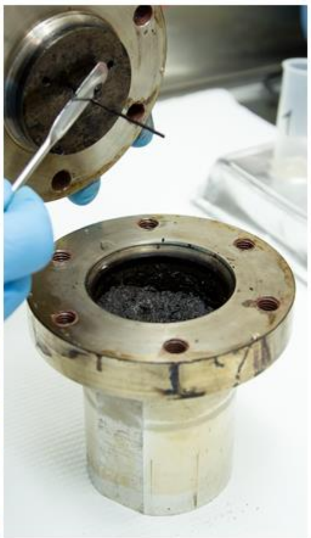
The crop as part of a biorefinery





Current and future works at the department of:

Conversion Technologies of Biobased Resources

Prof. Dr. Andrea Kruse

University of Hohenheim

Institute of Agricultural Engineering (440)
Conversion Technologies
of Biobased Resources (440f)

Imprint (German)

Authors

Prof. Dr. Andrea Kruse
Dr. Catalina Rodriguez Correa
Manuel Bauer
David Steinbach
Gero Becker

Photos/illustrations

Conversion Technologies of Biobased Resources, University of Hohenheim
German Academic Exchange Service DAAD / Focke Strangmann
Wikipedia
HTCycle

Published in April 2019

Content

1. Conversion Technologies at the Institute of Agricultural Engineering

The mission statement: **Nature-adapted technology**

Animals locked in small stalls and cages, environmentally unconscious agriculture in a monotonous landscape and the ongoing extinction of species. These are the consequences when nature is adapted to technology. The Institute of Agricultural Engineering at the University of Hohenheim is taking a different approach: Here technology is adapted to nature (Figure 1). We want to learn from nature and thus follow the principles of the "biologization of technology".

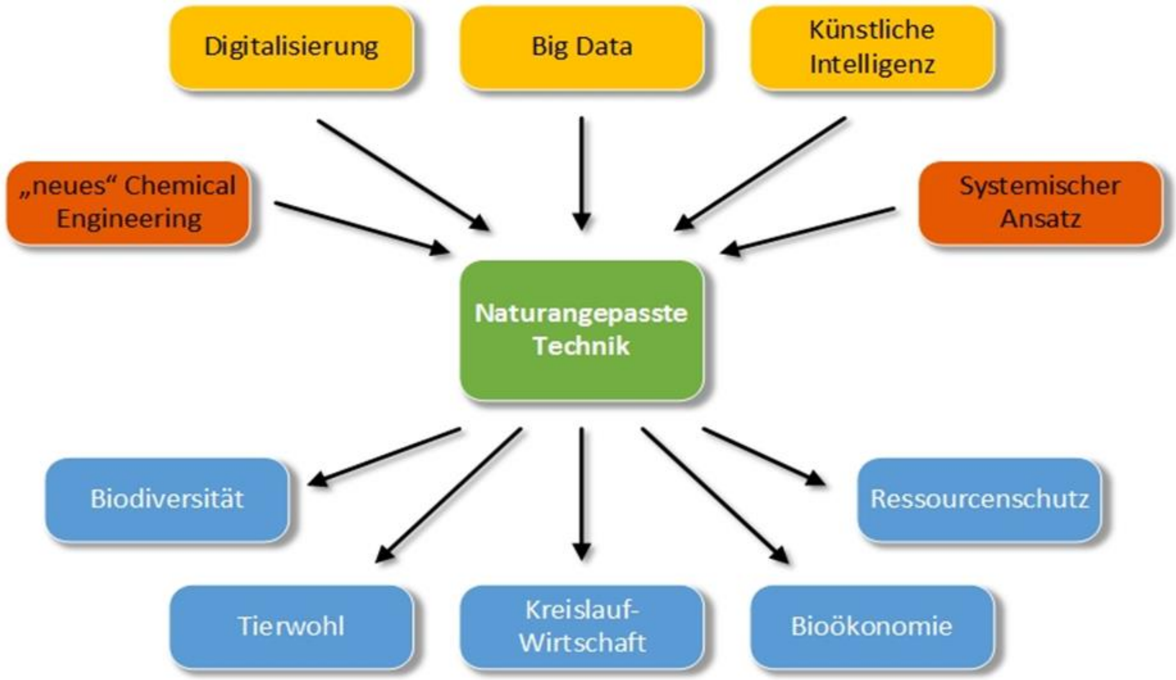


Figure 1: Nature-adapted technology with, for example, digitalisation and artificial intelligence as a basis for resource protection and food safety.

Soil-conserving agricultural practices protect the soil as a resource and safeguard the food supply of future generations. Animal-friendly stables with cleaned exhaust air not only secure animal welfare, but also guarantee the highest quality and safety of food. Small agricultural robots apply fertilizers and insecticides exactly where they are needed.

Hedgerows are preserved and allow the cohabitation of a large diversity of species within the agricultural system. The most important resource, water, is protected by innovative irrigation methods. In addition, phosphate and nitrogen recovery, for example from liquid manure and sewage sludge, combined with the precise application of fertilizers, ensure nutrient availability for plants without polluting groundwater or rivers. Residues from the food production are processed into new materials, e.g. for the electro-mobility, thus increasing the added-value of agriculture (bio-economy). These are just a few examples of the technological developments in agricultural engineering at the University of Hohenheim. They result in complex systems with large amounts of data (big data), which become manageable through digitalization and can be efficiently controlled with emerging artificial intelligence (Figure 1).

The activities of the department "Conversion Technologies of Biobased Resources" contribute to this mission statement. We adapt our technologies to the plant realm and in a second step to the agricultural structures. The fundamental principle and basis of our activities is the use of molecules and functional structures formed by the plants themselves. In addition, the department works intensively in the field of nutrient recovery and utilization.

2. Guiding principles in the department

Crops build-up chemical structures, which can be used as substitute for fossil-based products. Nutrients and the amount of carbon required for humus formation are returned to the field or remain there. This approach, known as circular or bio-economy, is implemented in biorefineries closely connected with agriculture.

Our focus is the development of carbon materials and platform chemicals that canbe used e.g. in the production of biogenic plastics. The carbon materials can be applied in energy storage systems for the electromobility, in hydrogen storage for fuel cells or in electrode materials for fuel cells and batteries.

In order to ensure sustainability of the processes, the entire value chain is considered: "From the field to the product" as well as from the product, at the end of its lifecycle, back to the field (e.g. in the form of nutrients, released during production).

In bioeconomy, however, there is a fundamental dilemma: the economy of scale and the necessary infrastructure favour very large conversion plants. This is often referred to as "Bio-BASF". Within this context and due to its extensive volume and quantities, biomass must be transported over long distances, which challenges the sustainability of the “bio-BASF” approach. Our proposalare modular, decentralised biorefineries that require only one (existing) biogas plant as additional infrastructure. Such modules can be manufactured in large quantities, thus reducing the cost per module. On decentralised on-farm biorefineries, intermediate products are obtained and transported to a central plant. This is where the mass production of marketable goods, such as car seats, clothing or batteries, takes place. Such an approach reduces transporting costs and brings together intermediate products from different biorefineries with variable starting materials. At the same time, different final goods can be manufactured from a single intermediate product, which makes the system flexible and enables a quick reaction to changes on the market.

Preferred raw materials are biomass residues and by-products from the food production, since this evades the food-vs.-fuel dilemma. In fact with a larger food production, more residues such as chicory roots or straw are available that can be used as feedstock for conversion. Figure 2 shows an example: the production of supercapacitors and batteries from maizecob residues, which fall as by-products from the corn maize production.

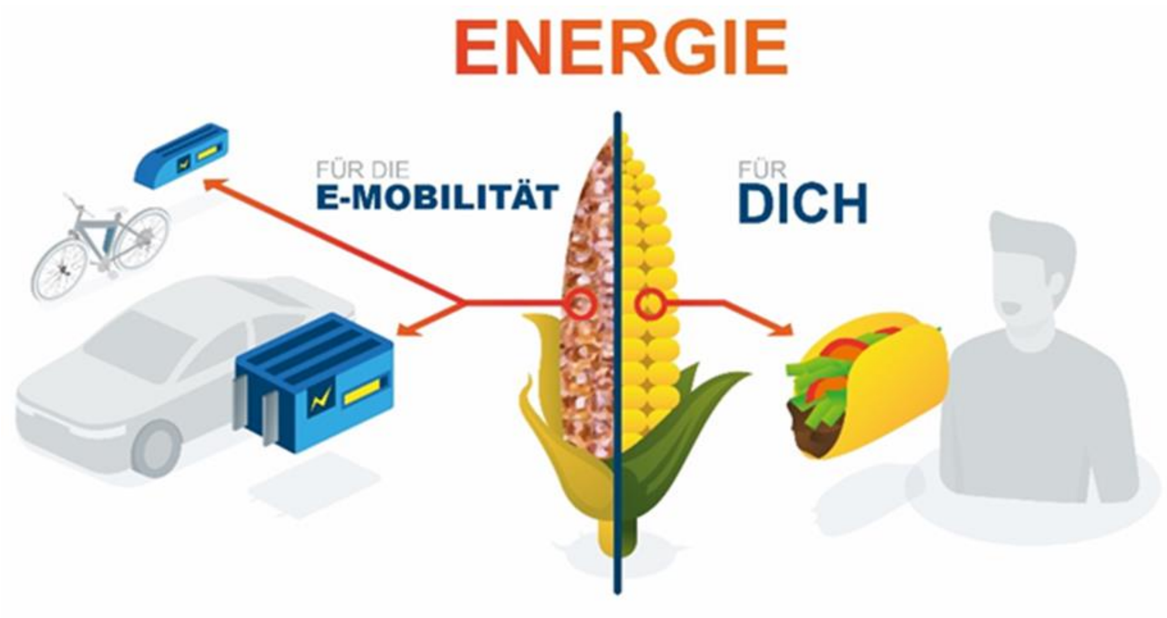


Figure 2: Production of carbon materials from the corncob after the corn grains have been removed for food usage. These carbon materials can be applied in the production of supercapacitors and battery electrodes.

3. The methodology

The methodology follows the classical rules of scale-up, to develop a technical process (Figure 3).

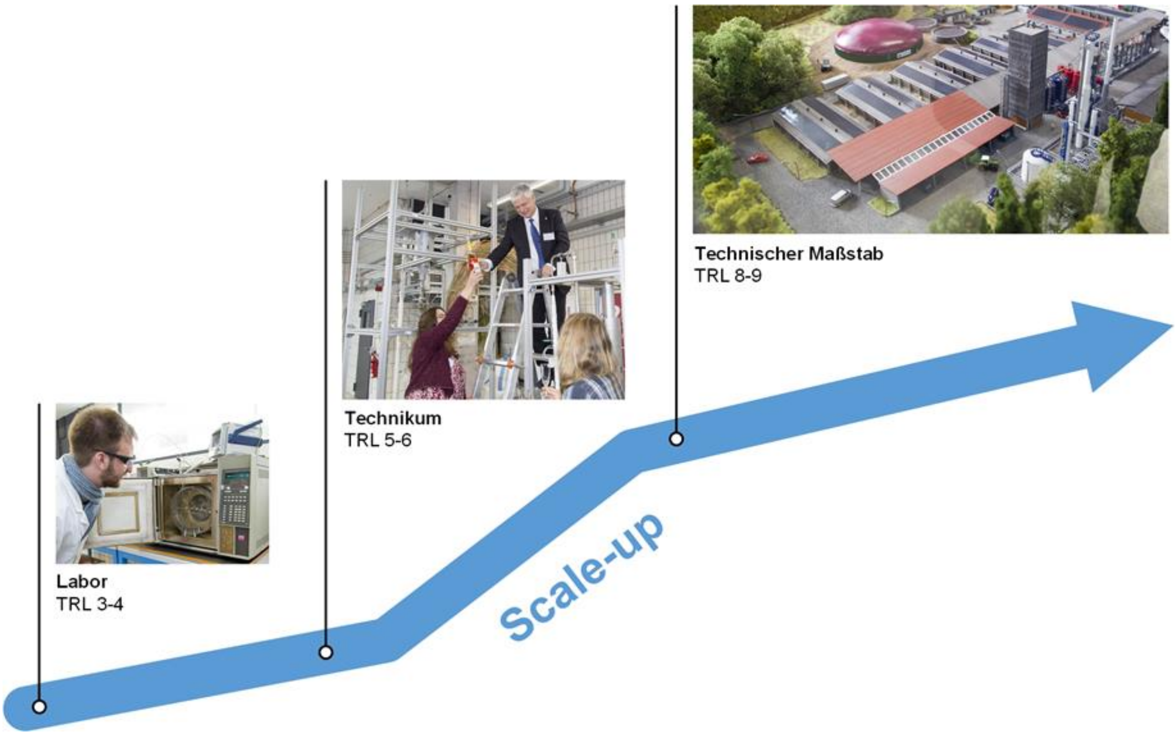


Figure 3: Visualization of scale-up (each with a factor of approx. 100).

As a first step, the production of certain materials or platform chemicals is tested, in the laboratory. Here, the relevant chemical reactions are "measured" and additional parameters and functions, such as kinetics of the chemical reactions, are modelled (Jung et al. 2018; Steinbach et al. 2018). On this basis, the technical reaction design is carried out, using mathematical models or, in simpler cases, "classically" with dimensionless numbers. Separation unit operations are designed in parallel. A platform chemical, such as 5-hydroxymethylfurfural (HMF) from chicory roots, first accumulates in aqueous solution and must be isolated afterwards. This requires the identification of appropriate separation methods (e.g. distillation, extraction, adsorption, etc.) and the determination of basic data. Finally, flow diagrams of a process can be set up (Schwiderski and Kruse 2016). Figure 4 shows an example of such a flow diagram.

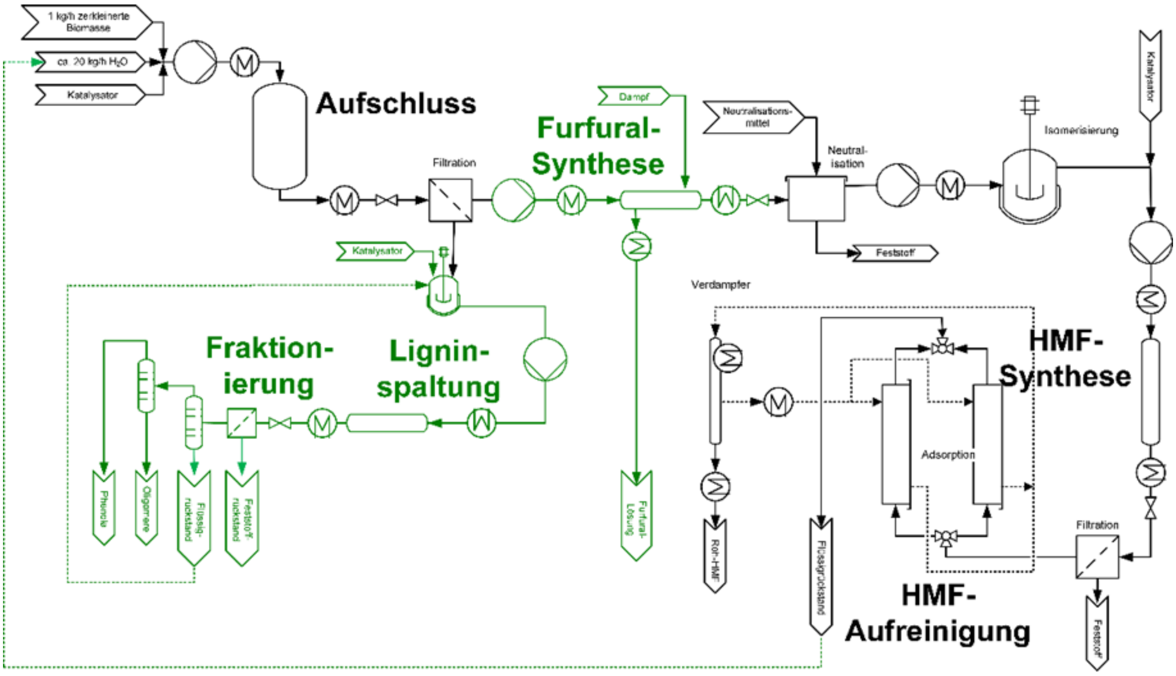


Figure 4: Flow chart of the B4B project (Biorefinery for Baden-Württemberg). Expansion of the plant in the biorefinery pilot plant to include the production of phenols and furfural as further platform chemicals in addition to hydroxymethyl-furfural.

Subsequently, the reactor is designed, i.e. material, size, type of heating, temperature range, fastening method, etc. are determined. If the plant components for a process are engineered and manufactured in accordance with the up-scaled design, the entire production process is assembled as a pilot or mini-plant. At the University of Hohenheim this takes place at the biorefinery pilot hall at the agricultural experiment station “Unterer Lindenhof”. This means that the unit operations, which were developed individually, are combined into one continuous process. An exemplary interconnection of different basic operations is presented in Figure 5.

The progress of a process can be expressed in Technology Readiness Levels (TRL). Pilot plants usually can only be operated in campaigns and working in shifts. They provide the necessary basic data for a scale-up to the industrial scale. In addition, samples of the product can be obtained, which is useful for a following market development. Often, pilot plants’ main purpose is to convince investors, because the mandatory last step is the industrial implementation and construction of a production plant.

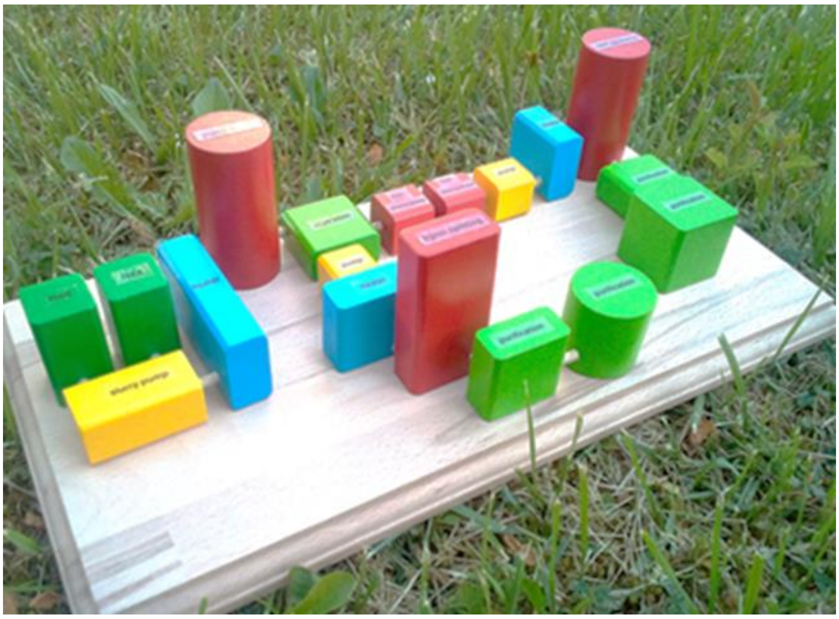


Figure 5: Model of the plant for the production of HMF and phenols from lignocellulose. Each building block corresponds to a unit operation.

4. Main working areas

The main activities of the department are the development of separation unit operations, the development of platform chemicals and novel carbon materials as well as their manufacturing processes. However, it is not possible to fully draw the line between these areas, since; for example, separation processes are always involved in the development of production processes for platform chemicals.

The individual focal points of the work and the respective stage of development are described below (Figure 6). Up to TRL 3, the laboratory infrastructure of the experimental hall of the Institute of Agricultural Engineering is used for research and development. A typical example is shown in Figure 3 at the bottom left part of the figure. Here, individual unit operations are developed and small systems are implemented. In order to achieve TRL 5 or 6, a plant has to be set up in the biorefinery pilot hall, where several unit operations are combined to form a single process. Higher TRLs can only be achieved with a close cooperation with industrial partners.

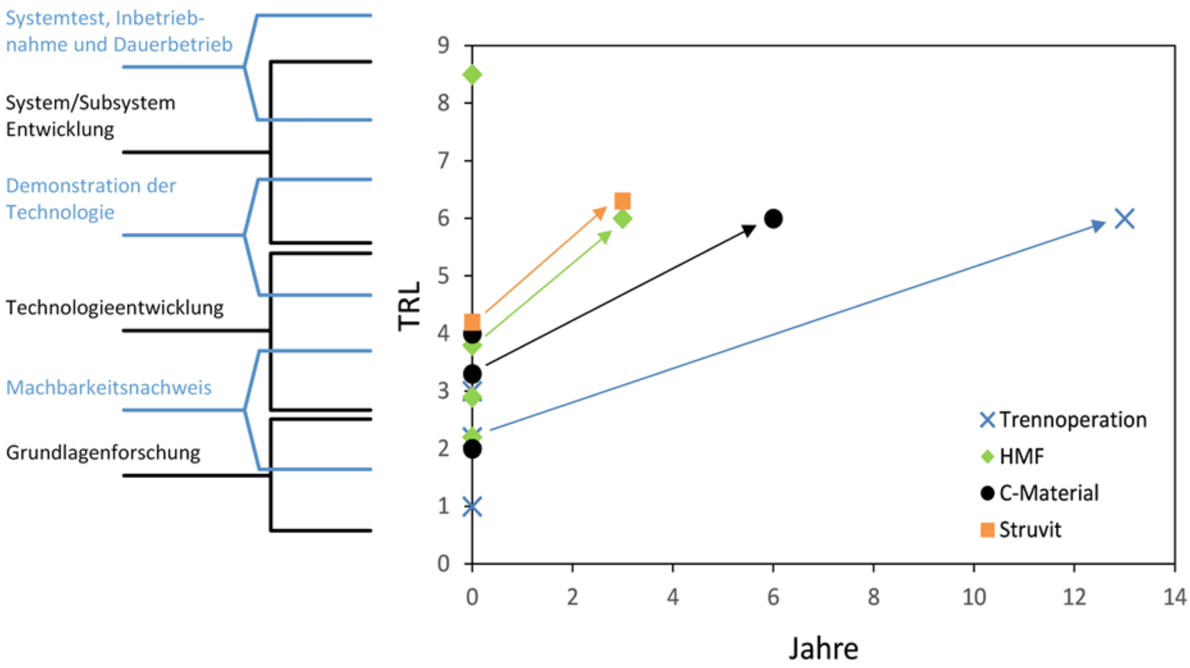


Figure 6: Technology Readiness Level (TRL) of different work areas. Process development in the fields of platform chemicals ("HMF"), carbon materials ("C-material"), phosphate recovery by carbonisation ("struvite") and separation operations.

4.1 Platform Chemicals from Biomass: "Plastics from the Field”

Cellulose, inulin and other carbohydrates made up of C6 sugars can be converted to 5-hydroxymethylfurfural (HMF) (Figure 7). HMF is regarded as one of the most important platform chemicals of the bioeconomy. It can be used to produce beverage bottles (PEF), food packaging, fibres for car seats, nylon for stockings, sportswear, car parts, etc.

Currently, work is underway with chicory roots, old bakery products and Miscanthus as feedstock materials. Nutrient recovery is achieved by coupling with a biogas plant. The implementation of Miscanthus is currently being developed on a pilot scale.

The use of chicory roots presents an interesting particularity: The first reaction step occurs in the beet itself! During the forcing for salad production, enzymes are released in the beets, which split long-chain inulin. In this way, inulin solubility in water and, consequently, its consecutive conversion to HMF improves. The first unit operation, therefore, takes place in the forcing chamber, not in a metal reactor. For this reason, the process for this specific biomass is relatively simple and consists of a small number of modules (

Figure ***7*** and Figure 8, Variant A).

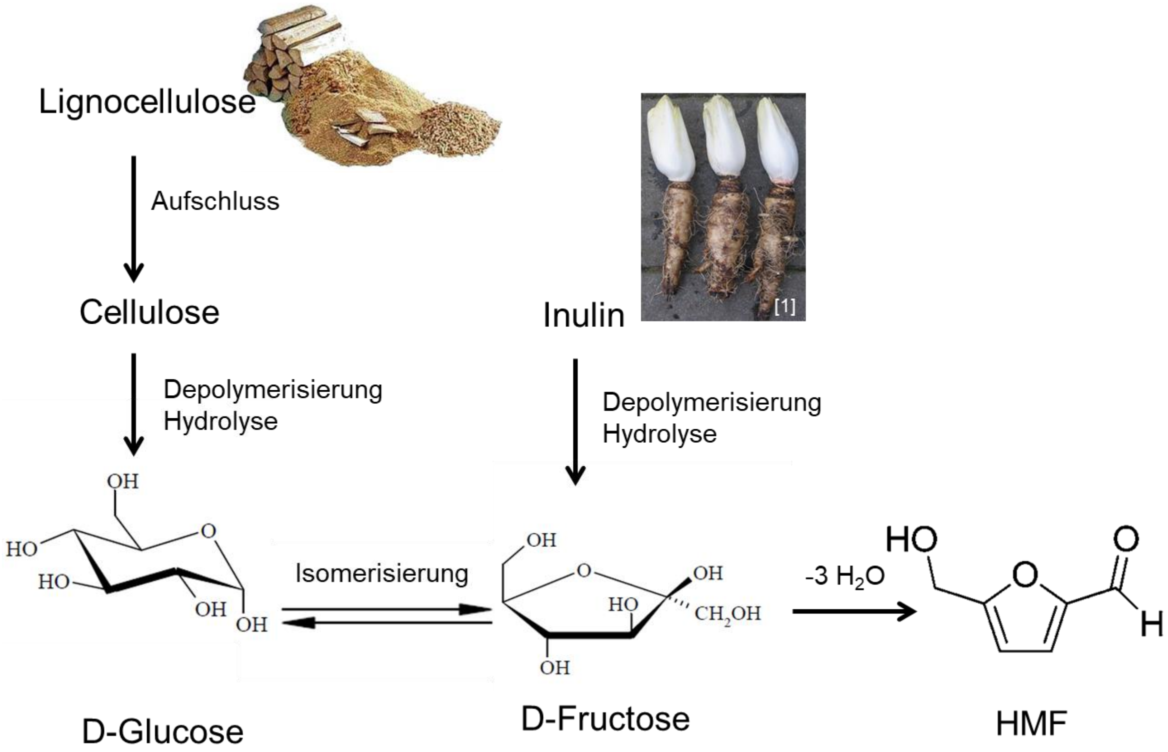


Figure 7: Production of HMF from lignocellulose (wood) and inulin (chicory root beet).

The pilot plant for HMF production at the biorefinery pilot station follows the modular concept, as a future biorefinery would do.

Compared to chicory roots, a system for converting old bakery products into HMF has an additional module, which ensures the isomerization of glucose into fructose (see Figure 7 and variant B in Figure 8). The design of the plant components for chicory and old bakery products is currently in preparation (sections A and B, Figure 8). The Miscanthus to HMF conversion plant consists of a lignocellulose splitting module, an isomerisation module, and the HMF modules themselves. The latter comprises a reactor for conversion to HMF and a unit for separating HMF from water (Section C, Figure 8).

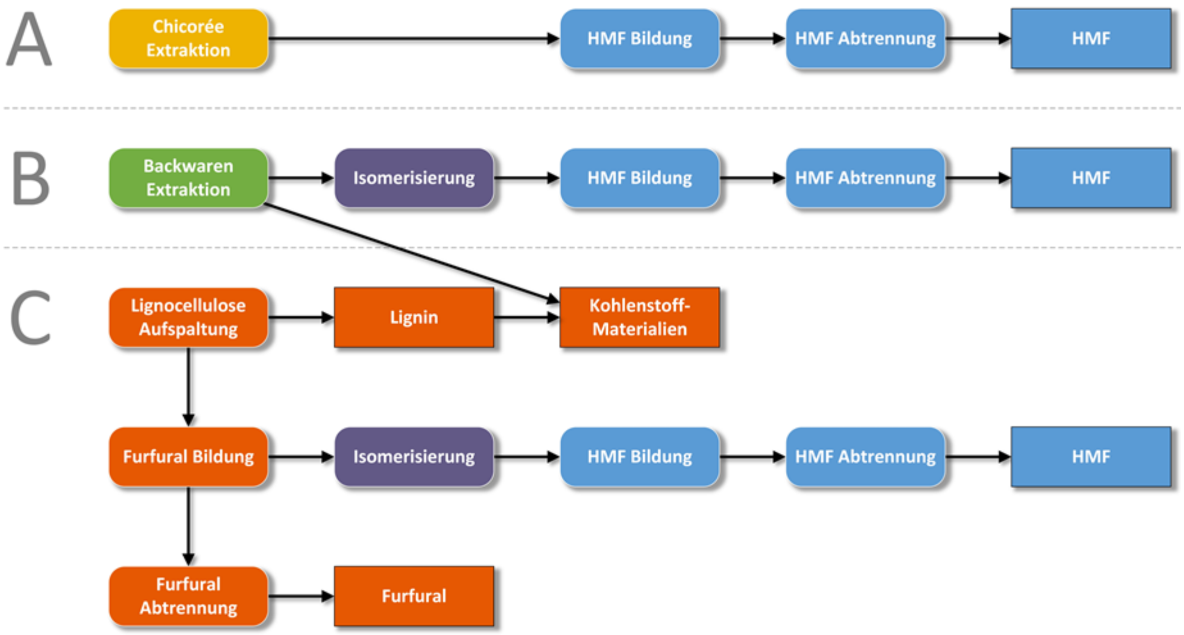


Figure 8: Modules of a biorefinery for the production of platform chemicals. A: Extraction of HMF from chicory; B: Old bakery products to HMF and as a by-product carbon materials; C: Grass or wood to HMF, furfural and carbon materials.

The production of furfural and phenols, both starting materials for synthetic resins, is implemented within the framework of the B4B (Biorefinery for Baden-Württemberg) project (Section C, Figure 8 and Figures 4 and 9). These are, again, individual modules, which can be combined. Thus way, the production of biogenic chipboard and plywood is possible. Alternatively, the residual lignin can be used for developing carbon materials (see Figure 8).

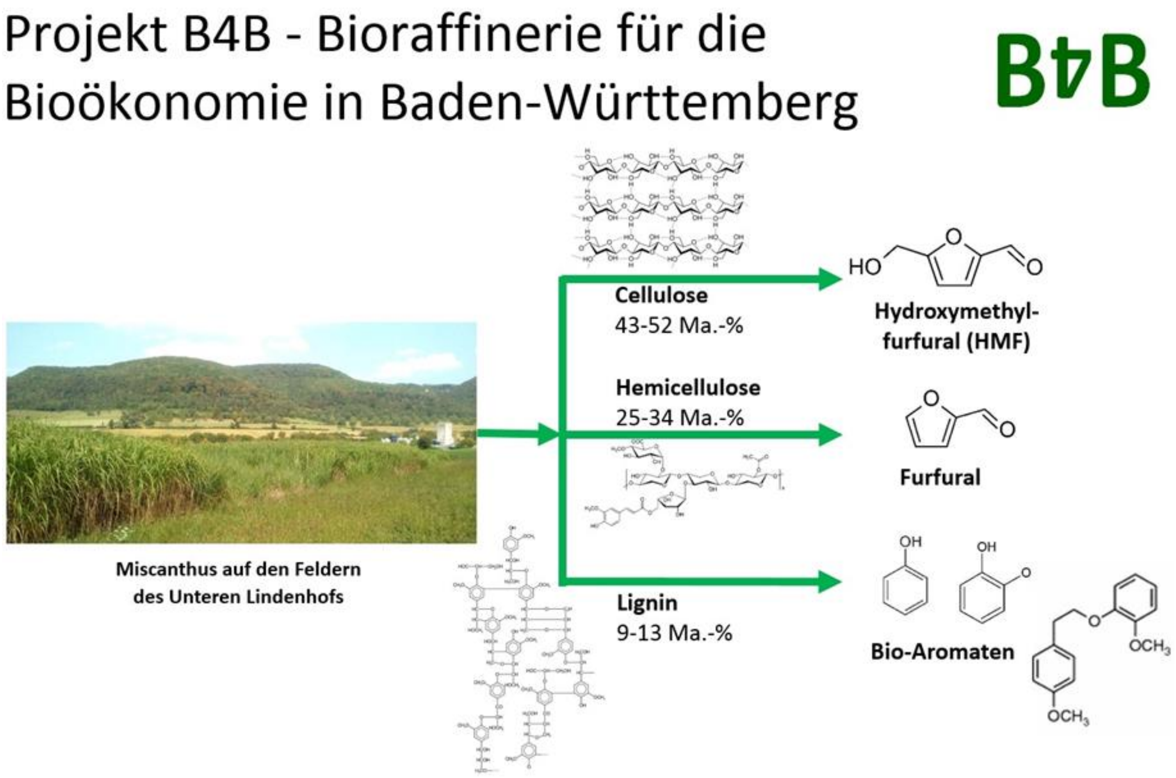


Figure 9: Production of different platform chemicals (here HMF, furfural and phenols) from lignocelluloses as part of the "B4B" research project funded by the state of Baden-Württemberg.

Together with the company AVA-Biochem and based on previous works developed at KIT, a process to produce HMF from fructose, was developed. This process is now commercially implemented. For this reason, it has been classified with TRL 9 in Figure 6. The activities for HMF production have been completely transferred from KIT to Hohenheim. The existence of the company AVA-Biochem, which focuses exclusively on HMF production and further processing, shows the principal feasibility and the availability of an interesting market for HMF, albeit still small. Furthermore, the complex extraction process shown in

Figure *10* suggests that the separation operations are usually the greatest challenge with regard to the costs of a process.

Figure 10: Counter-current extraction by AVA Biochem to extract HMF from the aqueous product solution. (Image: AVA Biochem)

Future Activities

An expansion of the pilot plant is currently being planned. It would enable the production of significant amounts of different samples, i.e. quantities of a few kilograms, which can be processed into the corresponding products and prototypes. In this way, a market launch is enabled, since companies are mainly interested in finished products, such as a bottles or chicory based stockings. Technical implementation with an industrial partner should be possible in approx. 3-4 years. Additional optimization would take another 3-4 years.

4.2 Carbon materials with nutrient recovery

Various biomasses can be converted into carbon materials by carbonization processes (Rodriguez Correa and Kruse 2018; Rodriguez Correa et al. 2018; Figure 11). In the case of dry biomass, this is done by using the so-called “slow pyrolysis”. Hydrothermal carbonization is preferred for wet substrates. In both cases, the chars obtained can be subsequently activated by different methods.

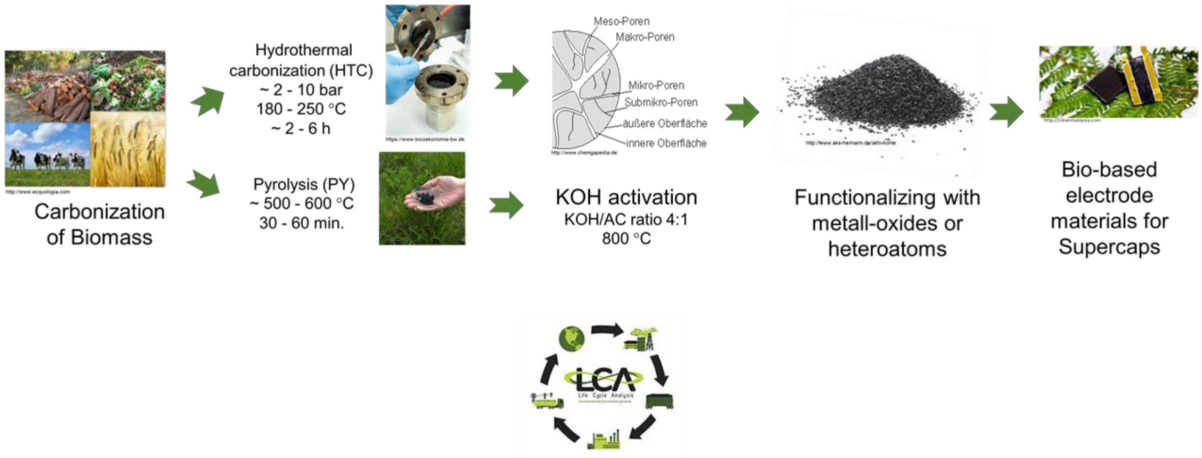


Figure 11: Activated carbon production from dry and wet biomass

Our carbon materials are characterised and analysed with regard to their quality and the respective field of application. Possible applications of activated carbon are air or water purification, storage media for hydrogen, electrode materials for batteries and fuel cells, supercapacitors and material in adsorption columns, e.g. for the separation of methane and CO_2. Here, again, the close connection to biogas plants is evident, because materials can be produced from fermentation residues (digestate) which, in turn, upgrade biogas by separating carbon dioxide.

In general, electrochemical applications, supercapacitors and electrodes for batteries and fuel cells are of particular interest. Due to the use of biomass as feedstock, the obtained carbon materials can have better properties than those available on the market. One reason is the integration of nitrogen from the biomass and the formation of special structures, the so-called "hard carbon". Supercapacitors and sodium batteries, which require hard carbon electrodes are particularly interesting in the context of e-mobility (see alsoFigure 2).

Another promising application of carbon materials is as an electrode for microbial fuel cells (MFC; Figure 12), which is being developed together with the State Institute of Agricultural Engineering and Bioenergy and the Department of Microbiology, led by Prof. Dr. Julia Fritz-Steuber. In this system, organic substances from wastewater are decomposed by bacteria from the biogas reactor and as a result, electricity is generated. Coupling MFCs with biogas plants can be of advantage as some metabolic processes overlap in both processes.

Figure 12: Presentation of the model of a microbial fuel cell at the Open Day 2018. The electrode from a carbonated corncob is visible in the right vessel.

Currently, the focus in the field of material development is on applied basic research, i.e. on a relatively low TRL. These developments will also take a few more years.

An exception is the hydrothermal carbonization with separation of phosphate as struvite. There are several processes for obtaining struvite, but usually they take place in the liquid phase. The Hohenheim process is one of the few that is able to extract phosphate from the solid phase of sewage sludge or fermentation residues to approx. 80 % as struvite (

Figure ***13***). A larger laboratory plant for carbonisation and another one for struvite separation have been designed for this purpose. Currently, there is an increased effort to raise third-party funds for the construction of a pilot plant at the biorefinery pilot station. Here, the required quantities of struvite fertilizer for field trials shall be produced, which are also needed within a large graduate program between the University of Hohenheim and the China Agricultural University.

In the case of sewage sludge as feedstock material, a scale-up to technical implementation would be possible today with the help of our industry partner HTCycle. The activated carbon obtained during this process could also be used in wastewater treatment processes (Benstoem et al. 2018).

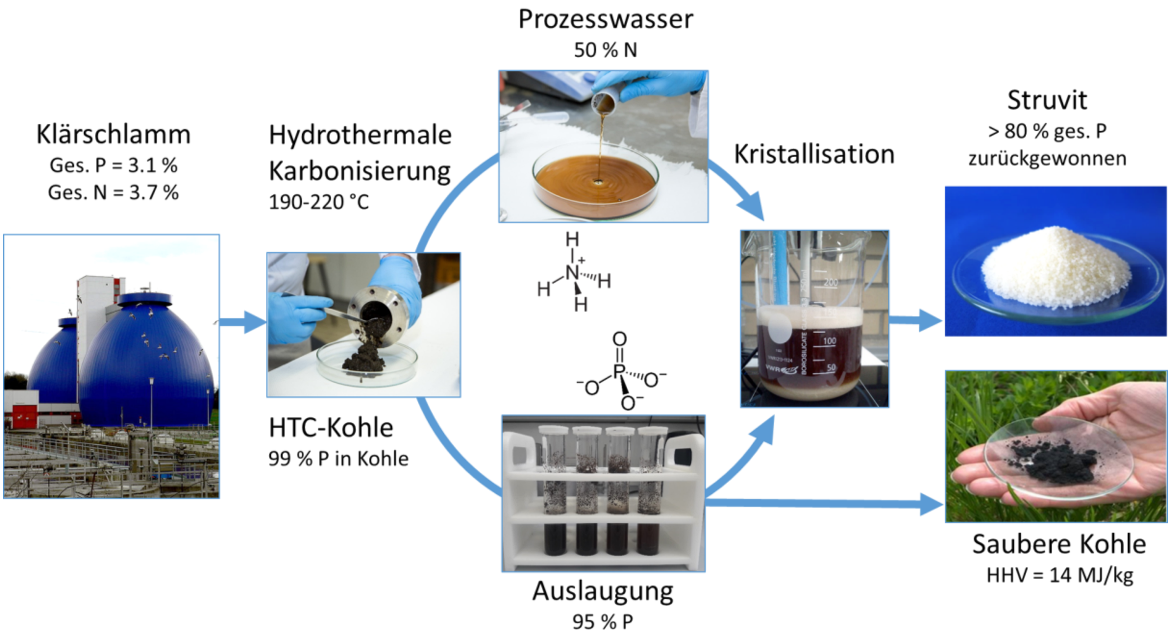


Figure 13: Nutrient balance during phosphate recovery from sewage sludge according to the Hohenheim process (Becker et al. 2019).

Future Activities

Further process development is being planned to demonstrate the production of carbon materials in a pilot plant. In the future, additional synergies e.g. with biogas production can be expected. The production of platform chemicals (which is already under development) often produces a lignin-rich residue, which is a very interesting starting material for carbon materials.

Furthermore, the development towards material applications is being intensified, e.g. in the field of battery electrodes. The aim is to develop new applications in the future, such as carrier materials for fertilizers, direct carbon fuel cells, substitutes for carbon black and raw materials for basic chemicals.

Within the framework of the foundation of a wood research center for Baden-Württemberg that uses solely hardwood as feedstock, the work on the production of biogenic electrodes has attracted great attention, called the "wood battery" here. The hardwood research center would open up the possibility to advance the development of several carbon materials up to their industrial utilisation.

4.3 New separation processes

A decentralised biorefinery requires separation operations that are economical on a small scale. Also, they must not rely on toxic chemicals, which can contaminate the end product and lead to high technical costs (i.e. plant safety). Current activities are the separation of proteins and fats from algae. In the first case, water is used (subcritical and supercritical) and in the second case dimethyl ether. Both solvents do not leave any harmful residues in the wastewater or product.
Furthermore, processes are being developed to separate platform chemicals such as HMF and furfural from aqueous solutions (see Figure 8). The challenge is to separate the valuable products from complex biomass-based mixtures of substances at reasonable technical costs.

Future Activities

Separation processes for recyclable materials will be expanded in future, especially with regard to the combination with the biorefinery concepts mentioned above. For example, protein separation from ryegrass would be useful prior to HMF production. In addition, it could be used to obtain other platform chemicals (a corresponding project application has been submitted). As a new approach, innovative separation processes that

- are profitable on a small scale and
- can be used on an agricultural biorefinery, or
- enable cost-effective separation of biochemically or microbiologically produced platform chemicals

are being developed. Specifically, the separation of lactic acid by reactive extraction is one of the topics to be addressed in the future.

5. The Team

Currently (March 2019), the Department of Conversion Technologies of Biobased Resources consists of 20 doctoral candidates, a postdoctoral scientist, two senior engineers, two technicians and a secretary. The group is led by Prof. Dr. Andrea Kruse (Figure 14).

The team of young scientists is multidisciplinary and broadly diverse: six have completed a Master or Diploma in chemical engineering, four in "Renewable Resources and

Bioenergy", two in chemistry (organic and physical chemistry), two in agricultural engineering and two in environmental technology. The others come from different areas of agricultural sciences as well as microbiology, risk management and materials science.

The two senior engineers are responsible for the lab plants on the Hohenheim campus and the biorefinery facilities in the pilot hall. The post-doc scientist works in the field of carbon materials.

In 2018, 18 publications (peer-reviewed, Scopus) were published. In addition, the total third-party funding received for new projects was approximately € 1.5 million (department share).

Figure 14: Employees of department 440F (October 2018, two employees absent).

6. Education

The vision of decentralised agricultural biorefineries is also reflected in teaching. In the degree programmes "Renewable Resources and Bioenergy" (Bachelor and Master) students are taught basic knowledge in the fields of economics, agriculture, and process engineering. Those who specialise in "technology" de facto have an engineering education. Today, these students usually find a job in industry, where they collaborate with other engineers and supervise sustainability projects.

For the future, there will be new opportunities: In the Master's programme "Renewable Resources and Bioenergy", students are already learning about the unit operations of a biorefinery and simulate such biorefineries with corresponding mass and energy flows. One of the tools used is the computer program "AspenPlus", which is common in the chemical industry. Together with the process engineering education, the graduates are able to plan and operate a decentralised biorefinery. For illustration purposes, the biorefinery pilot station is included in the syllabus.

7. Equipment

The departmentoperates a laboratory and an experimental hall in the Institute of Agricultural Engineering on the university campus. Furthermore, the facilities in the biorefinery pilot hall operates at the experimental station "Unterer Lindenhof" near Eningen. Process development starts in the laboratory and smaller test rigs can be set up in the experimental hall. The pilot plant scale is implemented in the biorefinery pilot hall.
Our department works closely with the Core Facility of the University of Hohenheim and the Institute for Catalysis Research and Technology at the KIT to characterise solid, liquid and gaseous samples. Among others, the following analytical instruments are available on site:

Structural analysis of solids:
Surface determination (BET), thermogravimetry (TGA), thermogravimetry coupled with chromatography and mass spectrometry (TGA-GC-MS)

Spectroscopy:
atomic spectrometry (ICP-OES), infrared spectroscopy (FTIR), UV-Vis spectroscopy

Chromatography:
Elemental analyzer (CHNOS), Liquid chromatography (HPLC), Gas chromatography (GC), Ion chromatography (IC)

8. Collaborations

The department works along the value chain "from field to product" in an interdisciplinary manner with various partners from academia and industry, some of which are listed below.

- State institute of agricultural engineering and bioenergy (740): Fermentation of process water, pre-treatments for biogas processes, microbial fuel cells
- Institute of Crop Sciences (340): Miscanthus for lignocellulosic biorefinery, LCA of biobased process chains

- Karlsruher Institut für Technologie: Lignocellulose-Biorefinery, Techno-economic Process Chain Assessment, Oxidation of HMF
- AVA-biochem: HMF production
- HTCycle: Hydrothermal Carbonization
- Carbonauten: dry carbonization and production of composite materials

9. Financing Bodies

Bundesministerium für Bildung und Forschung

Baden-Württemberg Ministerium für Wissenschaft, Forschung und Kunst

DFG Deutsche Forschungsgemeinschaft

Bundesministerium für Ernährung und Landwirtschaft

DBU

Horizon 2020 European Union Funding for Research & Innovation

Bio-Based Industries Public-Private Partnership

Bio-based Industries Consortium

VolkswagenStiftung

10. Selected References

Becker, G., Wüst, D., Köhler, H., Lautenbach, A. & Kruse, A. 2019. Novel approach of phosphate-reclamation as struvite from sewage sludge by utilising hydrothermal carbonization. Journal of Environmental Management, **238**, 119-125

Benstoem, F., Becker, G., Firk, J., Kaless, M., Wuest, D., Pinnekamp, J., & Kruse, A. 2018. Elimination of micropollutants by activated carbon produced from fibers taken from wastewater screenings using hydrothermal carbonization. *Journal of Environmental Management*, **211**, 278-286

Rodriguez Correa, C. & Kruse, A. 2018. Biobased functional carbon materials: Production, characterization, and applications-A Review. *Materials*, **11**, (9)

Jung, D., Zimmermann, M., & Kruse, A. 2018. Hydrothermal Carbonization of Fructose: Growth Mechanism and Kinetic Model. *ACS Sustainable Chemistry and Engineering* **6**, (11) 13877-13887

Rodríguez Correa, C., Ngamying, C., Klank, D., & Kruse, A. 2018. Investigation of the textural and adsorption properties of activated carbon from HTC and pyrolysis carbonizates. *Biomass Conversion and Biorefinery*, **8**, (2) 317-328

Schwiderski, M. & Kruse, A. 2016. Process design and economics of an aluminium chloride catalysed organosolv process. *Biomass Conversion and Biorefinery*, **6**, (3) 335-345

Steinbach, D., Kruse, A., Sauer, J., & Vetter, P. 2018. Sucrose is a promising feedstock for the synthesis of the platform chemical hydroxymethylfurfural. *Energies*, **11**, (3)

A complete list of publications is available under the Orchid and Scopus identification number of **Andrea Kruse.**

Scopus Author ID: 16316292300

ORCHID: https://orcid.org/0000-0002-8156-139X

UNIVERSITY OF HOHENHEIM
Institute of Agricultural Engineering
Conversion Technologies of Biobased Resources (440f)
Garbenstrasse 9
70599 Stuttgart, Germany

T: +49 711 459 247-01
F: +49 711 459 247-02
M: bioraffinerie@uni-hohenheim.de