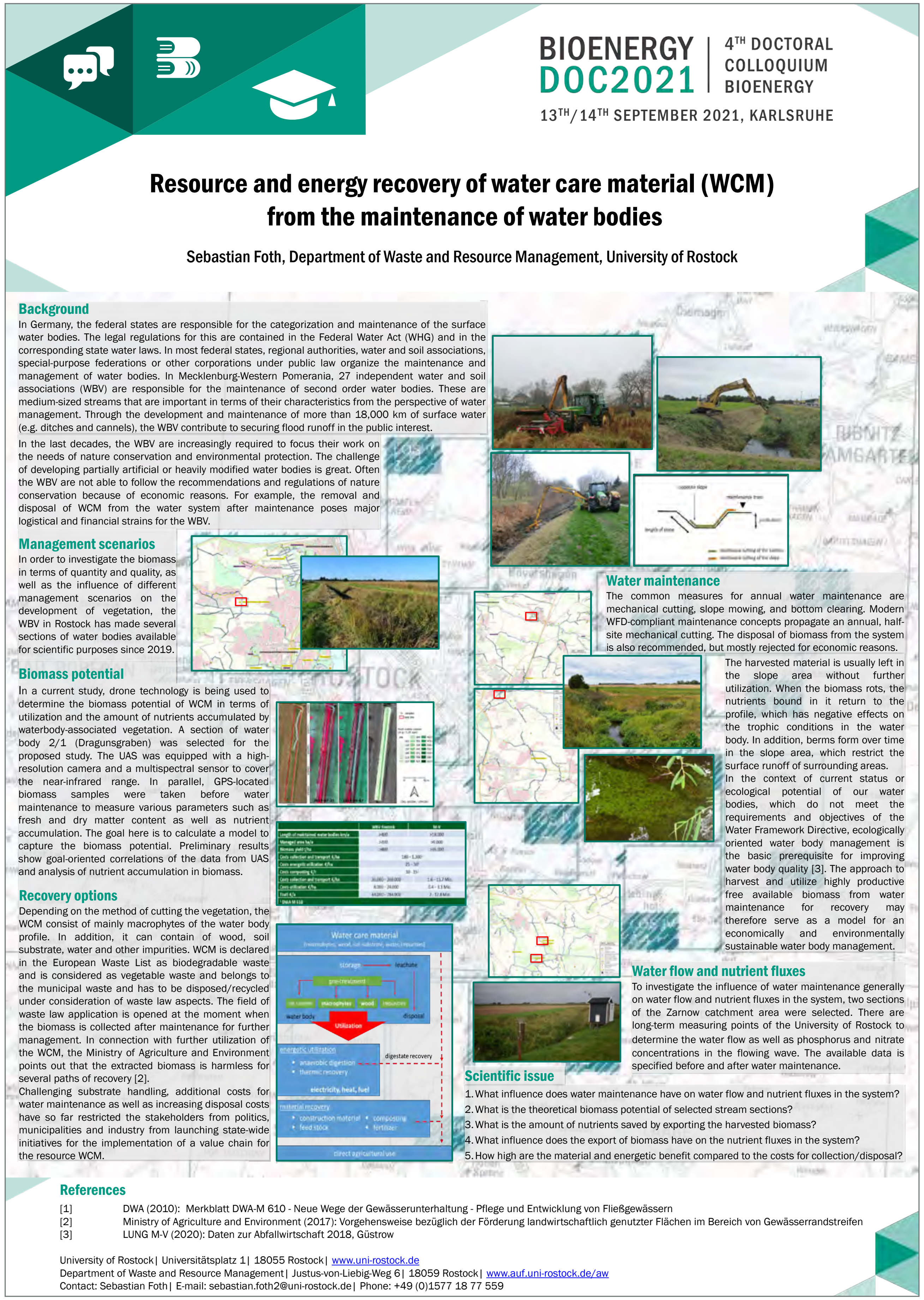
The water and soil associations (WBV) in Mecklenburg-Western Pomerania do important work for flood protection as well as for the management of agricultural land. In the past decade, they have been increasingly required to focus their activities on ecological aspects. The challenge of developing partly artificial, partly underground water bodies in highly manipulated catchment areas is great. Often, they are not able to make the desired/required adaptations to environmental conservation concerns for economic reasons. For example, the removal and disposal of water care material (WCM) from the water system after mowing poses problems for the WBV, since area-wide concepts for the economic management of WCM are missing so far. However, material and energy recovery offer the opportunity to refinance costs incurred for disposal of WCM. Additionally, the nutrient recovery is a valuable addition to efforts to reduce eutrophication in water bodies.



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Resource and energy recovery of water care material (WCM) from the maintenance of water bodies

Sebastian Foth, Department of Waste and Resource Management, University of Rostock

Background

In Germany, the federal states are responsible for the categorization and maintenance of the surface water bodies. The legal regulations for this are contained in the Federal Water Act (WHG) and in the corresponding state water laws. In most federal states, regional authorities, water and soil associations, special-purpose federations or other corporations under public law organize the maintenance and management of water bodies. In Mecklenburg-Western Pomerania, 27 independent water and soil associations (WBV) are responsible for the maintenance of second order water bodies. These are medium-sized streams that are important in terms of their characteristics from the perspective of water management. Through the development and maintenance of more than 18,000 km of surface water (e.g. ditches and cannels), the WBV contribute to securing flood runoff in the public interest.

In the last decades, the WBV are increasingly required to focus their work on the needs of nature conservation and environmental protection. The challenge of developing partially artificial or heavily modified water bodies is great. Often the WBV are not able to follow the recommendations and regulations of nature conservation because of economic reasons. For example, the removal and disposal of WCM from the water system after maintenance poses major logistical and financial strains for the WBV.

Management scenarios

In order to investigate the biomass in terms of quantity and quality, as well as the influence of different management scenarios on the development of vegetation, the WBV in Rostock has made several sections of water bodies available for scientific purposes since 2019.

Biomass potential

In a current study, drone technology is being used to determine the biomass potential of WCM in terms of utilization and the amount of nutrients accumulated by waterbody-associated vegetation. A section of water body 2/1 (Dragunsgraben) was selected for the proposed study. The UAS was equipped with a high-resolution camera and a multispectral sensor to cover the near-infrared range. In parallel, GPS-located biomass samples were taken before water maintenance to measure various parameters such as fresh and dry matter content as well as nutrient accumulation. The goal here is to calculate a model to capture the biomass potential. Preliminary results show goal-oriented correlations of the data from UAS and analysis of nutrient accumulation in biomass.

Recovery options

Depending on the method of cutting the vegetation, the WCM consist of mainly macrophytes of the water body profile. In addition, it can contain of wood, soil substrate, water and other impurities. WCM is declared in the European Waste List as biodegradable waste and is considered as vegetable waste and belongs to the municipal waste and has to be disposed/recycled under consideration of waste law aspects. The field of waste law application is opened at the moment when the biomass is collected after maintenance for further management. In connection with further utilization of the WCM, the Ministry of Agriculture and Environment points out that the extracted biomass is harmless for several paths of recovery [2].
Challenging substrate handling, additional costs for water maintenance as well as increasing disposal costs have so far restricted the stakeholders from politics, municipalities and industry from launching state-wide initiatives for the implementation of a value chain for the resource WCM.

Water maintenance

The common measures for annual water maintenance are mechanical cutting, slope mowing, and bottom clearing. Modern WFD-compliant maintenance concepts propagate an annual, half-site mechanical cutting. The disposal of biomass from the system is also recommended, but mostly rejected for economic reasons.

The harvested material is usually left in the slope area without further utilization. When the biomass rots, the nutrients bound in it return to the profile, which has negative effects on the trophic conditions in the water body. In addition, berms form over time in the slope area, which restrict the surface runoff of surrounding areas.
In the context of current status or ecological potential of our water bodies, which do not meet the requirements and objectives of the Water Framework Directive, ecologically oriented water body management is the basic prerequisite for improving water body quality [3]. The approach to harvest and utilize highly productive free available biomass from water maintenance for recovery may therefore serve as a model for an economically and environmentally sustainable water body management.

Water flow and nutrient fluxes

To investigate the influence of water maintenance generally on water flow and nutrient fluxes in the system, two sections of the Zarnow catchment area were selected. There are long-term measuring points of the University of Rostock to determine the water flow as well as phosphorus and nitrate concentrations in the flowing wave. The available data is specified before and after water maintenance.

Scientific issue

1. What influence does water maintenance have on water flow and nutrient fluxes in the system?
2. What is the theoretical biomass potential of selected stream sections?
3. What is the amount of nutrients saved by exporting the harvested biomass?
4. What influence does the export of biomass have on the nutrient fluxes in the system?
5. How high are the material and energetic benefit compared to the costs for collection/disposal?

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Sören Richter, University of Leipzig/Deutsches Biomasseforschungszentrum

Drivers for a sustainable future bioeconomy in Germany

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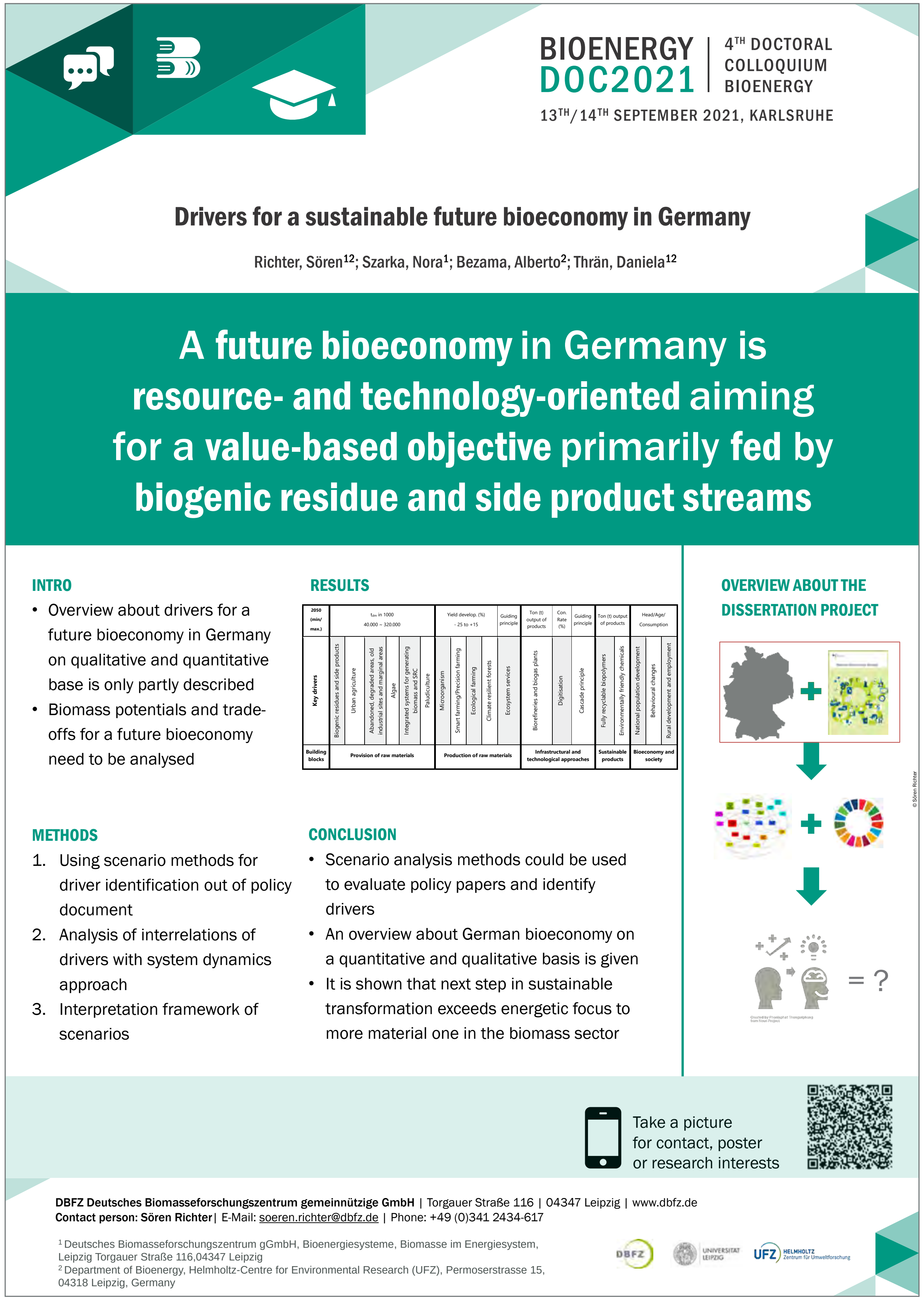
Bioeconomy is seen as beneficial concept for the aim of reaching the Sustainable Development Goals, maintain provision systems for future societies as well as reaching climate neutrality in Germany. Although approaches such as biorefineries or fuels from algae biomass have been developed, the systemic impacts on different value chains when changing the resource base from fossil to biogenic are still very uncertain. Thus study activities need to focus on impacts to the resource base itself and on emerging trade-offs among the various approaches to gain understanding into reducing negative consequences. By investigating the research question of how bioeconomy approaches can support a sustainable development of material and energy flows in Germany until 2050 on a qualitative and quantitative basis, the PhD study will contribute to broadening the knowledge base with insights into possible future developments of material flows. To approach this, the method of scenario analysis is used for the development of bioeconomy scenarios in Germany until the year 2050. Therefore scenario drivers will be composed based on the German National Bioeconomy Strategy 2020. In the following, bioeconomy scenarios are generated in relation to the uncertainty and quality of the data gathered for describing the drivers. By analysing the biogenic material and energy flows with an system dynamics methodology trade-offs and interrelationships between the elaborated drivers of the scenarios will be identified. In the last step of the study the emphasis is on the interpretation and communication of scenarios. This will support the methodological development of the field of scenario interpretation as well as the overall systemic description of a future sustainable bioeconomy in Germany. In the present state a narrative analysis of the German National Bioeconomy Strategy 2020 was conducted and scenario drivers were compiled. In relation to the evaluated narrative, scenario drivers have been described on qualitative and quantitative base. While the qualitative aspects include a general description, the quantifiable data are used to form scenario funnels that describe possible future developments of biogenic material and energy flows. The presentation for the PhD colloquium will give an overview of the methods used and preliminary results from the strategy analysis but the focus will be on the methodology of scenario generation and system dynamics. This will provide an overview of central drivers of a future bioeconomy in Germany as well as an outlook on possible interrelationships of the drivers themselves. Describing possible future pathways supports the process of creating a sustainable bioeconomy and a more sustainable means of living for societies as a whole.

References/Articles to be submitted:

Working Title: A scenario framework: Key drivers for a sustainable bioeconomy based on the German National Bioeconomy Strategy 2020



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Drivers for a sustainable future bioeconomy in Germany

Richter, Sören[1][2]; Szarka, Nora[1]; Bezama, Alberto[2]; Thrän, Daniela[1][2]

A future bioeconomy in Germany is resource- and technology-oriented aiming for a value-based objective primarily fed by biogenic residue and side product streams

INTRO

- Overview about drivers for a future bioeconomy in Germany on qualitative and quantitative base is only partly described
- Biomass potentials and trade-offs for a future bioeconomy need to be analysed

RESULTS

2050 (min/ max.)	t_{dm} in 1000 40.000 ~ 320.000						Yield develop. (%) - 25 to +15				Guiding principle	Ton (t) output of products	Con. Rate (%)	Guiding principle	Ton (t) output of products		Head/Age/ Consumption		
Key drivers	Biogenic residues and side products	Urban agriculture	Abandoned, degraded areas, old industrial sites and marginal areas	Algae	Integrated systems for generating biomass and SRC	Paludiculture	Microorganism	Smart farming/Precision farming	Ecological farming	Climate resilient forests	Ecosystem services	Biorefineries and biogas plants	Digitisation	Cascade principle	Fully recyclable biopolymers	Environmentally friendly chemicals	National population development	Behavioural changes	Rural development and employment
Building blocks	**Provision of raw materials**						**Production of raw materials**					**Infrastructural and technological approaches**			**Sustainable products**		**Bioeconomy and society**		

OVERVIEW ABOUT THE DISSERTATION PROJECT

METHODS

1. Using scenario methods for driver identification out of policy document
2. Analysis of interrelations of drivers with system dynamics approach
3. Interpretation framework of scenarios

CONCLUSION

- Scenario analysis methods could be used to evaluate policy papers and identify drivers
- An overview about German bioeconomy on a quantitative and qualitative basis is given
- It is shown that next step in sustainable transformation exceeds energetic focus to more material one in the biomass sector

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Martin Dotzauer, University of Leipzig/Deutsches Biomasseforschungszentrum

Empirical greenhouse gas assessment for flexible bioenergy in interaction with the German power sector

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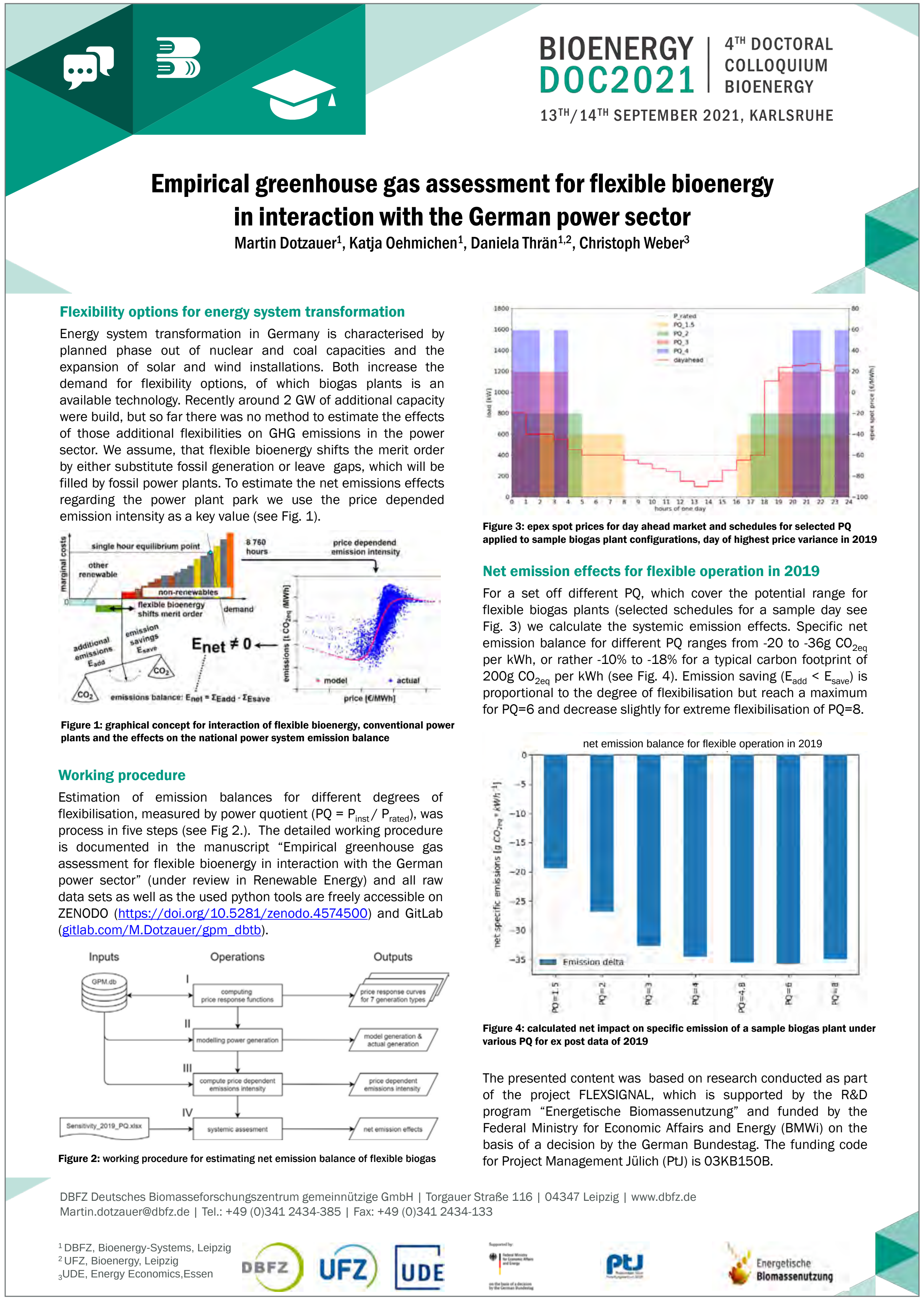
INTRODUCTION:
The renewable energy act (EEG) is a major policy instrument in Germany within the context of the global trend towards an energy transition. Wind and solar power are already the major pillars of renewable power generation and are set to become even more dominant in the future due to their low electricity generation costs and expansion potentials. At the same time, dispatchable power plants are being substantially phased out. Both trends heighten the demand for flexible options to balance increasing fluctuations in the residual load. Within the EEG, special incentives for flexible bioenergy generation aim to provide flexible bioenergy to counterbalance residual load. The provision of flexible bioenergy also contributes to the reduction of greenhouse gas emissions (GHG), a major goal of the energy transition. However, there is currently no assessment approach for quantifying the systemic GHG impacts of flexible operation of bioenergy plants.

APPROACH AND METHODS:
Based on the merit order concept, we develop an empirical approach to systemically assess the GHG emissions impact for electricity generated by flexible bioenergy plants. We estimate price response functions using the historical data of market prices and feed-in time series for the different forms of dispatchable non-renewable power generation (NRPG). By calculating the expected generation from NRPG based on these functions, and using specific emission factors, we are able to estimate the net impact for flexible versus continuous bioenergy generation.

RESULTS:
We apply the new approach to a sample biogas plant setup in order to obtain net emission reductions for flexible power generation in 2019. We place all raw data in an SQLite database. The calculation tools are written in Python and freely accessible on ZENODO and GitLab.
We calculate the specific decrease in emissions for selected flexible operation modes. The net impact ranges from -20 to -36 g CO_2eq per kWh, which is equivalent to a benefit of 10 % and 18 % respectively for an average carbon footprint of 200 g CO_2eq per kWh. In short, the shift to a flexible operation mode increases power generation during times of high prices and high emissions. Power generation decreases during periods of lower prices and emissions. Hence power generation replaced by biogas plants is more emission intensive than NRDG, which is filling the gaps.

CONCLUSION:
The proposed approach for an empirical assessment of the impact of GHG emissions from flexible bioenergy operation is based on a detailed analysis of power market data and thus provides empirically founded estimates.



Empirical greenhouse gas assessment for flexible bioenergy in interaction with the German power sector

Martin Dotzauer[1], Katja Oehmichen[1], Daniela Thrän[1,2], Christoph Weber[3]

Flexibility options for energy system transformation

Energy system transformation in Germany is characterised by planned phase out of nuclear and coal capacities and the expansion of solar and wind installations. Both increase the demand for flexibility options, of which biogas plants is an available technology. Recently around 2 GW of additional capacity were build, but so far there was no method to estimate the effects of those additional flexibilities on GHG emissions in the power sector. We assume, that flexible bioenergy shifts the merit order by either substitute fossil generation or leave gaps, which will be filled by fossil power plants. To estimate the net emissions effects regarding the power plant park we use the price depended emission intensity as a key value (see Fig. 1).

Figure 1: graphical concept for interaction of flexible bioenergy, conventional power plants and the effects on the national power system emission balance

Working procedure

Estimation of emission balances for different degrees of flexibilisation, measured by power quotient ($PQ = P_{inst} / P_{rated}$), was process in five steps (see Fig 2.). The detailed working procedure is documented in the manuscript "Empirical greenhouse gas assessment for flexible bioenergy in interaction with the German power sector" (under review in Renewable Energy) and all raw data sets as well as the used python tools are freely accessible on ZENODO (https://doi.org/10.5281/zenodo.4574500) and GitLab (gitlab.com/M.Dotzauer/gpm_dbtb).

Figure 2: working procedure for estimating net emission balance of flexible biogas

Figure 3: epex spot prices for day ahead market and schedules for selected PQ applied to sample biogas plant configurations, day of highest price variance in 2019

Net emission effects for flexible operation in 2019

For a set off different PQ, which cover the potential range for flexible biogas plants (selected schedules for a sample day see Fig. 3) we calculate the systemic emission effects. Specific net emission balance for different PQ ranges from -20 to -36g CO_{2eq} per kWh, or rather -10% to -18% for a typical carbon footprint of 200g CO_{2eq} per kWh (see Fig. 4). Emission saving ($E_{add} < E_{save}$) is proportional to the degree of flexibilisation but reach a maximum for PQ=6 and decrease slightly for extreme flexibilisation of PQ=8.

Figure 4: calculated net impact on specific emission of a sample biogas plant under various PQ for ex post data of 2019

The presented content was based on research conducted as part of the project FLEXSIGNAL, which is supported by the R&D program "Energetische Biomassenutzung" and funded by the Federal Ministry for Economic Affairs and Energy (BMWi) on the basis of a decision by the German Bundestag. The funding code for Project Management Jülich (PtJ) is 03KB150B.

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Technical and economic evaluation of follow-up concepts for agricultural biogas plants

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Introduction: In the EEG 2000, a minimum remuneration for biogas plants (BGP) was stipulated for a period of 20 years, which currently leads to the fact that the support tariff is continuously expiring. Further operation of existing BGPs should be analyzed regarding the aspects technical feasibility and economic efficiency. Operators face the challenge of having to make highly complex decisions about follow-up investments. Within the frame of this PhD thesis, an evaluation of the value of investment decisions for agricultural biogas plants with the different methods (net present value method and real options approach) based on a simulation model is aimed to solve these valuation problems for previously selected follow-up concepts.

Approach and methods: A combined technical and economic analysis is carried out with the help of a simulation model. Starting with cash-flow models of basic biogas plants of different sizes, the effects of individual revenue and cost factors on the economic viability are to be determined. Based on this, the changes necessary for the implementation of follow-up concepts will be analyzed. Different evaluation methods for the evaluation of the investment decisions are to be used. The fundamental applicability of the real options approach for the evaluation of investment decisions of BGPs will be examined.

Interim Results: Different follow-up concepts especially those that are expected to require a high level of investment like flexibilisation of the power production and gas treatment with the possibility of CNG/LNG use in the mobility sector were identified and the necessary technological changes examined [1,2]. The simulation model can be divided into several individual modules: plant configuration, cash flows to costs and revenues, and cash flows to financing. Based on this, project-relevant key figures (DSCR) can be determined. It was found that an economical evaluation using the real options approach would make sense due to the „option character“ of the decisions to be made.

Outlook: By using a simulation model and different valuation approaches (net present value method and real options approach), a technical and economic analysis will take place. Through this procedure, different investment decisions for BGPs will be transparently presented and subsequently evaluated. The aim is to carry out a comparative analysis and evaluation of selected follow-up concepts for further operation.

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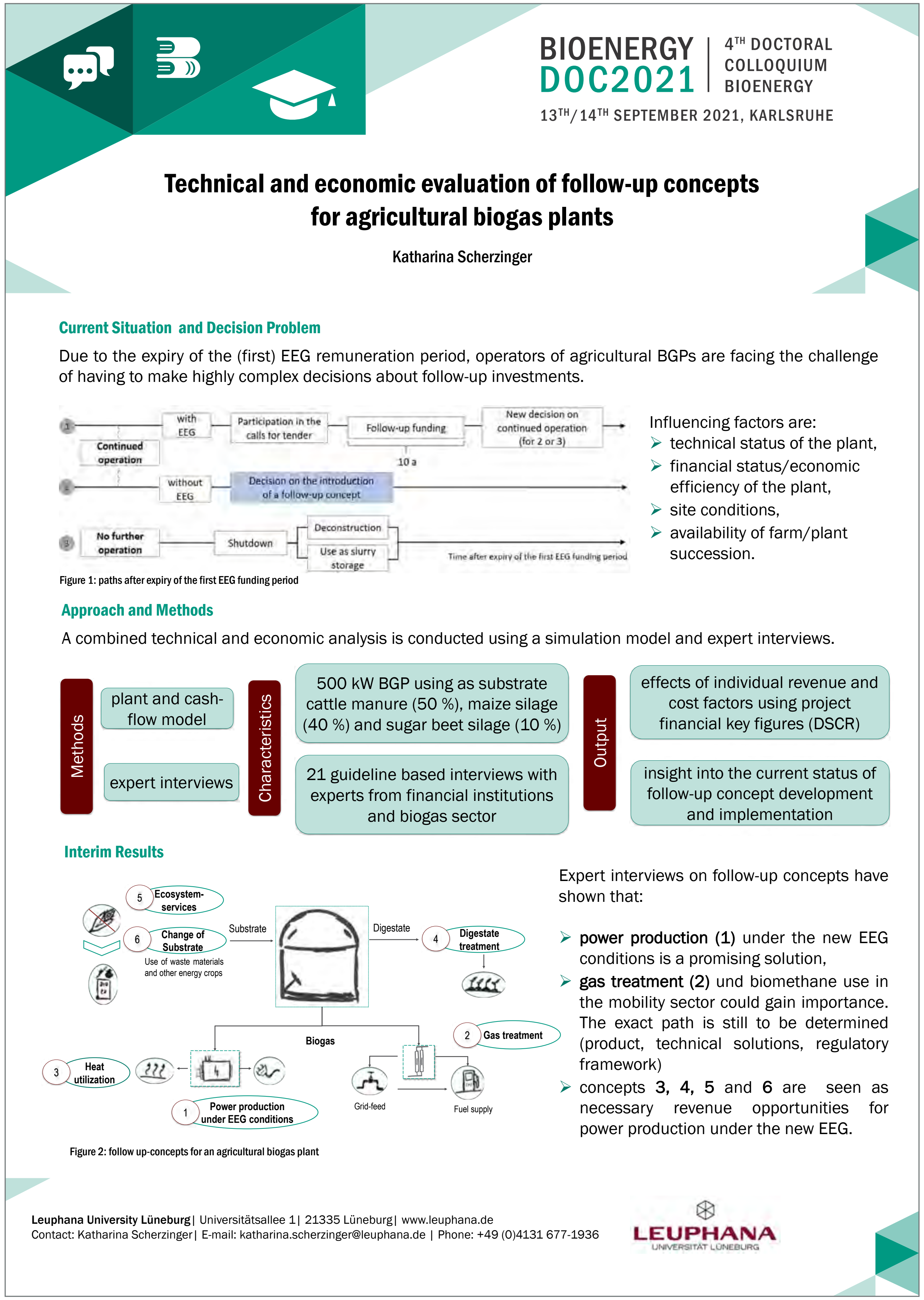

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Technical and economic evaluation of follow-up concepts for agricultural biogas plants

Katharina Scherzinger

Current Situation and Decision Problem

Due to the expiry of the (first) EEG remuneration period, operators of agricultural BGPs are facing the challenge of having to make highly complex decisions about follow-up investments.

Figure 1: paths after expiry of the first EEG funding period

Influencing factors are:

- technical status of the plant,
- financial status/economic efficiency of the plant,
- site conditions,
- availability of farm/plant succession.

Approach and Methods

A combined technical and economic analysis is conducted using a simulation model and expert interviews.

Methods
- plant and cash-flow model
- expert interviews

Characteristics
- 500 kW BGP using as substrate cattle manure (50 %), maize silage (40 %) and sugar beet silage (10 %)
- 21 guideline based interviews with experts from financial institutions and biogas sector

Output
- effects of individual revenue and cost factors using project financial key figures (DSCR)
- insight into the current status of follow-up concept development and implementation

Interim Results

Figure 2: follow up-concepts for an agricultural biogas plant

Expert interviews on follow-up concepts have shown that:

- **power production (1)** under the new EEG conditions is a promising solution,
- **gas treatment (2)** und biomethane use in the mobility sector could gain importance. The exact path is still to be determined (product, technical solutions, regulatory framework)
- concepts **3, 4, 5** and **6** are seen as necessary revenue opportunities for power production under the new EEG.

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How changing diets could reduce climate burdens in the German society

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Introduction: Many studies have analysed the climate impact of vegan, classic vegetarian, and/or reduced meat diets [1], [2]. To date, literature has not evaluated how diet transitions, reflecting personal nutrition preference, affects greenhouse gas emissions (GHGE), primary energy use (PEU), and land use (LU), and costs in Germany. Reflecting the nutrition preference of the German population outlines how holistic diet transitions could decrease climate impacts, compared to business as usual. Further, changing diets affects land availability, and thus, increases the options for GHG abatement within Germany through land-based mitigation strategies.

Approach and methods: To find how diet transitions, reflecting personal nutrition preference, affect GHGE, PEU, and LU in Germany, we define 13 different diets. We find the climate impacts of these diets. Further, we define diet scenarios to reflect interim diet transitions as well as diet choice within the population. In the end, we capture how changing diets affects land availability and increases the options for GHG abatement in Germany. We do so by making a contextualisation using the newly available land from these transitions to compare biomethane production and afforestation. This gives an overview of the overall potential for GHG emission savings between two land-based climate change mitigation strategies.

Results: We find that all defined diets have climate impact savings above 35 % when compared to the Business as Usual (BAU) diet. Additionally, we find that our different diet portfolios reflect a variety of climate impact savings, ranging from 6 % to 76 % in all impact categories and cost savings between 4 % -42 %. As well, we find that using newly available land from the diet transitions for afforestation or biomethane production can sequester a further 1 % to 29 % of GHGE.

Conslusion: Our research indicates that there are various short-term pathways to reduce GHGE with nutrition. For example, through diets which do not completely exclude meat or through our defined scenarios, in which only half the population changes diet. Lastly, further GHGE can be saved through land-based climate change mitigation strategies.

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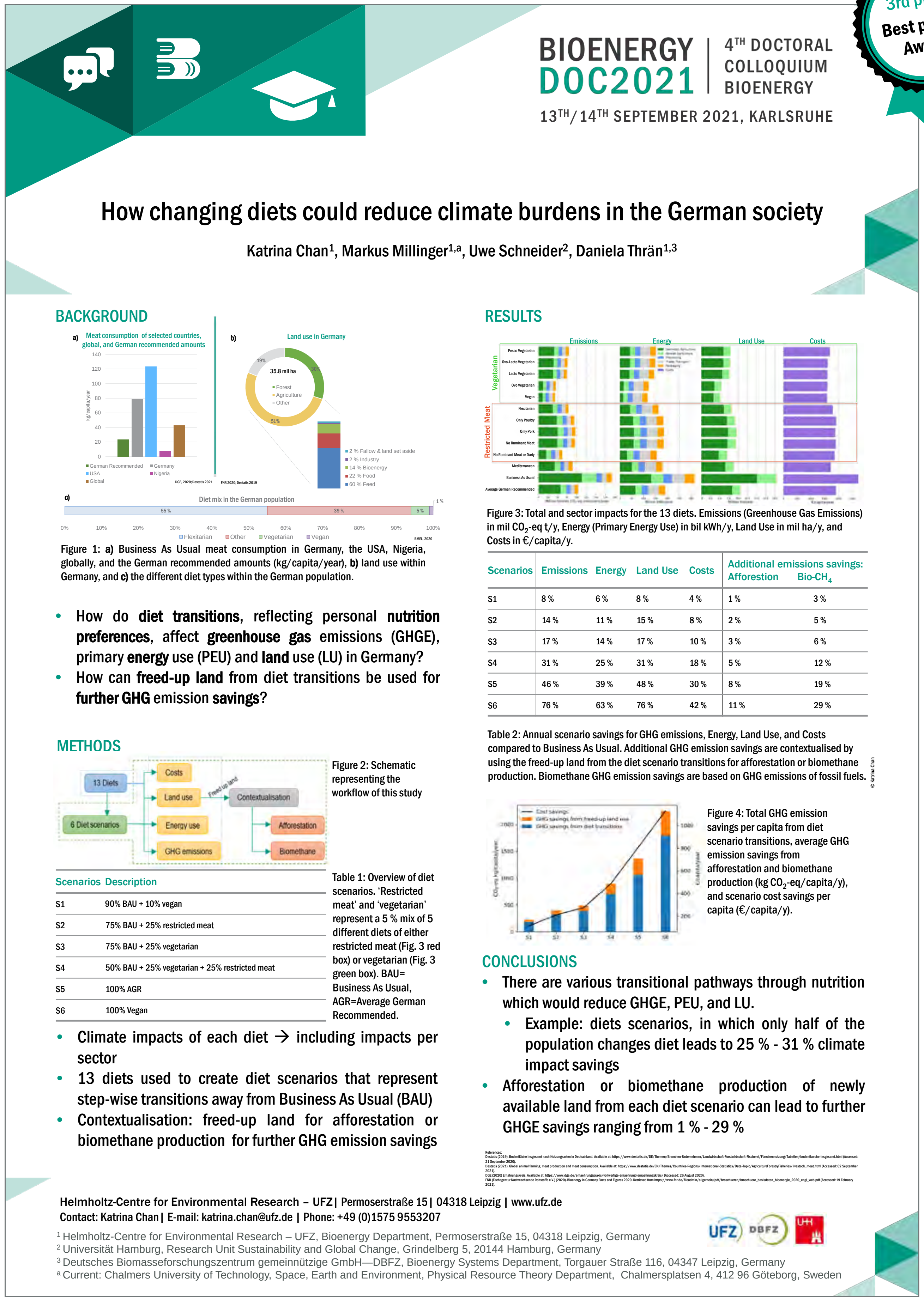
3rd place
Best poster
Award



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13TH/14TH SEPTEMBER 2021, KARLSRUHE

How changing diets could reduce climate burdens in the German society

Katrina Chan[1], Markus Millinger[1,a], Uwe Schneider[2], Daniela Thrän[1,3]

BACKGROUND

Figure 1: **a)** Business As Usual meat consumption in Germany, the USA, Nigeria, globally, and the German recommended amounts (kg/capita/year), **b)** land use within Germany, and **c)** the different diet types within the German population.

- How do **diet transitions**, reflecting personal **nutrition preferences**, affect **greenhouse gas** emissions (GHGE), primary **energy** use (PEU) and **land** use (LU) in Germany?
- How can **freed-up land** from diet transitions be used for **further GHG** emission **savings**?

METHODS

Figure 2: Schematic representing the workflow of this study

Scenarios	Description
S1	90% BAU + 10% vegan
S2	75% BAU + 25% restricted meat
S3	75% BAU + 25% vegetarian
S4	50% BAU + 25% vegetarian + 25% restricted meat
S5	100% AGR
S6	100% Vegan

Table 1: Overview of diet scenarios. ‘Restricted meat’ and ‘vegetarian’ represent a 5 % mix of 5 different diets of either restricted meat (Fig. 3 red box) or vegetarian (Fig. 3 green box). BAU= Business As Usual, AGR=Average German Recommended.

- Climate impacts of each diet → including impacts per sector
- 13 diets used to create diet scenarios that represent step-wise transitions away from Business As Usual (BAU)
- Contextualisation: freed-up land for afforestation or biomethane production for further GHG emission savings

RESULTS

Figure 3: Total and sector impacts for the 13 diets. Emissions (Greenhouse Gas Emissions) in mil CO_2-eq t/y, Energy (Primary Energy Use) in bil kWh/y, Land Use in mil ha/y, and Costs in €/capita/y.

Scenarios	Emissions	Energy	Land Use	Costs	Additional emissions savings: Afforestion	Bio-CH_4
S1	8 %	6 %	8 %	4 %	1 %	3 %
S2	14 %	11 %	15 %	8 %	2 %	5 %
S3	17 %	14 %	17 %	10 %	3 %	6 %
S4	31 %	25 %	31 %	18 %	5 %	12 %
S5	46 %	39 %	48 %	30 %	8 %	19 %
S6	76 %	63 %	76 %	42 %	11 %	29 %

Table 2: Annual scenario savings for GHG emissions, Energy, Land Use, and Costs compared to Business As Usual. Additional GHG emission savings are contextualised by using the freed-up land from the diet scenario transitions for afforestation or biomethane production. Biomethane GHG emission savings are based on GHG emissions of fossil fuels.

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Figure 4: Total GHG emission savings per capita from diet scenario transitions, average GHG emission savings from afforestation and biomethane production (kg CO_2-eq/capita/y), and scenario cost savings per capita (€/capita/y).

CONCLUSIONS

- There are various transitional pathways through nutrition which would reduce GHGE, PEU, and LU.
  - Example: diets scenarios, in which only half of the population changes diet leads to 25 % - 31 % climate impact savings
- Afforestation or biomethane production of newly available land from each diet scenario can lead to further GHGE savings ranging from 1 % - 29 %

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POSTER SESSIONS

SESSION II

BIOREFINERIES/BIOFUELS

Lukas Perret, Karlsruhe Institute of Technology (KIT)

Efficiency enhancement of synthesis gas fermentation with Clostridium ljungdahlii by the use of cell retention in a continuously operated stirred tank reactor (CSTR)

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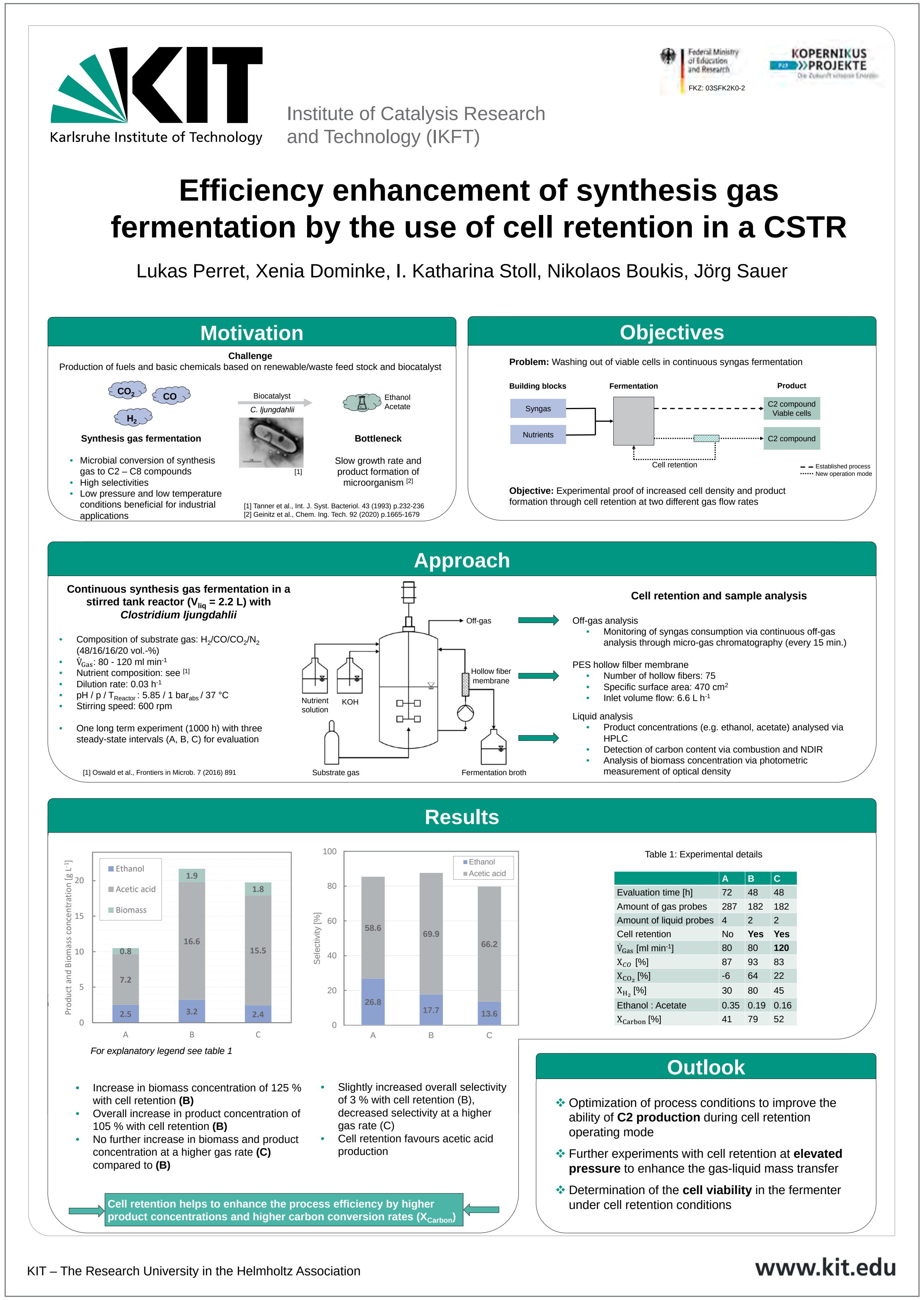
The fermentation of synthesis gas mixtures with anaerobic bacteria as biocatalysts represents a promising process for the production of fuels and basic chemicals. In this process, gas mixtures of H_2, CO_2 and CO are converted by microorganisms (as whole-cell catalysts) to alcohols and organic acids. Besides the main products acetic acid and ethanol, C_4 - C_8 compounds are possible, especially in co-cultures with various bacteria. The microbial conversion of synthesis gas offers the potential of simplification and efficiency increase compared to classical thermocatalytic processes. For example, upstream gas purification can be omitted because microorganisms are much less sensitive to interfering substances such as sulfur components than chemical catalysts. However, low cell density as well as low product formation still represent current challenges on the way to commercialization of syngas fermentation. At the Institute of Catalysis Research and Technology (IKFT) at the Karlsruhe Institute of Technology (KIT), experimental and conceptual work is being carried out to optimize fermentation in a continuously operated stirred tank reactor (CSTR). A major goal of this investigation is to increase the overall efficiency. Important contributing factors seem to be the composition of the synthesis gas, gas flow rate, cell density in the reactor and process pressure.

The influence of gas composition and cell retention on fermentation performance is investigated in a laboratory study. The anaerobic bacterium Clostridium ljungdahlii is used as the biocatalyst and the volume of the fermentation broth is 2.2 liters. The syngas is composed of H_2, CO, CO_2 and N_2 as inert standard. A hollow fiber filter module from Repligen is used for cell retention.

Cell retention can significantly increase the biomass concentration in the reactor so that an increase of more than 100 % can be achieved. In addition, an increase in the hydrogen uptake rate of approximately 60 % as well as a net CO_2 uptake can be observed after implementing the cell retention system. The product concentration of ethanol and acetic acid also increases by more than 40 %. A higher supply of nutrient media leads to a further increase in biomass concentration, gas uptake rates and product formation.

Finally, the gas flow rate and gas composition can be used to influence the product concentration as well as the overall efficiency. A reduction of hydrogen uptake in favor of a higher CO uptake is observed.

This abstract has already been presented at the 29th European Biomass Conference & Exhibition 2021.



Institute of Catalysis Research and Technology (IKFT)

Federal Ministry of Education and Research
FKZ: 03SFK2K0-2
KOPERNIKUS PROJEKTE

Efficiency enhancement of synthesis gas fermentation by the use of cell retention in a CSTR

Lukas Perret, Xenia Dominke, I. Katharina Stoll, Nikolaos Boukis, Jörg Sauer

Motivation

Challenge

Production of fuels and basic chemicals based on renewable/waste feed stock and biocatalyst

Synthesis gas fermentation

- Microbial conversion of synthesis gas to C2 – C8 compounds
- High selectivities
- Low pressure and low temperature conditions beneficial for industrial applications

Bottleneck

Slow growth rate and product formation of microorganism [2]

[1] Tanner et al., Int. J. Syst. Bacteriol. 43 (1993) p.232-236
[2] Geinitz et al., Chem. Ing. Tech. 92 (2020) p.1665-1679

Objectives

Problem: Washing out of viable cells in continuous syngas fermentation

Objective: Experimental proof of increased cell density and product formation through cell retention at two different gas flow rates

Approach

Continuous synthesis gas fermentation in a stirred tank reactor (V_{liq} = 2.2 L) with *Clostridium ljungdahlii*

- Composition of substrate gas: $H_2/CO/CO_2/N_2$ (48/16/16/20 vol.-%)
- $\dot{V}_{Gas}$: 80 - 120 ml min^{-1}
- Nutrient composition: see [1]
- Dilution rate: 0.03 h^{-1}
- pH / p / $T_{Reactor}$: 5.85 / 1 bar_{abs} / 37 °C
- Stirring speed: 600 rpm

- One long term experiment (1000 h) with three steady-state intervals (A, B, C) for evaluation

[1] Oswald et al., Frontiers in Microb. 7 (2016) 891

Cell retention and sample analysis

Off-gas analysis
- Monitoring of syngas consumption via continuous off-gas analysis through micro-gas chromatography (every 15 min.)

PES hollow filber membrane
- Number of hollow fibers: 75
- Specific surface area: 470 cm^2
- Inlet volume flow: 6.6 L h^{-1}

Liquid analysis
- Product concentrations (e.g. ethanol, acetate) analysed via HPLC
- Detection of carbon content via combustion and NDIR
- Analysis of biomass concentration via photometric measurement of optical density

Results

For explanatory legend see table 1

Table 1: Experimental details

	A	B	C
Evaluation time [h]	72	48	48
Amount of gas probes	287	182	182
Amount of liquid probes	4	2	2
Cell retention	No	**Yes**	**Yes**
$\dot{V}_{Gas}$ [ml min^{-1}]	80	80	**120**
X_{CO} [%]	87	93	83
X_{CO_2} [%]	-6	64	22
X_{H_2} [%]	30	80	45
Ethanol : Acetate	0.35	0.19	0.16
X_{Carbon} [%]	41	79	52

- Increase in biomass concentration of 125 % with cell retention **(B)**
- Overall increase in product concentration of 105 % with cell retention **(B)**
- No further increase in biomass and product concentration at a higher gas rate **(C)** compared to **(B)**

- Slightly increased overall selectivity of 3 % with cell retention (B), decreased selectivity at a higher gas rate (C)
- Cell retention favours acetic acid production

Cell retention helps to enhance the process efficiency by higher product concentrations and higher carbon conversion rates (X_{Carbon})

Outlook

- ❖ Optimization of process conditions to improve the ability of **C2 production** during cell retention operating mode
- ❖ Further experiments with cell retention at **elevated pressure** to enhance the gas-liquid mass transfer
- ❖ Determination of the **cell viability** in the fermenter under cell retention conditions

KIT – The Research University in the Helmholtz Association

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Jakob Köchermann, Technical University of Berlin/Deutsches Biomasseforschungszentrum

Hydrothermal production of furfural and hydrochar using a vapor releasing reactor system

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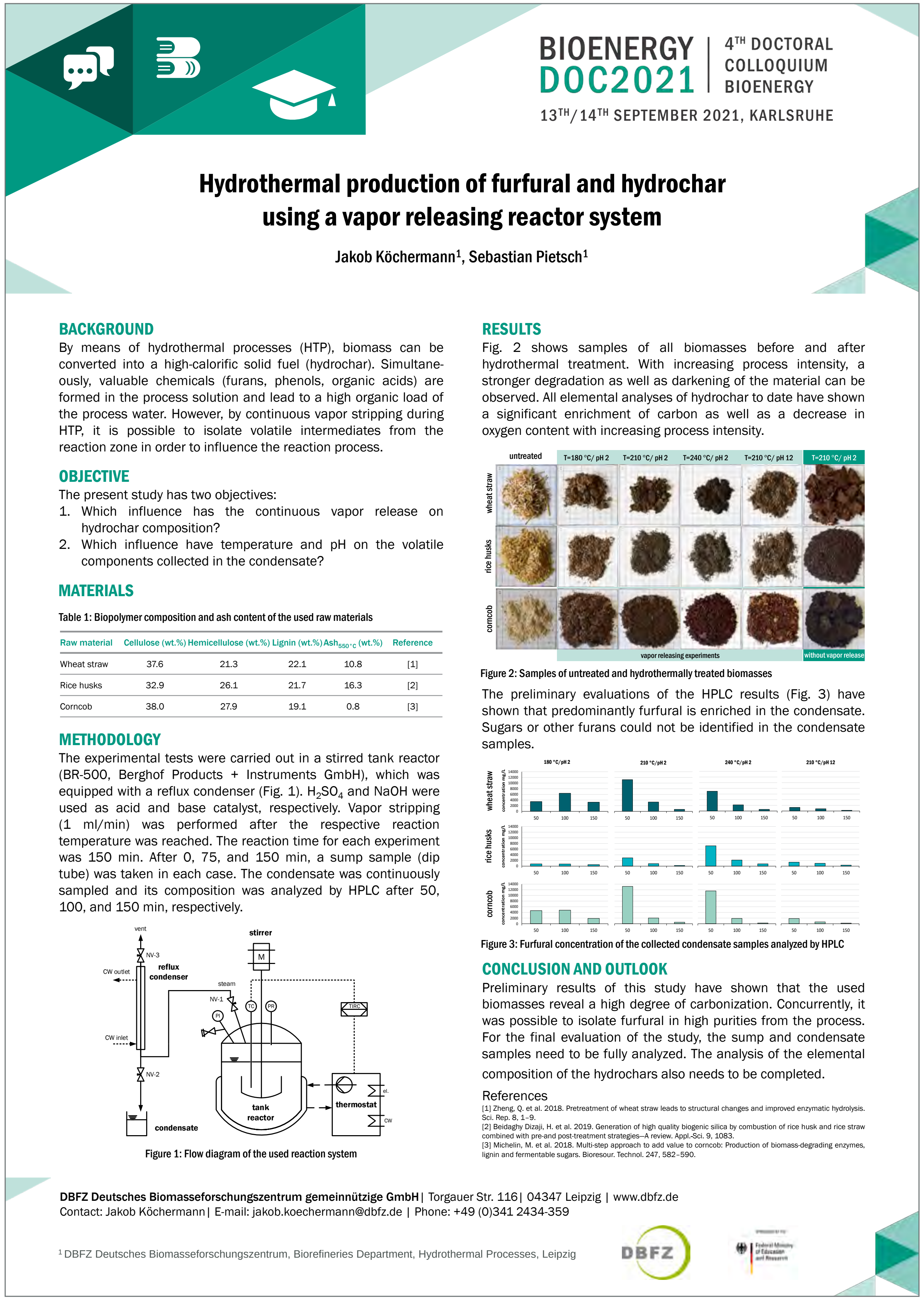
Hydrothermal treatment of lignocellulosic biomass is characterized through rapid hydrolysis of hemicellulose. The pentoses (xylose and arabinose) that pass into the solution during this process are dehydrated to furfural. Furfural is a versatile platform chemical from which plastics, resins, or biofuels can be produced. However, under the conditions prevailing in hydrothermal reactions, furfural tends to polymerize with itself. The resulting polycondensates (humins or secondary char) are deposited on the surface of the biomass and cause the typical darkening of the substrate. Cellulose and lignin are much more stable than hemicellulose and begin to hydrolyze later and at higher temperatures. Decomposition products that cannot polymerize accumulate in the liquid phase, causing a disposal problem.

In this contribution, we will present a new approach in which a continuous vapor stream is stripped and condensed during hydrothermal treatment. In contrast to the C_6 sugar-based 5-hydroxymethylfurfural (HMF), furfural is volatile and forms a minimum azeotrope together with water and, therefore, it can be discharged from the process without polymerizing. The immediate condensation of the vapor prevents further decomposition of the molecule. With the help of this approach, the simultaneous production of furfural, as well as hydrochar, can succeed. The experiments were carried out with three classical lignocelluloses (wheat straw, rice husk, and corn straw). First results based on lignocellulose showed a very good separation of furfural combined with the production of a promising hydrochar. It will also be investigated whether the absence of secondary char based on furfural influences cellulose and lignin decomposition.



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Hydrothermal production of furfural and hydrochar using a vapor releasing reactor system

Jakob Köchermann[1], Sebastian Pietsch[1]

BACKGROUND

By means of hydrothermal processes (HTP), biomass can be converted into a high-calorific solid fuel (hydrochar). Simultaneously, valuable chemicals (furans, phenols, organic acids) are formed in the process solution and lead to a high organic load of the process water. However, by continuous vapor stripping during HTP, it is possible to isolate volatile intermediates from the reaction zone in order to influence the reaction process.

OBJECTIVE

The present study has two objectives:

1. Which influence has the continuous vapor release on hydrochar composition?
2. Which influence have temperature and pH on the volatile components collected in the condensate?

MATERIALS

Table 1: Biopolymer composition and ash content of the used raw materials

Raw material	Cellulose (wt.%)	Hemicellulose (wt.%)	Lignin (wt.%)	$Ash_{550\,°C}$ (wt.%)	Reference
Wheat straw	37.6	21.3	22.1	10.8	[1]
Rice husks	32.9	26.1	21.7	16.3	[2]
Corncob	38.0	27.9	19.1	0.8	[3]

METHODOLOGY

The experimental tests were carried out in a stirred tank reactor (BR-500, Berghof Products + Instruments GmbH), which was equipped with a reflux condenser (Fig. 1). H_2SO_4 and NaOH were used as acid and base catalyst, respectively. Vapor stripping (1 ml/min) was performed after the respective reaction temperature was reached. The reaction time for each experiment was 150 min. After 0, 75, and 150 min, a sump sample (dip tube) was taken in each case. The condensate was continuously sampled and its composition was analyzed by HPLC after 50, 100, and 150 min, respectively.

Figure 1: Flow diagram of the used reaction system

RESULTS

Fig. 2 shows samples of all biomasses before and after hydrothermal treatment. With increasing process intensity, a stronger degradation as well as darkening of the material can be observed. All elemental analyses of hydrochar to date have shown a significant enrichment of carbon as well as a decrease in oxygen content with increasing process intensity.

Figure 2: Samples of untreated and hydrothermally treated biomasses

The preliminary evaluations of the HPLC results (Fig. 3) have shown that predominantly furfural is enriched in the condensate. Sugars or other furans could not be identified in the condensate samples.

Figure 3: Furfural concentration of the collected condensate samples analyzed by HPLC

CONCLUSION AND OUTLOOK

Preliminary results of this study have shown that the used biomasses reveal a high degree of carbonization. Concurrently, it was possible to isolate furfural in high purities from the process. For the final evaluation of the study, the sump and condensate samples need to be fully analyzed. The analysis of the elemental composition of the hydrochars also needs to be completed.

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Water selective membranes for the methanation of CO_2

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Introduction

Based on the concept of power-to-gas, the usage of synthetic methane is a storage option for excess renewable electricity in the gas grid. This process is economically not feasible at the moment [1]. By using a water-permeable membrane, water can be extracted as a by-product of methane, thus increasing CO_2 turnover according to LeChatelier‘s principle [2].

A membrane used for such applications must withstand the high temperatures in the reaction zone and additionally be as selective and permeable for water as possible.

Methods and Results

The research focuses on the question which membrane is best suitable for selectively removing water from the reaction zone of a methanation reactor and why. In order to answer this question different membranes need to be tested and mathematically described. There are different candidates that might be suitable to be applied in this field.

One promising candidate of these membranes was produced and characterized in the present work following a the sol-gel preparation route [3]. The prepared membranes are cylindrical ceramics with an outer diameter of 9 mm and a thickness of 2 mm. The system was tested in regard to their surface and water separation properties. The mostly underwhelming results are presented.

Membrane samples from Fraunhofer IKTS with different separation principles are being tested at DBFZ to compare the results of the self-prepared membrane to state-of-the-art membranes and have an insight into the

Outlook

In the next step the available mass transport description [4] for the different membranes will be implemented in a membrane reactor model. The possible best candidate from the used membrane can be defined by comparing the results from experiments and simulation work. By using these results a deeper understanding of the membrane-reactor system can be achieved and possible operation points can be defined.

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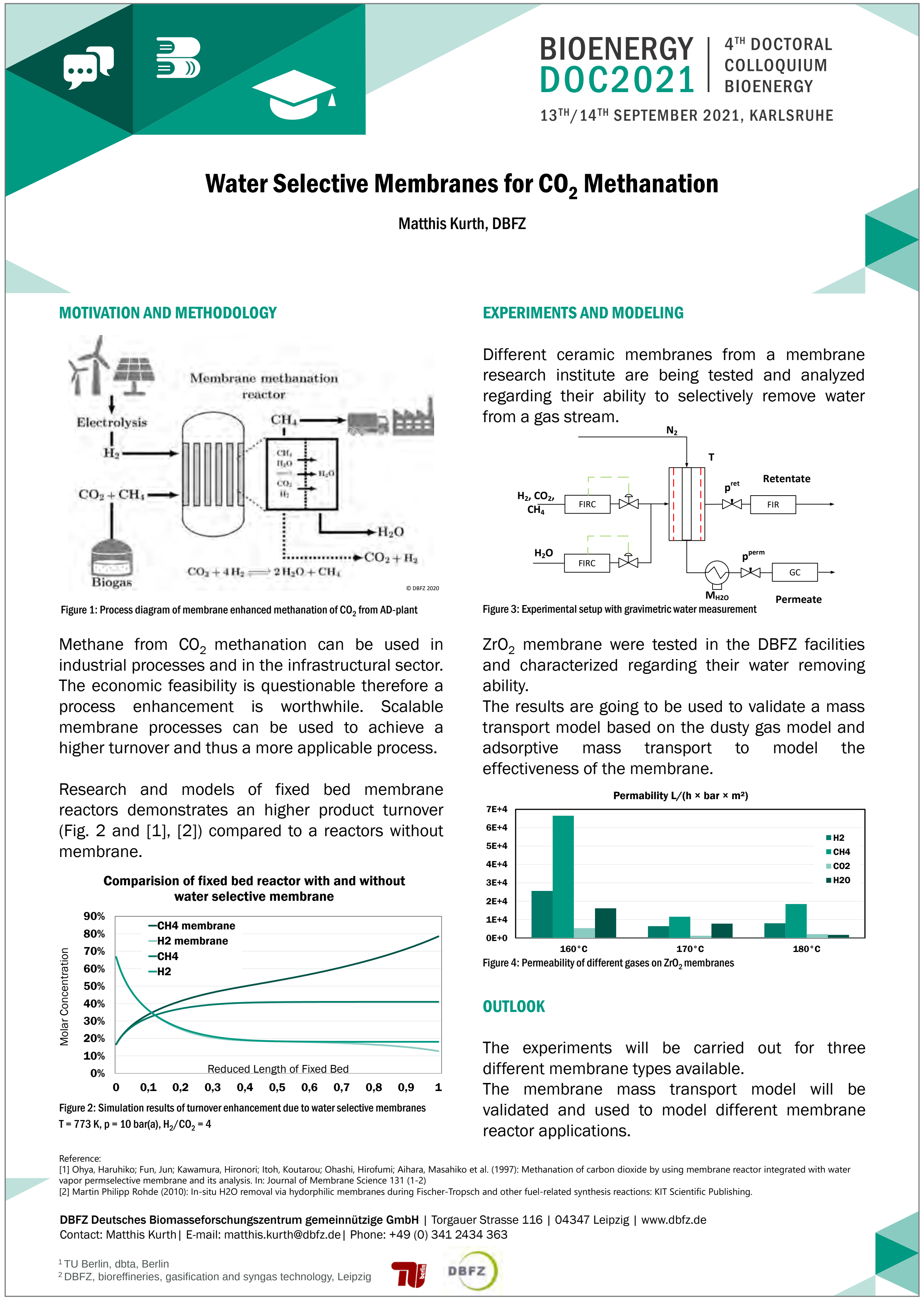

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Water Selective Membranes for CO_2 Methanation

Matthis Kurth, DBFZ

MOTIVATION AND METHODOLOGY

Figure 1: Process diagram of membrane enhanced methanation of CO_2 from AD-plant

Methane from CO_2 methanation can be used in industrial processes and in the infrastructural sector. The economic feasibility is questionable therefore a process enhancement is worthwhile. Scalable membrane processes can be used to achieve a higher turnover and thus a more applicable process.

Research and models of fixed bed membrane reactors demonstrates an higher product turnover (Fig. 2 and [1], [2]) compared to a reactors without membrane.

Figure 2: Simulation results of turnover enhancement due to water selective membranes
T = 773 K, p = 10 bar(a), $H_2/CO_2 = 4$

EXPERIMENTS AND MODELING

Different ceramic membranes from a membrane research institute are being tested and analyzed regarding their ability to selectively remove water from a gas stream.

Figure 3: Experimental setup with gravimetric water measurement

ZrO_2 membrane were tested in the DBFZ facilities and characterized regarding their water removing ability.

The results are going to be used to validate a mass transport model based on the dusty gas model and adsorptive mass transport to model the effectiveness of the membrane.

Figure 4: Permeability of different gases on ZrO_2 membranes

OUTLOOK

The experiments will be carried out for three different membrane types available.

The membrane mass transport model will be validated and used to model different membrane reactor applications.

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Production of platform chemicals in on-farm biorefinery

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The production of bio-based platform chemicals has recently been the subject of wide research interest. Biomass can be used to synthesized various platform chemicals like levulinic acid, furfural, or 5-hydroxymethylfurfural. The HMF is a versatile intermediate that offers a wide range of applications, e.g. bio-polymer production. The large-scale production of HMF has not yet been realized, even though the synthesis of HMF from fructose is highly efficient. Agricultural raw materials, which contains cellulose, sucrose or inulin, are low-priced starting materials for the manufacture of hexoses. Key step in transformation of biomass to furfurals is hydrolysis. Pretreatment experiments in a semi-continuous plant were carried out to measure the time-dependent formation of sugars, furfurals, and organic acids at different hydrolysis temperatures of lignocelluloses. Increase of the reaction temperature increased the formation of furfurals and organic acids, regardless of biomass type. The results obtained in this study can be used for the optimisation of the hydrolysis conditions and reactor design to maximise the yields of desired products. Finding low-priced feedstock may be an opportunity for large-scale HMF production. Unfortunately, the use of biomass is still a challenge due to the heterogeneity of the feedstock‘s plant material and interactions between biomass components. For this purpose, comparison of HMF synthesis from hexoses- fructose and glucose, with biomass-miscanthus and chicory roots was made. The study shows that biomass has the potential for the production of HMF as part of an environmentally friendly process in a biorefinery. Nevertheless, further research in this direction is needed, especially in the techno-economic field. Some results from the conversion of hydrolysates solutions are unexpected and shows a need for further investigations. In the course of bioeconomy, HMF production from biomass could be conducted in decentralized biorefineries that work with agricultural residues. However, HMF-production is only a part of the biorefinery concept developed. In a biorefinery, also furfural from hemicellulose and the solid fraction can be produced. In addition, the solved organic compounds can be used to generate heat for the process by a biogas production combined with a power plant. Therefore, a stream coupling between the biorefinery and the biogas plant is currently being developed with the help of the AspenPlus. A holistic approach to the on-farm biorefinery concept in coupling with a biogas plant is crucial for the efficient large-scale production of platform chemicals.

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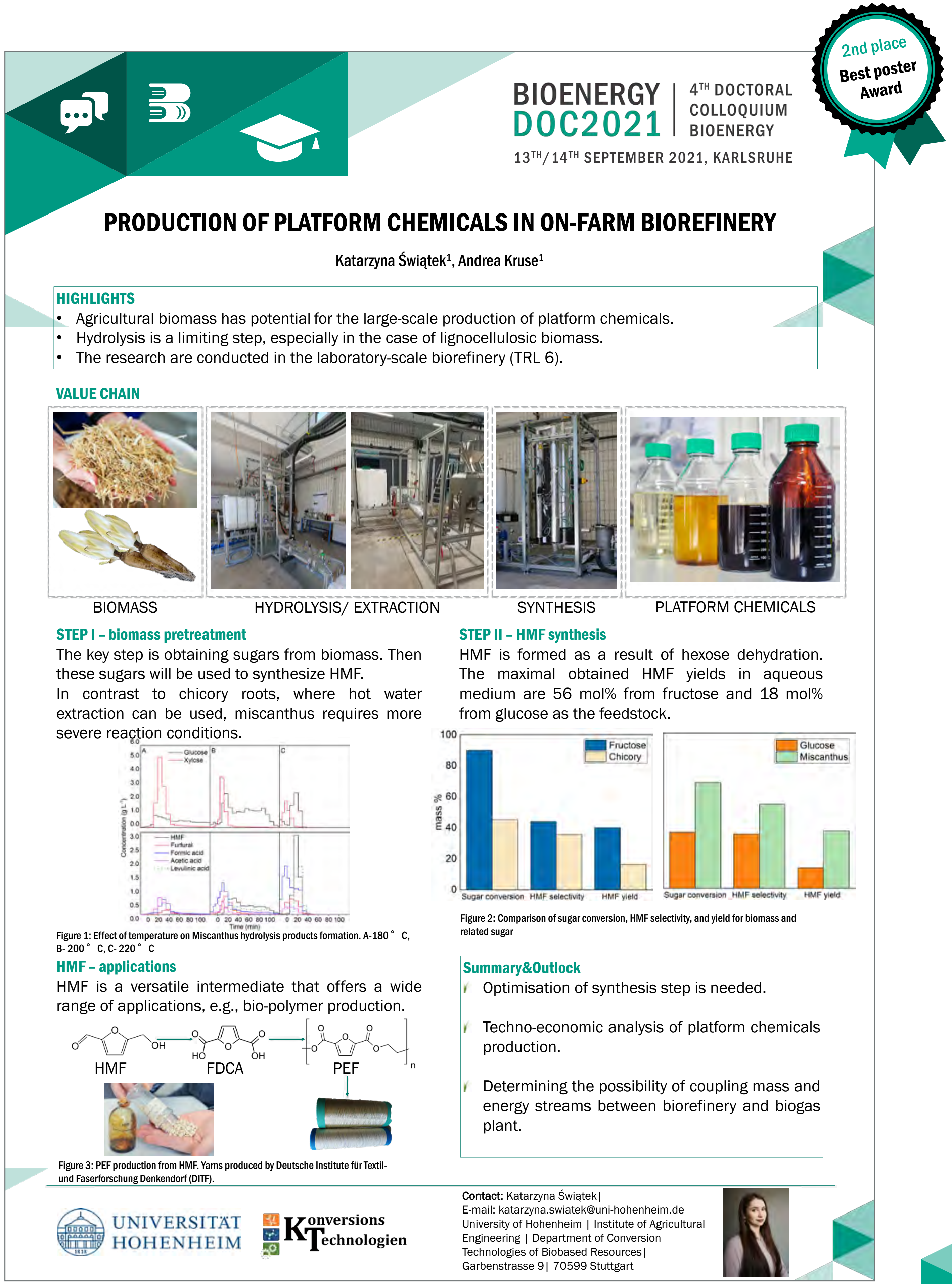

PRODUCTION OF PLATFORM CHEMICALS IN ON-FARM BIOREFINERY

Katarzyna Świątek[1], Andrea Kruse[1]

HIGHLIGHTS

- Agricultural biomass has potential for the large-scale production of platform chemicals.
- Hydrolysis is a limiting step, especially in the case of lignocellulosic biomass.
- The research are conducted in the laboratory-scale biorefinery (TRL 6).

VALUE CHAIN

BIOMASS — HYDROLYSIS/ EXTRACTION — SYNTHESIS — PLATFORM CHEMICALS

STEP I – biomass pretreatment

The key step is obtaining sugars from biomass. Then these sugars will be used to synthesize HMF.

In contrast to chicory roots, where hot water extraction can be used, miscanthus requires more severe reaction conditions.

Figure 1: Effect of temperature on Miscanthus hydrolysis products formation. A-180 ° C, B- 200 ° C, C- 220 ° C

HMF – applications

HMF is a versatile intermediate that offers a wide range of applications, e.g., bio-polymer production.

Figure 3: PEF production from HMF. Yarns produced by Deutsche Institute für Textil- und Faserforschung Denkendorf (DITF).

STEP II – HMF synthesis

HMF is formed as a result of hexose dehydration. The maximal obtained HMF yields in aqueous medium are 56 mol% from fructose and 18 mol% from glucose as the feedstock.

Figure 2: Comparison of sugar conversion, HMF selectivity, and yield for biomass and related sugar

Summary&Outlock

- ✓ Optimisation of synthesis step is needed.
- ✓ Techno-economic analysis of platform chemicals production.
- ✓ Determining the possibility of coupling mass and energy streams between biorefinery and biogas plant.

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Investigation of catalysts for direct biogas methanation

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The biggest climate challenge is the reduction of CO_2 emissions, especially in the transport sector. Future-oriented solutions for alternative fuels are therefore necessary. One potential way to produce synthetic natural gas is to upgrade biogas. By using residual materials like agricultural residues or waste as substrates, as planned in the Pilot-SBG project, no energy crops need to be cultivated. Biogas mainly consists of methane (CH_4) and carbon dioxide (CO_2), as well as other minor components such as hydrogen sulfide (H_2S), siloxanes or ammonia (NH_3). To increase the methane content, hydrogen (H_2) is added to react with CO_2 on a methanation catalyst. However, certain trace compounds inhibit the reaction, which is why biogas purification is necessary before methanation. Direct biogas methanation without prior CO_2 separation is a fairly new field of research. Further research into the influences of biogas components on the reaction, as well as possible materials for biogas purification and methanation can drive the commercialisation of the process and thus the use of residues for the production of fuels.

To investigate direct biogas methanation in more detail, three research questions were formulated. First, the biogas composition is clarified, with respect to the presence of trace components and their concentrations. For this purpose, biogas measurements were carried out at four biogas plants with different substrates. Secondly, there is the question of biogas purification and suitable materials for the removal of minor components from the biogas. H_2S will be used as a test molecule to record breakthrough curves of different adsorbents. Finally, methanation catalysts are tested with regard to their methanation activity and sulfur resistance to answer the question of which catalysts are suitable for the direct conversion of biogas to biomethane.

The biogas measurements have shown that agricultural substrates lead to an increased NH_3 concentration in the biogas, while sewage sludge as substrate promotes the formation of siloxanes and biowaste together with green waste leads to sulfur compounds and ketones in the resulting biogas. Initial results have also been obtained on Ni and Ru based methanation catalysts on Al_2O_3. In the laboratory, a product gas with a methane content of 97 Vol.- % was obtained, while the H_2 content remained below 2 Vol.- %. A biogas composition and recirculation of a part of the product gas were simulated as reactant gas. H_2 was added in a substoichiometric amount. CH_4 in the reactant gas has no limiting effect on the reaction.

In future experiments, the long-term activities of the catalysts will be analyzed, as well as their deactivation by poisoning with H_2S. Together with the experiments on biogas purification, an overall strategy is to be developed in which the adsorbent and the catalyst are tailored to each other in such a way that the longest possible lifetime of the materials can be expected for their application.

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Investigation of catalysts for direct biogas methanation

Selina Nieß, DBFZ

BIORESOURCES AND HYDROGEN TO METHANE AS A FUEL

Within the scope of the Pilot-SBG project, a pilot plant will be realized, which maps the entire process chain of biomethane production from residues and waste materials (Figure 1).

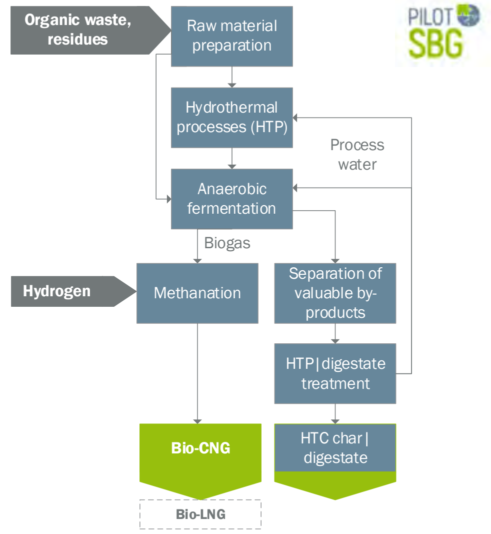
Organic waste, residues
Raw material preparation
Hydrothermal processes (HTP)
Process water
Anaerobic fermentation
Biogas
Hydrogen
Methanation
Separation of valuable by-products
HTP|digestate treatment
Bio-CNG
HTC char|digestate
Bio-LNG

Figure 1: Process Chain of the individual technologies in the Pilot-SBG Plant

The biogas produced during anaerobic digestion is upgraded by the addition of hydrogen (H_2). In this process, the carbon dioxide (CO_2) contained in the biogas reacts with H_2 in presence of a catalyst to generate biomethane (CH_4). In contrast to pure CO_2 methanation, during direct biogas methanation the activity of the catalyst can be influenced by the high methane content and gas by-products.

EXPERIMENTAL PROCEDURE

The activity of six incipient wetness impregnated catalysts (Figure 2) was studied in a fixed bed reactor ($p = 8$ bar, $CH_4 \approx 82$ Vol.-%). T, gas hourly space velocity (GHSV) and H_2/CO_2 ratio were varied using a response surface model (Figure 3).

The aim was to find a combination of T, H_2/CO_2 ratio and GHSV to produce a product gas with less than 2 Vol.-% H_2 and the highest possible CH_4 content. As a reference, the same experiment was performed with a commercial catalyst in a temperature range of 340 – 440 °C.

Catalyst Name	Temperature range
$Ni20/Al_2O_3$	250 – 350 °C
$Ru0.3/Al_2O_3$	300 – 400 °C
$Ru1/Al_2O_3$	250 – 350 °C
$Ni20/CeO_2$	250 – 350 °C
$Ru0.3/CeO_2$	250 – 350 °C
$Ru1/CeO_2$	250 – 350 °C

Figure 2: Investigated catalysts and T range

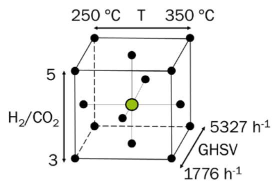

Figure 3: Response surface model

RESULTS

For each catalyst except $Ru0.3/Al_2O_3$, at least one combination of the three parameters was found, where the H_2 concentration in the product gas was below 2 Vol.-%. The results, which had the highest methane concentrations in the product gas, are shown in Figure 4. $Ni20/CeO_2$ showed the highest H_2 conversion at 97 %, reaching 0,5 Vol.-% H_2.

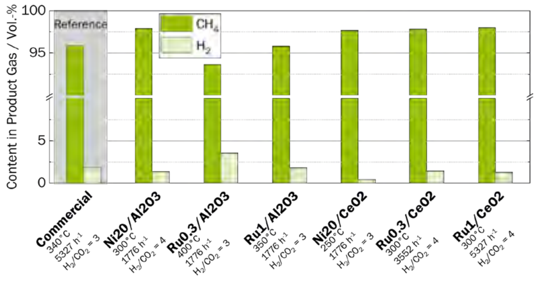

Figure 4: Results from the selected optimal conditions for the tested catalysts

OUTLOOK

The catalysts show high activities at high amounts of CH_4 in the reaction gas. In the next experiments, the influence of H_2S will be investigated.

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Niobium containing catalysts for pyrolysis oil HDO

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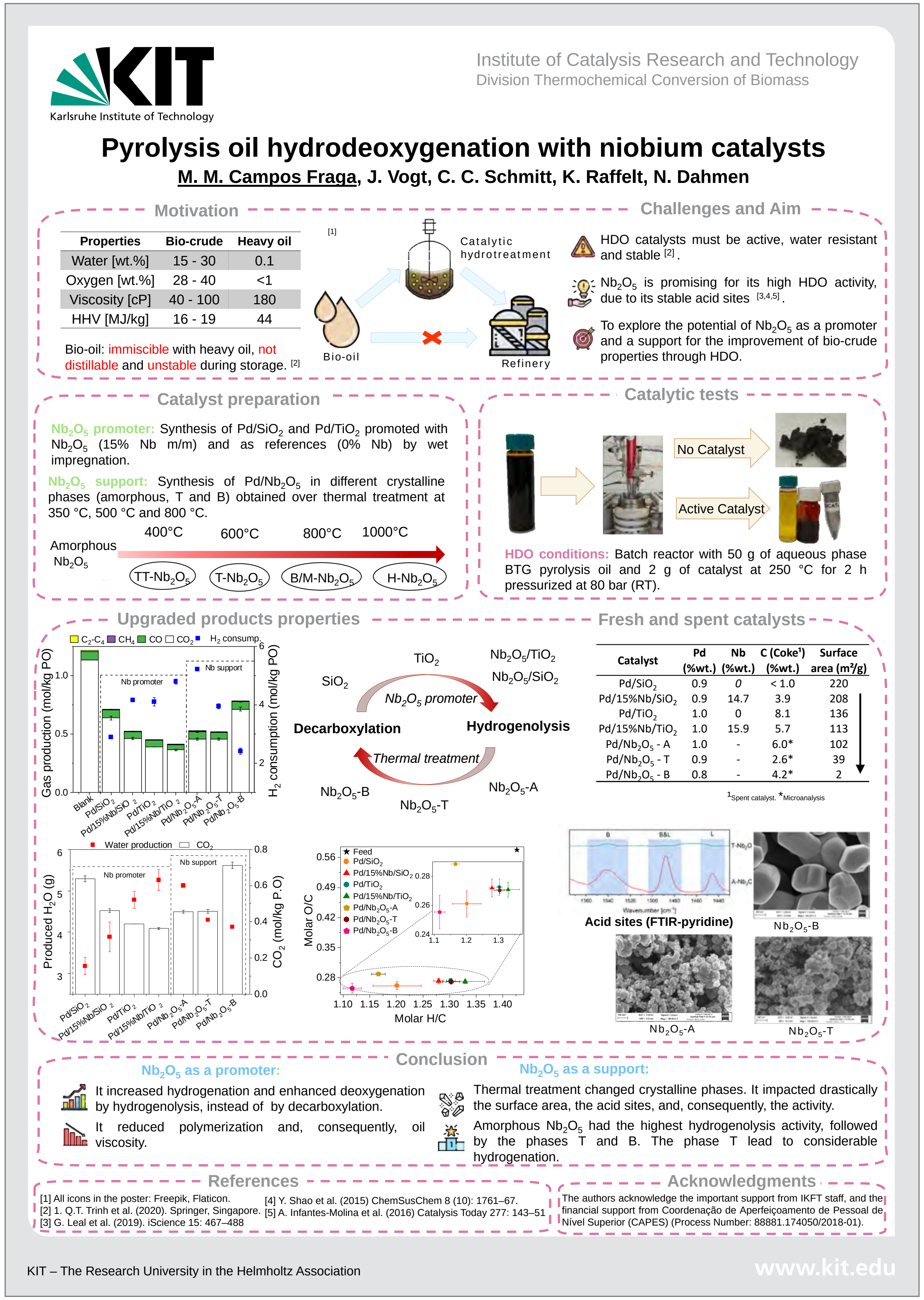
Biomass is a renewable and abundant source of carbon. It can be converted by many ways, including fast pyrolysis. The main product of fast pyrolysis is the bio-crude. The bio-crude is a complex mixture of oxygenated hydrocarbons. It contains between 15 – 35 % wt. water and 18 – 40 % wt. oxygen, from which most of its undesired properties as high viscosity, high acidity and low heating value comes from. Similar to the removal of nitrogen and sulfur from heavy oil, the bio-crude requires upgrading such as catalytic hydrodeoxygenation (HDO) for further use.

Niobium has been investigated as a promoter and as a support for biomass HDO, in most cases with model compounds. The excellent performance observed was attributed to the high stability, presence of water tolerant Lewis acidity and C-O bond cleavage ability. Although model compounds allow fundamental studies on the catalyst behavior, it has several limitations on catalyst designing for HDO of the whole bio-crude. Thus, there is a necessity of comprehensive studies with niobium containing catalysts for HDO of whole bio-crude.

In this work, the improvement of bio-crude properties through HDO with niobium containing catalysts were evaluated, especially in terms of the reduction of oxygen and water contents. The impact of Nb_2O_5 as a promoter in several loadings on Pd/SiO_2 and Pd/TiO_2 was analyzed. Besides that, the HDO of bio-crude with Nb_2O_5 as a support (Pd/Nb_2O_5) was also investigated. The catalysts were prepared by wet impregnation and tested in a batch reactor pressurized at 80 bar – RT for 2h at 250 °C. Nb_2O_5 promoted catalysts presented higher hydrogenation/HDO activity, reflected on a higher H_2 consumption. Related to it, the amount of water produced via promoted silica catalysts (15 % wt. Nb) was 22 % wt. higher than over not promoted ones. In contrast, the generated CO_2 was reduced by niobium addition. This indicates that Nb_2O_5 enhanced HDO via hydrogenolysis and reduced HDO via decarboxylation. The reduction of decarboxylation pathway plus the increasing on hydrogenation reflected in a beneficial reduction of viscosity of oils. In terms of organic compounds, nio-bium promoted a higher selectivity towards ketones and a higher sugar conversion.

A similar tendency was observed when Nb_2O_5 was used as a support. Hydrogenation increased over Pd/Nb_2O_5 in comparison with Pd/SiO_2 leading to a smaller viscosity. Niobium supported catalysts produced circa 50 % wt. more water than Pd/SiO_2 and a similar amount Pd/TiO_2. In terms of oxygen content, the SiO_2 supported ones was slightly better than Nb_2O_5 and TiO_2 supported catalysts, explained by reduction of the decarboxylation. All tested catalysts compositions successfully densified the energy from the bio-crude oil onto upgraded oils. The oxygen content was reduced from 40.7 % wt. (light phase) to 22.8 – 24.7 % wt. (upgraded oils). Niobium beneficial impacts reflected on an increasing hydrogenation/hydrogenolysis activity as well on the reduction on the viscosity of upgraded oils.



Karlsruhe Institute of Technology

Institute of Catalysis Research and Technology
Division Thermochemical Conversion of Biomass

Pyrolysis oil hydrodeoxygenation with niobium catalysts

M. M. Campos Fraga, J. Vogt, C. C. Schmitt, K. Raffelt, N. Dahmen

Motivation

Properties	Bio-crude	Heavy oil
Water [wt.%]	15 - 30	0.1
Oxygen [wt.%]	28 - 40	<1
Viscosity [cP]	40 - 100	180
HHV [MJ/kg]	16 - 19	44

Bio-oil: immiscible with heavy oil, not distillable and unstable during storage. [2]

Challenges and Aim

HDO catalysts must be active, water resistant and stable [2].

Nb_2O_5 is promising for its high HDO activity, due to its stable acid sites [3,4,5].

To explore the potential of Nb_2O_5 as a promoter and a support for the improvement of bio-crude properties through HDO.

Catalyst preparation

Nb_2O_5 promoter: Synthesis of Pd/SiO_2 and Pd/TiO_2 promoted with Nb_2O_5 (15% Nb m/m) and as references (0% Nb) by wet impregnation.

Nb_2O_5 support: Synthesis of Pd/Nb_2O_5 in different crystalline phases (amorphous, T and B) obtained over thermal treatment at 350 °C, 500 °C and 800 °C.

Catalytic tests

HDO conditions: Batch reactor with 50 g of aqueous phase BTG pyrolysis oil and 2 g of catalyst at 250 °C for 2 h pressurized at 80 bar (RT).

Upgraded products properties

Fresh and spent catalysts

Catalyst	Pd (%wt.)	Nb (%wt.)	C (Coke¹) (%wt.)	Surface area (m²/g)
Pd/SiO_2	0.9	0	< 1.0	220
$Pd/15\%Nb/SiO_2$	0.9	14.7	3.9	208
Pd/TiO_2	1.0	0	8.1	136
$Pd/15\%Nb/TiO_2$	1.0	15.9	5.7	113
Pd/Nb_2O_5 - A	1.0	-	6.0*	102
Pd/Nb_2O_5 - T	0.9	-	2.6*	39
Pd/Nb_2O_5 - B	0.8	-	4.2*	2

¹Spent catalyst. *Microanalysis

Acid sites (FTIR-pyridine)

Nb_2O_5-B

Nb_2O_5-A

Nb_2O_5-T

Conclusion

Nb_2O_5 as a promoter:

It increased hydrogenation and enhanced deoxygenation by hydrogenolysis, instead of by decarboxylation.

It reduced polymerization and, consequently, oil viscosity.

Nb_2O_5 as a support:

Thermal treatment changed crystalline phases. It impacted drastically the surface area, the acid sites, and, consequently, the activity.

Amorphous Nb_2O_5 had the highest hydrogenolysis activity, followed by the phases T and B. The phase T lead to considerable hydrogenation.

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Musa Bishir, University of Hohenheim

Conductive Materials from Pyrolysis of Corncobs for Application as Electrodes in Microbial Fuel

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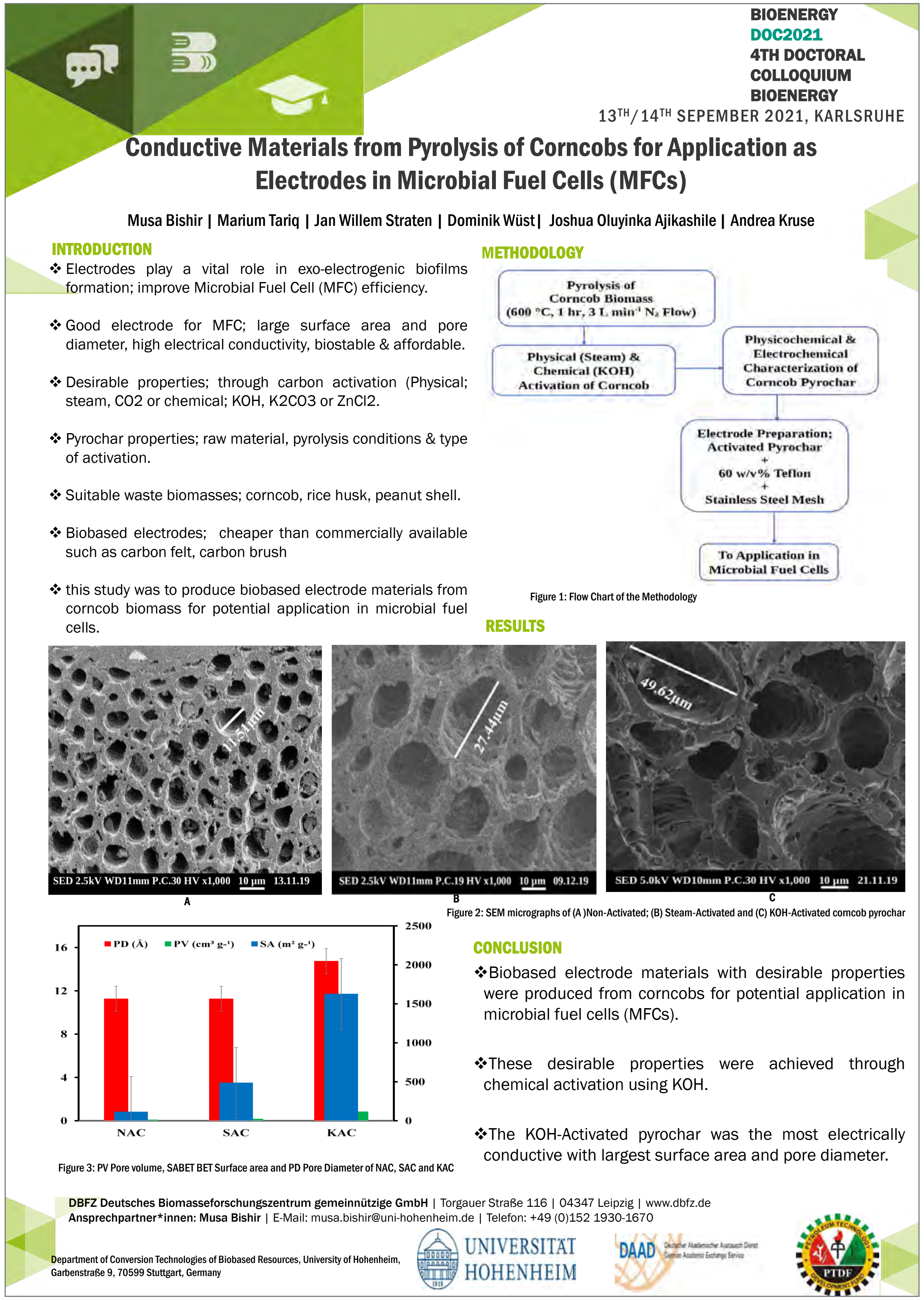
Despite the large varieties of commercially available electrodes, only few are suitable for electro-active bacterial colonization during biofilm formation in microbial fuel cells (MFCs), and yet most of these electrodes are cost prohibitive. Hence the need to search for low-cost alternative electrodes for MFCs. In this study, pyrochars (which are the conductive materials from corncobs) were produced were produced by pyrolysis at a predetermined reaction conditions (600 °C, a constant nitrogen flow of 3 L/min for 30 min) and subsequently steam and potassium hydroxide (KOH) activation of the pyrochar at 600 °C were carried out accordingly. Physicochemical, structural, and electrochemical properties of the activated and non-activated pyrochars were determined according to standardized analytical methods. The highest specific surface area of 1626 $m^2\ g^{-1}$ according to BET and highest medium pore diameter of 14.74 Å were obtained from the KOH-activated pyrochar which was also the most conductive (0.26 S m-1). It was observed that chemical activation of pyrochar with KOH resulted in an improved specific surface area and medium pore size diameter as well as increased poly-condensed aromatic structure and graphitized carbon, thus higher EC. In conclusion, KOH-activated corncob pyrochar holds potentials for producing carbonaceous materials with high electrochemical performance. They showed greater performance in microbial fuel cells in comparison to non-activated and steam-activated pyrochars of the same biomass.



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Conductive Materials from Pyrolysis of Corncobs for Application as Electrodes in Microbial Fuel Cells (MFCs)

Musa Bishir | Marium Tariq | Jan Willem Straten | Dominik Wüst | Joshua Oluyinka Ajikashile | Andrea Kruse

INTRODUCTION

- ❖ Electrodes play a vital role in exo-electrogenic biofilms formation; improve Microbial Fuel Cell (MFC) efficiency.
- ❖ Good electrode for MFC; large surface area and pore diameter, high electrical conductivity, biostable & affordable.
- ❖ Desirable properties; through carbon activation (Physical; steam, CO2 or chemical; KOH, K2CO3 or ZnCl2.
- ❖ Pyrochar properties; raw material, pyrolysis conditions & type of activation.
- ❖ Suitable waste biomasses; corncob, rice husk, peanut shell.
- ❖ Biobased electrodes; cheaper than commercially available such as carbon felt, carbon brush
- ❖ this study was to produce biobased electrode materials from corncob biomass for potential application in microbial fuel cells.

METHODOLOGY

Pyrolysis of
Corncob Biomass
(600 °C, 1 hr, 3 L min^{-1} N_2 Flow)

Physical (Steam) &
Chemical (KOH)
Activation of Corncob

Physicochemical &
Electrochemical
Characterization of
Corncob Pyrochar

Electrode Preparation;
Activated Pyrochar
+
60 w/v% Teflon
+
Stainless Steel Mesh

To Application in
Microbial Fuel Cells

Figure 1: Flow Chart of the Methodology

RESULTS

A
B
C

Figure 2: SEM micrographs of (A)Non-Activated; (B) Steam-Activated and (C) KOH-Activated corncob pyrochar

Figure 3: PV Pore volume, SABET BET Surface area and PD Pore Diameter of NAC, SAC and KAC

CONCLUSION

- ❖ Biobased electrode materials with desirable properties were produced from corncobs for potential application in microbial fuel cells (MFCs).
- ❖ These desirable properties were achieved through chemical activation using KOH.
- ❖ The KOH-Activated pyrochar was the most electrically conductive with largest surface area and pore diameter.

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Fractional extraction and physiochemical characterization of Biocrude from Hydrothermal Liquefaction of Sewage Sludge

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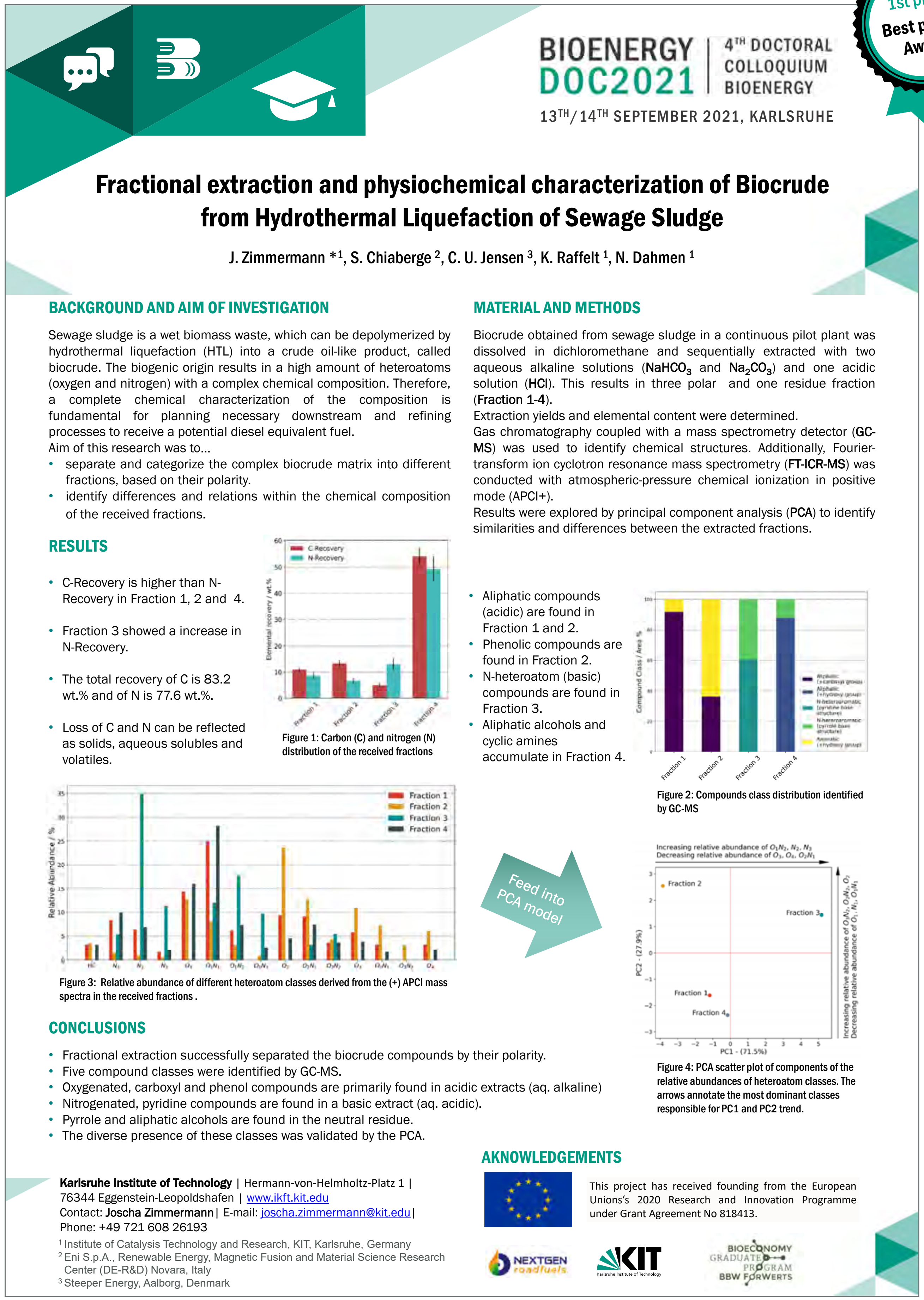
The valorization of wet biowastes to valuable products has the potential to increase carbon-neutral production of chemicals and fuels and tackle disposal issues. However, due to high water content, they are not particularly well suited for a number of thermochemical conversion processes, which require a dry feedstock, e.g., incineration, fast pyrolysis, and gasification. A technology that tolerates and even needs high water content is hydrothermal liquefaction (HTL). The viscous oil-like biocrude product is comparable with the vacuum gas oil cut of a heavy petroleum crude oil, but it is richer in heteroatoms that are unwanted in final products and subsequent upgrading processes is needed. Especially protein-rich biowaste (like sewage sludge) result in biocrude with high content of N-heteroatom compounds with a complex chemical composition. Therefore a complete chemical characterization of the composition is fundamental for planning necessary downstream processes to improve its technological properties.

This study aims to physically separate and simplify the complex biocrude matrix produced from sewage sludge. The biocrude is therefore solubilized in dichloromethane (DCM) and fractioned by liquid-liquid extraction with acid or alkaline aqueous solutions. The separation takes advantage of the changing solubility of different biocrude components at different pH values. This should provide a deeper understanding of the behaviour of different compound classes in the biocrude in downstream processes. The recovered amount of these fractions would allow their subsequent analysis by a set of experimental techniques. The mass balances and extraction yields were carefully determined for the potential recovery or removal of valuable or harming organic components.

This study is embedded in the NextGenRoadFuels project and has received funding from the European Unions‘s 2020 Research and Innovation Programme under Grant Agreement No 818413.

1st place
Best poster
Award



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Fractional extraction and physiochemical characterization of Biocrude from Hydrothermal Liquefaction of Sewage Sludge

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BACKGROUND AND AIM OF INVESTIGATION

Sewage sludge is a wet biomass waste, which can be depolymerized by hydrothermal liquefaction (HTL) into a crude oil-like product, called biocrude. The biogenic origin results in a high amount of heteroatoms (oxygen and nitrogen) with a complex chemical composition. Therefore, a complete chemical characterization of the composition is fundamental for planning necessary downstream and refining processes to receive a potential diesel equivalent fuel.

Aim of this research was to…

- separate and categorize the complex biocrude matrix into different fractions, based on their polarity.
- identify differences and relations within the chemical composition of the received fractions.

RESULTS

- C-Recovery is higher than N-Recovery in Fraction 1, 2 and 4.
- Fraction 3 showed a increase in N-Recovery.
- The total recovery of C is 83.2 wt.% and of N is 77.6 wt.%.
- Loss of C and N can be reflected as solids, aqueous solubles and volatiles.

Figure 1: Carbon (C) and nitrogen (N) distribution of the received fractions

Figure 3: Relative abundance of different heteroatom classes derived from the (+) APCI mass spectra in the received fractions .

MATERIAL AND METHODS

Biocrude obtained from sewage sludge in a continuous pilot plant was dissolved in dichloromethane and sequentially extracted with two aqueous alkaline solutions (**$NaHCO_3$** and **Na_2CO_3**) and one acidic solution (**HCl**). This results in three polar and one residue fraction (**Fraction 1-4**).

Extraction yields and elemental content were determined.

Gas chromatography coupled with a mass spectrometry detector (**GC-MS**) was used to identify chemical structures. Additionally, Fourier-transform ion cyclotron resonance mass spectrometry (**FT-ICR-MS**) was conducted with atmospheric-pressure chemical ionization in positive mode (APCI+).

Results were explored by principal component analysis (**PCA**) to identify similarities and differences between the extracted fractions.

- Aliphatic compounds (acidic) are found in Fraction 1 and 2.
- Phenolic compounds are found in Fraction 2.
- N-heteroatom (basic) compounds are found in Fraction 3.
- Aliphatic alcohols and cyclic amines accumulate in Fraction 4.

Figure 2: Compounds class distribution identified by GC-MS

Figure 4: PCA scatter plot of components of the relative abundances of heteroatom classes. The arrows annotate the most dominant classes responsible for PC1 and PC2 trend.

CONCLUSIONS

- Fractional extraction successfully separated the biocrude compounds by their polarity.
- Five compound classes were identified by GC-MS.
- Oxygenated, carboxyl and phenol compounds are primarily found in acidic extracts (aq. alkaline)
- Nitrogenated, pyridine compounds are found in a basic extract (aq. acidic).
- Pyrrole and aliphatic alcohols are found in the neutral residue.
- The diverse presence of these classes was validated by the PCA.

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The generation of a functional catalytic support system from silicon rich biomass residues for low-temperature methane oxidation operations

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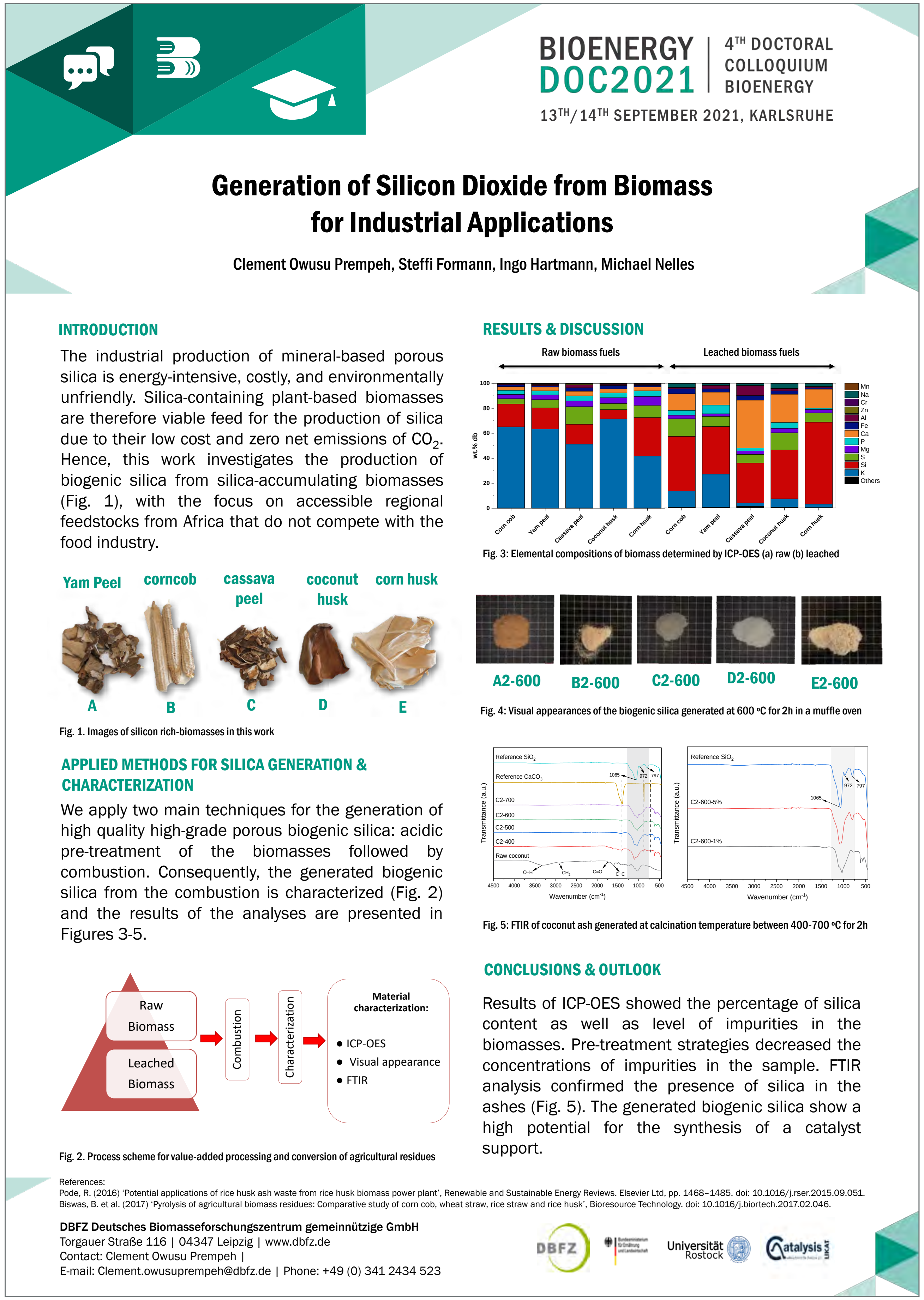
The development of a functional catalytic system for low-temperature methane oxidation has received considerable interest over the years. Methane (CH_4) is emitted from daily operations such as the production and transport of biogas, coal, natural gas and oil, and it possesses a global warming potential of 15-35 times higher than that of carbon dioxide (CO_2). The transportation industry is a major contributor to methane emissions through the combustion of natural gas as a fuel source. One approach to mitigate the expulsion of unburned CH_4 from natural gas vehicles (NGVs) is by the catalytic conversion of CH_4 to more climate-neutral CO_2 ($CH_4 + O_2 \rightarrow H_2O + CO_2$) over noble metal catalysts. Potential candidates for such an operation are supported catalysts containing Palladium (Pd) and Platinum (Pt). These catalysts have the highest activity for CH_4 oxidation, but their activity is tuned by an appropriate support system. However, the current support systems in use (for e.g., alumina and carbon) is associated with certain operational deficiencies that affect their optimal performance as a catalyst. These include poor heat conductivity and chemical reactivity of the support as well as mass transfer limitation of gases during operations. These setbacks are offset by the introduction of other porous structures such as controlled porous glass (CPG) and silica (SiO_2) as carrier materials for the catalysts. With CPG, the industrial production route is expensive as it involves a high-energy process, whereas the conventional production of SiO_2 from the hydrolysis of Tetraethyl orthosilicate (TEOS) is environmentally unfriendly. Therefore, there is a need to find a more sustainable approach to produce SiO_2. Si-containing plant-based biomasses present a viable alternative for SiO_2 production via thermochemical conversion. This process offers significant environmental advantages (zero net emissions) as well as cost-effective options for generating high-quality biogenic silica. Hence, the present study is focused on exploring possible alternatives of preparing catalyst supports from silicon-rich agricultural residues that can exhibit enhanced and stable catalytic activity at conditions (low temperatures) relevant for total methane oxidation.



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Generation of Silicon Dioxide from Biomass for Industrial Applications

Clement Owusu Prempeh, Steffi Formann, Ingo Hartmann, Michael Nelles

INTRODUCTION

The industrial production of mineral-based porous silica is energy-intensive, costly, and environmentally unfriendly. Silica-containing plant-based biomasses are therefore viable feed for the production of silica due to their low cost and zero net emissions of CO_2. Hence, this work investigates the production of biogenic silica from silica-accumulating biomasses (Fig. 1), with the focus on accessible regional feedstocks from Africa that do not compete with the food industry.

Fig. 1. Images of silicon rich-biomasses in this work

APPLIED METHODS FOR SILICA GENERATION & CHARACTERIZATION

We apply two main techniques for the generation of high quality high-grade porous biogenic silica: acidic pre-treatment of the biomasses followed by combustion. Consequently, the generated biogenic silica from the combustion is characterized (Fig. 2) and the results of the analyses are presented in Figures 3-5.

Fig. 2. Process scheme for value-added processing and conversion of agricultural residues

RESULTS & DISCUSSION

Fig. 3: Elemental compositions of biomass determined by ICP-OES (a) raw (b) leached

Fig. 4: Visual appearances of the biogenic silica generated at 600 °C for 2h in a muffle oven

Fig. 5: FTIR of coconut ash generated at calcination temperature between 400-700 °C for 2h

CONCLUSIONS & OUTLOOK

Results of ICP-OES showed the percentage of silica content as well as level of impurities in the biomasses. Pre-treatment strategies decreased the concentrations of impurities in the sample. FTIR analysis confirmed the presence of silica in the ashes (Fig. 5). The generated biogenic silica show a high potential for the synthesis of a catalyst support.

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POSTER SESSIONS

SESSION III

THERMOCHEMICAL CONVERSION

Mario König, University of Halle-Wittenberg/Deutsches Biomasseforschungszentrum

Development and application of novel catalysts for the low-temperature NOX abatement at combustion of biogenic solid fuels

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Alongside particulate matter emissions and hydrocarbons, nitrogen oxides (NOx) are the most problematic group of pollutants in the thermal conversion of biomass. Due to the increasing material use of wood, non-wood biomasses from residues has to be utilized for energy production. These fuels have an increased nitrogen content with correspondingly increased NOx emissions during combustion. Existing reduction measures for NOx do not have the technical and economic potential for an application in decentralized bioenergy plants. For the effective abatement of NOx from biomass furnaces, suitable catalysts for the low-temperature range must be developed. The aim of the PhD is research for low-temperature SCR-catalyst which can be produced, applied and disposed of in an economical and environmentally friendly manner.

Approach and Methods

The approach of the presented PhD is a systematic screening on suitable active components, carriers and synthesis methods for the preparation of a suitable SCR catalyst. Based on a literature survey catalyst precursors and carrier materials has been selected. A synthesis route based on Excess Solution Impregnation was developed and several powder catalysts were synthesized. The catalyst screening took place on a laboratory scale reactor with a synthetic gas mixture in the low temperature range. Temperature-conversion charts were recorded in order to select suitable catalyst. Beside the NOx- and NH_3-conversion also the formation of N_2O was studied and the N_2-selectivity of the different catalysts were compared. To characterize the catalysts, standard methods were applied: BET surface area, pore volume, H_2-TPR, XRD. Theses data is needed to understand the different performance of the synthesized catalysts for further improvement of suitable catalysts.

Interim results

The synthesis route consists of the following steps:
- 15 min stirring at 20 °C
- 45 min stirring at 70 °C
- 2 h drying at 120 °C
- 4 h calcination at 400 °C

The synthesized powder catalysts were examined on the laboratory scale reactor in a temperature range between 120 up to 250 °C at a space velocity of 38,000 h^{-1}.

The most promising catalyst was prepared with Manganese(II) nitrate tetrahydrate as precursor and SiO_2-powder with a high pore volume as carrier. For this catalyst the content of Mn was varied from 5 to 30 wt. %. Further, the influence of different operation conditions such as space velocity, SO_2 and H_2O content were investigated.

Ongoing research

The next steps in the PhD work are the investigation of the mechanism that are leading to high SCR-activity and N_2-selectivity including possible deactivation by SO_2 and H_2O. In order to improve the catalyst performance a mix of Mn with other metal oxides such as Cu or Fe will be investigated. The suitability of the studied catalyst will be demonstrated by tests at a pilot scale biomass boiler.

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13TH/14TH SEPTEMBER 2021, KARLSRUHE

Development and application of novel SCR catalysts for the low-temperature denitrification of exhaust gases from the thermo-chemical conversion of biogenic solid fuels

Mario König

BACKGROUND AND GOAL

Alongside particulate emissions and airborne hydrocarbons, nitrogen oxides (NO_x) are the most problematic group of pollutants in the thermal conversion of biomass. Due to the increasing material use of wood, non-woody biomass has to be utilized for energy production. Non-woody biomasses have an increased nitrogen content with correspondingly increased NO_x emissions during combustion. Existing reduction measures for NO_x do not have the technical and economic potential for an application in decentralized bioenergy plants. For the effective abatement of NO_x from biomass furnaces, suitable catalysts for the low-temperature range must be developed. The aim of the PhD is to find a low-temperature SCR-catalyst which can be produced, applied and disposed of in an economical and environmentally friendly manner.

APPROACH AND METHODS

- Systematic screening on suitable active catalyst components and carriers for low-temperature SCR
- Synthesis of different catalyst powders with optimized impregnation method
- Determination of catalyst properties with standard characterization methods (TGA, Physisorption, Chemisorption, XRD, SEM-EDX)
- Determination of the $DeNO_x$-activity of the catalysts on a laboratory-scale-reactor
- Influence of operating conditions (exhaust gas temperature, space velocity, SO_2 and H_2O)

CATALYST SYNTHESIS

- Appropriate synthesis route has been found:
  1) Solution of the precursor in distilled water
  2) Immersion of the support in the solution
  3) 15 min stirring at 20 ˚C
  4) 45 min stirring at 70 ˚C (dehydrate)
  5) 2 h drying at 120 ˚C @ air
  6) 4 h calcination at 400 ˚C
- Synthesis based on Mn-precursor and SiO_2:
  - Mn-Acetat and Mn-Nitrat as Precursor
  - SiO_2 powder with different surface properties
  - Variation of the mass ratio of Manganese (5, 10, 15, 20, 25, 30 % Mn)

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Figure 1: Catalyst suspension before, during and after stirring

RESULTS

Test of activity in the laboratory reactor schowed:
- Precursor Mn-Nitrate better than Mn-Acetat
- SiO_2 carrier with higher pore volume and lower BET-surface more active

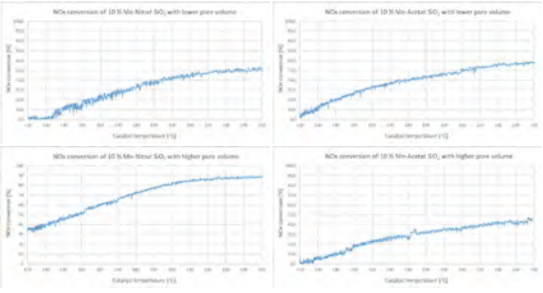

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Figure 2: $DeNO_x$ activity dependend on precursor and carrier surface properties.

- Activity increases from 5 to 15 % Mn-ratio and decreases from 20 - 30 % Mn-ratio
- BET surface and pore volume decreases with increasing Mn-ratio

Catalyst	BET-surface [m^2/g]	Pore Volume [cm^3/g]
SiO_2 with low PV (pure)	316	0,73
SiO_2 with high PV (pure)	232	2,10
5 % Mn-Nitrat on SiO_2 with high PV	222	1,46
10 % Mn-Nitrat on SiO_2 with high PV	204	1,35
15 % Mn-Nitrat on SiO_2 with high PV	188	1,22
20 % Mn-Nitrat on SiO_2 with high PV	173	1,16
25 % Mn-Nitrat on SiO_2 with high PV	154	1,10
30 % Mn-Nitrat on SiO_2 with high PV	138	0,96

Figure 3: Results of physisorption analysis

ONGOING RESEARCH

- Variation of calcination temperature
- Blend of different carriers (SiO_2, Al_2O_3, TiO_2)
- Doping with further metal oxides to increase SO_2/H_2O-resistance and N_2 selectivity

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Simon Markthaler, Friedrich-Alexander University Erlangen/Nürnberg

Direct catalytic methanation of biogas: From laboratory experiments to demonstration scale

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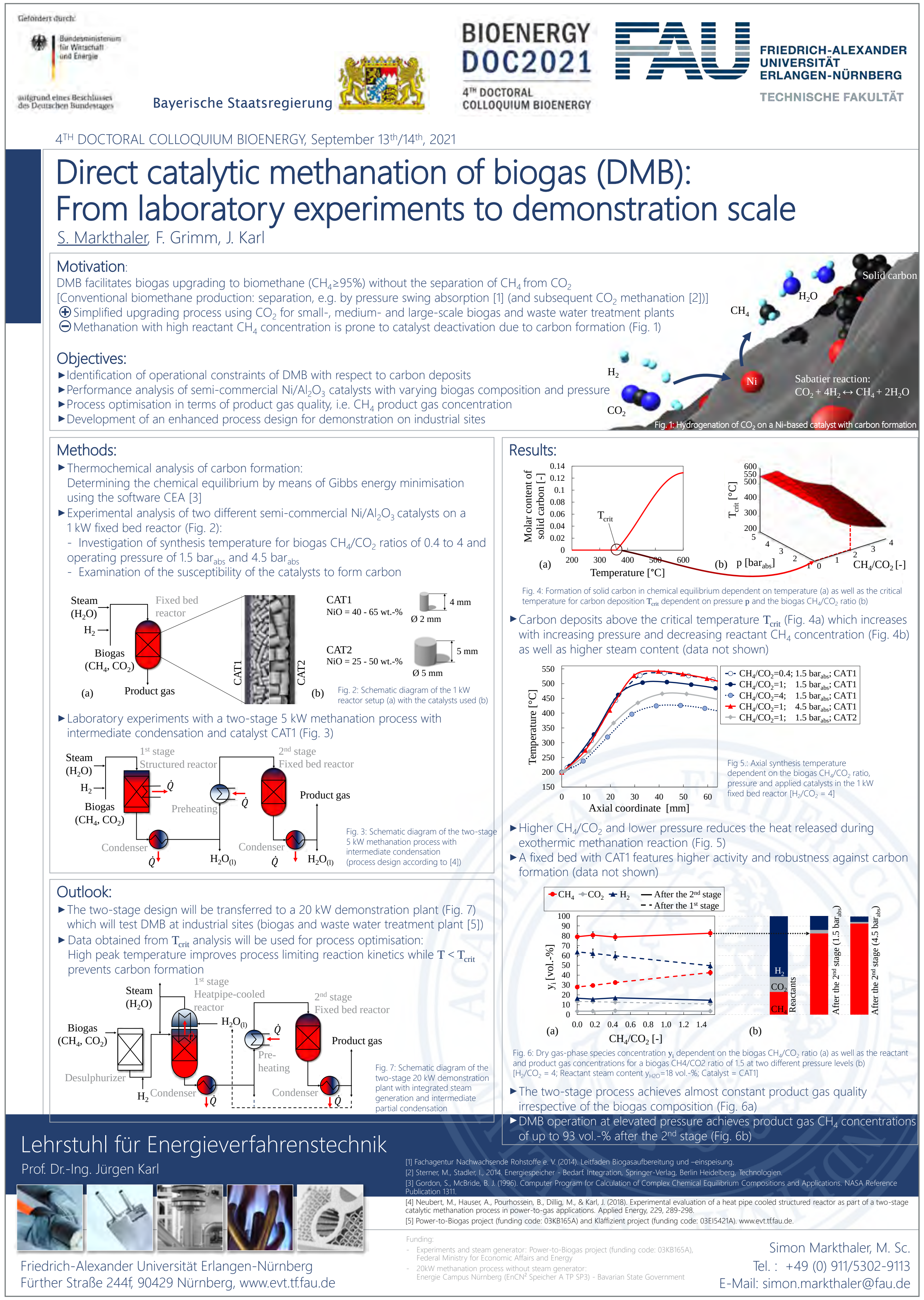
Direct methanation of biogas involves the conversion of carbon dioxide (CO_2), a major component of biogas, with hydrogen (H_2) into methane (CH_4). Using hydrogen from renewable energy sources, this approach enables the conversion of surplus electrical energy into the chemical energy carrier, methane. The synthetically produced methane can either be stored in local gas storage facilities or utilized in gas engines for cogeneration of heat and power. Due to its high gas quality, injection into the gas grid is moreover possible, which may contribute to long-term chemical storage and sector coupling, i.e. methane utilization for heat, mobility and electricity applications.

The present work portrays an approach from laboratory experiments to a demonstration plant dedicated to biogas methanation. Starting with the systematic analysis of chemical equilibrium, the maximum synthesis temperatures are explored which enable process optimization with respect to reaction kinetics without being inflicted by the most prominent catalyst deactivation mechanisms of direct biogas methanation, i.e. carbon formation. On the basis of this thermochemical analysis, experimental investigations in a 1 kW adiabatic fixed bed reactor reveal the performance of two different Ni/Al2O3 catalysts (CAT1: NiO ≈ 40 – 65 wt.- %; CAT2: NiO ≈ 25 – 50 wt.- %) for varying biogas composition (CH_4/CO_2 = 0 – 4; desulfurized) and pressure (1.5 bar_{abs}, 4.5 bar_{abs}). Due to higher activity and robustness of CAT1, this catalyst was employed in a second experimental step: A two-stage 5 kW methanation process with intermediate condensation. The two-stage process demonstrates excellent performance on biogas methanation with methane product gas concentrations of y_{CH4} = 93 – 95 Vol.- % at elevated pressure p = 4.5 barabs for reactant gas compositions of CH_4/CO_2 = 0 - 1.5.

Bridging the gap between laboratory experiments and industrial application, the knowledge and experience of the present work are applied to a 20 kW demonstration plant. Based on the two-stage design, the new enhanced demonstration plant incorporates a heatpipe-cooled reactor with integrated steam generation. Furthermore, precise control of intermediate condensation and reaction temperature obviates carbon formation in the second methanation stage. These measures, in combination with a desulphurizer and autonomous plant control, will aim for upcoming long-term operation at several industrial sites (biogas plant/ waste water treatment plant) and the proof-of-concept of efficient direct methanation of biogas.



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4TH DOCTORAL COLLOQUIUM BIOENERGY

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

4TH DOCTORAL COLLOQUIUM BIOENERGY, September 13th/14th, 2021

Direct catalytic methanation of biogas (DMB): From laboratory experiments to demonstration scale

S. Markthaler, F. Grimm, J. Karl

Motivation:

DMB facilitates biogas upgrading to biomethane (CH_4≥95%) without the separation of CH_4 from CO_2
[Conventional biomethane production: separation, e.g. by pressure swing absorption [1] (and subsequent CO_2 methanation [2])]
⊕ Simplified upgrading process using CO_2 for small-, medium- and large-scale biogas and waste water treatment plants
⊖ Methanation with high reactant CH_4 concentration is prone to catalyst deactivation due to carbon formation (Fig. 1)

Objectives:

- Identification of operational constraints of DMB with respect to carbon deposits
- Performance analysis of semi-commercial Ni/Al_2O_3 catalysts with varying biogas composition and pressure
- Process optimisation in terms of product gas quality, i.e. CH_4 product gas concentration
- Development of an enhanced process design for demonstration on industrial sites

Fig. 1: Hydrogenation of CO_2 on a Ni-based catalyst with carbon formation

Methods:

- Thermochemical analysis of carbon formation:
  Determining the chemical equilibrium by means of Gibbs energy minimisation using the software CEA [3]
- Experimental analysis of two different semi-commercial Ni/Al_2O_3 catalysts on a 1 kW fixed bed reactor (Fig. 2):
  - Investigation of synthesis temperature for biogas CH_4/CO_2 ratios of 0.4 to 4 and operating pressure of 1.5 bar_{abs} and 4.5 bar_{abs}
  - Examination of the susceptibility of the catalysts to form carbon

Fig. 2: Schematic diagram of the 1 kW reactor setup (a) with the catalysts used (b)

- Laboratory experiments with a two-stage 5 kW methanation process with intermediate condensation and catalyst CAT1 (Fig. 3)

Fig. 3: Schematic diagram of the two-stage 5 kW methanation process with intermediate condensation (process design according to [4])

Outlook:

- The two-stage design will be transferred to a 20 kW demonstration plant (Fig. 7) which will test DMB at industrial sites (biogas and waste water treatment plant [5])
- Data obtained from T_{crit} analysis will be used for process optimisation:
  High peak temperature improves process limiting reaction kinetics while $T < T_{crit}$ prevents carbon formation

Fig. 7: Schematic diagram of the two-stage 20 kW demonstration plant with integrated steam generation and intermediate partial condensation

Results:

Fig. 4: Formation of solid carbon in chemical equilibrium dependent on temperature (a) as well as the critical temperature for carbon deposition T_{crit} dependent on pressure p and the biogas CH_4/CO_2 ratio (b)

- Carbon deposits above the critical temperature T_{crit} (Fig. 4a) which increases with increasing pressure and decreasing reactant CH_4 concentration (Fig. 4b) as well as higher steam content (data not shown)

Fig 5.: Axial synthesis temperature dependent on the biogas CH_4/CO_2 ratio, pressure and applied catalysts in the 1 kW fixed bed reactor [H_2/CO_2 = 4]

- Higher CH_4/CO_2 and lower pressure reduces the heat released during exothermic methanation reaction (Fig. 5)
- A fixed bed with CAT1 features higher activity and robustness against carbon formation (data not shown)

Fig. 6: Dry gas-phase species concentration y_i dependent on the biogas CH_4/CO_2 ratio (a) as well as the reactant and product gas concentrations for a biogas CH4/CO2 ratio of 1.5 at two different pressure levels (b) [H_2/CO_2 = 4; Reactant steam content y_{H2O}=18 vol.-%; Catalyst = CAT1]

- The two-stage process achieves almost constant product gas quality irrespective of the biogas composition (Fig. 6a)
- DMB operation at elevated pressure achieves product gas CH_4 concentrations of up to 93 vol.-% after the 2nd stage (Fig. 6b)

Lehrstuhl für Energieverfahrenstechnik
Prof. Dr.-Ing. Jürgen Karl

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- 20kW methanation process without steam generator: Energie Campus Nürnberg (EnCN² Speicher A TP SP3) - Bavarian State Government

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Thomas Schliermann, Deutsches Biomasseforschungszentrum

Synthesis and property optimization of biogenic silica by thermochemical conversion of rice husk in conversion reactors of variable size from laboratory to kilogram scale

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Biogenic silica can be a sustainable alternative to commercially available silica products such as precipitated silica or fumed silica, which currently have to be manufactured using energy-intensive processes. Such biogenic silica can be obtained from cheap and abundantly available Si-containing agricultural residues such as rice husks or straw by thermo-chemical conversion, with biogenic silica being obtained from the Si-containing ash as a second product in addition to heat.

So far, extensive work has been carried out by researchers on laboratory scale (gram scale) on pre-treatment strategies of Si-containing agro-residues and thermochemical conversion providing a broad knowledge base on main parameters influencing the properties of the biogenic silica, especially using muffle furnaces and thermogravimetric analyzers. However, there is a lack of research activities on upscaling the process to conversion apparatuses relevant in practical application such as boilers while simultaneously still producing high quality biogenic silica ash in terms of purity, homogeneity, crystallinity, surface area and porosity. In upscaled conversion systems additional aspects such as inhomogeneities of gaseous atmospheres, flow profiles and temperatures have to be taken into account too. Furthermore, for application the processes must be adapted and optimized for sustainability and ressource efficiency.

The focus of this research work is on the investigation and optimization of conversion processes using different conversion systems up to several kg of fuel supply as an intermediate step towards understanding the necessary measures for upscaling and practical conversion systems. Thermogravimetric balances of different scales and small-scale furnaces are used in this study. For this paper the principal approach comprising specially designed experiments, computer modeling and extensive characterization of the obtained ashes will be presented. Furthermore, first results will be discussed.

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Synthesis and property optimization of biogenic silica by thermochemical conversion of rice husk in conversion reactors of variable size from laboratory to kilogram scale

Thomas Schliermann

BACKGROUND AND GOALS

Biogenic silica can be a sustainable alternative to commercially available silica products, which currently have to be manufactured using energy-intensive processes. Such biogenic silica can be obtained from cheap and abundantly available Si-containing agricultural residues such as rice husks by thermo-chemical conversion, with biogenic silica being obtained from the Si-containing ash as a second product in addition to heat.

So far, extensive work has been carried out by researchers on laboratory scale (gram scale) on pre-treatment strategies of Si-containing agro-residues and thermochemical conversion providing a broad knowledge base on main parameters influencing the properties of the biogenic silica, especially using muffle furnaces and thermogravimetric analyzers. However, there is a lack of research activities on upscaling the process to conversion apparatuses relevant in practical application such as boilers while simultaneously still producing high quality biogenic silica ash in terms of purity, homogeneity, crystallinity, surface area and porosity.

The focus of this research work is on the investigation and optimization of conversion processes using different conversion systems up to several kg of fuel supply as an intermediate step towards understanding the necessary measures for upscaling and practical conversion systems.

LABORATORY SCALE

Muffle furnaces

Rice husk

High purity
300 m²/g
0,4 cm³/g

Laboratory ash

Upscaling: additional knowledge needed

- Temperature distribution in bed and overbed
  → Ash crystallization; emissions
- Gas atmosphere (primary / secondary air)
- Fuel density / fuel segregation / dust
- Bed porosity
- Huge ash volumes
  (rice husk: 10 – 25 wt.% ash content)
- Modes of operation

MacroTGA

- kg scale; flexible gas supply
- Monitoring of mass
- Temperature sensors
- Gaseous products
- Adjustable boundary conditions

Deeper understanding of combustion process

APPLICATION SCALE

Boiler (with heat provision)

Impurities,
carbon
185 m²/g
0,25 cm³/g

Boiler ash

Improved properties of biogenic silica ashes

APPROACH

- Experiments using MacroTGA, small-scale combustors and boilers
- Modeling of specific partial aspects
- Optimized operation conditions and components

CURRENT ACTIVITIES

- MacroTGA put into operation
- First experiments with rice husks (raw, pretreated, pelletized) carried out
- Familiarization with modeling approaches

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René Bindig, University of Halle-Wittenberg/Deutsches Biomasseforschungszentrum

Procedure for the development of catalysts for the reduction of emissions from small-scale combustion

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The basis for almost all industrial processes and exhaust aftertreatments are catalysts. Catalyst development is a topic of constant high relevance, because process optimizations and adaptations to changed boundary conditions require new and further developed catalysts.

The greatest difficulties encountered in development arise during the transition from one stage of development to the next. A reliable estimation of the behaviour of a newly developed catalyst in real applications based on laboratory results would minimize the risk of having to repeat especially the final, very cost-intensive development step several times. This could significantly reduce the overall development costs.

Furthermore, on a laboratory scale, and under otherwise identical conditions a more exact recording of the temperature or temperature distribution over a catalyst sample is possible. This allows a more detailed investigation of the various factors that influence the observed effective kinetics of that catalyst sample.

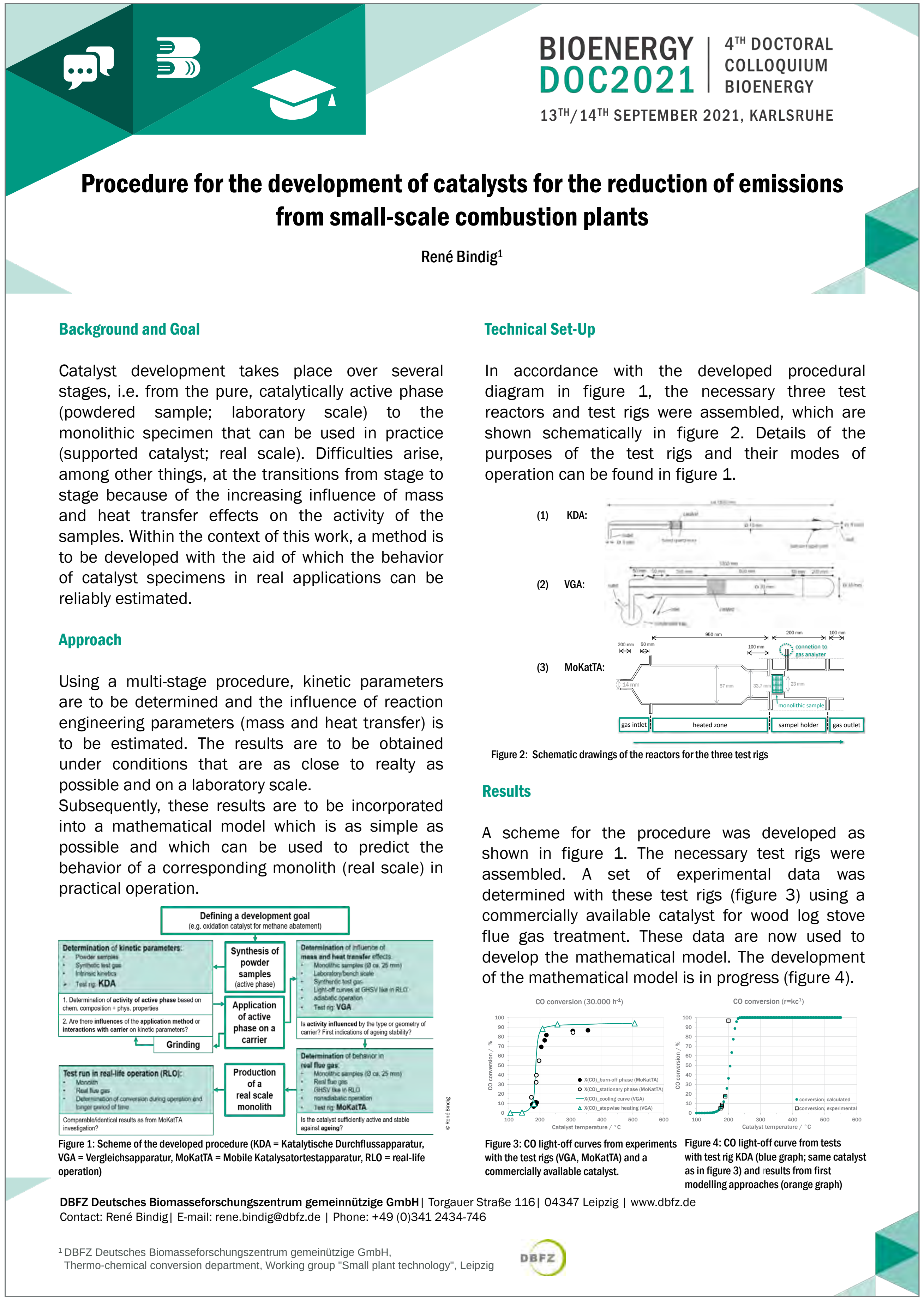
The aim of the thesis is the development of a multi-stage procedure with which the behaviour of a full-scale, newly developed catalyst can be reliably estimated.

For this purpose, experimental data are generated in suitable test rigs, using samples on a laboratory scale. These data are to be incorporated into a mathematical model. This model will be used to describe the conversion-temperature behaviour of the full-scale catalyst under the conditions in a real combustion plant.

The scope of application is restricted initially to the development of catalyts for exhaust aftertreatment of combustion plants in the small capacity range (i.e. combined heat and power plants and small-scale combustion units).

The test rigs, which are required for the procedure, have been designed and setted up. With the help of a commercially available catalyst, the suitability of the test rigs for this procedure is to be proven and the mathematical model to be derived.

The test rigs and the data obtained with these test rigs are presented and discussed. Also, the concepts for the model development are presented.



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Procedure for the development of catalysts for the reduction of emissions from small-scale combustion plants

René Bindig[1]

Background and Goal

Catalyst development takes place over several stages, i.e. from the pure, catalytically active phase (powdered sample; laboratory scale) to the monolithic specimen that can be used in practice (supported catalyst; real scale). Difficulties arise, among other things, at the transitions from stage to stage because of the increasing influence of mass and heat transfer effects on the activity of the samples. Within the context of this work, a method is to be developed with the aid of which the behavior of catalyst specimens in real applications can be reliably estimated.

Approach

Using a multi-stage procedure, kinetic parameters are to be determined and the influence of reaction engineering parameters (mass and heat transfer) is to be estimated. The results are to be obtained under conditions that are as close to realty as possible and on a laboratory scale.
Subsequently, these results are to be incorporated into a mathematical model which is as simple as possible and which can be used to predict the behavior of a corresponding monolith (real scale) in practical operation.

Defining a development goal
(e.g. oxidation catalyst for methane abatement)

Determination of **kinetic parameters**:
- Powder samples
- Synthetic test gas
- Intrinsic kinetics
- Test rig: **KDA**

1. Determination of **activity of active phase** based on chem. composition + phys. properties
2. Are there **influences** of the **application method** or **interactions with carrier** on kinetic parameters?

Grinding

Synthesis of powder samples (active phase)

Application of active phase on a carrier

Production of a real scale monolith

Determination of influence of **mass and heat transfer** effects:
- Monolithic samples (Ø ca. 25 mm)
- Laboratory/bench scale
- Synthetic test gas
- Light-off curves at GHSV like in RLO
- adiabatic operation
- Test rig: **VGA**

Is **activity influenced** by the type or geometry of carrier? First indications of ageing stability?

Determination of behavior in **real flue gas**:
- Monolithic samples (Ø ca. 25 mm)
- Real flue gas
- GHSV like in RLO
- nonadiabatic operation
- Test rig: **MoKatTA**

Is the catalyst sufficiently active and stable against **ageing**?

Test run in real-life operation (RLO):
- Monolith
- Real flue gas
- Determination of conversion during operation and longer period of time

Comparable/identical results as from MoKatTA investigation?

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Figure 1: Scheme of the developed procedure (KDA = Katalytische Durchflussapparatur, VGA = Vergleichsapparatur, MoKatTA = Mobile Katalysatortestapparatur, RLO = real-life operation)

Technical Set-Up

In accordance with the developed procedural diagram in figure 1, the necessary three test reactors and test rigs were assembled, which are shown schematically in figure 2. Details of the purposes of the test rigs and their modes of operation can be found in figure 1.

Figure 2: Schematic drawings of the reactors for the three test rigs

Results

A scheme for the procedure was developed as shown in figure 1. The necessary test rigs were assembled. A set of experimental data was determined with these test rigs (figure 3) using a commercially available catalyst for wood log stove flue gas treatment. These data are now used to develop the mathematical model. The development of the mathematical model is in progress (figure 4).

Figure 3: CO light-off curves from experiments with the test rigs (VGA, MoKatTA) and a commercially available catalyst.

Figure 4: CO light-off curve from tests with test rig KDA (blue graph; same catalyst as in figure 3) and results from first modelling approaches (orange graph)

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Stella Walker, Karlsruhe Institute of Technology (KIT)

Investigations on reaction kinetics of biogenic solid fuel for Entrained Flow Gasification

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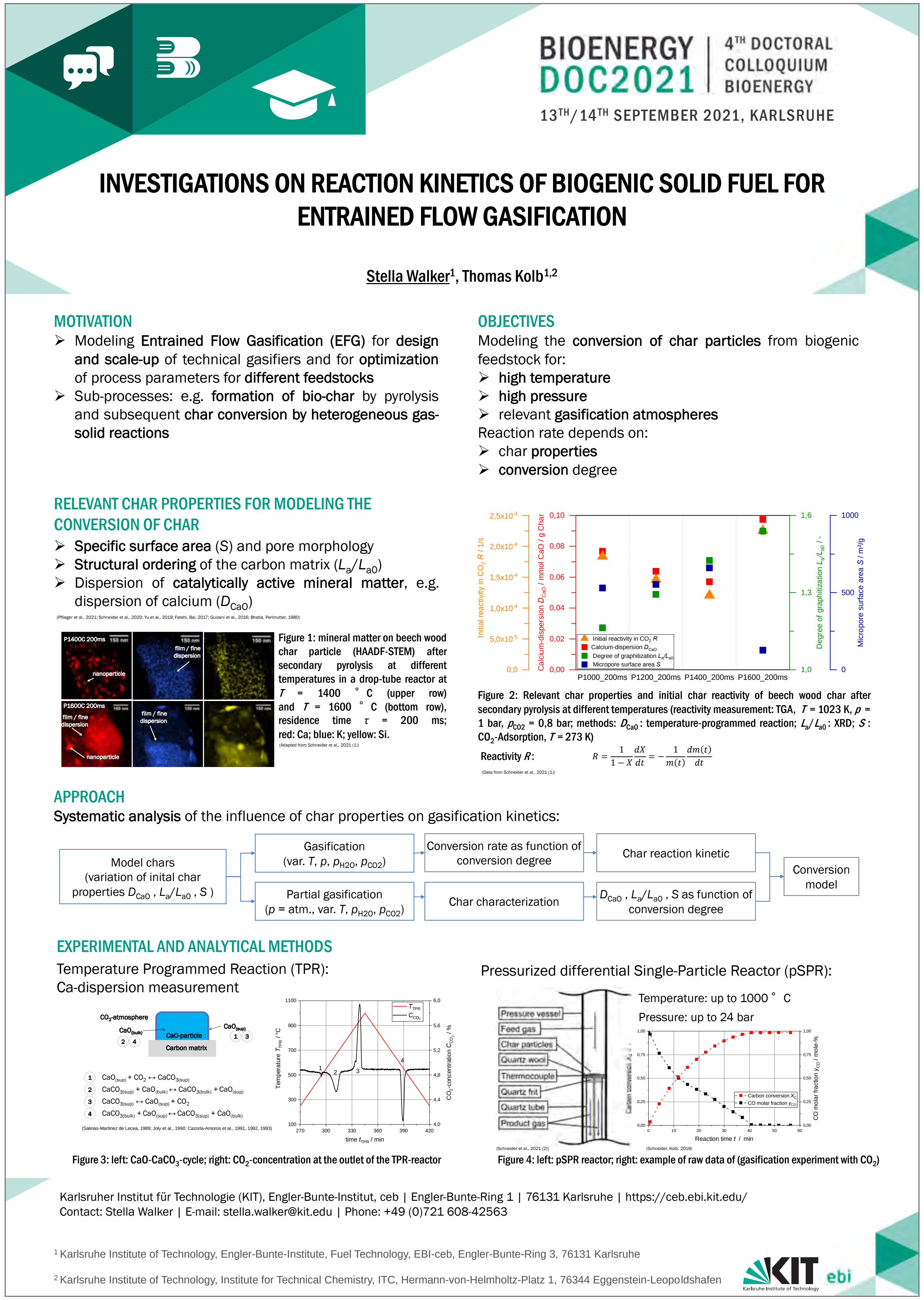
Entrained-flow gasification allows for the sustainable production of chemicals and synthetic fuels from low-grade biogenic feedstock via syngas.

The conversion of biogenic fuels consists of multiple steps such as formation of bio-char by pyrolysis and subsequent heterogeneous gas-solid reactions. Kinetic investigations of biogenic char contribute to the determination of the conversion rate at process conditions and are crucial for design and operation of entrained-flow gasifiers.



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INVESTIGATIONS ON REACTION KINETICS OF BIOGENIC SOLID FUEL FOR ENTRAINED FLOW GASIFICATION

Stella Walker[1], Thomas Kolb[1,2]

MOTIVATION

- Modeling **Entrained Flow Gasification (EFG)** for **design and scale-up** of technical gasifiers and for **optimization** of process parameters for **different feedstocks**
- Sub-processes: e.g. **formation of bio-char** by pyrolysis and subsequent **char conversion by heterogeneous gas-solid reactions**

OBJECTIVES

Modeling the **conversion of char particles** from biogenic feedstock for:

- **high temperature**
- **high pressure**
- relevant **gasification atmospheres**

Reaction rate depends on:

- char **properties**
- **conversion** degree

RELEVANT CHAR PROPERTIES FOR MODELING THE CONVERSION OF CHAR

- **Specific surface area** (S) and pore morphology
- **Structural ordering** of the carbon matrix (L_a/L_{a0})
- Dispersion of **catalytically active mineral matter**, e.g. dispersion of calcium (D_{CaO})

(Pflieger et al., 2021; Schneider et al., 2020; Yu et al., 2019; Fatehi, Bai, 2017; Guizani et al., 2016; Bhatia, Perlmutter, 1980)

Figure 1: mineral matter on beech wood char particle (HAADF-STEM) after secondary pyrolysis at different temperatures in a drop-tube reactor at T = 1400 ° C (upper row) and T = 1600 ° C (bottom row), residence time τ = 200 ms; red: Ca; blue: K; yellow: Si.

(Adapted from Schneider et al., 2021 (1))

Figure 2: Relevant char properties and initial char reactivity of beech wood char after secondary pyrolysis at different temperatures (reactivity measurement: TGA, T = 1023 K, p = 1 bar, p_{CO2} = 0,8 bar; methods: D_{CaO}: temperature-programmed reaction; L_a/L_{a0}: XRD; S: CO_2-Adsorption, T = 273 K)

Reactivity R: $$R = \frac{1}{1-X}\frac{dX}{dt} = -\frac{1}{m(t)}\frac{dm(t)}{dt}$$

(Data from Schneider et al., 2021 (1))

APPROACH

Systematic analysis of the influence of char properties on gasification kinetics:

Model chars (variation of inital char properties D_{CaO} , L_a/L_{a0} , S)
Gasification (var. T, p, p_{H2O}, p_{CO2})
Partial gasification (p = atm., var. T, p_{H2O}, p_{CO2})
Conversion rate as function of conversion degree
Char characterization
Char reaction kinetic
D_{CaO} , L_a/L_{a0} , S as function of conversion degree
Conversion model

EXPERIMENTAL AND ANALYTICAL METHODS

Temperature Programmed Reaction (TPR):
Ca-dispersion measurement

① $CaO_{(sup)} + CO_2 \leftrightarrow CaCO_{3(sup)}$
② $CaCO_{3(sup)} + CaO_{(bulk)} \leftrightarrow CaCO_{3(bulk)} + CaO_{(sup)}$
③ $CaCO_{3(sup)} \leftrightarrow CaO_{(sup)} + CO_2$
④ $CaCO_{3(bulk)} + CaO_{(sup)} \leftrightarrow CaCO_{3(sup)} + CaO_{(bulk)}$

(Salinas-Martinez de Lecea, 1989; Joly et al., 1990; Cazorla-Amoros et al., 1991, 1992, 1993)

Figure 3: left: CaO-$CaCO_3$-cycle; right: CO_2-concentration at the outlet of the TPR-reactor

Pressurized differential Single-Particle Reactor (pSPR):

Temperature: up to 1000 ° C
Pressure: up to 24 bar

(Schneider et al., 2021 (2)) (Schneider, Kolb, 2019)

Figure 4: left: pSPR reactor; right: example of raw data of (gasification experiment with CO_2)

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Experimental screening of process parameters for the hydrothermal liquefaction of digestate

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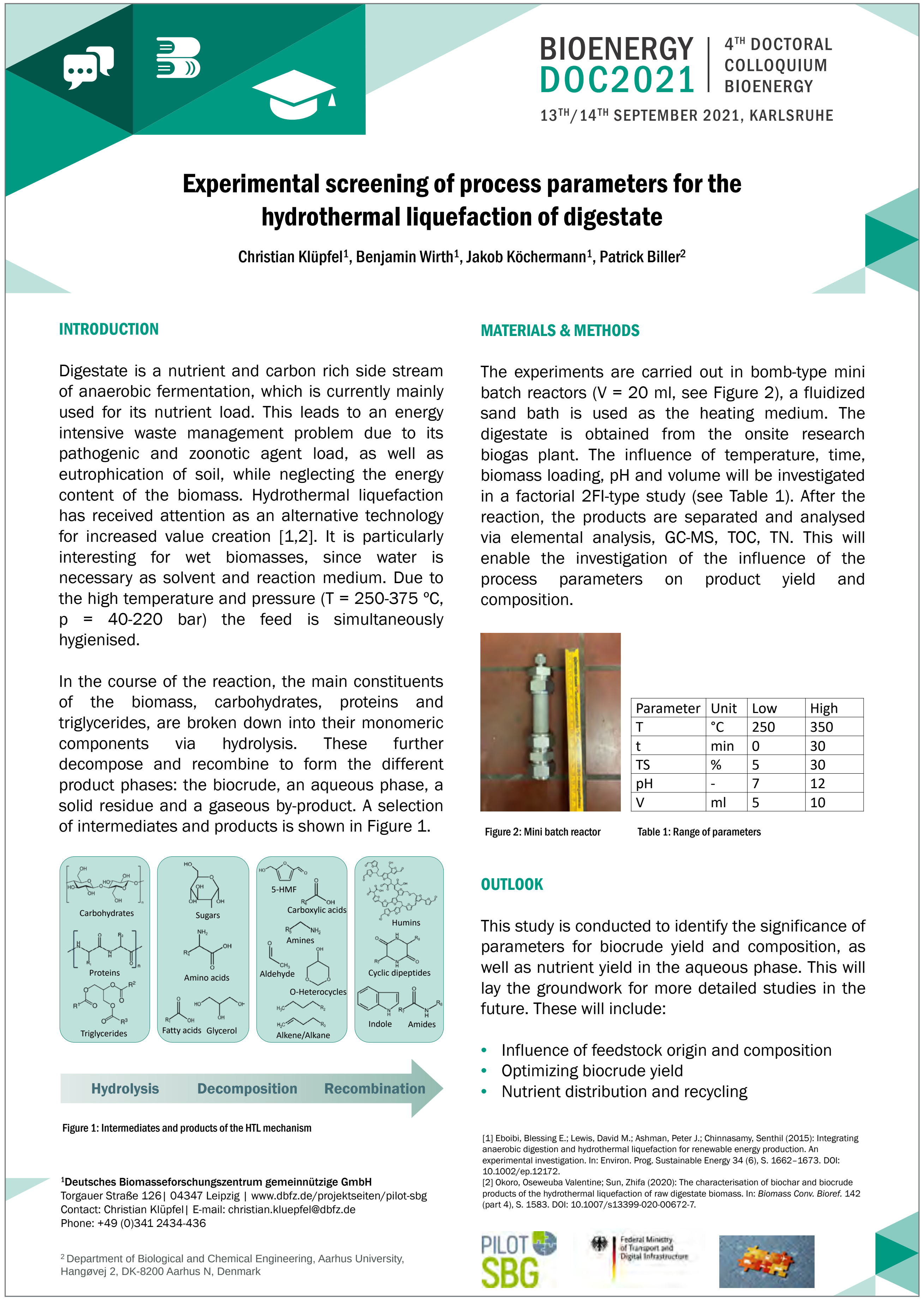
Digestate, a side stream of anaerobic fermentation of wet biomass, is a carbon and nutrient rich biomass, which requires further treatment due to pathogen and zoonotic agent load. Established schemes involve energy intensive drying and hygienisation, as well as storing prior to its use for plant cultivation, neglecting the energy content of the biomass. Hydrothermal liquefaction can be used as an alternative technology for increased value creation, by producing an energy dense bio-crude and a nutrient rich process water. This explorative study investigates various process parameters besides the usually studied ones as temperature and residence time. This is done to identify significant parameters to maximize biocrude yield by means of a maximized carbon yield and the nitrogen yield to the aqueous phase. The experiments are carried out in a mini batch (20 mL) setup in a factorial 2FI-type study. The biocrude is studied for its elemental and molecular composition, while the process water and solid residue will be studied for their nutrient load. The results will allow further understanding the influence of those process parameters and are used as a basis for more detailed studies in the future.



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Experimental screening of process parameters for the hydrothermal liquefaction of digestate

Christian Klüpfel[1], Benjamin Wirth[1], Jakob Köchermann[1], Patrick Biller[2]

INTRODUCTION

Digestate is a nutrient and carbon rich side stream of anaerobic fermentation, which is currently mainly used for its nutrient load. This leads to an energy intensive waste management problem due to its pathogenic and zoonotic agent load, as well as eutrophication of soil, while neglecting the energy content of the biomass. Hydrothermal liquefaction has received attention as an alternative technology for increased value creation [1,2]. It is particularly interesting for wet biomasses, since water is necessary as solvent and reaction medium. Due to the high temperature and pressure (T = 250-375 °C, p = 40-220 bar) the feed is simultaneously hygienised.

In the course of the reaction, the main constituents of the biomass, carbohydrates, proteins and triglycerides, are broken down into their monomeric components via hydrolysis. These further decompose and recombine to form the different product phases: the biocrude, an aqueous phase, a solid residue and a gaseous by-product. A selection of intermediates and products is shown in Figure 1.

Figure 1: Intermediates and products of the HTL mechanism

MATERIALS & METHODS

The experiments are carried out in bomb-type mini batch reactors (V = 20 ml, see Figure 2), a fluidized sand bath is used as the heating medium. The digestate is obtained from the onsite research biogas plant. The influence of temperature, time, biomass loading, pH and volume will be investigated in a factorial 2FI-type study (see Table 1). After the reaction, the products are separated and analysed via elemental analysis, GC-MS, TOC, TN. This will enable the investigation of the influence of the process parameters on product yield and composition.

Figure 2: Mini batch reactor

Parameter	Unit	Low	High
T	°C	250	350
t	min	0	30
TS	%	5	30
pH	-	7	12
V	ml	5	10

Table 1: Range of parameters

OUTLOOK

This study is conducted to identify the significance of parameters for biocrude yield and composition, as well as nutrient yield in the aqueous phase. This will lay the groundwork for more detailed studies in the future. These will include:

- Influence of feedstock origin and composition
- Optimizing biocrude yield
- Nutrient distribution and recycling

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[2] Okoro, Oseweuba Valentine; Sun, Zhifa (2020): The characterisation of biochar and biocrude products of the hydrothermal liquefaction of raw digestate biomass. In: *Biomass Conv. Bioref.* 142 (part 4), S. 1583. DOI: 10.1007/s13399-020-00672-7.

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Catalytic hydrothermal gasification of glycerol. Focus on chemical deactivation pathways.

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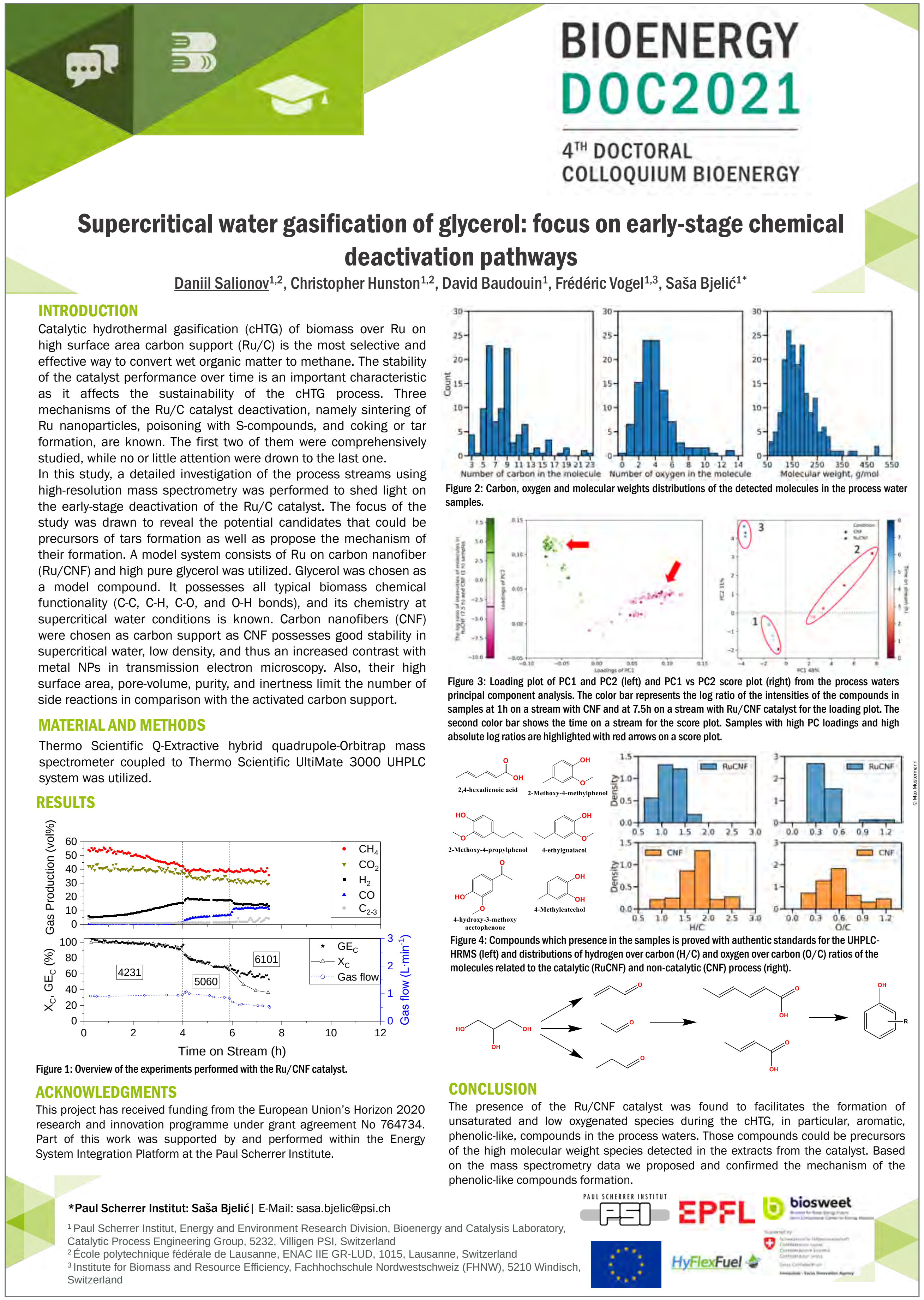
Catalytic hydrothermal gasification (cHTG) of biomass over Ru on high surface area carbon support (Ru/C) is the most selective and effective way to convert wet organic matter to methane. It is in particular interest to investigate the deactivation mechanisms of such catalysts to understand the origin of this process with the following development of the methods for the catalyst reactivation to increase its longevity and thus improve the sustainability of the cHTG process. In the previous studies, the main focus was drawn to understand the deactivation process by the poisoning of Ru/C with sulfur compounds or by nanoparticle sintering. Recently, another way of deactivation, namely the adsorption of larger organic molecules on the Ru nanoparticles, was proposed; however, it was not supported by analytical data. Also, the role of the catalyst in the formation of such species is still yet unknown. To understand this phenomenon, a comparison of the chemical compositions of the effluents (liquid phase) of catalytical and non-catalytical conversion of glycerol and extracts from the Ru/C catalyst using high-resolution mass spectrometry was made. Glycerol was chosen as a model compound. It possesses all typical biomass chemical functionality (C-C, C-H, C-O, and O-H bonds), and its chemistry at supercritical water conditions is known. The most abundant species detected in the liquid phase of the non-catalytical process were found to be different products of glycerol degradation and condensation, such as acrolein, acetaldehyde, 1-hydroxypropyl-2-one, and diglycerol. Also, the presence of long-chain ethers, consist of C_2H_4O structural elements, was observed. The average hydrogen to carbon (H/C) and oxygen to carbon (O/C) values of the detected compounds was found to be 2 and 0.6, respectively, with the mean molecular weight of 118 g/mole and double bond equivalent (DBE) value equal to 0.6. In contrast, in the liquid phase of the catalytical conversion of glycerol, a higher share of unsaturated species was observed. The average H/C and O/C values were shifted toward lower numbers and equal to 1.2 and 0.2. The mean molecular weight and DBE values increased to 152 g/mole and 1.2, respectively. Further investigation showed that these unsaturated species belong to different phenolic compounds. Using authentic standards, we confirmed the presence of dimethoxy-phenols, hydroxy-benzyl alcohols, and hydroxy-dimethoxyacetophenons in the sample. The analysis of the adsorbates extracted from the Ru/C catalyst showed the presence of different high molecular weight compounds with the mean molecular weight of 343 g/mole and DBE value of 5, which could be products of phenolics compound polymerization observed in the liquid phase. These findings indicate that the Ru/C catalyst facilitates the formation of unsaturated compounds from glycerol. The following polymerization of such species could be a potential source of the tar and thus leads to the catalyst deactivation.



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Supercritical water gasification of glycerol: focus on early-stage chemical deactivation pathways

Daniil Salionov[1,2], Christopher Hunston[1,2], David Baudouin[1], Frédéric Vogel[1,3], Saša Bjelić[1*]

INTRODUCTION

Catalytic hydrothermal gasification (cHTG) of biomass over Ru on high surface area carbon support (Ru/C) is the most selective and effective way to convert wet organic matter to methane. The stability of the catalyst performance over time is an important characteristic as it affects the sustainability of the cHTG process. Three mechanisms of the Ru/C catalyst deactivation, namely sintering of Ru nanoparticles, poisoning with S-compounds, and coking or tar formation, are known. The first two of them were comprehensively studied, while no or little attention were drown to the last one.

In this study, a detailed investigation of the process streams using high-resolution mass spectrometry was performed to shed light on the early-stage deactivation of the Ru/C catalyst. The focus of the study was drawn to reveal the potential candidates that could be precursors of tars formation as well as propose the mechanism of their formation. A model system consists of Ru on carbon nanofiber (Ru/CNF) and high pure glycerol was utilized. Glycerol was chosen as a model compound. It possesses all typical biomass chemical functionality (C-C, C-H, C-O, and O-H bonds), and its chemistry at supercritical water conditions is known. Carbon nanofibers (CNF) were chosen as carbon support as CNF possesses good stability in supercritical water, low density, and thus an increased contrast with metal NPs in transmission electron microscopy. Also, their high surface area, pore-volume, purity, and inertness limit the number of side reactions in comparison with the activated carbon support.

MATERIAL AND METHODS

Thermo Scientific Q-Extractive hybrid quadrupole-Orbitrap mass spectrometer coupled to Thermo Scientific UltiMate 3000 UHPLC system was utilized.

RESULTS

Figure 1: Overview of the experiments performed with the Ru/CNF catalyst.

Figure 2: Carbon, oxygen and molecular weights distributions of the detected molecules in the process water samples.

Figure 3: Loading plot of PC1 and PC2 (left) and PC1 vs PC2 score plot (right) from the process waters principal component analysis. The color bar represents the log ratio of the intensities of the compounds in samples at 1h on a stream with CNF and at 7.5h on a stream with Ru/CNF catalyst for the loading plot. The second color bar shows the time on a stream for the score plot. Samples with high PC loadings and high absolute log ratios are highlighted with red arrows on a score plot.

2,4-hexadienoic acid
2-Methoxy-4-methylphenol
2-Methoxy-4-propylphenol
4-ethylguaiacol
4-hydroxy-3-methoxy acetophenone
4-Methylcatechol

Figure 4: Compounds which presence in the samples is proved with authentic standards for the UHPLC-HRMS (left) and distributions of hydrogen over carbon (H/C) and oxygen over carbon (O/C) ratios of the molecules related to the catalytic (RuCNF) and non-catalytic (CNF) process (right).

ACKNOWLEDGMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 764734. Part of this work was supported by and performed within the Energy System Integration Platform at the Paul Scherrer Institute.

CONCLUSION

The presence of the Ru/CNF catalyst was found to facilitates the formation of unsaturated and low oxygenated species during the cHTG, in particular, aromatic, phenolic-like, compounds in the process waters. Those compounds could be precursors of the high molecular weight species detected in the extracts from the catalyst. Based on the mass spectrometry data we proposed and confirmed the mechanism of the phenolic-like compounds formation.

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Anthanasios Angelos Vadarlis, Karlsruhe Institute of Technology (KIT)

Hydrogen Production from wet waste biomass via Supercritical Water Gasification and sequential steam reforming of the hydrocarbons: A simulation study

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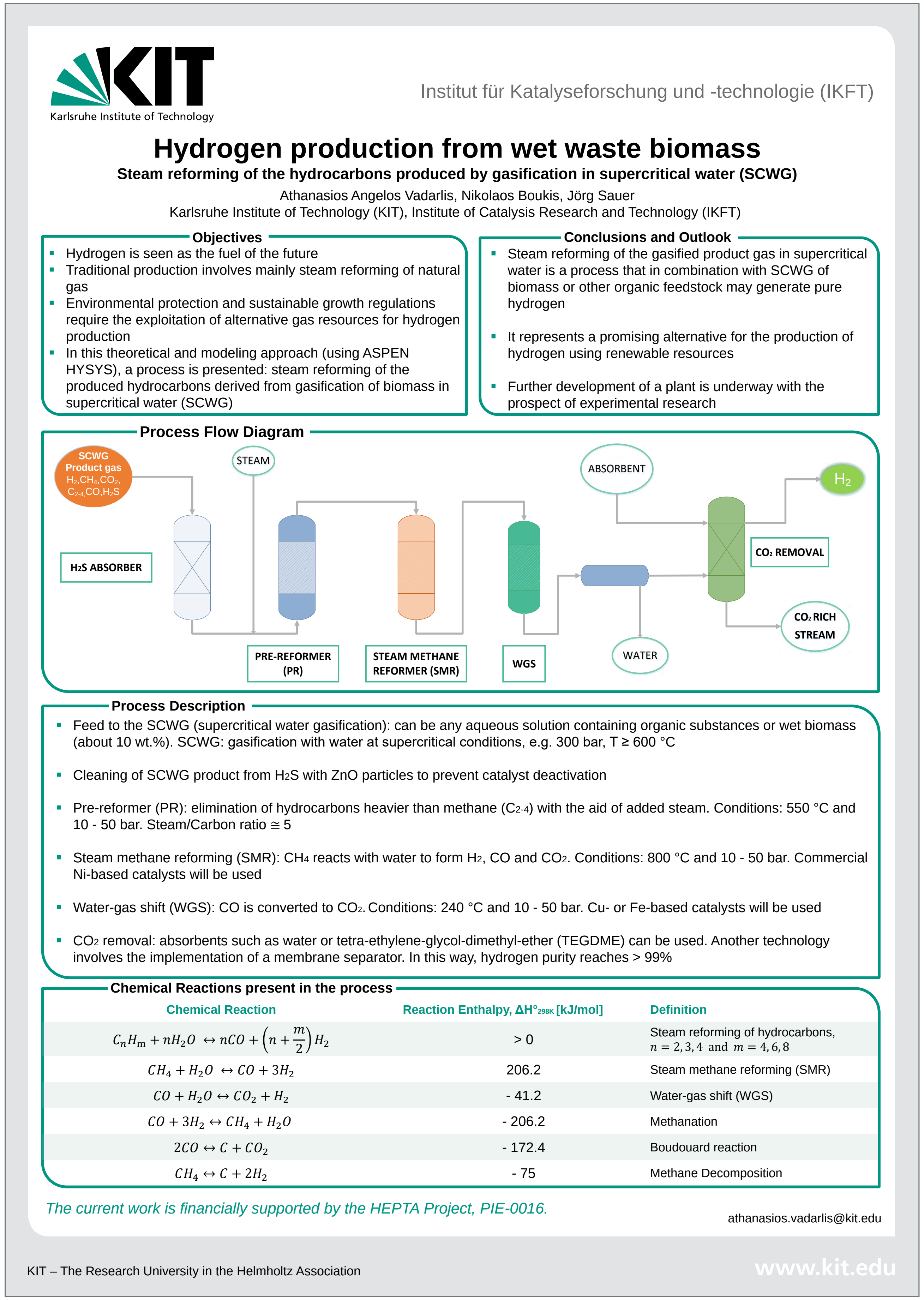
Hydrogen is considered to be the fuel of the future since it can replace hydrocarbons and provide a combustion without carbon oxides emissions, is suitable as an energy carrier instead of electricity and it is an intermediate product for the production of other widely used chemicals such as methanol and ammonia. It derives from fossil fuels and is produced by an intermediate product gas mixture consisted of H_2 and CO (syngas) via steam reforming of natural gas. Recent trends regarding environmental protection and sustainable growth have led to the application of a product gas from various biomass resources. This gas is comprised mainly of hydrogen, methane and carbon dioxide and can be produced via a process called Super Critical Water Gasification (SCWG). A sequential steam reforming process can result to a product gas highly pure in H_2. The current work focuses on a new process for the combination of the SCWG with the conventional steam reforming process. This process will be further designed and experimentally tested.

The feed to the SCWG is an 8wt. % ethanol aqueous solution as a model substance for wet biomass. In a later stage of the project also wet biomass waste will be applied. Data regarding the gasification of an ethanol solution under supercritical water conditions are given from previous experiments at IKFT. The gasification is carried out under supercritical conditions, more specifically at 280 bar and 600 °C. The product gas consists of supercritical water (92 vol. %), hydrogen (3.49 vol. %), methane (2.32 vol. %), higher hydrocarbons such as ethane (0.2 vol. %), propane (0.01 vol. %), carbon monoxide (0.04 vol. %) and carbon dioxide (1.85 vol. %).

After SCWG, a pre-reformer operated at 550 °C and 30bar is used for the conversion of any hydrocarbons except from methane to H_2, CO_2, CO and CH_4. The pre-reformed product is fed to the steam methane reformer (SMR) where, under 800 °C and 30bar methane reacts with steam to form CO and H_2. CO_2 and H_2 are already present in the SMR feed and therefore water has to be in excess, so a larger Steam/Carbon ratio than that applied in industry is used. Due to the high temperature in the reactor, the water-gas shift (WGS) reaction cannot take place extensively and CO has to be converted to CO_2 in a sequential reactor operated at lower temperature (240-250 °C) but at the same pressure. Commercial Ni-based catalysts will be used in the reforming reactors and Cu- or Fe-based catalysts in the WGS reactor. The product from the last reactor is cooled enough for steam to condense and then to be separated. The last step of the process is related to hydrogen purification. For this purpose, water or tetra-ethylene-glycol-dimethyl-ether (TEGDME) can be used for the absorption of CO_2. Other technologies such as a membrane separator may be applied. The product gas is rich in hydrogen and its purity, which is above 98 % is a matter of optimization.



Karlsruhe Institute of Technology

Institut für Katalyseforschung und -technologie (IKFT)

Hydrogen production from wet waste biomass

Steam reforming of the hydrocarbons produced by gasification in supercritical water (SCWG)

Athanasios Angelos Vadarlis, Nikolaos Boukis, Jörg Sauer
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Objectives

- Hydrogen is seen as the fuel of the future
- Traditional production involves mainly steam reforming of natural gas
- Environmental protection and sustainable growth regulations require the exploitation of alternative gas resources for hydrogen production
- In this theoretical and modeling approach (using ASPEN HYSYS), a process is presented: steam reforming of the produced hydrocarbons derived from gasification of biomass in supercritical water (SCWG)

Conclusions and Outlook

- Steam reforming of the gasified product gas in supercritical water is a process that in combination with SCWG of biomass or other organic feedstock may generate pure hydrogen
- It represents a promising alternative for the production of hydrogen using renewable resources
- Further development of a plant is underway with the prospect of experimental research

Process Flow Diagram

Process Description

- Feed to the SCWG (supercritical water gasification): can be any aqueous solution containing organic substances or wet biomass (about 10 wt.%). SCWG: gasification with water at supercritical conditions, e.g. 300 bar, T ≥ 600 °C
- Cleaning of SCWG product from H_2S with ZnO particles to prevent catalyst deactivation
- Pre-reformer (PR): elimination of hydrocarbons heavier than methane (C_{2-4}) with the aid of added steam. Conditions: 550 °C and 10 - 50 bar. Steam/Carbon ratio ≅ 5
- Steam methane reforming (SMR): CH_4 reacts with water to form H_2, CO and CO_2. Conditions: 800 °C and 10 - 50 bar. Commercial Ni-based catalysts will be used
- Water-gas shift (WGS): CO is converted to CO_2. Conditions: 240 °C and 10 - 50 bar. Cu- or Fe-based catalysts will be used
- CO_2 removal: absorbents such as water or tetra-ethylene-glycol-dimethyl-ether (TEGDME) can be used. Another technology involves the implementation of a membrane separator. In this way, hydrogen purity reaches > 99%

Chemical Reactions present in the process

Chemical Reaction	Reaction Enthalpy, ΔH°_{298K} [kJ/mol]	Definition
$C_nH_m + nH_2O \leftrightarrow nCO + \left(n + \frac{m}{2}\right) H_2$	> 0	Steam reforming of hydrocarbons, $n = 2,3,4$ and $m = 4,6,8$
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	206.2	Steam methane reforming (SMR)
$CO + H_2O \leftrightarrow CO_2 + H_2$	- 41.2	Water-gas shift (WGS)
$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	- 206.2	Methanation
$2CO \leftrightarrow C + CO_2$	- 172.4	Boudouard reaction
$CH_4 \leftrightarrow C + 2H_2$	- 75	Methane Decomposition

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Production of a mineral fertilizer in a multi-stage process for phosphorus recovery of sewage sludge

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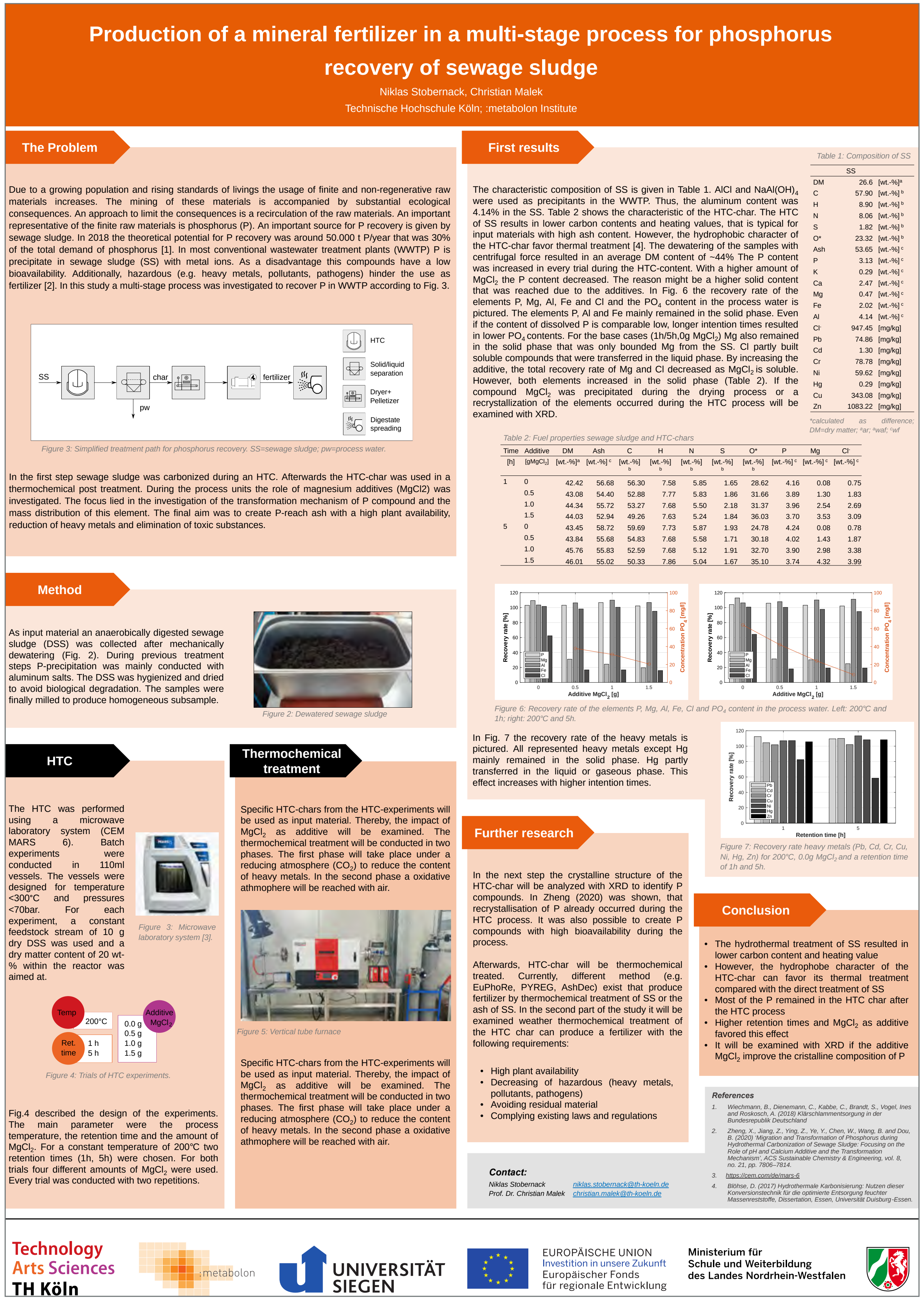
Due to a growing population and rising living standards the usage of finite and non-regenerative raw materials increases. The mining of these materials is accompanied by substantial ecological consequences. An approach to limit the consequences is a recirculation of the raw materials. An important representative of the finite raw materials is phosphorus. Phosphorus is essential for many biological processes and can neither be substituted nor synthesized. The increasing scarcity leads to precarious mining situations which are accompanied by drastic social and ecologic consequences. Additionally, to counteract a dependence from provider countries a focus on closing nutrient cycles is needed.

An important source for phosphorus recovery is provided by municipal sewage plants. In Germany, the operator of sewage plants will be continuously obliged to recover phosphorus from sewage sludge or its ash from 2029 on. Thus, alternative or complementary technologies have to be integrated into the waste water treatment plants (WWTP). Hydrothermal carbonization (HTC) has emerged as an energy-efficient technology for the treatment of sewage sludge. HTC can be used to convert sewage sludge in a coal-like intermediate product, which can be further used for an energetic exploitation. Thereby, the process enables the recovery of phosphorus.

In this study a multi-stage process was investigated to recover phosphorus in WWTP. In the first step sewage sludge was carbonized during HTC. Afterwards the HTC-char was utilized in a thermochemical post treatment step. During the process magnesium chloride ($MgCl_2$) was added to investigate the transformation mechanisms of phosphorus compounds and the mass distribution of this element. The final aim was to produce an ash which was (i) rich in phosphorus, (ii) characterized by a high plant availability, (iii) a reduction of heavy metals and (iv) an elimination of toxic substances.



Production of a mineral fertilizer in a multi-stage process for phosphorus recovery of sewage sludge

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The Problem

Due to a growing population and rising standards of livings the usage of finite and non-regenerative raw materials increases. The mining of these materials is accompanied by substantial ecological consequences. An approach to limit the consequences is a recirculation of the raw materials. An important representative of the finite raw materials is phosphorus (P). An important source for P recovery is given by sewage sludge. In 2018 the theoretical potential for P recovery was around 50.000 t P/year that was 30% of the total demand of phosphorus [1]. In most conventional wastewater treatment plants (WWTP) P is precipitate in sewage sludge (SS) with metal ions. As a disadvantage this compounds have a low bioavailability. Additionally, hazardous (e.g. heavy metals, pollutants, pathogens) hinder the use as fertilizer [2]. In this study a multi-stage process was investigated to recover P in WWTP according to Fig. 3.

Figure 3: Simplified treatment path for phosphorus recovery. SS=sewage sludge; pw=process water.

In the first step sewage sludge was carbonized during an HTC. Afterwards the HTC-char was used in a thermochemical post treatment. During the process units the role of magnesium additives (MgCl2) was investigated. The focus lied in the investigation of the transformation mechanism of P compound and the mass distribution of this element. The final aim was to create P-reach ash with a high plant availability, reduction of heavy metals and elimination of toxic substances.

Method

As input material an anaerobically digested sewage sludge (DSS) was collected after mechanically dewatering (Fig. 2). During previous treatment steps P-precipitation was mainly conducted with aluminum salts. The DSS was hygienized and dried to avoid biological degradation. The samples were finally milled to produce homogeneous subsample.

Figure 2: Dewatered sewage sludge

HTC

The HTC was performed using a microwave laboratory system (CEM MARS 6). Batch experiments were conducted in 110ml vessels. The vessels were designed for temperature <300°C and pressures <70bar. For each experiment, a constant feedstock stream of 10 g dry DSS was used and a dry matter content of 20 wt-% within the reactor was aimed at.

Figure 3: Microwave laboratory system [3].

Figure 4: Trials of HTC experiments.

Fig.4 described the design of the experiments. The main parameter were the process temperature, the retention time and the amount of $MgCl_2$. For a constant temperature of 200°C two retention times (1h, 5h) were chosen. For both trials four different amounts of $MgCl_2$ were used. Every trial was conducted with two repetitions.

Thermochemical treatment

Specific HTC-chars from the HTC-experiments will be used as input material. Thereby, the impact of $MgCl_2$ as additive will be examined. The thermochemical treatment will be conducted in two phases. The first phase will take place under a reducing atmosphere (CO_2) to reduce the content of heavy metals. In the second phase a oxidative athmophere will be reached with air.

Figure 5: Vertical tube furnace

Specific HTC-chars from the HTC-experiments will be used as input material. Thereby, the impact of $MgCl_2$ as additive will be examined. The thermochemical treatment will be conducted in two phases. The first phase will take place under a reducing atmosphere (CO_2) to reduce the content of heavy metals. In the second phase a oxidative athmophere will be reached with air.

First results

The characteristic composition of SS is given in Table 1. AlCl and $NaAl(OH)_4$ were used as precipitants in the WWTP. Thus, the aluminum content was 4.14% in the SS. Table 2 shows the characteristic of the HTC-char. The HTC of SS results in lower carbon contents and heating values, that is typical for input materials with high ash content. However, the hydrophobic character of the HTC-char favor thermal treatment [4]. The dewatering of the samples with centrifugal force resulted in an average DM content of ~44% The P content was increased in every trial during the HTC-content. With a higher amount of $MgCl_2$ the P content decreased. The reason might be a higher solid content that was reached due to the additives. In Fig. 6 the recovery rate of the elements P, Mg, Al, Fe and Cl and the PO_4 content in the process water is pictured. The elements P, Al and Fe mainly remained in the solid phase. Even if the content of dissolved P is comparable low, longer intention times resulted in lower PO_4 contents. For the base cases (1h/5h,0g $MgCl_2$) Mg also remained in the solid phase that was only bounded Mg from the SS. Cl partly built soluble compounds that were transferred in the liquid phase. By increasing the additive, the total recovery rate of Mg and Cl decreased as $MgCl_2$ is soluble. However, both elements increased in the solid phase (Table 2). If the compound $MgCl_2$ was precipitated during the drying process or a recrystallization of the elements occurred during the HTC process will be examined with XRD.

Table 1: Composition of SS

	SS	
DM	26.6	[wt.-%]^a
C	57.90	[wt.-%]^b
H	8.90	[wt.-%]^b
N	8.06	[wt.-%]^b
S	1.82	[wt.-%]^b
O*	23.32	[wt.-%]^b
Ash	53.65	[wt.-%]^c
P	3.13	[wt.-%]^c
K	0.29	[wt.-%]^c
Ca	2.47	[wt.-%]^c
Mg	0.47	[wt.-%]^c
Fe	2.02	[wt.-%]^c
Al	4.14	[wt.-%]^c
Cl^-	947.45	[mg/kg]
Pb	74.86	[mg/kg]
Cd	1.30	[mg/kg]
Cr	78.78	[mg/kg]
Ni	59.62	[mg/kg]
Hg	0.29	[mg/kg]
Cu	343.08	[mg/kg]
Zn	1083.22	[mg/kg]

*calculated as difference; DM=dry matter; ^{a}ar; ^{a}waf; ^{c}wf

Table 2: Fuel properties sewage sludge and HTC-chars

Time	Additive	DM	Ash	C	H	N	S	O*	P	Mg	Cl^-
[h]	[$gMgCl_2$]	[wt.-%]^a	[wt.-%]^c	[wt.-%]^b	[wt.-%]^b	[wt.-%]^b	[wt.-%]^b	[wt.-%]^b	[wt.-%]^c	[wt.-%]^c	[wt.-%]^c
1	0	42.42	56.68	56.30	7.58	5.85	1.65	28.62	4.16	0.08	0.75
	0.5	43.08	54.40	52.88	7.77	5.83	1.86	31.66	3.89	1.30	1.83
	1.0	44.34	55.72	53.27	7.68	5.50	2.18	31.37	3.96	2.54	2.69
	1.5	44.03	52.94	49.26	7.63	5.24	1.84	36.03	3.70	3.53	3.09
5	0	43.45	58.72	59.69	7.73	5.87	1.93	24.78	4.24	0.08	0.78
	0.5	43.84	55.68	54.83	7.68	5.58	1.71	30.18	4.02	1.43	1.87
	1.0	45.76	55.83	52.59	7.68	5.12	1.91	32.70	3.90	2.98	3.38
	1.5	46.01	55.02	50.33	7.86	5.04	1.67	35.10	3.74	4.32	3.99

Figure 6: Recovery rate of the elements P, Mg, Al, Fe, Cl and PO_4 content in the process water. Left: 200°C and 1h; right: 200°C and 5h.

In Fig. 7 the recovery rate of the heavy metals is pictured. All represented heavy metals except Hg mainly remained in the solid phase. Hg partly transferred in the liquid or gaseous phase. This effect increases with higher intention times.

Figure 7: Recovery rate heavy metals (Pb, Cd, Cr, Cu, Ni, Hg, Zn) for 200°C, 0.0g $MgCl_2$ and a retention time of 1h and 5h.

Further research

In the next step the crystalline structure of the HTC-char will be analyzed with XRD to identify P compounds. In Zheng (2020) was shown, that recrystallisation of P already occurred during the HTC process. It was also possible to create P compounds with high bioavailability during the process.

Afterwards, HTC-char will be thermochemical treated. Currently, different method (e.g. EuPhoRe, PYREG, AshDec) exist that produce fertilizer by thermochemical treatment of SS or the ash of SS. In the second part of the study it will be examined weather thermochemical treatment of the HTC char can produce a fertilizer with the following requirements:

- High plant availability
- Decreasing of hazardous (heavy metals, pollutants, pathogens)
- Avoiding residual material
- Complying existing laws and regulations

Conclusion

- The hydrothermal treatment of SS resulted in lower carbon content and heating value
- However, the hydrophobe character of the HTC-char can favor its thermal treatment compared with the direct treatment of SS
- Most of the P remained in the HTC char after the HTC process
- Higher retention times and $MgCl_2$ as additive favored this effect
- It will be examined with XRD if the additive $MgCl_2$ improve the cristalline composition of P

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Prof. Dr. Christian Malek christian.malek@th-koeln.de

References
1. Wiechmann, B., Dienemann, C., Kabbe, C., Brandt, S., Vogel, Ines and Roskosch, A. (2018) Klärschlammentsorgung in der Bundesrepublik Deutschland
2. Zheng, X., Jiang, Z., Ying, Z., Ye, Y., Chen, W., Wang, B. and Dou, B. (2020) 'Migration and Transformation of Phosphorus during Hydrothermal Carbonization of Sewage Sludge: Focusing on the Role of pH and Calcium Additive and the Transformation Mechanism', ACS Sustainable Chemistry & Engineering, vol. 8, no. 21, pp. 7806–7814.
3. https://cem.com/de/mars-6
4. Blöhse, D. (2017) Hydrothermale Karbonisierung: Nutzen dieser Konversionstechnik für die optimierte Entsorgung feuchter Massenreststoffe, Dissertation, Essen, Universität Duisburg-Essen.

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:metabolon
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ORAL PRESENTATIONS

SESSION III/IV

BIOCHEMICAL CONVERSION

Daniel Dzofou Ngoumelah, Leipzig University/Deutsches Biomasseforschungszentrum/Helmholtz Centre for Environmental Research - UFZ

Interaction between Geobacter spp. dominated biofilms and methanogens from anaerobic digestion

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Combination of microbial electrochemical technologies (MET) and anaerobic digestion (AD) have been examined in recent years to, e.g., 1) remove monovalent ions as ammonium from AD, 2) remove COD from AD effluent also known as effluent polishing, 3) upgrade biogas or 4) monitor AD using microbial electrochemical sensors. All these applications bear quite some advantages for improving the efficiency and environmental impact of AD but research is still at laboratory level. One limiting factor for combining microbial electrochemical systems with AD is the observed loss of electrochemical activity of Geobacter spp. dominated biofilms at graphite electrodes. It was found that biofilms leave the electrode surface when adding AD effluents or incorporating them in AD processes. The cause of this inhibition is unclear so far but several hypothesis exist. Inhibition can be induced, e.g. by toxic compounds (e.g. high $N\text{-}NH_4+$), alternative dissolved electron acceptors (sulfate, nitrate or humic substances) or even methanogens itself. The latter is probably connected to direct interspecies electron transfer (DIET) where methanogens accept electrons directly from electroactive bacteria.

Therefore, the aim is to investigate optimal conditions for Geobacter spp. dominated biofilms to survive for a long time-period in AD processes using AD effluents from different reactors fed with either a mixture of C5 and C6 sugars (hemicellulose) or cow manure and wheat straw and then identify parameters that trigger the inhibition process. Several adaptation and shock experiments were performed using different concentrations of AD effluents (0 - 100 %).

Experiments using different concentrations of AD effluent from reactors fed with hemicellulose showed negative effects on the performance and the resistance of pre-grown mature biofilms from 50 % AD effluent (v/v) onwards. Contrary, the use of 2-BES and filtration at 0.2 µm stabilized biofilm performance for over 4 weeks at 50 % AD, indicating an inhibitory effect of methanogens. Using AD effluent from reactors fed with cow manure and wheat straw, showed no significant inhibition either by applying different filtration and centrifugation steps or by varying the potential applied to the anode. Characterization of the microbial community of AD effluents and anodic biofilms by Amplicon sequencing will allow differentiation of the methanogenic groups in each of these specific AD effluents to better understand why strong inhibition occurred in one case and not in the other.

Deutsches Biomasseforschungszentrum
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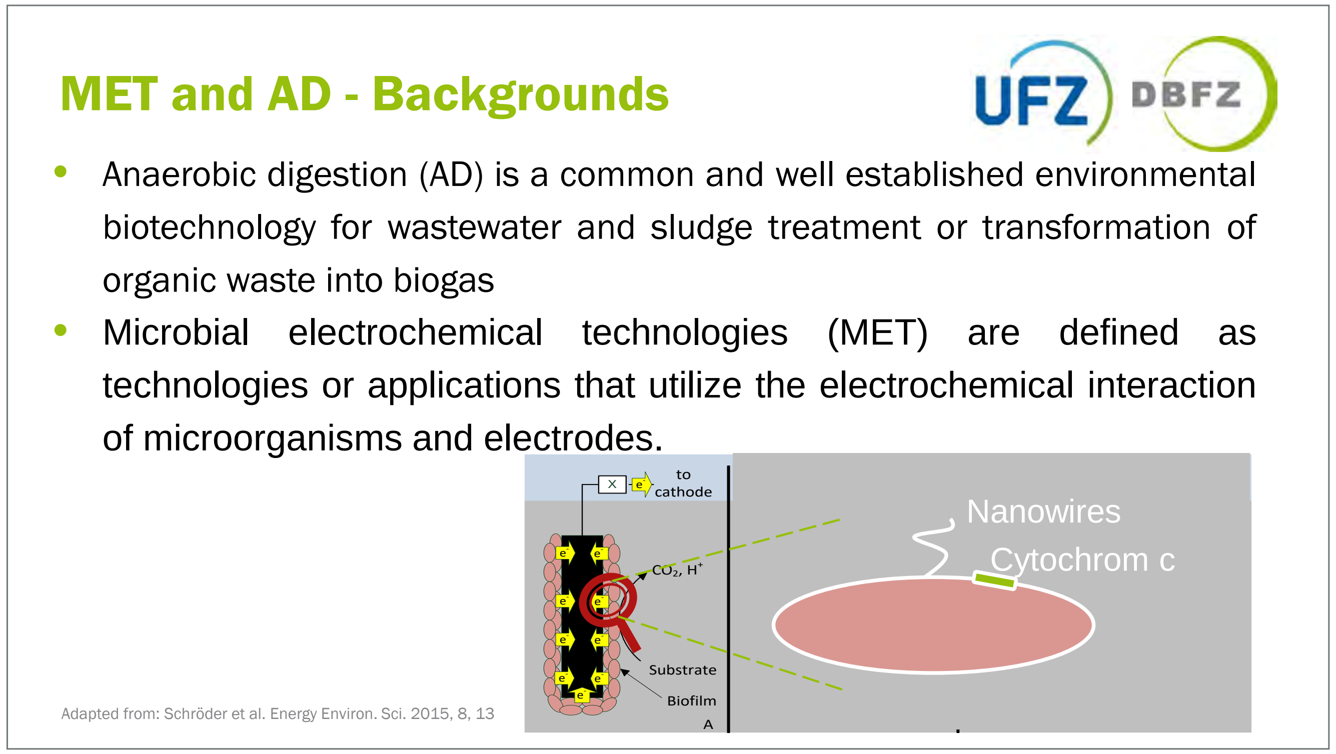
Interaction between *Geobacter* spp. dominated biofilms and methanogens from anaerobic digestion

Daniel Dzofou Ngoumelah, Falk Harnisch, Jörg Kretzschmar

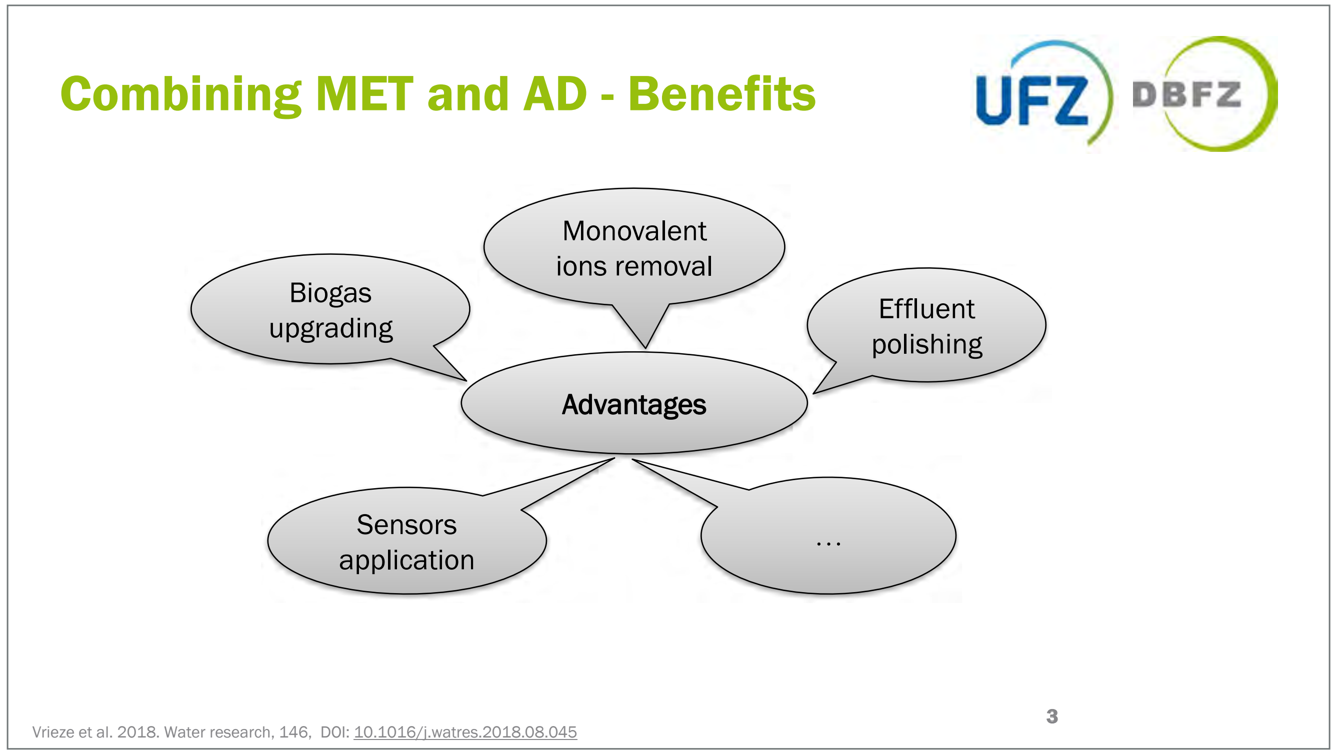
4th DOCTORAL COLLOQUIUM BIOENERGY | 13.-14.09.2021 |



MET and AD - Backgrounds

- Anaerobic digestion (AD) is a common and well established environmental biotechnology for wastewater and sludge treatment or transformation of organic waste into biogas
- Microbial electrochemical technologies (MET) are defined as technologies or applications that utilize the electrochemical interaction of microorganisms and electrodes.

Adapted from: Schröder et al. Energy Environ. Sci. 2015, 8, 13



Combining MET and AD - Benefits

Monovalent ions removal

Biogas upgrading

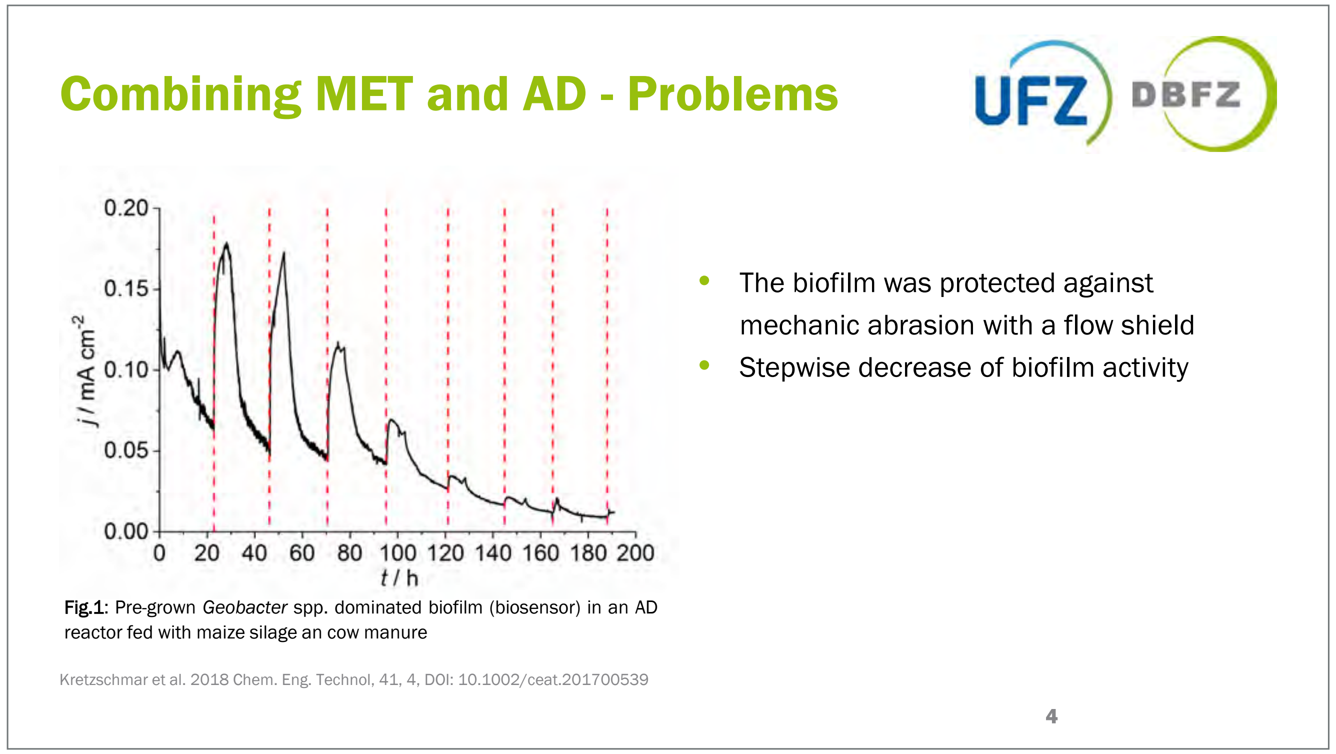
Effluent polishing

Advantages

Sensors application

…

Vrieze et al. 2018. Water research, 146, DOI: 10.1016/j.watres.2018.08.045

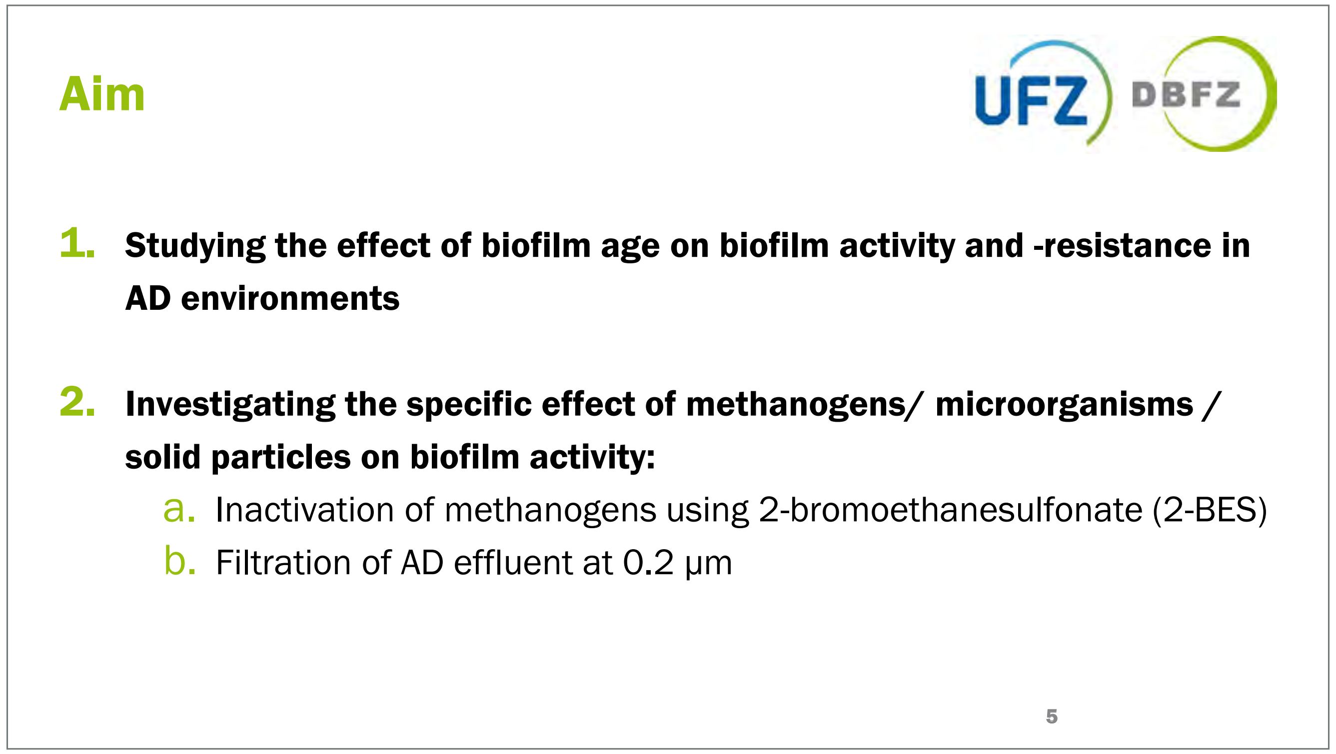


Combining MET and AD - Problems

Fig.1: Pre-grown *Geobacter* spp. dominated biofilm (biosensor) in an AD reactor fed with maize silage an cow manure

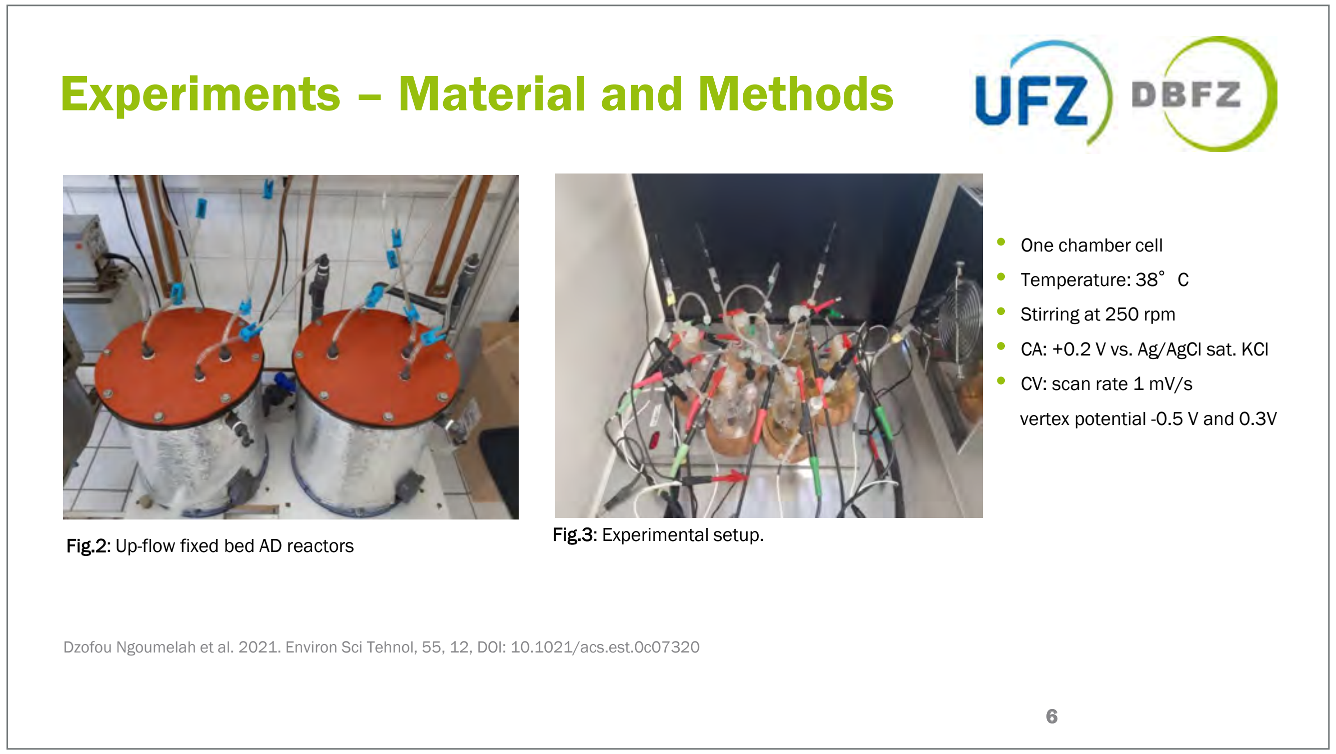
- The biofilm was protected against mechanic abrasion with a flow shield
- Stepwise decrease of biofilm activity

Kretzschmar et al. 2018 Chem. Eng. Technol, 41, 4, DOI: 10.1002/ceat.201700539



Aim

1. **Studying the effect of biofilm age on biofilm activity and -resistance in AD environments**
2. **Investigating the specific effect of methanogens/ microorganisms / solid particles on biofilm activity:**
   a. Inactivation of methanogens using 2-bromoethanesulfonate (2-BES)
   b. Filtration of AD effluent at 0.2 µm



Experiments – Material and Methods

Fig.2: Up-flow fixed bed AD reactors

Fig.3: Experimental setup.

- One chamber cell
- Temperature: 38° C
- Stirring at 250 rpm
- CA: +0.2 V vs. Ag/AgCl sat. KCl
- CV: scan rate 1 mV/s
  vertex potential -0.5 V and 0.3V

Dzofou Ngoumelah et al. 2021. Environ Sci Tehnol, 55, 12, DOI: 10.1021/acs.est.0c07320

Experiments

Table 1. Parameters of the performed experiments

Name of the experiment	Age of the biofilms / weeks	AD effluent concentration in the growth media / % (v/v)	New biofilms for each AD effluent concentration	Duration / batch cycles (weeks)
AD shock young	3 (young)	0, 10, 25, 50, 75, 100	Yes	2
AD shock old	5 (old)	0, 10, 25, 50, 75, 100	Yes	2
AD adaptation	5 (old)	0, 10, 25, 50, 75, 100	No	2
2-BES	5 (old)	0[1], 50	No	4
Filtration	5 (old)	0[1], 50	No	5

[1] Controls were performed for two weeks only

Dzofou Ngoumelah et al. 2021. Environ Sci Tehnol, 55, 12, DOI: 10.1021/acs.est.0c07320

Results - Impact of biofilm age

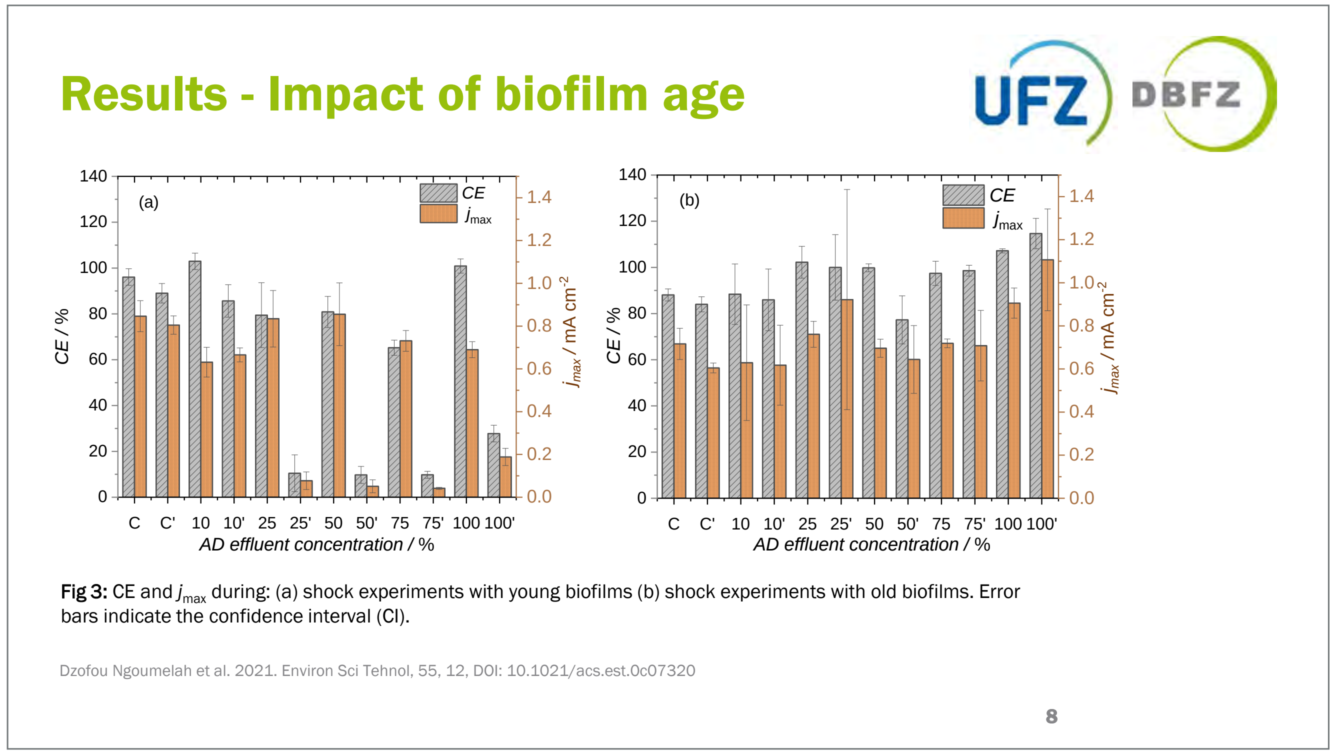


Fig 3: CE and j_{max} during: (a) shock experiments with young biofilms (b) shock experiments with old biofilms. Error bars indicate the confidence interval (CI).

Dzofou Ngoumelah et al. 2021. Environ Sci Tehnol, 55, 12, DOI: 10.1021/acs.est.0c07320

Results – Adaptation of old Biofilm

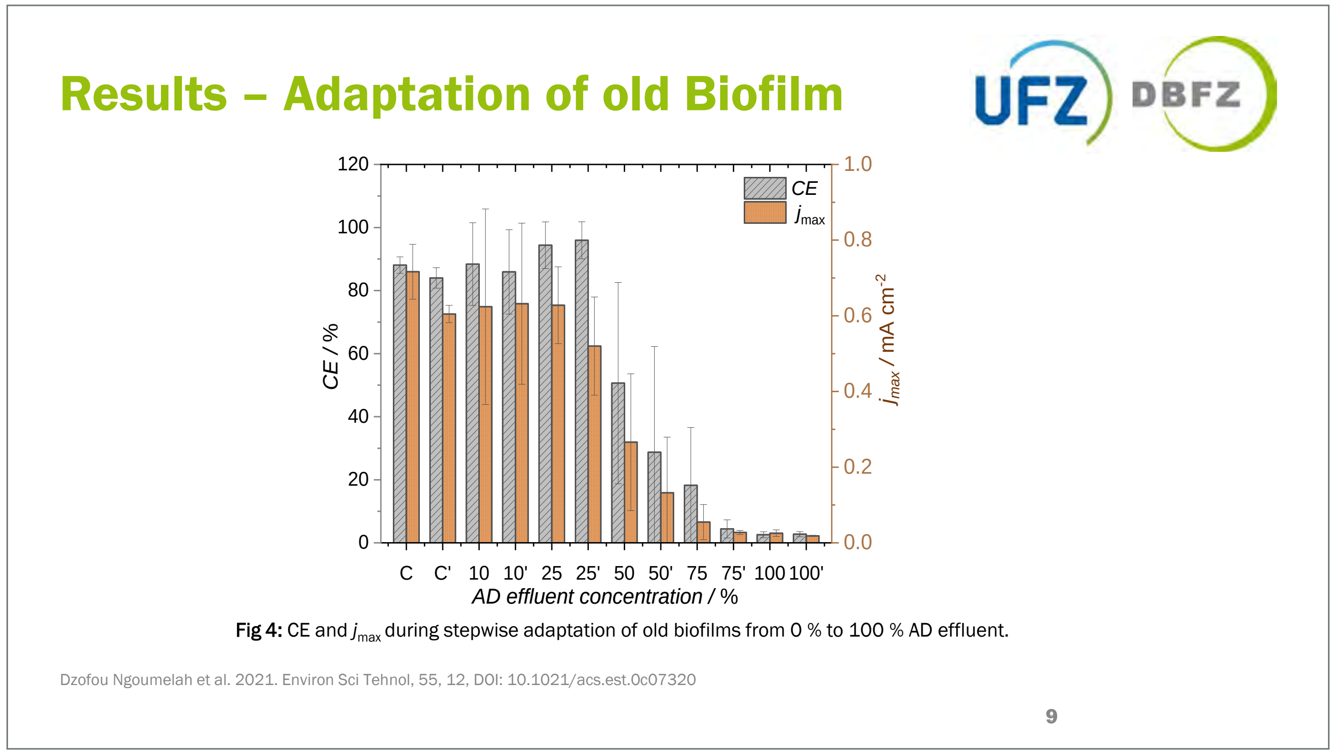


Fig 4: CE and j_{max} during stepwise adaptation of old biofilms from 0 % to 100 % AD effluent.

Dzofou Ngoumelah et al. 2021. Environ Sci Tehnol, 55, 12, DOI: 10.1021/acs.est.0c07320

Results – Removal and inhibition of methanogens

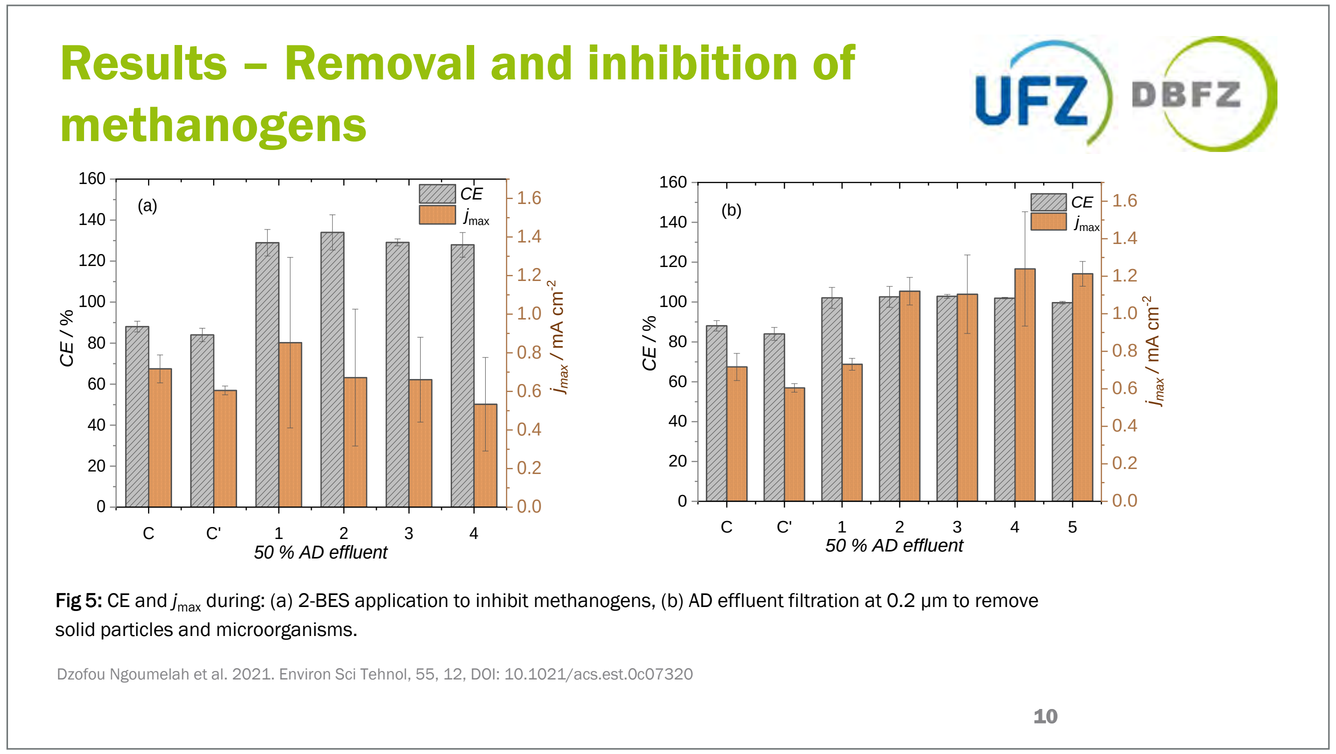


Fig 5: CE and j_{max} during: (a) 2-BES application to inhibit methanogens, (b) AD effluent filtration at 0.2 µm to remove solid particles and microorganisms.

Dzofou Ngoumelah et al. 2021. Environ Sci Tehnol, 55, 12, DOI: 10.1021/acs.est.0c07320

Results – Microbial community analysis

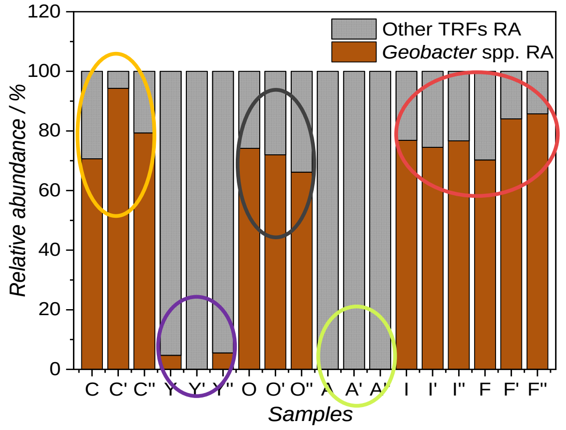
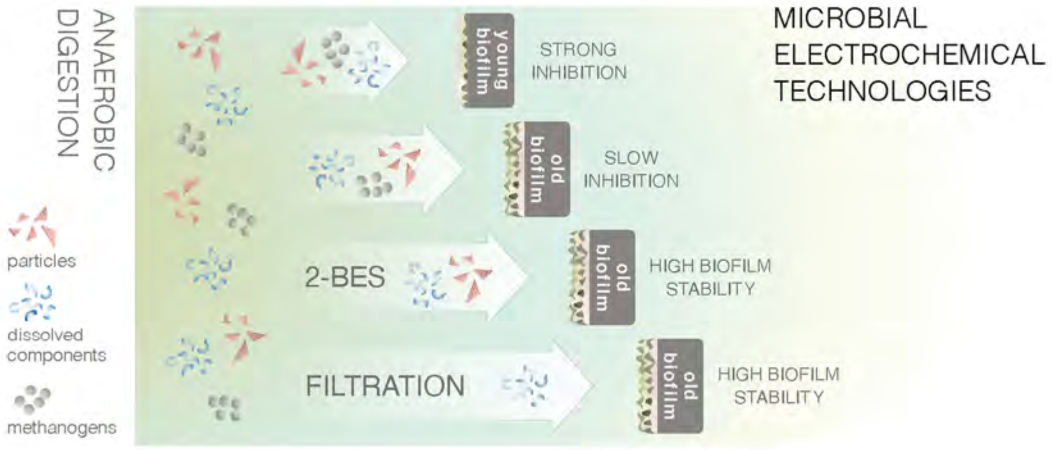


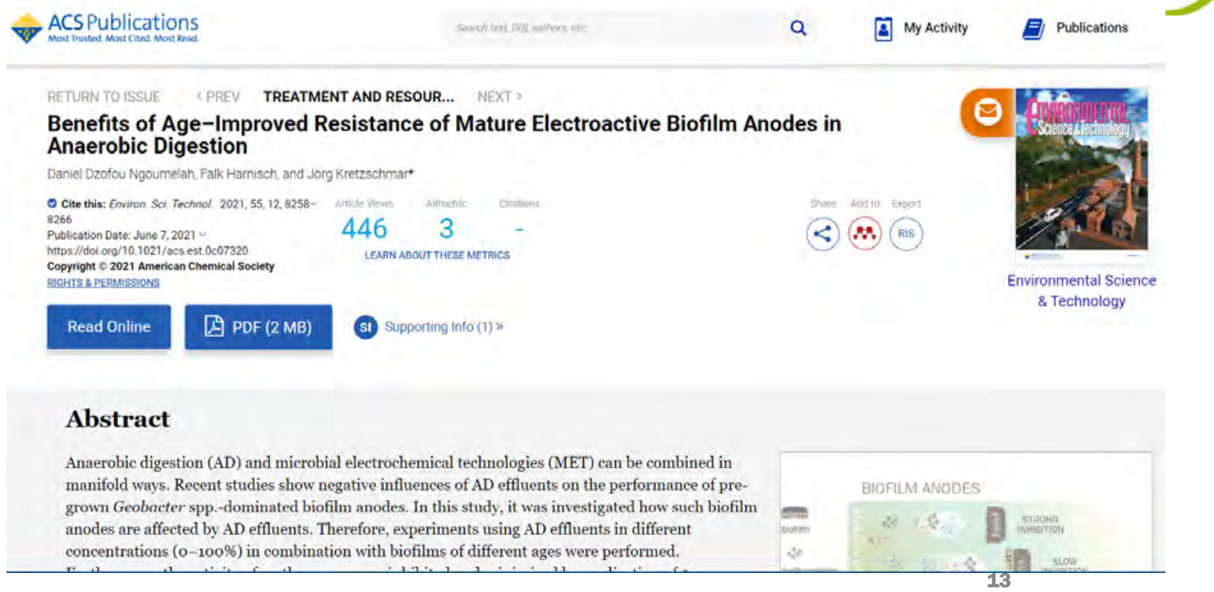
Fig 6: Relative abundance of the bacterial 16S rRNA gene. C: control, Y: AD shock young biofilms , O: AD shock old biofilms, A: AD adaption, I: 2-BES experiment, F: Filtration experiment.

Dzofou Ngoumelah et al. 2021. Environ Sci Tehnol, 55, 12, DOI: 10.1021/acs.est.0c07320

Conclusion



Dzofou Ngoumelah et al. 2021. Environ Sci Tehnol, 55, 12, DOI: 10.1021/acs.est.0c07320



Benefits of Age–Improved Resistance of Mature Electroactive Biofilm Anodes in Anaerobic Digestion

Daniel Dzofou Ngoumelah, Falk Harnisch, and Jorg Kretzschmar*

Cite this: *Environ. Sci. Technol.* 2021, 55, 12, 8258–8266
Publication Date: June 7, 2021
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Abstract

Anaerobic digestion (AD) and microbial electrochemical technologies (MET) can be combined in manifold ways. Recent studies show negative influences of AD effluents on the performance of pre-grown *Geobacter* spp.-dominated biofilm anodes. In this study, it was investigated how such biofilm anodes are affected by AD effluents. Therefore, experiments using AD effluents in different concentrations (0–100%) in combination with biofilms of different ages were performed.

Outlook

- Assess how abiotic particles and methanogens from other AD effluent might affect the activity and stability of *Geobacter* spp. dominated biofilm.
- Check if and how the applied potential to the working electrode could influence the reaction of the electroactive microorganisms.

Deutsches Biomasseforschungszentrum
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Thank you for your attention!

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Fotos: DBFZ, Jan Gutzeit, DREWAG/Peter Schubert (Titelfolie, rechts), Pixabay / CC0 Public Domain

Matheus de Oliveira Pessoa, Technical University of Berlin

The use of biomagnetism for biogas production from sugar beet pulp

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1. Introduction.

There are several strategies reported in the literature regarding the application of a magnetic field to biogas production, like constant magnetization of the fermentation broth, introduction of magnetic particles in the fermentation broth, use of rotating magnetic fields or magnetic mills. The present research explores the use of biomagnetism to increase the biogas/biomethane production from sugar beet pulp (SBP). As enzymes can increase their activity and substrates can increase its degradability when exposed to a magnetic field, the present research exposed an enzyme-substrate complex to a stable magnetic field (solenoid) in the weak range (smaller than 1 mT) and an increase in methane production and content was observed. The main motivation for developing this research is to establish a magnetic pretreatment with negligible energy costs and of easy applicability that enables a high biogas/methane production.

2. Approach and methods.

In which configuration can we use a solenoid to increase biogas production?

The strategy adopted in this set of experiments consist in apply a magnetic pretreatment to an enzyme-substrate complex, incubation at 50 °C for activation of the enzyme, fermentation experiments to quantify the application of the pretreatment, and check the influence of sonication in the process.

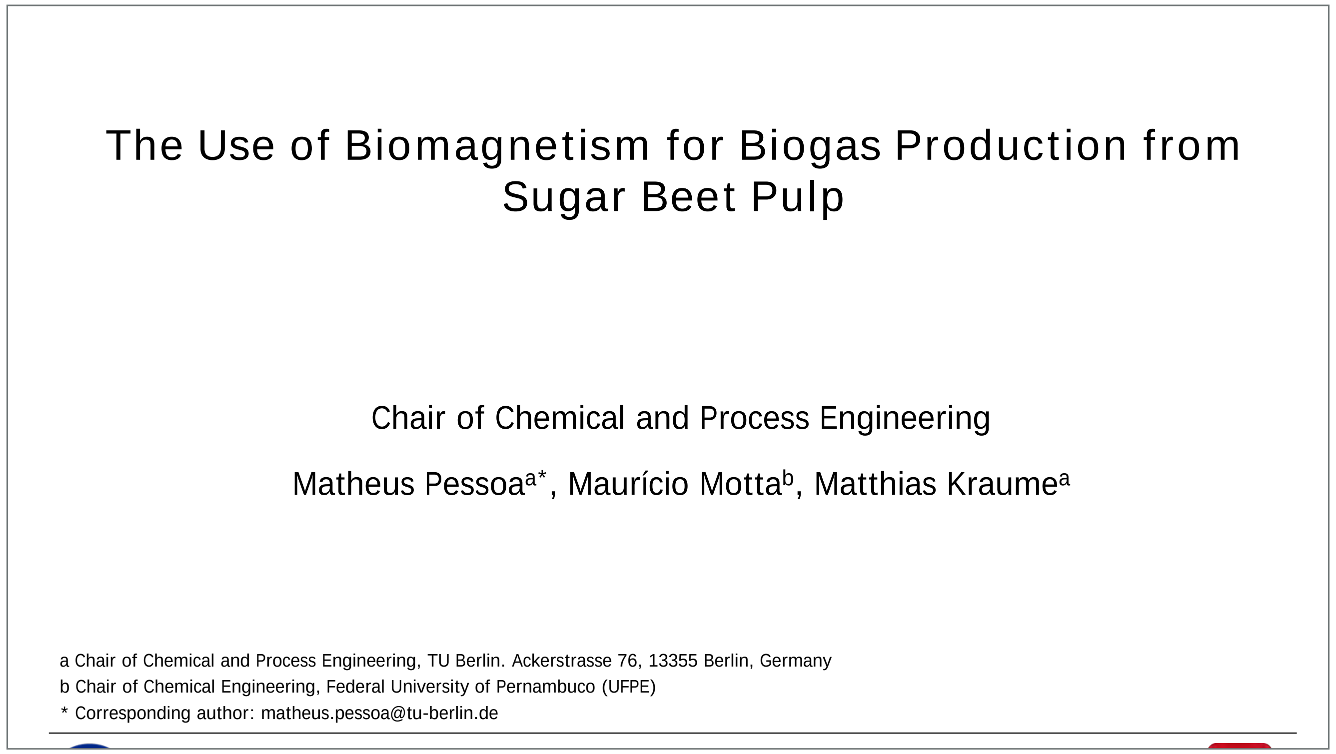
After establishing the magnetic field exposure time, soluble sugar release from SBP according to different pretreatments were quantified. The Michaelis-Menten equation was used to analyze the enzymatic activity. Fermentation experiments were operated to quantify the increase in biogas/methane production.

3. Results.

Hydrolysis experiments indicated that pectinase can increase its activity when exposed for 4 hours to a magnetic field (0.2mT). Batch experiments indicated that when SBP was exposed to a magnetic field, or when SBP was treated with pectinase, an increase in biogas/methane production was observed but not statistically higher than the control. The exposure of the enzyme-substrate complex increased the biogas/methane production with statistical differences. Specific energy gain calculations indicated that the highest balance is accounted to the magnetization of the enzyme-substrate complex although its variation with sonication produced more biogas/methane. Fed-batch monitoring indicated that the magnetization of the enzyme-substrate complex can increase the biogas/methane production, decrease the residence time and promote a more stable fermentation process.

4. Conclusion / Outlook

The magnetization of the enzyme substrate complex was successfully applied to the fermentation of sugar beet pulp. This process can easily be applied and promotes a faster a more stable biogas/methane production.



The Use of Biomagnetism for Biogas Production from Sugar Beet Pulp

Chair of Chemical and Process Engineering

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M.Sc. Matheus de Oliveira Pessoa

Graduation: Agricultural and Environmental Engineering – UFRPE - Brazil
Master: Civil Engineering – UFPE - Brazil
PhD: Chair of Chemical and Process Engineering – TU Berlin

Motivation

- Use a magnetic field (Solenoid) as substrate pretreatment for anaerobic digestion.

Objectives

- Magnetize an enzyme-substrate mixture before fermentation;
- Check the influence of sonication on the process.

- Biomagnetism is the effect of magnetic fields on biological systems;

- Exposure of enzymes to magnectic fields can increase its activity, depending on the enzyme, type of magnetic field, intensity and exposure time;

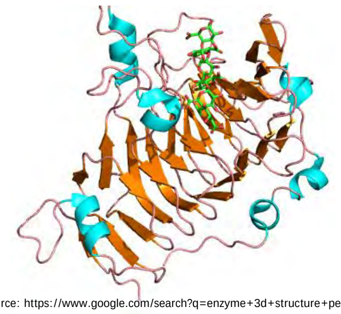
- The application of MF can be done by:
  - Continuously pumping of fermentation broth into a magnetic field column and back to the fermenter;
  - Use o magnets near by the reactor;
  - Use of magnetic particles inside the fermenter;
  - Use of a magnetic mill;
  - Application of rotating magnetic fieds and etc.

Physical effect

Enzymes are 3D structures and its exposure to a magnetic field can induce conformational changes (changes in the structure)

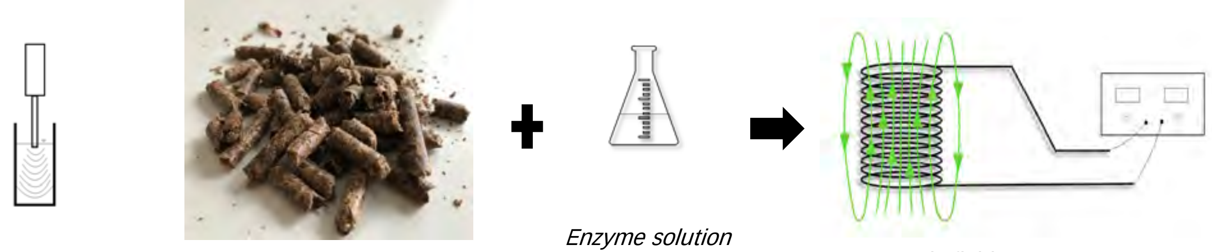
Energetic effect

The radical pair mechanism is a theoretical principle, that explains how magnetic fields can influence chemical reactions



Source: https://www.google.com/search?q=enzyme+3d+structure+pectinase...

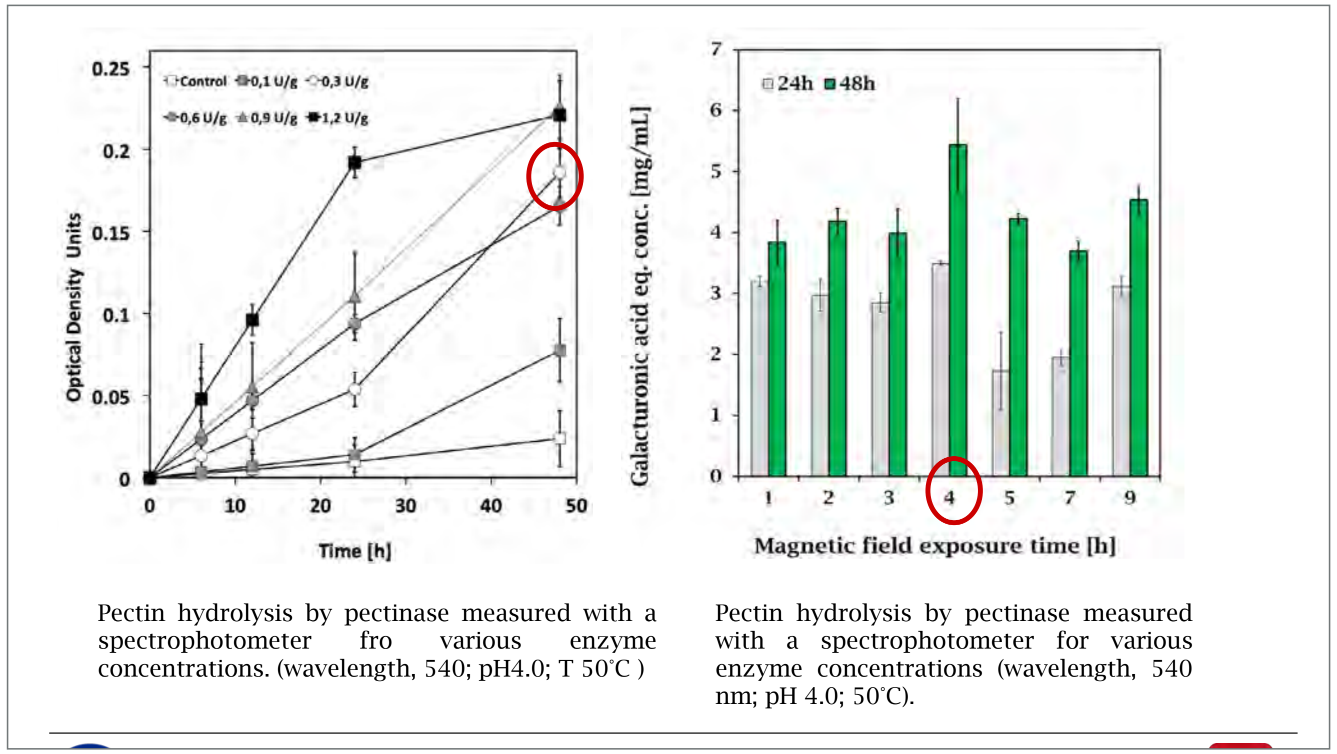
- ➢ Sonication: specific energy *2100 kJ/kg*
- ➢ Substrate: Sugar beet pulp *(10 % VS solution)*
- ➢ Enzyme: Pectinase *(0,3 U/g substrate)*
- ➢Magnetic field: Solenoid *(0.2 mT)(4 h)*



Sugar beet pulp

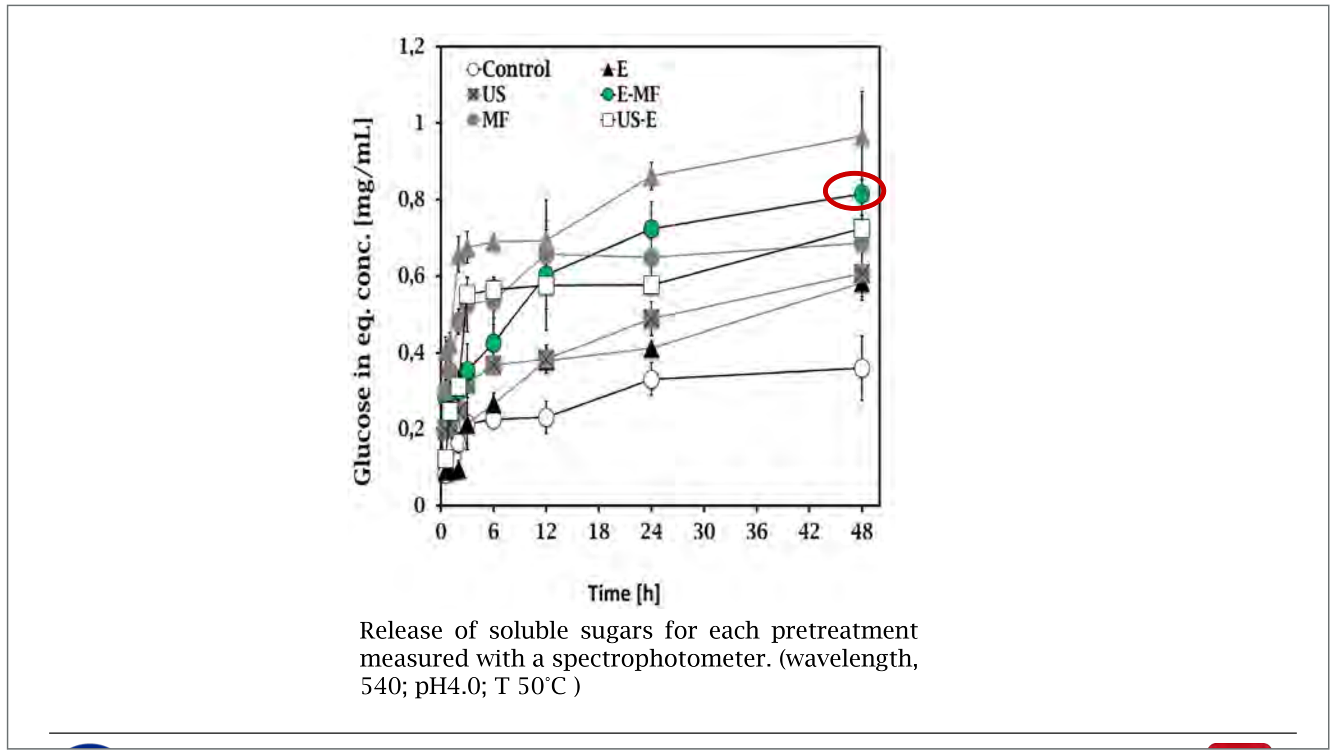
Enzyme solution

Magnetic field



Pectin hydrolysis by pectinase measured with a spectrophotometer fro various enzyme concentrations. (wavelength, 540; pH4.0; T 50˚C)

Pectin hydrolysis by pectinase measured with a spectrophotometer for various enzyme concentrations (wavelength, 540 nm; pH 4.0; 50˚C).



Release of soluble sugars for each pretreatment measured with a spectrophotometer. (wavelength, 540; pH4.0; T 50˚C)

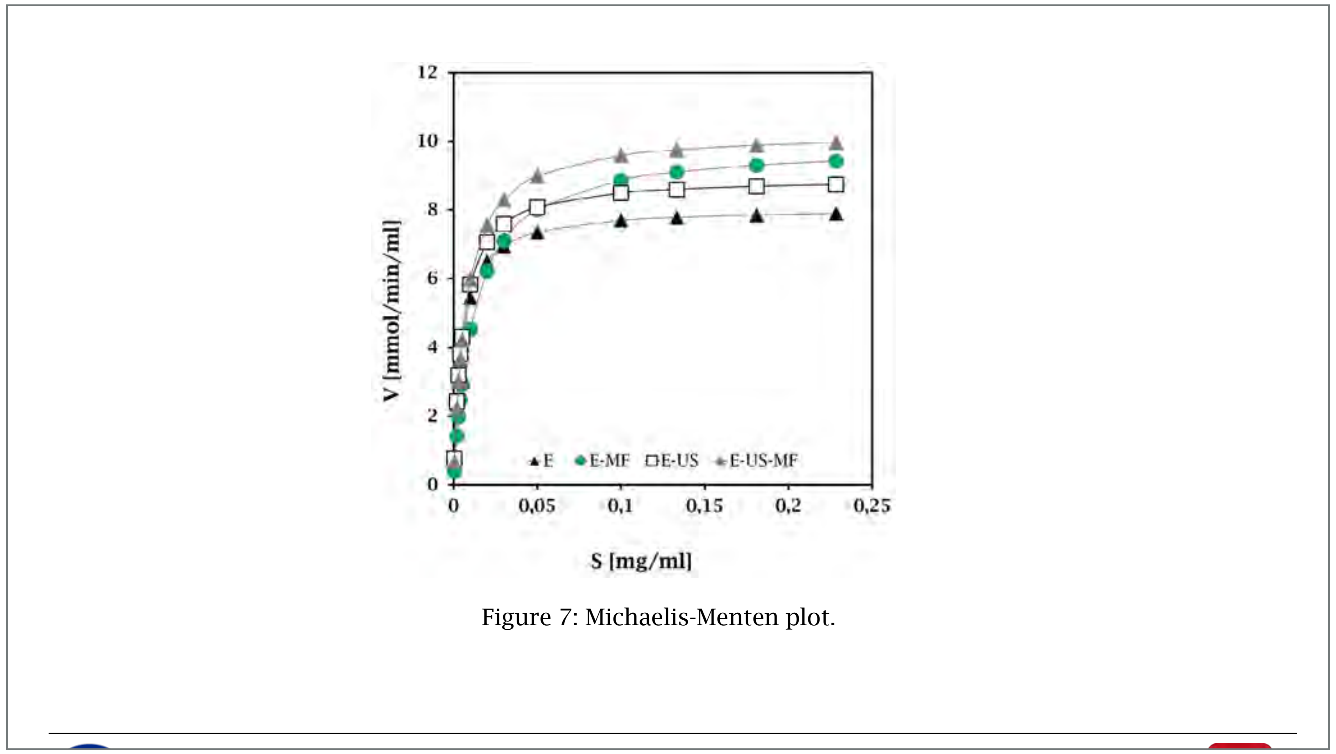
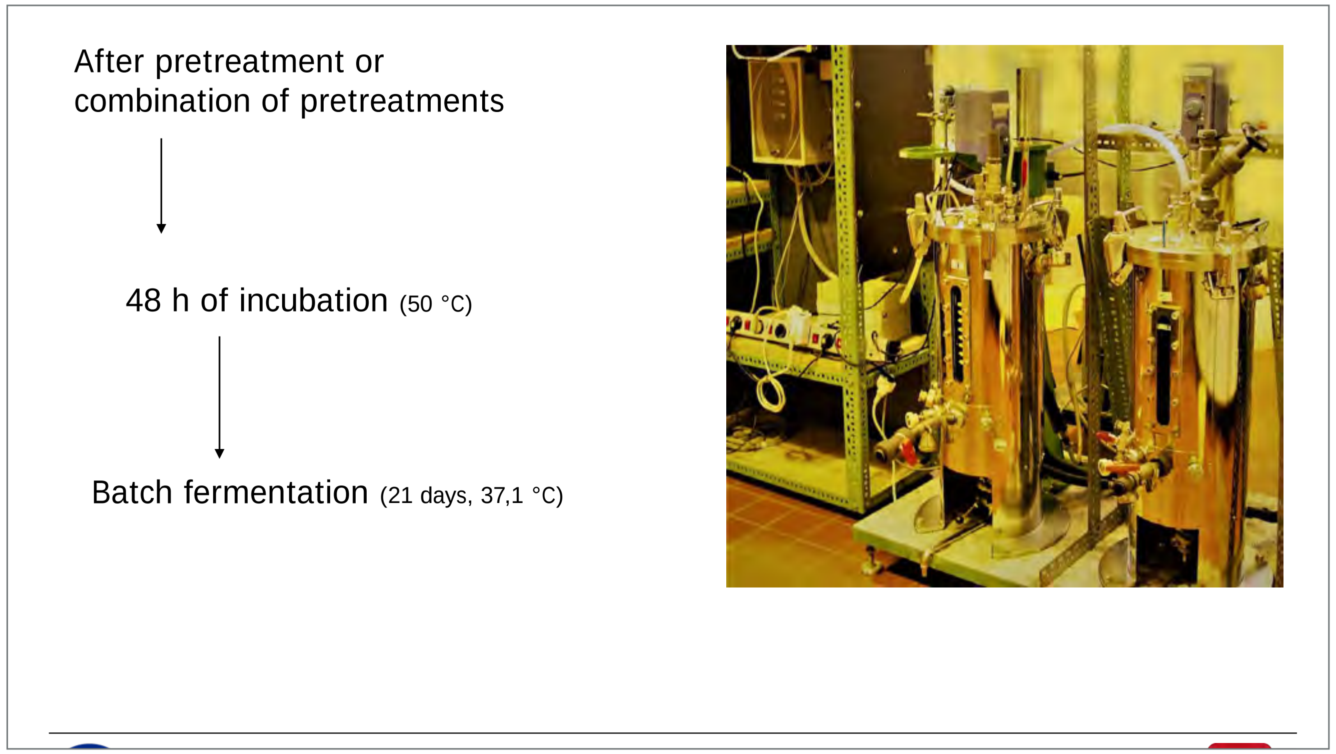
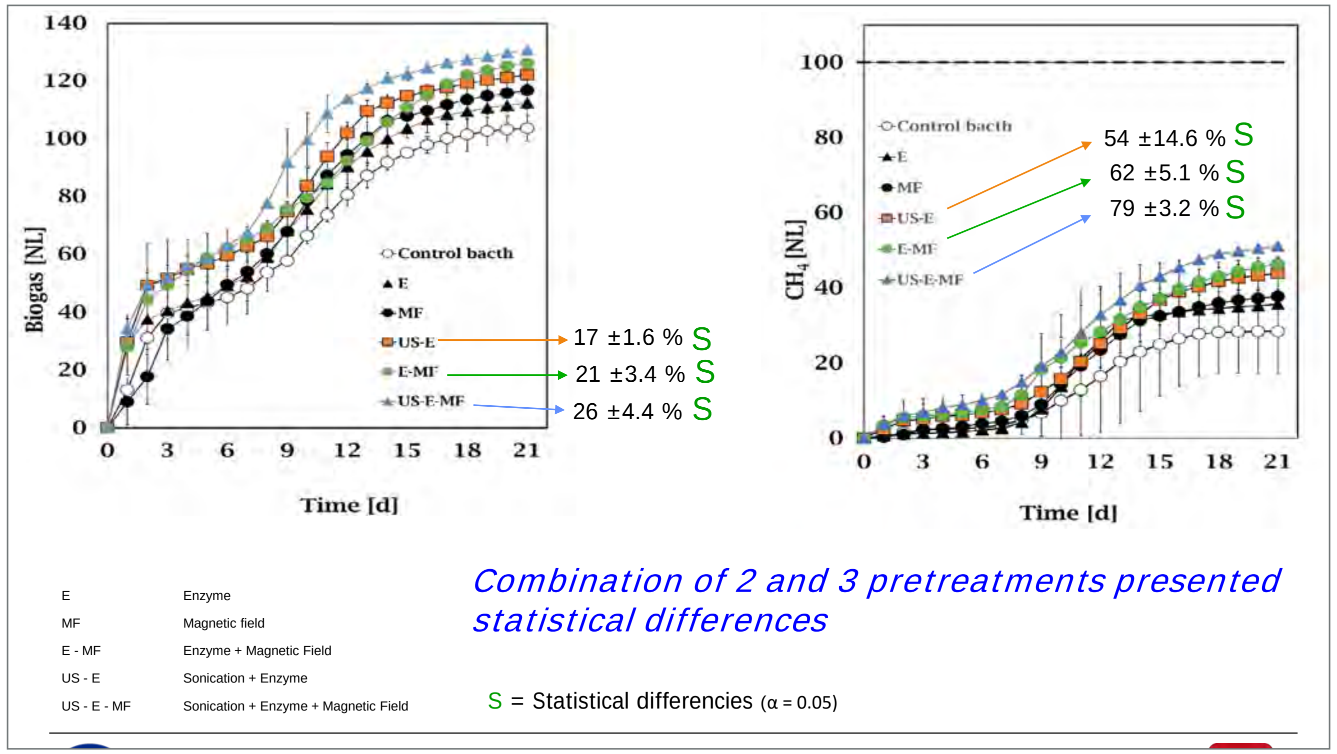


Figure 7: Michaelis-Menten plot.


After pretreatment or
combination of pretreatments

48 h of incubation (50 °C)

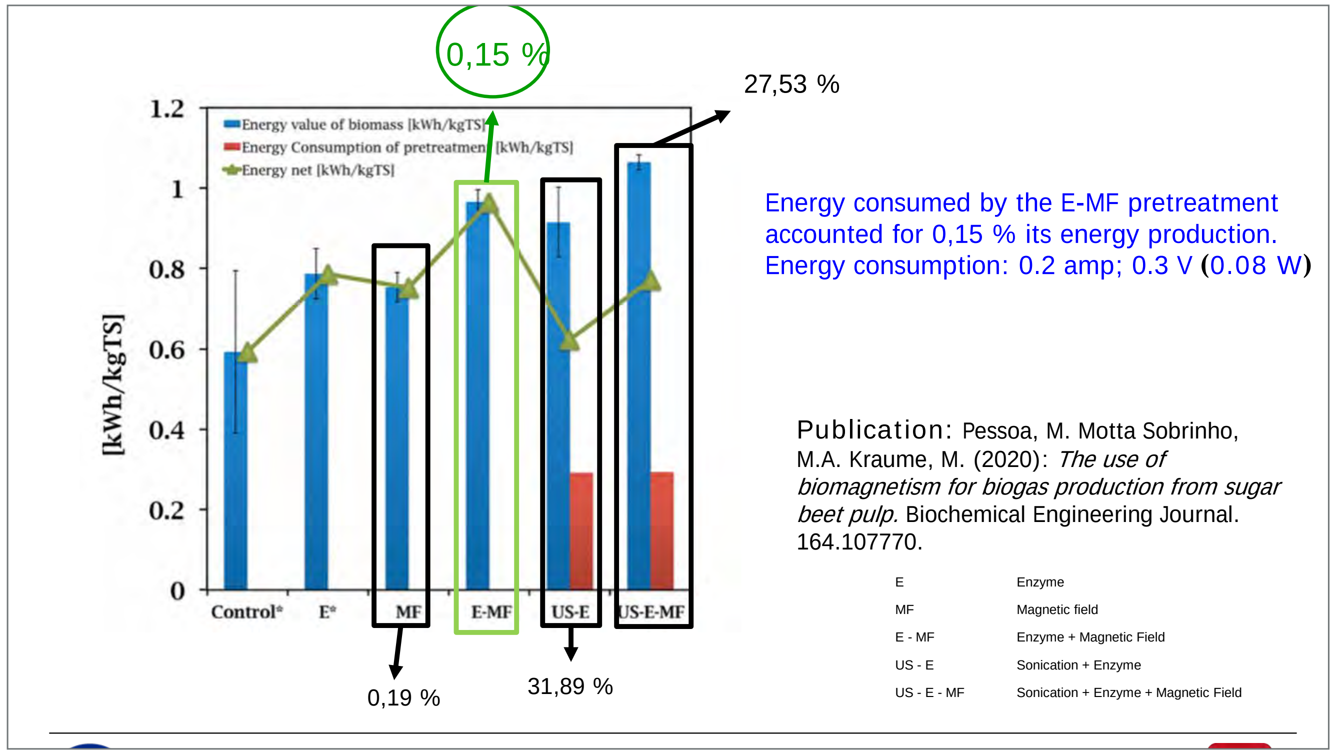
Batch fermentation (21 days, 37,1 °C)



E	Enzyme
MF	Magnetic field
E - MF	Enzyme + Magnetic Field
US - E	Sonication + Enzyme
US - E - MF	Sonication + Enzyme + Magnetic Field

Combination of 2 and 3 pretreatments presented statistical differences

S = Statistical differencies (α = 0.05)



Energy consumed by the E-MF pretreatment accounted for 0,15 % its energy production.
Energy consumption: 0.2 amp; 0.3 V (0.08 W)

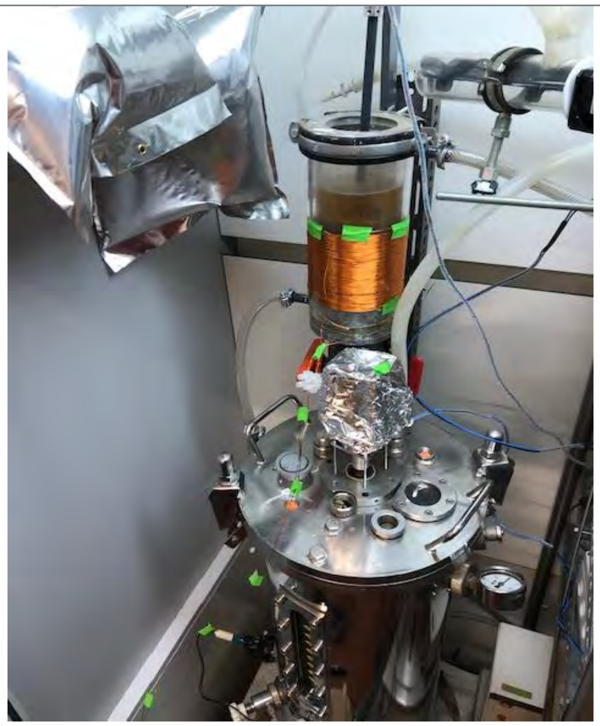
Publication: Pessoa, M. Motta Sobrinho, M.A. Kraume, M. (2020): *The use of biomagnetism for biogas production from sugar beet pulp.* Biochemical Engineering Journal. 164.107770.

E	Enzyme
MF	Magnetic field
E - MF	Enzyme + Magnetic Field
US - E	Sonication + Enzyme
US - E - MF	Sonication + Enzyme + Magnetic Field

- ◆ 150 g SBP
  - ◆ Every 3.5 days
  - ◆ TS: 92%
- ◆ V = 10 L
- ◆ Temp = 37°C
- ◆ HRT = 20 d
- ◆ OLR = 0.75 kg/m3*d

➡

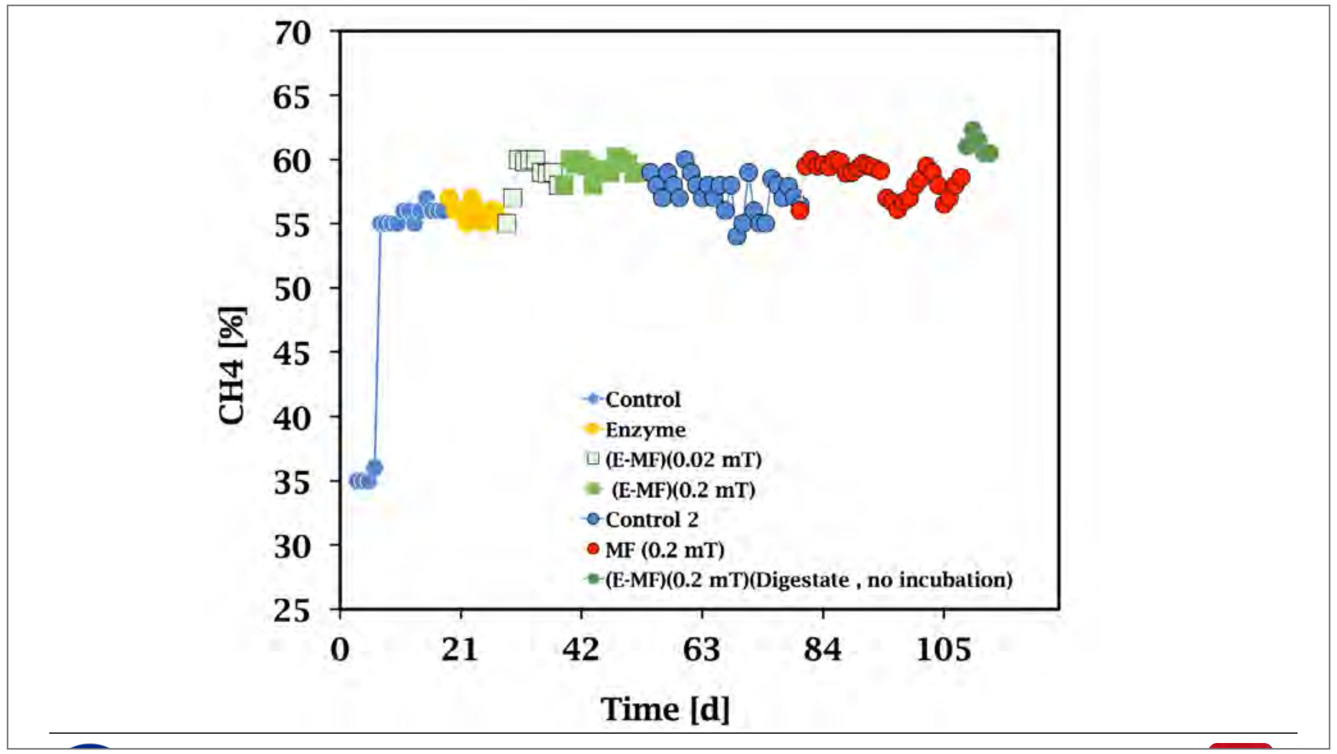
- ➢ 150 g SBP
  - ➢ Every 3.5 days
  - ➢ TS: 25 %
- ➢ V = 10 L
- ➢ Temp = 46 °C
- ➢ HRT = 50 d
- ➢ OLR = 0.75 kg/m3*d

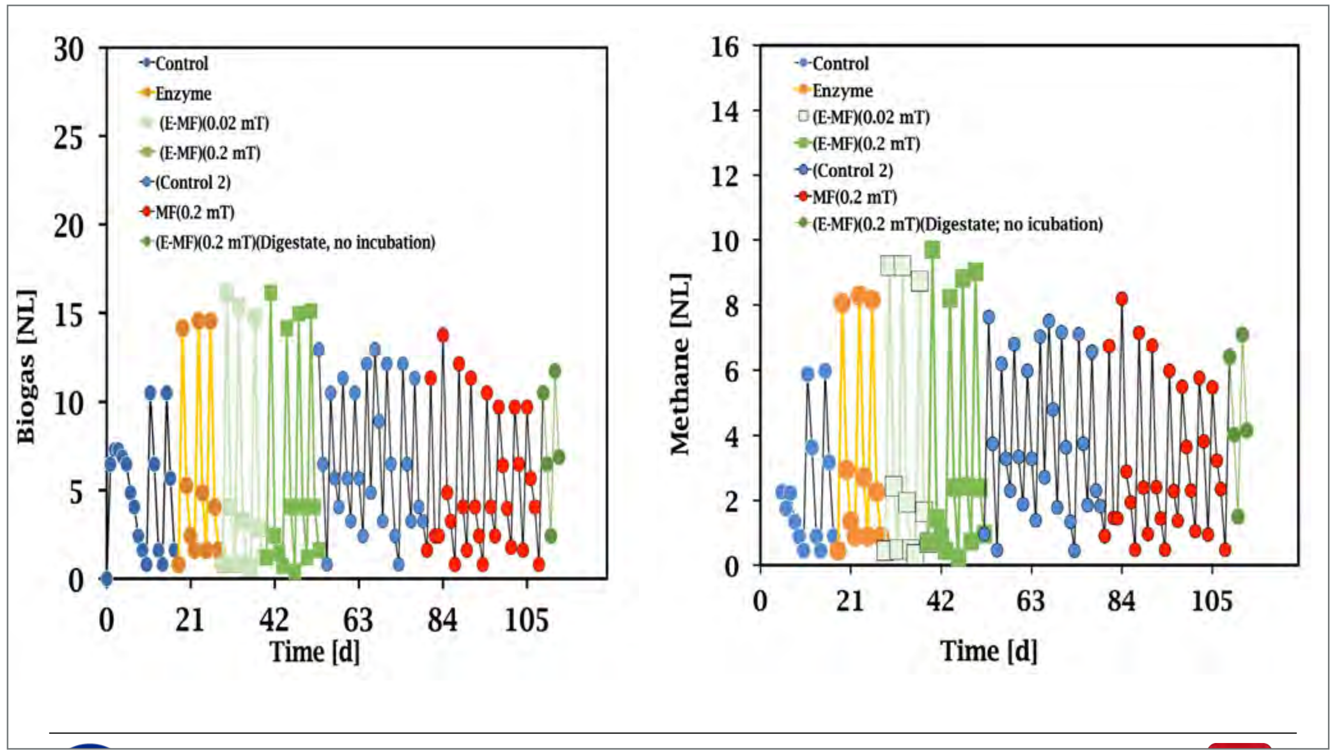


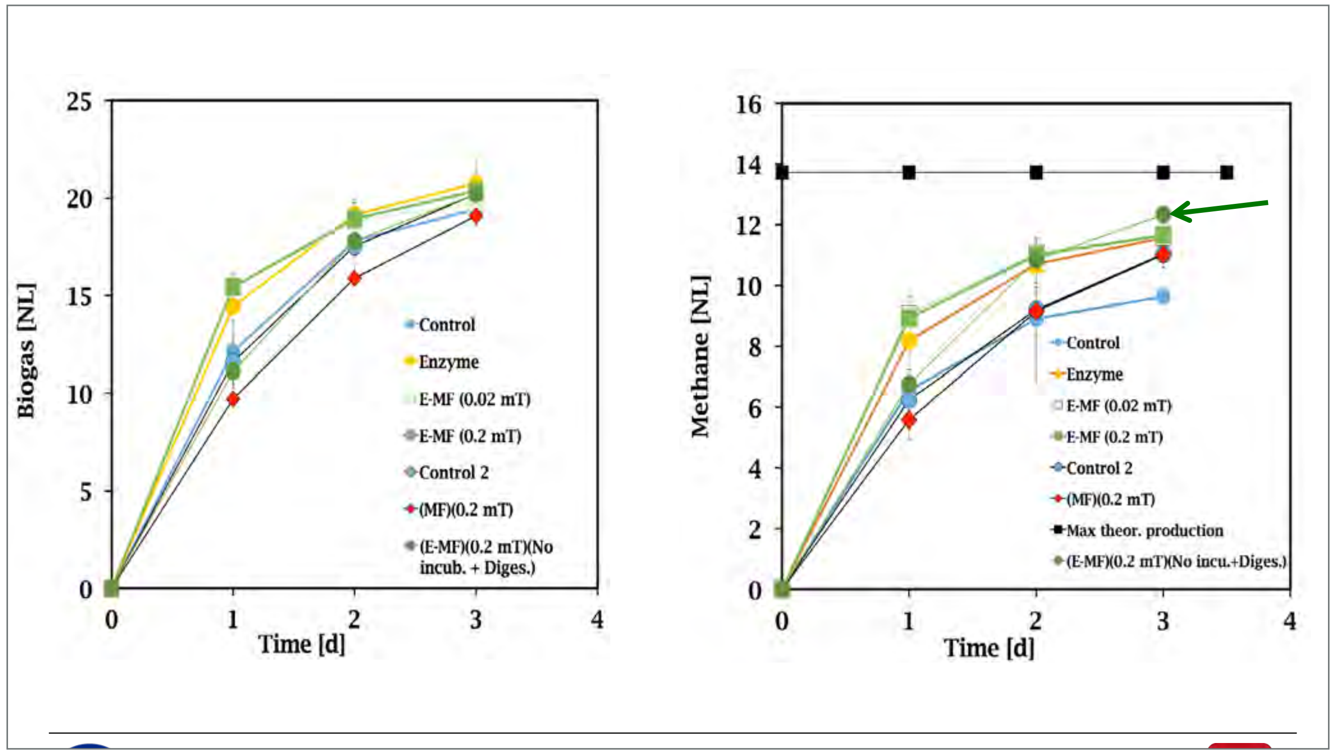
Solenoid
(0.2mT)

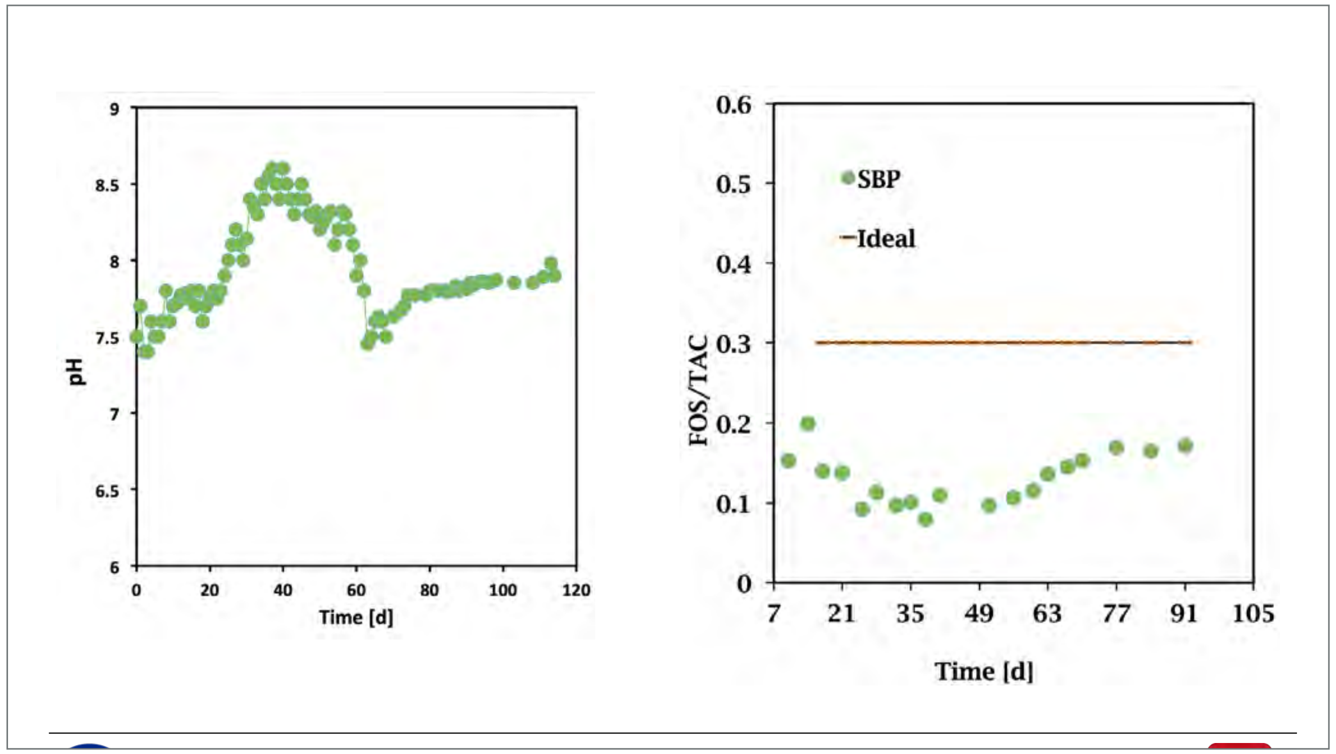
Pretreatment
(50 ˚C)

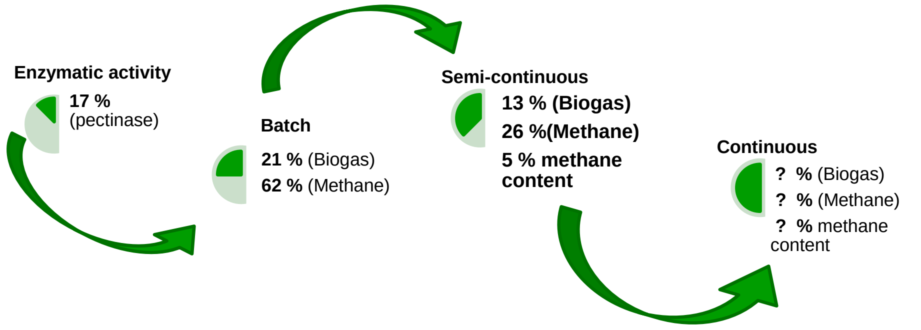
Fermenter
(46 ˚C)


CH4 [%]
70
65
60
55
50
45
40
35
30
25
0
21
42
63
84
105
Time [d]
Control
Enzyme
(E-MF)(0.02 mT)
(E-MF)(0.2 mT)
Control 2
MF (0.2 mT)
(E-MF)(0.2 mT)(Digestate , no incubation)


Biogas [NL]
30
25
20
15
10
5
0
0
21
42
63
84
105
Time [d]
Control
Enzyme
(E-MF)(0.02 mT)
(E-MF)(0.2 mT)
(Control 2)
MF(0.2 mT)
(E-MF)(0.2 mT)(Digestate, no incubation)
Methane [NL]
16
14
12
10
8
6
4
2
0
0
21
42
63
84
105
Time [d]
Control
Enzyme
(E-MF)(0.02 mT)
(E-MF)(0.2 mT)
(Control 2)
MF(0.2 mT)
(E-MF)(0.2 mT)(Digestate; no icubation)


Biogas [NL]
25
20
15
10
5
0
0
1
2
3
4
Time [d]
Control
Enzyme
E-MF (0.02 mT)
E-MF (0.2 mT)
Control 2
(MF)(0.2 mT)
(E-MF)(0.2 mT)(No incub. + Diges.)
Methane [NL]
16
14
12
10
8
6
4
2
0
0
1
2
3
4
Time [d]
Control
Enzyme
E-MF (0.02 mT)
E-MF (0.2 mT)
Control 2
(MF)(0.2 mT)
Max theor. production
(E-MF)(0.2 mT)(No incu.+Diges.)


pH
9
8.5
8
7.5
7
6.5
6
0
20
40
60
80
100
120
Time [d]
FOS/TAC
0.6
0.5
0.4
0.3
0.2
0.1
0
7
21
35
49
63
77
91
105
Time [d]
SBP
Ideal



Enzymatic activity
17 %
(pectinase)

Batch
21 % (Biogas)
62 % (Methane)

Semi-continuous
13 % (Biogas)
26 %(Methane)
5 % methane content

Continuous
? % (Biogas)
? % (Methane)
? % methane content

- Increase in methane concetration;
- Stable process;
- Decrease in FOS TAC
- Low energy consumption

Future work:

- Fermenter of 200 L

Thank you for your attention

Katrin Salbrechter, Montanuniversität Leoben

Single-stage fixed bed methanation reactor for biogas upgrading

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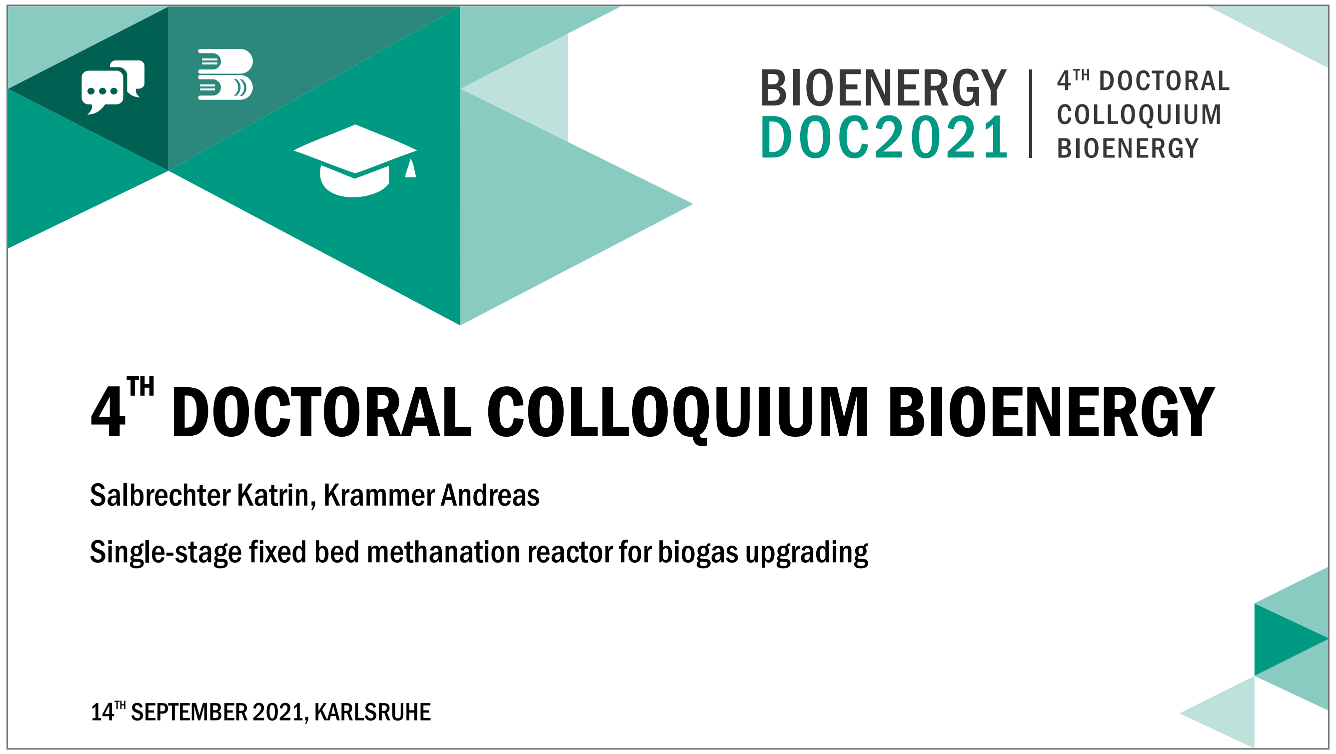
The catalytic fixed bed methanation with two or more reactors in series is an established concept developed and realized in demonstration and commercial scale (e.g. Lurgi [1], TREMP [2]). Even cooled reactor systems for enhanced methanation performance have been designed, e.g. by the company Linde but have never been brought to commercial scale [3]. The challenge of methanation operation in fixed bed reactors consists in heat management as temperature hot spots and high gas output temperatures thermodynamically limit full conversion of COx in the feedgas.

At the Chair of Process Technology at Montanuniversität Leoben a new single-stage methanation reactor set-up has been designed. The new lab-scale reactor design was characterized by a minimization of the reactor diameter (di=14 mm, l=84mm), resulting in higher gas turbulences to enhance heat and mass transfer and limit local temperature peaks in the bulk. The reactor was filled with commercial bulk catalyst. Eight thermocouples were used to measure the axial temperature profile during operation. In preliminary experiments the high performance of the new reactor design for biogas upgrading at 7 bar pressure, a hydrogen surplus of 4 % and a gas hourly space velocity (GHSV) of 15000 h^{-1} was proven. To illustrate the influence of the reactor diameter the results were compared to those of an existing fixed bed reactor with a diameter of 80 mm.

Although catalyst load was increased, high COx conversion of 95.5 % at GHSV = 15000 h^{-1} could be achieved with the new single stage concept compared to the existing reactor system after one reactor stage (94 % at GHSV = 3000 h^{-1})). The increased heat removal due to enhanced intra-bed heat transfer and higher reactor surface area-to-volume ratio leads to lower output temperatures and therefore high methane equilibrium concentrations. At the same time the systems complexity was significantly reduced to a single-stage reactor ensuring simplified operation and lower investment costs. In a future step, active cooling with water will be realized in a tube-in-tube reactor system to further increase the methanation performance through enhanced heat removal. The aim of these efforts is to meet the quality requirements for injection into the natural gas grid in Austria with a methane share of higher 96 mol % [4].

Additionally, it is planned to operate the improved cooled reactor system within a power-to-gas demo plant for biogas upgrading in Gabersdorf (Styria, AUT) within the project "Renewable Gasfield". This project aims at demonstrating biogas upgrading to green synthetic natural gas and feed it into the gas grid. Furthermore, CFD-based simulations coupled with reaction kinetics and heat transfer calculations will be conducted for the comparison of achieved and predicted methanation results. The new set-up serves as the basis for a further up-scale to an industrial scale tube-bundle methanation reactor.



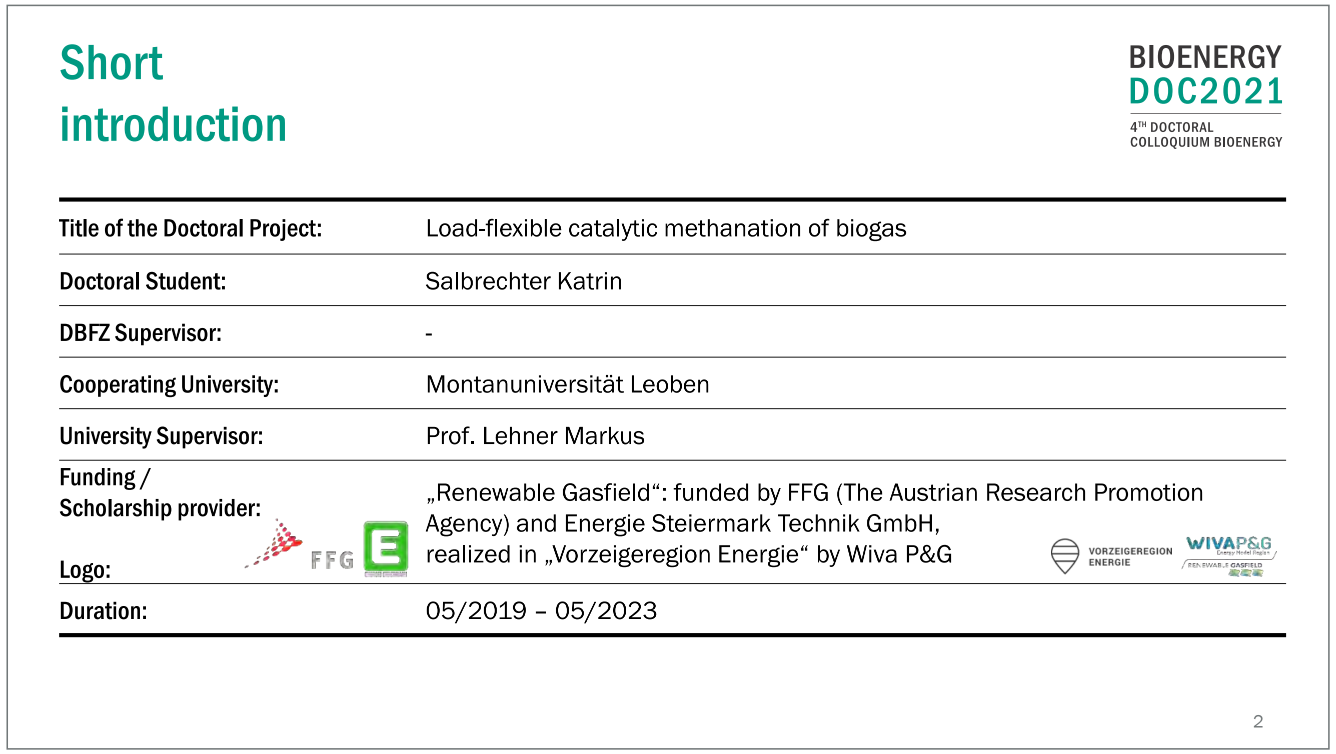
BIOENERGY DOC2021 | 4TH DOCTORAL COLLOQUIUM BIOENERGY

4TH DOCTORAL COLLOQUIUM BIOENERGY

Salbrechter Katrin, Krammer Andreas

Single-stage fixed bed methanation reactor for biogas upgrading

14TH SEPTEMBER 2021, KARLSRUHE



Short introduction

BIOENERGY DOC2021
4TH DOCTORAL COLLOQUIUM BIOENERGY

Title of the Doctoral Project:	Load-flexible catalytic methanation of biogas
Doctoral Student:	Salbrechter Katrin
DBFZ Supervisor:	-
Cooperating University:	Montanuniversität Leoben
University Supervisor:	Prof. Lehner Markus
Funding / Scholarship provider: **Logo:**	„Renewable Gasfield": funded by FFG (The Austrian Research Promotion Agency) and Energie Steiermark Technik GmbH, realized in „Vorzeigeregion Energie" by Wiva P&G
Duration:	05/2019 – 05/2023

2

Biogas upgrading via catalytic methanation (Scientific background and target)

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$CO_2 + 4\ H_2 \Leftrightarrow CH_4 + 2\ H_2O$ $\Delta H^{R(553K)} = -\ 176{,}4$ kJ/mol

- ≈ 50 vol.% CO_2 in biogas → upgrading potential → project „Renewable Gasfield"
  PV park + PEM Electrolysis + Catalytic methanation
  = energy model region for usage of green gases (H_2 (→ trailer) and SNG (→ grid injection))

Different reactor set-ups for catalytic methanation

- Investigations on advanced **fixed-bed set-up** in laboratory @VTiU Leoben
- Laboratory scale → plant set-up under real test conditions (*Renewable Gasfield*)
  - synthetic gases - purified biogas + green H_2
- Target: Improved heat management for even temperature distribution in reactor
  (results from laboratory tests → future scale up)

Laboratory test rigs for catalytic methanation @ MUL (Approach / Methods)

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Existing set-up

Three-stage polytropic fixed-bed set-up

- Max 700° C, 1-20 bar
- Q= 50 L_{STP}/min
- GHSV = 1 000 – 8 000 h^{-1}

New set-up

Single-stage fixed bed reactor

- Max 700° C, 1-20 bar
- Q = 50 L_{STP}/min
- GHSV =
  15 000 – 20 000 h^{-1}

Laboratory test rigs for catalytic methanation @ MUL (Approach / Methods)

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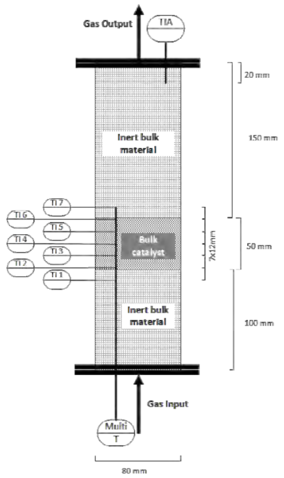
Three-stage fixed bed set up (cascade)

$d_{Reactor}$= 80 mm
$h_{Catalyst}$= 50 mm

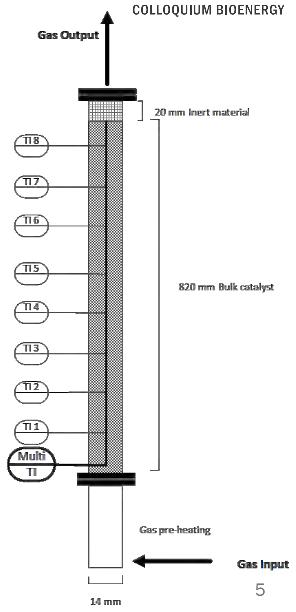
➢ Temperature hot spots in bulk



Single-stage fixed bed reactor

$d_{Reactor}$= 14 mm
$h_{Catalyst}$= 820 mm

➢ Higher turbulences for better heat and mass transfer
➢ Limitation of temperature peaks



Results Comparison of reactor models

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Biogas upgrading at 7 bar, H_2/CO_2 = 4,16 (4% surplus)

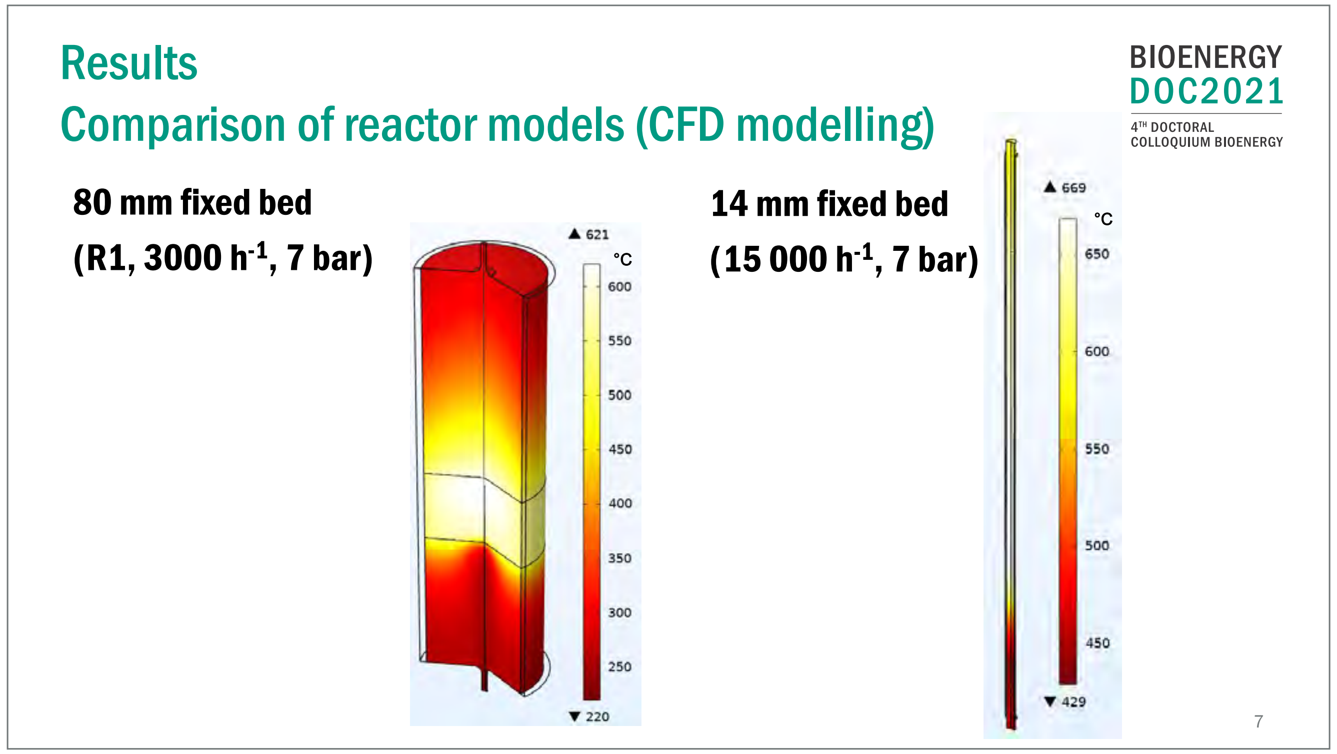
Comparison of CO_2-Conversion rate (CR %)

80 mm fixed bed reactor (R1)

- GHSV = 3 000 h^{-1}
- CR = 94.7%
- Product gas composition (dry)
  - CH_4 = 74.6 vol.%
  - CO_2 = 3.95 vol.%
  - H_2 = 20.73 vol.%
- T_{out}= 466.8 ° C

14 mm fixed bed reactor

- GHSV = 15 000 h^{-1}
- CR = 95.5%
- Product gas composition (dry)
  - CH_4 = 75.7 vol.%
  - CO_2 = 3.53 vol.%
  - H_2 = 20.54 vol.%
- T_{out}= 409.7 ° C



Results
Comparison of reactor models (CFD modelling)

80 mm fixed bed
(R1, 3000 h^{-1}, 7 bar)

14 mm fixed bed
(15 000 h^{-1}, 7 bar)

Results
Comparison of reactor models

Biogas upgrading at 7 bar, H_2/CO_2 = 4,16 with new reactor set-up

- Slightly higher conversion rate (measured results)
- Higher reactor surface area-to-volume ratio → Lower output temperature → higher methane yield
- Reduced system complexity → simplified operation & lower investment

Future steps

Upgrade to tube-in-tube reactor with active cooling and heating

set-up of inner pipe remains unchanged (variable: $h_{Catalyst}$ → heat removal)

outer pipe: oil-tempered (25 - 320 ° C)

- cooling at reactor inlet
- heating at reactor outlet

installation planned in Dec 2021

further test runs with commercial bulk and self-made honeycomb catalysts will be conducted

results serve as basis for future plant scale up realized in „Renewable Gasfield“ – Styria AUT in summer 2022

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Yingmu Chang, Deutsches Biomasseforschungszentrum/University of Leipzig

Potential of agricultural residues and biogas develpment in China

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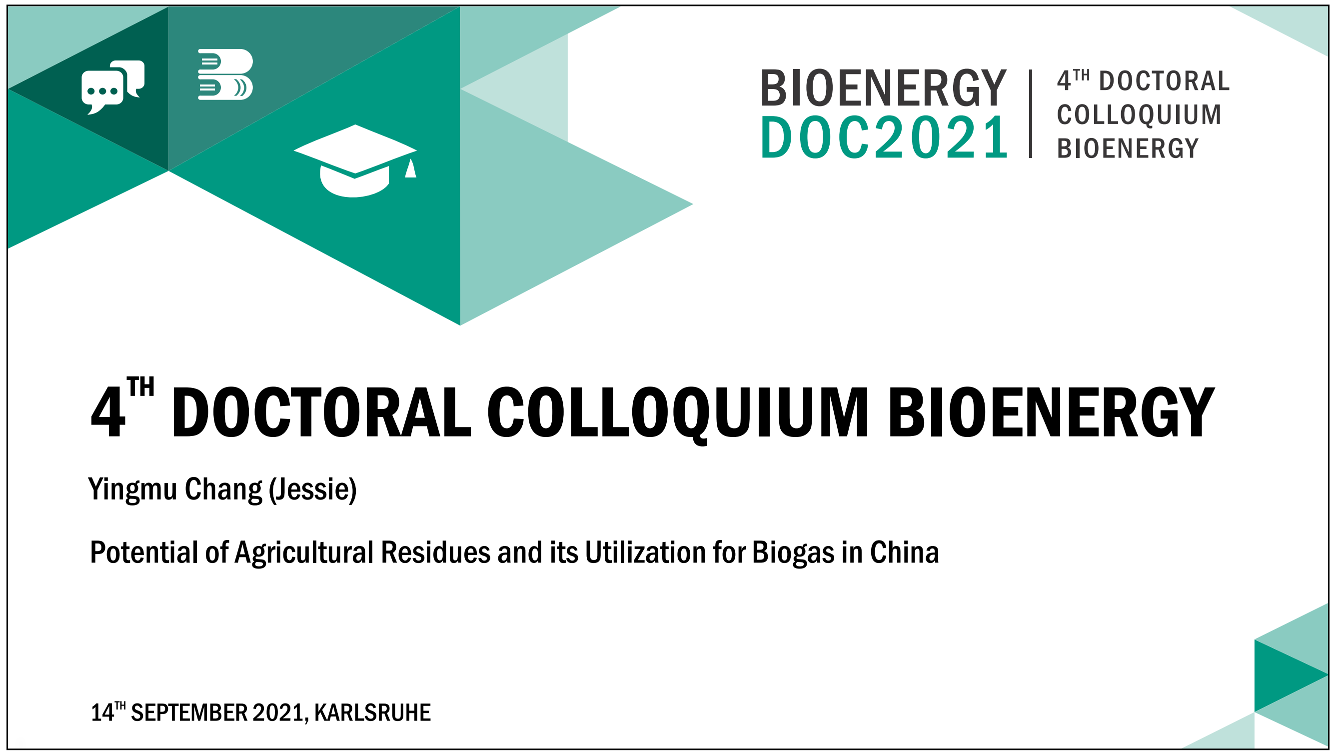
As the second economy in the world, China is one of the world's top energy-consuming countries and largest carbon emitter. Faced with the pressure of both energy supply and environmental protection, China has determination to develop non-fossil fuels, which will account for 20 % of the total energy consumption in 2030. China also sets goal to achieve carbon peak in 2030, and carbon neutrality in 2060. Compared with other renewable energy sources, biogas has its unique advantages, not weather dependent, relatively easy for storage, and is a "joker" in the whole energy structure. China is a large agricultural and breeding country with huge output of straw and animal manure, which provides a superior prerequisite for the development of biogas industry. From 2008 to now, the number of biogas plants increases quickly.

Mainland China is the biggest meat producer in the world. There are nearly 4 billion tons of livestock manure and 800 million tons of crop residues every year generated in mainland China. However, the utilization of agricultural residues is still low. According to the data of the Ministry of Agriculture and Rural Areas of People's Republic of China, the comprehensive utilization rate is less than 60 %, and more than 30 % of livestock manure is directly discharged into the surface water, which brings environmental problems especially in rural area.

Biogas has long history in China. The development of China's biogas industry has gone through three stages. Currently Chinese government vigorously support effective utilization of agricultural residues in large-scale biogas and bio-methane projects, which is mainly for the comprehensive utilization of renewable energy. However, the scale development of biogas industry is in the primary stage and China's biogas industry still has many problems. For example, there are still difficulties in whole industry chain in material collection, storage, transportation and utilization. High-quality systems often show a lack of efficiency due to planning, which is difficult to reconcile with the cost pressure in China. In the aspect of development mode of overall industry, there are also shortcomings in the top-level design and business model. It focuses on policy formulation and project construction, but which lacks effective incentives. Additionally, there is a lack of knowledge-based infrastructure, lack of competence in efficiency-oriented planning in engineering, plant construction and planning companies. The cash flow generated by project operations is not ideal, but many projects did not actually operate sustainably and profitably. China's biogas industry generally lacks a sustainable business model. These problems are common in projects, "emphasizing construction and neglecting management".



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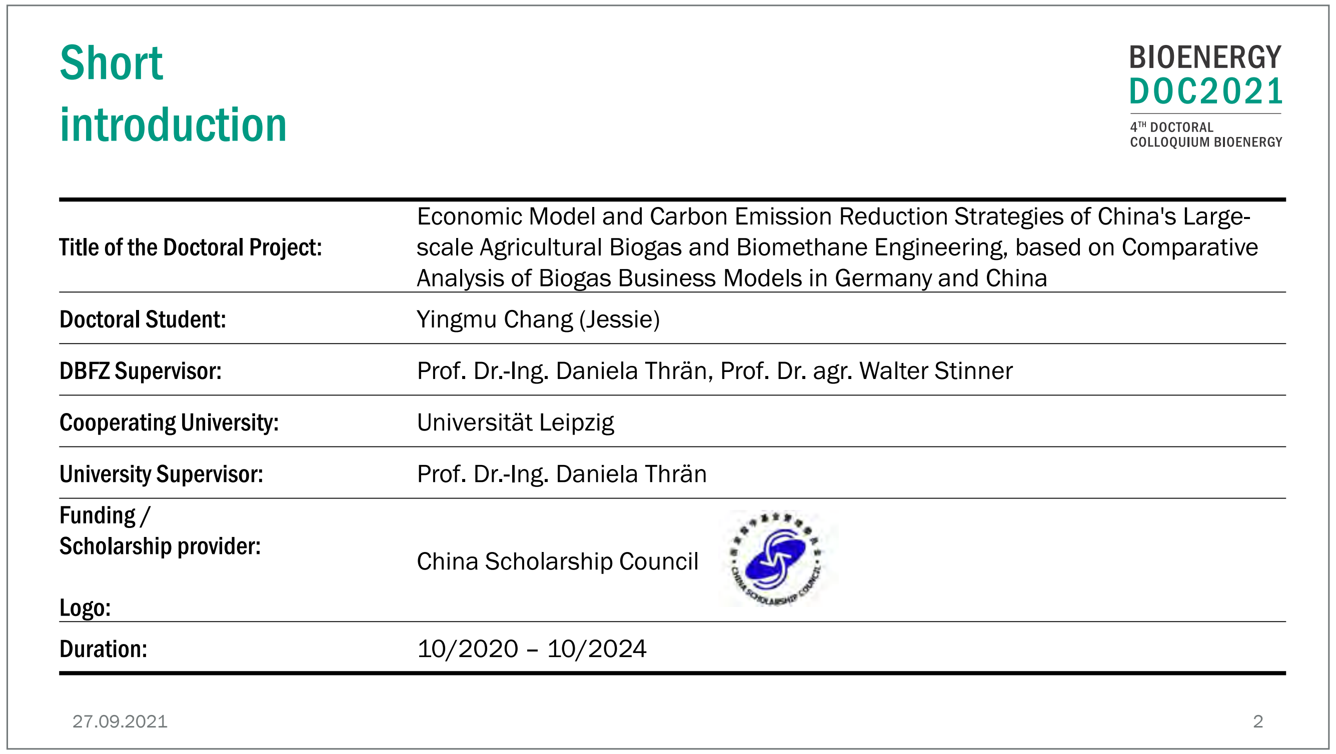
4TH DOCTORAL COLLOQUIUM BIOENERGY

Yingmu Chang (Jessie)

Potential of Agricultural Residues and its Utilization for Biogas in China

14TH SEPTEMBER 2021, KARLSRUHE



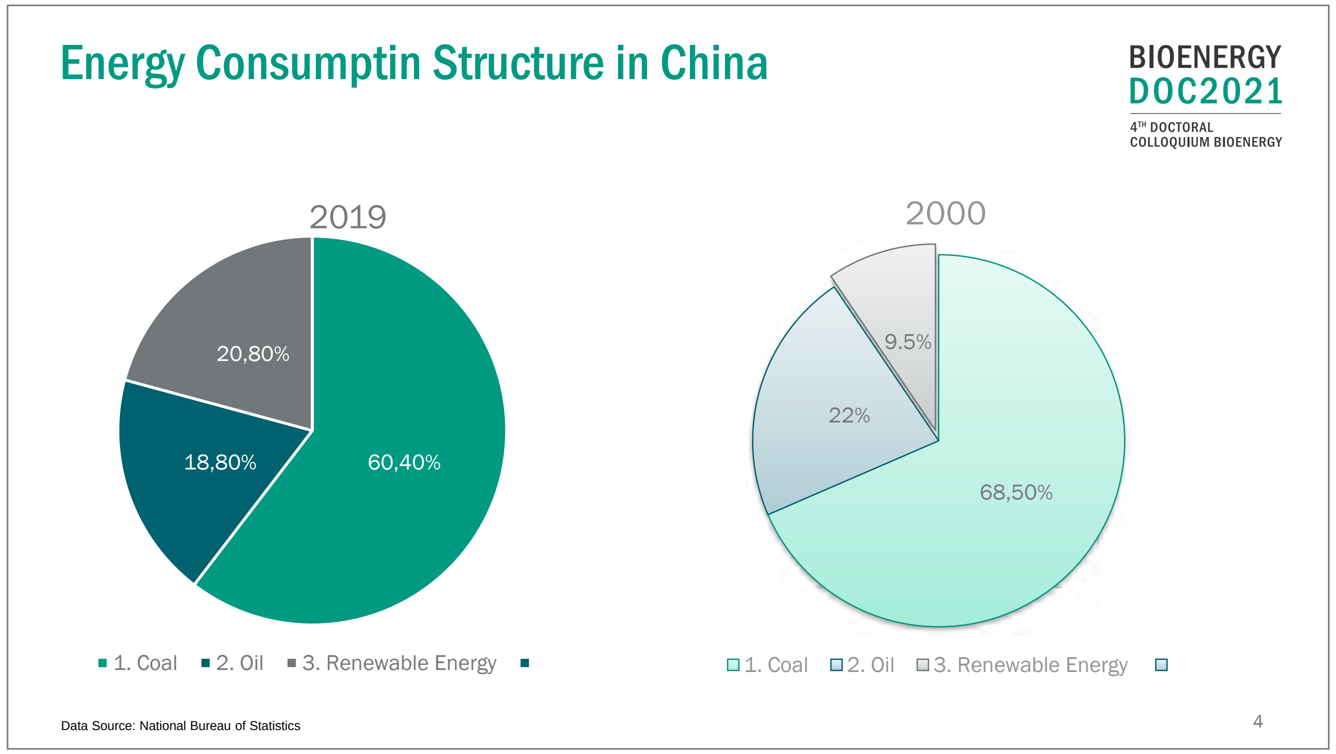
Short introduction

BIOENERGY DOC2021 4TH DOCTORAL COLLOQUIUM BIOENERGY

Title of the Doctoral Project:	Economic Model and Carbon Emission Reduction Strategies of China's Large-scale Agricultural Biogas and Biomethane Engineering, based on Comparative Analysis of Biogas Business Models in Germany and China
Doctoral Student:	Yingmu Chang (Jessie)
DBFZ Supervisor:	Prof. Dr.-Ing. Daniela Thrän, Prof. Dr. agr. Walter Stinner
Cooperating University:	Universität Leipzig
University Supervisor:	Prof. Dr.-Ing. Daniela Thrän
Funding / Scholarship provider: **Logo:**	China Scholarship Council
Duration:	10/2020 – 10/2024

27.09.2021 2

2nd Economy	The largest carbon emitter 2030, Carbon peak 2060, Carbon Neutrality	One of the world's top energy-consuming countries
The biggest meat producer	Year 2019 Total power generation: 7503.43 billion kWh Total energy production: 3.97 billion tons of standard coal Total energy consumption: 4.86 billion tons of standard coal	4 billion tons of livestock manure +800 million tons of crop residues/year



Energy Consumptin Structure in China

Data Source: National Bureau of Statistics

Biomass Energy

- In 2019, China's biomass energy installed capacity and power generation accounted for 2.54% and 6.31% of renewable energy.
- The annual power generation capacity is 33.3 billion kWh, which accounts for 2.1% of the renewable energy power generation and 9.0% of the non-aqueous renewable energy power.
- 254 agricultural and forestry biomass power generation projects have been put into operation in 23 provinces, with an installed capacity of 6.36 million kilowatts, accounting for 1.1% of the installed capacity of renewable energy.
- The average annual utilization hours are 5835 hours.

Data Source: National Bureau of Statistics

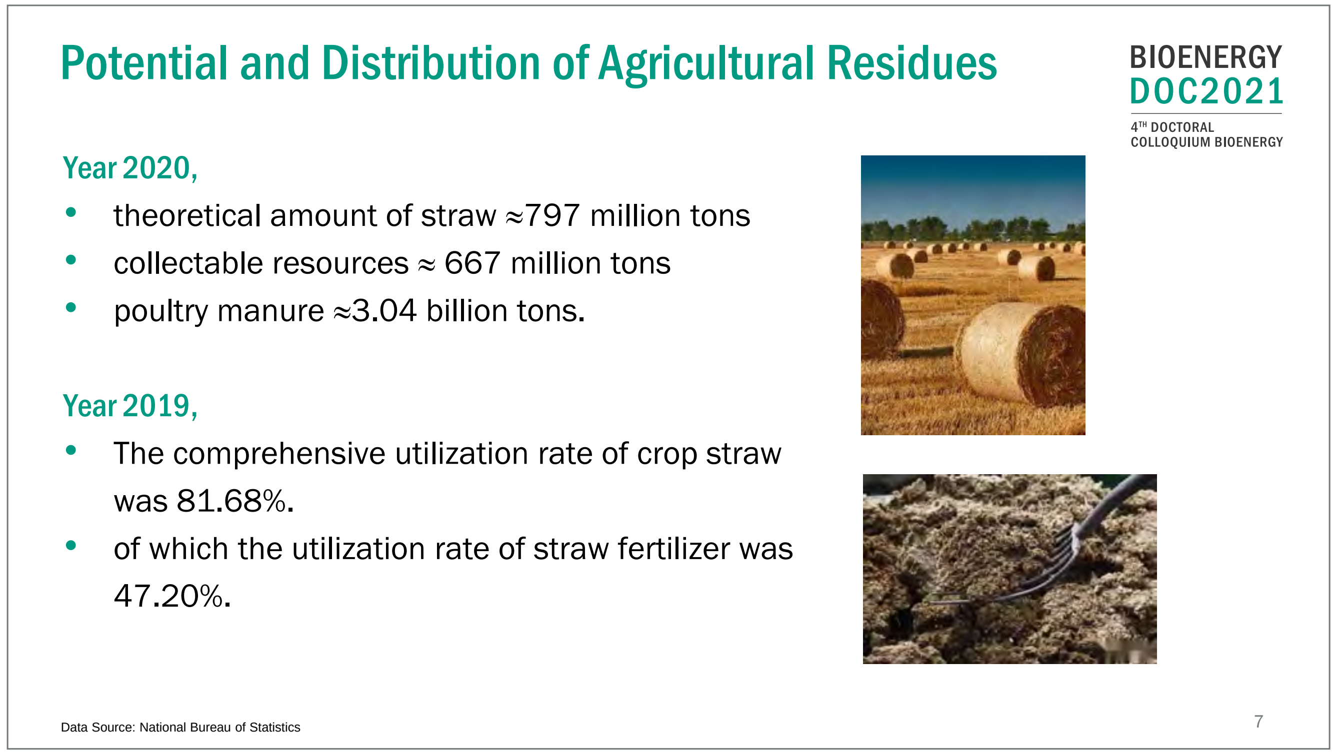
Utilization of Agricultural Residues

Crop Straw

- Direct-application into fields
- Burning on field not allowed any more
- Anaerobic treatment of straw-e.g. Large-scale biological natural gas demonstration project

Livestock and poultry manure

- Rural household biogas
- Large and medium-sized biogas



Potential and Distribution of Agricultural Residues

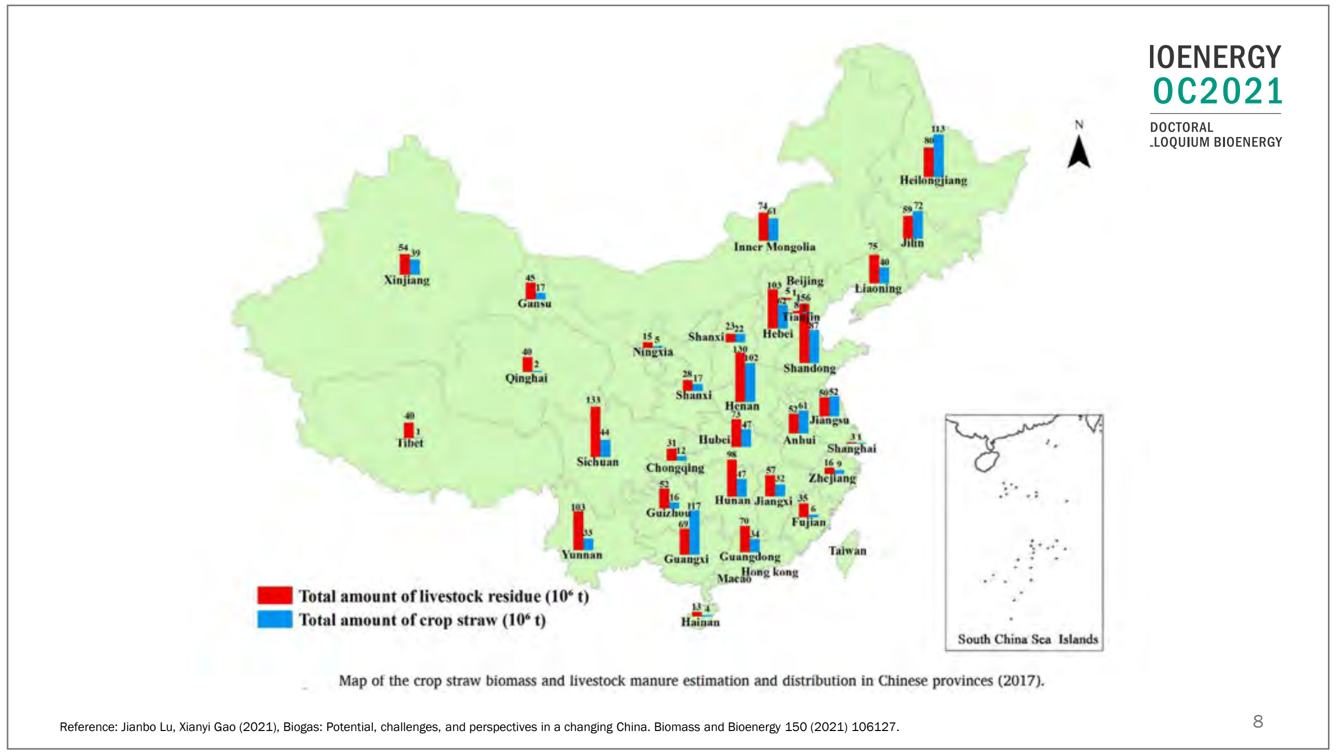
Year 2020,

- theoretical amount of straw ≈797 million tons
- collectable resources ≈ 667 million tons
- poultry manure ≈3.04 billion tons.

Year 2019,

- The comprehensive utilization rate of crop straw was 81.68%.
- of which the utilization rate of straw fertilizer was 47.20%.

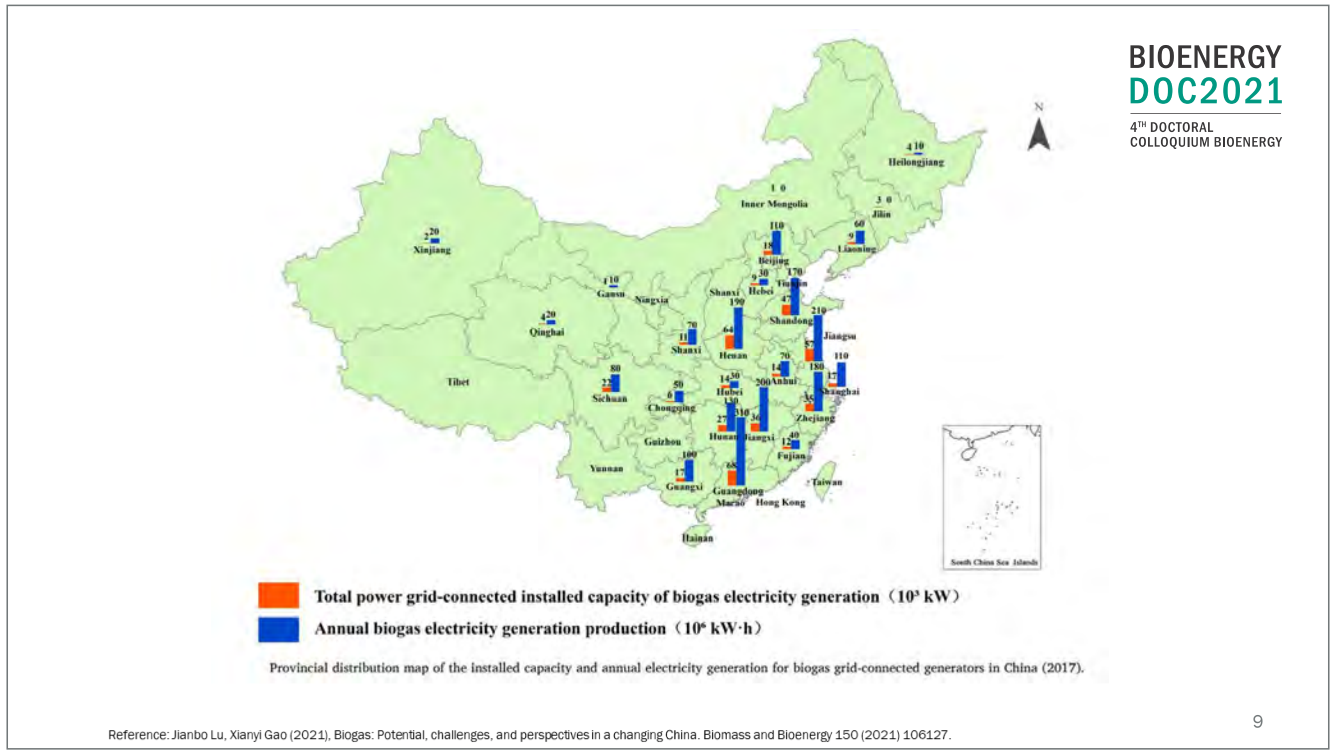
Data Source: National Bureau of Statistics



🟥 Total amount of livestock residue (10^6 t)
🟦 Total amount of crop straw (10^6 t)

Map of the crop straw biomass and livestock manure estimation and distribution in Chinese provinces (2017).

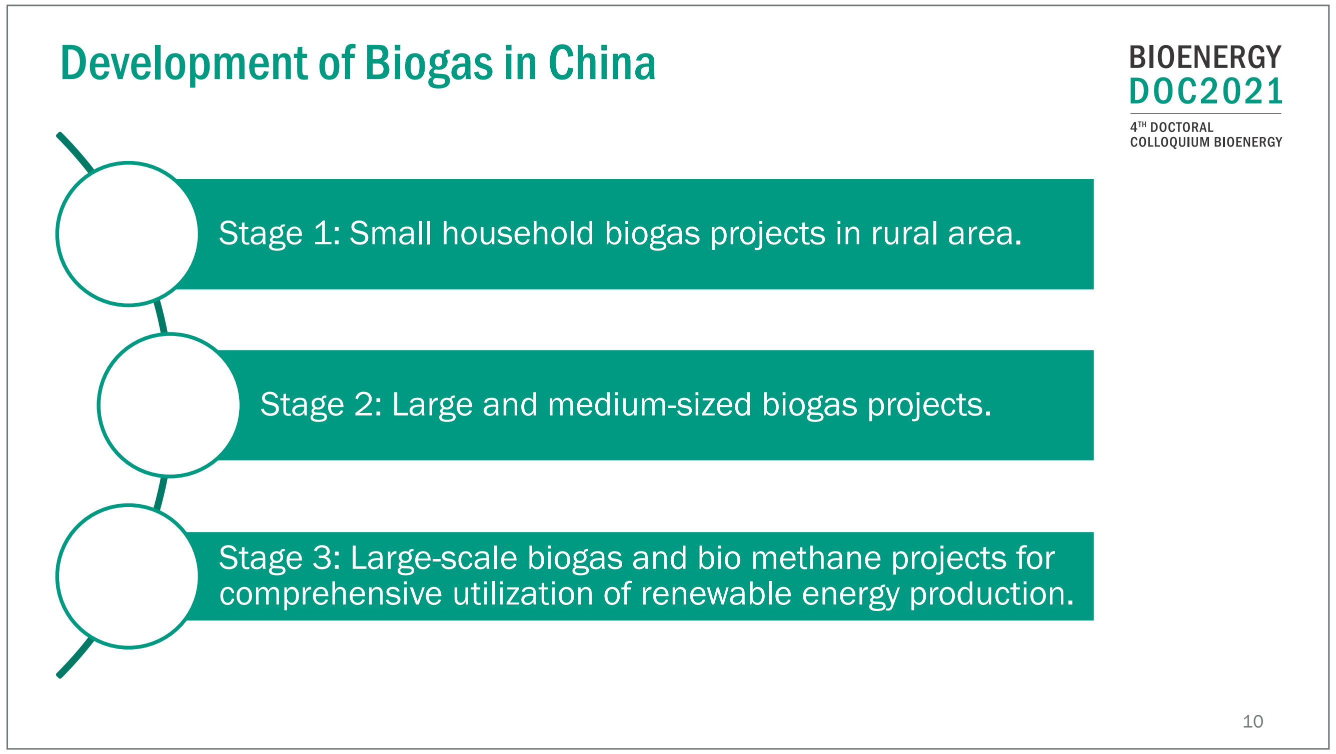
Reference: Jianbo Lu, Xianyi Gao (2021), Biogas: Potential, challenges, and perspectives in a changing China. Biomass and Bioenergy 150 (2021) 106127.



🟧 Total power grid-connected installed capacity of biogas electricity generation（10^3 kW）
🟦 Annual biogas electricity generation production（10^6 kW·h）

Provincial distribution map of the installed capacity and annual electricity generation for biogas grid-connected generators in China (2017).

Reference: Jianbo Lu, Xianyi Gao (2021), Biogas: Potential, challenges, and perspectives in a changing China. Biomass and Bioenergy 150 (2021) 106127.

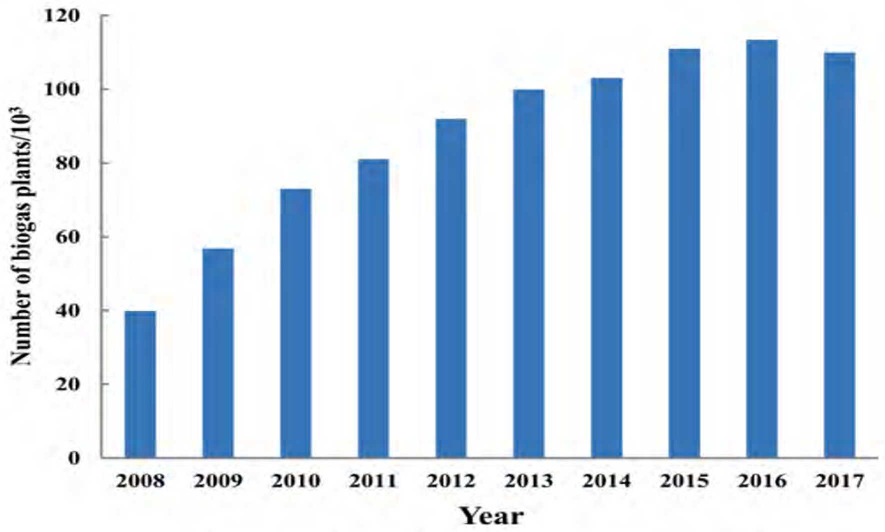


Development of Biogas in China

Stage 1: Small household biogas projects in rural area.

Stage 2: Large and medium-sized biogas projects.

Stage 3: Large-scale biogas and bio methane projects for comprehensive utilization of renewable energy production.



Changes in the number of biogas plants (2008–2017).

Reference: Jianbo Lu, Xianyi Gao (2021), Biogas: Potential, challenges, and perspectives in a changing China. Biomass and Bioenergy 150 (2021) 106127.

Problems and Opportunity

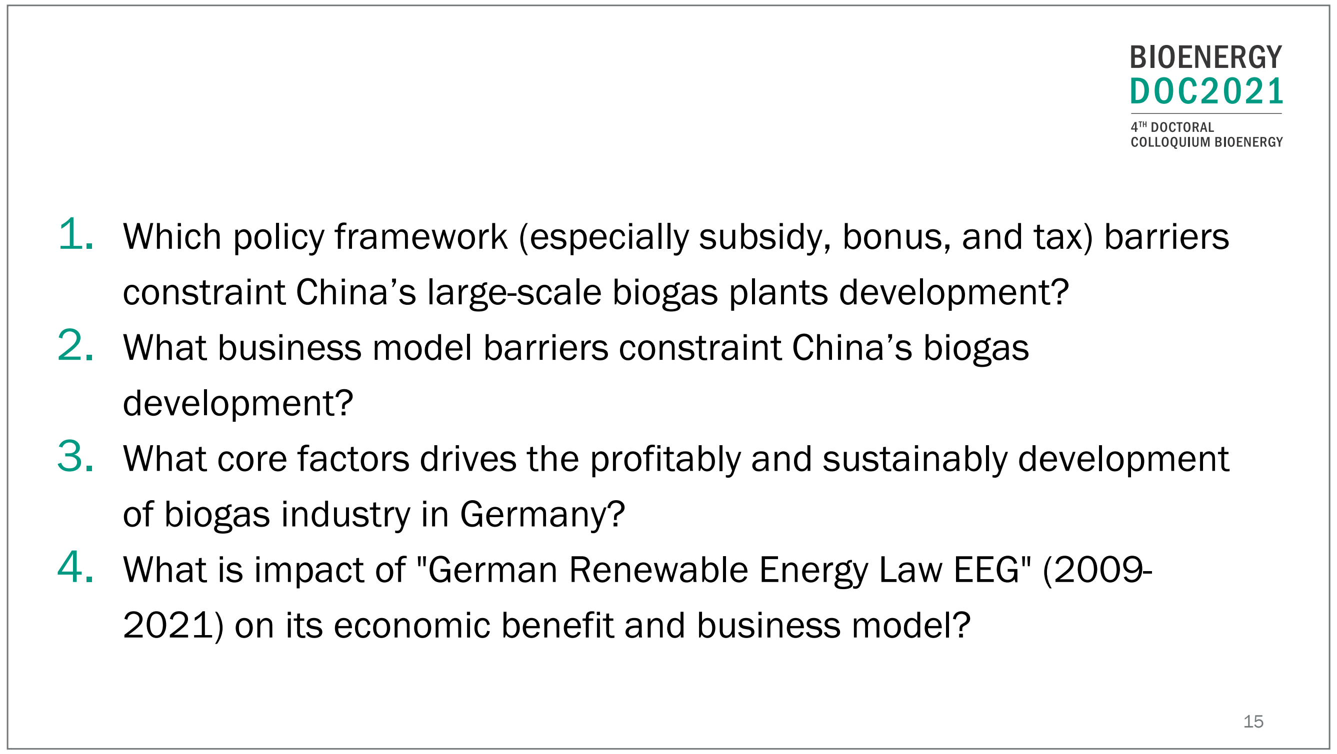
- China's biogas market is large, and the government also strongly supports the development of large-scale biogas projects. However, it is still in primary stage, which is far from forming a long-term stable business model and industrialization operation.
- There are few analyses on business models and their economics. Many projects have been abandoned due to cost pressure.
- There are still difficulties in material collection, storage, transportation and utilization. It has not formed an effective whole industry chain.

- Compared with international advanced technology, there is a certain gap in key equipment such as power generation and purification. Not only technical components are the problem, even high-quality systems often show a lack of efficiency due to planning, which is difficult to reconcile with the cost pressure in China.
- Shortcomings in the top-level design, lack of efficient incentives and price system.
- Lack of knowledge-based infrastructure (specialist laboratories and experts for advice, ideally independent of the company, e.g., organized by state institutions and universities), of competence in efficiency-oriented planning in engineering, plant construction and planning companies.

Research Question

How to promote the industrialization upgrading of large-scale agricultural and biomethane engineering in China combing with Germany's experience?

The following sub-questions will be asked and shall be answered:



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1. Which policy framework (especially subsidy, bonus, and tax) barriers constraint China’s large-scale biogas plants development?
2. What business model barriers constraint China’s biogas development?
3. What core factors drives the profitably and sustainably development of biogas industry in Germany?
4. What is impact of "German Renewable Energy Law EEG" (2009-2021) on its economic benefit and business model?

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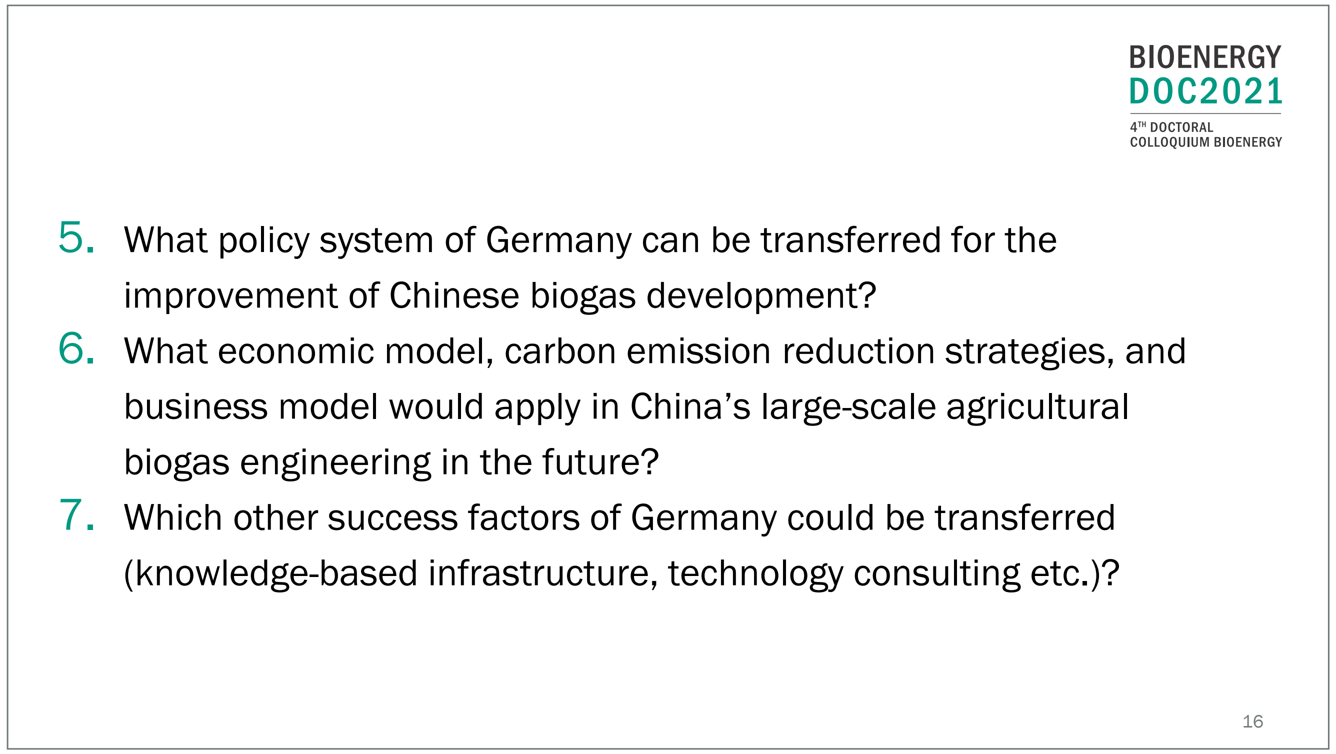

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5. What policy system of Germany can be transferred for the improvement of Chinese biogas development?
6. What economic model, carbon emission reduction strategies, and business model would apply in China’s large-scale agricultural biogas engineering in the future?
7. Which other success factors of Germany could be transferred (knowledge-based infrastructure, technology consulting etc.)?

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ORAL PRESENTATIONS

SESSION V

BIOREFINERIES/BIOFUELS

Michael Bampaou, University of Thessaloniki

Integrating bio-oils into petrochemical refineries

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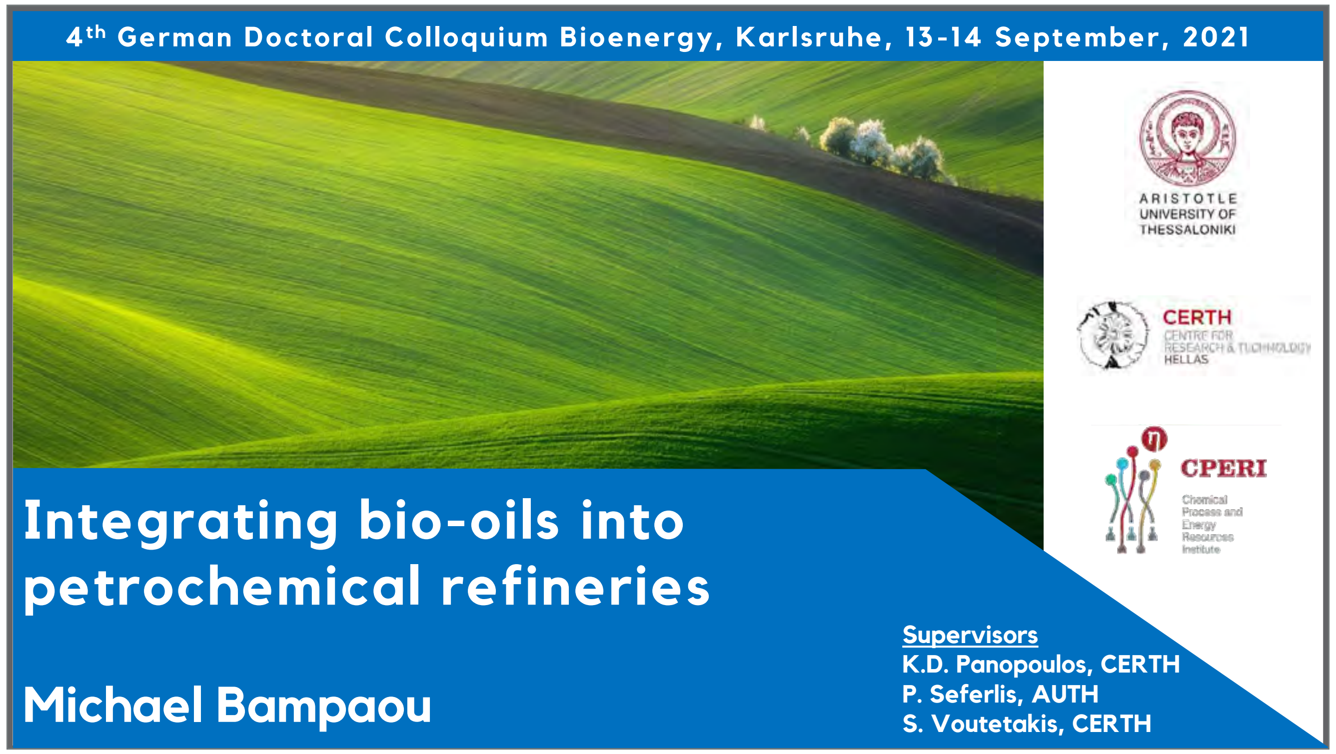
The scope of this work is the efficient integration of pyrolysis oils into existing refinery operations for the production of drop-in fuels. The first part of this work investigates the proposed biorefinery concept that converts the initial biomass feedstock to a treatable, bio-intermediate. The proposed concept consists of the following systems: pyrolysis, hydrotreatment, gas cleaning, hydrogen production and hydrogen recirculation (electrochemical compression, pressure swing adsorption). Crucial operating parameters are investigated that affect the overall economic and energetic performance, focusing especially on H2 since it is the most expensive component in this scheme. This study was conducted using flowsheet simulations in AspenPlusTM. The second part, involves the investigation and discussion of potential entry points of the produced bio-crudes into the EU refinery ecosystem. The suitability of each insertion point is investigated based on the composition and properties of the bio-intermediates as well as on the desired final product and the potential environmental/economic benefits.

European refineries are currently challenged by strict emission regulations and international competition from non-European countries. Biomass integration into refinery operations has been proposed as an option to cope up with these challenges. It allows to utilize existing infrastructures without deviating from established production routes and partially substitute fossil- with renewable-carbon molecules. In particular, biomass after being thermochemically converted by pyrolysis into bio-oil, it is further upgraded in the hydrotreatment (HDT) section due to the contained oxygen and water. Finally, the higher-value, bio-intermediate is inserted for co-processing into existing refinery operations (such as in the FCC unit). Pyrolysis oils as well as upgraded oils are investigated as potential candidates for co-processing.

Hydrogen is a key component in the HDT process. It is used in high excess for removing the contained O_2 and is renewable (produced by water electrolysis) in order to reduce the carbon intensity of the final fuel. During HDT a large amount of the added H_2 remains unreacted in the off-gases and therefore, recovering and reusing it, could prove beneficial for the economic viability of the process. Along with the state-of-the-art pressure swing adsorption, an alternative technology to recover H_2 from a gaseous stream is electrochemical compression. An electrochemical hydrogen compressor (EHC) has similar construction to a PEM fuel cell. It has the ability to recover H_2 from a gaseous mixture and, simultaneously, compress it, within a single step. Prior to entering the EHC, the HDT off-gases require conditioning to remove the contained H_2S and CO, which is conducted via a ZnO Bed and a CO methanation reactor.

This work was conducted within European Union's Horizon 2020 Research and Innovation Programme BRISK2 under Grant Agreement Nr. 731101.



4th German Doctoral Colloquium Bioenergy, Karlsruhe, 13-14 September, 2021

Integrating bio-oils into petrochemical refineries

Michael Bampaou

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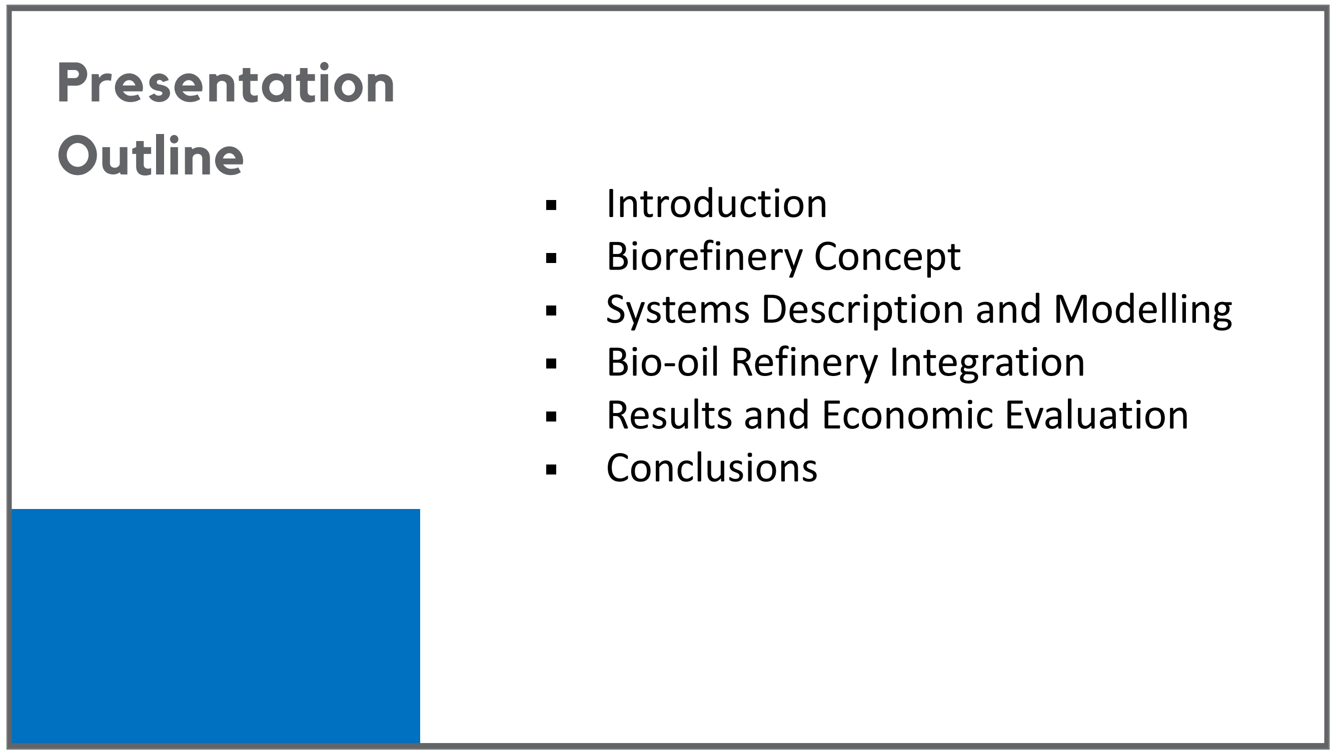
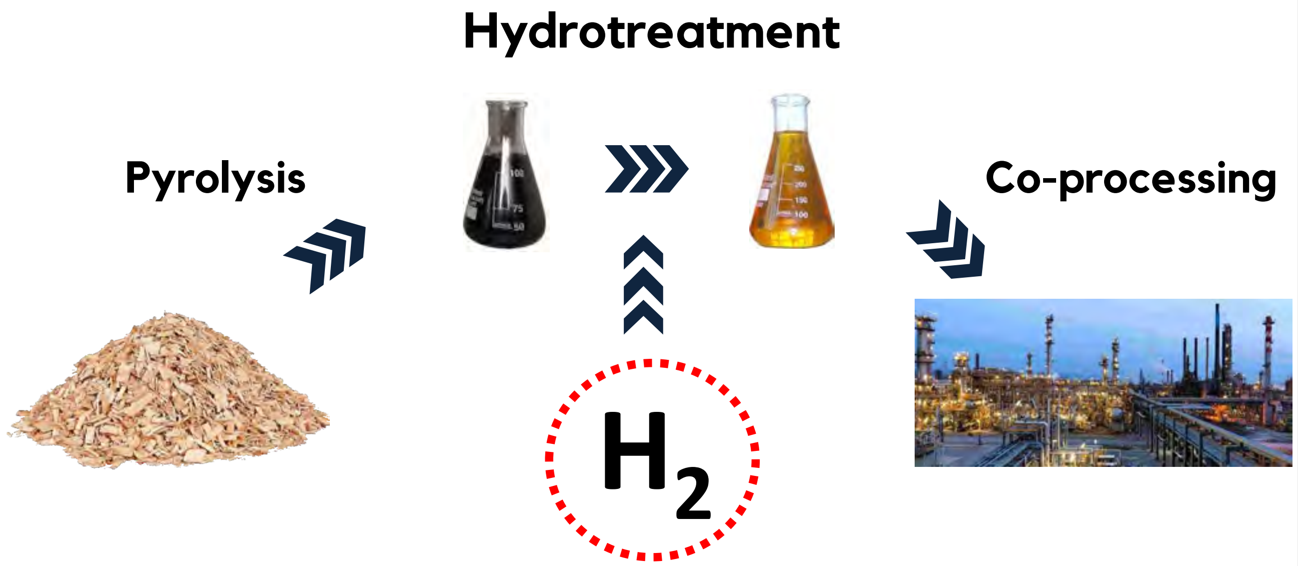
P. Seferlis, AUTH
S. Voutetakis, CERTH



Presentation Outline

- Introduction
- Biorefinery Concept
- Systems Description and Modelling
- Bio-oil Refinery Integration
- Results and Economic Evaluation
- Conclusions

Problem Definition



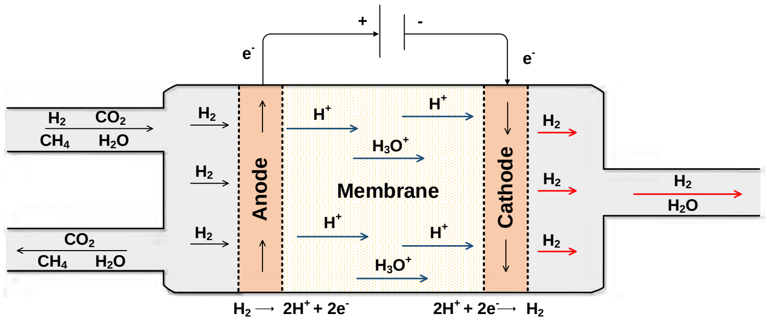
Hydrotreatment

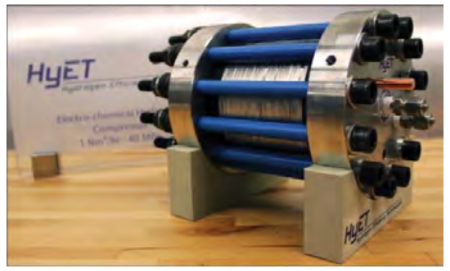
Pyrolysis

Co-processing

H_2

Electrochemical Hydrogen Compression (EHC)



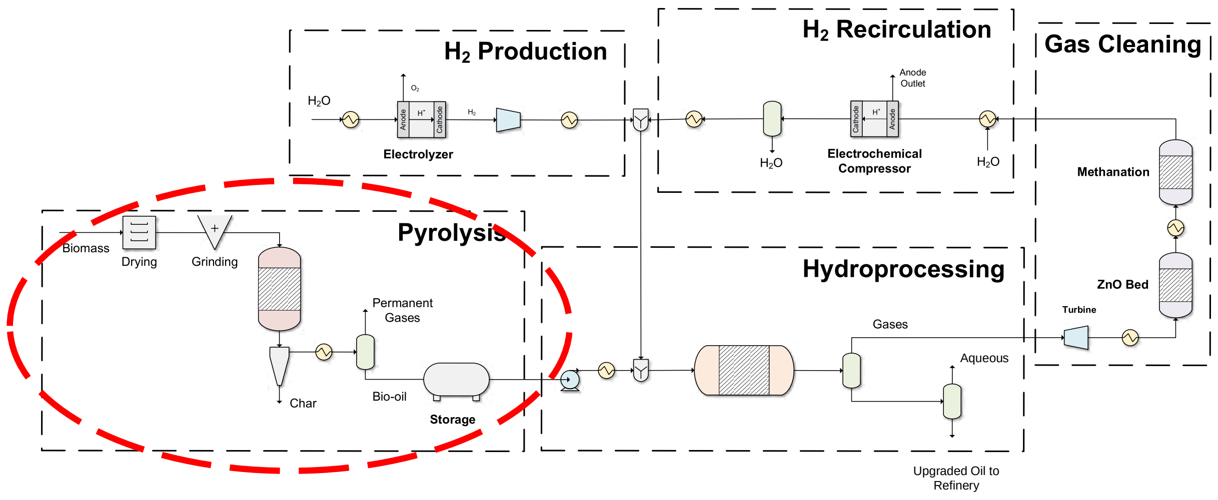


*Source: Bouwman P. Electrochemical Hydrogen Compression (EHC) solutions for hydrogen infrastructure. Fuel Cells Bull. 2014;2014(5):12–6.

- Single stage recovery and compression
- Similar construction to PEMFC: Pt electrodes/Nafion® membrane
- No moving parts and noiseless operation

- Isothermal and Faradaic Process
- T = 30 – 70 ºC, P_{in}<10 bar, P_{out} < 150 bar
- Susceptible to CO and H_2S impurities

Process Flowsheet

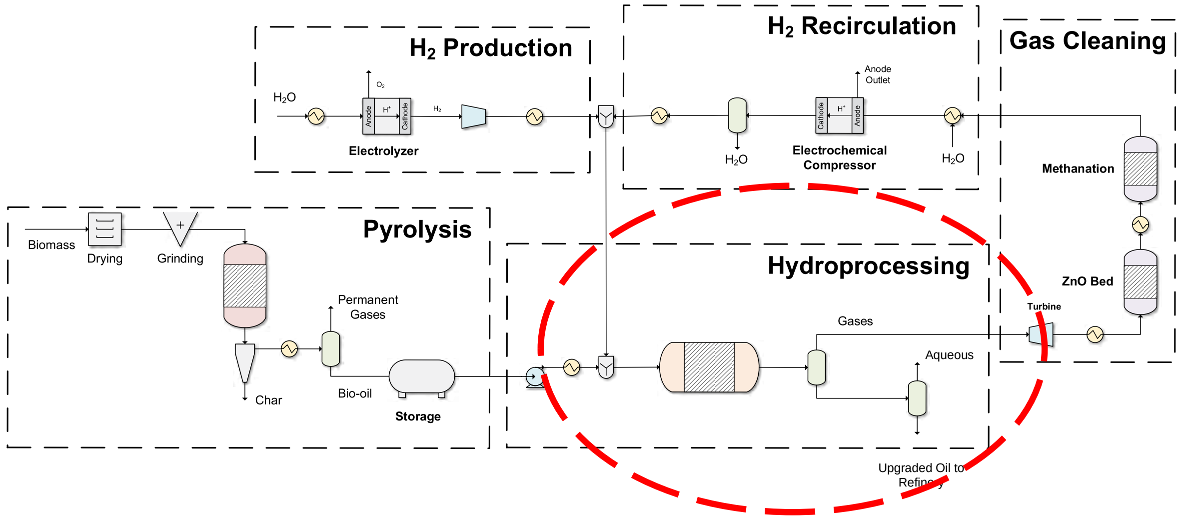


Pyrolysis

- Thermal decomposition of biomass in the absence of O_2
- Main products: bio-oil, char, permanent gases
- Bio-oil main product of interest - fast pyrolysis conditions suitable (short vapor residence time, T = 500 ºC)
- Scope is to accurately predict the mass balances, compositions and energetic value of pyrolysis products
- Developed model (AspenPlus™) is based on semi-empirical correlations available in literature*

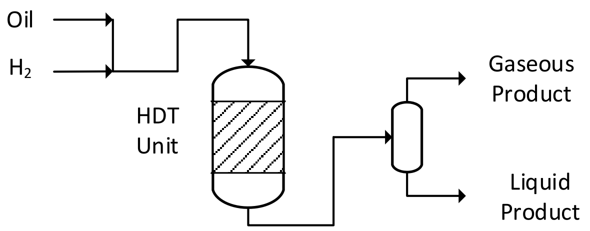
*D. Neves, H. Thunman, A. Matos, L. Tarelho, A. Gómez-Barea, Characterization and prediction of biomass pyrolysis products, Prog. Energy Combust. Sci. 37 (2011) 611–630.

Process Flowsheet



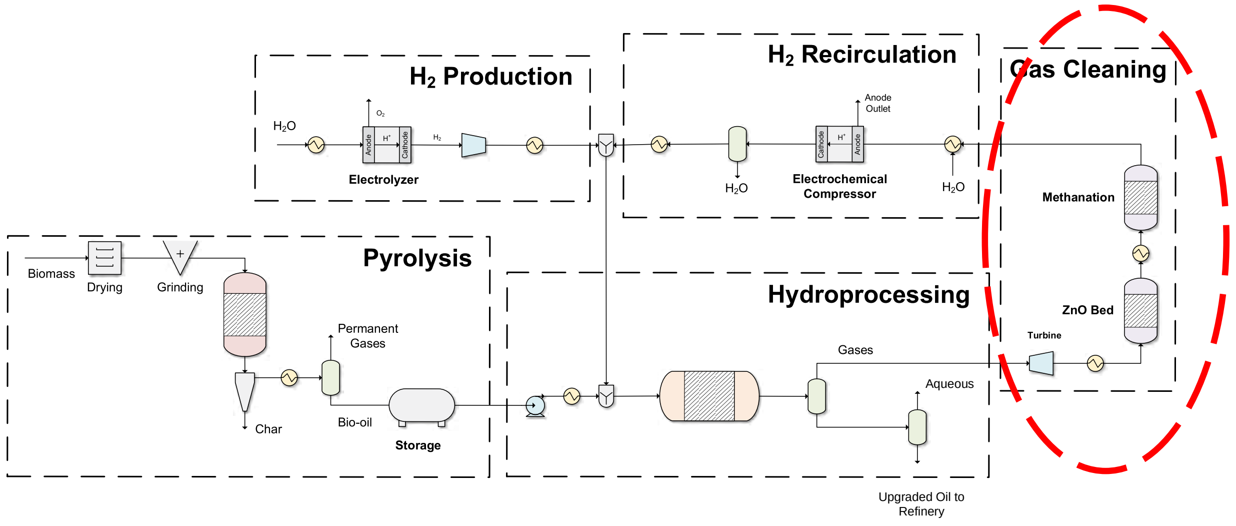
Bio-oil mild Hydrotreatment

- Hydrotreating (HDT): removal of O heteroatoms and moisture
- Exothermic at T = 250 – 400 ºC, P = 50 – 150 bar, H_2 excess
- Reactor outlet phases: organic (upgraded oil to refinery), aqueous & gaseous (contains unreacted H_2, CO, CO_2, CH_4)
- Variety of experimental data types: Ultimate analysis used as basis for the calculations[1]



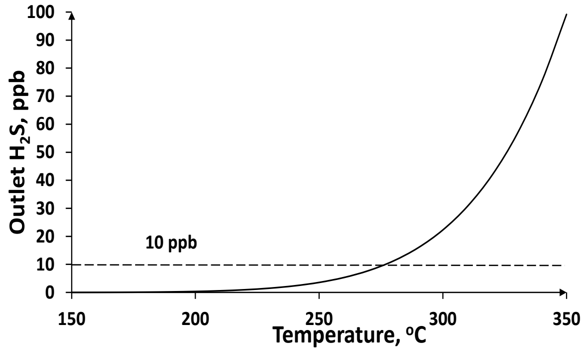
[1] **M. Bampaou**, K.D. Panopoulos, A.I. Papadopoulos, S. Bezergianni, P. Seferlis, S. Voutetakis, "Hydroprocessing Modelling Toolkit for Process Design", European Biomass Conference and Exhibition, EUBCE 2018, Copenhagen, Denmark, 2018.

Process Flowsheet

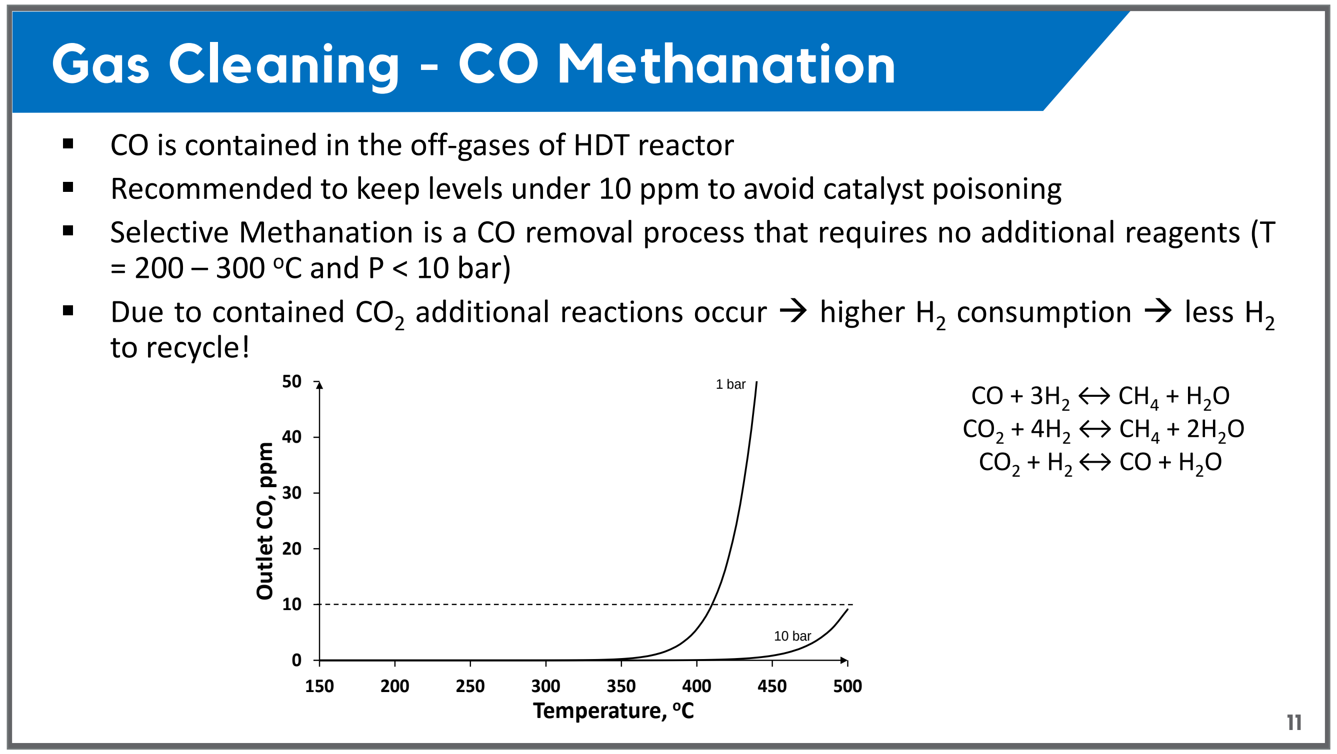


Gas Cleaning - ZnO Bed

- Use of sulphided NiMo and CoMo HDT catalyst → H_2S contained in off-gases
- H_2S is corrosive and toxic to the EHC catalyst and membrane → low S contents required before entering EHC (<10 ppb)
- Deep S removal process is H_2S adsorption using ZnO bed: S is removed in the form of ZnS



$$ZnO_{(s)} + H_2S \leftrightarrow ZnS_{(s)} + H_2O$$
$$H_2S + CO \leftrightarrow COS + H_2$$
$$H_2S + CO_2 \leftrightarrow COS + H_2O$$



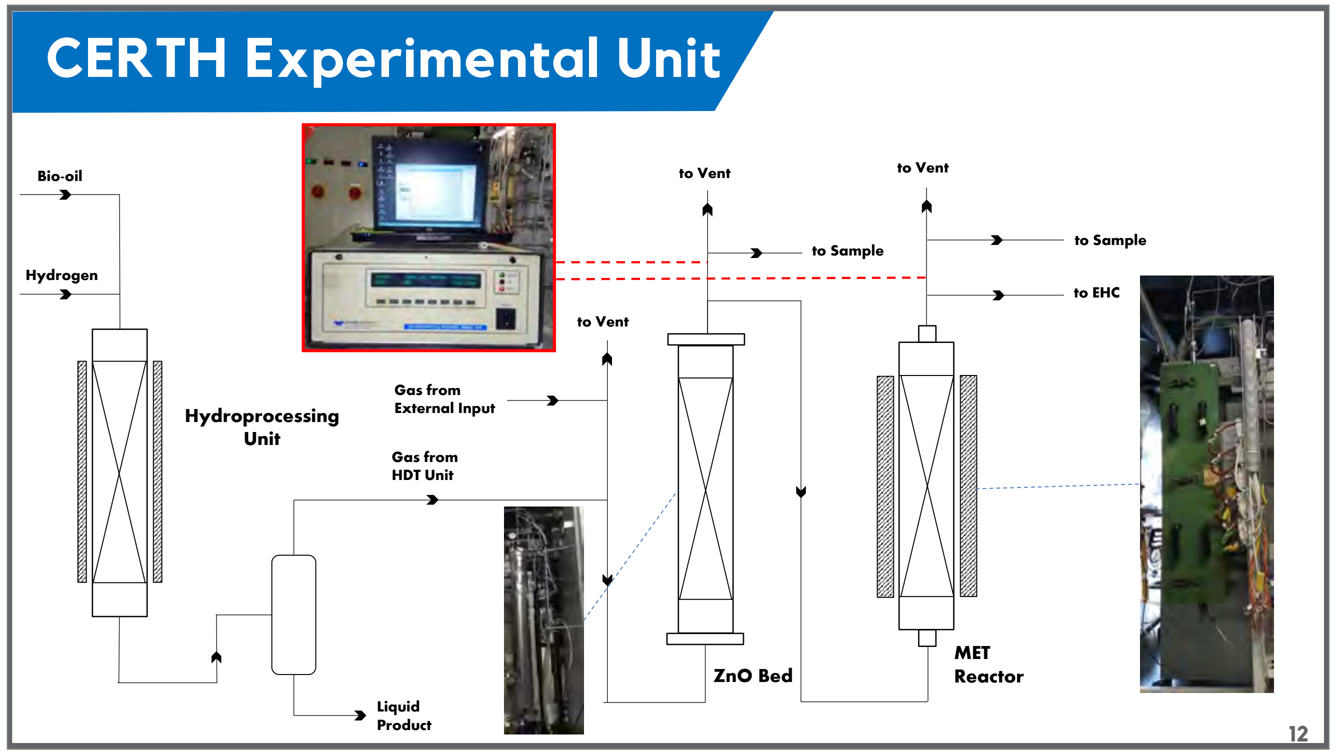
Gas Cleaning - CO Methanation

- CO is contained in the off-gases of HDT reactor
- Recommended to keep levels under 10 ppm to avoid catalyst poisoning
- Selective Methanation is a CO removal process that requires no additional reagents (T = 200 – 300 °C and P < 10 bar)
- Due to contained CO_2 additional reactions occur → higher H_2 consumption → less H_2 to recycle!

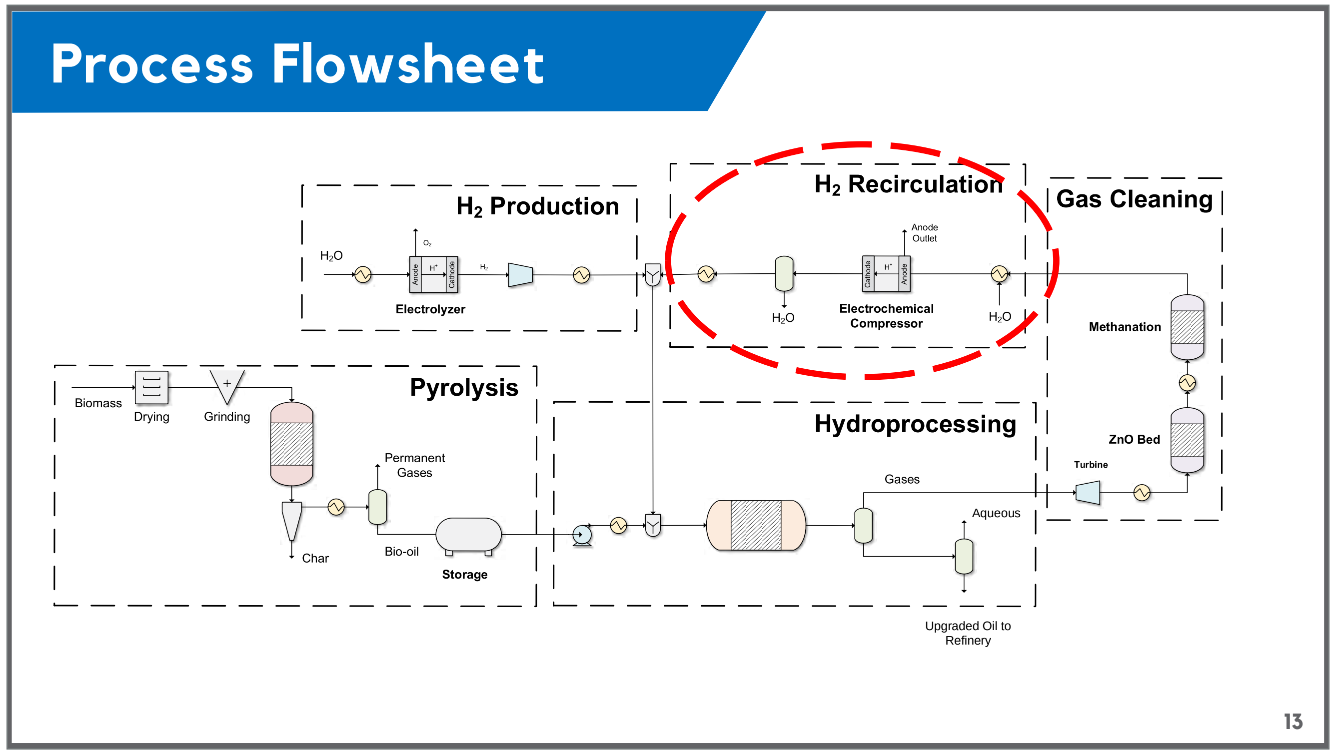
$$CO + 3H_2 \leftrightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$$

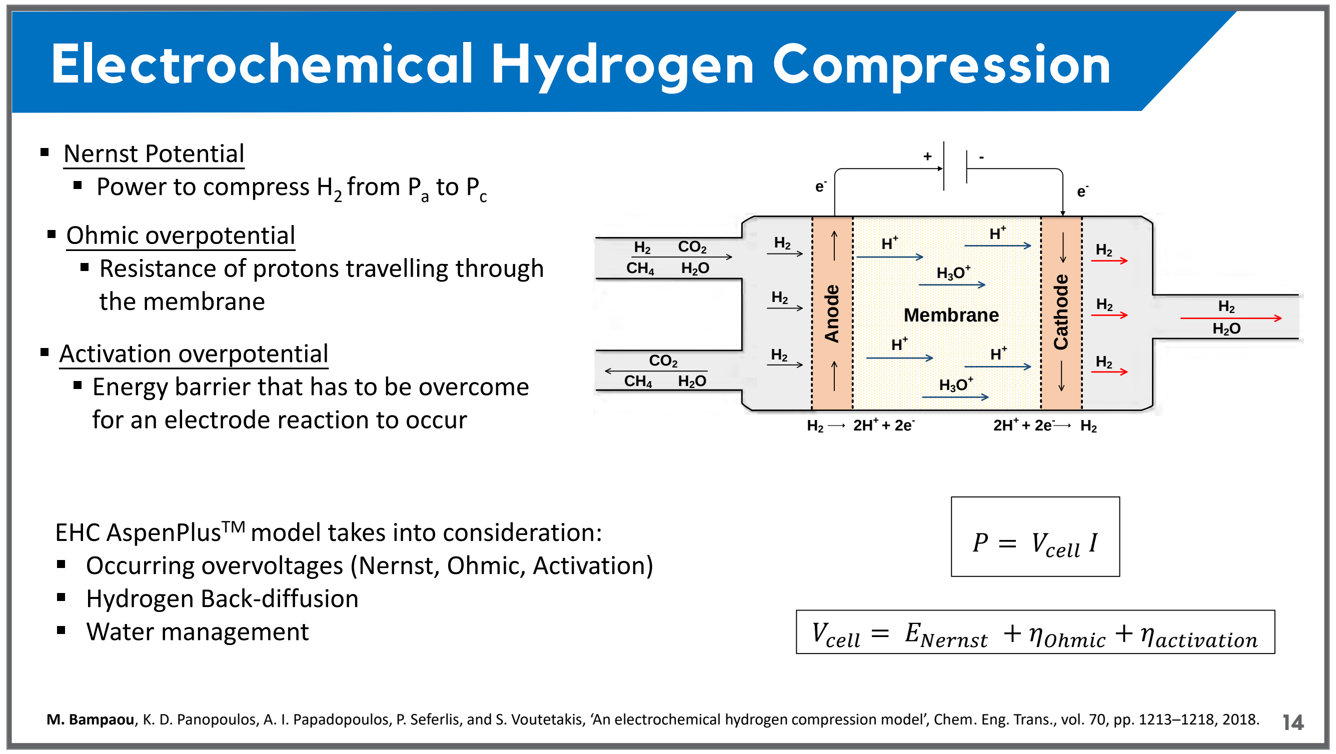
$$CO_2 + H_2 \leftrightarrow CO + H_2O$$



CERTH Experimental Unit



Process Flowsheet



Electrochemical Hydrogen Compression

- Nernst Potential
  - Power to compress H_2 from P_a to P_c
- Ohmic overpotential
  - Resistance of protons travelling through the membrane
- Activation overpotential
  - Energy barrier that has to be overcome for an electrode reaction to occur

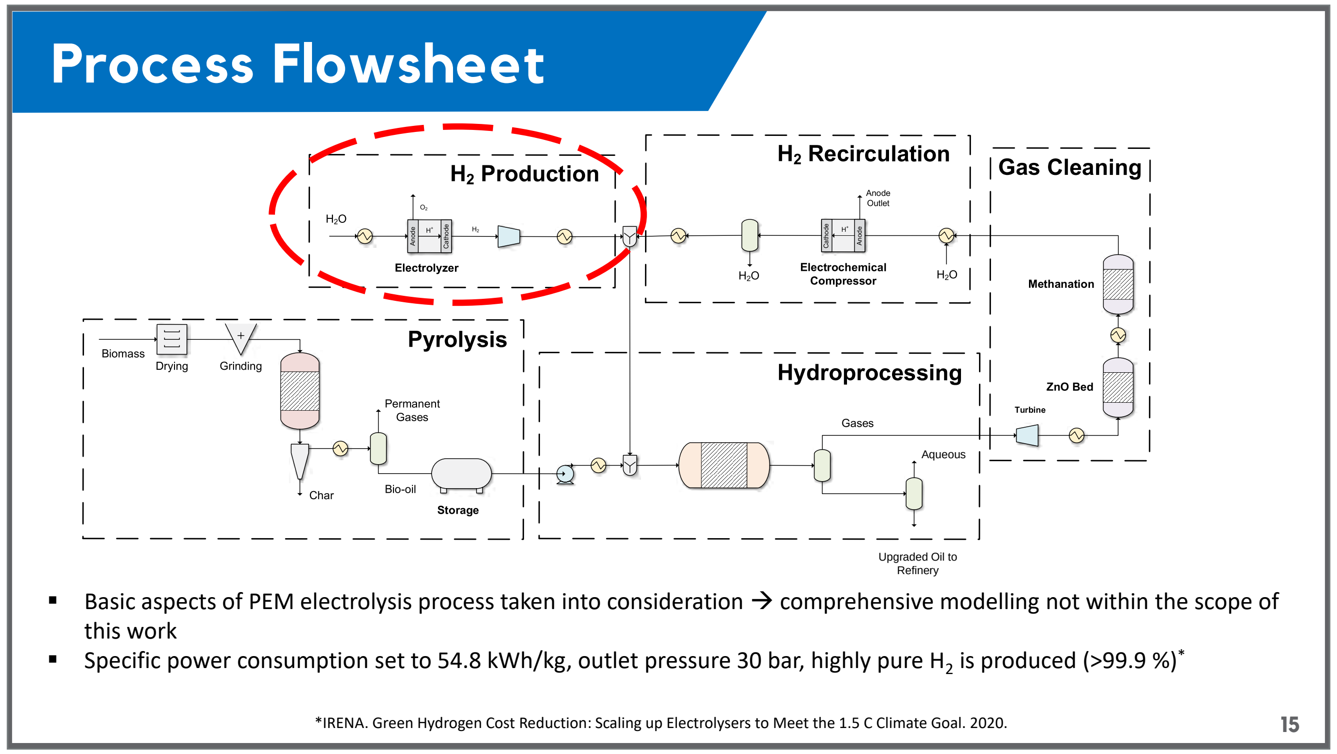
EHC AspenPlus^{TM} model takes into consideration:

- Occurring overvoltages (Nernst, Ohmic, Activation)
- Hydrogen Back-diffusion
- Water management

$$\boxed{P = V_{cell}\, I}$$

$$\boxed{V_{cell} = E_{Nernst} + \eta_{Ohmic} + \eta_{activation}}$$

M. Bampaou, K. D. Panopoulos, A. I. Papadopoulos, P. Seferlis, and S. Voutetakis, 'An electrochemical hydrogen compression model', Chem. Eng. Trans., vol. 70, pp. 1213–1218, 2018.



Process Flowsheet

- Basic aspects of PEM electrolysis process taken into consideration → comprehensive modelling not within the scope of this work
- Specific power consumption set to 54.8 kWh/kg, outlet pressure 30 bar, highly pure H_2 is produced (>99.9 %)*

*IRENA. Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.5 C Climate Goal. 2020.

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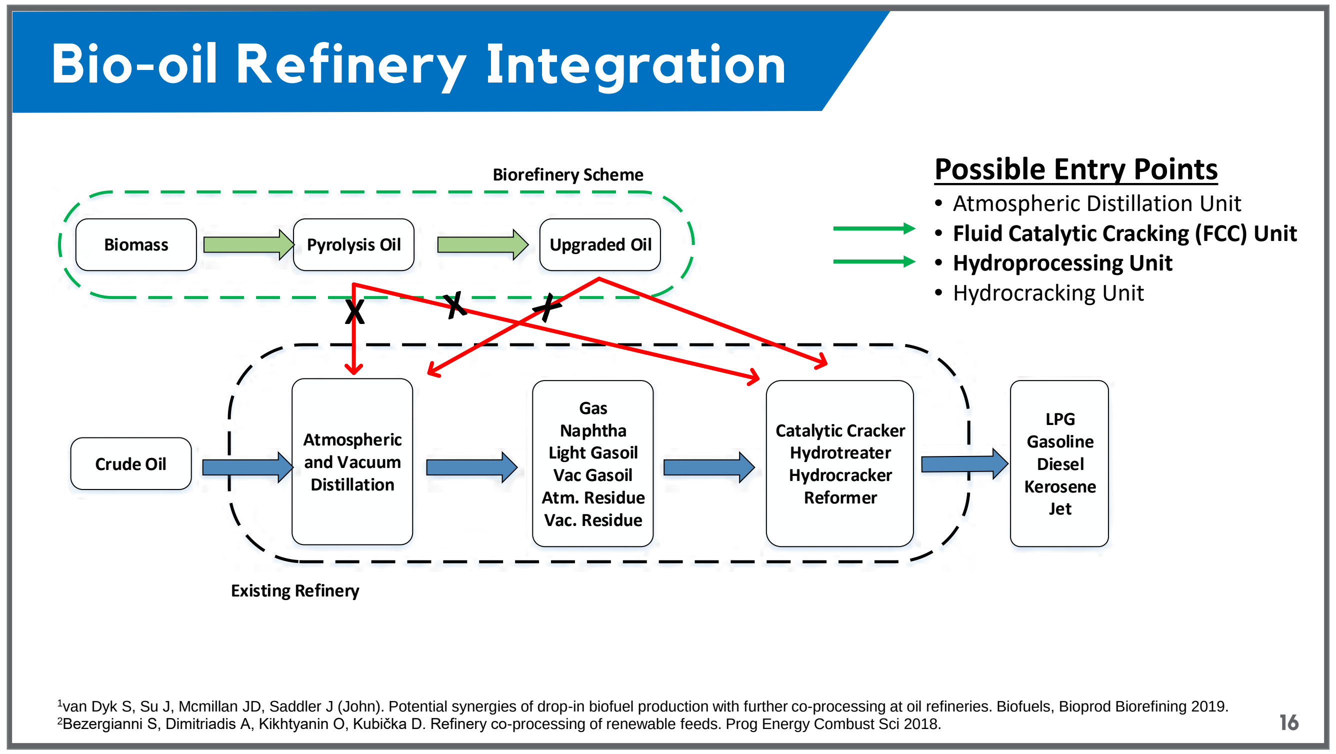

Bio-oil Refinery Integration

Biorefinery Scheme

Biomass → Pyrolysis Oil → Upgraded Oil

Crude Oil → Atmospheric and Vacuum Distillation → Gas Naphtha Light Gasoil Vac Gasoil Atm. Residue Vac. Residue → Catalytic Cracker Hydrotreater Hydrocracker Reformer → LPG Gasoline Diesel Kerosene Jet

Existing Refinery

Possible Entry Points

- Atmospheric Distillation Unit
- **Fluid Catalytic Cracking (FCC) Unit**
- **Hydroprocessing Unit**
- Hydrocracking Unit

[1]van Dyk S, Su J, Mcmillan JD, Saddler J (John). Potential synergies of drop-in biofuel production with further co-processing at oil refineries. Biofuels, Bioprod Biorefining 2019.
[2]Bezergianni S, Dimitriadis A, Kikhtyanin O, Kubička D. Refinery co-processing of renewable feeds. Prog Energy Combust Sci 2018.

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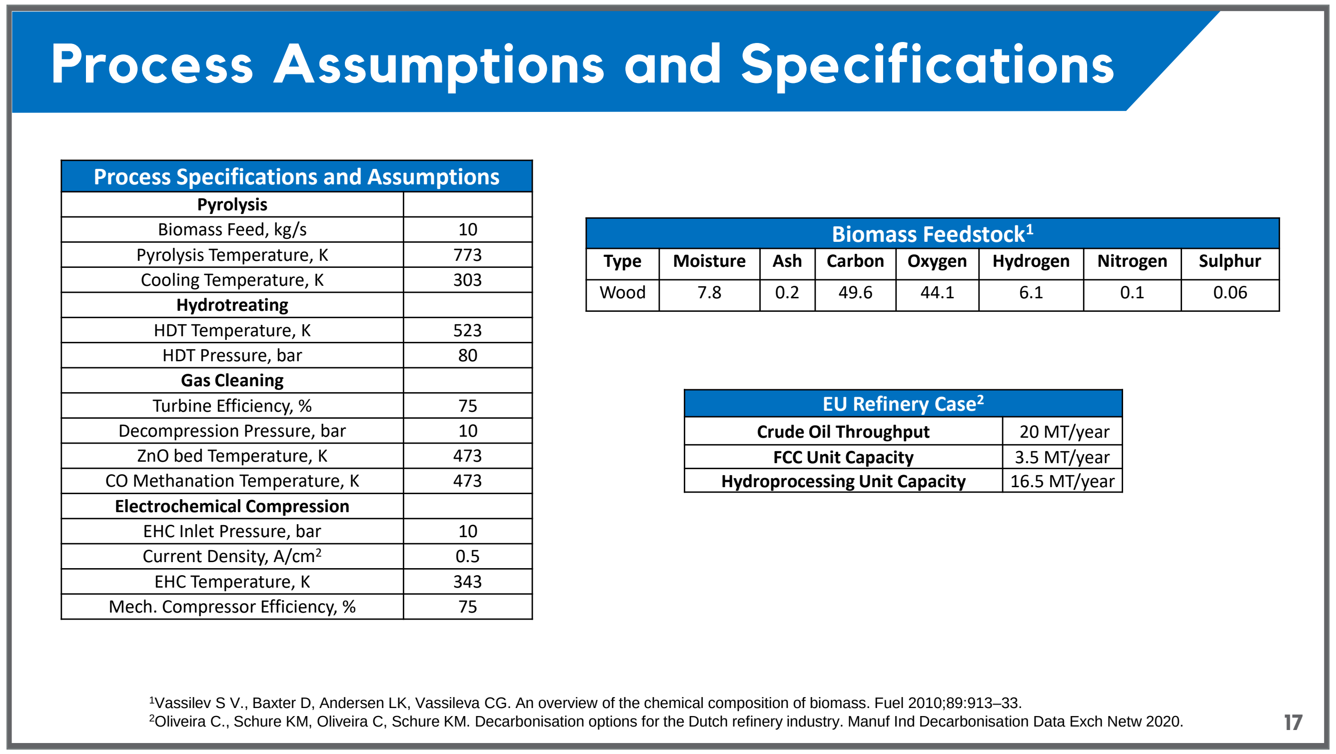

Process Assumptions and Specifications

Process Specifications and Assumptions	
Pyrolysis	
Biomass Feed, kg/s	10
Pyrolysis Temperature, K	773
Cooling Temperature, K	303
Hydrotreating	
HDT Temperature, K	523
HDT Pressure, bar	80
Gas Cleaning	
Turbine Efficiency, %	75
Decompression Pressure, bar	10
ZnO bed Temperature, K	473
CO Methanation Temperature, K	473
Electrochemical Compression	
EHC Inlet Pressure, bar	10
Current Density, A/cm^2	0.5
EHC Temperature, K	343
Mech. Compressor Efficiency, %	75

Biomass Feedstock[1]

Type	Moisture	Ash	Carbon	Oxygen	Hydrogen	Nitrogen	Sulphur
Wood	7.8	0.2	49.6	44.1	6.1	0.1	0.06

EU Refinery Case[2]	
Crude Oil Throughput	20 MT/year
FCC Unit Capacity	3.5 MT/year
Hydroprocessing Unit Capacity	16.5 MT/year

[1]Vassilev S V., Baxter D, Andersen LK, Vassileva CG. An overview of the chemical composition of biomass. Fuel 2010;89:913–33.
[2]Oliveira C., Schure KM, Oliveira C, Schure KM. Decarbonisation options for the Dutch refinery industry. Manuf Ind Decarbonisation Data Exch Netw 2020.

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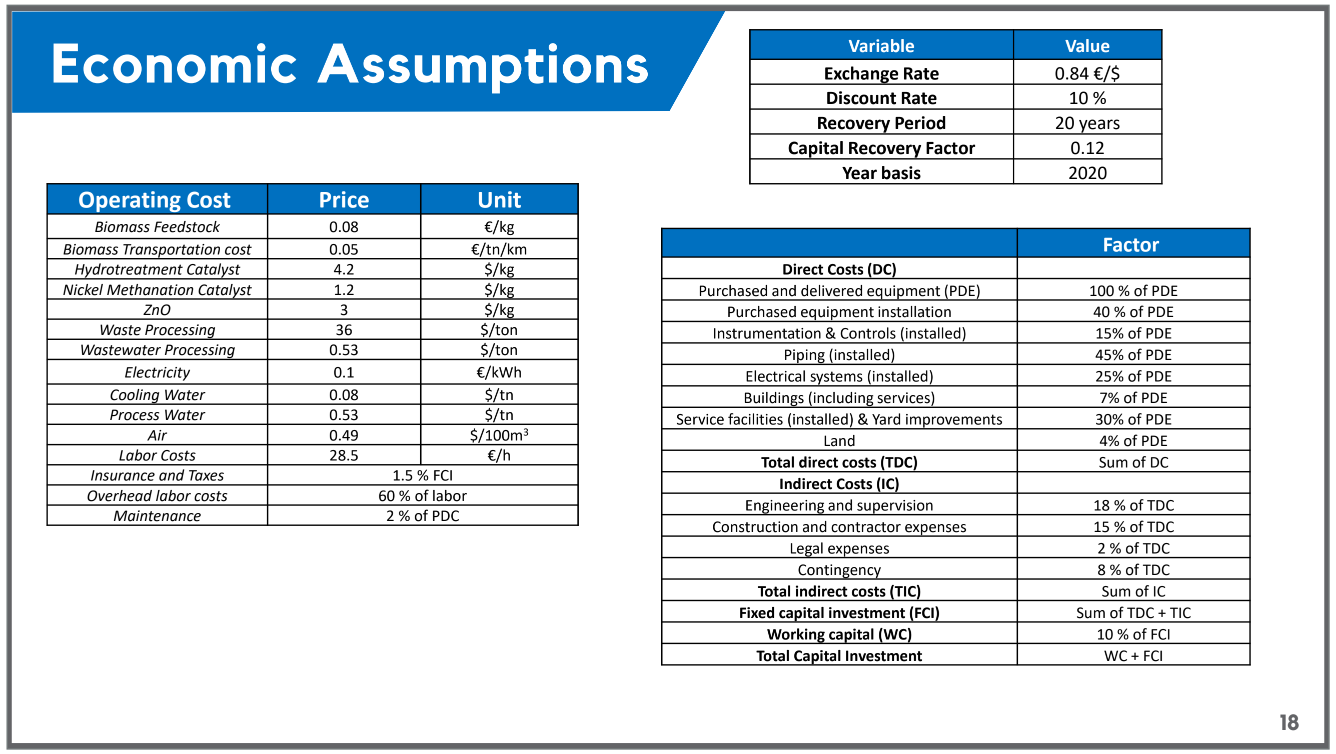

Economic Assumptions

Variable	Value
Exchange Rate	0.84 €/$
Discount Rate	10 %
Recovery Period	20 years
Capital Recovery Factor	0.12
Year basis	2020

Operating Cost	Price	Unit
Biomass Feedstock	0.08	€/kg
Biomass Transportation cost	0.05	€/tn/km
Hydrotreatment Catalyst	4.2	$/kg
Nickel Methanation Catalyst	1.2	$/kg
ZnO	3	$/kg
Waste Processing	36	$/ton
Wastewater Processing	0.53	$/ton
Electricity	0.1	€/kWh
Cooling Water	0.08	$/tn
Process Water	0.53	$/tn
Air	0.49	$/100m^3
Labor Costs	28.5	€/h
Insurance and Taxes	1.5 % FCI	
Overhead labor costs	60 % of labor	
Maintenance	2 % of PDC	

	Factor
Direct Costs (DC)	
Purchased and delivered equipment (PDE)	100 % of PDE
Purchased equipment installation	40 % of PDE
Instrumentation & Controls (installed)	15% of PDE
Piping (installed)	45% of PDE
Electrical systems (installed)	25% of PDE
Buildings (including services)	7% of PDE
Service facilities (installed) & Yard improvements	30% of PDE
Land	4% of PDE
Total direct costs (TDC)	Sum of DC
Indirect Costs (IC)	
Engineering and supervision	18 % of TDC
Construction and contractor expenses	15 % of TDC
Legal expenses	2 % of TDC
Contingency	8 % of TDC
Total indirect costs (TIC)	Sum of IC
Fixed capital investment (FCI)	Sum of TDC + TIC
Working capital (WC)	10 % of FCI
Total Capital Investment	WC + FCI

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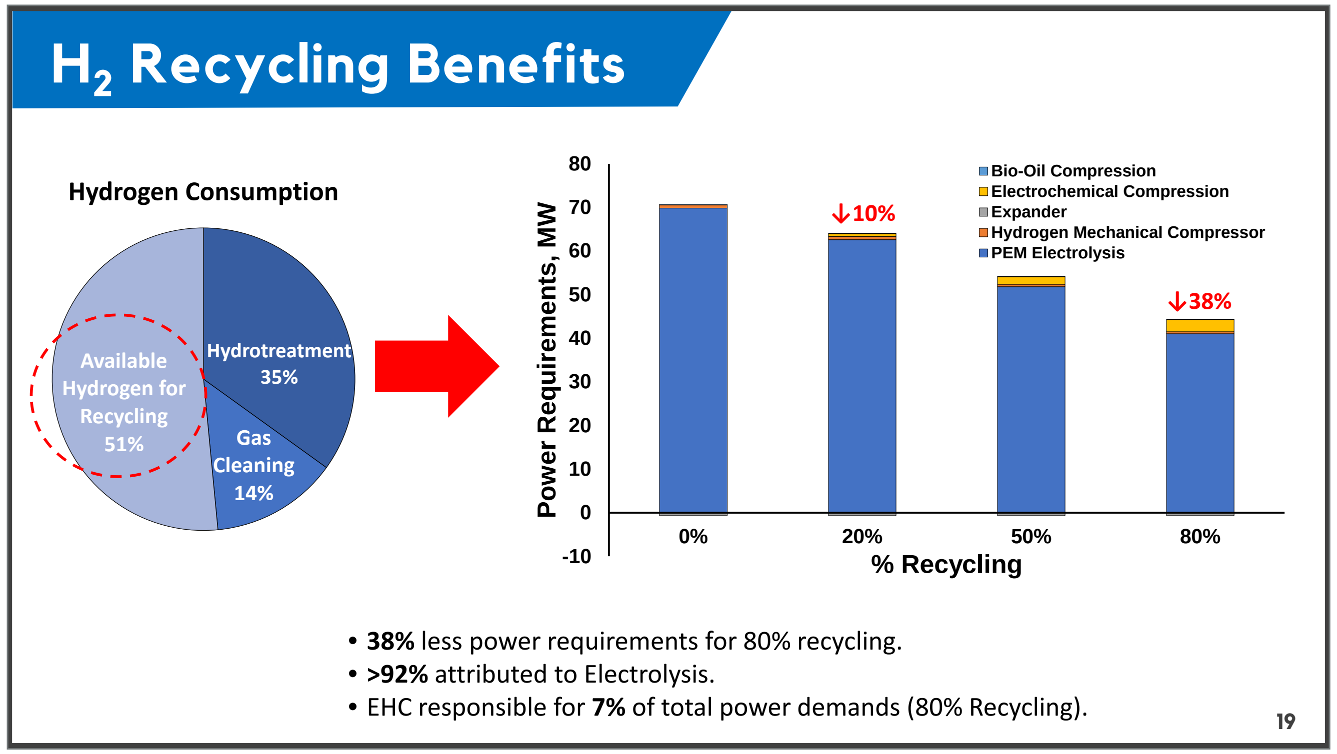
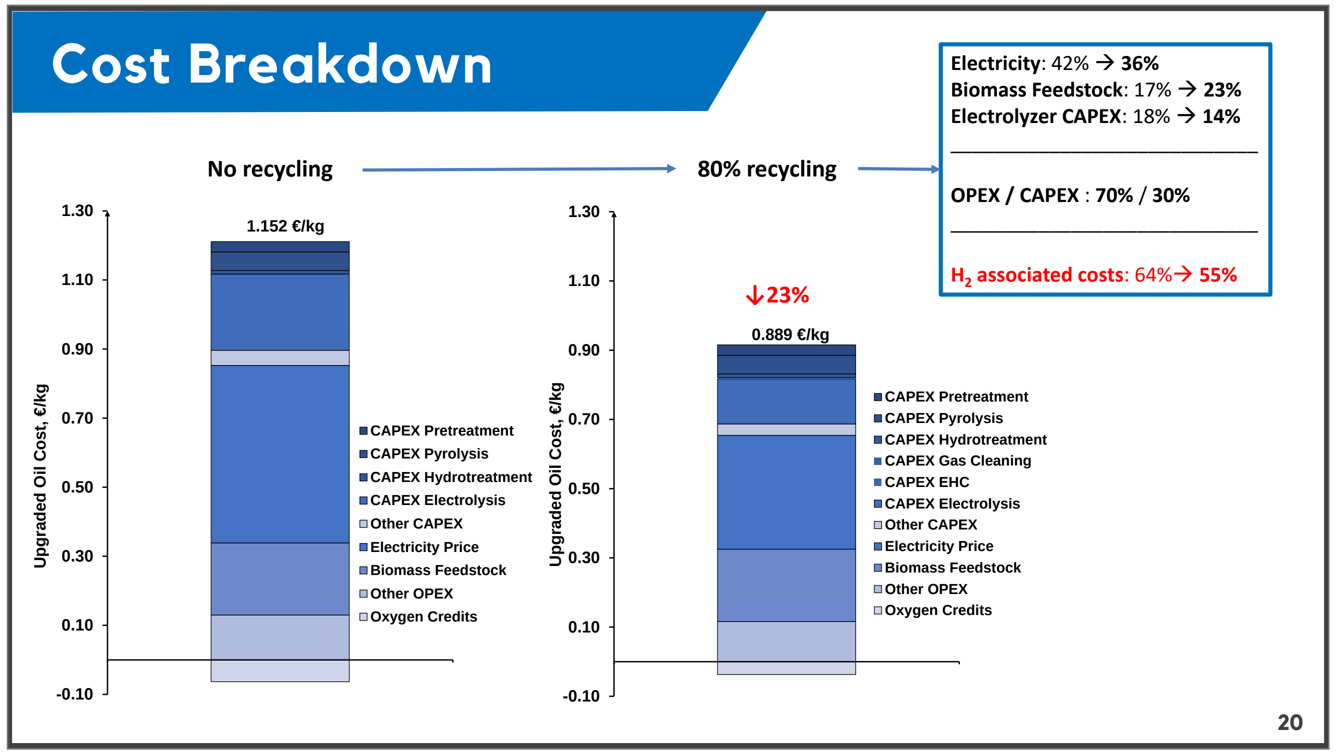


H_2 Recycling Benefits

- **38%** less power requirements for 80% recycling.
- **>92%** attributed to Electrolysis.
- EHC responsible for **7%** of total power demands (80% Recycling).

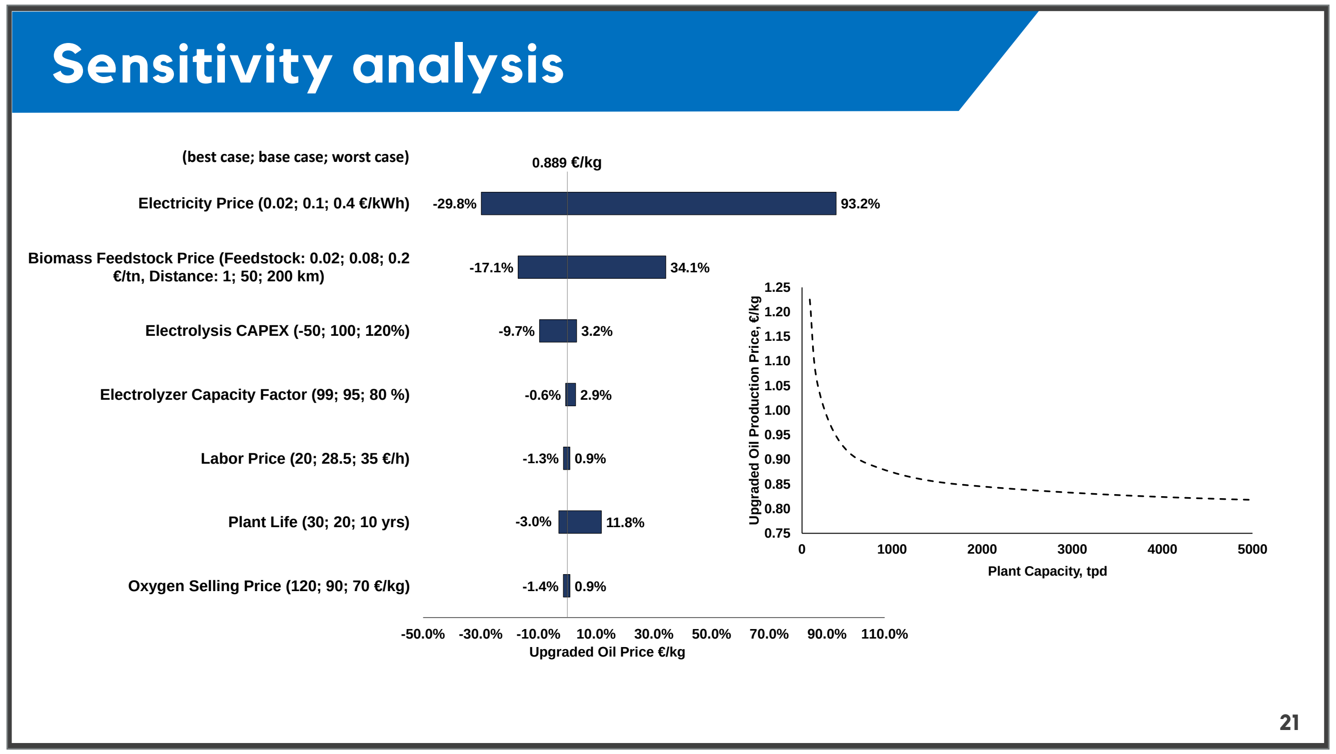


Cost Breakdown

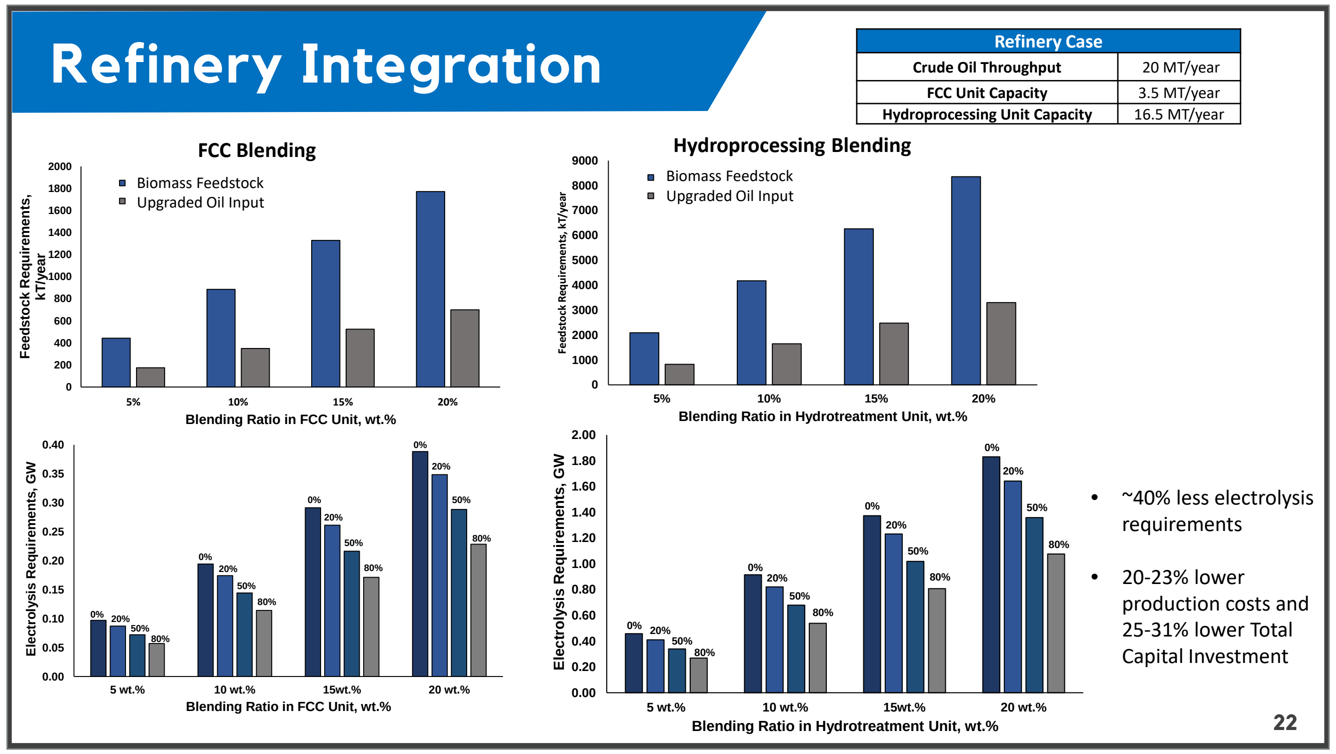
Electricity: 42% → **36%**
Biomass Feedstock: 17% → **23%**
Electrolyzer CAPEX: 18% → **14%**

OPEX / CAPEX : **70% / 30%**

H_2 associated costs: 64%→ **55%**



Sensitivity analysis



Refinery Integration

Refinery Case	
Crude Oil Throughput	20 MT/year
FCC Unit Capacity	3.5 MT/year
Hydroprocessing Unit Capacity	16.5 MT/year

- ~40% less electrolysis requirements
- 20-23% lower production costs and 25-31% lower Total Capital Investment

Conclusions

- The integration of bio-oils into refinery operations was investigated using flowsheet simulations and economic analysis tools.
- Hydrogen recycling using an electrochemical compressor has significant benefits to the overall system: 38% lower power requirements and 23% lower production costs.
- 70% of the costs associated to OPEX and 30% to CAPEX; H_2 production and management is responsible for 55-64% of the costs.
- The variable electricity and biomass feedstock costs can influence the total production costs (strategic placement); technology can benefit from the “economies of scale”.
- Progress in the hydrogen economy is necessary for the establishment of this technology.

Thank you for your attention

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CERTH CENTRE FOR RESEARCH & TECHNOLOGY HELLAS

CPERI Chemical Process and Energy Resources Institute

BRISK2 BIOFUELS RESEARCH INFRASTRUCTURE

Sebastian Dietrich, Technical University of Berlin/Deutsches Biomasseforschungszentrum

Fischer-Tropsch synthesis for biogas upgrading

Sebastian Dietrich, Marco Klemm, Selina Nieß
Technical University of Berlin
Marchstraße 23
10587 Berlin
E-mail: **sebastian.dietrich@dbfz.de**

Introduction

In a fossil-free future, it is very important to use available biogenic carbon sources as effectively as possible. During anaerobic digestion of biomass, a mixture of methane and carbon dioxide, biogas, is produced which is most often converted to electricity directly on-site. However, feeding biogas into the existing natural gas grid is advantageous, as it can then be stored for a demand-oriented conversion into electricity and/or heat. To generate a gas that can be fed into the grid, carbon dioxide is normally separated to produce almost pure methane. This biomethane, however, does not meet the German H-gas feed-in requirements yet, as the natural gas to be substituted contains certain amounts of gaseous C_2-C_4 hydrocarbons. In order to adjust the calorific value of the biomethane to equal that of natural gas, usually fossil liquid petroleum gas (LPG) is added.

Biogas upgrading by synthesis

Another way to increase the calorific value of biogas is the Fischer-Tropsch synthesis of light hydrocarbons using the carbon dioxide and added hydrogen. Depending on the reaction and possible intermediate steps, either only carbon dioxide or possibly also the methane from the biogas is used to produce gaseous alkenes and alkanes (C_2-C_4). The aim is to produce a biogenic substitute natural gas (SNG), a mixture of methane and a certain proportion of higher hydrocarbons, which in its composition and properties (with focus on calorific value) is similar to natural gas and can be fed into the natural gas network without further upgrading.

Methodology and results

In the course of the work, both the synthesis with CO_2 and CO were investigated in a test rig using a fixed-bed reactor. In the latter case, an intermediate step for the conversion of CO_2 into CO (e.g. dry reforming or co-electrolysis) would be necessary. As the performance of the synthesis is mainly dependent on the suitability of the catalyst, different catalysts were investigated for both syntheses at different temperatures, pressures and space velocities. The synthesis with CO achieved better experimental results as the synthesis with CO_2. Selectivities of up to 27 vol.- % to C_2-C_4 hydrocarbons were reached, but a visible decrease of catalyst activity over time has to be determined. A flow sheet simulation is being developed to investigate various possible designs of a biogas upgrading plant using different conversions steps to produce hydrocarbons while taking the impact of the omitted CHP plant into account.

Conclusion

The synthesis of light hydrocarbons to produce H-gas was experimentally demonstrated for a framework defined by the biogas upgrading application. Stable but low yields of C_2-C_4 hydrocarbons were achieved and could be increased to 16 vol.- % but with a visible catalyst deactivation. The whole provision chain will be analysed in flowsheet simulation implementing the experimental results in order to evaluate different possible synthesis routes.

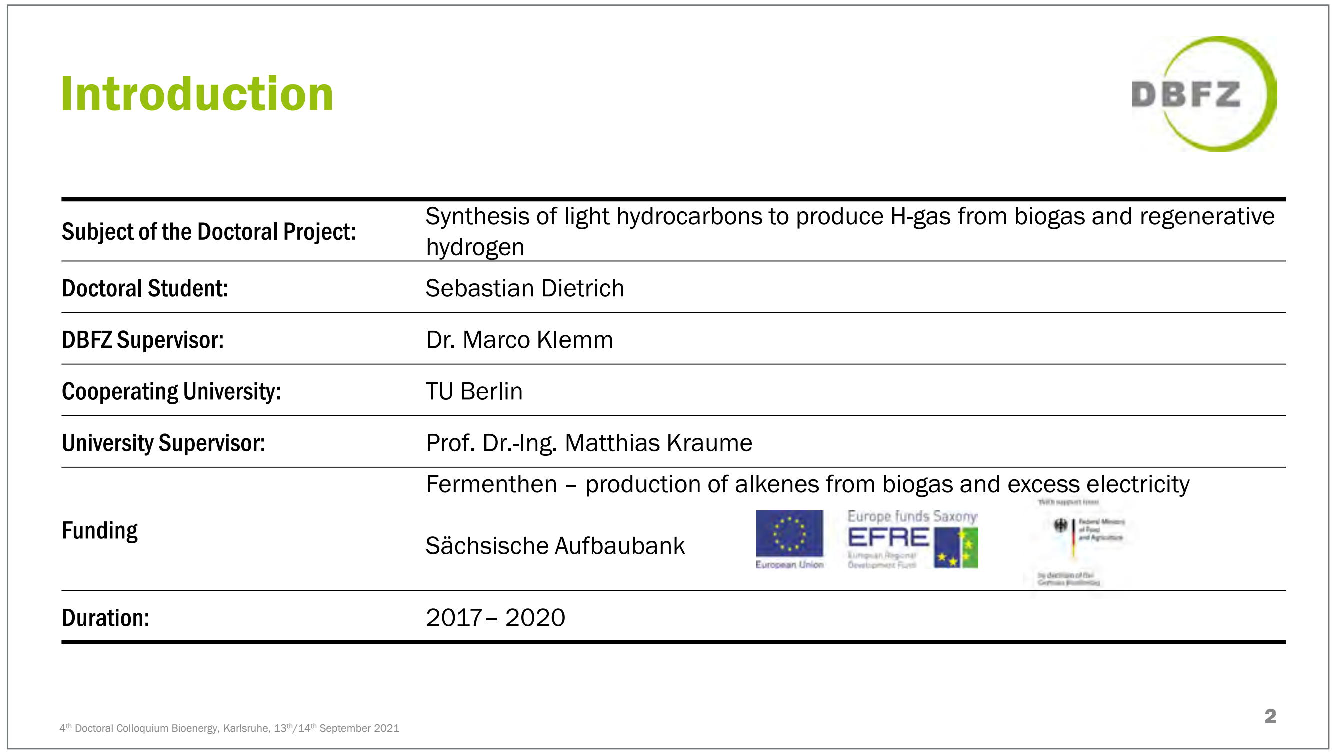
Deutsches Biomasseforschungszentrum
gemeinnützige GmbH

Fischer-Tropsch synthesis for biogas upgrading

Sebastian Dietrich

Selina Nieß, Marco Klemm

4th Doctoral Colloquium Bioenergy, Karlsruhe, 13th/14th September 2021



Introduction

Subject of the Doctoral Project:	Synthesis of light hydrocarbons to produce H-gas from biogas and regenerative hydrogen
Doctoral Student:	Sebastian Dietrich
DBFZ Supervisor:	Dr. Marco Klemm
Cooperating University:	TU Berlin
University Supervisor:	Prof. Dr.-Ing. Matthias Kraume
Funding	Fermenthen – production of alkenes from biogas and excess electricity Sächsische Aufbaubank
Duration:	2017– 2020

4th Doctoral Colloquium Bioenergy, Karlsruhe, 13th/14th September 2021

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Agenda

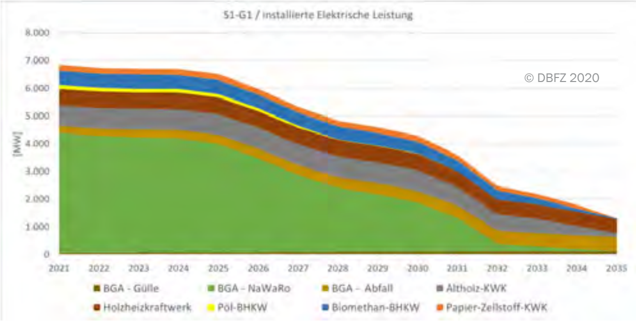
- Motivation and objective
- Methodology
- Results
- Conclusion and outlook

Motivation and objective

Motivation and objective

Background

- EEG 2017 - Expiring fixed tariff for electricity generated by biogas plants through direct electricity generation
- Alternative: Processing and biomethane injection into the existing natural gas grid



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- German feed-in requirements call for certain gas properties
  → Conditioning of biomethane necessary

Motivation and objective

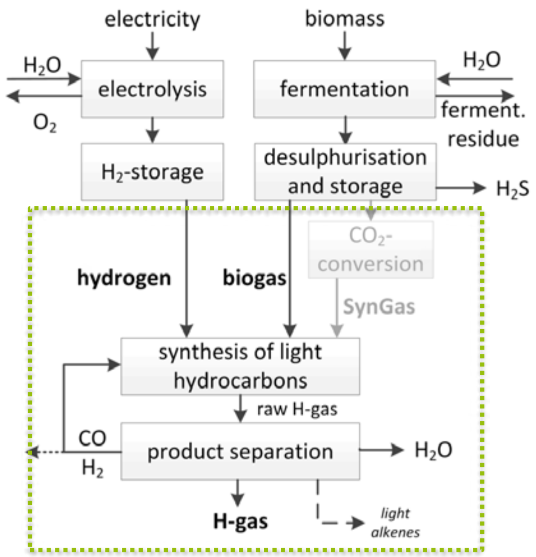
Objective and procedure

Objective:

- Increase calorific value through synthesis of light hydrocarbons (C_2-C_4)
- Reach feed-in quality without the admixture of fossil LPG

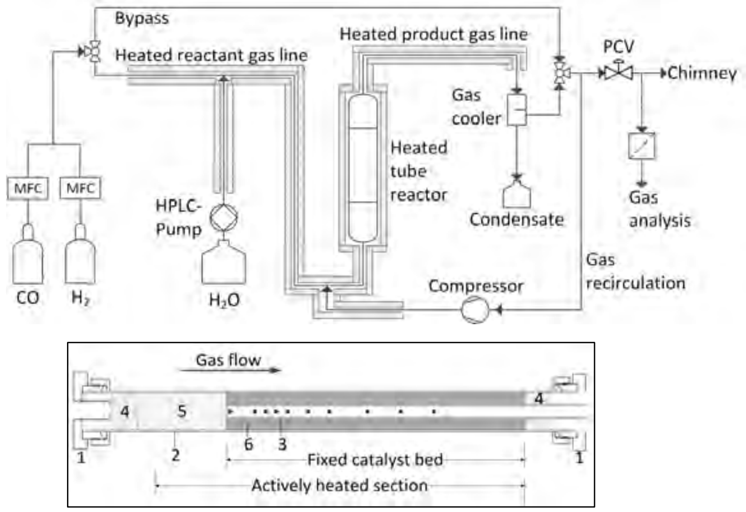
Work stages:

- Experimental studies
- Process simulation (Aspen Plus)
- Analysis of the production costs



Methodology

Methodology
experimental rig



- Tube reactor (22x2 mm, 400 mm length) heated by tube furnace
- Fully automated for unmanned long term experiments
- operating pressure up to 9 bar(a)
- Gasanalysis by GC-TCD

Source: Dietrich, S., Nieß, S., Rönsch, S., & Kraume, M. (2020). Synthesis of Light Hydrocarbons from Biogas and Hydrogen: Investigation of a Fe-Mn-K/MgO Catalyst. Chemical Engineering & Technology, 43(8), 1547-1553.

Methodology
Preliminary tests for synthesis with CO_2

- Fe/MgO- and Fe-Mn-K/MgO-catalyst
- low conversion rates (X_{CO_2} = 1.1 – 40.8 %)
- mainly reverse water gas shift reaction (S_{CO} = 14 – 100 %) and methanation (S_{CH_4} = 0 – 41 %)
- light hydrocarbons (C_2-C_4) below detection limit

→ synthesis with CO and H_2
conversion from CO_2 to CO necessary

Methodology
Catalyst for synthesis with CO

- Fe-Mn-K/MgO catalyst (11.5 wt % Fe, 10.2 wt % Mn, 1.1 wt % K)
- per incipient wetness impregnation
- dried for 6 h at 110 °C
- calcinated for 4h at 600 °C with air
- BET surface (N_2-adsorption)
  - dried: 107 $m^2 g^{-1}$
  - calcinated: 64 $m^2 g^{-1}$
- activation with H_2, ~18 h at 400 °C

Methodology

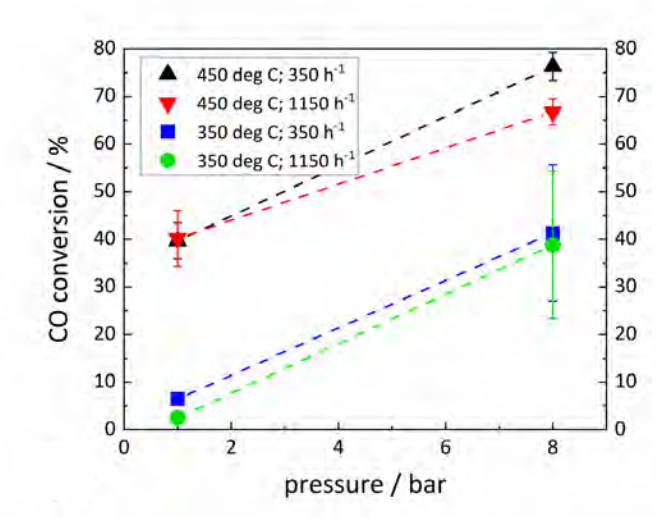
experimental plan for synthesis with CO

run	method	pressure bar(a)	temperature °C	GHSV h^{-1}	Steam content vol. %	Catalyst preparation
1	Parameter screening	1; 4,5; 8	350; 400; 450	350; 750; 1150	20 %	Dried
2	Long-term (90 h)	8	450	350	20 %	Dried
3	Long-term (27 h)	8	450	350	0 %	Dried

Results

Results

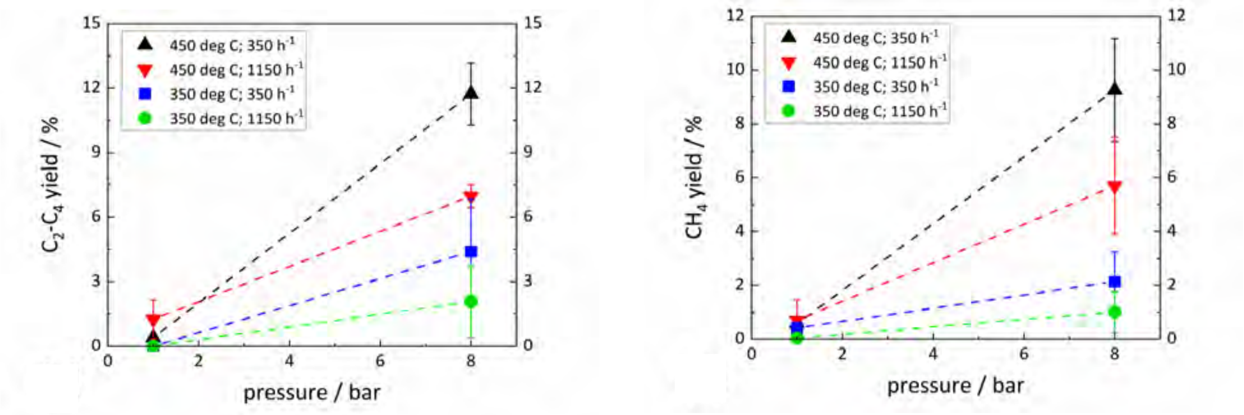
Parameter screening I



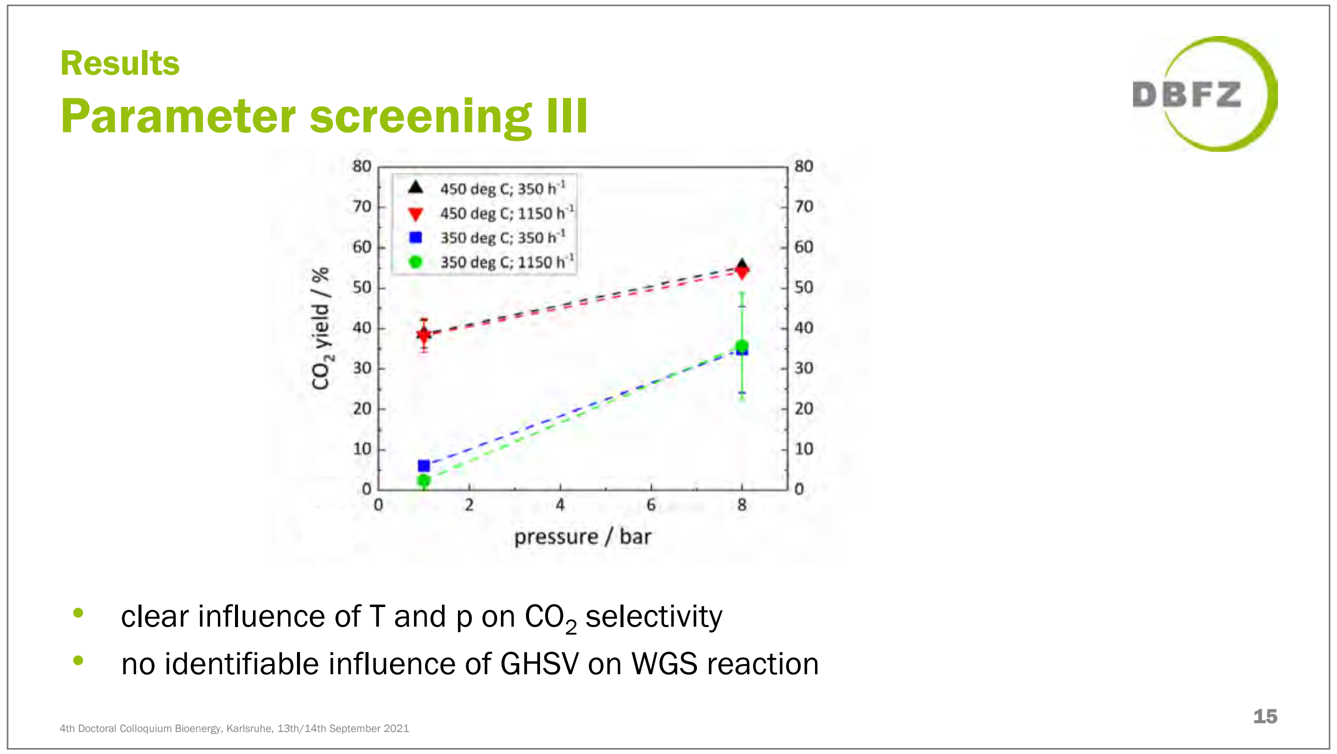
- CO conversion mainly determined by temperature and pressure
- Clear influence of space velocity on conversion rate only at p_{max} and T_{max}

Results

Parameter screening II



- hydrocarbon yield increases with rising pressure and temperature
- formation of hydrocarbons preferably at low GHSV



Results

Parameter screening III

- clear influence of T and p on CO_2 selectivity
- no identifiable influence of GHSV on WGS reaction

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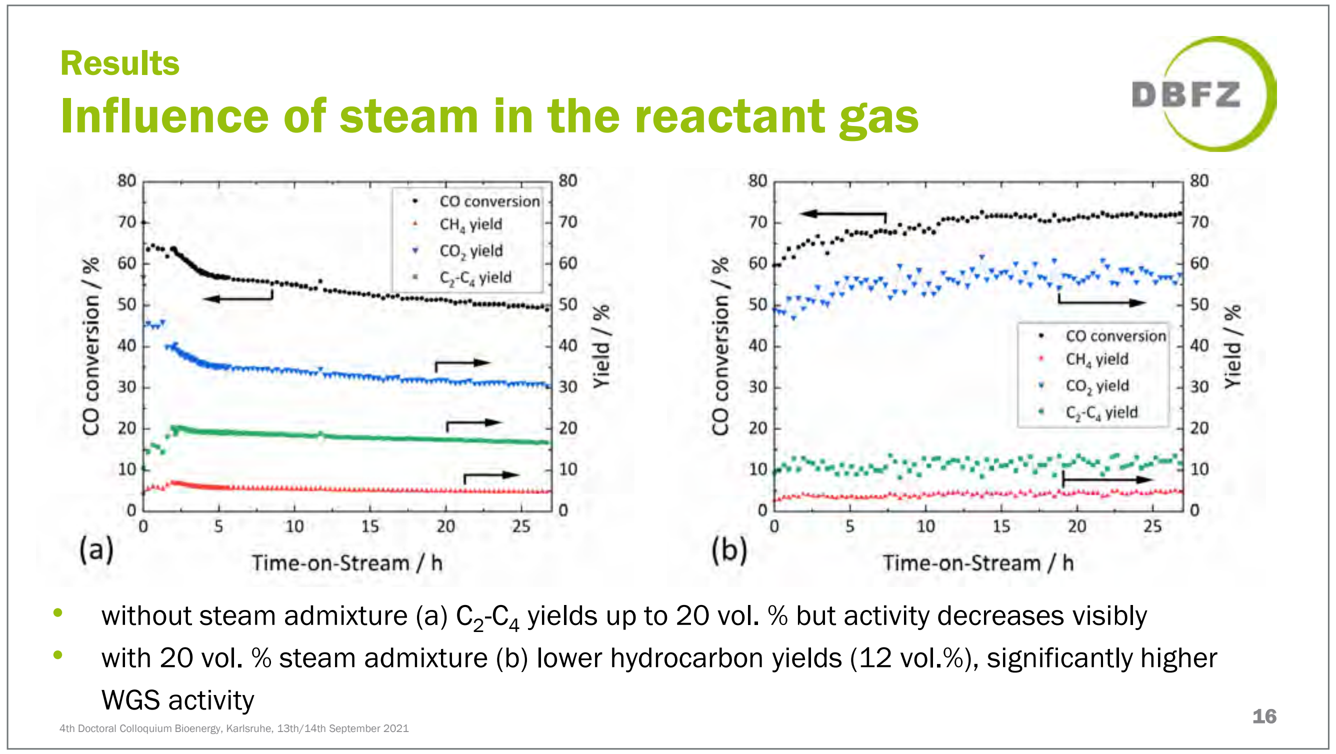

Results

Influence of steam in the reactant gas

- without steam admixture (a) C_2-C_4 yields up to 20 vol. % but activity decreases visibly
- with 20 vol. % steam admixture (b) lower hydrocarbon yields (12 vol.%), significantly higher WGS activity

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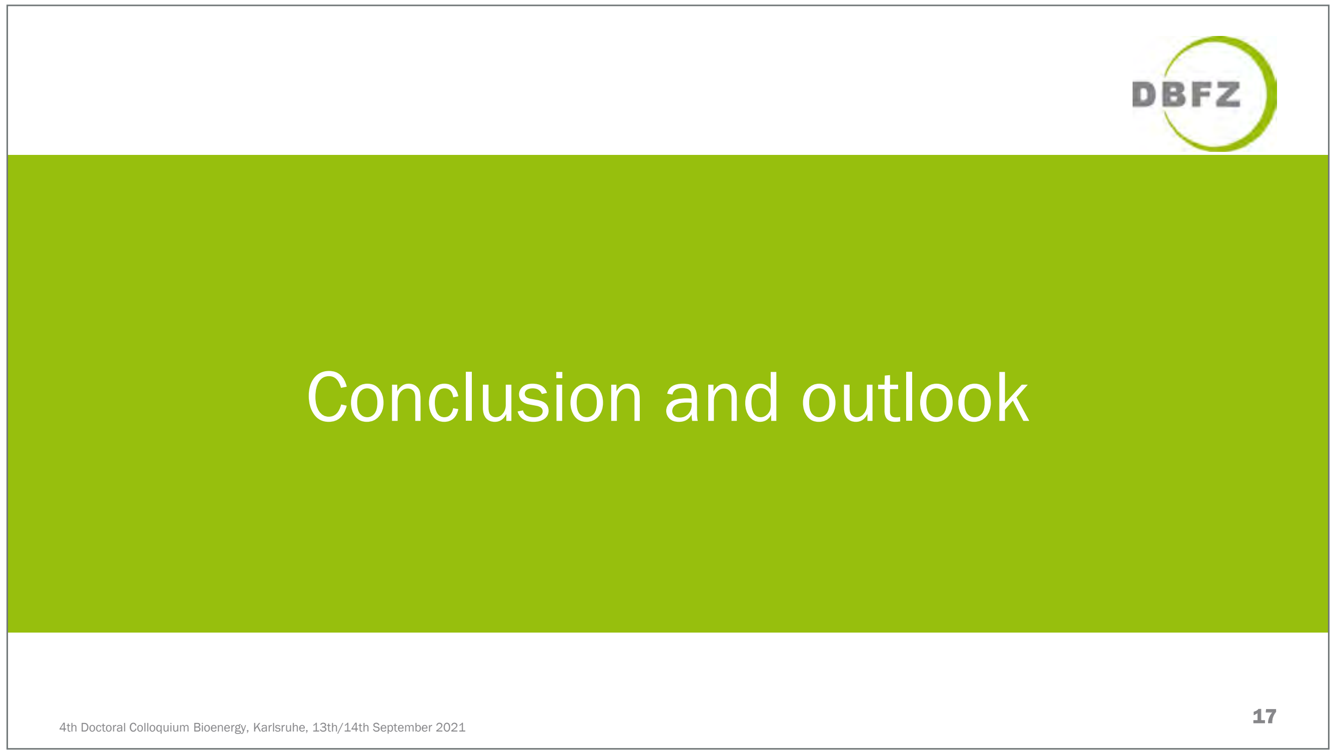

Conclusion and outlook

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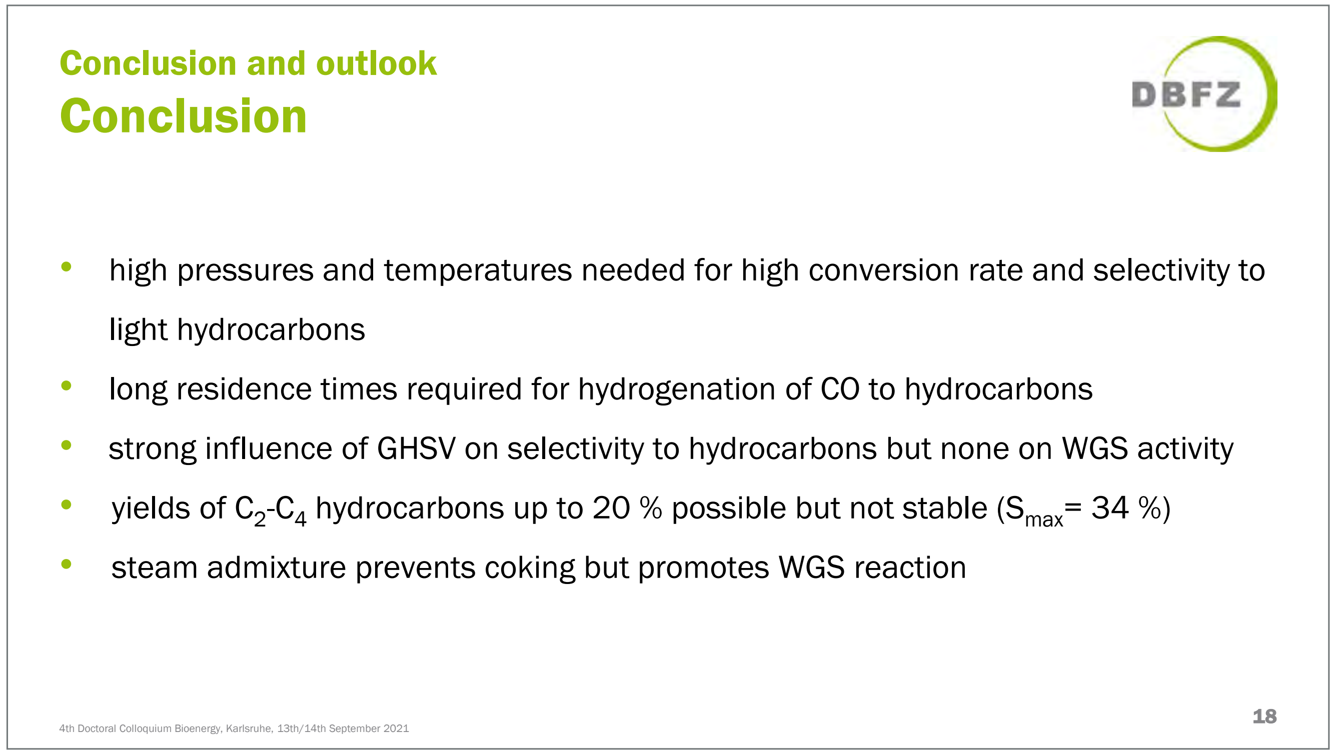

Conclusion and outlook

Conclusion

- high pressures and temperatures needed for high conversion rate and selectivity to light hydrocarbons
- long residence times required for hydrogenation of CO to hydrocarbons
- strong influence of GHSV on selectivity to hydrocarbons but none on WGS activity
- yields of C_2-C_4 hydrocarbons up to 20 % possible but not stable (S_{max}= 34 %)
- steam admixture prevents coking but promotes WGS reaction

4th Doctoral Colloquium Bioenergy, Karlsruhe, 13th/14th September 2021

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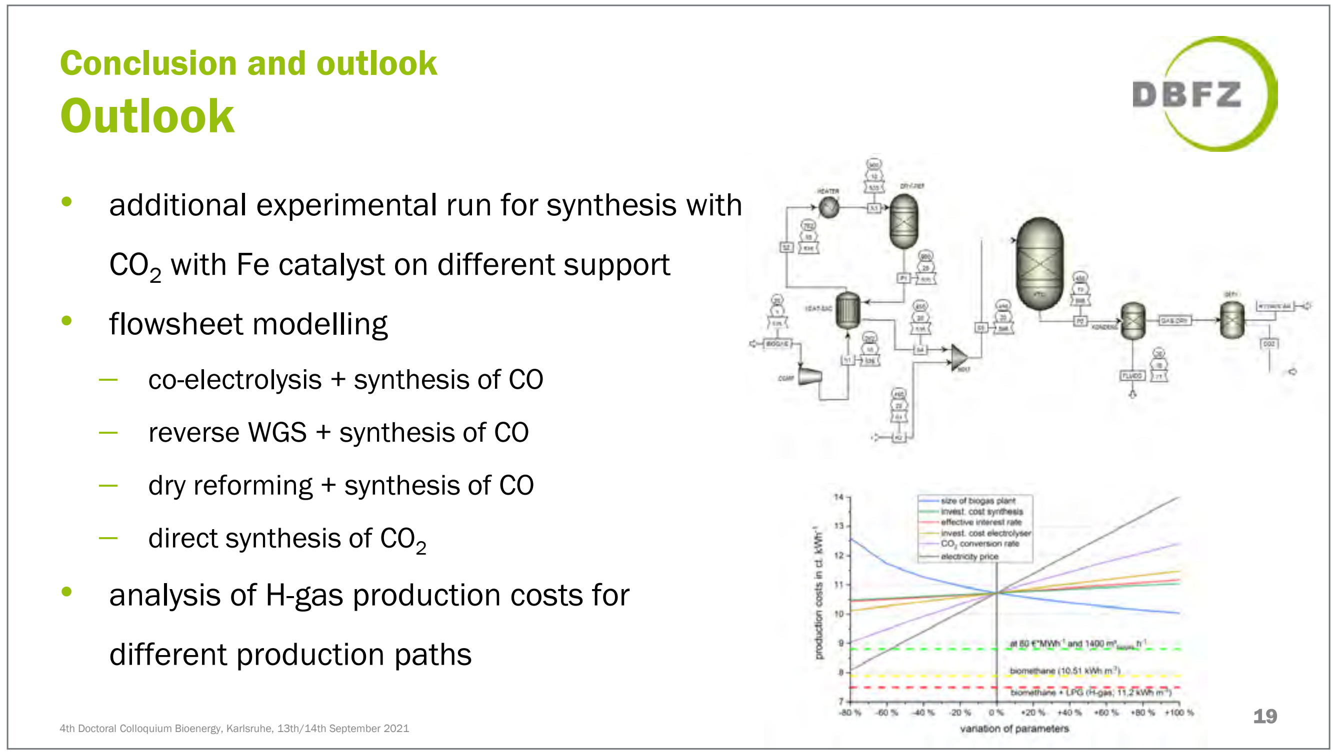

Conclusion and outlook

Outlook

- additional experimental run for synthesis with CO_2 with Fe catalyst on different support
- flowsheet modelling
  - co-electrolysis + synthesis of CO
  - reverse WGS + synthesis of CO
  - dry reforming + synthesis of CO
  - direct synthesis of CO_2
- analysis of H-gas production costs for different production paths

4th Doctoral Colloquium Bioenergy, Karlsruhe, 13th/14th September 2021

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Deutsches Biomasseforschungszentrum
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Smart Bioenergy – Innovations for a sustainable future

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Maximilian Wörner, Karlsruhe Institute of Technology (KIT)

Investigations on the influence of sulfur-containing salts on HTL of black liquor by using model

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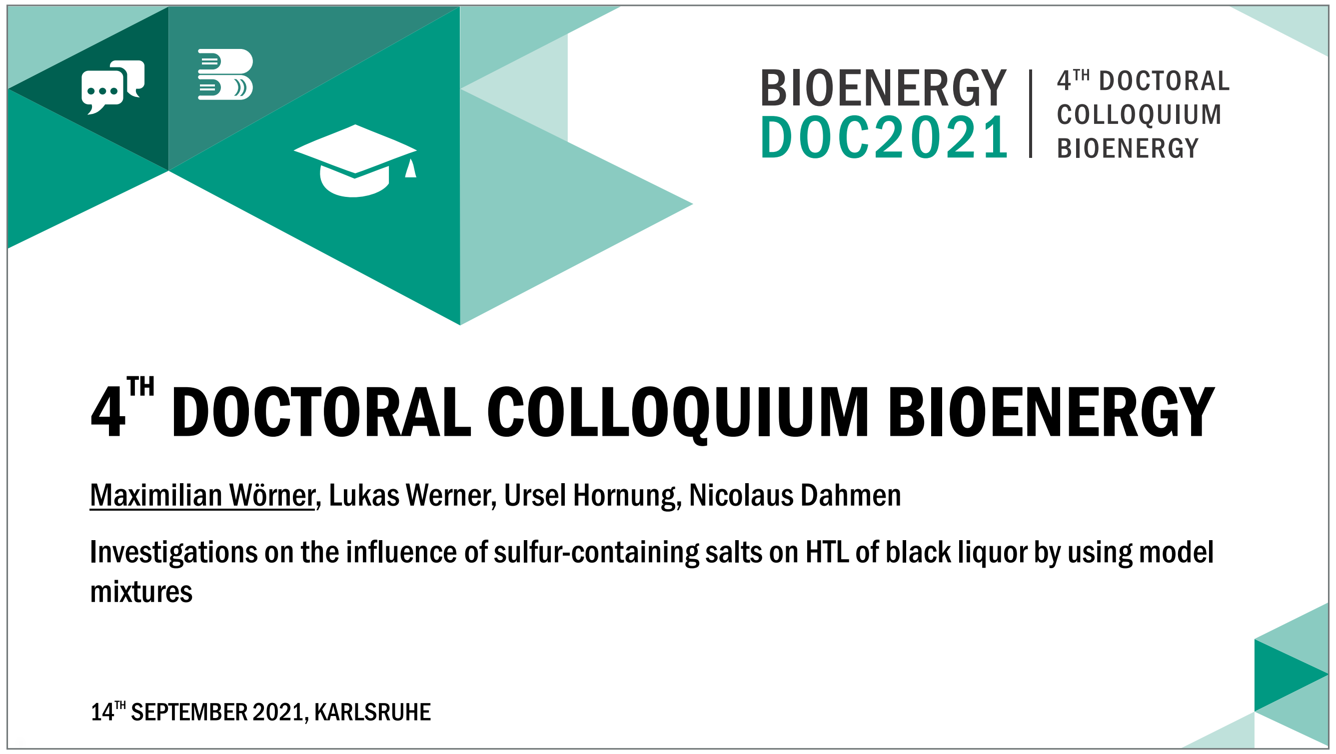
Hydrothermal liquefaction (HTL) is a thermochemical process to convert organic matter into biocrude for fuel applications or the production of useful chemical compounds. HTL is especially useful for wet biomass because it avoids drying prior to the process. One possible feedstock is lignin, which is produced in large quantities in the pulp & paper industry as a by-product for instance in the Kraft process. It is dissolved in an alkaline solution called black liquor. Desired products in HTL of lignin, besides biocrude, are aromatic compounds, which today are produced via fossil resources. Up to now, most research was performed with extracted and dried solid lignin. The EU project "BL2F" (Black Liquor to Fuels) explores the approach to liquefy the lignin directly in the black liquor via HTL. This eliminates the extracting and drying step to separate the lignin from the black liquor and also chemistry of decomposition may be different. In this study, the liquefaction of black liquor is investigated and compared with data from the HTL of dried lignin. The challenge is to study the influence of the pulping chemicals in form of salts one the hydrothermal depolymerisation of lignin. Of particular interest are salts containing sulfur, such as sulfides. Besides influencing the ongoing depolymerisation of lignin, the distribution of sulfur in the different product phases plays an important role for the applicability of such a process. For the required catalytic upgrading process steps, it is very helpful to know whether and in what form sulfur compounds occur.

In order to verify the feasibility of direct HTL of black liquor, we performed parameter studies in batch experiments using micro autoclaves. The product phases were separated and analyzed using different analytical methods. Our study shows that the typical depolymerisation products of lignin are found dependent on temperatures and residence times. In addition, dimethyl sulfide is found in significant concentration in the gas phase. This indicates that thiols are formed during the process, but continue to react immediately due to their high reactivity. For a deeper insight into these reactions, we prepared a model solution containing the lignin extracted from black liquor and the most important pulping salts. We used analytical data from the feedstock characterization of black liquor to prepare a representing salt concentration. The experiments with the model black liquor, so far, show that the typical reaction products after HTL are formed. Therefore, the model black liquor can be used to investigate the influence of the individual salts on HTL of lignin.



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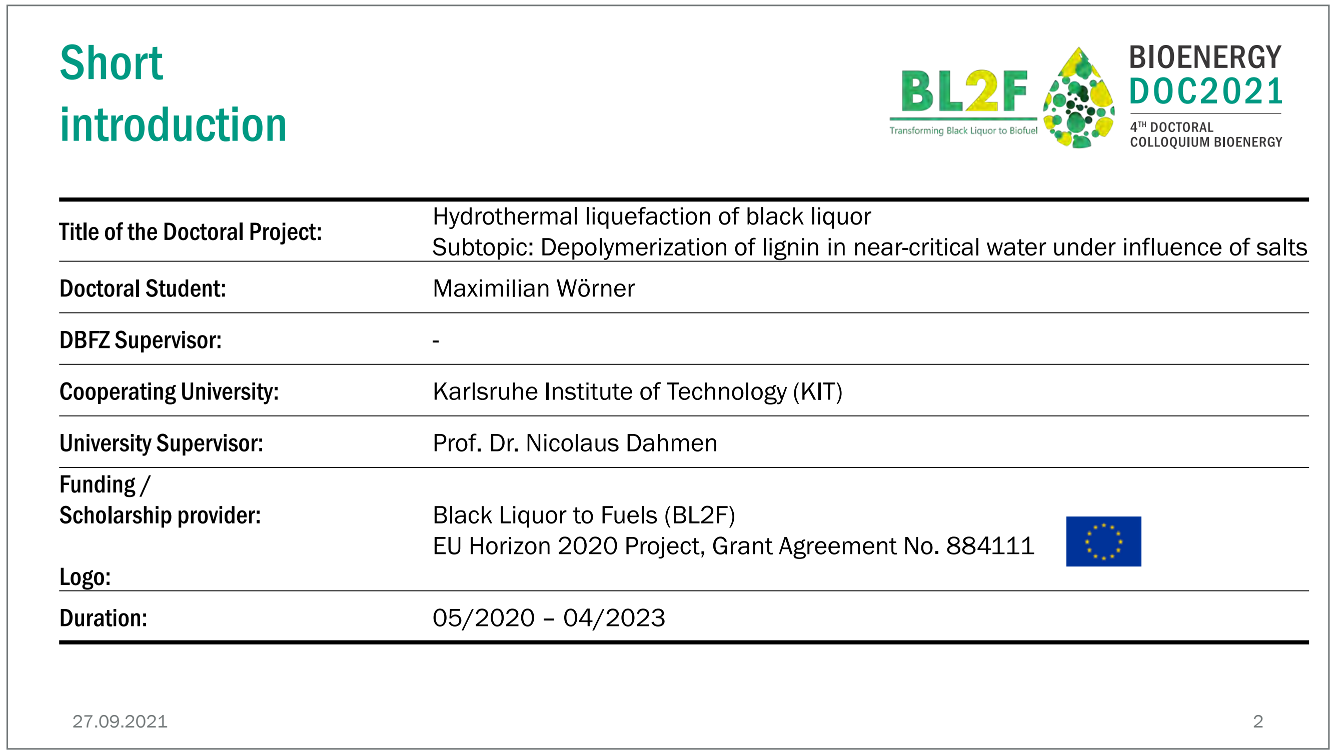
4TH DOCTORAL COLLOQUIUM BIOENERGY

Maximilian Wörner, Lukas Werner, Ursel Hornung, Nicolaus Dahmen

Investigations on the influence of sulfur-containing salts on HTL of black liquor by using model mixtures

14TH SEPTEMBER 2021, KARLSRUHE



Short introduction

BL2F Transforming Black Liquor to Biofuel

BIOENERGY DOC2021 4TH DOCTORAL COLLOQUIUM BIOENERGY

Title of the Doctoral Project:	Hydrothermal liquefaction of black liquor Subtopic: Depolymerization of lignin in near-critical water under influence of salts
Doctoral Student:	Maximilian Wörner
DBFZ Supervisor:	-
Cooperating University:	Karlsruhe Institute of Technology (KIT)
University Supervisor:	Prof. Dr. Nicolaus Dahmen
Funding / Scholarship provider:	Black Liquor to Fuels (BL2F) EU Horizon 2020 Project, Grant Agreement No. 884111
Logo:	
Duration:	05/2020 – 04/2023

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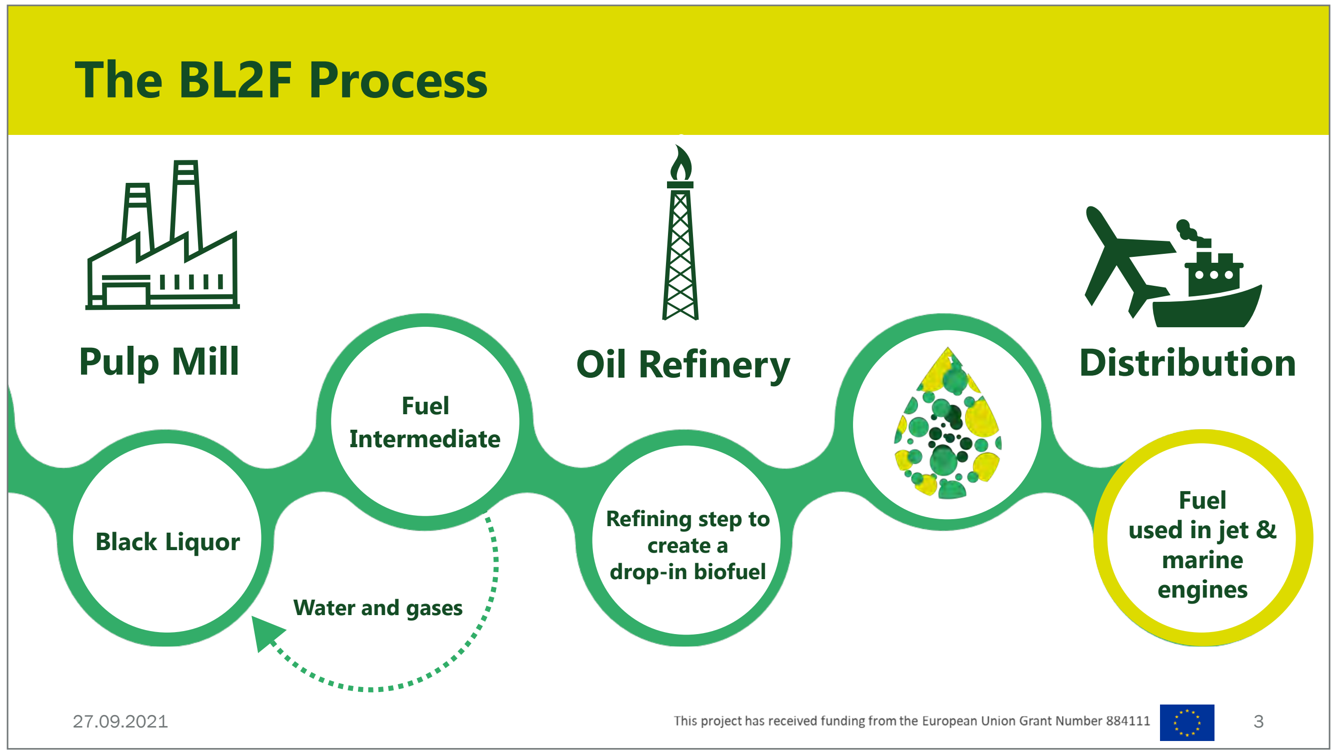


The BL2F Process

Pulp Mill

Oil Refinery

Distribution

Fuel Intermediate

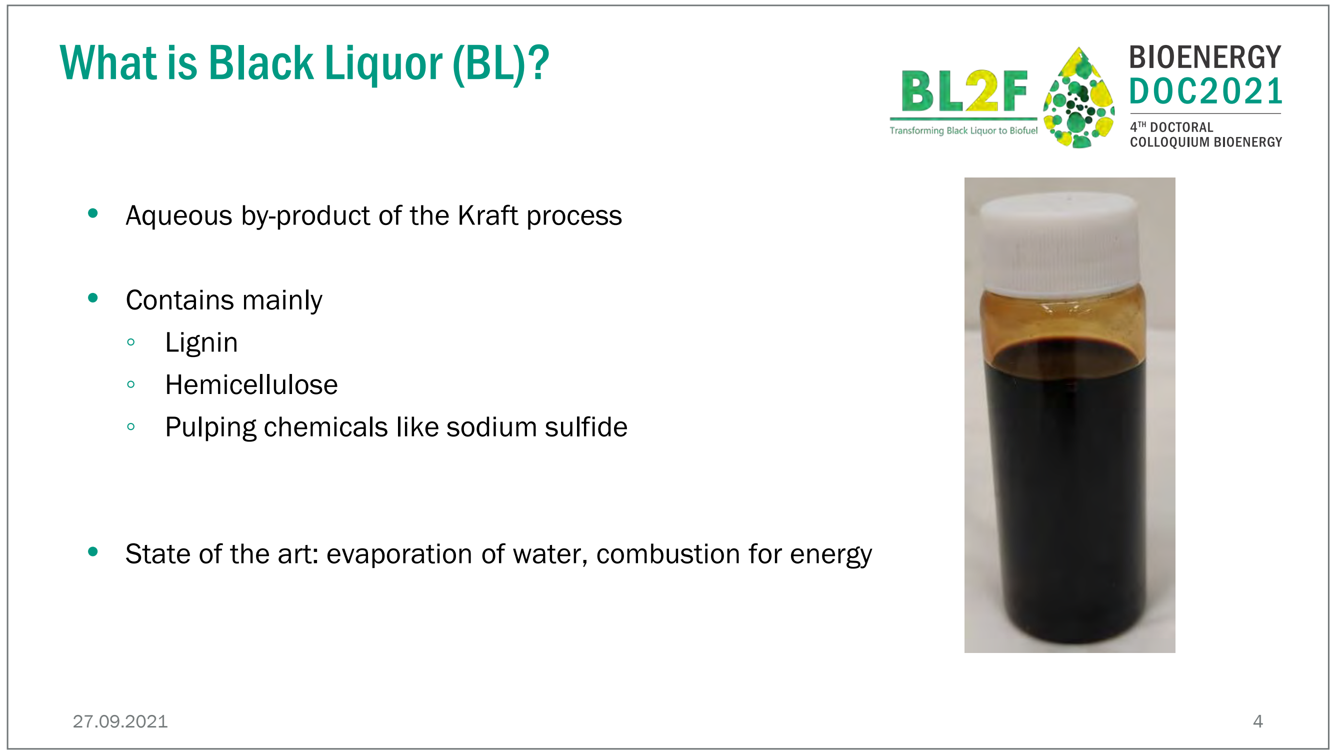
Black Liquor

Water and gases

Refining step to create a drop-in biofuel

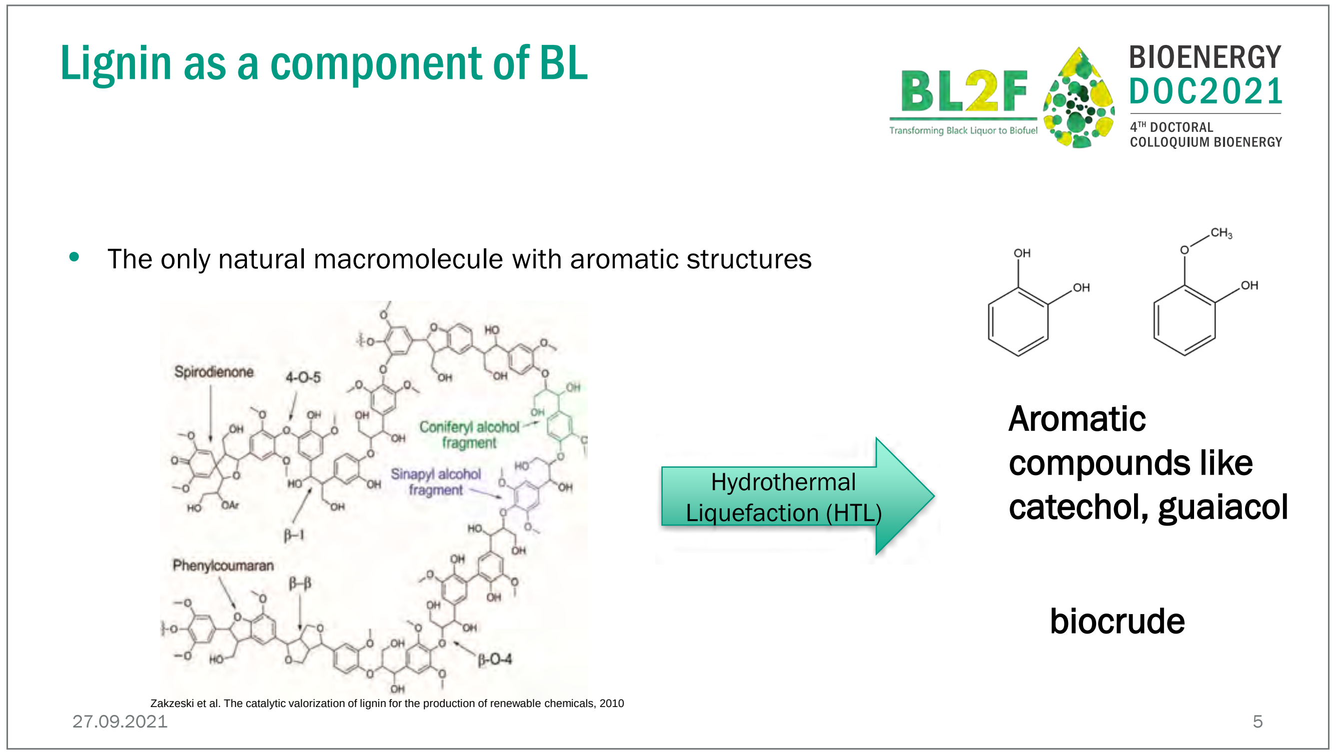
Fuel used in jet & marine engines

This project has received funding from the European Union Grant Number 884111



What is Black Liquor (BL)?

- Aqueous by-product of the Kraft process
- Contains mainly
    - Lignin
    - Hemicellulose
    - Pulping chemicals like sodium sulfide
- State of the art: evaporation of water, combustion for energy



Lignin as a component of BL

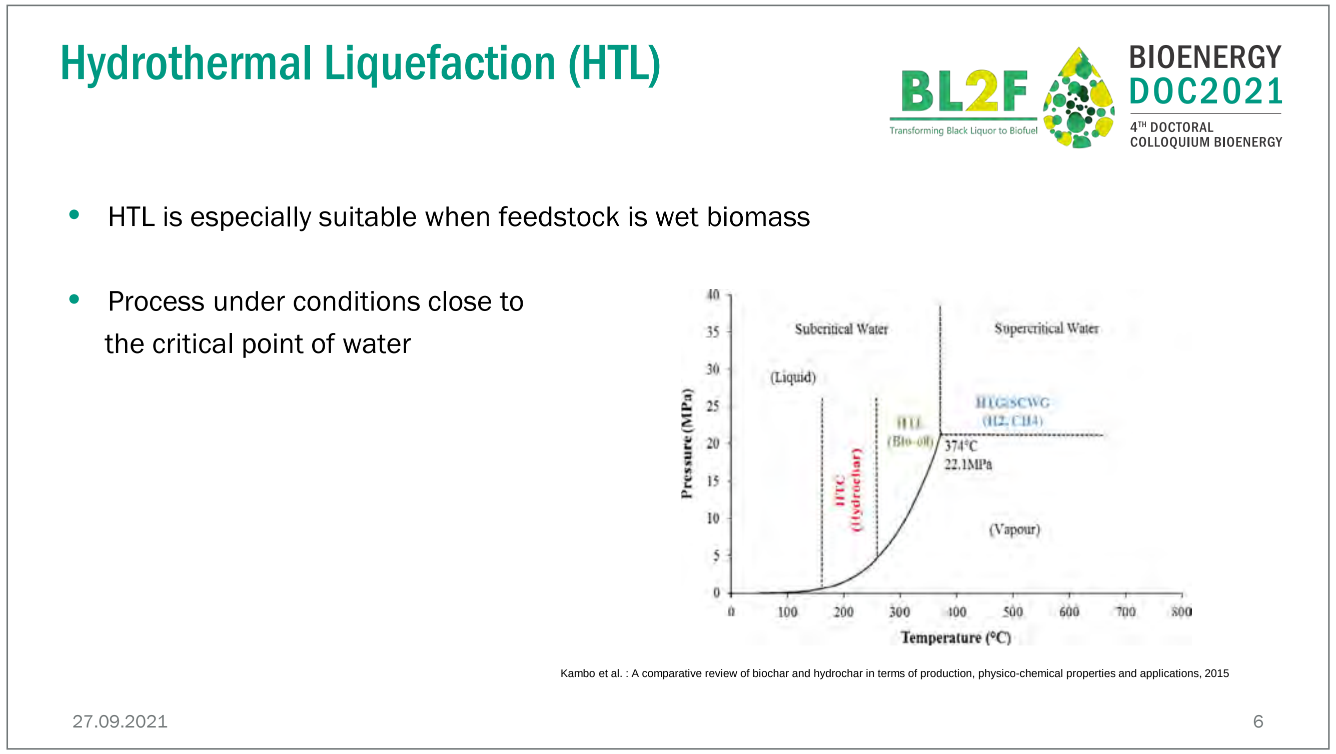
- The only natural macromolecule with aromatic structures

Hydrothermal Liquefaction (HTL)

Aromatic compounds like catechol, guaiacol

biocrude

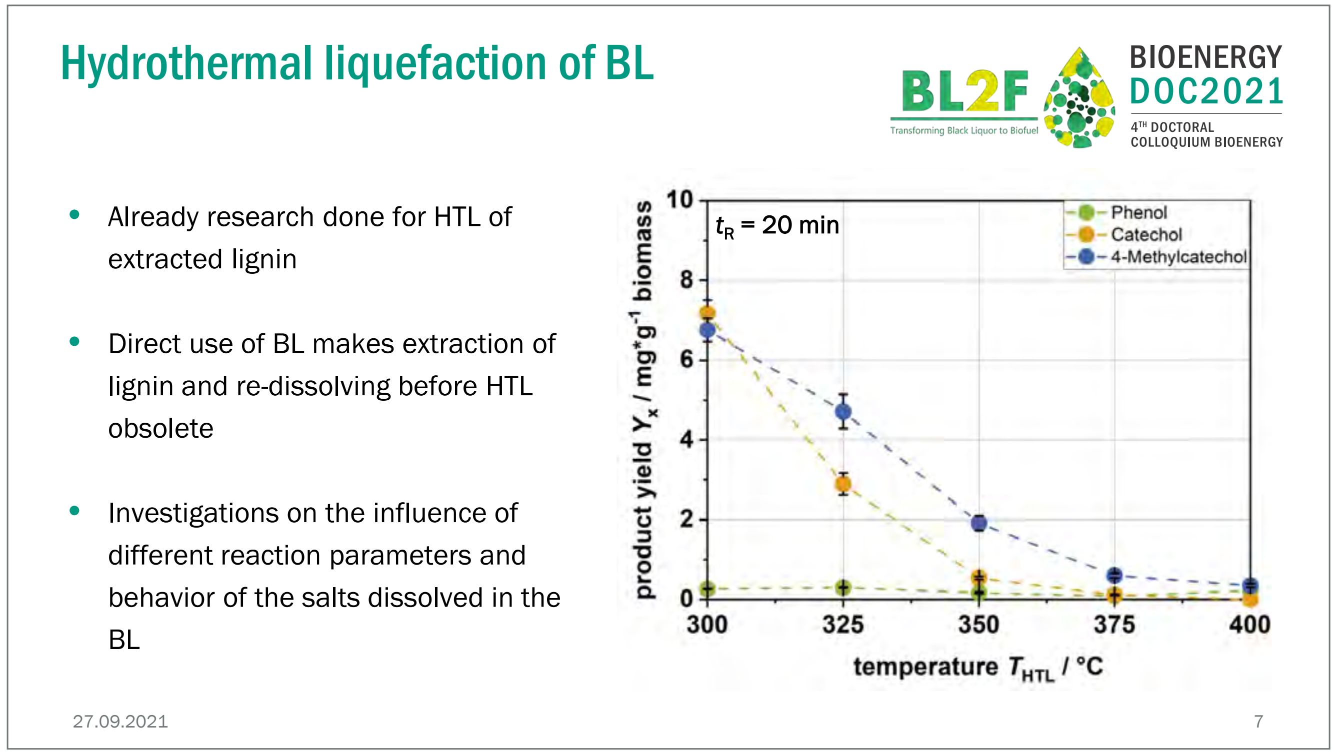
Zakzeski et al. The catalytic valorization of lignin for the production of renewable chemicals, 2010



Hydrothermal Liquefaction (HTL)

- HTL is especially suitable when feedstock is wet biomass
- Process under conditions close to the critical point of water

Kambo et al. : A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications, 2015



Hydrothermal liquefaction of BL

- Already research done for HTL of extracted lignin
- Direct use of BL makes extraction of lignin and re-dissolving before HTL obsolete
- Investigations on the influence of different reaction parameters and behavior of the salts dissolved in the BL

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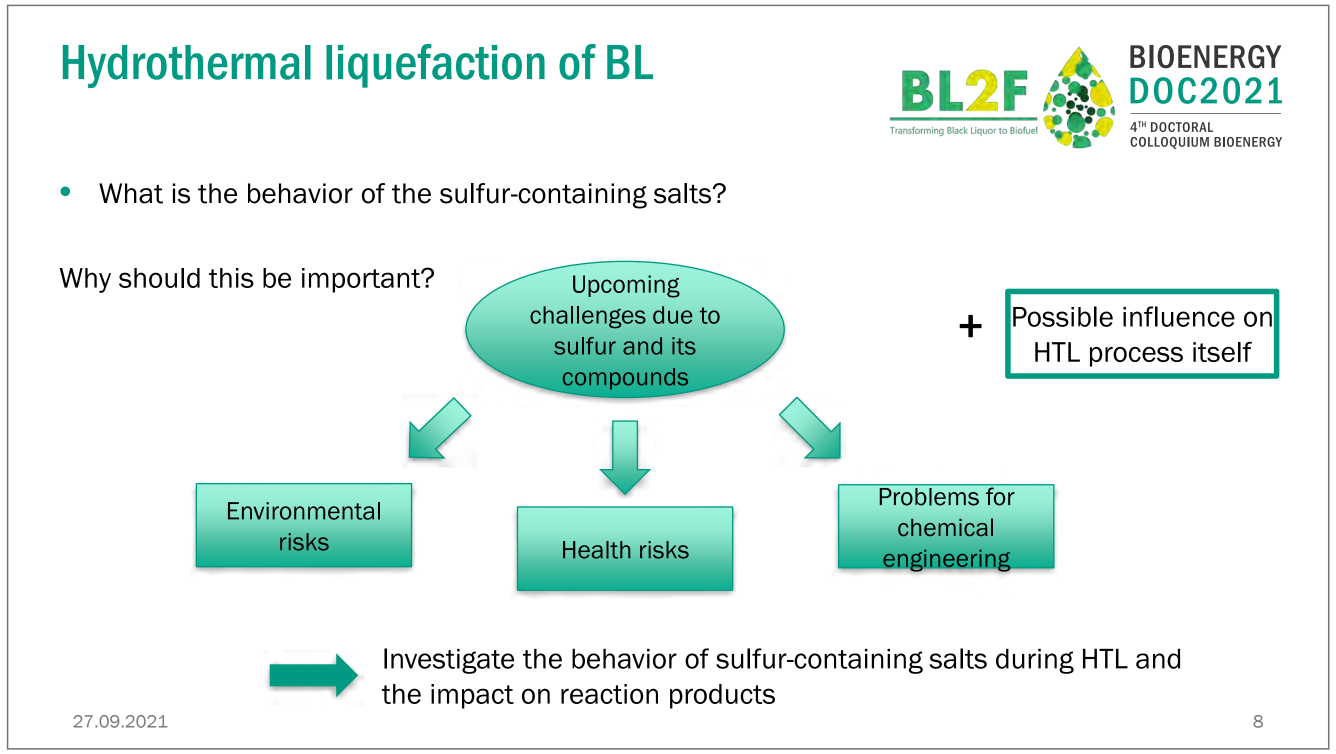

Hydrothermal liquefaction of BL

- What is the behavior of the sulfur-containing salts?

Why should this be important?

Upcoming challenges due to sulfur and its compounds

+ Possible influence on HTL process itself

Environmental risks

Health risks

Problems for chemical engineering

Investigate the behavior of sulfur-containing salts during HTL and the impact on reaction products

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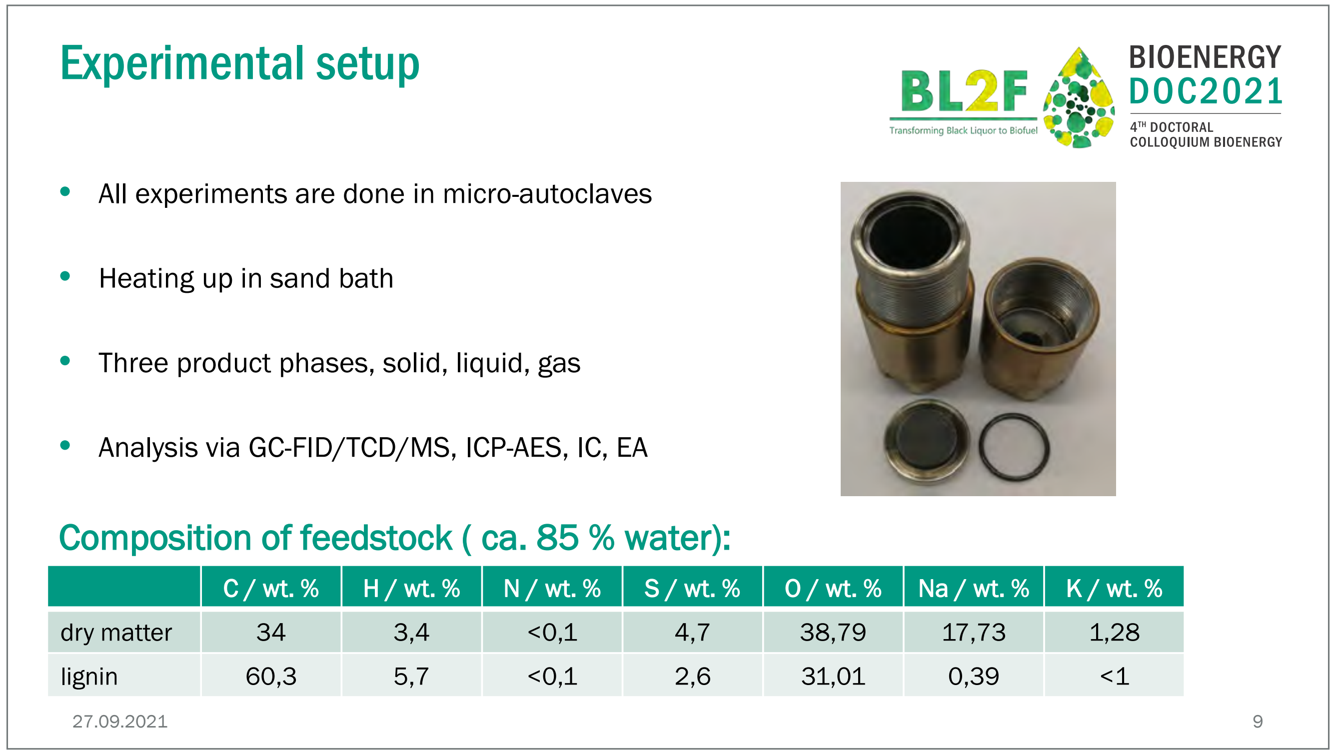

Experimental setup

- All experiments are done in micro-autoclaves
- Heating up in sand bath
- Three product phases, solid, liquid, gas
- Analysis via GC-FID/TCD/MS, ICP-AES, IC, EA

Composition of feedstock (ca. 85 % water):

	C / wt. %	H / wt. %	N / wt. %	S / wt. %	O / wt. %	Na / wt. %	K / wt. %
dry matter	34	3,4	<0,1	4,7	38,79	17,73	1,28
lignin	60,3	5,7	<0,1	2,6	31,01	0,39	<1

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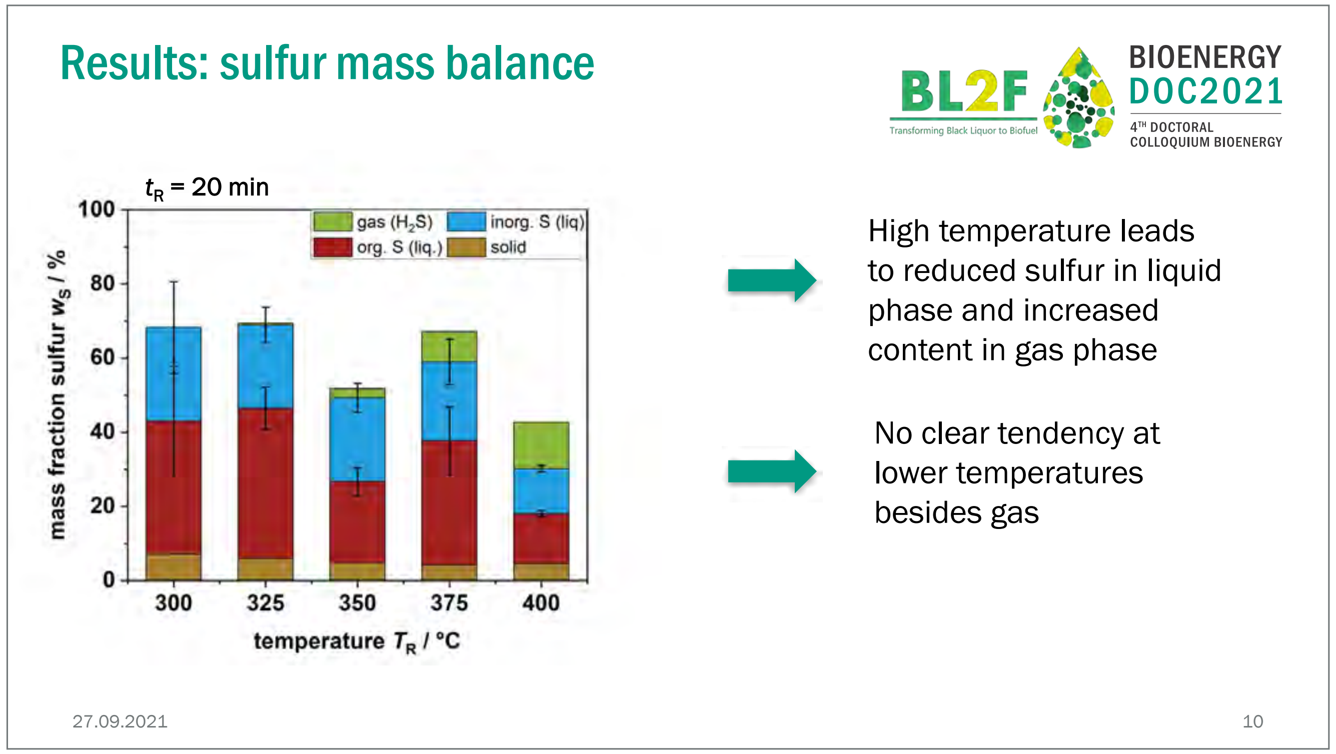

Results: sulfur mass balance

High temperature leads to reduced sulfur in liquid phase and increased content in gas phase

No clear tendency at lower temperatures besides gas

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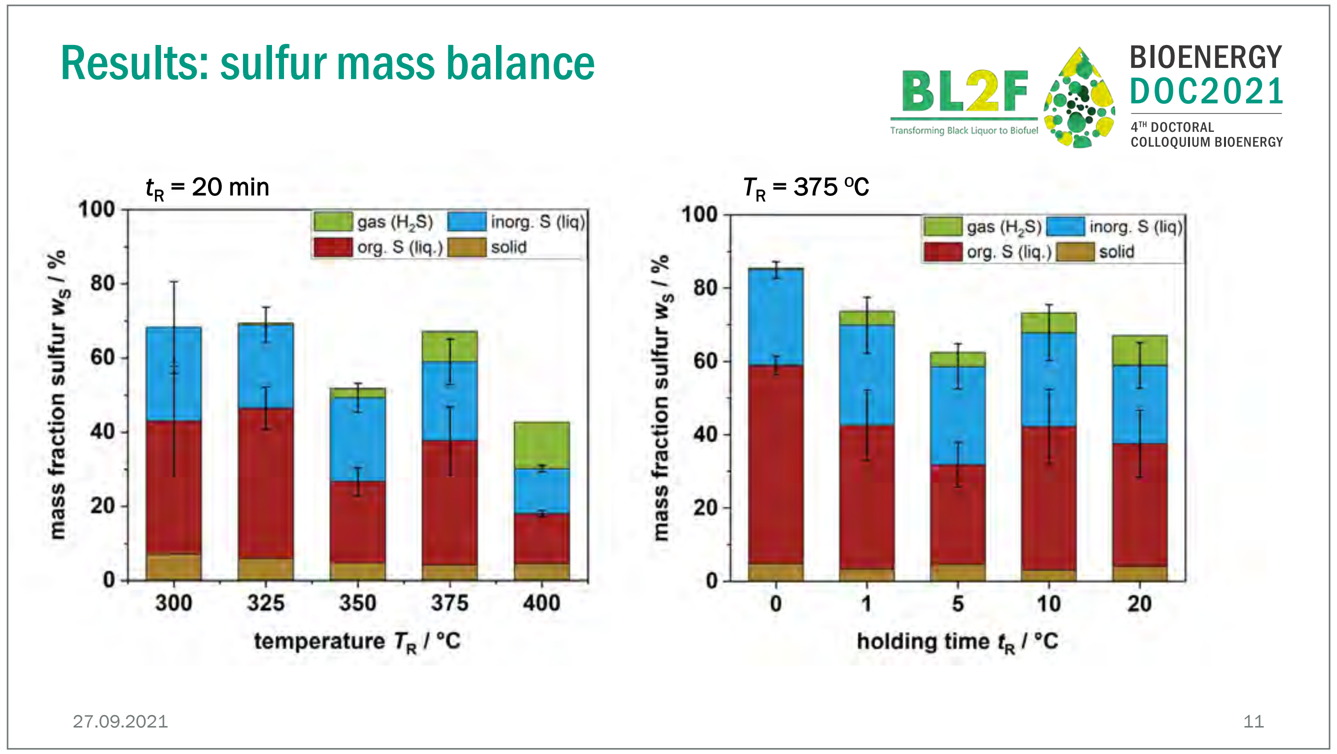

Results: sulfur mass balance

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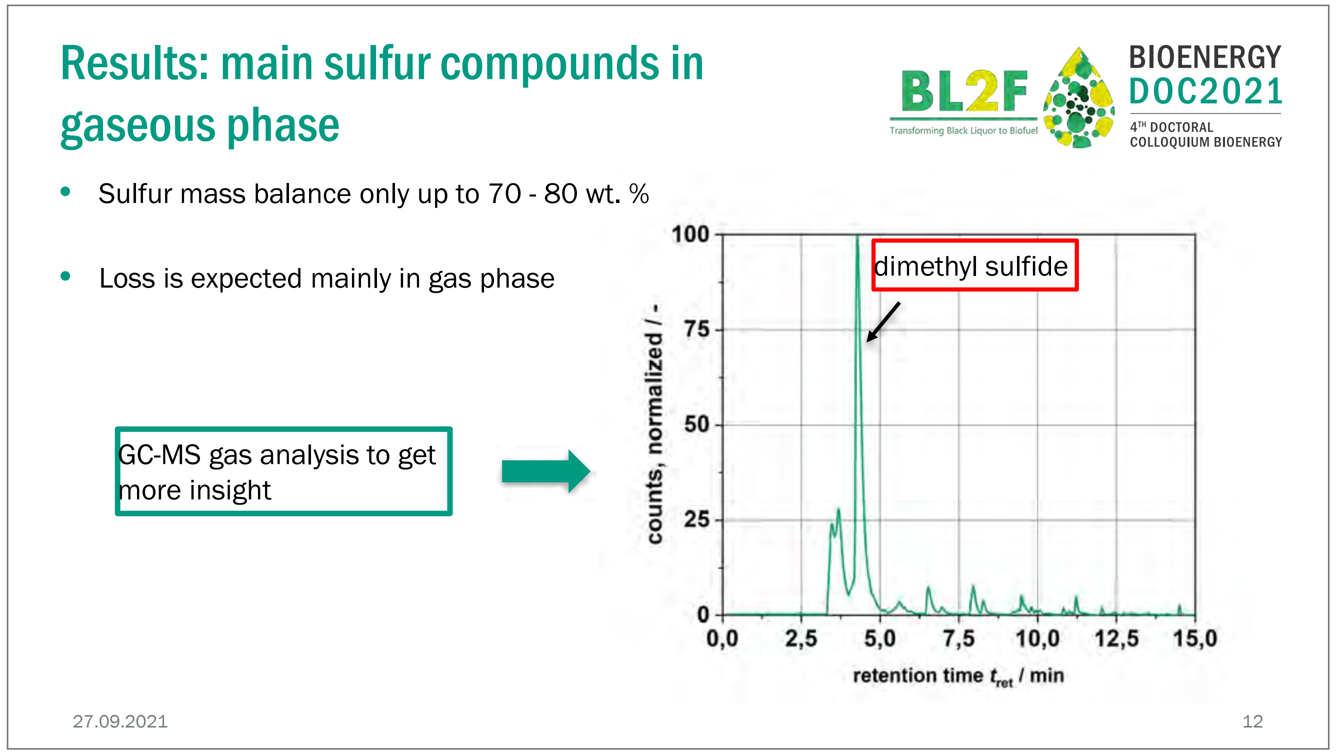

Results: main sulfur compounds in gaseous phase

- Sulfur mass balance only up to 70 - 80 wt. %
- Loss is expected mainly in gas phase

GC-MS gas analysis to get more insight

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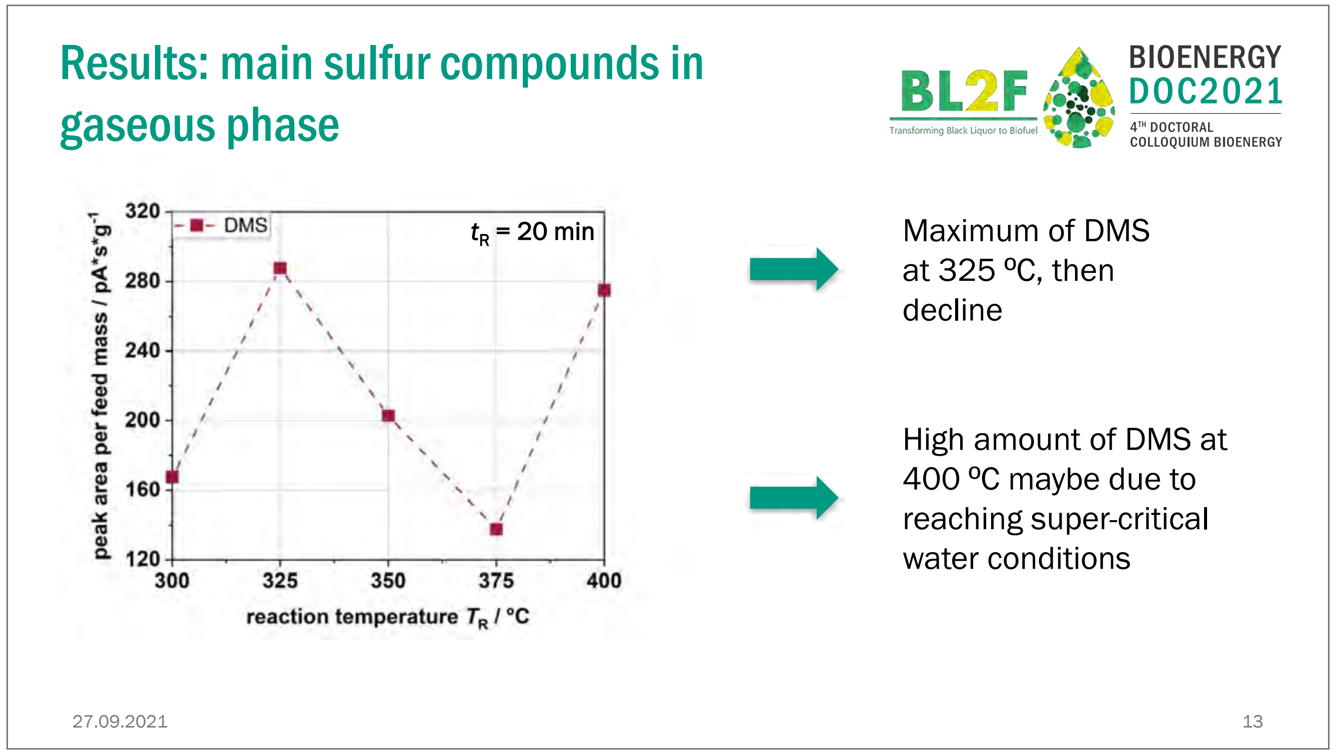

Results: main sulfur compounds in gaseous phase

Maximum of DMS at 325 °C, then decline

High amount of DMS at 400 °C maybe due to reaching super-critical water conditions

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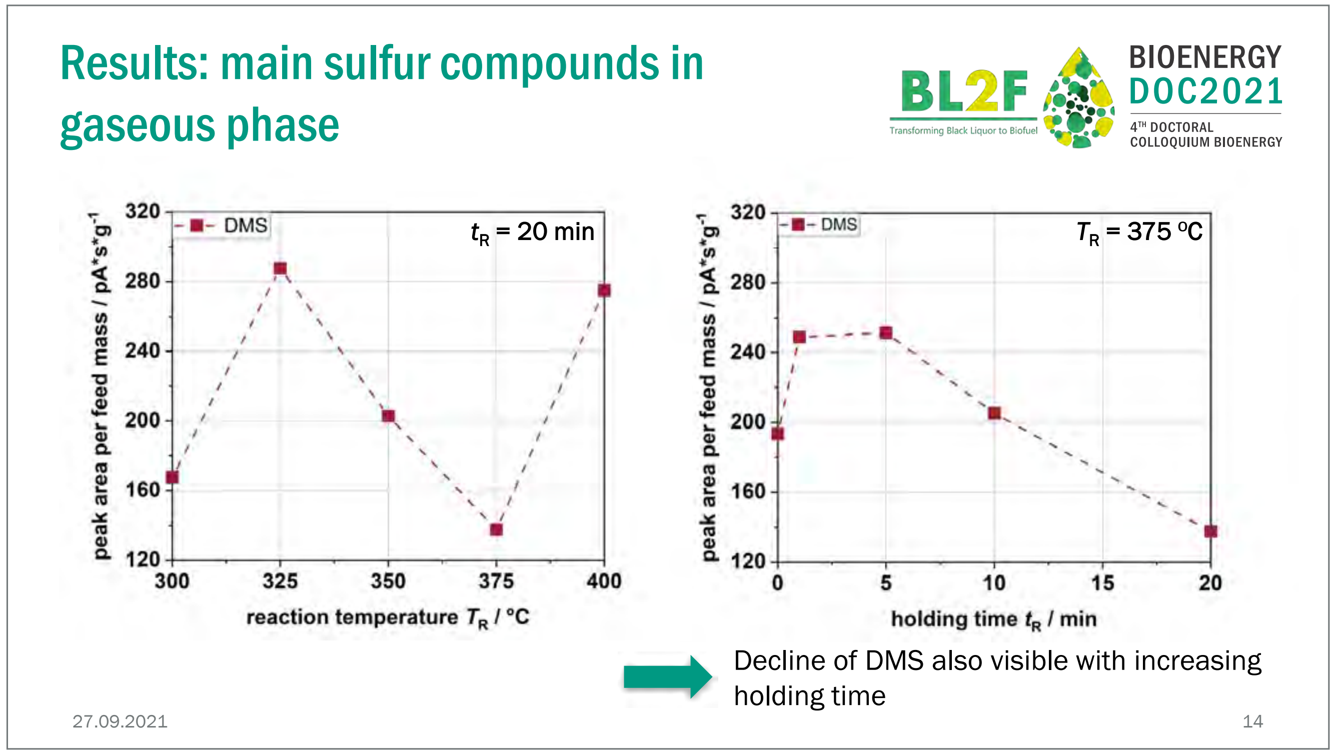

Results: main sulfur compounds in gaseous phase

Decline of DMS also visible with increasing holding time

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Results: main sulfur compounds in gaseous phase

- Possible reaction pathway given in Karnofski et al. 1975, Odor generation in the Kraft process

methyl mercaptane

$$HS^- + Lig - CH_3O \rightarrow \boxed{CH_3SH} + Lig - O^-$$

$$CH_3SH \ + \ OH^- \leftrightarrow CH_3S^- + H_2O$$

$$CH_3S^- + Lig - CH_3O \rightarrow \boxed{H_3CSCH_3} + Lig - O^-$$

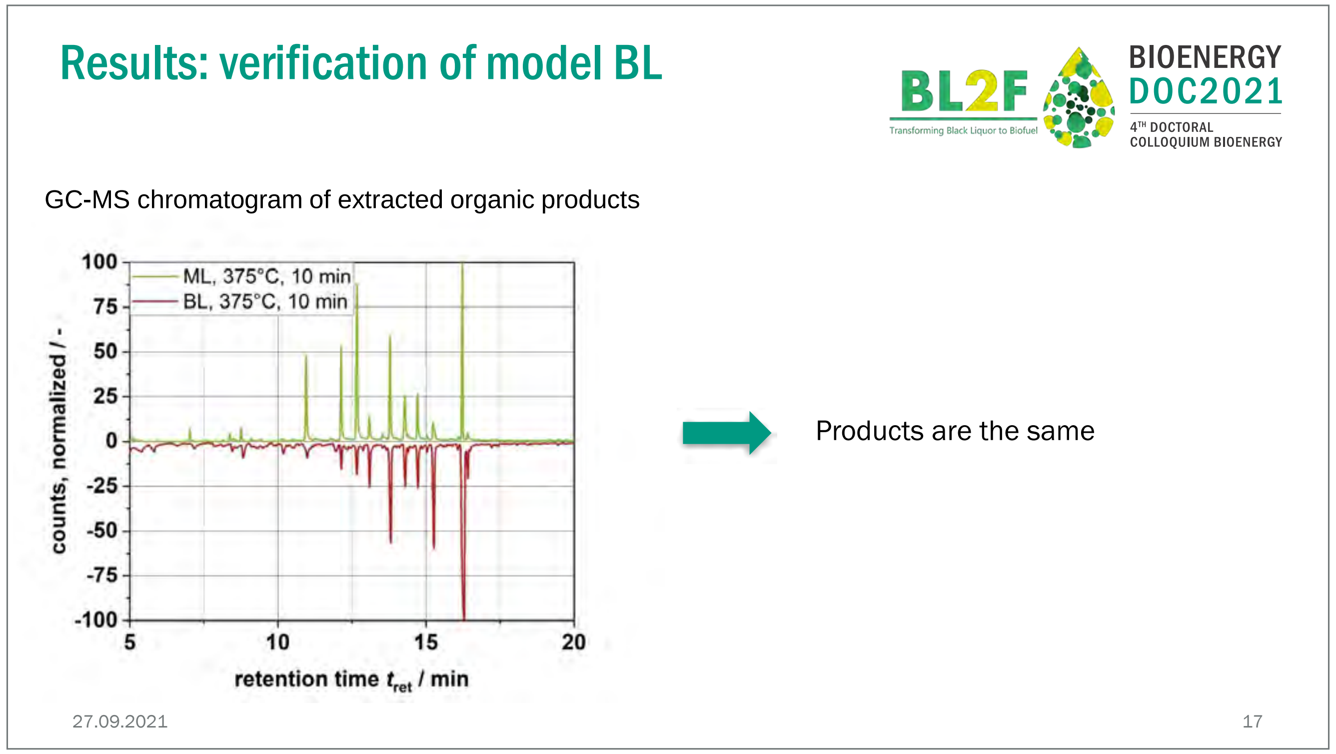
dimethyl sulifde

Usage of a model BL

- Difficult to analyze the influence of different salt concentrations by using real black liquor

→ model black liquor based on feedstock characterization needed

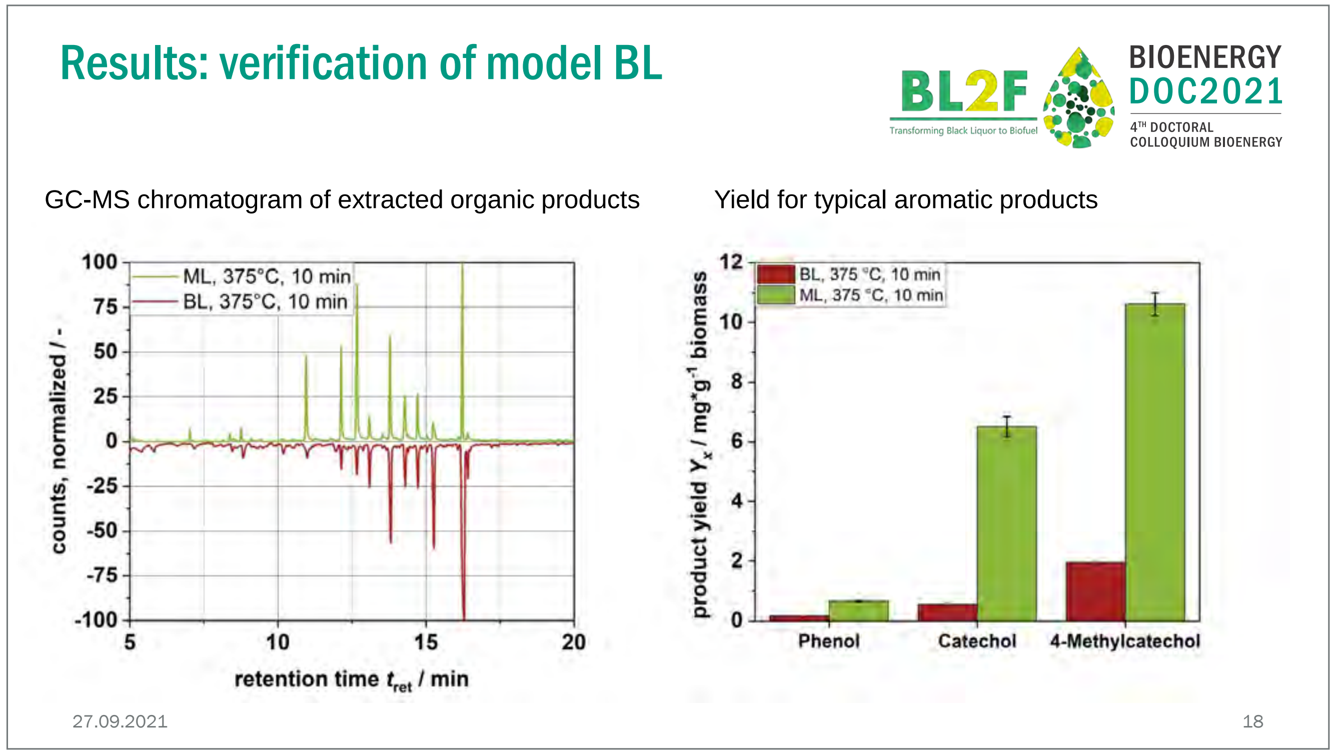
- Composition:
  - salts: Na_2CO_3, K_2CO_3, Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$, Na_2S
  - KOH/NaOH for pH adjustments
  - Lignin (extracted from BL)
- HTL at 375 °C, 10 min with different concentration for Na_2SO_4 and Na_2S



Results: verification of model BL

GC-MS chromatogram of extracted organic products

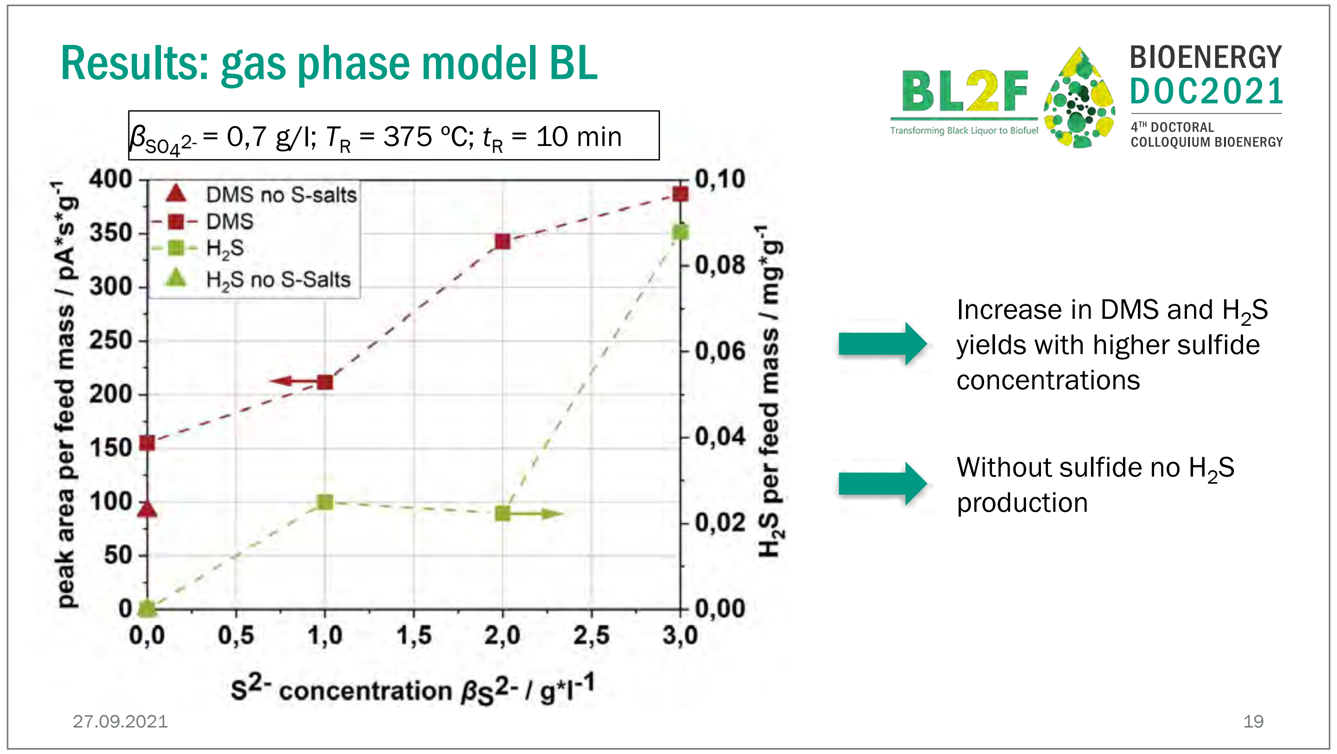
→ Products are the same



Results: verification of model BL

GC-MS chromatogram of extracted organic products

Yield for typical aromatic products



Results: gas phase model BL

$\beta_{SO_4^{2-}}$ = 0,7 g/l; T_R = 375 °C; t_R = 10 min

Increase in DMS and H_2S yields with higher sulfide concentrations

Without sulfide no H_2S production

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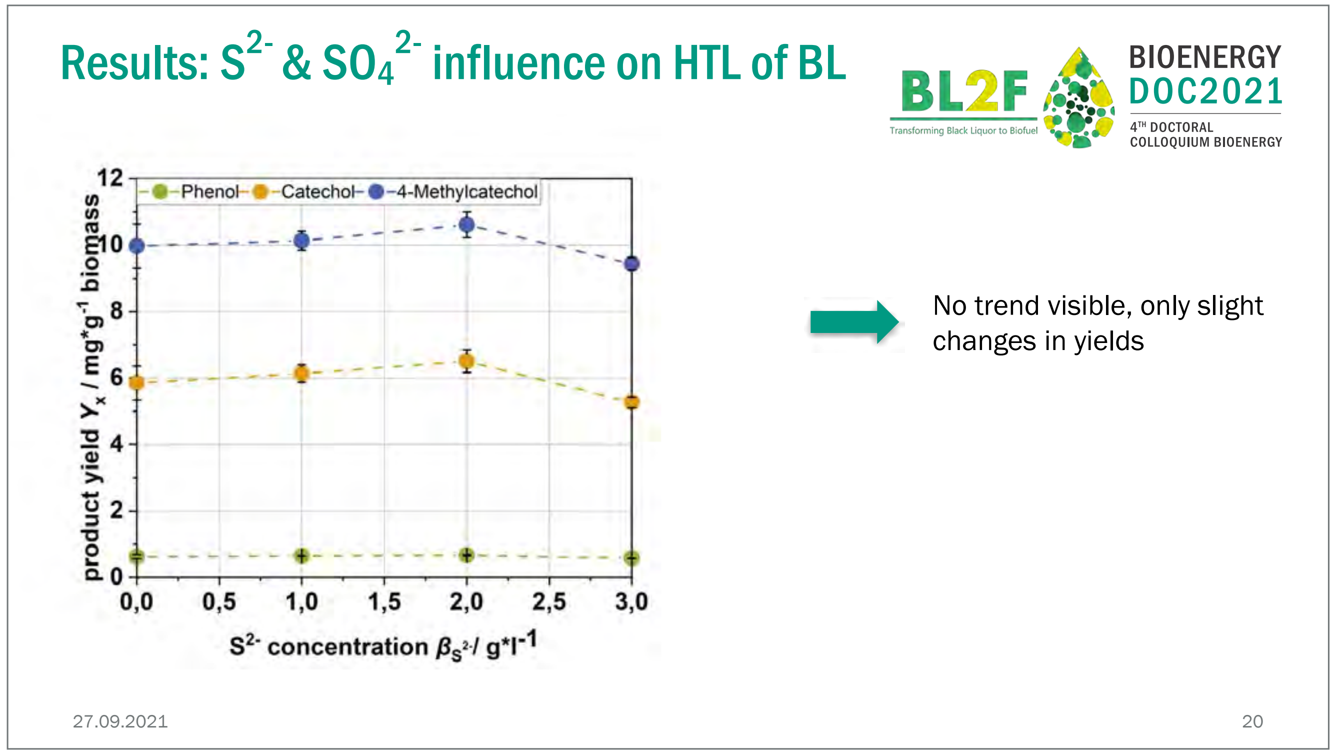

Results: S^{2-} & SO_4^{2-} influence on HTL of BL

No trend visible, only slight changes in yields

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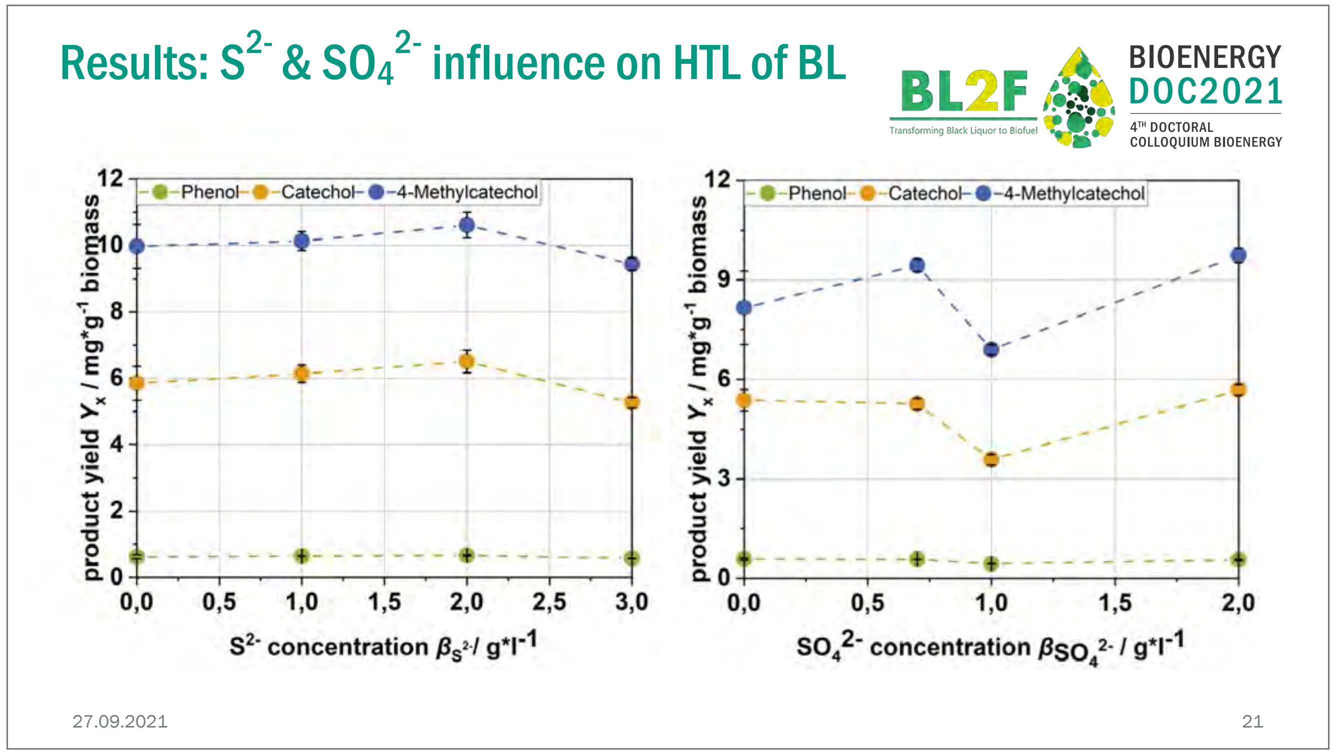

Results: S^{2-} & SO_4^{2-} influence on HTL of BL

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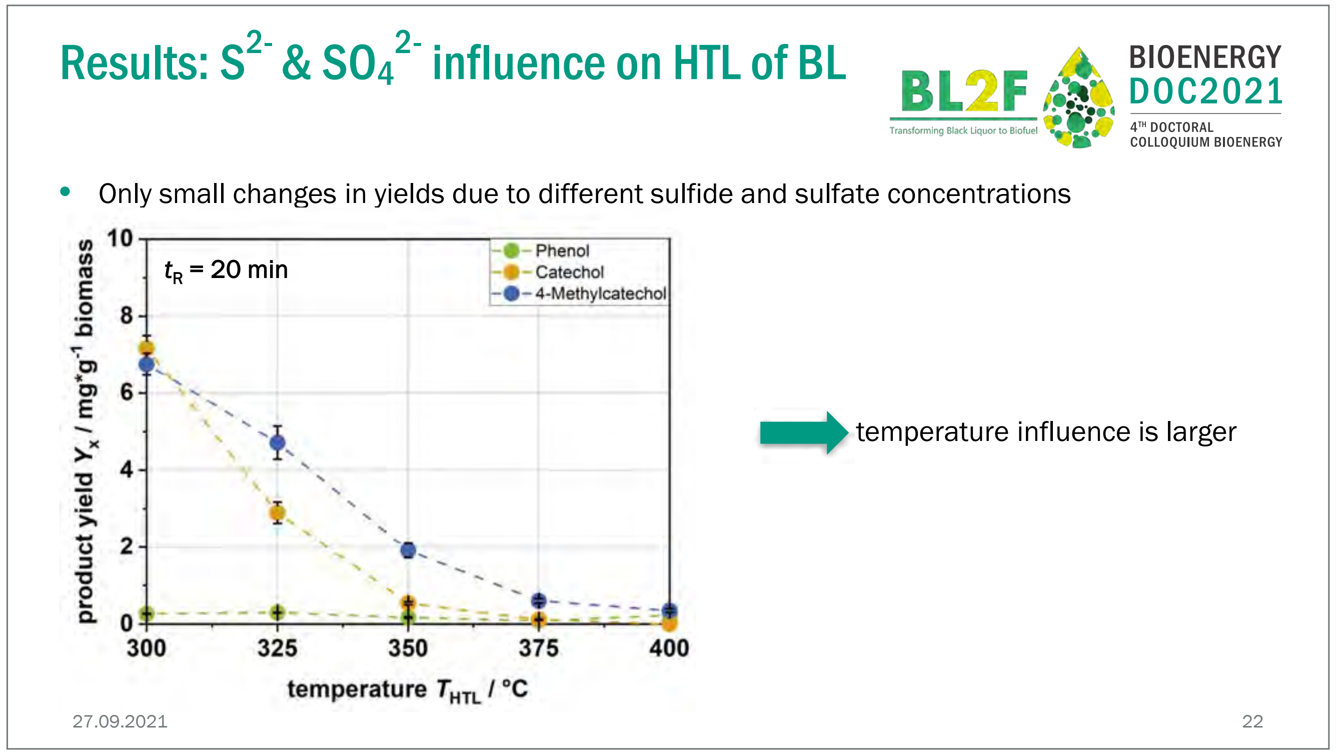

Results: S^{2-} & SO_4^{2-} influence on HTL of BL

- Only small changes in yields due to different sulfide and sulfate concentrations

temperature influence is larger

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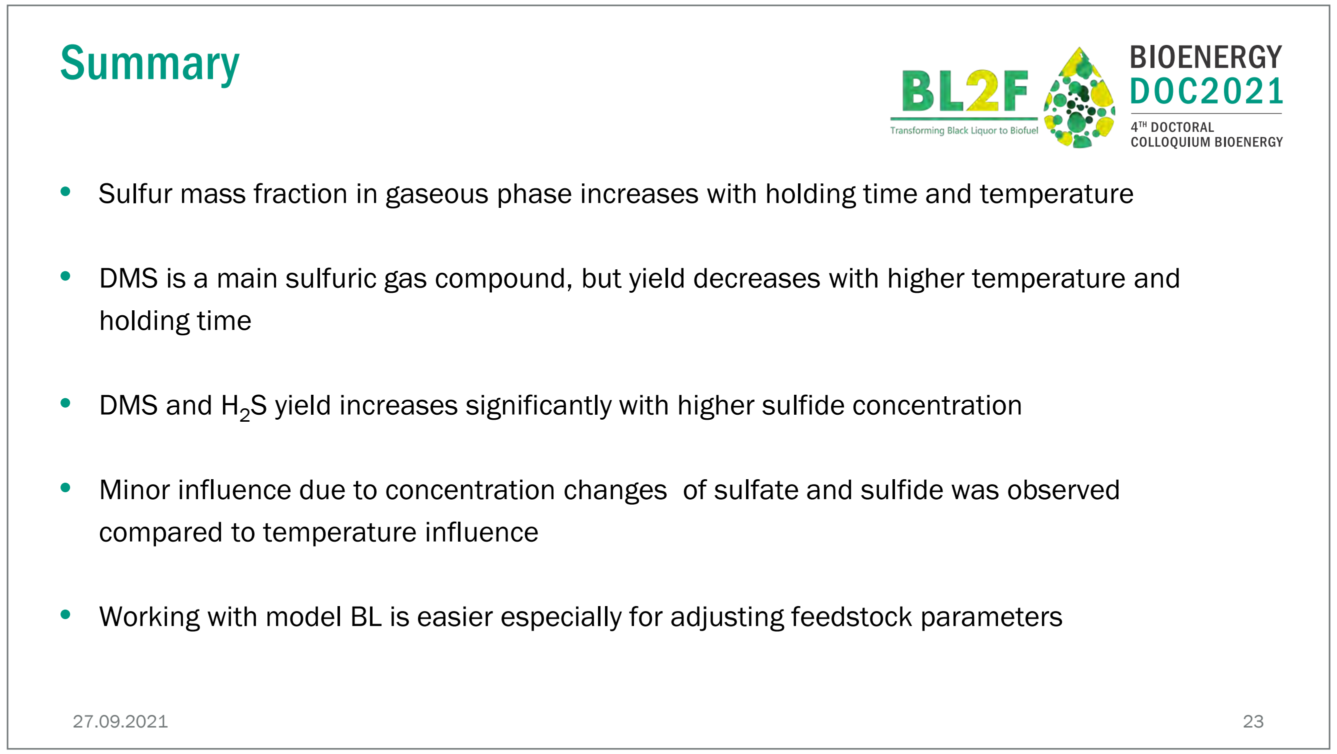
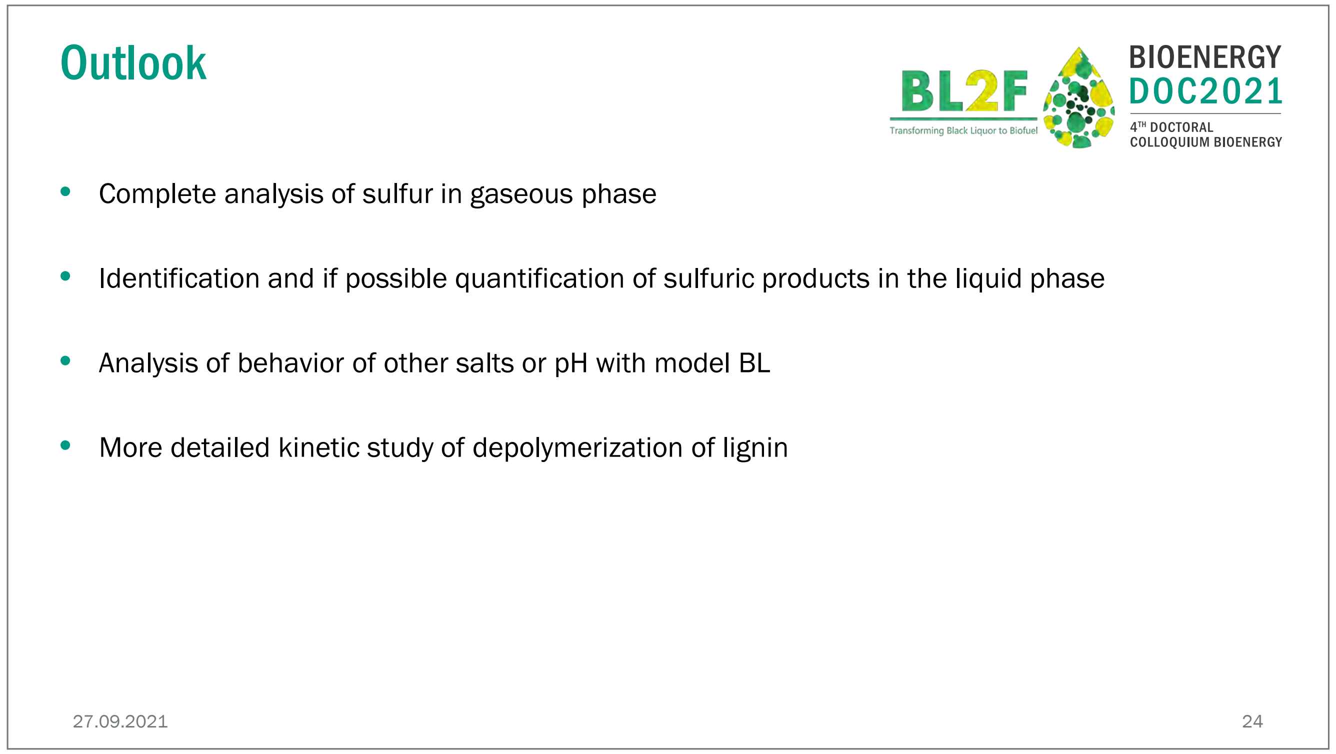


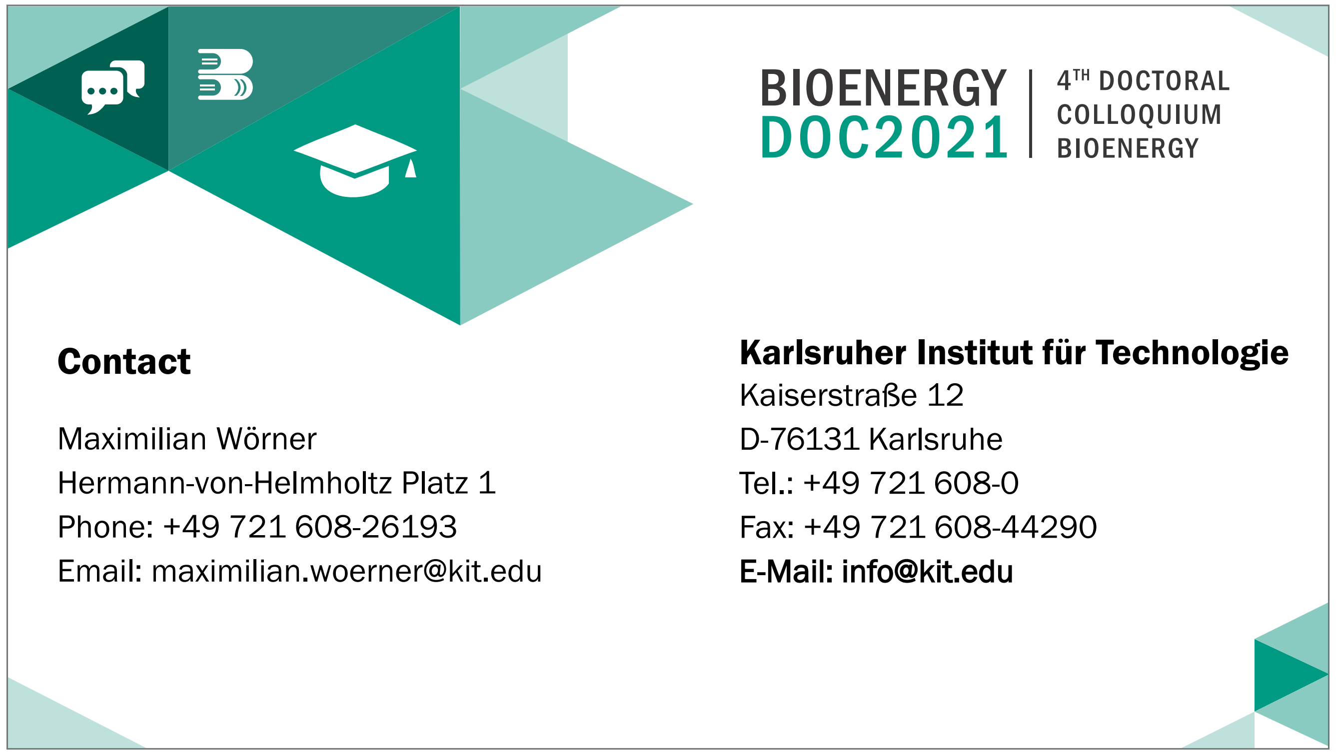
Summary

- Sulfur mass fraction in gaseous phase increases with holding time and temperature
- DMS is a main sulfuric gas compound, but yield decreases with higher temperature and holding time
- DMS and H_2S yield increases significantly with higher sulfide concentration
- Minor influence due to concentration changes of sulfate and sulfide was observed compared to temperature influence
- Working with model BL is easier especially for adjusting feedstock parameters



Outlook

- Complete analysis of sulfur in gaseous phase
- Identification and if possible quantification of sulfuric products in the liquid phase
- Analysis of behavior of other salts or pH with model BL
- More detailed kinetic study of depolymerization of lignin



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Roy Nizsche, Technical University of Berlin/Deutsches Biomasseforschungszentrum

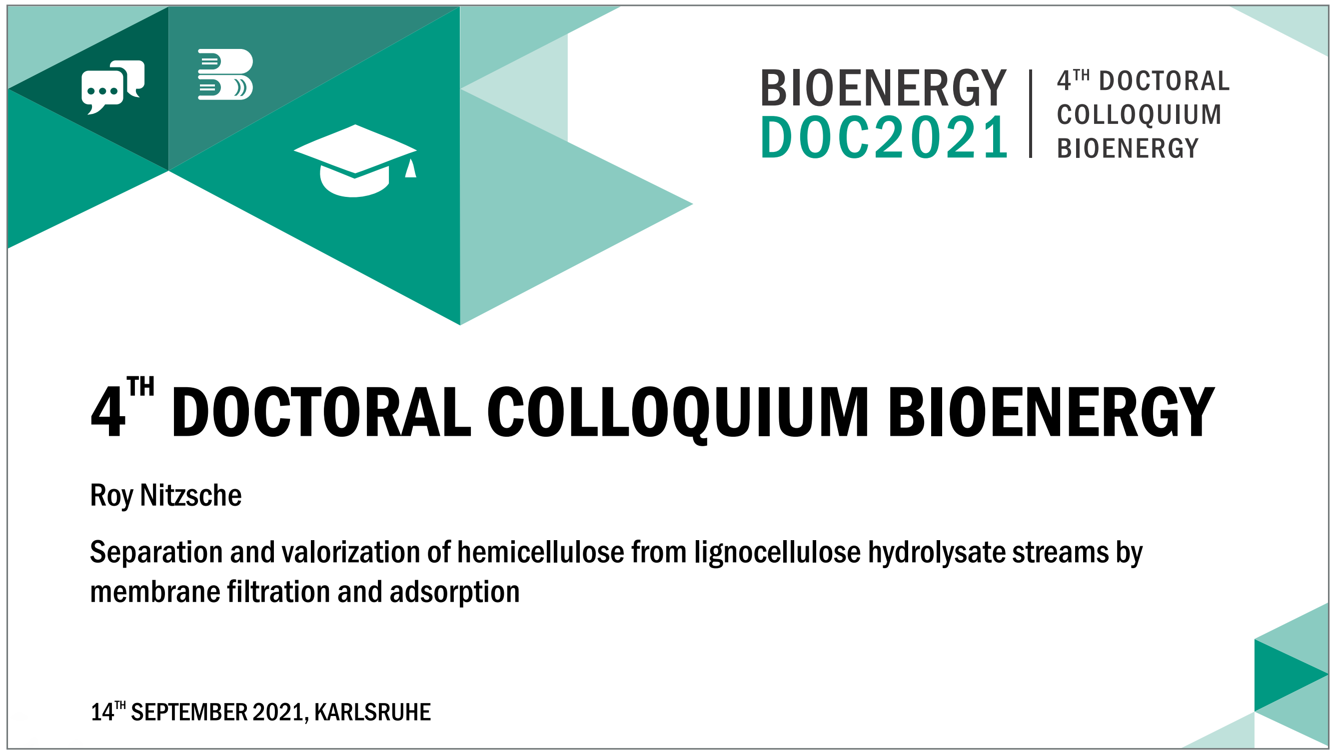
Separation and valorization of hemicellulose from lignocellulose hydrolysate streams by membrane filtration and adsorption

Roy Nitzsche, Jakob Köchermann, Hendrik Etzold, Arne Gröngröft
Technical University of Berlin
Straße des 17. Juni
10623 Berlin
E-mail: **roy.nitzsche@dbfz.de**

The utilization and conversion of lignocellulosic biomass to fuels and chemicals can help to cope with energy shortage, decreasing petroleum reserves and increasing climate change By means of biorefineries, lignocellulosic raw materials can be fractionated in its three main constituent's cellulose, hemicellulose and lignin. An appropriate process for fractionation is the organosolv process. The solid cellulose fraction can be processed to pulp. Dissolved lignin is precipitated and can be used in binding agents. A residual liquid fraction, so-called lignocellulose hydrolysate (LH), contains relevant amounts of hemicellulose and its monomeric degradation products. Due to low concentrations and inhomogeneous composition, this process stream has so far not been used. The aim of the research is the practical demonstration and assessment of two separation concepts (SC), including membrane filtration and adsorption, which enable the material use of LH from an organosolv pulping.

SC 1 consists of a hydrothermal pretreatment (HTP) of the LH to hydrolyze remaining hemicellulose into C5 sugars and nanofiltration (NF) for its separation from inhibitors and concentration. HTP was tested and optimized with the aim of maximizing the C5 sugar yield without the formation of chemical successors. Results showed conversion rates over 95 % under mild hydrothermal conditions. NF was investigated in terms of suitable process parameters and the influence of HTP on membrane performance and fouling. A transmembrane pressure (TMP) of 20 bar and a temperature (T) of 35 °C resulted in an efficient separation and purification of C5 sugars from inhibitors. Moreover, the HTP of LH had a positive influence on NF performance and fouling. On the other hand, SC 2 consists of an adsorption process to remove foulants (e.g. lignin) from the LH and ultrafiltration (UF) for the concentration of hemicellulose and simultaneous removal of remaining lignin fragments. In a fixed bed adsorption column 80 % of the lignin could be removed after feeding 5 bed volumes of LH at a hemicellulose recovery rate of 99.7 %. The adsorption process fitted best with the extended Freundlich isotherm. UF was designed on the basis of statistical experiments and multiobjective parameter optimization. A TMP of 9.5 bar, T of 55 °C and pH of 2.5 seemed appropriate for high permeate flux and hemicellulose retention as well as low lignin retention. Moreover, adsorption as a pretreatment step significantly increased the UF performance. Finally, mass and energy balances of both SC were simulated using Aspen Plus and specific production costs were calculated.

The SC's developed lead to higher yields of C5 sugars respectively hemicellulose in higher purity and concentration, which makes it possible to use it in subsequent applications (e.g. fermentation). Moreover, the results contribute to raising the technology readiness level (TRL) of the processes and expanding their application in real biomass substrates.



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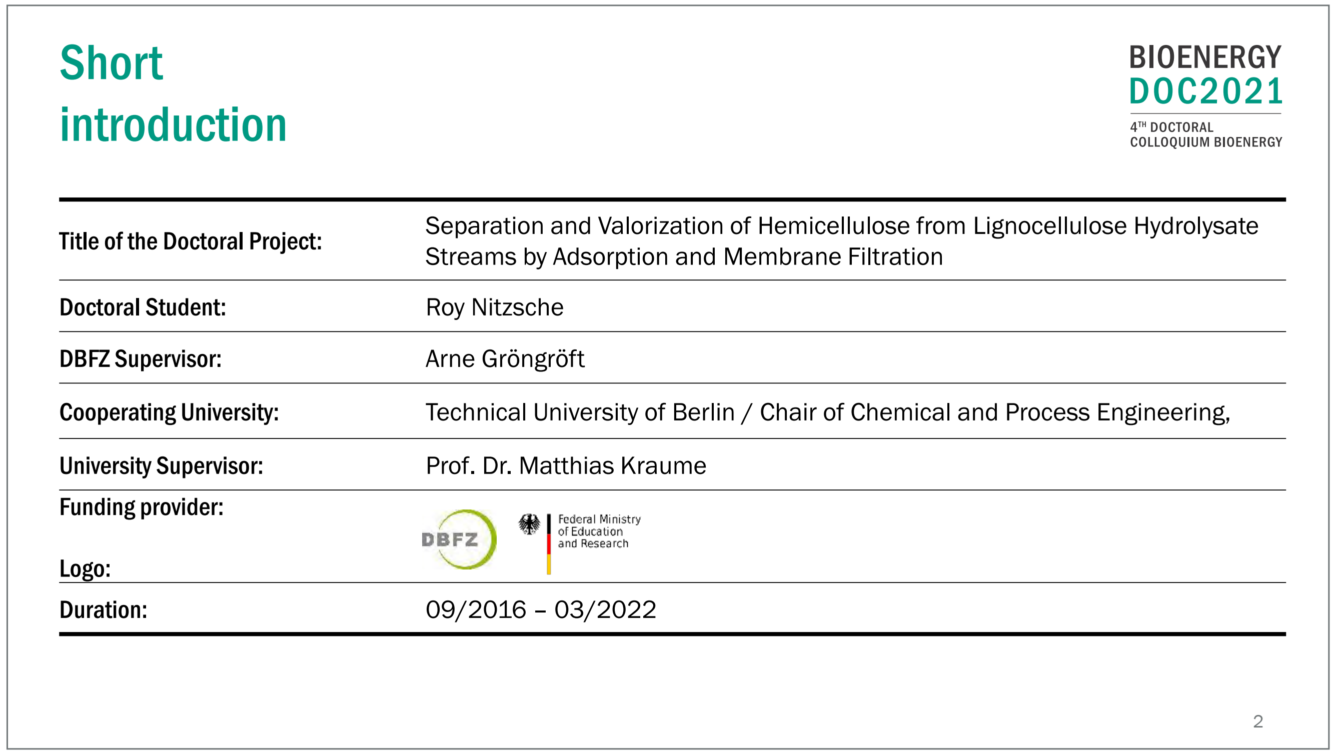
4TH DOCTORAL COLLOQUIUM BIOENERGY

Roy Nitzsche

Separation and valorization of hemicellulose from lignocellulose hydrolysate streams by membrane filtration and adsorption

14TH SEPTEMBER 2021, KARLSRUHE



Short introduction

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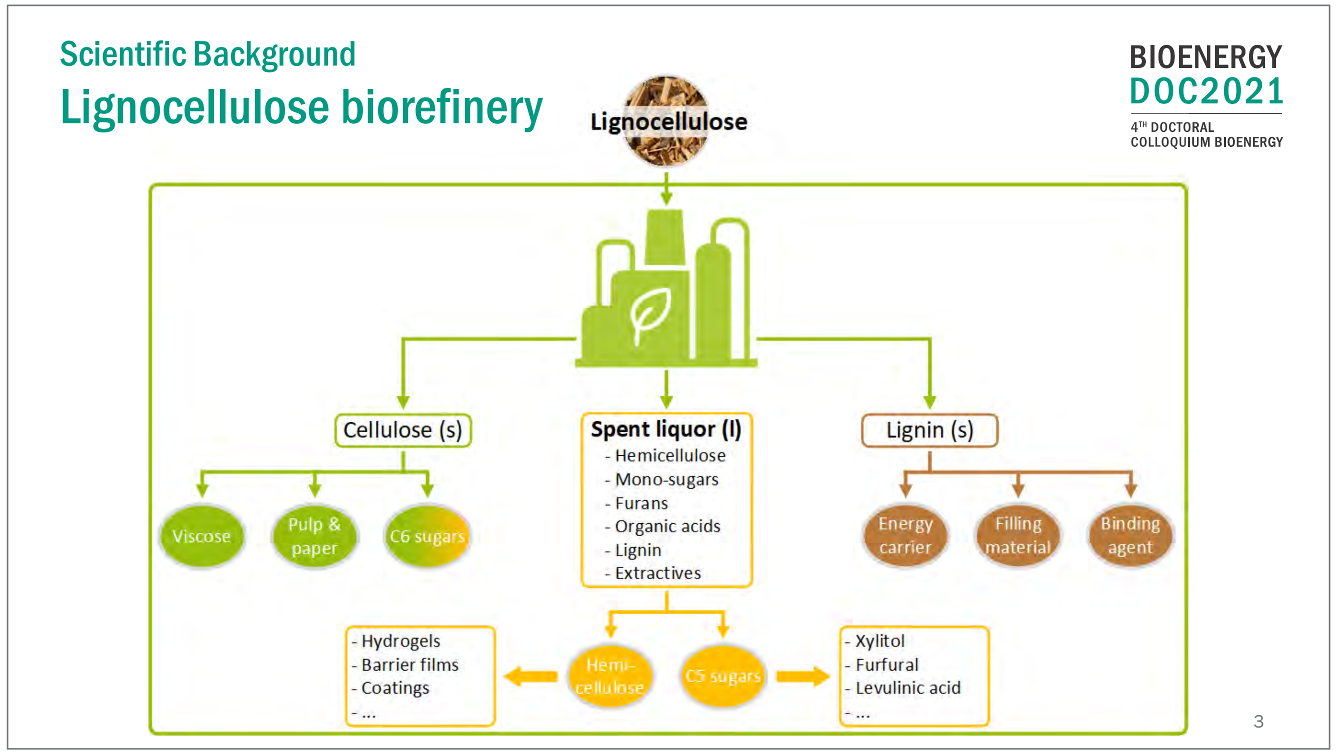
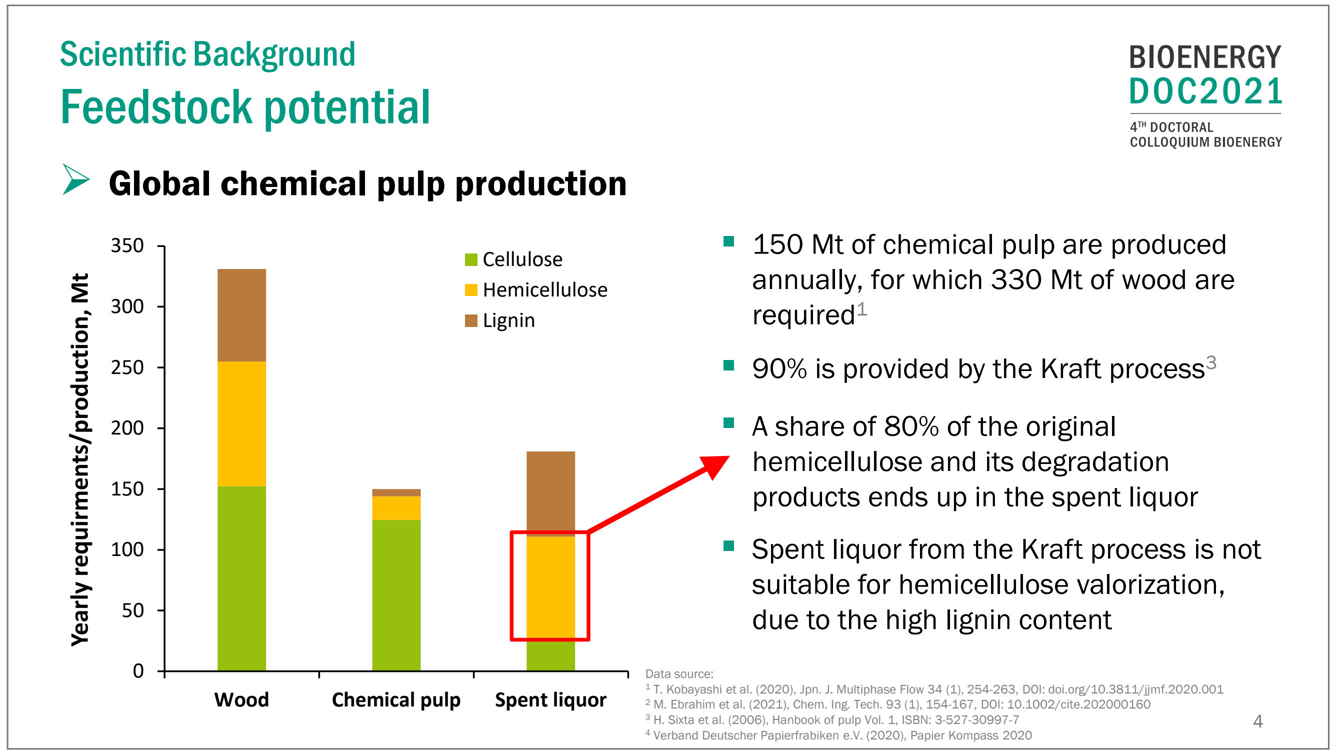
4TH DOCTORAL COLLOQUIUM BIOENERGY

Title of the Doctoral Project:	Separation and Valorization of Hemicellulose from Lignocellulose Hydrolysate Streams by Adsorption and Membrane Filtration
Doctoral Student:	Roy Nitzsche
DBFZ Supervisor:	Arne Gröngröft
Cooperating University:	Technical University of Berlin / Chair of Chemical and Process Engineering,
University Supervisor:	Prof. Dr. Matthias Kraume
Funding provider: **Logo:**	DBFZ Federal Ministry of Education and Research
Duration:	09/2016 – 03/2022



Scientific Background

Lignocellulose biorefinery



Scientific Background

Feedstock potential

➢ **Global chemical pulp production**

- 150 Mt of chemical pulp are produced annually, for which 330 Mt of wood are required[1]
- 90% is provided by the Kraft process[3]
- A share of 80% of the original hemicellulose and its degradation products ends up in the spent liquor
- Spent liquor from the Kraft process is not suitable for hemicellulose valorization, due to the high lignin content

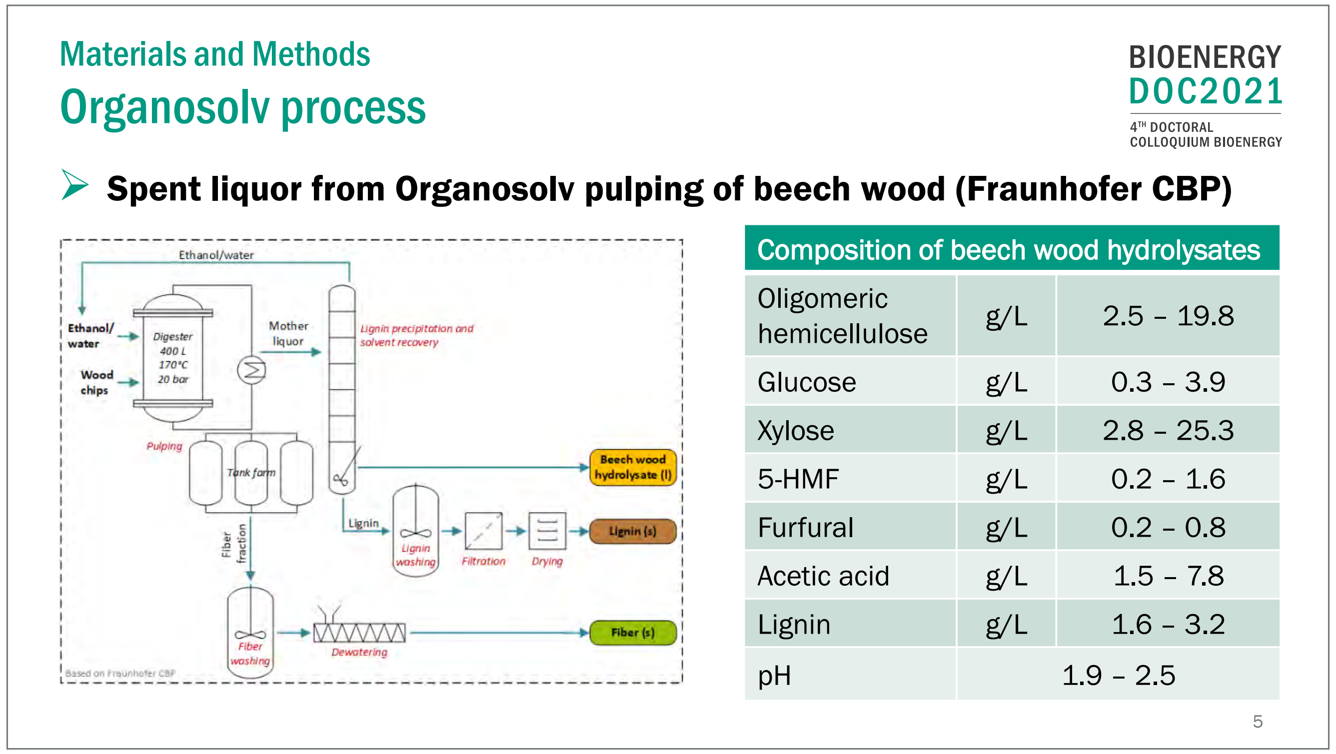
Data source:

[1] T. Kobayashi et al. (2020), Jpn. J. Multiphase Flow 34 (1), 254-263, DOI: doi.org/10.3811/jjmf.2020.001

[2] M. Ebrahim et al. (2021), Chem. Ing. Tech. 93 (1), 154-167, DOI: 10.1002/cite.202000160

[3] H. Sixta et al. (2006), Hanbook of pulp Vol. 1, ISBN: 3-527-30997-7

[4] Verband Deutscher Papierfrabiken e.V. (2020), Papier Kompass 2020



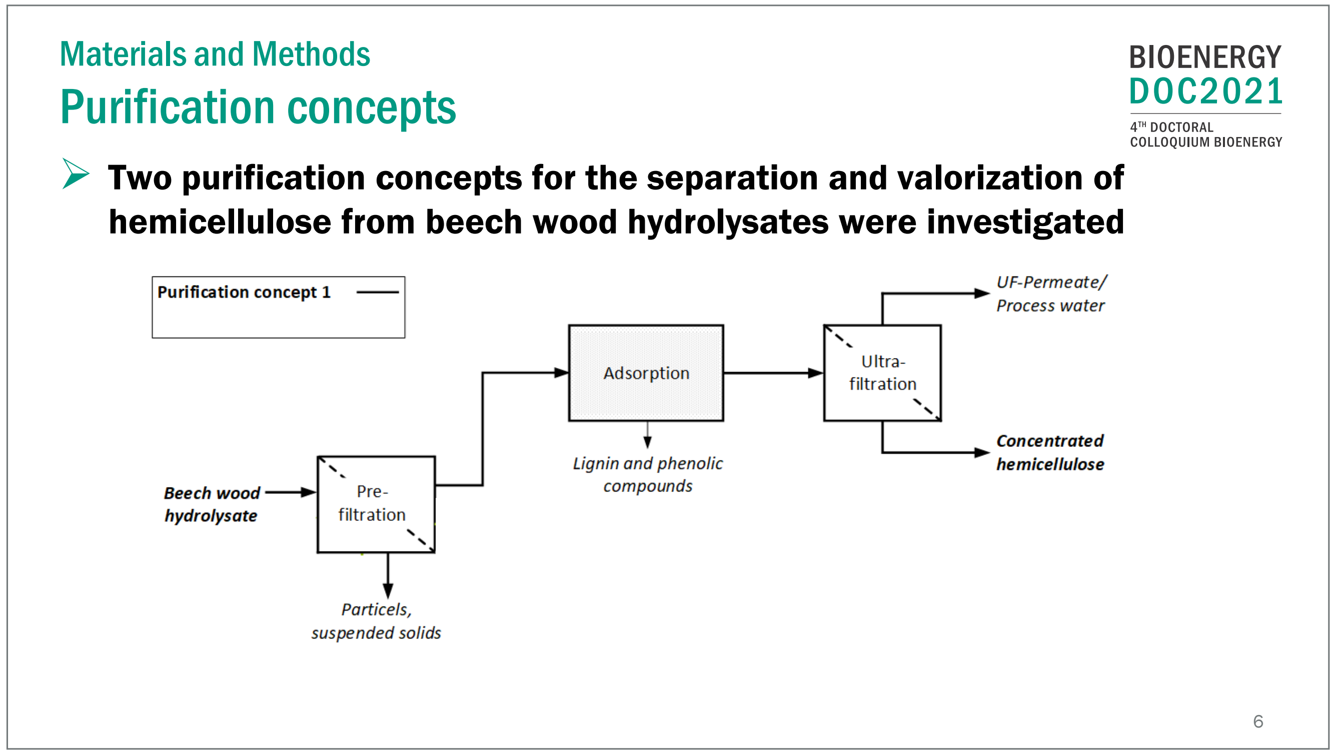
Materials and Methods

Organosolv process

➢ **Spent liquor from Organosolv pulping of beech wood (Fraunhofer CBP)**

Based on Fraunhofer CBP

Composition of beech wood hydrolysates		
Oligomeric hemicellulose	g/L	2.5 – 19.8
Glucose	g/L	0.3 – 3.9
Xylose	g/L	2.8 – 25.3
5-HMF	g/L	0.2 – 1.6
Furfural	g/L	0.2 – 0.8
Acetic acid	g/L	1.5 – 7.8
Lignin	g/L	1.6 – 3.2
pH	1.9 – 2.5	



Materials and Methods

Purification concepts

➢ **Two purification concepts for the separation and valorization of hemicellulose from beech wood hydrolysates were investigated**

Purification concept 1
Adsorption

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Removal of lignin from bee… hydrolysate by adsorption

- Adsorbent screening
- Ac
- Breakthrough curves (SP700)

Separation and Purification Technology

Separation of lignin from beech wood hydrolysate using polymeric resins and zeolites – Determination and application of adsorption isotherms

Roy Nitzsche, Arne Gröngröft, Matthias Kraume

Nitzsche, R., Gröngröft, A., Kraume, M., 2019. Separation of lignin from beech wood hydrolysate using polymer… s and zeolites – Determination and application of adsorption isotherms. Separation and Purification Technology 209, 491-502.

Purification concept 1
Ultrafiltration

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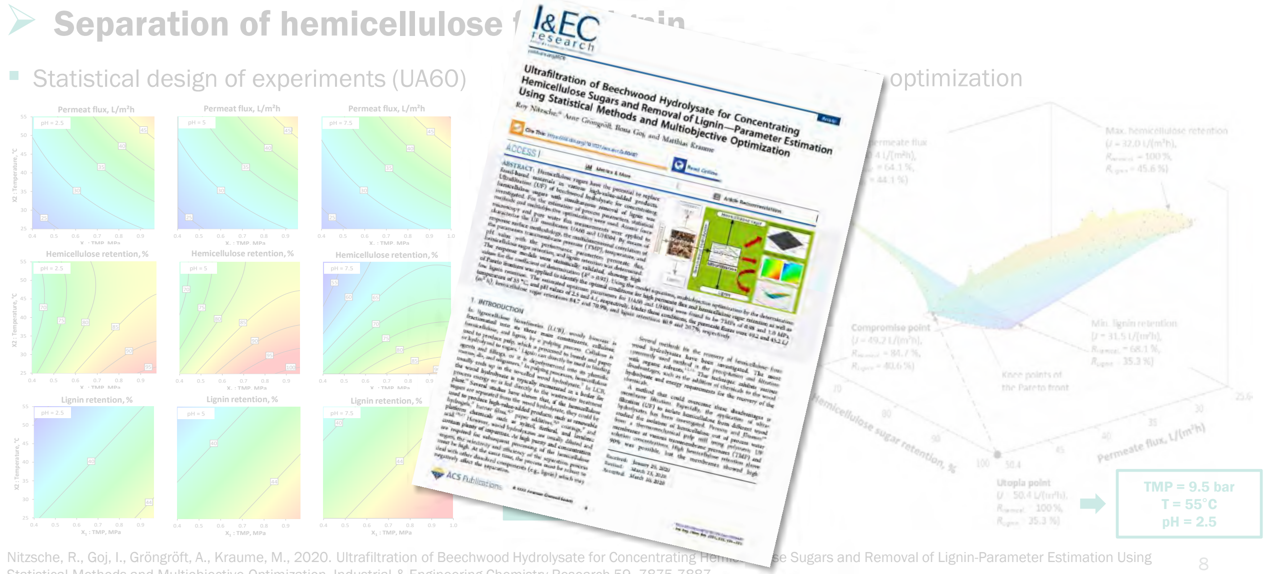
Separation of hemicellulose f… …nin

- Statistical design of experiments (UA60)
- …optimization



TMP = 9.5 bar
T = 55°C
pH = 2.5

I&EC research

Ultrafiltration of Beechwood Hydrolysate for Concentrating Hemicellulose Sugars and Removal of Lignin—Parameter Estimation Using Statistical Methods and Multiobjective Optimization

Roy Nitzsche, Arne Gröngröft, Ilona Goj, and Matthias Kraume

ACS Publications

Nitzsche, R., Goj, I., Gröngröft, A., Kraume, M., 2020. Ultrafiltration of Beechwood Hydrolysate for Concentrating Hemi… …se Sugars and Removal of Lignin-Parameter Estimation Using Statistical Methods and Multiobjective Optimization. Industrial & Engineering Chemistry Research 59, 7875-7887.

Purification concept 1
Adsorption + Ultrafiltration

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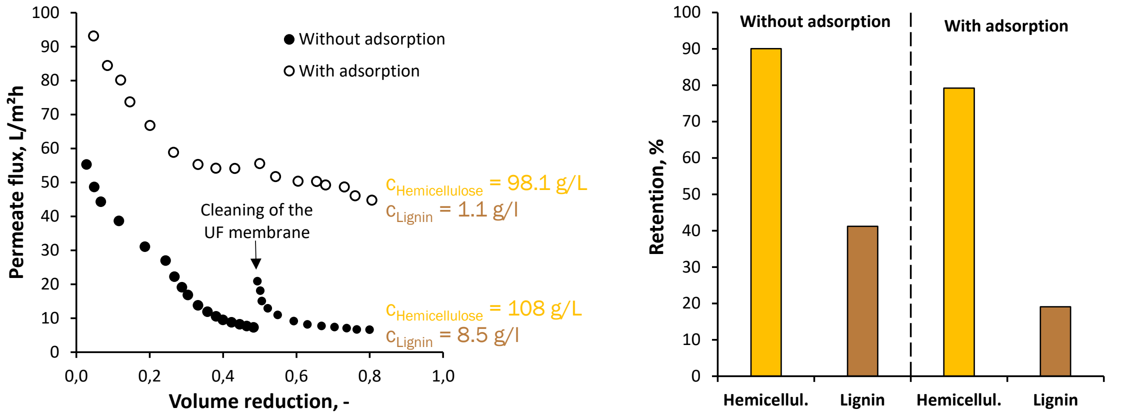
Enhanced UF by pretreatment of beech wood hydrolysate with adsorption



- Ø permeate flux increased by a factor of 3
- Adsorption minimizes membrane fouling

- Hemicellulose and lignin retention decreased
- Higher losses, but purer concentrate stream

Purification concept 2
Hydrothermal treatment

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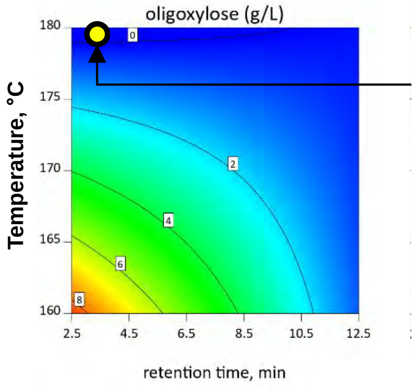
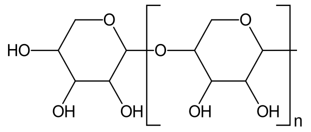
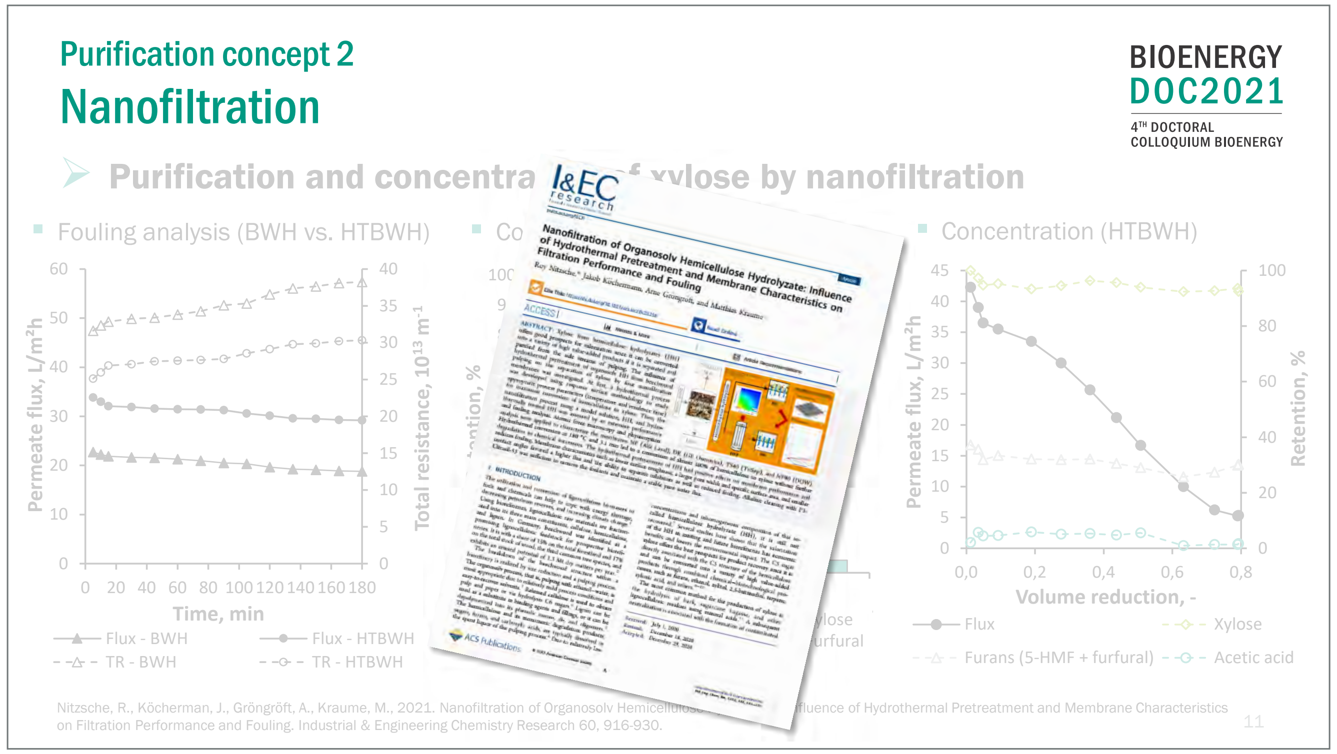
Conversion of oligomeric hemicellulose to monomeric xylose





Optimized parameters

***T* = 180°C**
***t* = 3.1 min**



Purification concept 2

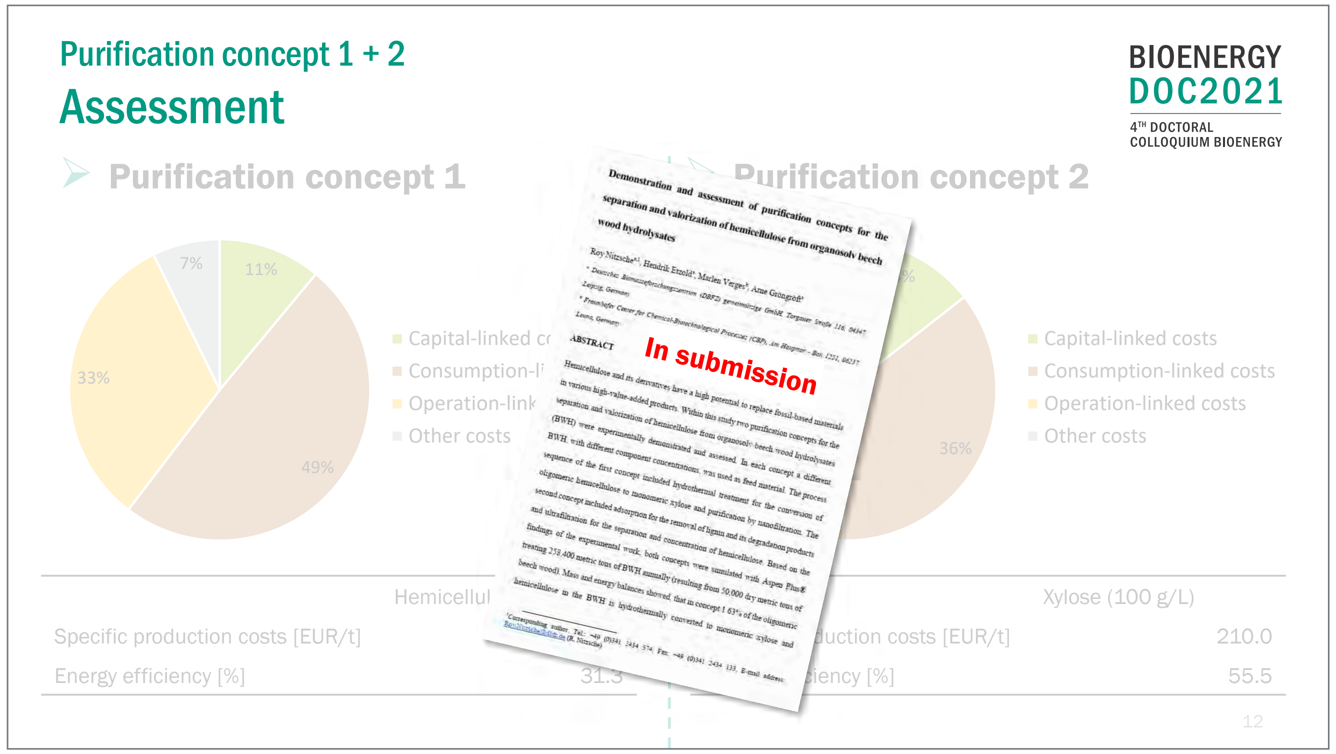
Nanofiltration

- Purification and concentra… xylose by nanofiltration

Nanofiltration of Organosolv Hemicellulose Hydrolyzate: Influence of Hydrothermal Pretreatment and Membrane Characteristics on Filtration Performance and Fouling

Roy Nitzsche,* Jakob Köchermann, Arne Gröngröft, and Matthias Kraume

Nitzsche, R., Köcherman, J., Gröngröft, A., Kraume, M., 2021. Nanofiltration of Organosolv Hemicellulose … fluence of Hydrothermal Pretreatment and Membrane Characteristics on Filtration Performance and Fouling. Industrial & Engineering Chemistry Research 60, 916-930.



Purification concept 1 + 2

Assessment

- Purification concept 1
- Purification concept 2

	Hemicellul
Specific production costs [EUR/t]	
Energy efficiency [%]	31.3

	Xylose (100 g/L)
duction costs [EUR/t]	210.0
iency [%]	55.5

Demonstration and assessment of purification concepts for the separation and valorization of hemicellulose from organosolv beech wood hydrolysates

Roy Nitzsche[a,*], Hendrik Etzold[a], Marlen Verges[b], Arne Gröngröft[a]

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[b] Fraunhofer Center for Chemical-Biotechnological Processes (CBP), Am Haupttor – Bau 1251, 06237 Leuna, Germany

In submission

ABSTRACT

Hemicellulose and its derivatives have a high potential to replace fossil-based materials in various high-value-added products. Within this study two purification concepts for the separation and valorization of hemicellulose from organosolv beech wood hydrolysates (BWH) were experimentally demonstrated and assessed. In each concept a different BWH with different component concentrations, was used as feed material. The process sequence of the first concept included hydrothermal treatment for the conversion of oligomeric hemicellulose to monomeric xylose and purification by nanofiltration. The second concept included adsorption for the removal of lignin and its degradation products and ultrafiltration for the separation and concentration of hemicellulose. Based on the findings of the experimental work, both concepts were simulated with Aspen Plus® treating 258,400 metric tons of BWH annually (resulting from 50,000 dry metric tons of beech wood). Mass and energy balances showed that in concept 1 63% of the oligomeric hemicellulose in the BWH is hydrothermally converted to monomeric xylose and

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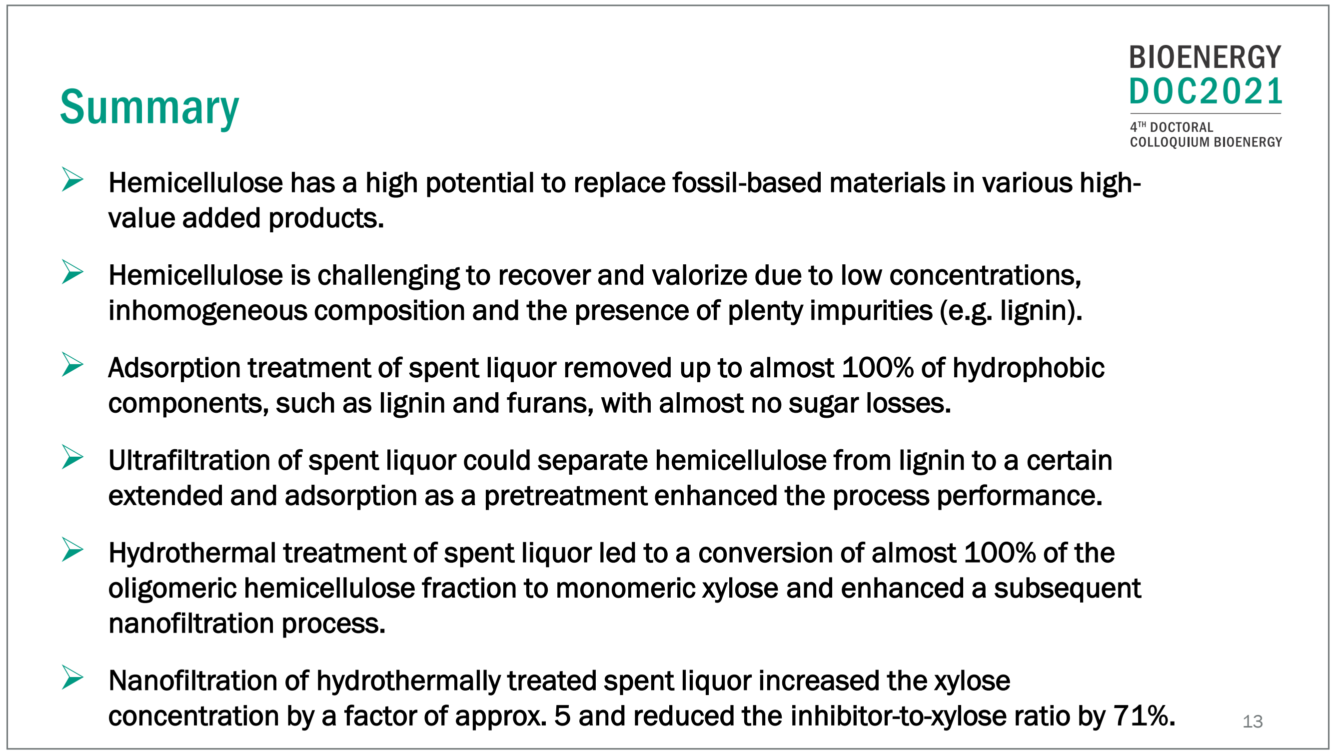

Summary

- Hemicellulose has a high potential to replace fossil-based materials in various high-value added products.
- Hemicellulose is challenging to recover and valorize due to low concentrations, inhomogeneous composition and the presence of plenty impurities (e.g. lignin).
- Adsorption treatment of spent liquor removed up to almost 100% of hydrophobic components, such as lignin and furans, with almost no sugar losses.
- Ultrafiltration of spent liquor could separate hemicellulose from lignin to a certain extended and adsorption as a pretreatment enhanced the process performance.
- Hydrothermal treatment of spent liquor led to a conversion of almost 100% of the oligomeric hemicellulose fraction to monomeric xylose and enhanced a subsequent nanofiltration process.
- Nanofiltration of hydrothermally treated spent liquor increased the xylose concentration by a factor of approx. 5 and reduced the inhibitor-to-xylose ratio by 71%.

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ORAL PRESENTATIONS

SESSION VI

THERMOCHEMICAL CONVERSION

Przemyslaw Maziarka, University of Hohenheim

Performance of the CFD model of the pyrolysis of a single cylindrical and spherical maple wood particles in a thermally thick regime over a range of temperatures and sizes

Przemyslaw Maziarka, Andrés Anca-Couce, Andrea Kruse, Frederik Ronsse
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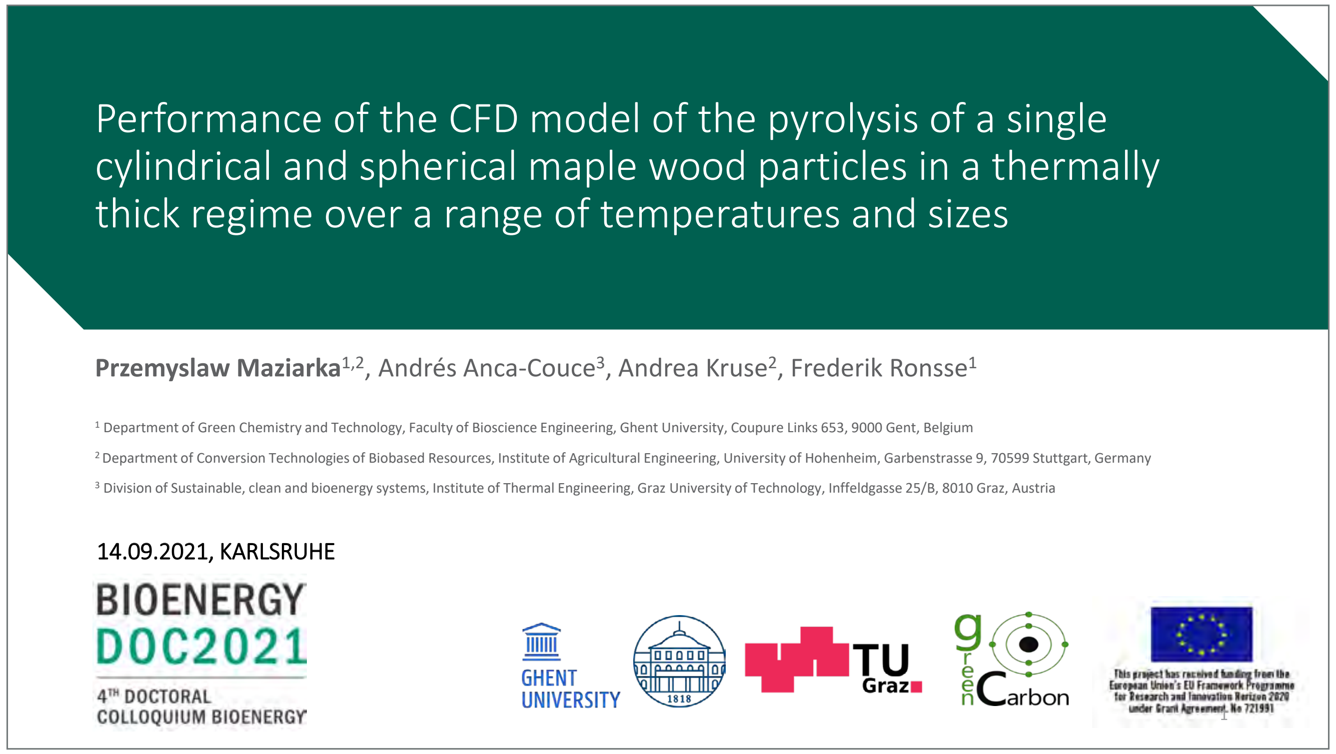
Predicting pyrolytic conversion of larger particles of wood (thermally thick regime) is a complex task due to heat transfer limitations, which detailed influence is still not fully known. The CFD modelling allows for the real-time investigation of parameters that are impossible to be analysed experimentally. That can provide new insights into the conversion mechanism and help to fill the knowledge gaps. The aim of this study was to establish a comprehensive single particle model of wood pyrolysis in the thick regime, valid over a wide range of parameters, to serve as a reliable tool for process optimisation and products tailoring.

The investigation was based on the 2D-axisymmetrical models of the particles (without surrounding), developed in the commercial software COMSOL (TM) v5.3. The particles were modelled as the porous matter with solid and fluid phase. As the kinetic was used the RAC scheme. Models included heat transfer (conduction, convection, and radiation), the vapours flow (Darcy's) and mass diffusion (Fick's), but not shrinking (software's limitations).

The thermochemical properties and the boundary conditions were based on the experimental data of (Attreya et al., 2017), also used for the validation. The experimental data consisted results of the maple wood particles with cylindrical shape (D/H [mm/mm] = 10/20, 15/20 and 20/20) and spherical shape (D [mm] = 10, 15 and 20), pyrolysed in temperatures 500 °C, 610 °C, 720 °C and 840 °C (in total 24 scenarios). All models were checked for grid independence to avoid numerical errors in the results of the simulations.

The fit of the predicted profiles of temperature at the centre and mass loss to experimental data was more than satisfactory, considering a broad range of conditions. The absolute error between experimental and predicted char yield was 1.3±0.7 wt. % and 1.8±1.5 wt. % for the spheres and cylinders, respectively. The yields of products per initial mass did not change linearly with the particle's size for the same shape. Such an outcome was assigned to the influence of the heat transfer limitations. The temperature distribution and the release profiles of vapours indicated the existence of the outer thermal layer (c.a. 2.5 mm thickness), which had a significantly higher heating rate than inner areas of a particle.

The developed model is suitable for the detailed investigation of the pyrolysis process. The particle shrinking and the adjustment of the heat transfer has to be implemented to increase the model's accuracy. The existence of the layer has to be experimentally proven considering the numerical foundation of the observation. If confirmed, the relation between, e.g., the thermal conductivity of the wood and the outer layer thickness should be investigated.



Performance of the CFD model of the pyrolysis of a single cylindrical and spherical maple wood particles in a thermally thick regime over a range of temperatures and sizes

Przemyslaw Maziarka[1,2], Andrés Anca-Couce[3], Andrea Kruse[2], Frederik Ronsse[1]

[1] Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, 9000 Gent, Belgium

[2] Department of Conversion Technologies of Biobased Resources, Institute of Agricultural Engineering, University of Hohenheim, Garbenstrasse 9, 70599 Stuttgart, Germany

[3] Division of Sustainable, clean and bioenergy systems, Institute of Thermal Engineering, Graz University of Technology, Inffeldgasse 25/B, 8010 Graz, Austria

14.09.2021, KARLSRUHE

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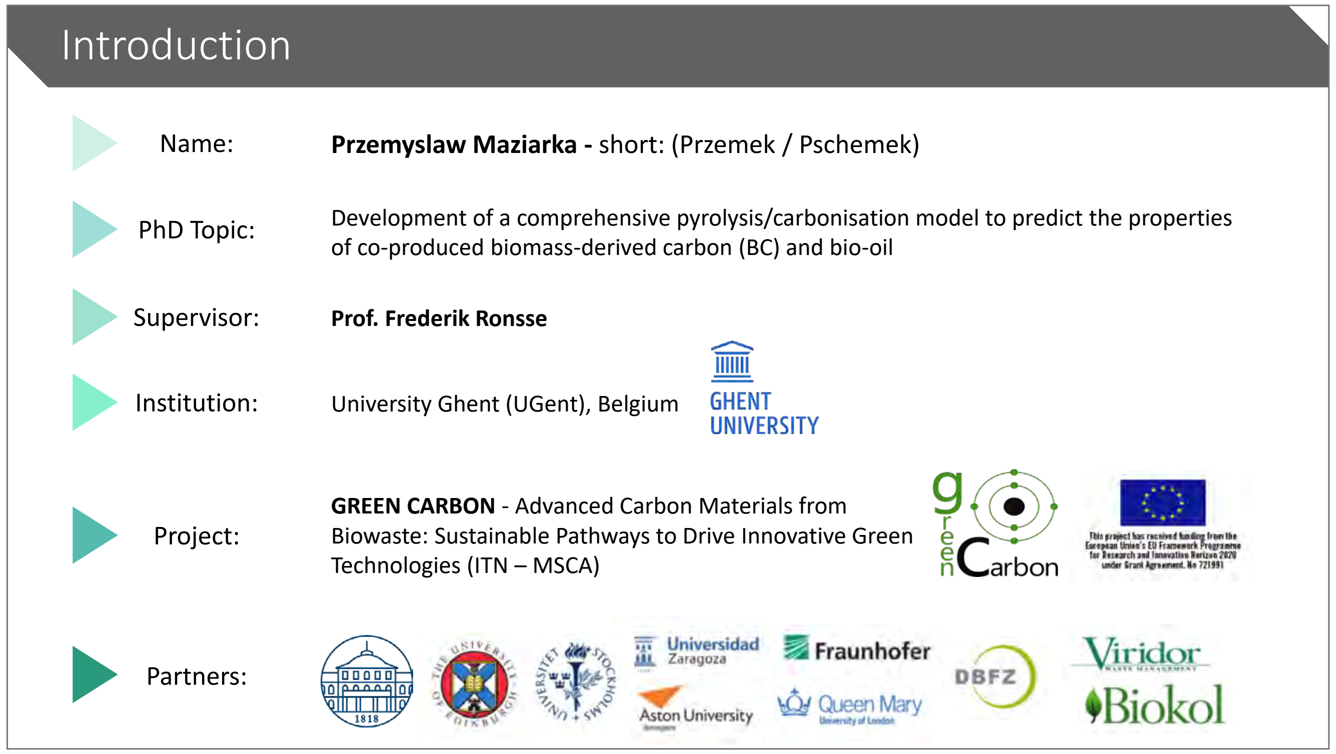
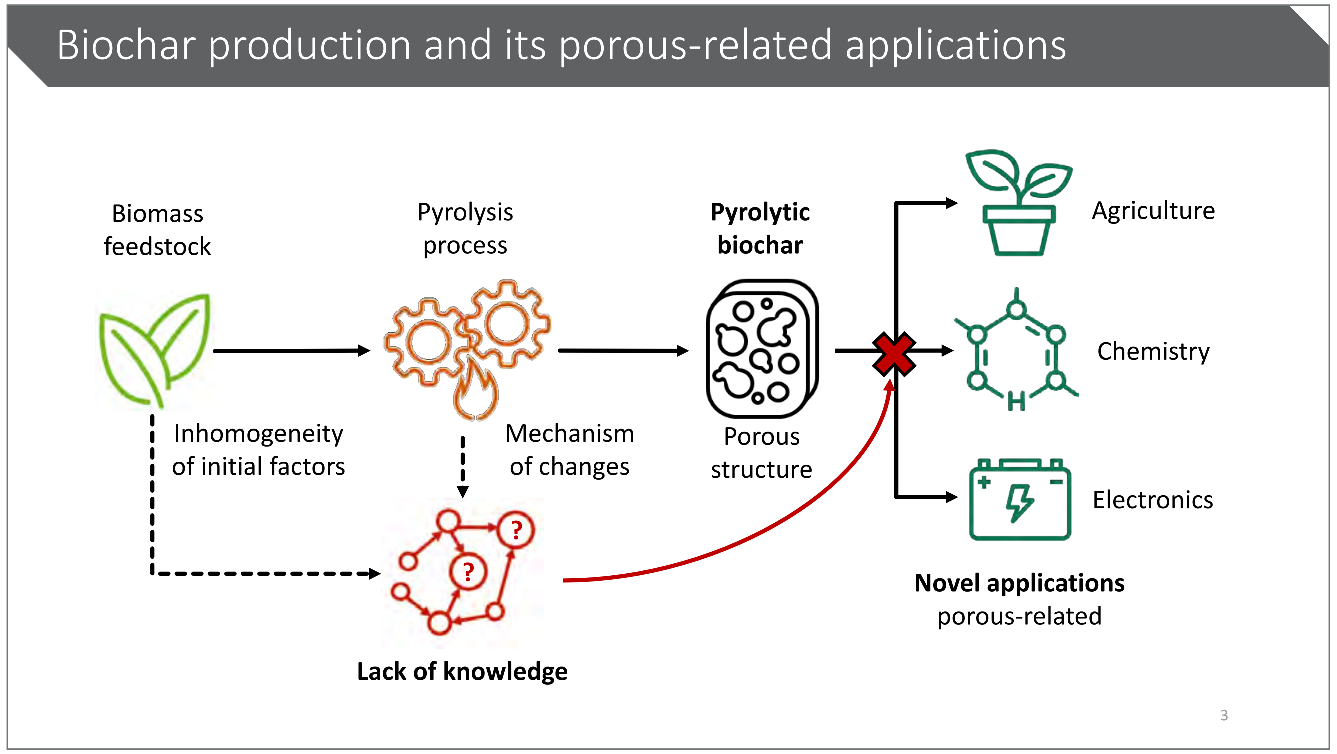
This project has received funding from the European Union's EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement. No 721991



Introduction

Name:	**Przemyslaw Maziarka -** short: (Przemek / Pschemek)
PhD Topic:	Development of a comprehensive pyrolysis/carbonisation model to predict the properties of co-produced biomass-derived carbon (BC) and bio-oil
Supervisor:	**Prof. Frederik Ronsse**
Institution:	University Ghent (UGent), Belgium
Project:	**GREEN CARBON** - Advanced Carbon Materials from Biowaste: Sustainable Pathways to Drive Innovative Green Technologies (ITN – MSCA)
Partners:	

This project has received funding from the European Union's EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement. No 721991



Biochar production and its porous-related applications

Biomass feedstock

Pyrolysis process

Pyrolytic biochar

Inhomogeneity of initial factors

Mechanism of changes

Porous structure

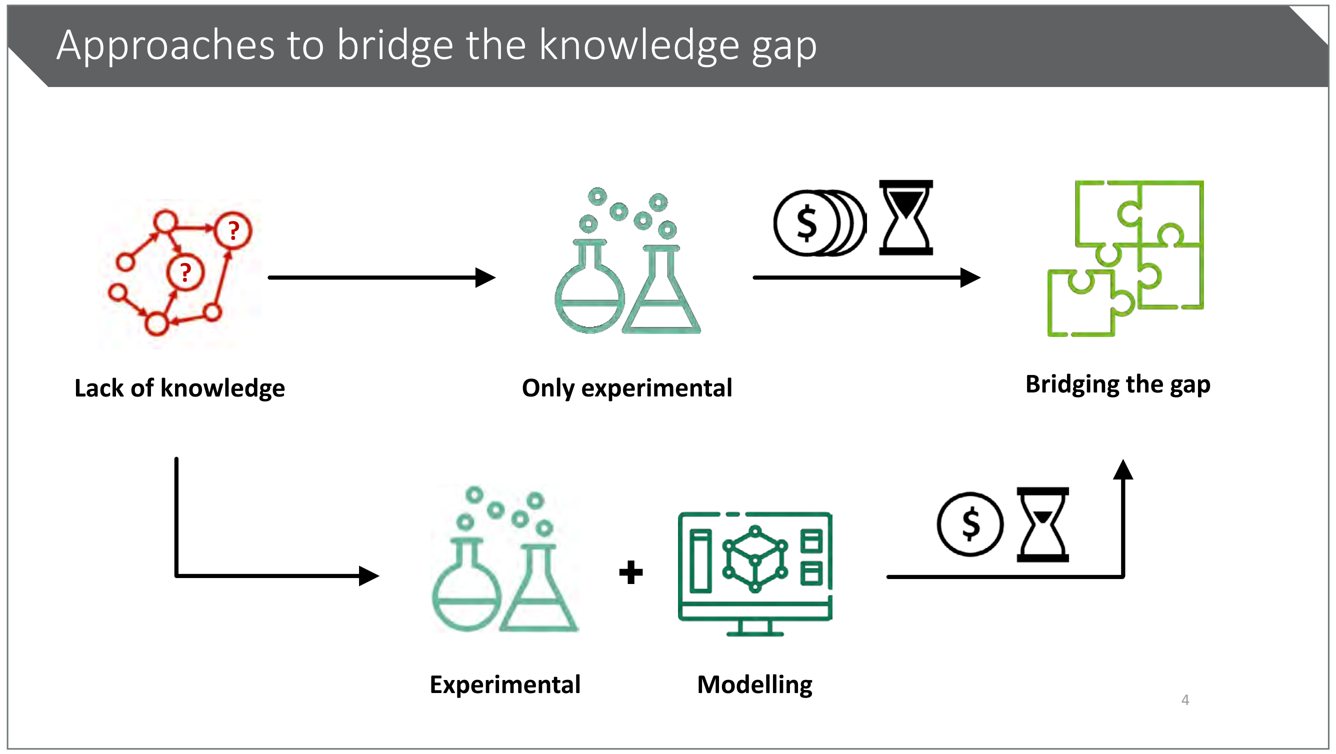
Agriculture

Chemistry

Electronics

Novel applications
porous-related

Lack of knowledge



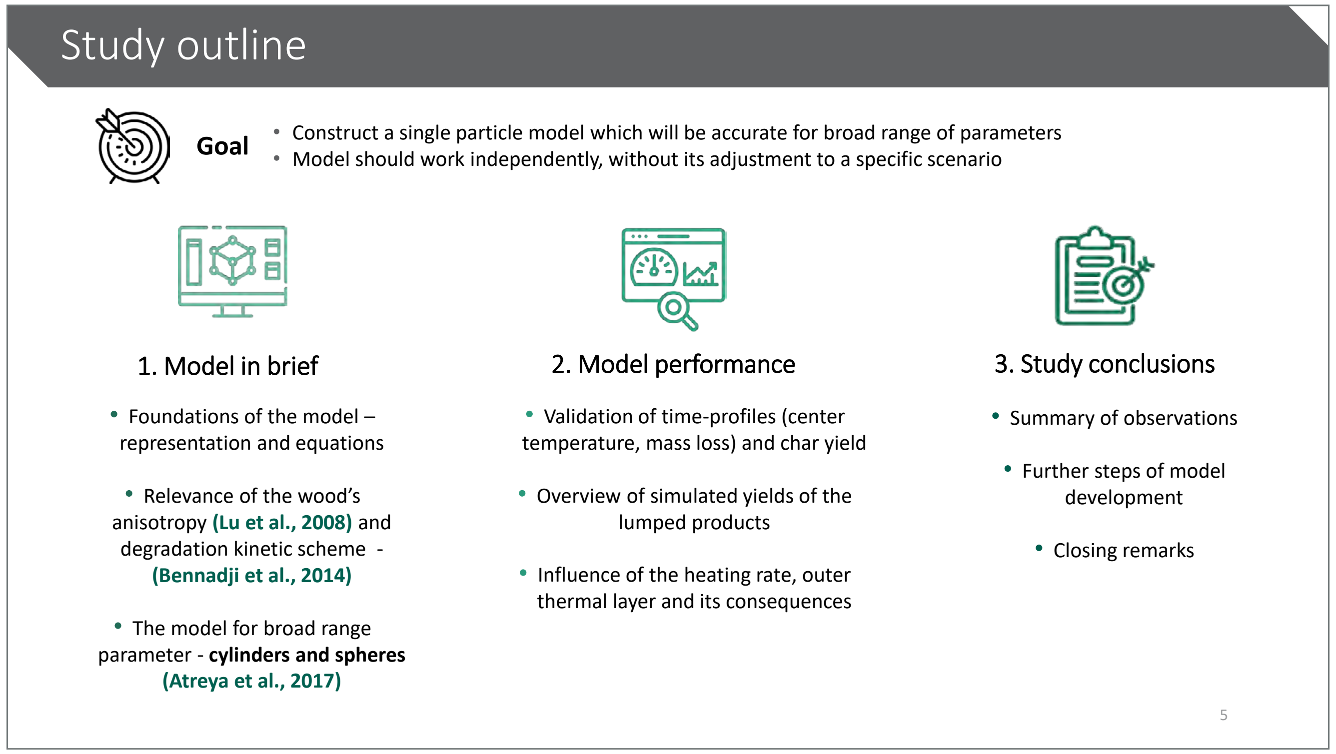
Approaches to bridge the knowledge gap

Lack of knowledge

Only experimental

Bridging the gap

Experimental + **Modelling**



Study outline

Goal

- Construct a single particle model which will be accurate for broad range of parameters
- Model should work independently, without its adjustment to a specific scenario

1. Model in brief

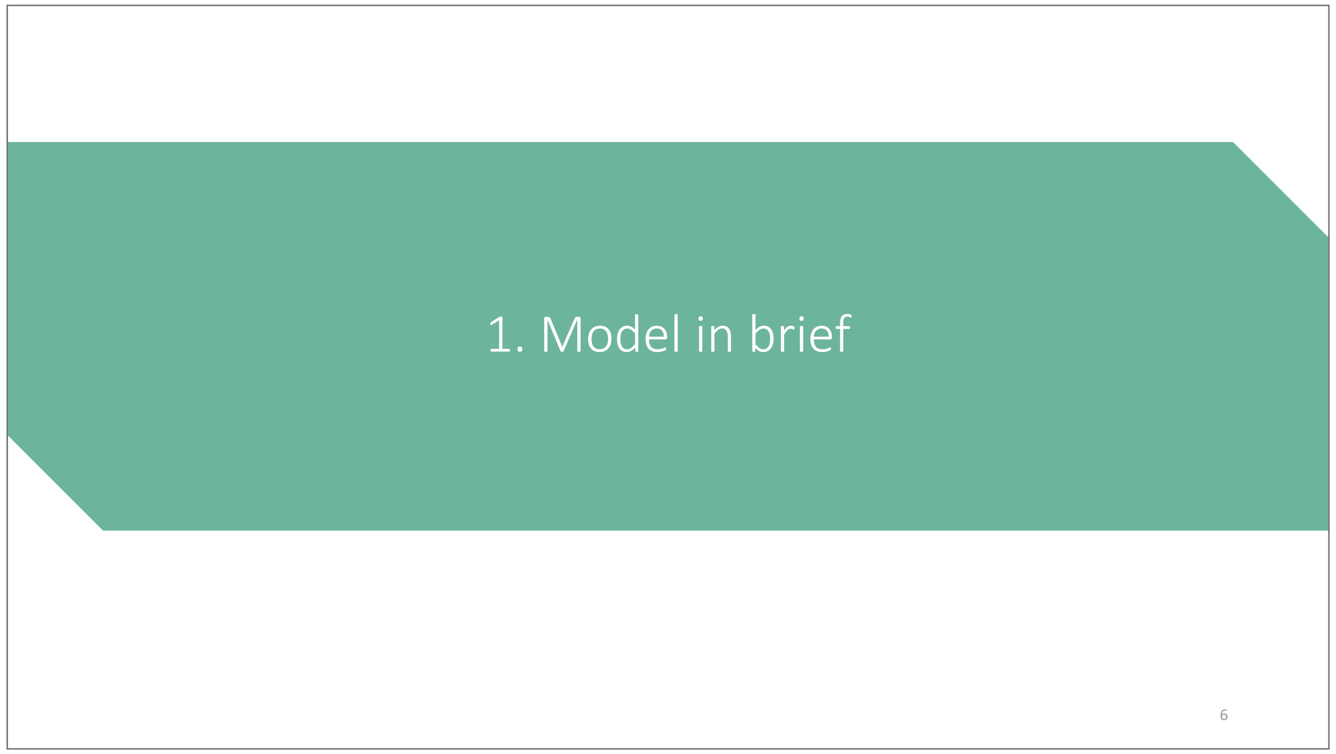
- Foundations of the model – representation and equations
- Relevance of the wood's anisotropy **(Lu et al., 2008)** and degradation kinetic scheme - **(Bennadji et al., 2014)**
- The model for broad range parameter - **cylinders and spheres** **(Atreya et al., 2017)**

2. Model performance

- Validation of time-profiles (center temperature, mass loss) and char yield
- Overview of simulated yields of the lumped products
- Influence of the heating rate, outer thermal layer and its consequences

3. Study conclusions

- Summary of observations
- Further steps of model development
- Closing remarks

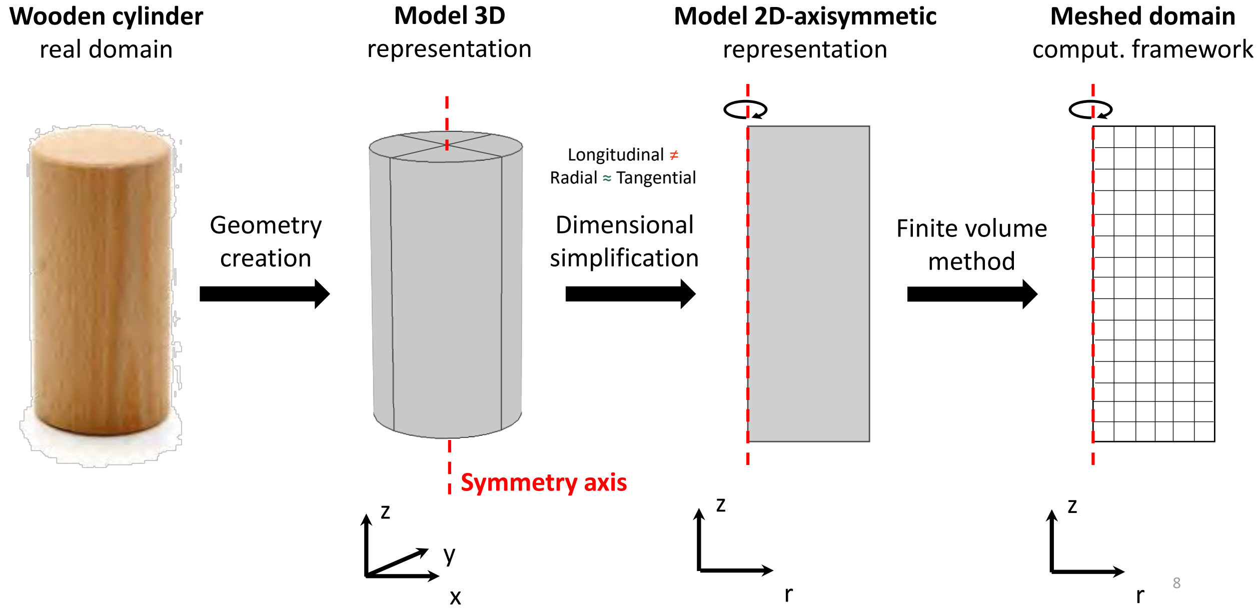


1. Model in brief

1. Model in brief - main assumptions

- The modelled particles = **porous material (wood and char).** No water phase (dry material).
- Intrinsic mass transport = **convection and diffusion**. The mass boundary condition = convective only. The fluid phase as an **ideal gas**.
- Woods and their chars - low gas permeability (flow does not exceed Re =10). The convective flow = **Darcy's description**. The diffusion = **Fick's binary diffusion law**.
- Internal heat transfer = **conduction, convection, and radiation**. The heat boundary = convective and radiative. Sufficiently large Péclet number = **thermal equilibrium** between solid and fluid phase.
- **Shrinking is neglected**. In the software (COMSOL^{TM}, v5.3), not possible to implement the shrinking.
- Model **only covers the particle**, the surrounding environment is not included. The model has **only the primary kinetic scheme** (biomass degradation) and secondary gas-phase reactions are not implemented.
- Wood is initially composed out of 3 base wood constituents: **cellulose, hemicellulose and lignin**.
- **Wood's and char's thermophysical parameters and bio-chemical composition in the model were used directly from the experimental work (if available) and if not, matched from the literature to be as close as possible to the species.**
- **For the main investigation the thermophysical parameters of model were not adjusted between scenario of investigated case, only the boundary temperatures and size and shape of particle.**

1. Model in brief - domain, dimensions and mesh



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1. Model in brief - governing equations and boundary conditions

Mass

Solids

D: $$\frac{\partial}{\partial t} < \rho_{i,s} >= \dot{\omega}_{i,s}$$

B: $$D_{eff}\nabla(< \rho_s >)\,|_{x=x_B} = 0$$

Fluid

D: $$\frac{\partial}{\partial t} < \rho_i > +\nabla < u_G \rho_i >= \dot{\omega}_i$$

B: $$D_{eff}\nabla(< \rho_i >^G)\,|_{x=x_B} = h_m[\,\rho_{i,\infty} - < \rho_i >^G\,|_{x=x_B}]$$

Flow

Fluid

D: $$< u_G >= \frac{K_{G,eff}}{\mu_G}\nabla(< P_G >)$$

B: $$< P_G >\,|_{x=x_B} = P_\infty$$

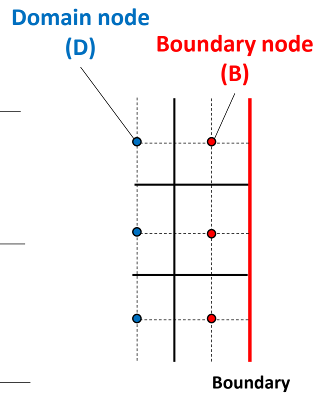
Energy

Accumulation — Convection — Conduction + Radiation — Reaction

D: $$\frac{\partial T}{\partial t}(< \rho_S > C_{P,S} + \varepsilon_G < \rho_G >^G C_{P,G}) + \nabla T\left(\varepsilon_G \sum_{i=1}^{N} < u_i \rho_i > C_{P,i}\right) = \nabla(\lambda_{eff}\nabla T) + Q$$

Conduction — Convection — Radiation

B: $$\nabla(\lambda_{eff}\nabla T)\,|_{x=x_B} = h_T(T_{flow,\infty} - T\,|_{x=x_B}) + \sigma\omega(T_{wall}^4 - T^4|_{x=x_B})$$



1. Model in brief – parameters of the main model

Accuracy over broad range based on **Atreya et al. (2017)**
Standard and missing, specific parameters (**maple wood**) from literature

Standard thermophysical parameters

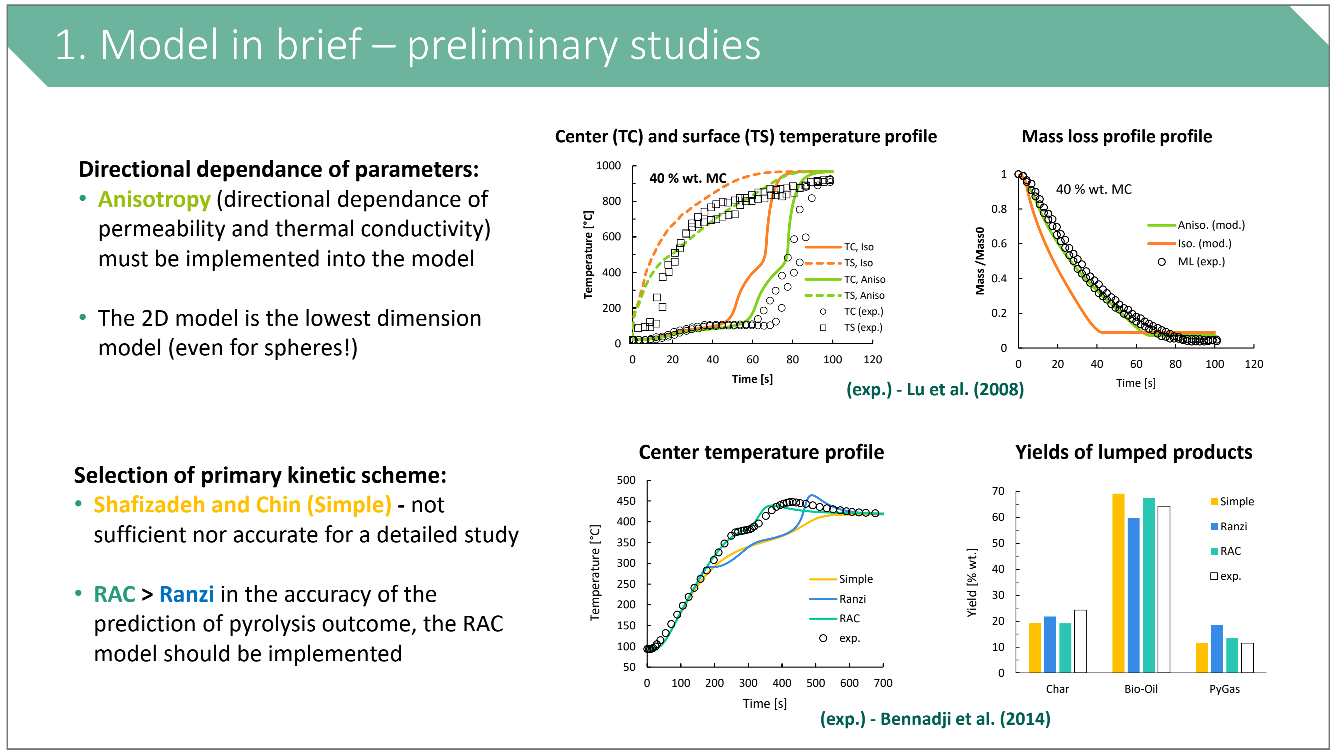
Parameter	Symbol	Unit	Formulation
True density			
Solid	$< \rho_S >^S$	[kg/m³]	1500
Thermal conductivity			
Gas	λ_G	[W/(m·K)]	0.026
Heat capacity			
Biomass (BS)	$C_{P,S}$	[kJ/(kg·K)]	$1.50 + (1 \cdot 10^{-3} \cdot T)$
Char/Metaphase (C/CM)	$C_{P,C}$	[kJ/(kg·K)]	$0.42 + (2.09 \cdot 10^{-3} \cdot T) - (6.85 \cdot 10^{-7} \cdot T^2)$
Pyrolysis gas (PG)	$C_{P,PG}$	[kJ/(kg·K)]	$0.77 + (6.29 \cdot 10^{-4} \cdot T) - (1.91 \cdot 10^{-7} \cdot T^2)$
Condensables Light/Heavy (CD/T)	$C_{P,CD}, C_{P,T}$	[kJ/(kg·K)]	$-0.10 + (4.40 \cdot 10^{-3} \cdot T) - (1.57 \cdot 10^{-6} \cdot T^2)$
Air	$C_{P,air}$	[kJ/(kg·K)]	$0.95 + (1.88 \cdot 10^{-4} \cdot T)$
Water Vapour (V)	$C_{P,V}$	[kJ/(kg·K)]	$1.67 + (6.40 \cdot 10^{-4} \cdot T)$
Viscosity			
Gas	μ_G	[Pa·s]	$3 \cdot 10^{-5}$
Surface emissivity			
Biomass	$\omega_{Biomass}$	[-]	0.70
Char/Metaphase	ω_{Char}	[-]	0.92
Macropore size			
Biomass	$d_{biomass}$	[m]	$5 \cdot 10^{-5}$
Char/Metaphase	d_{char}	[m]	$1 \cdot 10^{-4}$

Specific thermophysical parameters

Parameter	Symbol	Unit	Value
Particle	Cylinder, dry maple wood		
Diameters	$D1$	[mm]	10
	$D2$		15
	$D3$		20
Height	H	[mm]	20
Moisture content	MC	[-]	0
Bulk density (dry)	$< \rho_S >$	[kg/m³]	630
Biocomponents share			
Cellulose (CELL)	c_{CELL}	[wt. %]	42.20
Hemicellulose (HCE)	c_{HCE}	[wt. %]	32.30
H-rich lignin (LIG-H)	c_{LIGH}	[wt. %]	16.51
O-rich lignin (LIG-O)	c_{LIGO}	[wt. %]	5.59
C-rich lignin (LIG-C)	c_{LIGC}	[wt. %]	3.30
Thermal conductivity			
Biomass (L)	$\lambda_{Biomass,L}$	[W/(m·K)]	0.255
Biomass (R)	$\lambda_{Biomass,R}$	[W/(m·K)]	0.115
Char (L)	$\lambda_{Char,L}$	[W/(m·K)]	0.105
Char (R)	$\lambda_{Char,R}$	[W/(m·K)]	0.081
Permeability			
Biomass (L)	$K_{Biomass,L}$	[m²]	$1{\cdot}10^{-14}$
Biomass (R)	$K_{Biomass,R}$	[m²]	$1{\cdot}10^{-16}$
Char (L)	$K_{Char,L}$	[m²]	$5{\cdot}10^{-13}$
Char (R)	$K_{Char,R}$	[m²]	$5{\cdot}10^{-14}$
Boundary temperature			
Gas	$T_{Gas,500\,°C}$	[°C]	**494 ± 13**
	$T_{Gas,610\,°C}$		**603 ± 6**
	$T_{Gas,720\,°C}$		**714 ± 8**
	$T_{Gas,840\,°C}$		**838 ± 18**
Wall	$T_{Wall,500\,°C}$	[°C]	**509 ± 13**
	$T_{Wall,610\,°C}$		**618 ± 6**
	$T_{Wall,720\,°C}$		**726 ± 8**
	$T_{Wall,840\,°C}$		**850 ± 18**
Initial	T_{Ini}	[°C]	40

Modelled compounds and lumping (RAC)

Abbreviation	Name	Composition	Molar mass [kg/mol]
Biomass (BM)			
Cellulose (CELL)			
CELL	Cellulose raw	$C_5H_8O_4$	132.1
CELLA	Activated cellulose	$C_5H_8O_4$	132.1
Hemicellulose (HCE)			
HCE	Hemicellulose raw	$C_5H_8O_4$	132.1
HCE1	Activated hemicellulose 1	$C_5H_8O_4$	132.1
HCE2	Activated hemicellulose 2	$C_5H_8O_4$	132.1
Lignin (LIG)			
LIGC	Carbon-rich lignin	$C_{15}H_{14}O_4$	258.3
LIGH	Hydrogen-rich lignin	$C_{22}H_{28}O_9$	436.5
LIGO	Oxygen-rich lignin	$C_{20}H_{22}O_{10}$	422.4
LIGCC	Carbon-rich lignin 2	$C_{15}H_{14}O_4$	258.3
LIGOH	OH-rich lignin	$C_{19}H_{22}O_8$	378.4
LIG	Low molecular lignin	$C_{11}H_{12}O_4$	208.2
Biochar (BC)			
Metaphase (GX)			
G[H2]	Trapped H2	H_2	2.0
G[CO]	Trapped CO	CO	28.0
G[CO2]	Trapped CO2	CO_2	44.0
G[CH4]	Trapped CH4	CH_4	16.1
G[C2H4]	Trapped C2H4	C_2H_4	28.1
G[C2H6]	Trapped C2H6	C_2H_6	30.1
G[COH2]	Trapped COH2	CH_2O	30.0
G2[COH2]	Trapped COH2 (2)	CH_2O	30.0
G3[COH2]	Trapped COH2 (3)	CH_2O	30.0
G[COH2]S	Trapped COH2 stiff	CH_2O	30.0
G[COH2]L	Trapped COH2 loose	CH_2O	30.0
G[MeOH]	Trapped Methanol	CH_4O	30.0
G[PhOH]	Trapped Phenol	C_6H_6O	94.1
Char (Char)			
Char	Char	C	12.0
Volatiles (G)			
Permanent gases (PG)			
H2	Hydrogen	H_2	2.0
CO	Carbon monoxide	CO	28.0
CO2	Carbon dioxide	CO_2	44.0
CH4	Methane	CH_4	16.1
C2H4	Ethen	C_2H_4	28.1
C2H6	Ethan	C_2H_6	30.1
Light condensables (CM)			
H2O	Water vapour	H_2O	18.0
MeOH	Methanol	CH_4O	32.1
EtOH	Ethanol	C_2H_6O	46.1
MeALD	Formaldehyde	CH_2O	30.0
EtALD	Ethanal	C_2H_4O	44.1
GLYOX	Glyoxal	$C_2H_2O_2$	58.0
PrALD	Propanal	C_3H_6O	58.1
HPrALD	Hydroxypropanal	$C_3H_6O_2$	74.1
MeAC	Formic acid	CH_2O_2	46.0
EtAC	Acetic acid	$C_2H_4O_2$	60.1
HAA	Hydroxyacetaldehyde	$C_2H_4O_2$	60.1
ACROL	Acrolein	C_3H_4O	56.1
Heavy condensables (T)			
LVG	Levoglucosan	$C_6H_{10}O_5$	162.2
XYL	Xylose monomer	$C_5H_8O_4$	132.1
FURF	Furfural	$C_5H_4O_2$	96.1
HMFU	5-hydroxymethyl-furfural	$C_6H_6O_3$	126.1
PhOH	Phenol	C_6H_6O	94.1
pCUML	Paracoumaryl alcohol	$C_9H_{10}O_2$	150.2
FE2CR	Sinapyl aldehyde	$C_{11}H_{12}O_4$	208.2
VNL	Vanillin	$C_8H_8O_3$	152.2
ANISOL	Anisole	C_7H_8O	108.2
CRSL	Cresol	C_7H_8O	108.2
CHPRN	Chloropiryn	$C_{24}H_{28}O_4$	380.5



1. Model in brief – preliminary studies

Directional dependance of parameters:

- **Anisotropy** (directional dependance of permeability and thermal conductivity) must be implemented into the model
- The 2D model is the lowest dimension model (even for spheres!)

Selection of primary kinetic scheme:

- **Shafizadeh and Chin (Simple)** - not sufficient nor accurate for a detailed study
- **RAC** > **Ranzi** in the accuracy of the prediction of pyrolysis outcome, the RAC model should be implemented

Center (TC) and surface (TS) temperature profile

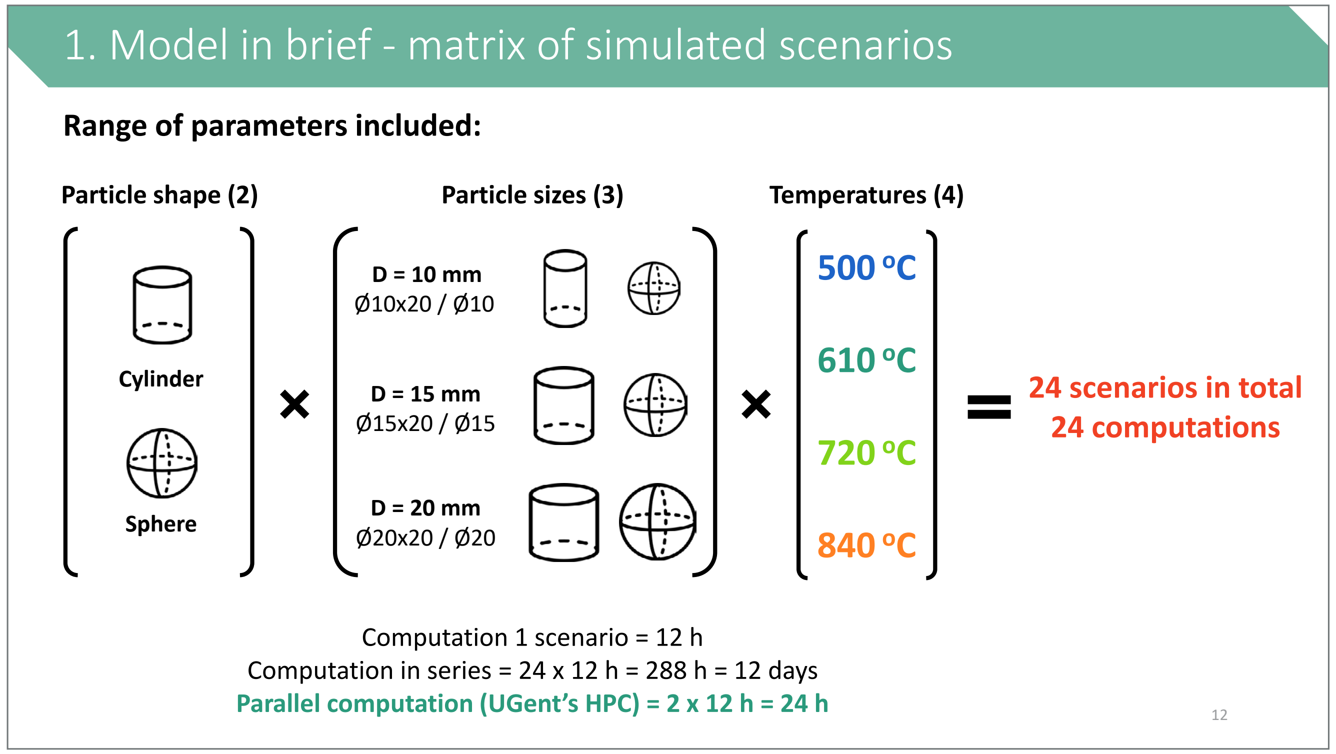
Mass loss profile profile

(exp.) - Lu et al. (2008)

Center temperature profile

Yields of lumped products

(exp.) - Bennadji et al. (2014)



1. Model in brief - matrix of simulated scenarios

Range of parameters included:

Particle shape (2)

Cylinder

Sphere

×

Particle sizes (3)

D = 10 mm
Ø10x20 / Ø10

D = 15 mm
Ø15x20 / Ø15

D = 20 mm
Ø20x20 / Ø20

×

Temperatures (4)

500 °C

610 °C

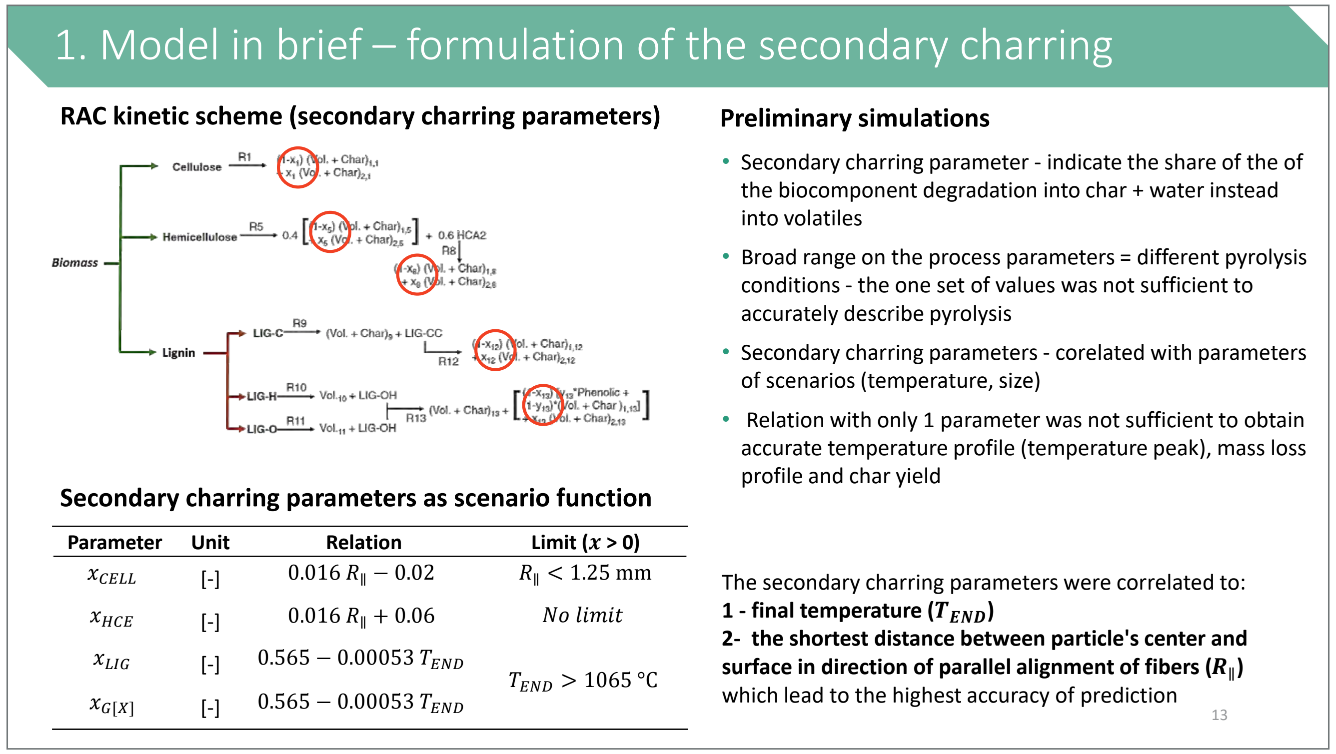
720 °C

840 °C

=

24 scenarios in total
24 computations

Computation 1 scenario = 12 h
Computation in series = 24 x 12 h = 288 h = 12 days
Parallel computation (UGent's HPC) = 2 x 12 h = 24 h



1. Model in brief – formulation of the secondary charring

RAC kinetic scheme (secondary charring parameters)

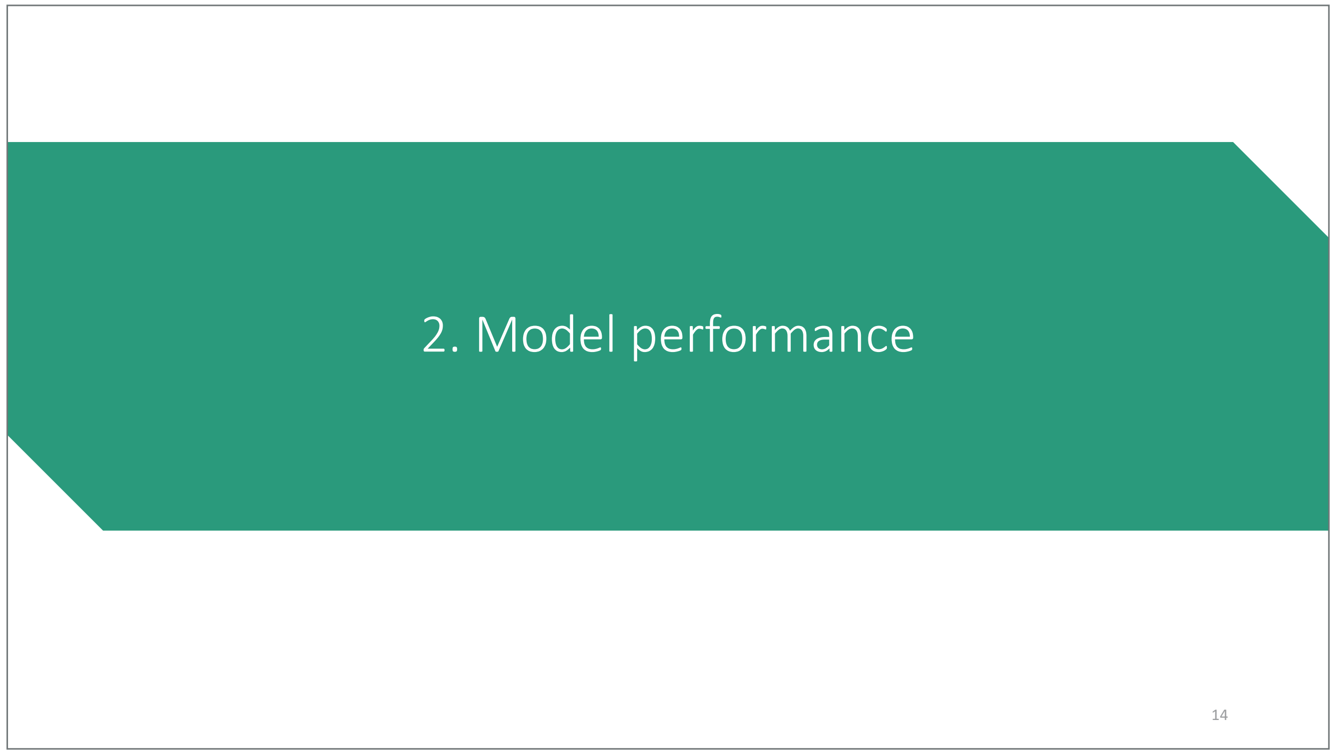
Secondary charring parameters as scenario function

Parameter	Unit	Relation	Limit ($x > 0$)
x_{CELL}	[-]	$0.016\,R_{\parallel} - 0.02$	$R_{\parallel} < 1.25$ mm
x_{HCE}	[-]	$0.016\,R_{\parallel} + 0.06$	*No limit*
x_{LIG}	[-]	$0.565 - 0.00053\,T_{END}$	$T_{END} > 1065$ °C
$x_{G[X]}$	[-]	$0.565 - 0.00053\,T_{END}$	

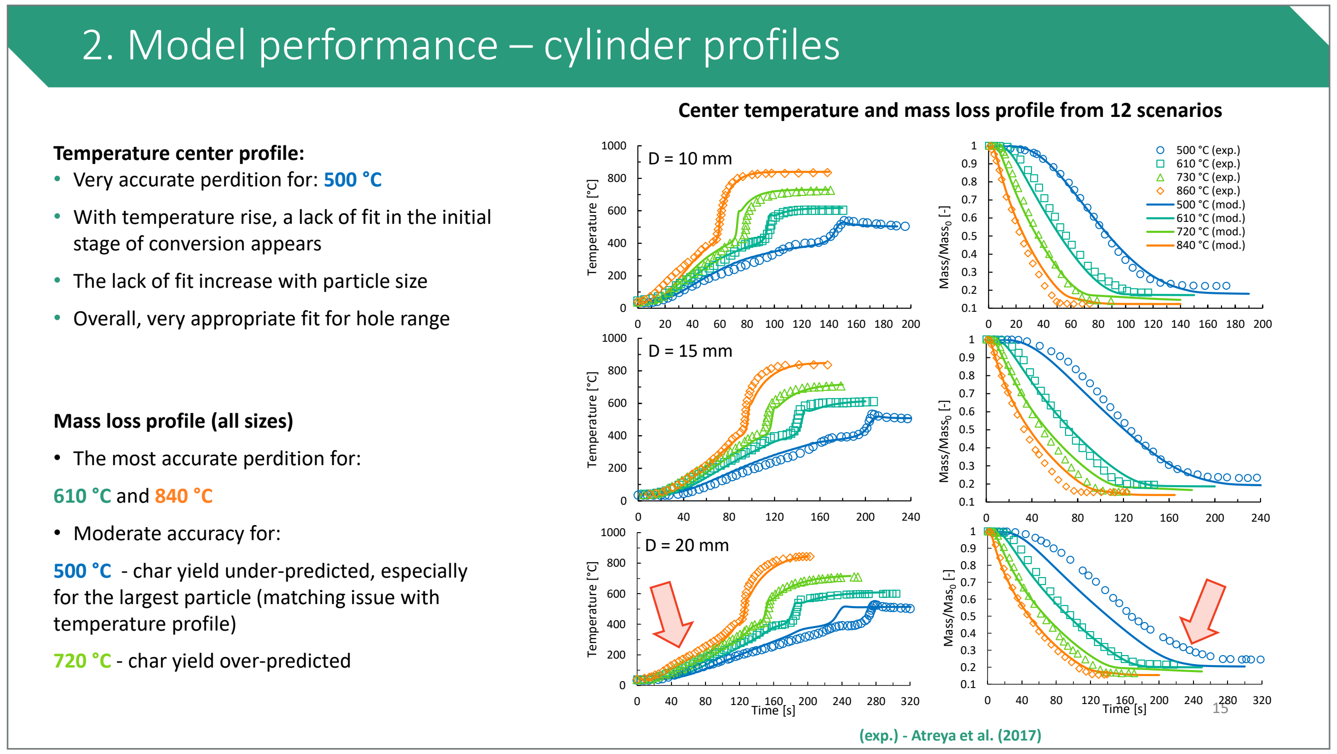
Preliminary simulations

- Secondary charring parameter - indicate the share of the of the biocomponent degradation into char + water instead into volatiles
- Broad range on the process parameters = different pyrolysis conditions - the one set of values was not sufficient to accurately describe pyrolysis
- Secondary charring parameters - corelated with parameters of scenarios (temperature, size)
- Relation with only 1 parameter was not sufficient to obtain accurate temperature profile (temperature peak), mass loss profile and char yield

The secondary charring parameters were correlated to:
1 - final temperature (T_{END})
2- the shortest distance between particle's center and surface in direction of parallel alignment of fibers ($R_{\parallel}$)
which lead to the highest accuracy of prediction



2. Model performance



2. Model performance – cylinder profiles

Center temperature and mass loss profile from 12 scenarios

Temperature center profile:

- Very accurate perdition for: 500 °C
- With temperature rise, a lack of fit in the initial stage of conversion appears
- The lack of fit increase with particle size
- Overall, very appropriate fit for hole range

Mass loss profile (all sizes)

- The most accurate perdition for:

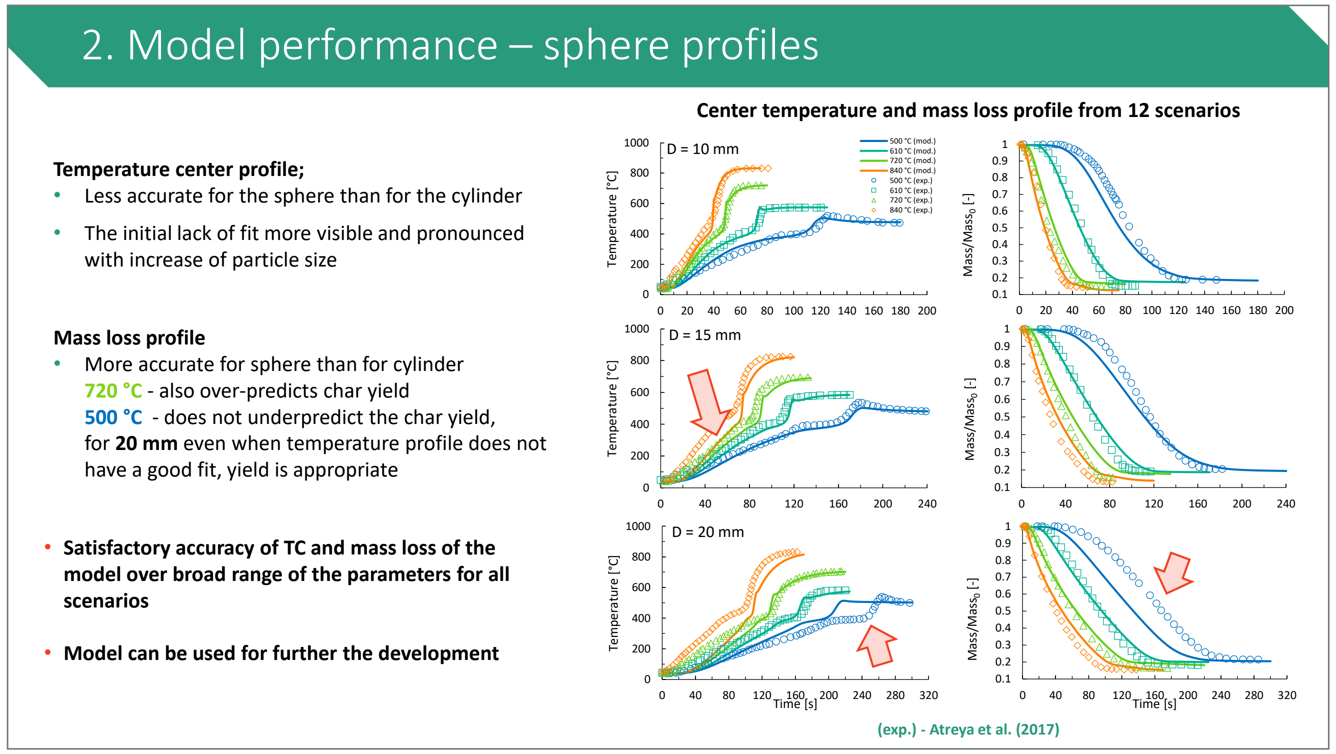
610 °C and 840 °C

- Moderate accuracy for:

500 °C - char yield under-predicted, especially for the largest particle (matching issue with temperature profile)

720 °C - char yield over-predicted

(exp.) - Atreya et al. (2017)



2. Model performance – sphere profiles

Center temperature and mass loss profile from 12 scenarios

Temperature center profile;

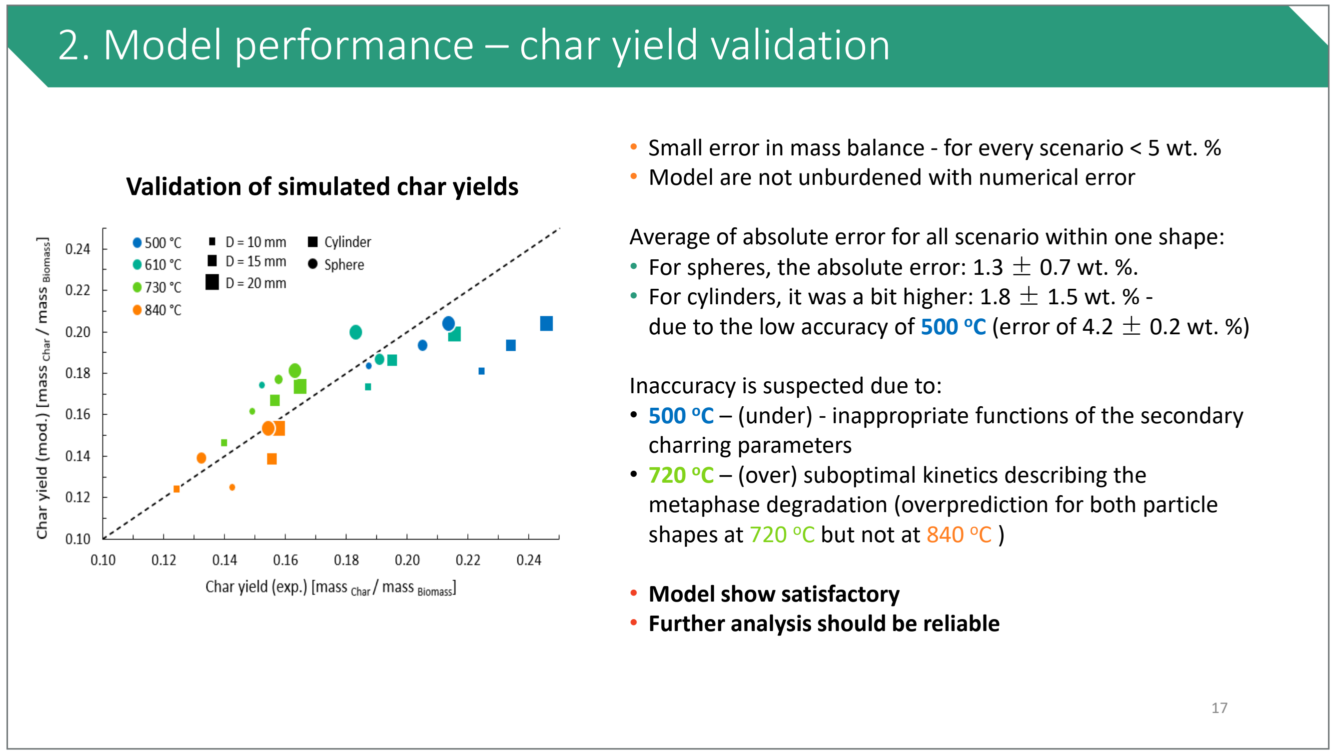
- Less accurate for the sphere than for the cylinder
- The initial lack of fit more visible and pronounced with increase of particle size

Mass loss profile

- More accurate for sphere than for cylinder
  720 °C - also over-predicts char yield
  500 °C - does not underpredict the char yield, for **20 mm** even when temperature profile does not have a good fit, yield is appropriate

- **Satisfactory accuracy of TC and mass loss of the model over broad range of the parameters for all scenarios**
- **Model can be used for further the development**

(exp.) - Atreya et al. (2017)



2. Model performance – char yield validation

Validation of simulated char yields

- Small error in mass balance - for every scenario < 5 wt. %
- Model are not unburdened with numerical error

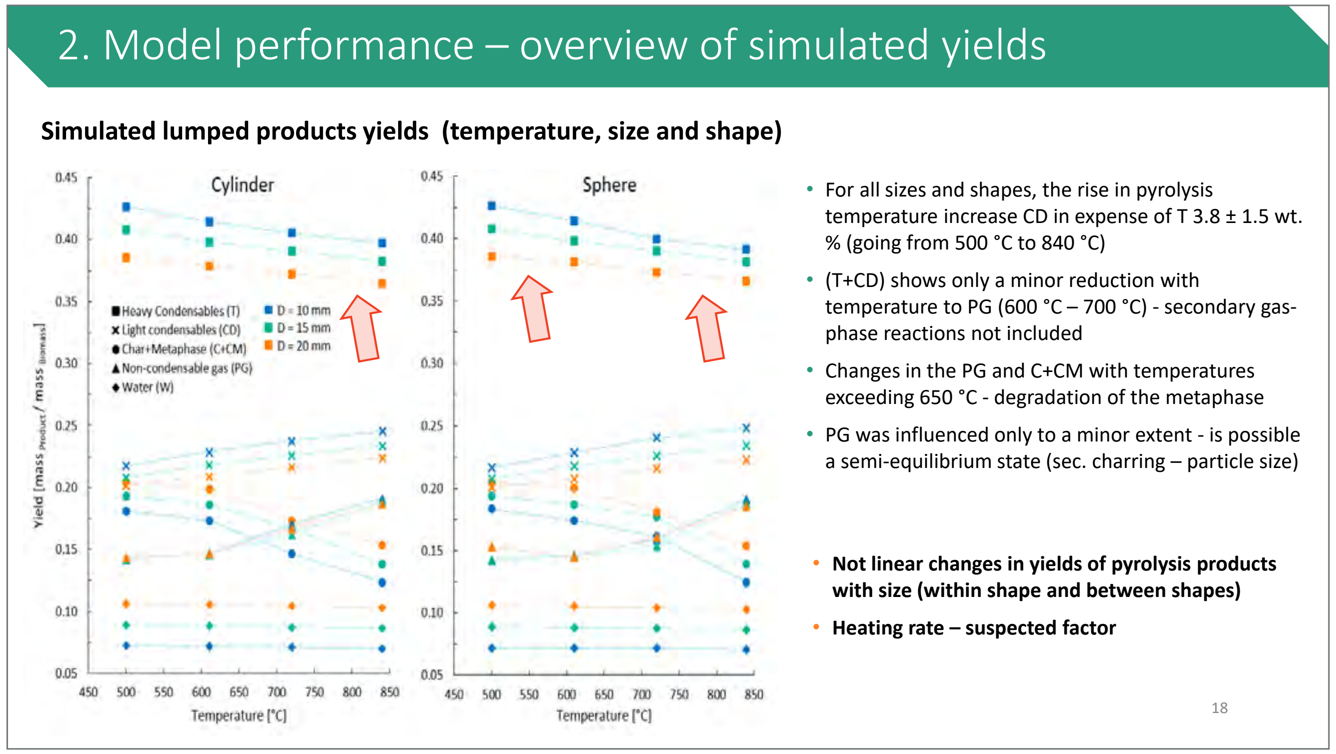
Average of absolute error for all scenario within one shape:

- For spheres, the absolute error: 1.3 ± 0.7 wt. %.
- For cylinders, it was a bit higher: 1.8 ± 1.5 wt. % - due to the low accuracy of 500 °C (error of 4.2 ± 0.2 wt. %)

Inaccuracy is suspected due to:

- 500 °C – (under) - inappropriate functions of the secondary charring parameters
- 720 °C – (over) suboptimal kinetics describing the metaphase degradation (overprediction for both particle shapes at 720 °C but not at 840 °C)

- **Model show satisfactory**
- **Further analysis should be reliable**

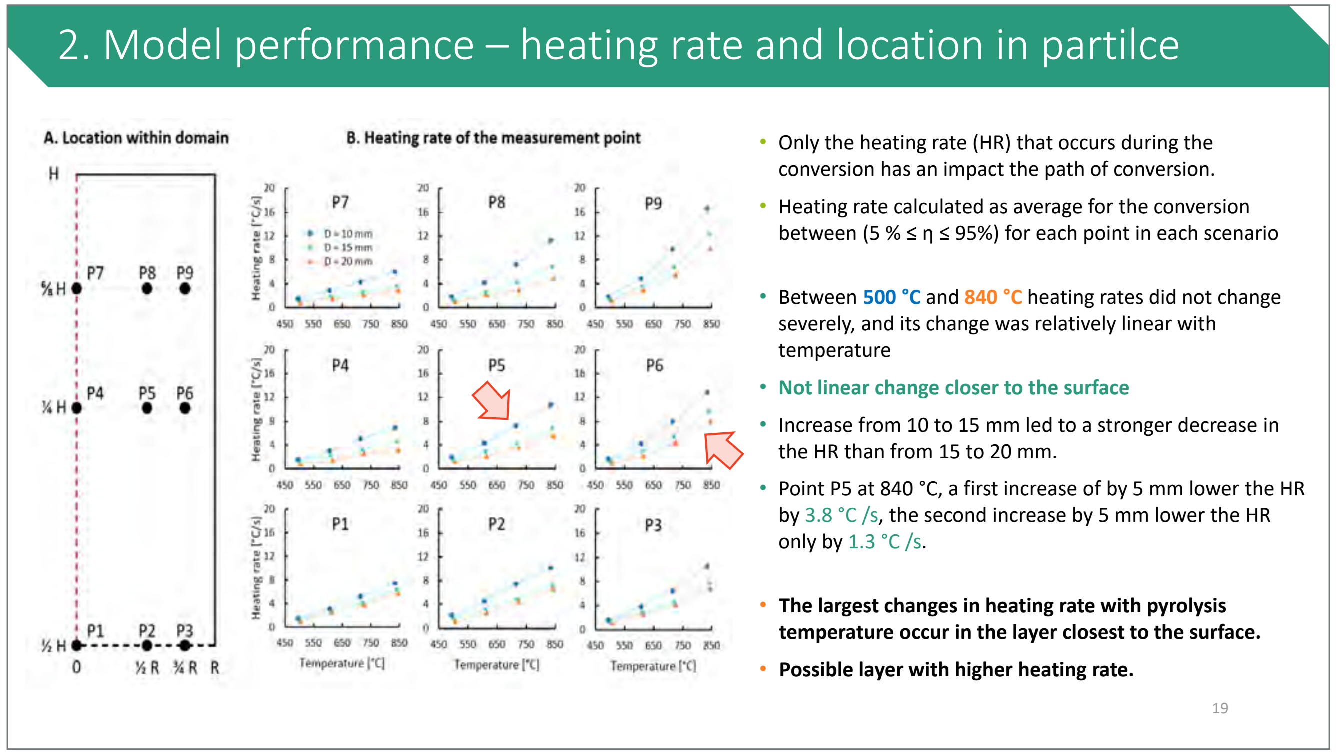


2. Model performance – overview of simulated yields

Simulated lumped products yields (temperature, size and shape)

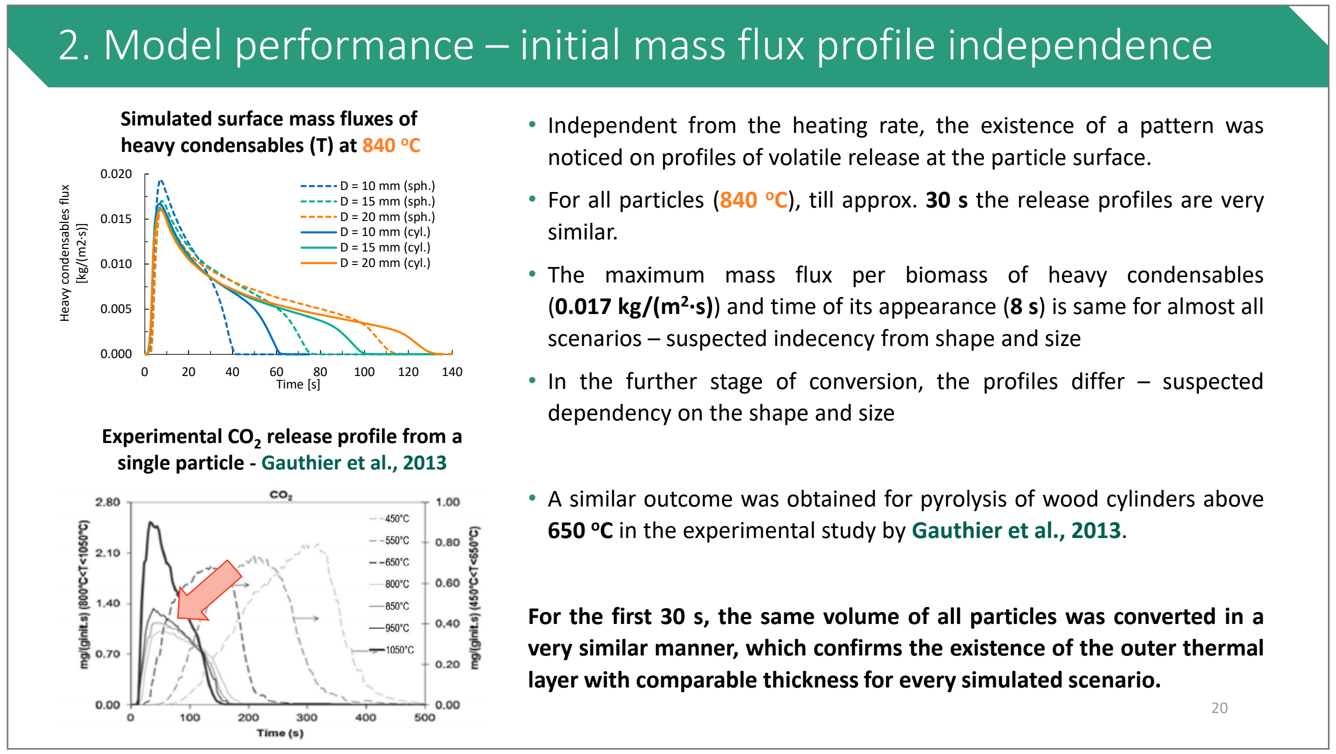
- For all sizes and shapes, the rise in pyrolysis temperature increase CD in expense of T 3.8 ± 1.5 wt. % (going from 500 °C to 840 °C)
- (T+CD) shows only a minor reduction with temperature to PG (600 °C – 700 °C) - secondary gas-phase reactions not included
- Changes in the PG and C+CM with temperatures exceeding 650 °C - degradation of the metaphase
- PG was influenced only to a minor extent - is possible a semi-equilibrium state (sec. charring – particle size)

- **Not linear changes in yields of pyrolysis products with size (within shape and between shapes)**
- **Heating rate – suspected factor**



2. Model performance – heating rate and location in partilce

- Only the heating rate (HR) that occurs during the conversion has an impact the path of conversion.
- Heating rate calculated as average for the conversion between (5 % ≤ η ≤ 95%) for each point in each scenario
- Between 500 °C and 840 °C heating rates did not change severely, and its change was relatively linear with temperature
- **Not linear change closer to the surface**
- Increase from 10 to 15 mm led to a stronger decrease in the HR than from 15 to 20 mm.
- Point P5 at 840 °C, a first increase of by 5 mm lower the HR by 3.8 °C /s, the second increase by 5 mm lower the HR only by 1.3 °C /s.
- **The largest changes in heating rate with pyrolysis temperature occur in the layer closest to the surface.**
- **Possible layer with higher heating rate.**



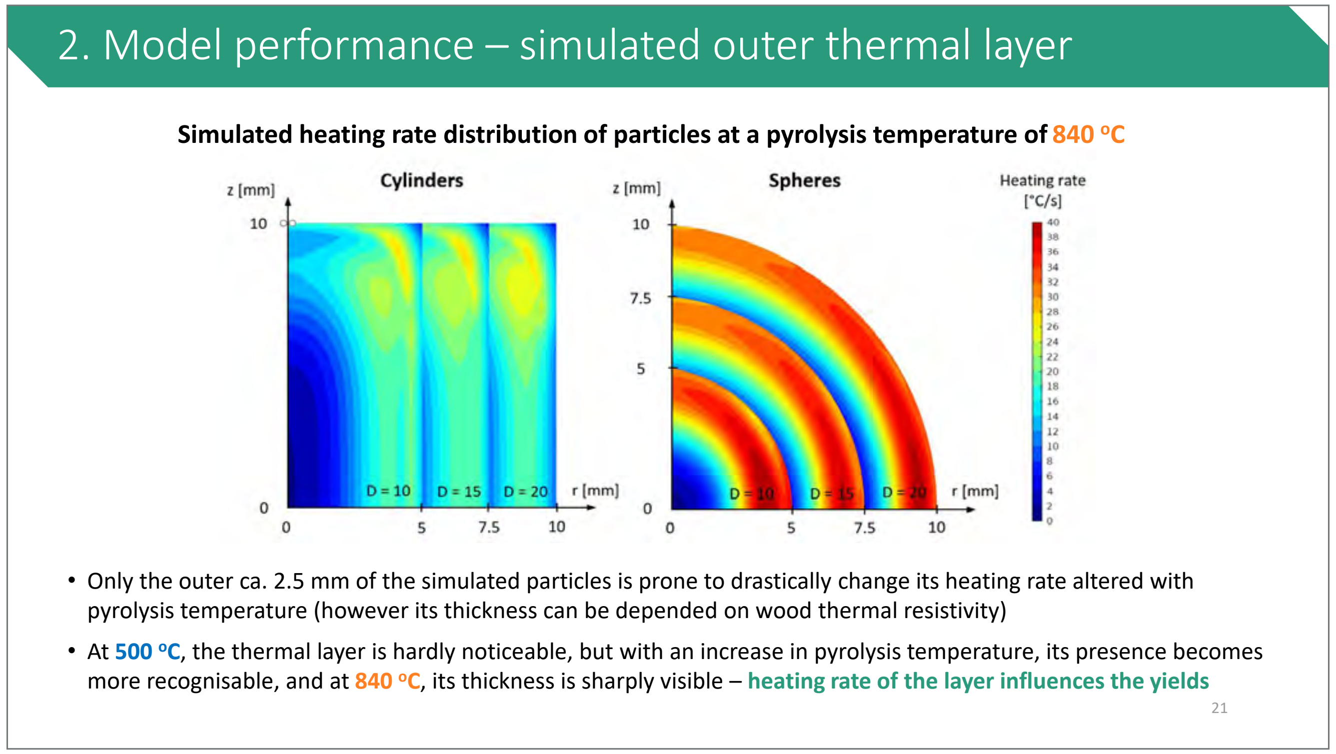
2. Model performance – initial mass flux profile independence

Simulated surface mass fluxes of heavy condensables (T) at 840 °C

Experimental CO_2 release profile from a single particle - Gauthier et al., 2013

- Independent from the heating rate, the existence of a pattern was noticed on profiles of volatile release at the particle surface.
- For all particles (840 °C), till approx. **30 s** the release profiles are very similar.
- The maximum mass flux per biomass of heavy condensables (**0.017 $kg/(m^2 \cdot s)$**) and time of its appearance (**8 s**) is same for almost all scenarios – suspected indecency from shape and size
- In the further stage of conversion, the profiles differ – suspected dependency on the shape and size
- A similar outcome was obtained for pyrolysis of wood cylinders above **650 °C** in the experimental study by **Gauthier et al., 2013**.

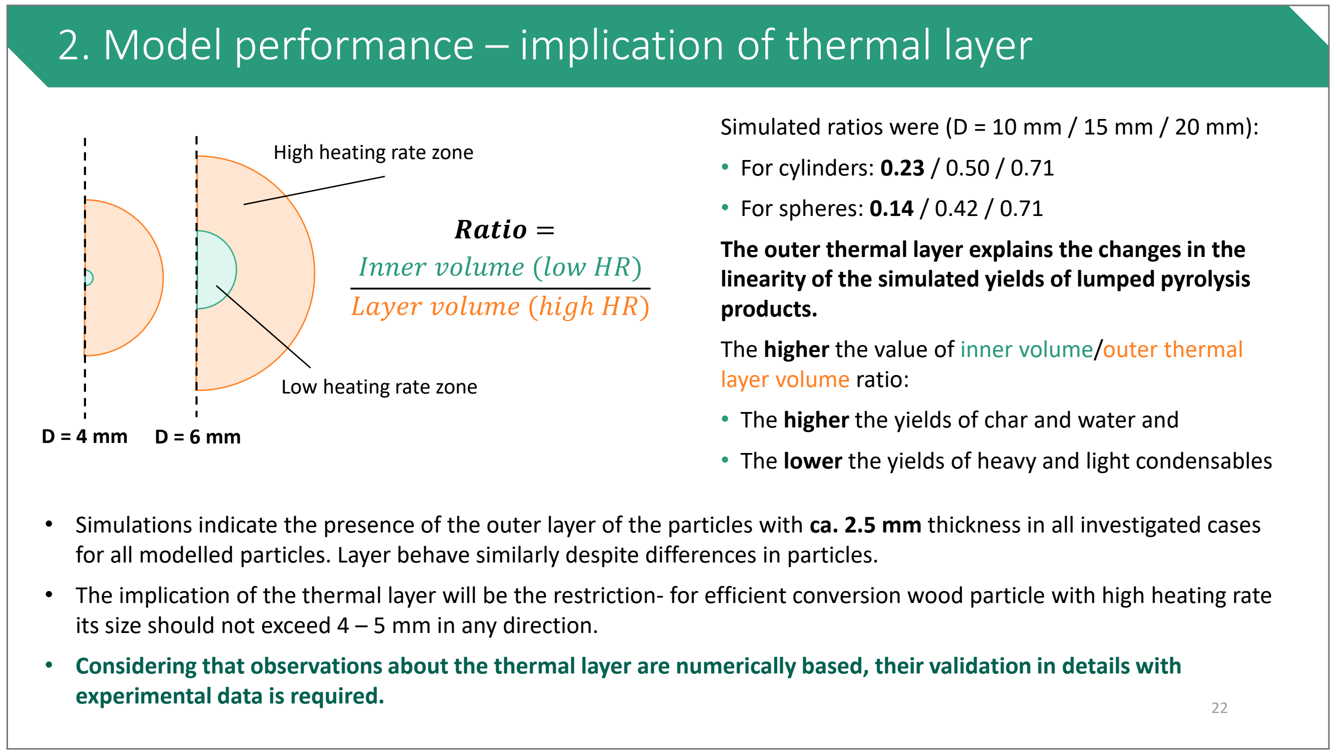
For the first 30 s, the same volume of all particles was converted in a very similar manner, which confirms the existence of the outer thermal layer with comparable thickness for every simulated scenario.



2. Model performance – simulated outer thermal layer

Simulated heating rate distribution of particles at a pyrolysis temperature of 840 °C

- Only the outer ca. 2.5 mm of the simulated particles is prone to drastically change its heating rate altered with pyrolysis temperature (however its thickness can be depended on wood thermal resistivity)
- At 500 °C, the thermal layer is hardly noticeable, but with an increase in pyrolysis temperature, its presence becomes more recognisable, and at 840 °C, its thickness is sharply visible – heating rate of the layer influences the yields



2. Model performance – implication of thermal layer

$$\textit{Ratio} = \frac{\textit{Inner volume (low HR)}}{\textit{Layer volume (high HR)}}$$

Simulated ratios were (D = 10 mm / 15 mm / 20 mm):

- For cylinders: **0.23** / 0.50 / 0.71
- For spheres: **0.14** / 0.42 / 0.71

The outer thermal layer explains the changes in the linearity of the simulated yields of lumped pyrolysis products.

The **higher** the value of inner volume/outer thermal layer volume ratio:

- The **higher** the yields of char and water and
- The **lower** the yields of heavy and light condensables

- Simulations indicate the presence of the outer layer of the particles with **ca. 2.5 mm** thickness in all investigated cases for all modelled particles. Layer behave similarly despite differences in particles.
- The implication of the thermal layer will be the restriction- for efficient conversion wood particle with high heating rate its size should not exceed 4 – 5 mm in any direction.
- **Considering that observations about the thermal layer are numerically based, their validation in details with experimental data is required.**

3. Study conclusions

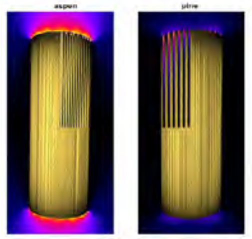
3. Study conclusions - summary

- Satisfactorily good fit of the model to the broad range of the experimental data (pyrolysis temperature, particle shape and size)
- Established model is not burdened by numerical error and is valid for board range of parameters (on char yield basis)
- Outer thermal layer observed, which implies different behavior (heating rate) of wood depending on the location within particle – only that layer is significantly influenced by pyrolysis temperature
- Simulations indicate that for efficient conversion in high heating rate the particle should not be larger than 4 – 5 mm – **However, that needs to be confirmed experimentally**
- Relation between secondary charring parameters and the heating rate needs to be calibrated better (continuous function)
- **Model still needs improvement and significant extension to improve its reliability and validated with vapors release profiles**

3. Study conclusions – required model's extentions

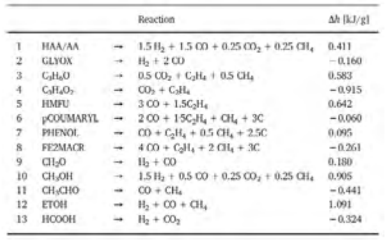
- **Secondary reactions in the gas phase**
  - particle's surrounding have to modeled
- **Validation of the results of the model with the GC/MS-FID bio-oil composition**
  - invalidation of the secondary gas phase reactions accuracy
- **Particle shrinking** - not possible to easily implement in the currently used software, although exp. data available
- **Implementation of the true density and porosity change, and the wood-dedicated thermal conductivity model** - data available, but shrinking have to be implemented first

Release of the vapours to the surrounding



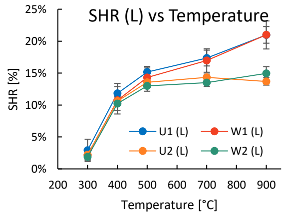
(Ciesielski et al., 2020)

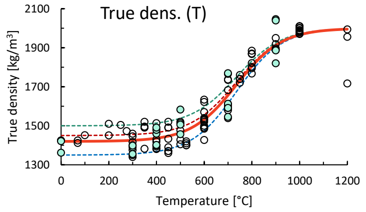
Secondary cracking reactions in the gas phase in temperatures above 500 °C



			Reaction	Δh [kJ/g]
1	HAA/AA	→	$1.5\,H_2 + 1.5\,CO + 0.25\,CO_2 + 0.25\,CH_4$	0.411
2	GLYOX	→	$H_2 + 2\,CO$	−0.160
3	C_3H_6O	→	$0.5\,CO_2 + C_2H_4 + 0.5\,CH_4$	0.583
4	$C_3H_4O_2$	→	$CO_2 + C_2H_4$	−0.915
5	HMFU	→	$3\,CO + 1.5C_2H_4$	0.642
6	pCOUMARYL	→	$2\,CO + 15C_2H_4 + CH_4 + 3C$	−0.060
7	PHENOL	→	$CO + C_2H_4 + 0.5\,CH_4 + 2.5C$	0.095
8	FE2MACR	→	$4\,CO + C_2H_4 + 2\,CH_4 + 3C$	−0.261
9	CH_2O	→	$H_2 + CO$	0.180
10	CH_3OH	→	$1.5\,H_2 + 0.5\,CO + 0.25\,CO_2 + 0.25\,CH_4$	0.905
11	CH_3CHO	→	$CO + CH_4$	−0.441
12	ETOH	→	$H_2 + CO + CH_4$	1.091
13	HCOOH	→	$H_2 + CO_2$	−0.324

(Anca-Couce et al., 2017)





3. Study conclusions - future read

Review of the properties of the wood and its char
Summary of the parameters and auxiliary functions

Book chapter

Production of Biofuels and Chemicals with Pyrolysis pp 373-438 | Cite as

Review on Modelling Approaches Based on Computational Fluid Dynamics for Biomass Pyrolysis Systems

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https://doi.org/10.1007/978-981-15-2732-6_13

Metanalysis of sub-models for single particle pyrolysis of wood
Practical information regarding establishing a model and its performance

Publication in preparation

The worst-case scenario - everything is relevant: A practical meta-analysis of thermo-physical and chemical aspects in CFD modelling of pyrolysis of a single wood particle in a thermally thick regime

Manuscript is finished and will be soon submitted

3. Study conclusions – invitation to PYRO2022

23rd edition of the International Conference on Analytical and Applied Pyrolysis in Ghent

Thank you for your attention!

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Optimisation of low-temperature, aqueous pyrolysis condensates for downstream microbial conversion

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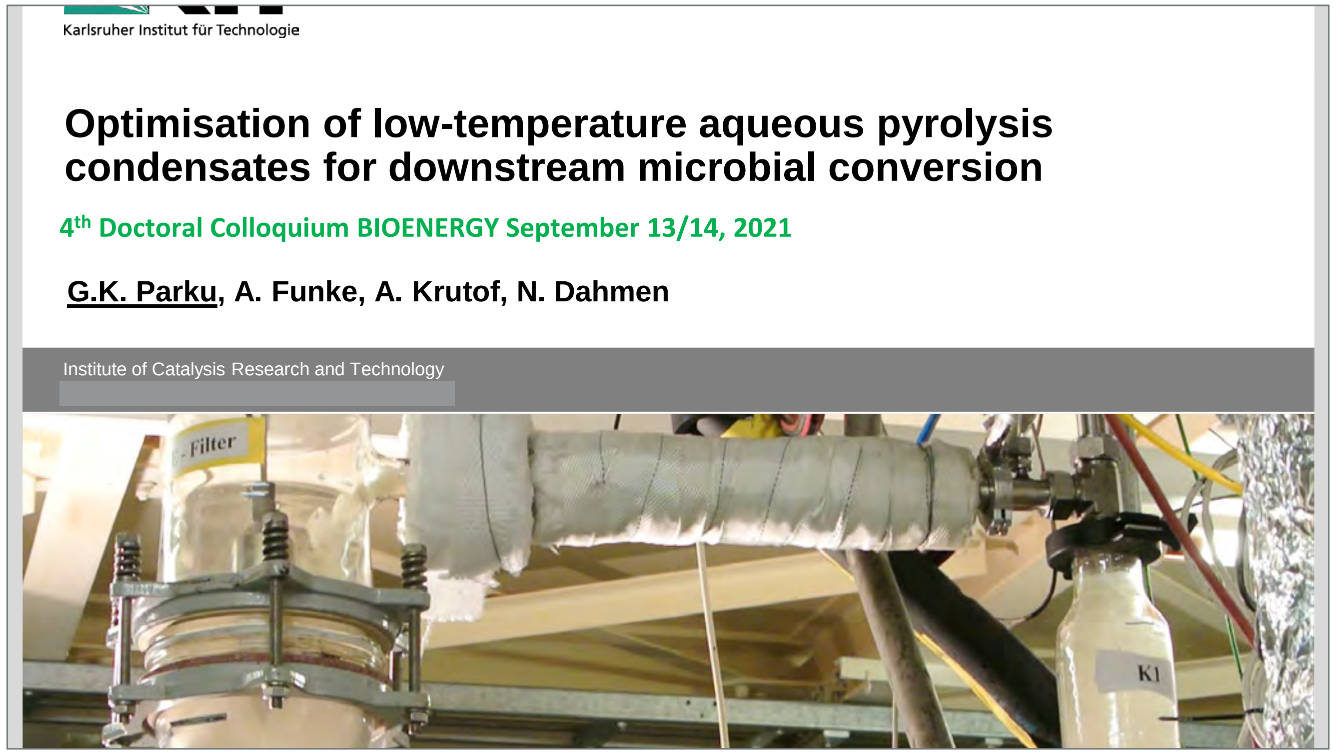
INTRODUCTION: Fractional condensation (FC) following fast pyrolysis of biomass to separate bio-oil into useful fractions has received increasing attention, due to its energy and economic advantages compared to other liquid-liquid separation technologies [1–3]. It enhances the recovery of different phases of bio-oil in the form of Organic Rich (ORC) and Aqueous Condensates (AC) [4]. ORC, because of its comparatively higher calorific value has been widely used for fuel applications. AC, which primarily comprises of up to 85 wt. % water has a high corrosivity and very low calorific value and usually undergoes costly treatment methods before being discarded. Studies on the use of the AC as carbon source for microbial cultivation have been reported to be possible [5]. This is because of the presence of compounds such as acetic acid, which facilitate microbial growth. However, the simultaneous presence of compounds such as furans and aldehydes in AC have also been reported to impede microbial cultivation. In this study, FC was employed following biomass fast pyrolysis to optimise the composition of AC for downstream microbial conversion by increasing and suppressing the concentrations of compounds that promote and impede microbial cultivation, respectively.

METHODS: Thermodynamic UNIFAC model was used to predict distribution of compounds in the AC following FC. Subsequently, an Advanced Distillation Curve (ADC) setup was used to validate this model. ADC generates thermodynamically accurate volatility measurements of a multicomponent fluid mixture as a function of its composition across a distillation curve. Afterwards, a central composite design (CCD) was then employed to determine the optimum temperature conditions (of the two-staged condensation unit) that promoted the production of compounds of interest (promoters) to microbes at the expense of compounds which did not (inhibitors). Temperature ranges of 80-120 °C and 10-50 °C were investigated for staged condensers 1 and 2, correspondingly. Optimum conditions were then mimicked on a 10 kg/h pyrolysis pilot unit for the production of 25 L of AC, which would be used to ascertain the validity of the optimum conditions.

RESULTS AND CONCLUSION: The CCD results showed a sharp increase in yield (from 13 to 17 wt. %) of promoter compounds (such as acetic acid, propionic acid and acetol) in AC as temperature rose from 80 to 120 °C. This was attributed to the higher volatility of these compounds, which meant they could only be recovered in the lower-temperature, stage 2 condenser. However, temperature variations of stage 2 condenser had no significant effect on promoter compounds. Furthermore, it was also inferred that yield of inhibiting compounds (such as furfural, syringol and cresols) were hardly influenced by temperature variations in both condensers. This was blamed on the majority of these compounds being retained in the first stage condenser by virtue of their higher molecular weight.In conclusion, a temperature of 120 °C on staged condenser 1, coupled with 50 °C on staged condenser 2 should return an optimum and minimum production of promoter and inhibitory compounds, respectively.



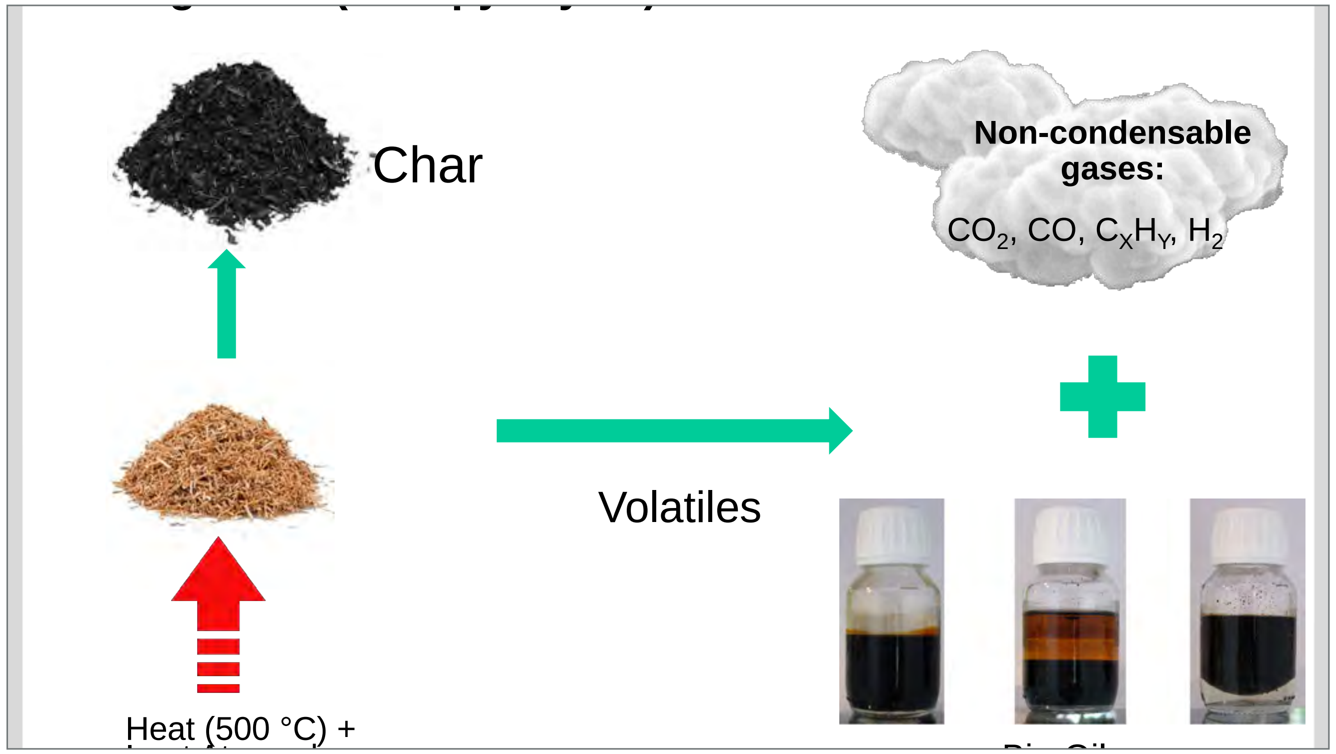
Karlsruher Institut für Technologie

Optimisation of low-temperature aqueous pyrolysis condensates for downstream microbial conversion

4th Doctoral Colloquium BIOENERGY September 13/14, 2021

G.K. Parku, A. Funke, A. Krutof, N. Dahmen

Institute of Catalysis Research and Technology

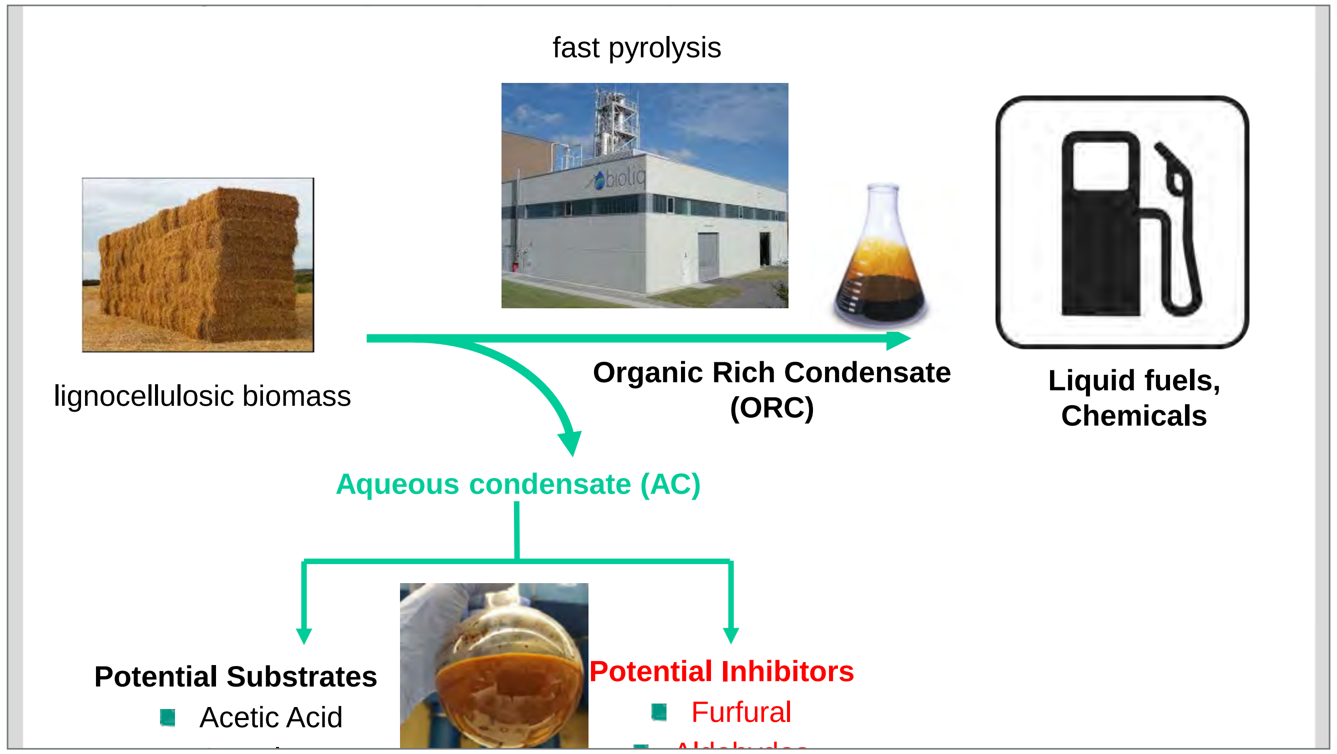


Char

Non-condensable gases:
CO_2, CO, C_XH_Y, H_2

Volatiles

Heat (500 °C) +



fast pyrolysis

lignocellulosic biomass

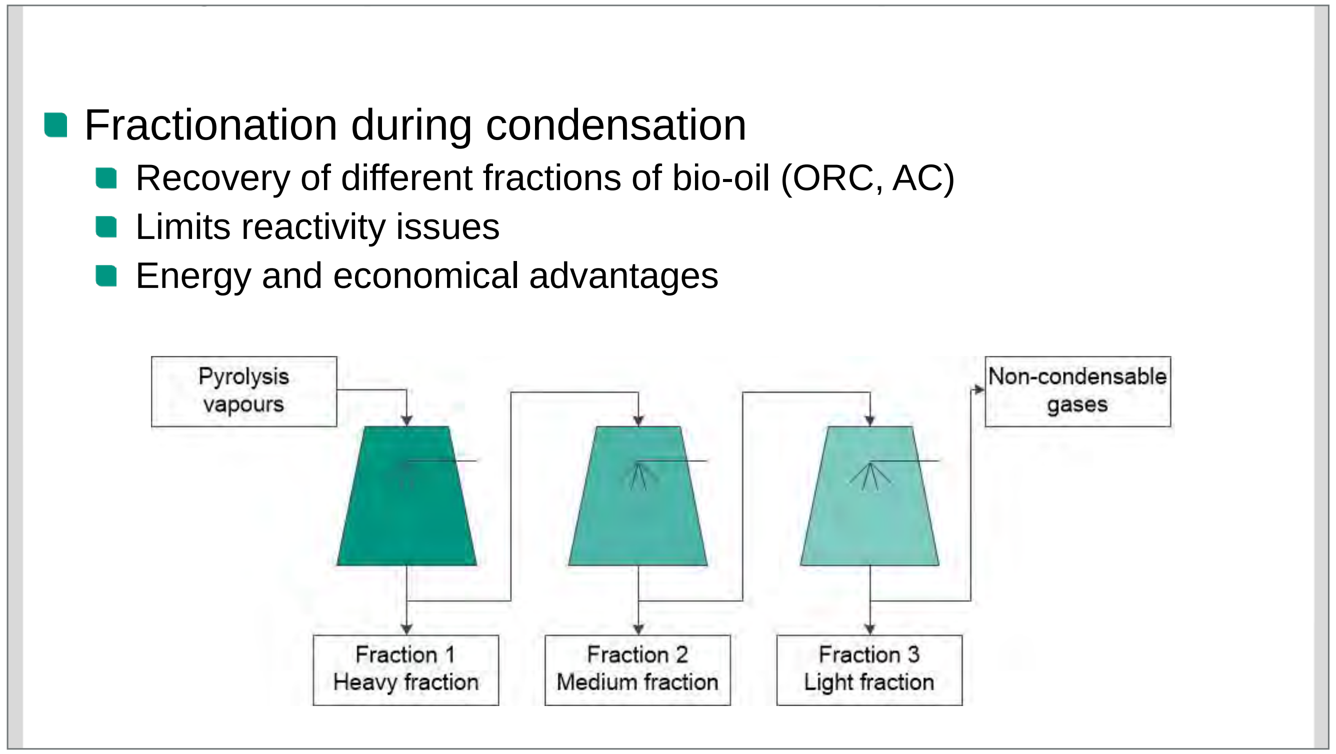
Organic Rich Condensate (ORC)

Liquid fuels, Chemicals

Aqueous condensate (AC)

Potential Substrates
- Acetic Acid

Potential Inhibitors
- Furfural



- Fractionation during condensation
  - Recovery of different fractions of bio-oil (ORC, AC)
  - Limits reactivity issues
  - Energy and economical advantages

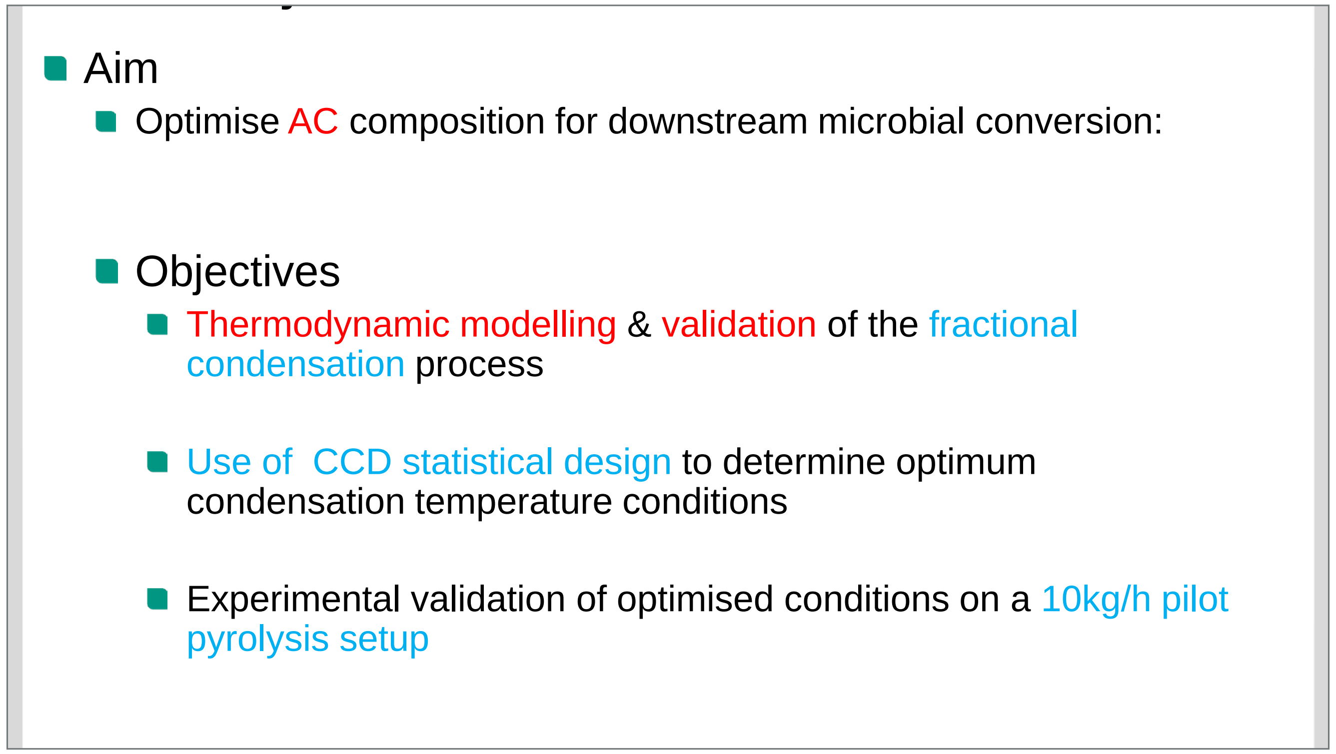
Pyrolysis vapours

Non-condensable gases

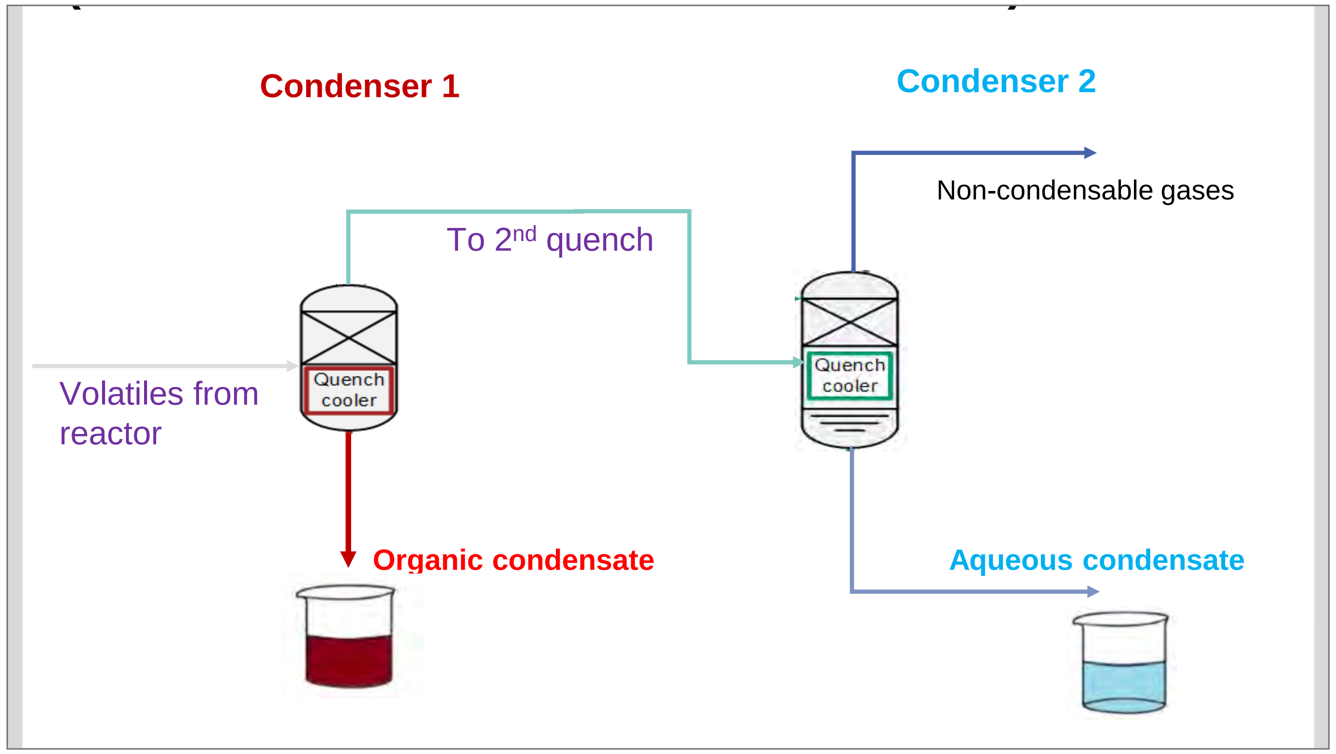
Fraction 1
Heavy fraction

Fraction 2
Medium fraction

Fraction 3
Light fraction



- Aim
  - Optimise AC composition for downstream microbial conversion:
  - Objectives
    - Thermodynamic modelling & validation of the fractional condensation process
    - Use of CCD statistical design to determine optimum condensation temperature conditions
    - Experimental validation of optimised conditions on a 10kg/h pilot pyrolysis setup



Condenser 1

Condenser 2

Non-condensable gases

To 2nd quench

Volatiles from reactor

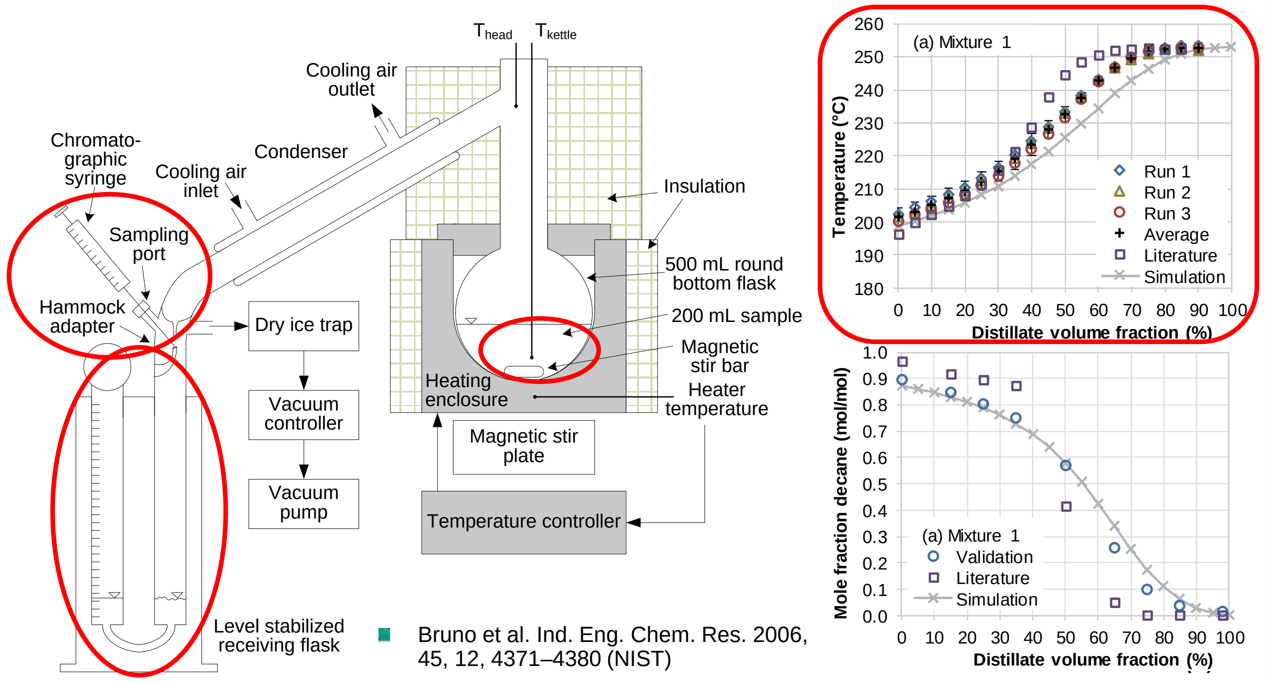
Organic condensate

Aqueous condensate

- UNIFAC-DMD (activity coefficient model)
- GCA-EoS (Group Contribution Assoc.)

Consider association reactions

- Studies so far indicate that both models describe the mixtures of interest equally well.
- UNIFAC-DMD used in this study



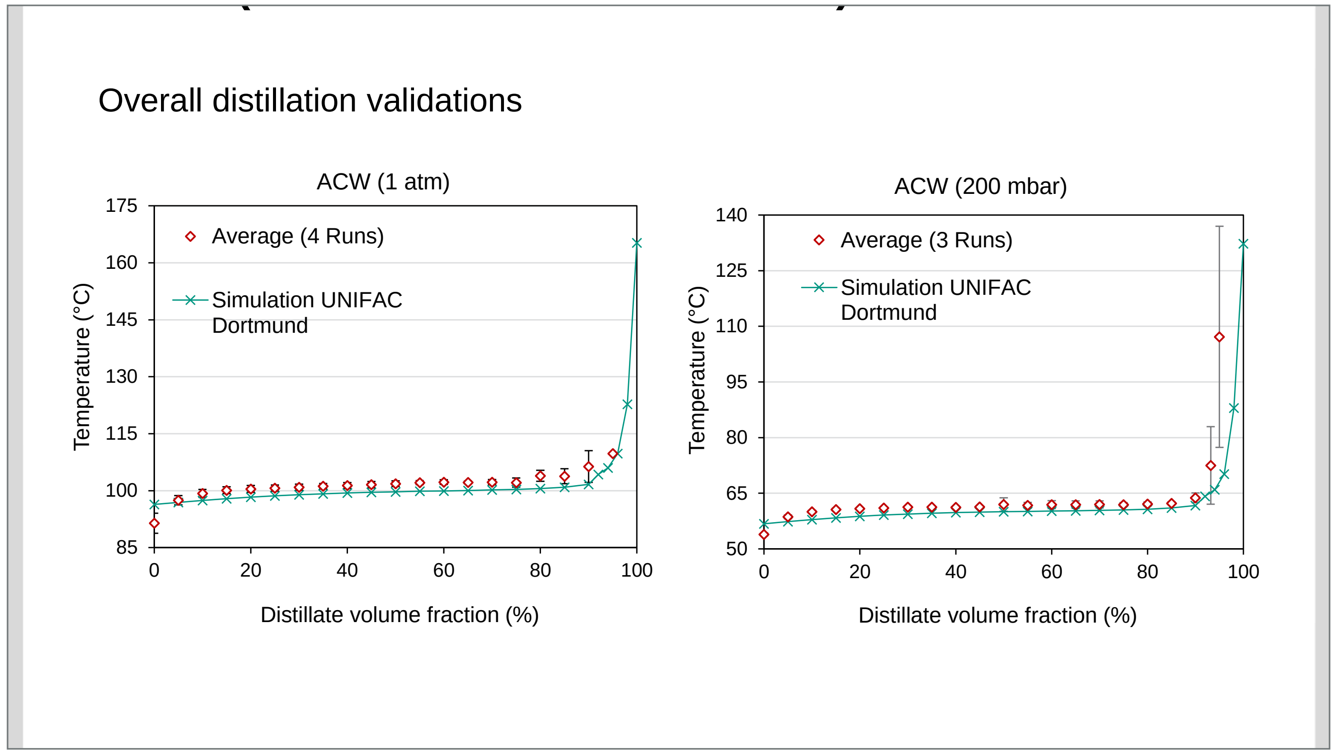
- Bruno et al. Ind. Eng. Chem. Res. 2006, 45, 12, 4371–4380 (NIST)

Promoters
Hydroxyacetaldehyde
Acetic Acid
Propionic Acid
Acetol
Phenol
Ethylenglycol
Guaiacol
2-methyl-Propanoic acid

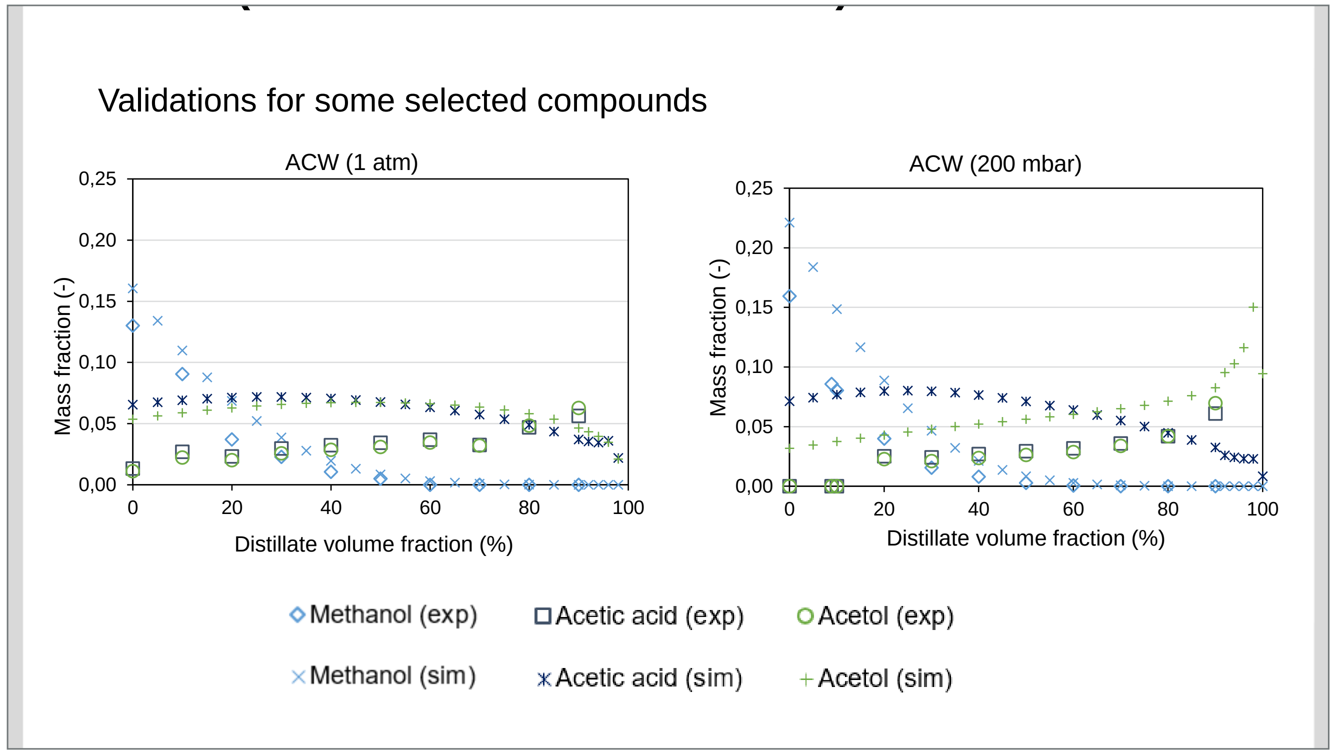
Inhibitors
3-hydroxy-propionaldehyde
Methanol
Furfural
O-Kresol
M-Kresol
Syringol / 2,6-Dimethoxyphenol
5-hydroxymethyl-2-Furaldehyde
Vanillin
2-Butanone
2,3-Butandione (Diacetyl)
1-hydroxy-2-butanone

- Grouped based on tolerance screening results

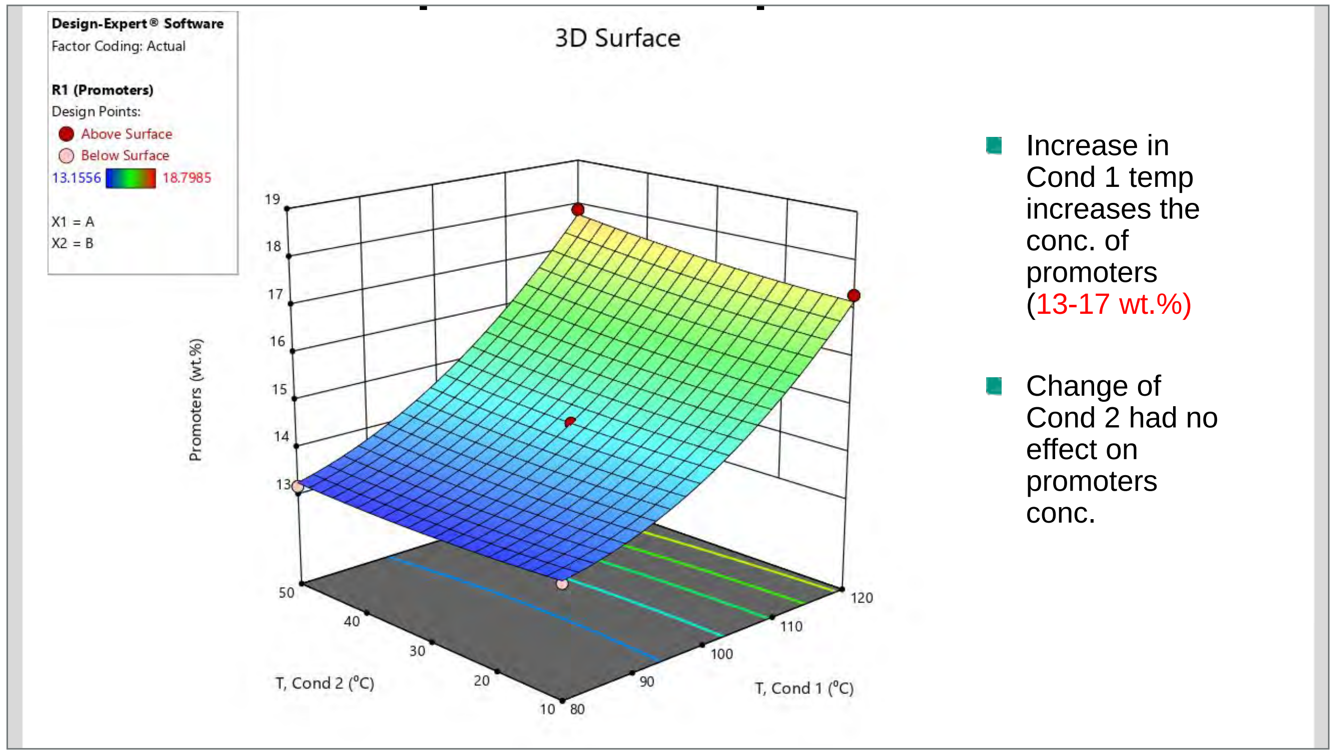
- Central composite Design (CCD)
  - Design-Expert® Software
- Factors:
  - Temperature, Condensers 1 (80-120ºC)
  - Temperature, Condensers 2 (10-50ºC)
- Responses:
  - wt.% of promoters
  - wt.% of inhibitors
  - yield of Aqueous condensate (AC)
  - Mass fraction of water in AC



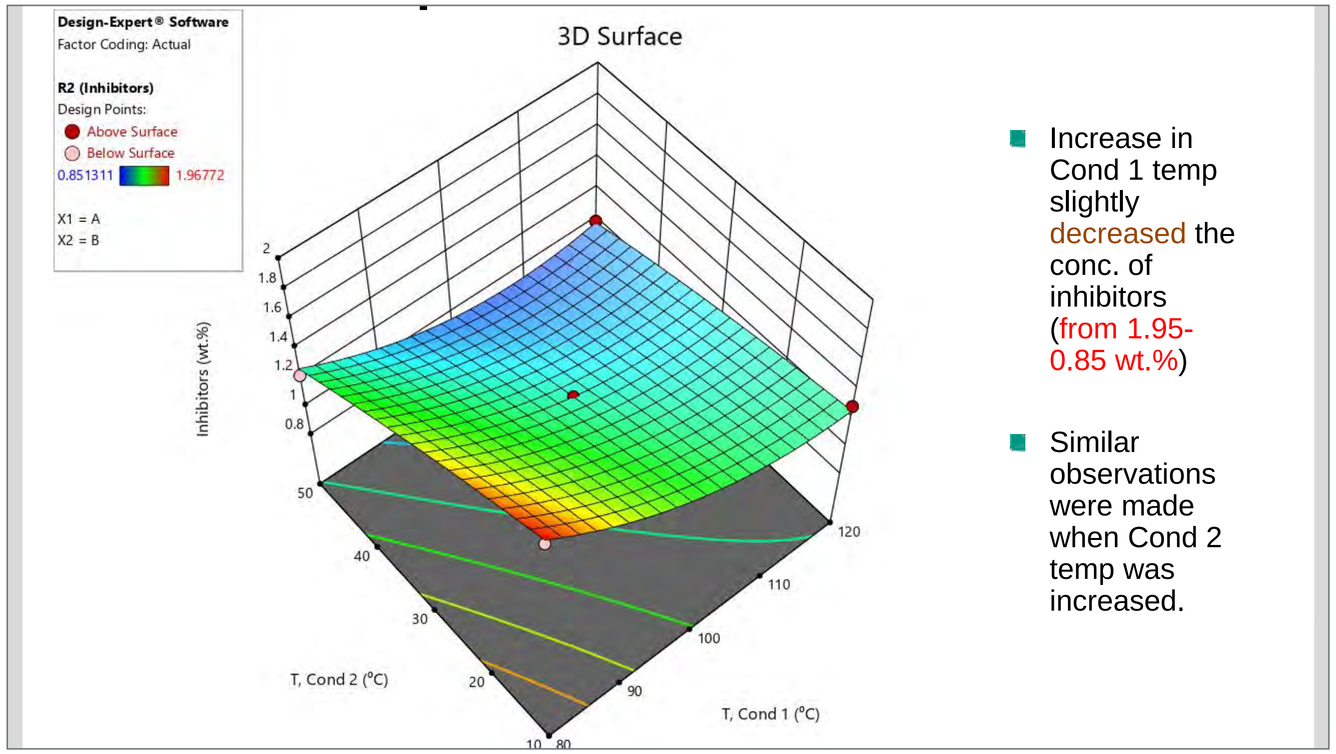
Overall distillation validations



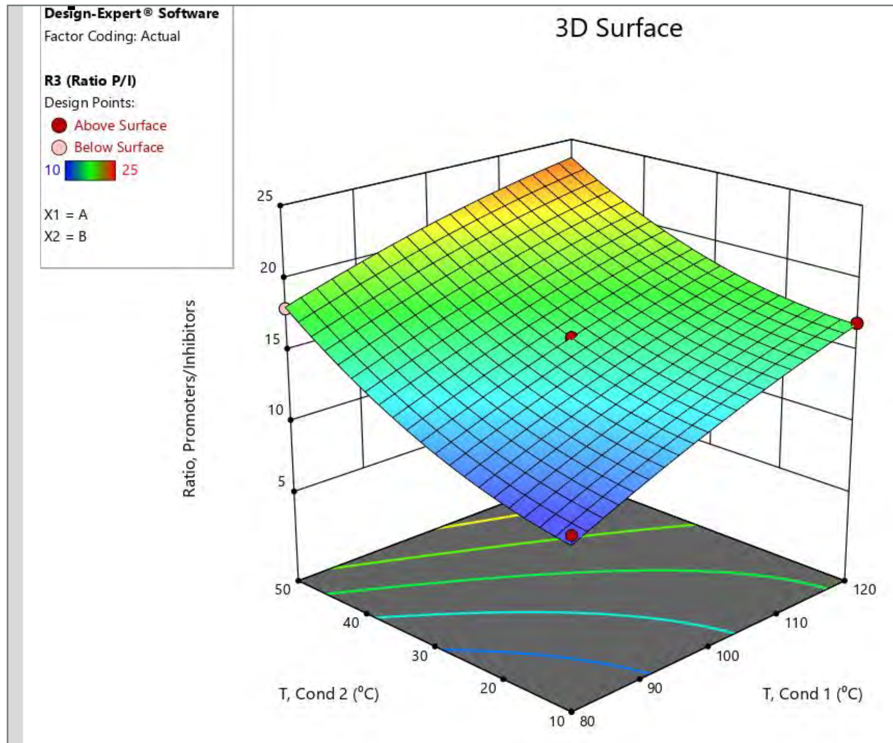
Validations for some selected compounds



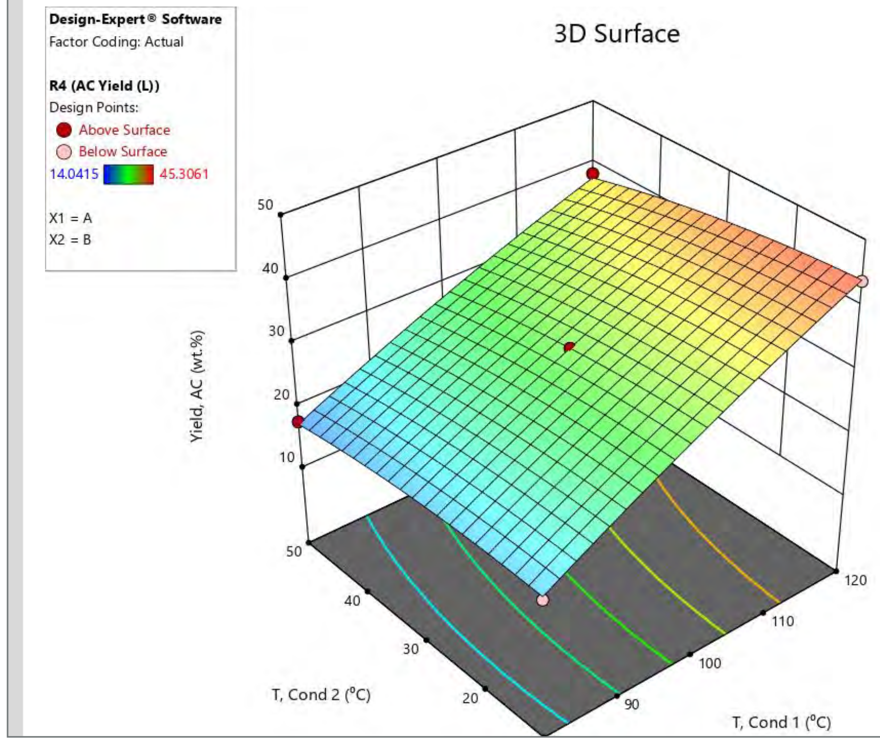
- Increase in Cond 1 temp increases the conc. of promoters (13-17 wt.%)
- Change of Cond 2 had no effect on promoters conc.



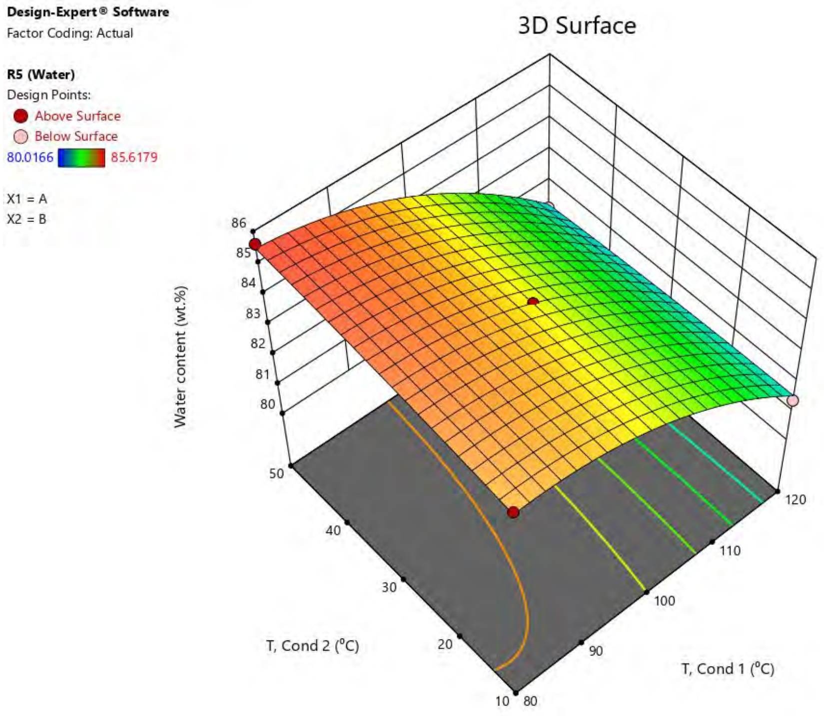
- Increase in Cond 1 temp slightly decreased the conc. of inhibitors (from 1.95-0.85 wt.%)
- Similar observations were made when Cond 2 temp was increased.



- Ratio of P/I gives a better impression of trends
- Increase in temps of both condensers suitable for promoters at the expense of inhibitors

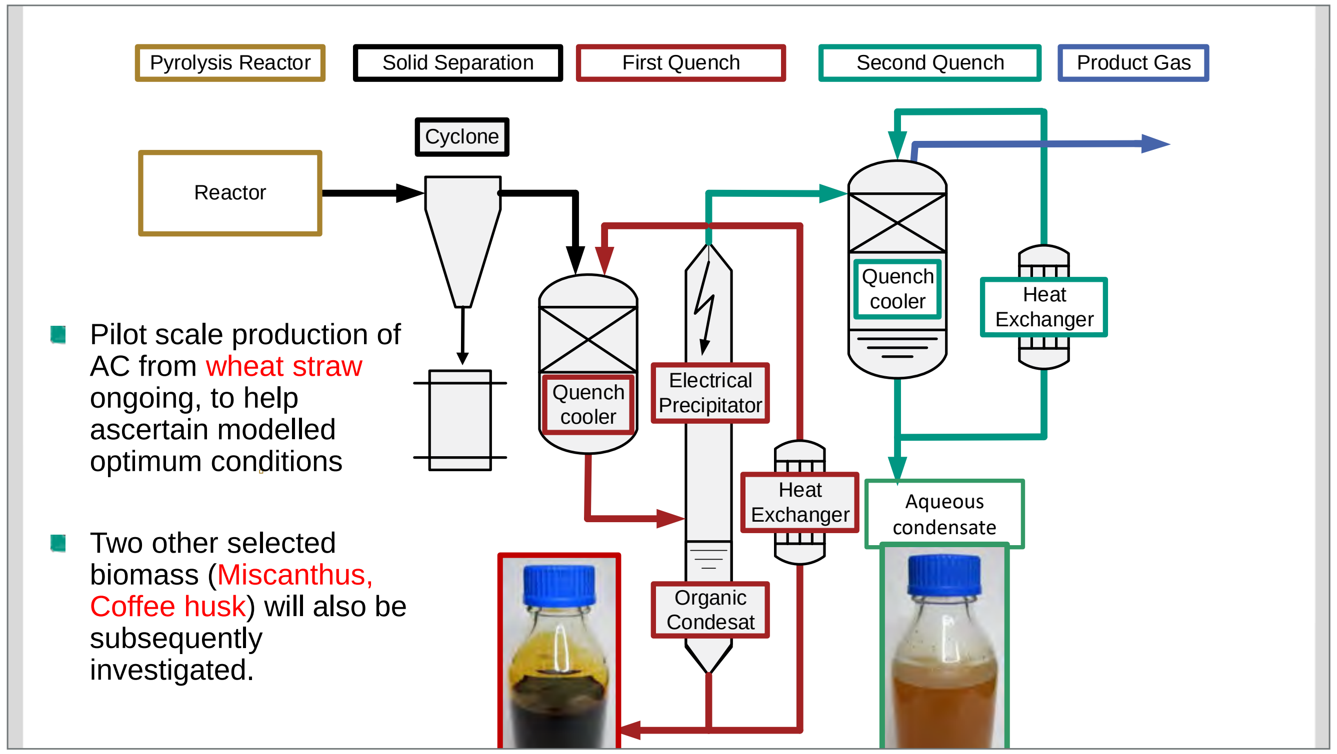


- Liquid media needed to hold the compounds
- Yield of AC favourable at higher Cond 1 Temp. (Increase from 19-44 wt.%)
- AC yield independent Cond 2 temperature



- Mass fraction of water slightly decreased with increase of Cond. 1 temp (3 wt.% decrease)
- Water mass fraction in AC is independent of Temp variation of Cond. 2

- Cond 1 temp of 120 ºC and Cond 2 temp of 50 ºC recommended to increase concentration of promoters at the expense of inhibitors in AC.
- These conditions to be mimicked on a 10 kg/h pilot pyrolysis setup



Pyrolysis Reactor
Solid Separation
First Quench
Second Quench
Product Gas

Reactor
Cyclone
Quench cooler
Electrical Precipitator
Heat Exchanger
Organic Condesat
Quench cooler
Heat Exchanger
Aqueous condensate

- Pilot scale production of AC from wheat straw ongoing, to help ascertain modelled optimum conditions
- Two other selected biomass (Miscanthus, Coffee husk) will also be subsequently investigated.

- Questions, comments welcomed!

contact: george.parku@kit.edu

Partners:

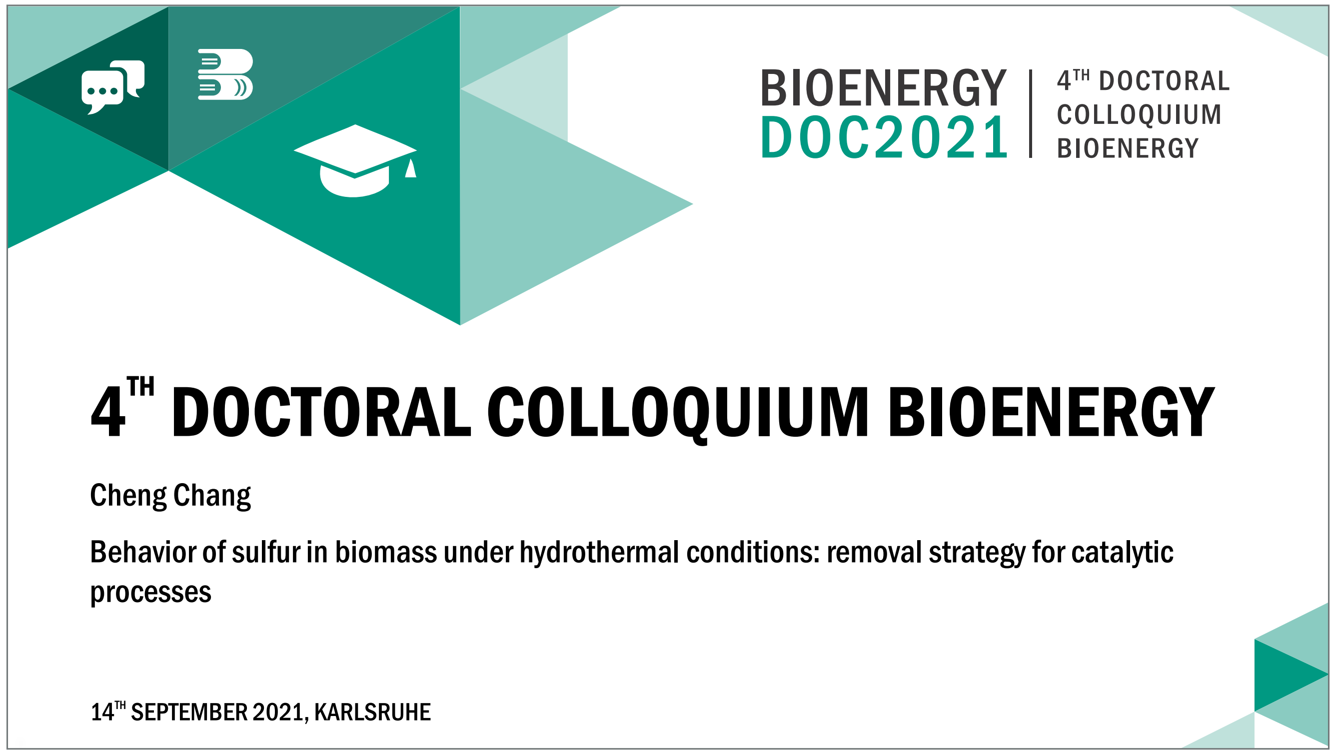
BLT

Cheng Chang, Paul Scherrer Institute

Behavior of sulfur in biomass under hydrothermal conditions: removal strategy for catalytic processes

Cheng Chang, David Baudouin, Frédéric Vogel, Oliver Kröcher
Paul Scherrer Institute
Forschungsstraße 111
5232 Villigen, Switzerland
E-mail: **cheng.chang@psi.ch**

Catalytic hydrothermal conversion of wet biomass to biofuels is a promising and sustainable route to generate energy and reduce the negative impact of human society on the natural environment. However, the sulfur contained in raw biomass has been an issue for metal catalysts (e.g. ruthenium), which are easily poisoned by sulfur-containing compounds. Therefore, the desulfurization of biomass is of significant value to the development of biofuel production in catalytic hydrothermal conversion. At Paul Scherrer Institute (PSI), a continuous catalytic hydrothermal gasification (cHTG) process for the production of synthetic natural gas has been under development. Yet even with the advantage of salt separator (to precipitate sulfate) and sulfur trap (to absorb hydrogen sulfide), a non-negligible amount of sulfate and organosulfur compounds flow into the catalytic reactor causing catalyst deactivation. How to efficiently remove sulfate and organosulfur compounds from the upstream of the cHTG process is the question worth to be dug into. Our strategy is to integrate an extensive sulfur removal step into the salt separator, extending the lifetime of sulfur trap and eliminating sulfur from entering the catalytic reactor. Benefiting from the supercritical condition in the salt separator, one approach, which is of special attraction in geochemistry, is planned to explore the removal of sulfur from hydrothermal process streams: Thermochemical Sulfate Reduction (TSR). Using ion chromatography (IC), gas chromatography-sulfur chemiluminescence detection (GC-SCD), ultraviolet-visible spectroscopy (UV-vis) for result analysis, we have optimized the reaction conditions (within 410 °C – 490 °C and pH 5 – pH 7) of model solution (2 wt % glycerol and 100 mg/L K_2SO_4) and devised reaction pathways with a single batch reactor in a non-catalytic environment. Results indicated that higher temperature (490 °C) and lower pH (5) would favor sulfate conversion. Interestingly, the stainless steel batch reactor itself showed a positive effect on sulfate conversion. Furthermore, how fast the reaction occurs in supercritical conditions and how to accelerate it with catalysts are important questions to be answered as well. The ultimate purpose is to convert the dissolved sulfate into sulfide and separate them from the cHTG process stream by absorption. The result would not only contribute to the practical application of catalytic hydrothermal gasification, but also bring insights to geochemistry in thermochemical sulfate reduction.



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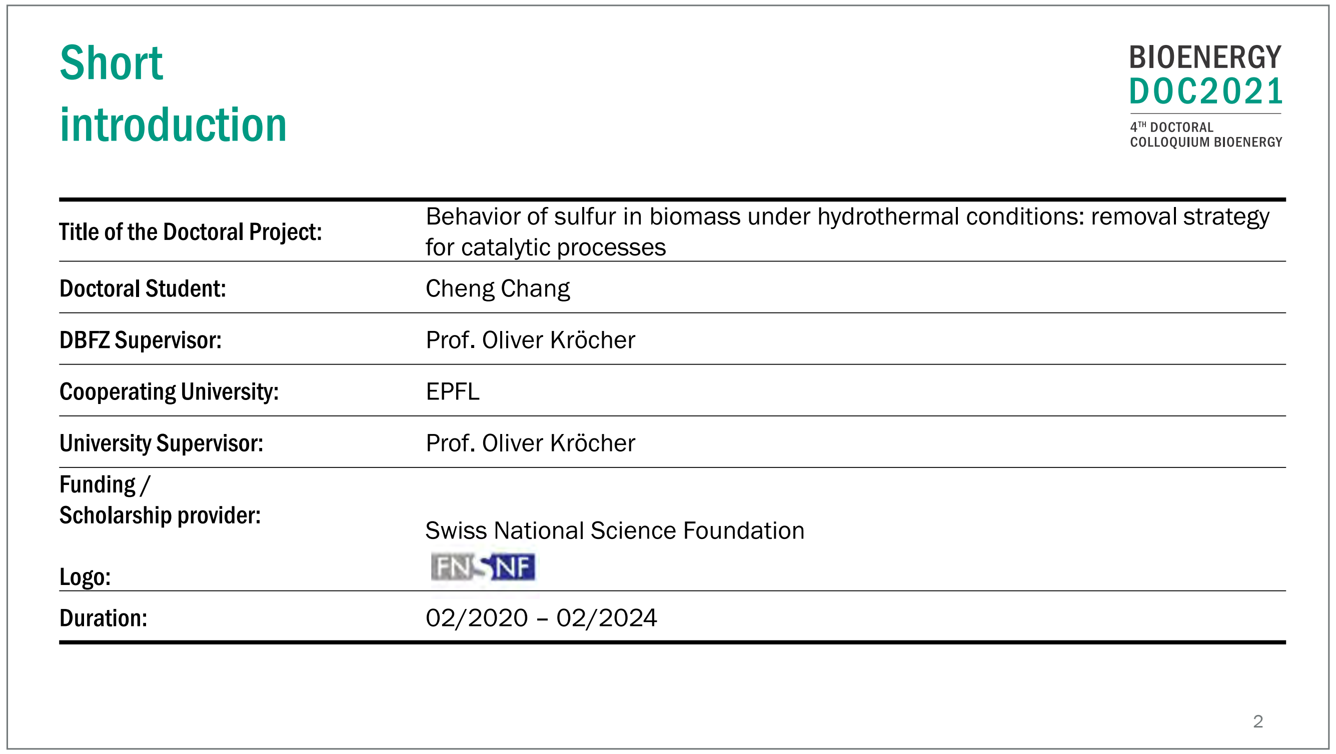
4TH DOCTORAL COLLOQUIUM BIOENERGY

Cheng Chang

Behavior of sulfur in biomass under hydrothermal conditions: removal strategy for catalytic processes

14TH SEPTEMBER 2021, KARLSRUHE



Short introduction

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4TH DOCTORAL COLLOQUIUM BIOENERGY

Title of the Doctoral Project:	Behavior of sulfur in biomass under hydrothermal conditions: removal strategy for catalytic processes
Doctoral Student:	Cheng Chang
DBFZ Supervisor:	Prof. Oliver Kröcher
Cooperating University:	EPFL
University Supervisor:	Prof. Oliver Kröcher
Funding / Scholarship provider:	Swiss National Science Foundation
Logo:	FNSNF
Duration:	02/2020 – 02/2024

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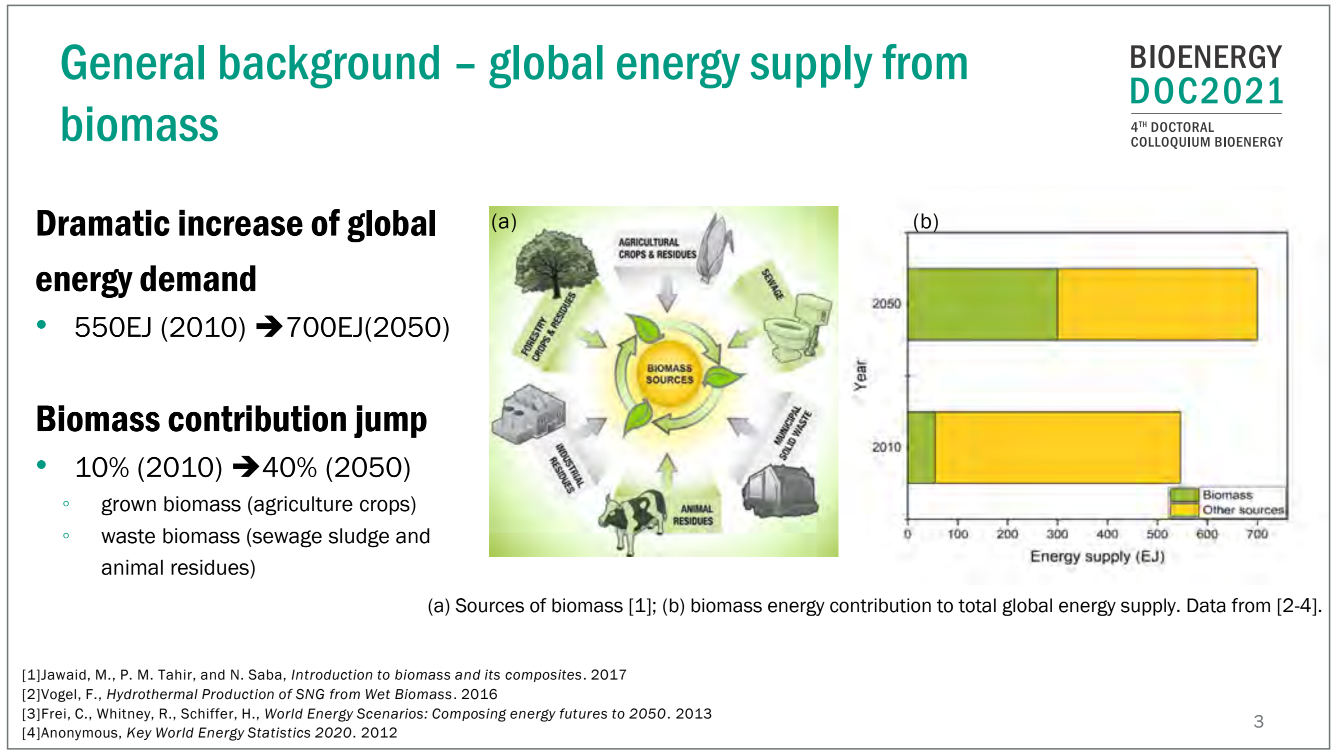

General background – global energy supply from biomass

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Dramatic increase of global energy demand

- 550EJ (2010) ➔700EJ(2050)

Biomass contribution jump

- 10% (2010) ➔40% (2050)
  - grown biomass (agriculture crops)
  - waste biomass (sewage sludge and animal residues)

(a) Sources of biomass [1]; (b) biomass energy contribution to total global energy supply. Data from [2-4].

[1]Jawaid, M., P. M. Tahir, and N. Saba, *Introduction to biomass and its composites*. 2017
[2]Vogel, F., *Hydrothermal Production of SNG from Wet Biomass*. 2016
[3]Frei, C., Whitney, R., Schiffer, H., *World Energy Scenarios: Composing energy futures to 2050*. 2013
[4]Anonymous, *Key World Energy Statistics 2020*. 2012

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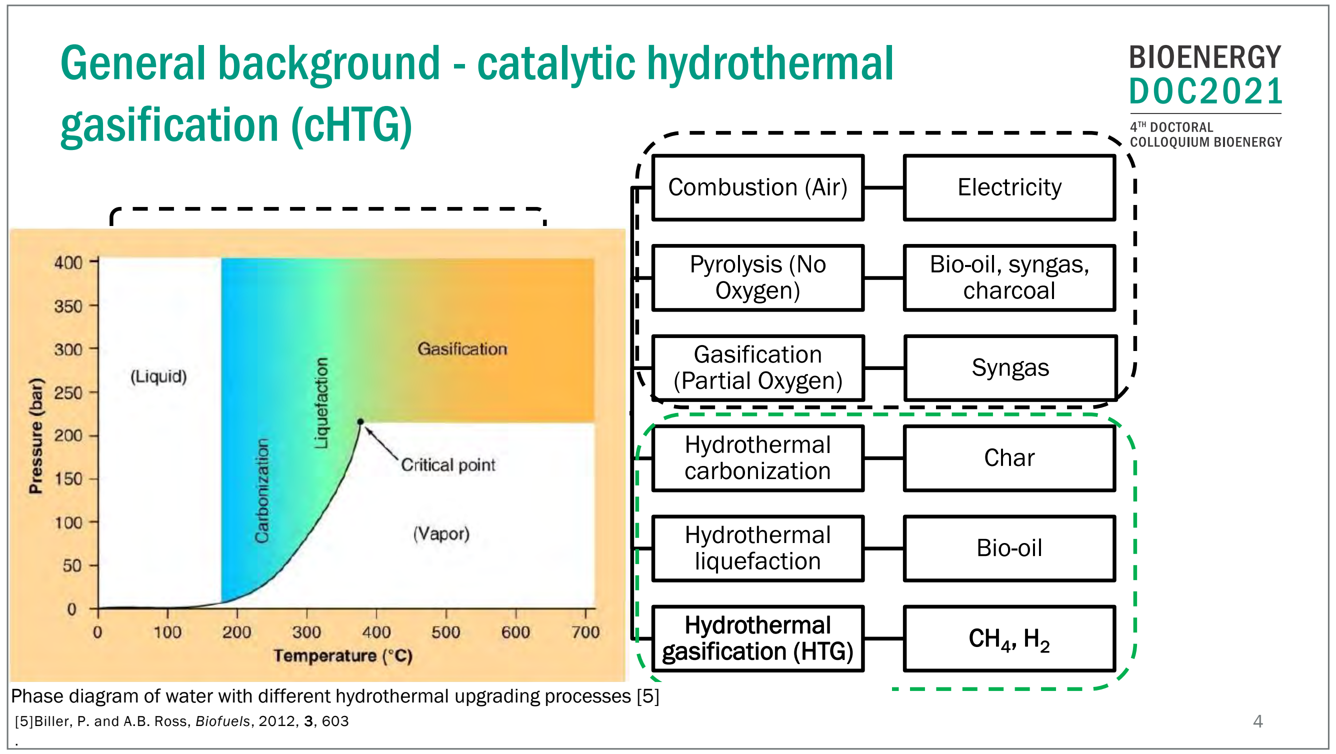

General background - catalytic hydrothermal gasification (cHTG)

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Combustion (Air) — Electricity
Pyrolysis (No Oxygen) — Bio-oil, syngas, charcoal
Gasification (Partial Oxygen) — Syngas
Hydrothermal carbonization — Char
Hydrothermal liquefaction — Bio-oil
Hydrothermal gasification (HTG) — CH_4, H_2

Phase diagram of water with different hydrothermal upgrading processes [5]

[5]Biller, P. and A.B. Ross, *Biofuels*, 2012, **3**, 603

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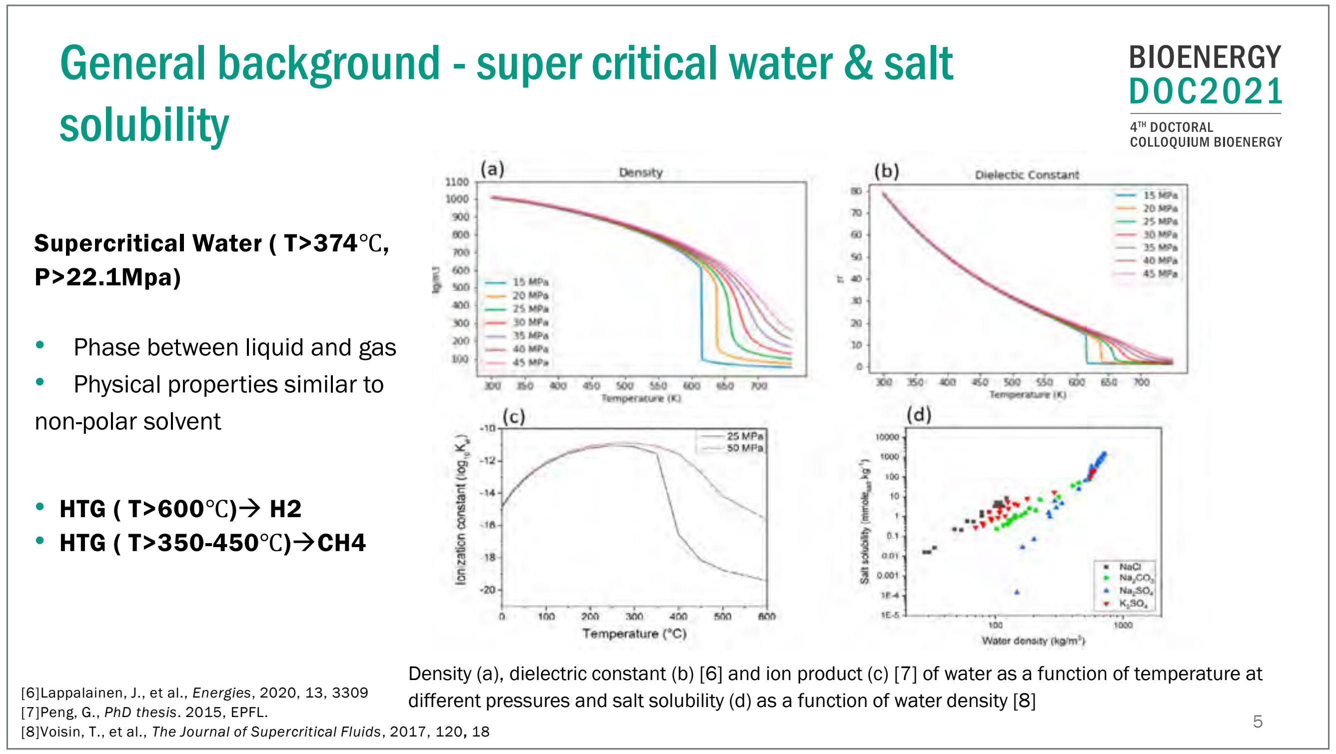

General background - super critical water & salt solubility

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Supercritical Water (T>374℃, P>22.1Mpa)

- Phase between liquid and gas
- Physical properties similar to non-polar solvent

- **HTG (T>600℃)→ H2**
- **HTG (T>350-450℃)→CH4**

Density (a), dielectric constant (b) [6] and ion product (c) [7] of water as a function of temperature at different pressures and salt solubility (d) as a function of water density [8]

[6]Lappalainen, J., et al., *Energies*, 2020, 13, 3309
[7]Peng, G., *PhD thesis*. 2015, EPFL.
[8]Voisin, T., et al., *The Journal of Supercritical Fluids*, 2017, 120, 18

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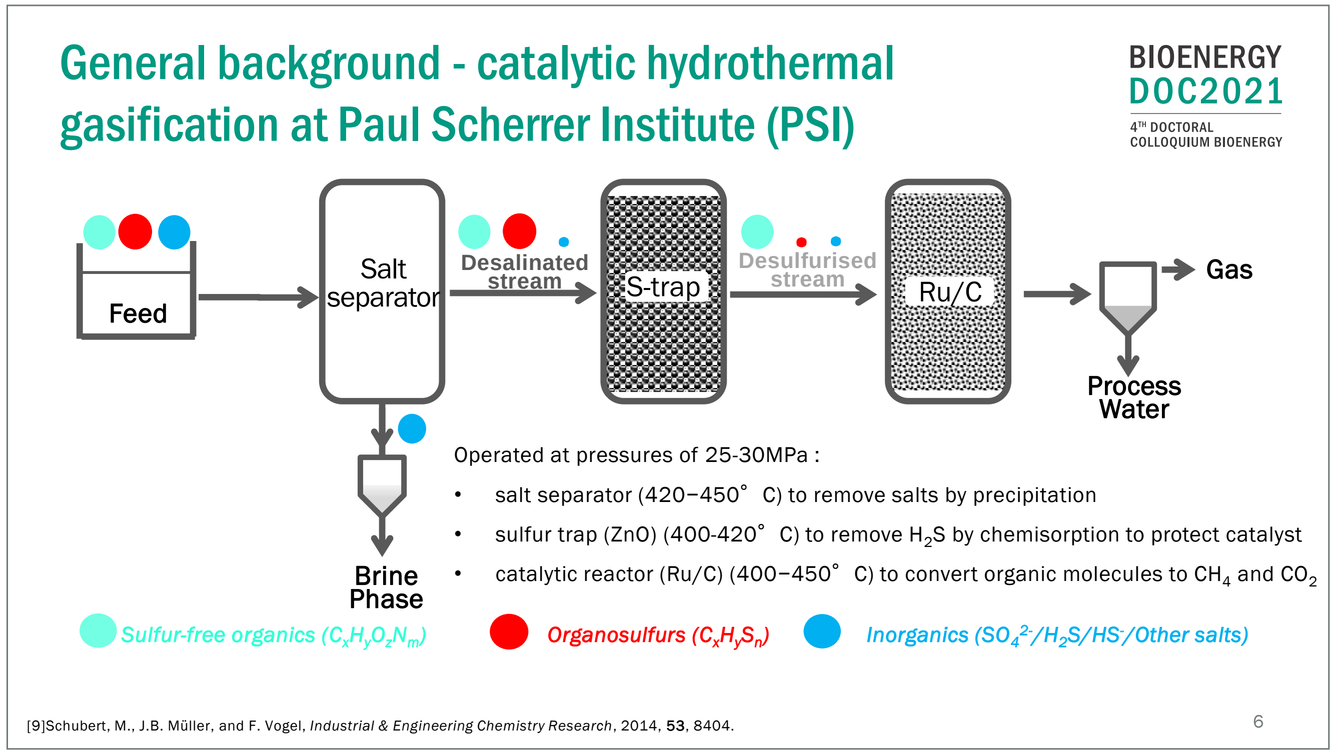

General background - catalytic hydrothermal gasification at Paul Scherrer Institute (PSI)

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Operated at pressures of 25-30MPa :

- salt separator (420−450° C) to remove salts by precipitation
- sulfur trap (ZnO) (400-420° C) to remove H_2S by chemisorption to protect catalyst
- catalytic reactor (Ru/C) (400−450° C) to convert organic molecules to CH_4 and CO_2

● *Sulfur-free organics ($C_xH_yO_zN_m$)* ● *Organosulfurs ($C_xH_yS_n$)* ● *Inorganics (SO_4^{2-}/H_2S/HS^-/Other salts)*

[9]Schubert, M., J.B. Müller, and F. Vogel, *Industrial & Engineering Chemistry Research*, 2014, **53**, 8404.

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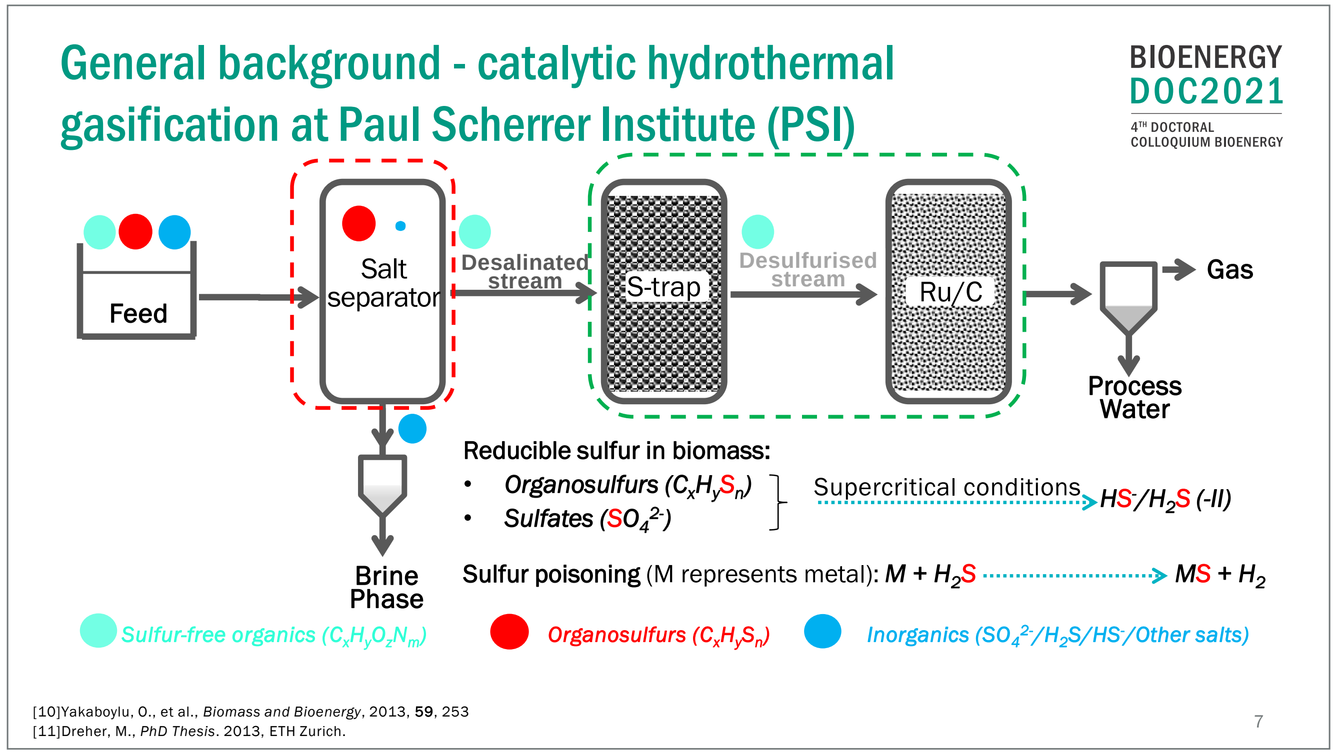

General background - catalytic hydrothermal gasification at Paul Scherrer Institute (PSI)

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Reducible sulfur in biomass:

- *Organosulfurs* ($C_xH_yS_n$)
- *Sulfates* (SO_4^{2-})

Supercritical conditions $\rightarrow$ HS^-/H_2S (-II)

Sulfur poisoning (M represents metal): $M + H_2S \rightarrow MS + H_2$

● Sulfur-free organics ($C_xH_yO_zN_m$) ● Organosulfurs ($C_xH_yS_n$) ● Inorganics ($SO_4^{2-}/H_2S/HS^-$/Other salts)

[10]Yakaboylu, O., et al., *Biomass and Bioenergy*, 2013, **59**, 253
[11]Dreher, M., *PhD Thesis*. 2013, ETH Zurich.

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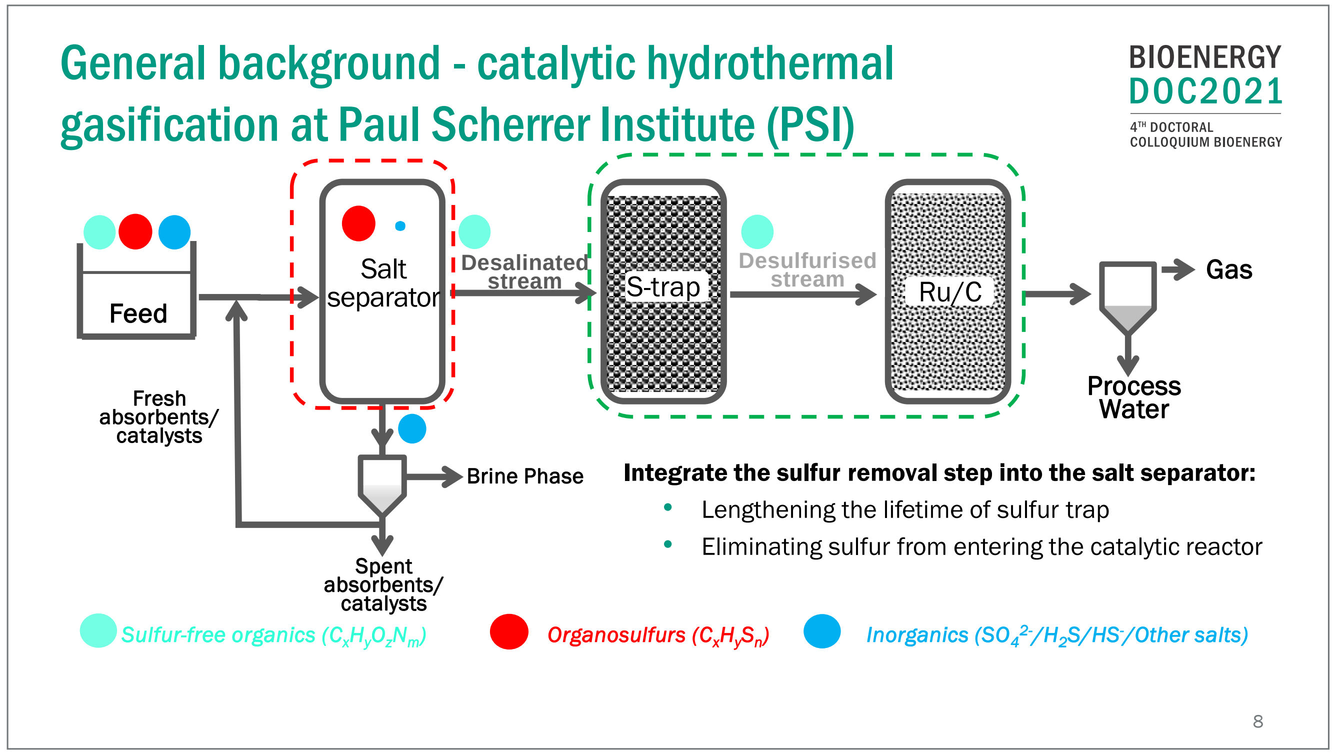

General background - catalytic hydrothermal gasification at Paul Scherrer Institute (PSI)

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Integrate the sulfur removal step into the salt separator:

- Lengthening the lifetime of sulfur trap
- Eliminating sulfur from entering the catalytic reactor

● Sulfur-free organics ($C_xH_yO_zN_m$) ● Organosulfurs ($C_xH_yS_n$) ● Inorganics ($SO_4^{2-}/H_2S/HS^-$/Other salts)

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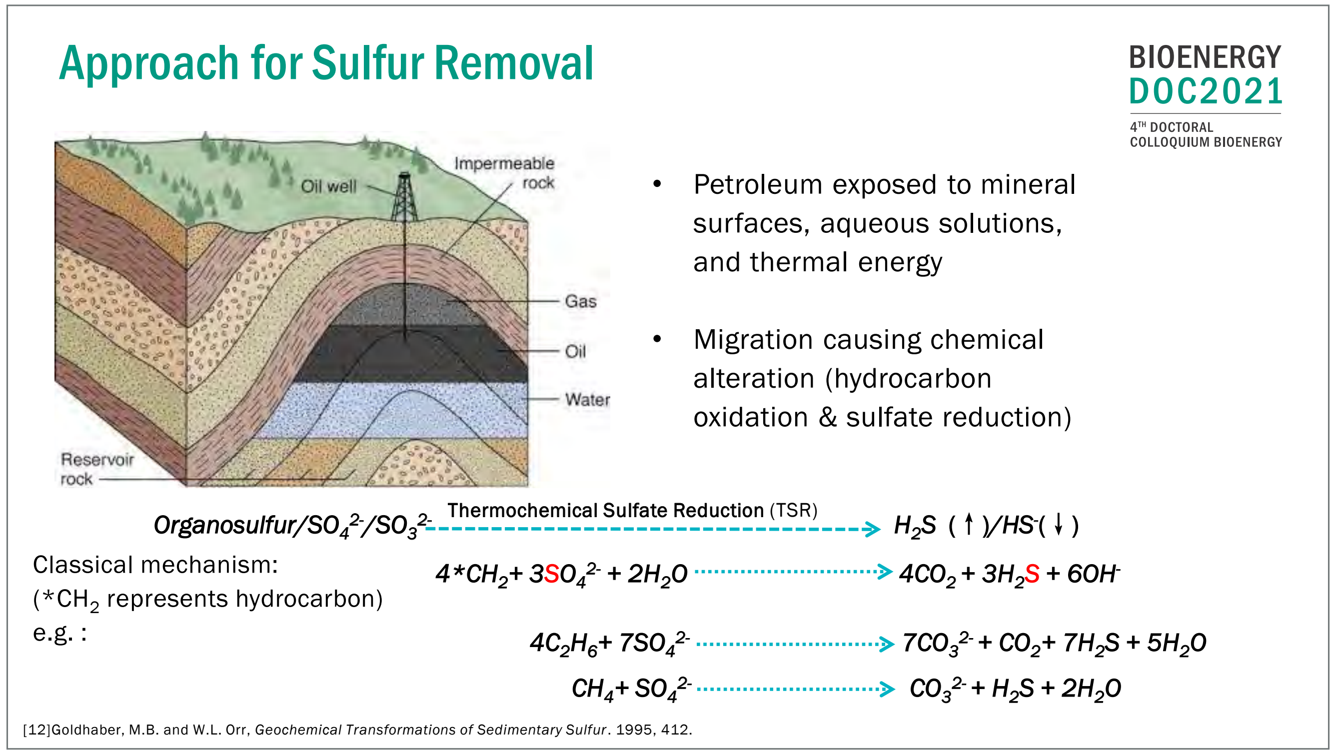

Approach for Sulfur Removal

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- Petroleum exposed to mineral surfaces, aqueous solutions, and thermal energy
- Migration causing chemical alteration (hydrocarbon oxidation & sulfate reduction)

$$Organosulfur/SO_4^{2-}/SO_3^{2-} \xrightarrow{\text{Thermochemical Sulfate Reduction (TSR)}} H_2S\ (\uparrow)/HS^-(\downarrow)$$

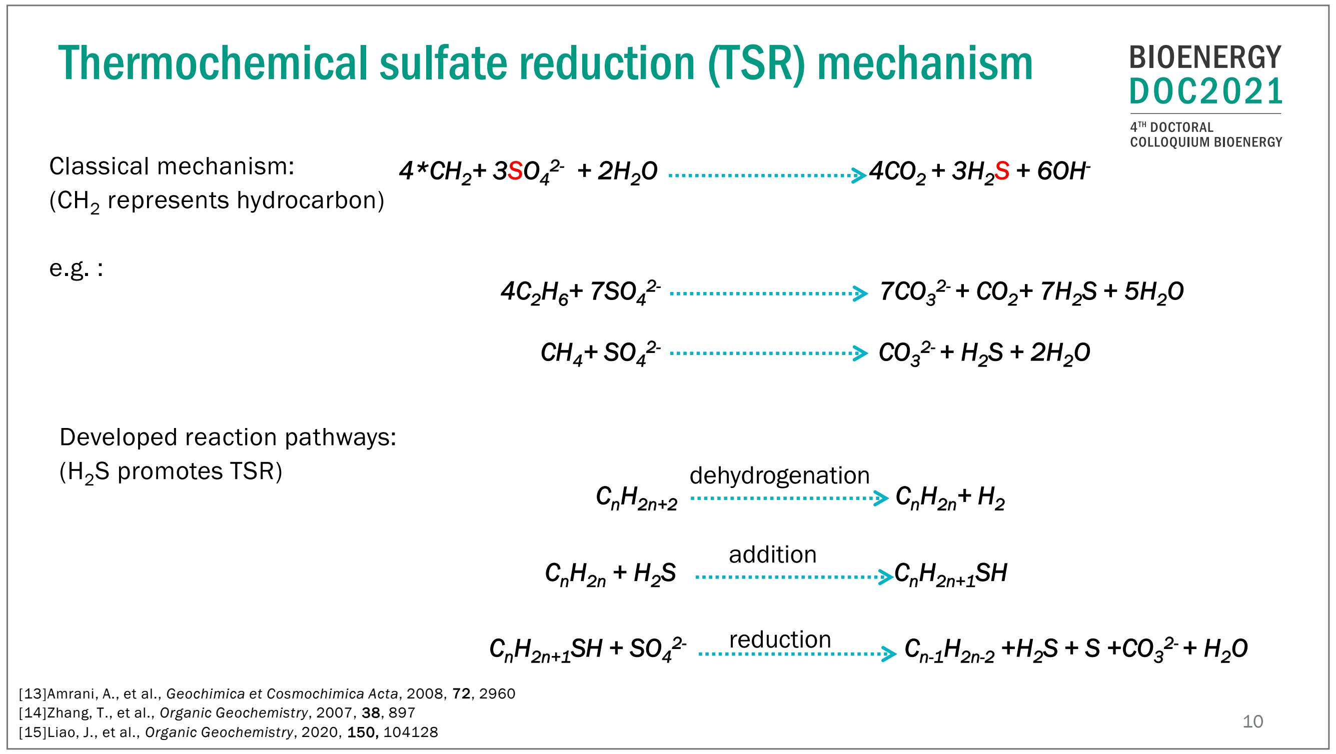
Classical mechanism:
(*CH_2 represents hydrocarbon)
e.g. :

$$4{*}CH_2 + 3SO_4^{2-} + 2H_2O \rightarrow 4CO_2 + 3H_2S + 6OH^-$$

$$4C_2H_6 + 7SO_4^{2-} \rightarrow 7CO_3^{2-} + CO_2 + 7H_2S + 5H_2O$$

$$CH_4 + SO_4^{2-} \rightarrow CO_3^{2-} + H_2S + 2H_2O$$

[12]Goldhaber, M.B. and W.L. Orr, *Geochemical Transformations of Sedimentary Sulfur*. 1995, 412.



Thermochemical sulfate reduction (TSR) mechanism

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Classical mechanism:
(CH_2 represents hydrocarbon)

$$4{*}CH_2 + 3SO_4^{2-} + 2H_2O \rightarrow 4CO_2 + 3H_2S + 6OH^-$$

e.g. :

$$4C_2H_6 + 7SO_4^{2-} \rightarrow 7CO_3^{2-} + CO_2 + 7H_2S + 5H_2O$$

$$CH_4 + SO_4^{2-} \rightarrow CO_3^{2-} + H_2S + 2H_2O$$

Developed reaction pathways:
(H_2S promotes TSR)

$$C_nH_{2n+2} \xrightarrow{\text{dehydrogenation}} C_nH_{2n} + H_2$$

$$C_nH_{2n} + H_2S \xrightarrow{\text{addition}} C_nH_{2n+1}SH$$

$$C_nH_{2n+1}SH + SO_4^{2-} \xrightarrow{\text{reduction}} C_{n-1}H_{2n-2} + H_2S + S + CO_3^{2-} + H_2O$$

[13]Amrani, A., et al., *Geochimica et Cosmochimica Acta*, 2008, **72**, 2960
[14]Zhang, T., et al., *Organic Geochemistry*, 2007, **38**, 897
[15]Liao, J., et al., *Organic Geochemistry*, 2020, **150**, 104128

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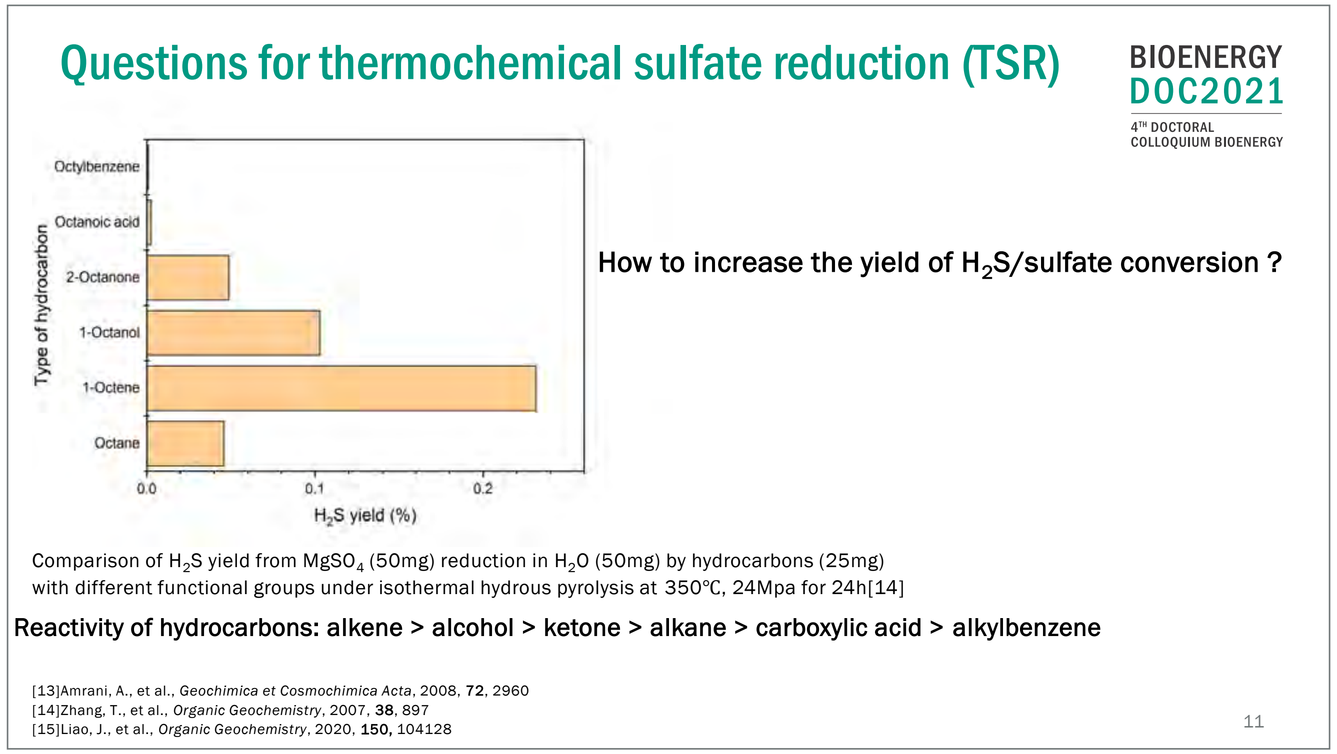

Questions for thermochemical sulfate reduction (TSR)

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How to increase the yield of H_2S/sulfate conversion ?

Comparison of H_2S yield from $MgSO_4$ (50mg) reduction in H_2O (50mg) by hydrocarbons (25mg) with different functional groups under isothermal hydrous pyrolysis at 350℃, 24Mpa for 24h[14]

Reactivity of hydrocarbons: alkene > alcohol > ketone > alkane > carboxylic acid > alkylbenzene

[13]Amrani, A., et al., *Geochimica et Cosmochimica Acta*, 2008, **72**, 2960
[14]Zhang, T., et al., *Organic Geochemistry*, 2007, **38**, 897
[15]Liao, J., et al., *Organic Geochemistry*, 2020, **150,** 104128

Sub-questions and objectives

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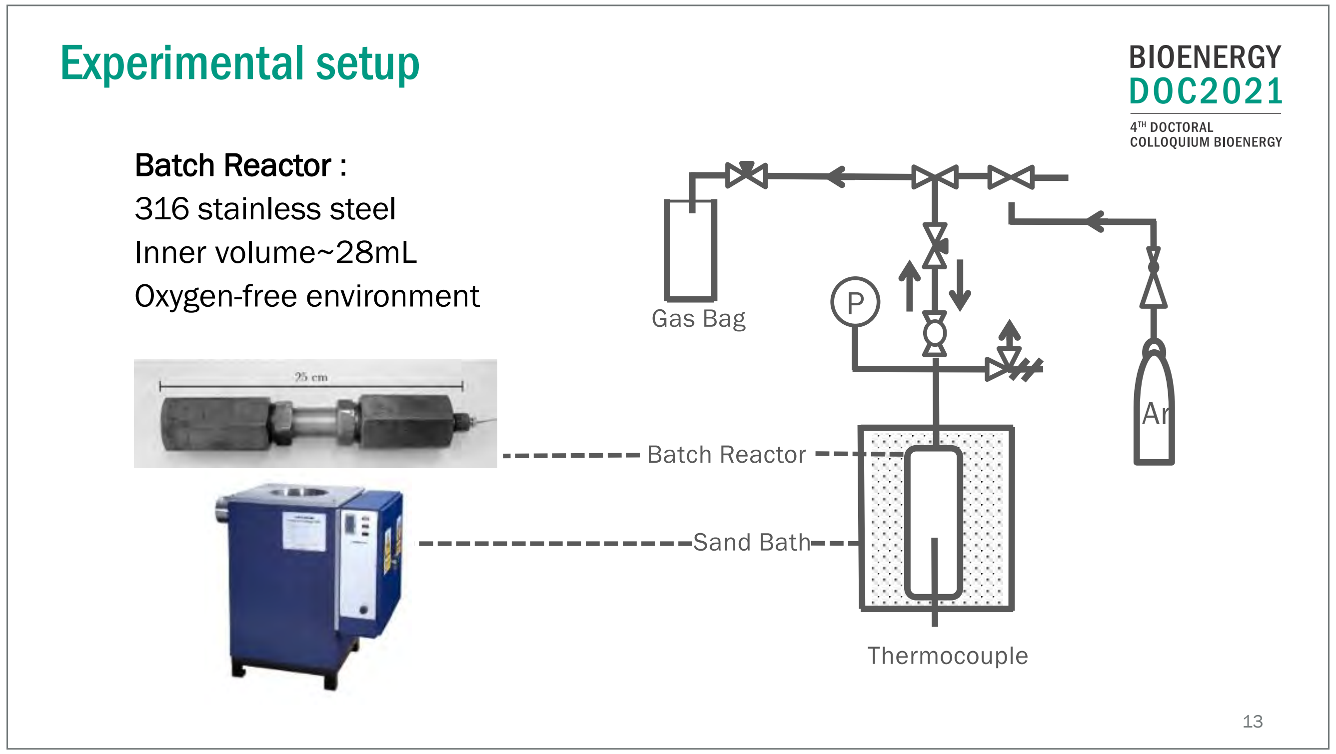
- What are the optimal reaction conditions (specific to HTG of biomass) for thermochemical sulfate reduction with model solution?
  - ➢ Identifying key parameters to find out optimal conditions of TSR with glycerol and potassium sulfate (temperature, reaction time, etc…) using IC for sulfate analysis.

- What is the reaction pathway and rate determining step of sulfate/organosulfurs with hydrocarbon in thermochemical sulfate reduction?
  - ➢ Investigating the transformation of different single reaction intermediates (by GC-SCD) under TSR conditions.

- What is the impact of catalysts/absorbents on TSR?
  - ➢ Investigating different catalysts/absorbents with model solution under TSR conditions.



Experimental setup

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Batch Reactor :
316 stainless steel
Inner volume~28mL
Oxygen-free environment

Thermochemical Sulfate Reduction (TSR) with Model Solution in Batch Reactor

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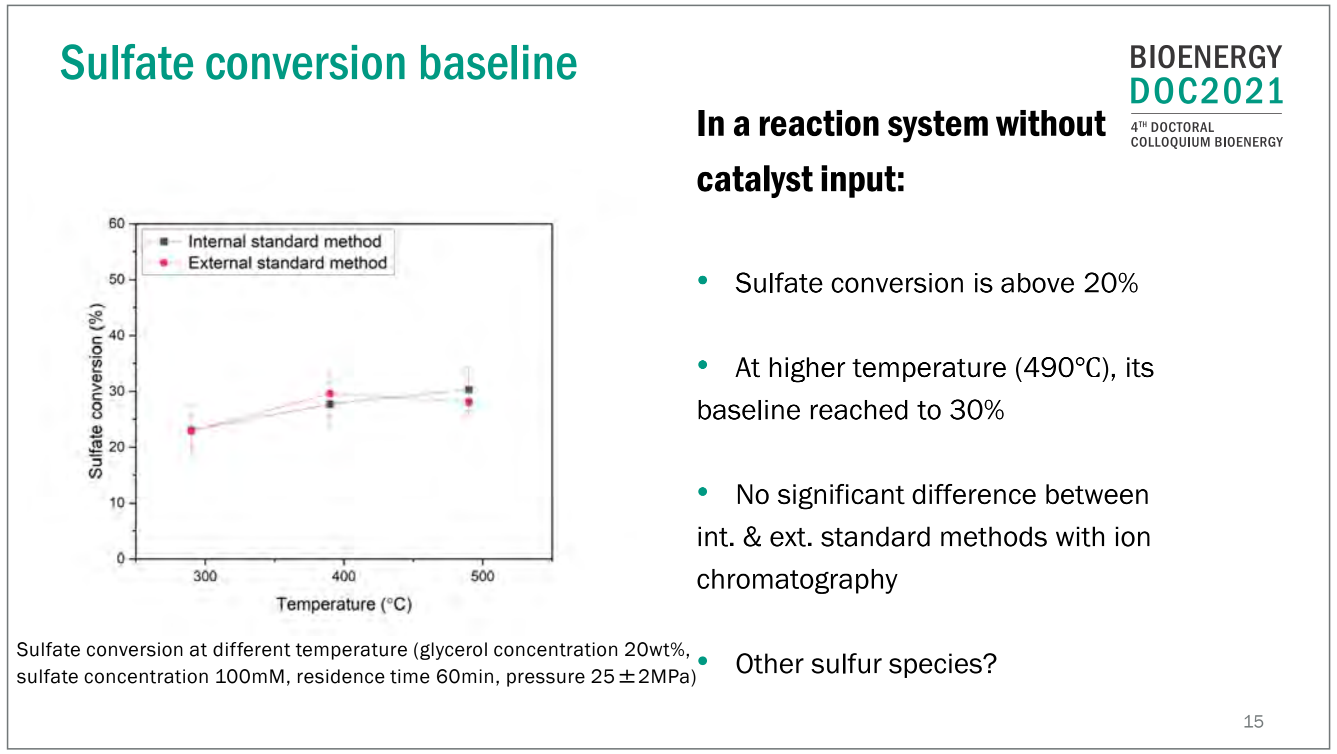
Table 1. Temperature effect on sulfate conversion based on internal standard method (glycerol concentration 20wt%, sulfate concentration 100mM, residence time 60min, pressure 25±2MPa)

Experiment No.	Temperature (℃)	Dosage (mL)	Initial sulfate amount (μmol)	Sulfate in product (μmol)	Sulfate balance (%)	Organosulfur balance (%)	Total sulfur balance (%)
Exp. 1	290	24.0	257±6	198±10.5	76.9 ±4.5	0.2±0.0	77.1±4.5
Exp. 2	390	6.7	72±2	51.9±7.3	72.3±10.4	6.2±0.2	78.5±11.3
Exp. 3	490	4.3	46±1	32.1±3.9	69.6±9.0	3.5±0.2	73.2±9.4

*Sulfite and sulfide are not detected due to limitations of analytical instruments. Sulfate was analyzed on ion chromatography (IC) with Zn nitrate as internal standard while organosulfur was analyzed on GC-SCD with dibenzothiophene as internal standard.

In a reaction system without catalyst input:

- Total sulfur balance is below 100%, there are other sulfur species besides sulfate and organosulfur.
- The amount of organosulfur is the highest at 390℃, indicating near-super critical point condition might benefit the generation of organosulfur the most.

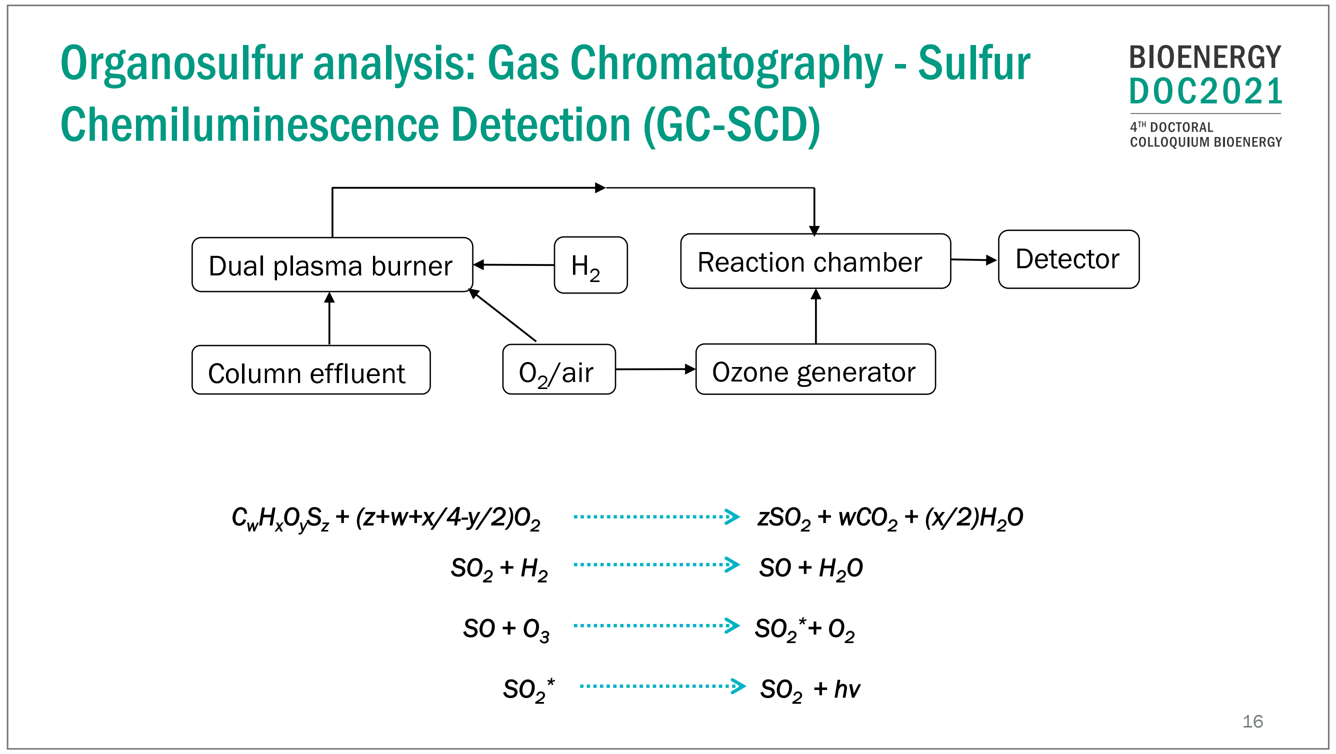


Sulfate conversion baseline

In a reaction system without catalyst input:

- Sulfate conversion is above 20%
- At higher temperature (490℃), its baseline reached to 30%
- No significant difference between int. & ext. standard methods with ion chromatography
- Other sulfur species?

Sulfate conversion at different temperature (glycerol concentration 20wt%, sulfate concentration 100mM, residence time 60min, pressure 25±2MPa)



Organosulfur analysis: Gas Chromatography - Sulfur Chemiluminescence Detection (GC-SCD)

Dual plasma burner

H_2

Reaction chamber

Detector

Column effluent

O_2/air

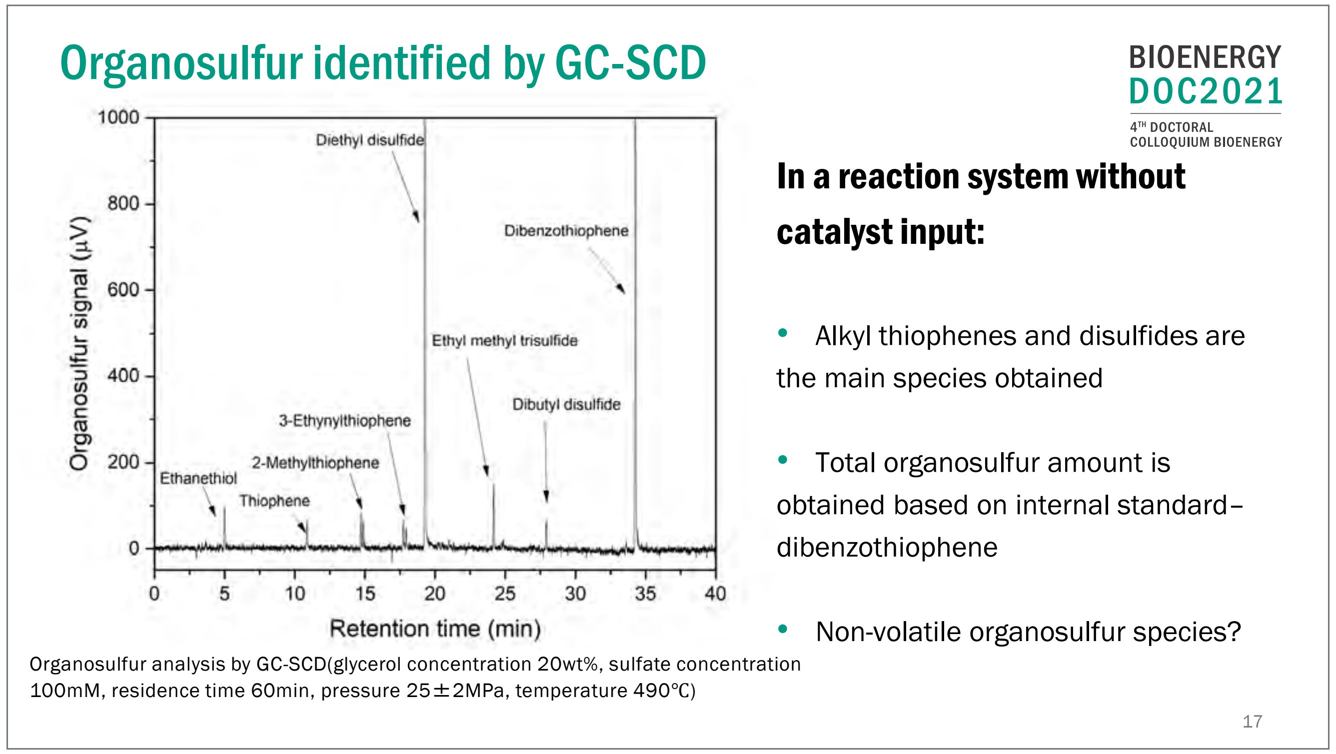
Ozone generator

$$C_wH_xO_yS_z + (z+w+x/4-y/2)O_2 \longrightarrow zSO_2 + wCO_2 + (x/2)H_2O$$

$$SO_2 + H_2 \longrightarrow SO + H_2O$$

$$SO + O_3 \longrightarrow SO_2^* + O_2$$

$$SO_2^* \longrightarrow SO_2 + hv$$



Organosulfur identified by GC-SCD

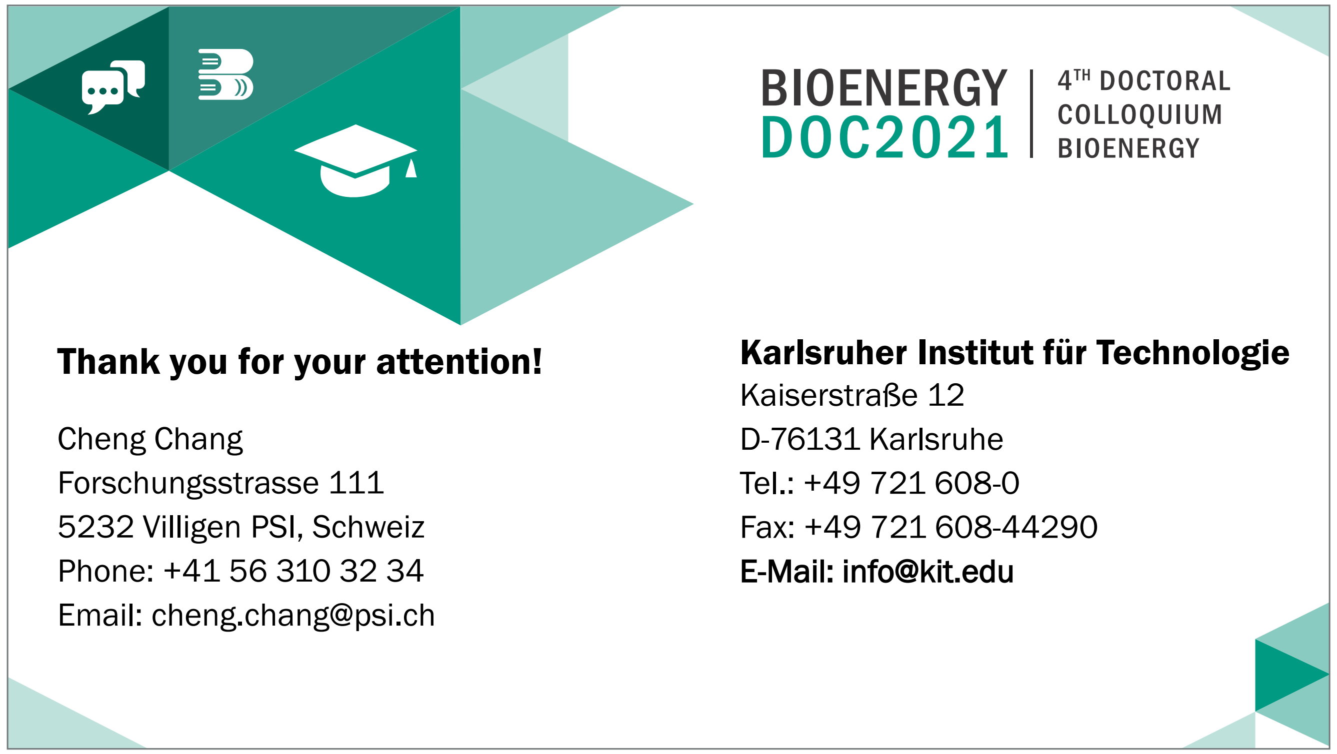
In a reaction system without catalyst input:

- Alkyl thiophenes and disulfides are the main species obtained
- Total organosulfur amount is obtained based on internal standard–dibenzothiophene
- Non-volatile organosulfur species?

Organosulfur analysis by GC-SCD(glycerol concentration 20wt%, sulfate concentration 100mM, residence time 60min, pressure 25±2MPa, temperature 490℃)

Next steps

- Closing the sulfur balance by using different analytical methods: HPLC for non-volatile organosulfur analysis, CHNS/ICP for total sulfur analysis, gas analyzer for H_2S.
- Conducting batch reactor experiments with model solution over different residence time and more temperature setting points to obtain the optimal condition.
- Composing reaction pathways based on the organosulfur species identified and find out the rate determining step by using intermediates as feedstock.
- Selecting and examining catalysts for sulfate reduction under supercritical conditions



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Thank you for your attention!

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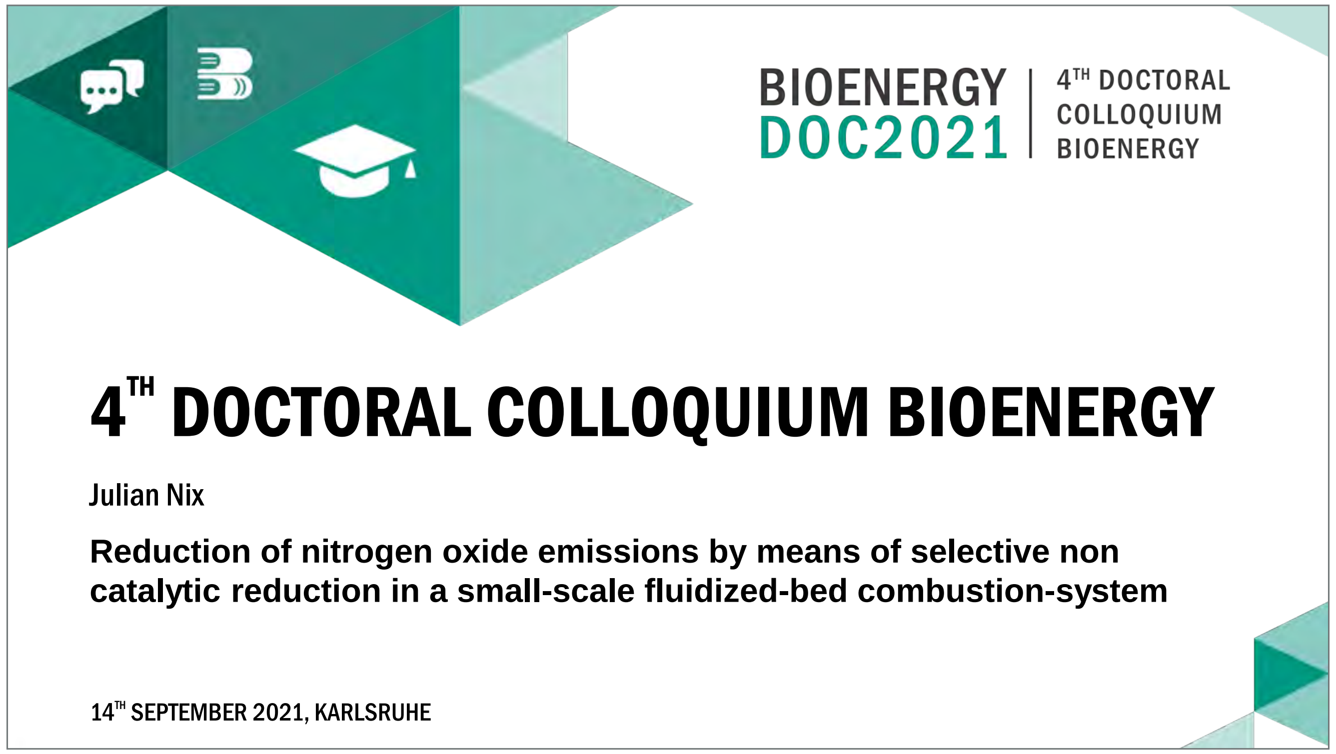
Julian Nix, Friedrich-Alexander-University Erlangen/Nürnberg

Reduction of nitric oxide emissions by means of selective non catalytic reduction in a small-scale fluidized-bed combustion-system

Julian Nix, Dominik Müller, Jürgen Karl
Friedrich-Alexander University of Erlangen-Nürnberg
Fürther Straße 244f
90429 Nürnberg
E-mail: **julian.nix@fau.de**

The energetic potential of residual biomass from agriculture and forestry has remained largely unexploited so far. The typically low ash melting temperatures of these fuels, inevitably lead to intensified slagging in conventional combustion plants. Within the past years, the chair for Energy Process Engineering developed and demonstrated an innovative concept of a small-scale fluidized-bed combustion-system. This system can be cooled actively by an integrated heat exchanger, allowing low combustion temperatures with less excess air and therefore higher combustion efficiencies. The combination of the small-scale fluidized-bed combustion system with a Stirling engine offers potential applications, not only for the supply of heat, but also for the co-generation of heat and power. Our recent work addresses further development of the system, focussing on the formation and reduction of nitric oxide emissions. To achieve better understanding for the formation of gaseous emissions inside the fluidized-bed combustion, we coupled the simulation of particle flow and -reactions in Barracuda VR with the gas-phase-reactions in Ansys Fluent. This procedure allows us to take transient effects of the fluidized bed into account, such as rising gas bubbles and include them in the inlet boundary conditions of the CFD-simulation. Initially, the particle dominated reactions during the fuel conversion inside the fluidized-bed are calculated with Barracuda VR. The results are than analysed and translated into a Fluent-compatible syntax with Matlab. As a final step, Ansys Fluent calculates the gas phase reactions. This leads to an overall simulative description, which simplifies the identification of suitable operating parameters for the application of the selective non catalytic reduction inside the cyclone of the system. The cyclone does not only separate particles from the exhaust gas flow, but also acts as thermal afterburning system, that proved to be responsible for the plant's typically very low CO-emissions. As it is equipped with a doubled wall, the cyclone can also be used as an air-preheater, to achieve higher electrical efficiencies in co-generation-mode, by increasing the combustion temperature. The high turbulence and the temperature range (750°-1000 °C) also qualify the cyclone as a reactor for the non-catalytic reduction of NOx-emissions. This new function is investigated in our recent work. The experiments show significant reduction of NOx-emissions, while the simulations indicate an even enhanced reduction of NOx. This conference contribution presents experimental and simulative results of the selective non catalytic reduction inside the cyclone of a small-scale fluidized bed combustion system. We investigated different influences on the reduction performance by the variation of stoichiometry, temperature, position and excess air ratio. The results can be used for an optimized operation and show points for further improvement of the application.



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Julian Nix

Reduction of nitrogen oxide emissions by means of selective non catalytic reduction in a small-scale fluidized-bed combustion-system

14TH SEPTEMBER 2021, KARLSRUHE

Overview on this presentation

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1. THE PROJECT „SmartWirbelschicht“
- Motivation and goals of the project

2. INTEGRATION OF SNCR
- experimental / simulative approach and results

3. CONCLUSION AND OUTLOOK

20.09.2021 2

Short introduction

Title of the Doctoral Project:	„SmartWirbelschicht“
Doctoral Student:	Julian Nix
University:	Friedrich-Alexander University Erlangen-Nürnberg
University Supervisor:	Prof. Dr.-Ing. Jürgen Karl
Funding :	BMEL, FNR Bundesministerium für Ernährung und Landwirtschaft FNR Fachagentur Nachwachsende Rohstoffe e.V.
Duration:	06/2019 – 05/2022

Motivation and goals of the project „SmartWirbelschicht“

MOTIVATION – A look back on previous work at EVT

Development of a micro CHP-system combining fluidized bed combustion with a Stirling engine:

- ✓ Wide fuel range
- ✓ Prevention of slagging
- ✓ Low emissions (CO & dust – with woody fuels)
- ✓ Air pre-heating with double-walled cyclone → increase of electrical efficiency

how it started…

Upscale and field test operation of a pilot-plant

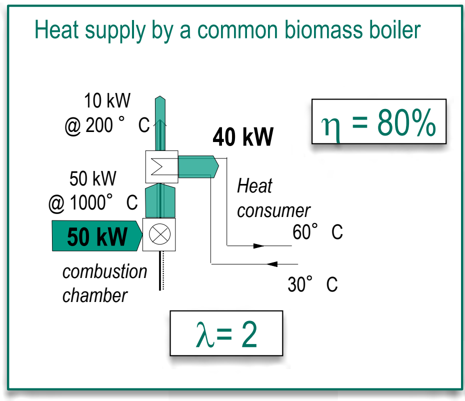
- ✓ Continous operation with several fuels (i.a. waste wood, sewage sludge)
- ✓ Detailed investigation of operation strategies and their effect on emissions

the next steps…

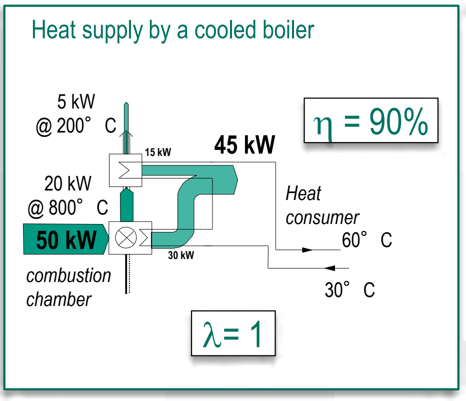
- ➢ Fuels with high nitrogen content e.g. hay-pellets require futher reduction measures

Motivation and goals of the project „SmartWirbelschicht“

MOTIVATION – fields of application (new: besides CHP)



Heat supply by a common biomass boiler



Heat supply by a cooled boiler

Motivation and goals of the project „SmartWirbelschicht“

MAIN GOALS

Identification of the „ideal application“ and acquisition of future partners

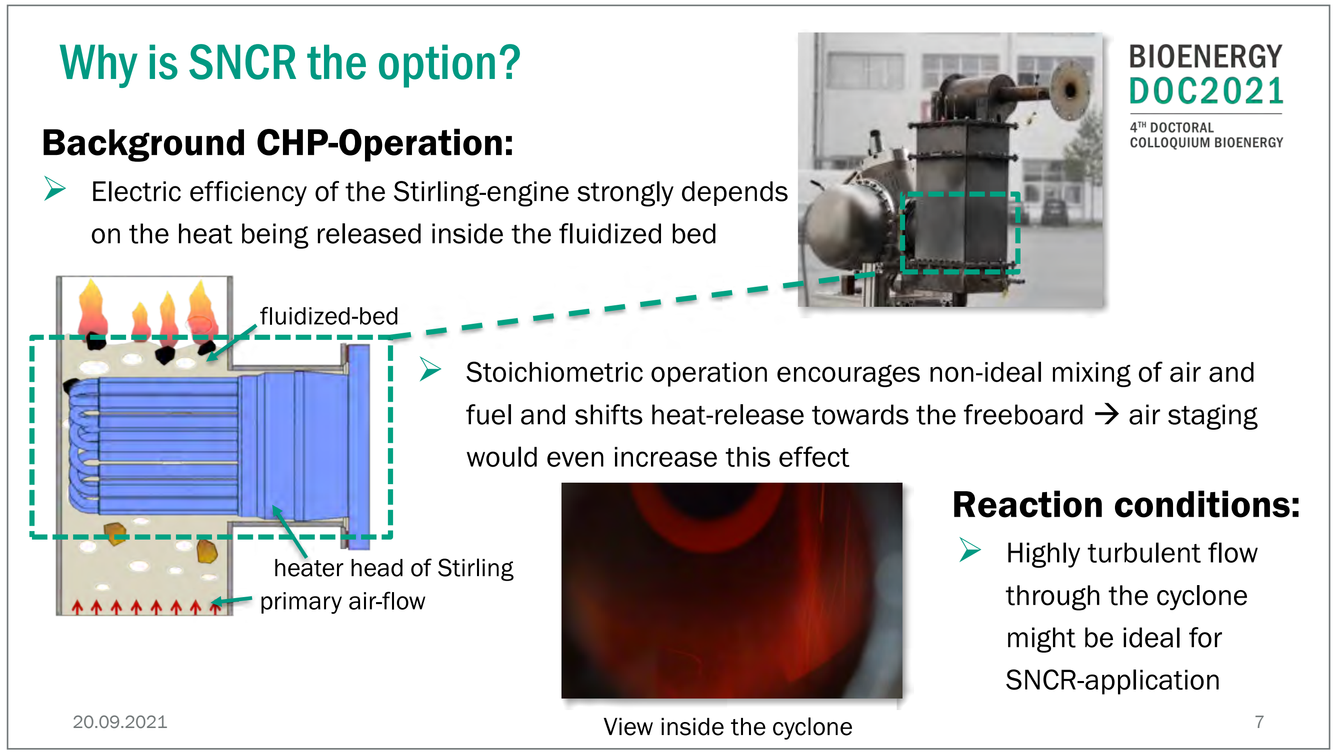
Economical- and thermodynamical evaluation of different application scenarios

- ➢ Evaluation with current customer needs/data
- ➢ Techno-economical analysis of future market potentials

eta Energieberatung DBFZ

Better understanding of NO_x-formation and modification of the lab system

- ➢ Particle resolved simulation of fuel conversion with CPFD-software Barracuda-VR
- ➢ Gas-phase reactions including NO_x-reduction by SNCR in ANSYS Fluent
- ➢ Experimental demonstration of SNCR
- ➢ Detailed emission measurements in full- and partial-load operation



Why is SNCR the option?

Background CHP-Operation:

- Electric efficiency of the Stirling-engine strongly depends on the heat being released inside the fluidized bed

- Stoichiometric operation encourages non-ideal mixing of air and fuel and shifts heat-release towards the freeboard → air staging would even increase this effect

Reaction conditions:

- Highly turbulent flow through the cyclone might be ideal for SNCR-application

View inside the cyclone

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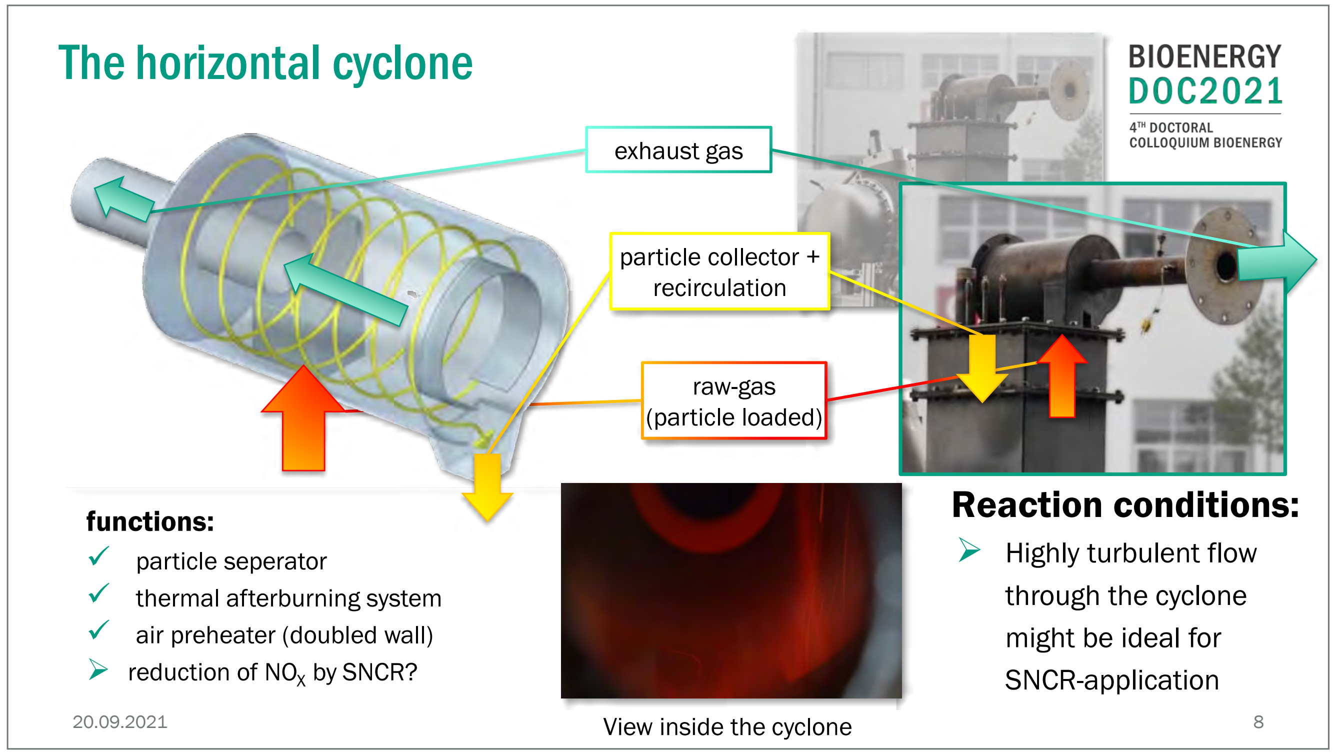

The horizontal cyclone

functions:

- ✓ particle seperator
- ✓ thermal afterburning system
- ✓ air preheater (doubled wall)
- ✓ reduction of NO_x by SNCR?

Reaction conditions:

- Highly turbulent flow through the cyclone might be ideal for SNCR-application

View inside the cyclone

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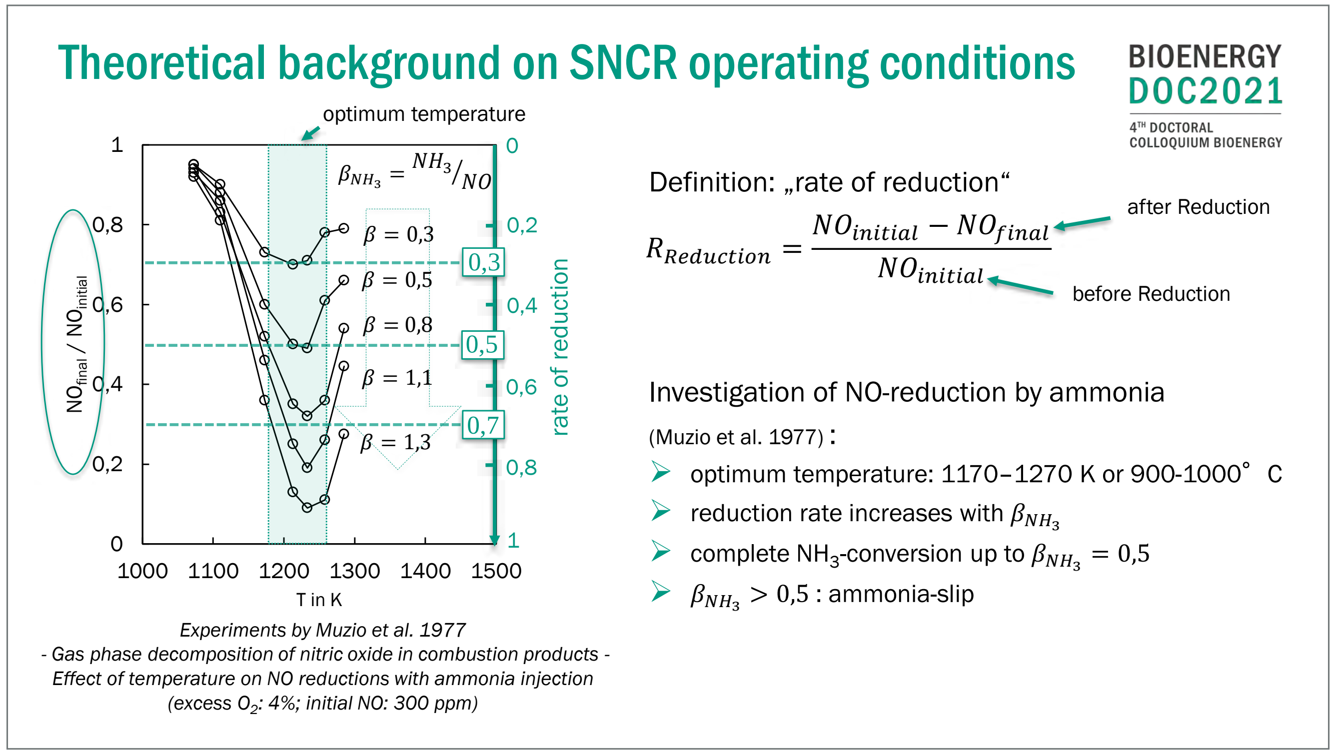


Theoretical background on SNCR operating conditions

Experiments by Muzio et al. 1977
- Gas phase decomposition of nitric oxide in combustion products -
Effect of temperature on NO reductions with ammonia injection
(excess O_2: 4%; initial NO: 300 ppm)

Definition: „rate of reduction“

$$R_{Reduction} = \frac{NO_{initial} - NO_{final}}{NO_{initial}}$$

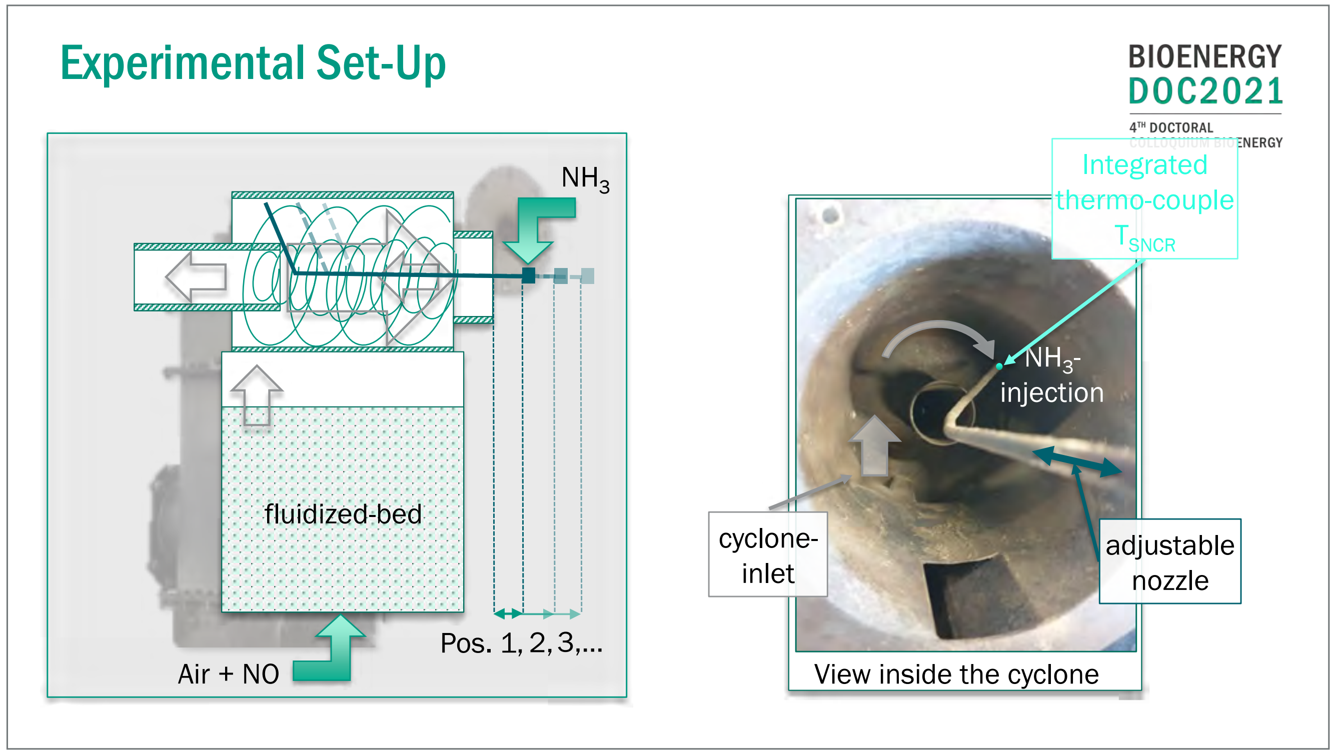
after Reduction

before Reduction

Investigation of NO-reduction by ammonia

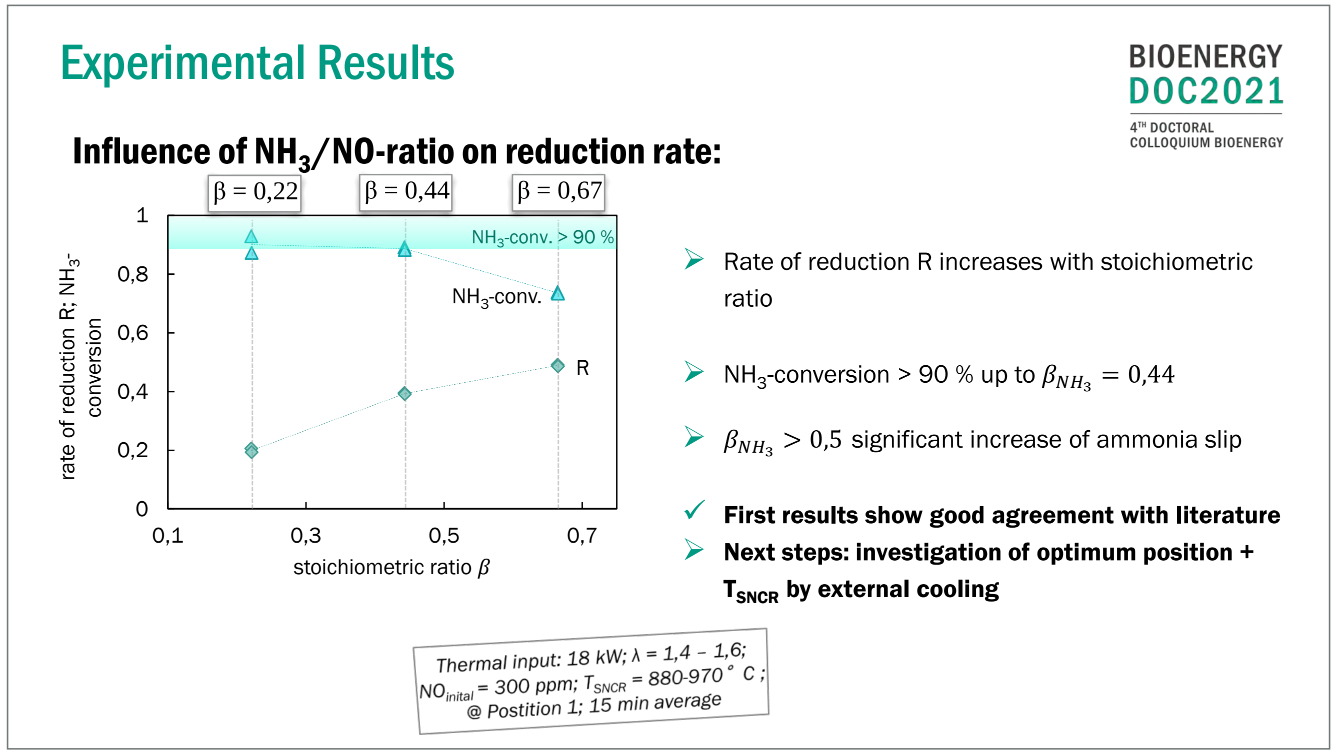
(Muzio et al. 1977) :

- optimum temperature: 1170–1270 K or 900-1000° C
- reduction rate increases with β_{NH_3}
- complete NH_3-conversion up to $\beta_{NH_3} = 0,5$
- $\beta_{NH_3} > 0,5$: ammonia-slip



Experimental Set-Up

View inside the cyclone



Experimental Results

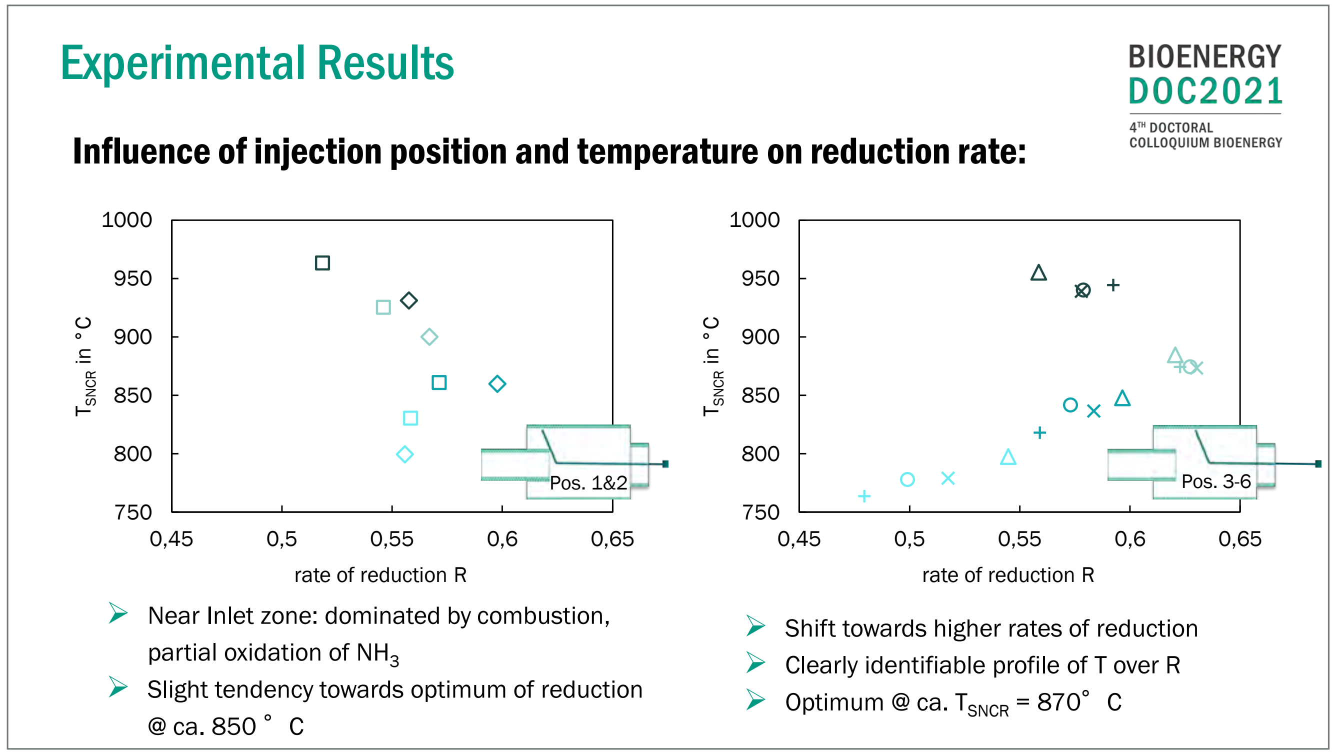
Influence of NH_3/NO-ratio on reduction rate:

- Rate of reduction R increases with stoichiometric ratio
- NH_3-conversion > 90 % up to $\beta_{NH_3} = 0{,}44$
- $\beta_{NH_3} > 0{,}5$ significant increase of ammonia slip

✓ **First results show good agreement with literature**

- **Next steps: investigation of optimum position + T_{SNCR} by external cooling**

Thermal input: 18 kW; λ = 1,4 – 1,6;
NO_{inital} = 300 ppm; T_{SNCR} = 880-970 ° C ;
@ Postition 1; 15 min average

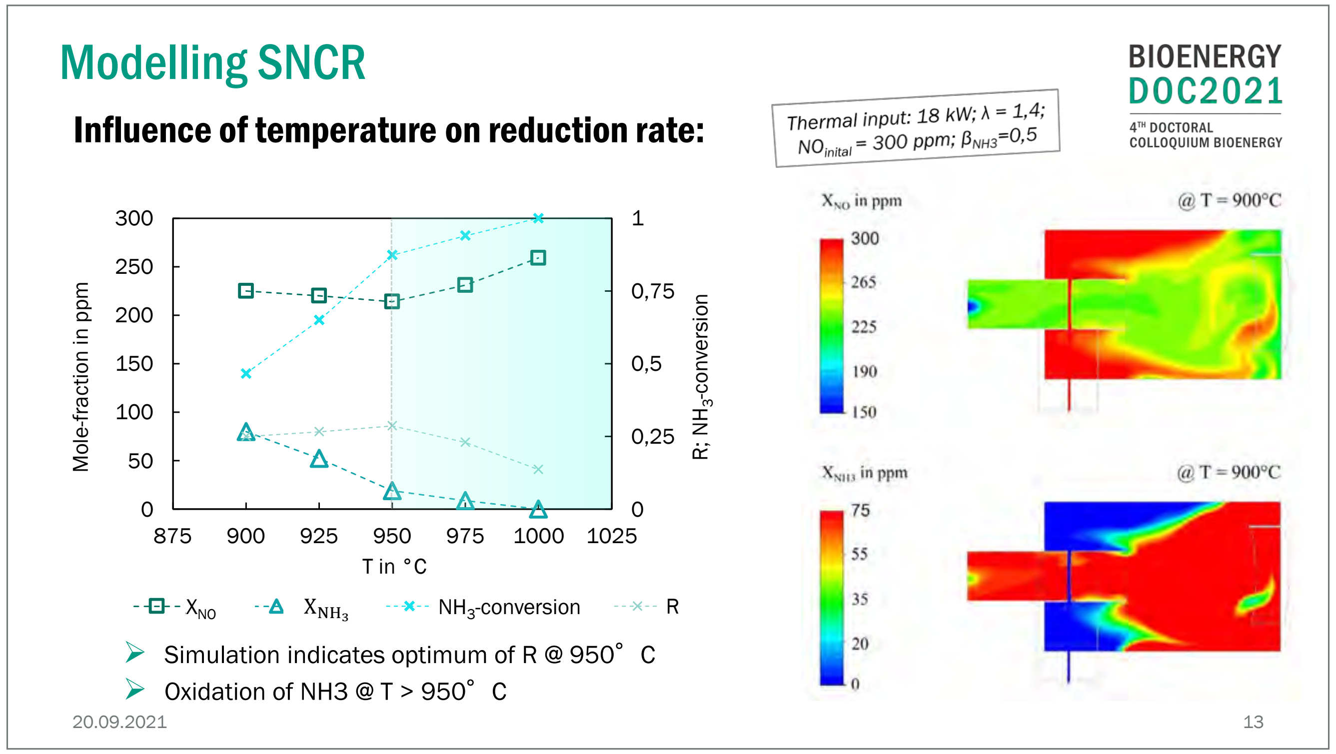


Experimental Results

Influence of injection position and temperature on reduction rate:

- Near Inlet zone: dominated by combustion, partial oxidation of NH_3
- Slight tendency towards optimum of reduction @ ca. 850 ° C

- Shift towards higher rates of reduction
- Clearly identifiable profile of T over R
- Optimum @ ca. T_{SNCR} = 870° C



Modelling SNCR

Influence of temperature on reduction rate:

Thermal input: 18 kW; λ = 1,4;
NO_{inital} = 300 ppm; β_{NH3}=0,5

- Simulation indicates optimum of R @ 950° C
- Oxidation of NH3 @ T > 950° C

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Conclusion

Experiments:

✓ SNCR can effectively be used for the reduction of NOx in the small-scale fluidized-bed system
✓ Highest rates of reduction were achieved with cooled cyclone → potential for air-preheating in CHP-mode
✓ Optimum position + „measured" temperature range for NH_3-injection identified

- Currently running: 36h tests with several fuels (unsteady NO_x-emissions)

SNCR -Modell

✓ Qualitative description of influence of Temperature on NO-reduction and NH_3-oxidation

Challenges

- Validation of heat-transfer
- Influence of radiation on temperature measurements
- Prediction of size of combustion-zone inside the cyclone requires consideration of the whole system

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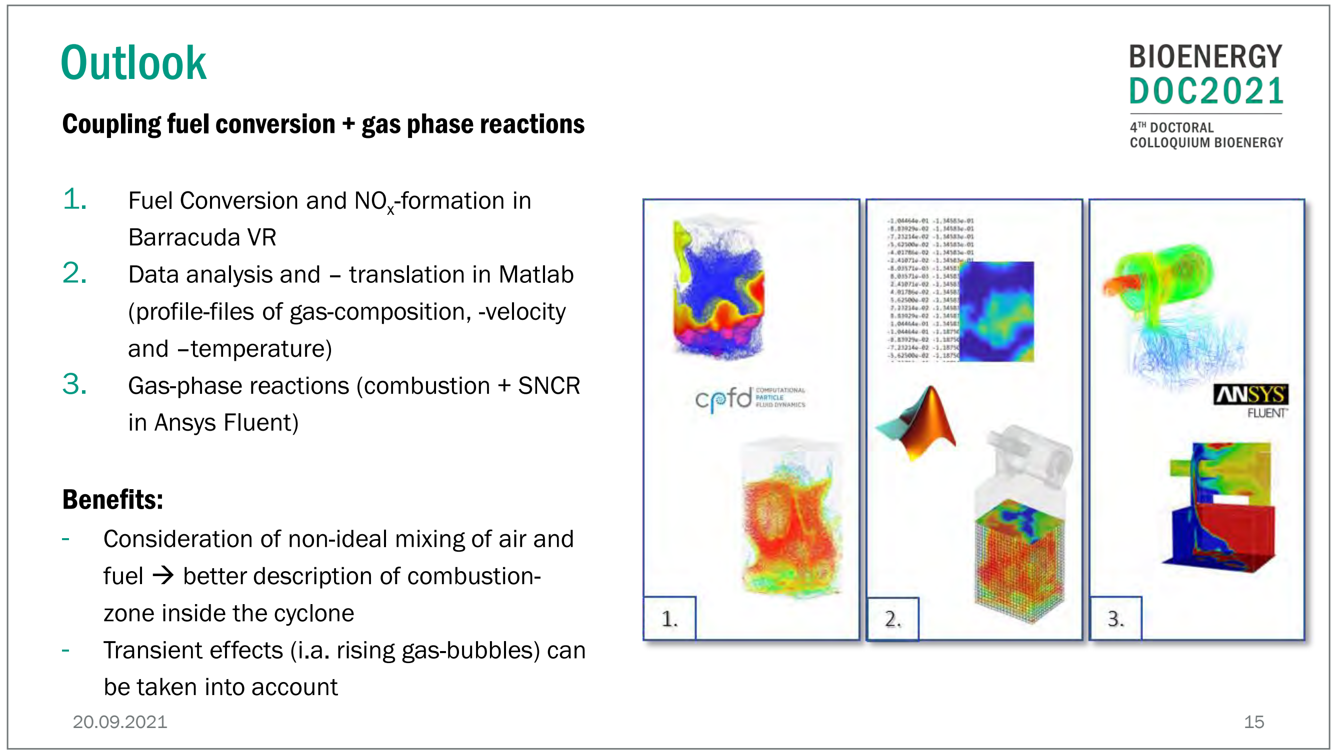

Outlook

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Coupling fuel conversion + gas phase reactions

1. Fuel Conversion and NO_x-formation in Barracuda VR
2. Data analysis and – translation in Matlab (profile-files of gas-composition, -velocity and –temperature)
3. Gas-phase reactions (combustion + SNCR in Ansys Fluent)

Benefits:

- Consideration of non-ideal mixing of air and fuel → better description of combustion-zone inside the cyclone
- Transient effects (i.a. rising gas-bubbles) can be taken into account

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