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Hrsg. Prof. Dr. Andrea Kruse

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A biorefinery approach for the valorization of agricultural residues using the example of sugar extraction from Cichorium intybus var. foliosum roots

Katrin Stökle

Band 5

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A biorefinery approach for the valorization of agricultural residues using the example of sugar extraction from Cichorium intybus *var.* foliosum *roots*

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Remember to look up at the stars and not down at your feet. Try to make sense of what you see and wonder about what makes the universe exist. Be curious. And however difficult life may seem, there is always something you can do and succeed at. It matters that you don't just give up.

Stephen Hawking (1942-2018)

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Declaration in lieu of an oath on independent work

The dissertation submitted on the topic

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is work done independently by me.

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Abstract

The use of fossil resources in conjunction with advancing technological progress leads to an increased release of CO_2, which contributes to climate change. Furthermore, fossil resources are finite. On the other hand, the use of biomass instead of fossil resources can have a positive effect on the climate, since only plant-bound carbon is released into the atmosphere during the utilization steps. In addition to the possibility of cultivating renewable raw materials, there are also numerous waste streams worldwide, such as agricultural residues, that potentially can be used to manufacture valuable products. These products aim is to replace the fossil-based components by bio-based components. They should therefore be at least efficient or, in the best-case scenario, have better properties than the conventional products. 5-Hydroxymethylfurfural (HMF) as a platform chemical can be a precursor for the production of bio-based plastics. This platform chemical can be obtained from carbohydrates.

The substitution of fossil-based products by bio-based products is best described as "circular bioeconomy", which represents an important step in the development of a more sustainable economy, both in the future and today. Chicory roots represent an agricultural residue in lettuce production. Without interfering in the food production chain, this residue can be used in a biorefinery for the production of HMF. The sugars required for this process are found in the form of inulin, a polyfructose. Inulin is found as storage carbohydrate in the roots and can be extracted with hot water.

In this dissertation, the conditions and kinetics of this above-mentioned sugar extraction are examined in detail. The aim here was to determine the best reaction conditions with the highest possible sugar yields. To produce extracts that are optimally suited for HMF production, the acid hydrolysis of these extracts was also investigated in order to increase their fructose content. In a further step, these extraction experiments were compared and evaluated in a biorefinery concept with conventional methods for the utilization of chicory roots.

Using the chicory root as an example, this work shows that valuable products can be obtained from a waste material via various routes. By means of additionally implemented unit operations, the potential of a residual material can be used sufficiently. Finally, it is not necessary to intervene in the food production chain, which is obligatory to avoid the conflict between fuel tank and plate.

Zusammenfassung

Die Verwendung fossiler Ressourcen in Verbindung mit dem voranschreitenden technologischen Fortschritt führt zu einer erhöhten Freisetzung von CO_2, welches zum Klimawandel beiträgt. Außerdem sind fossile Ressourcen endlich. Die Verwendung von Biomasse anstelle fossiler Ressourcen kann sich positiv auf das Klima auswirken, da bei den Verwertungsschritten lediglich pflanzengebundener Kohlenstoff in die Atmosphäre gelangt. Außerdem gibt es neben der Möglichkeit des Anbaus nachwachsender Rohstoffe auch weltweit zahlreiche Abfallströme, wie zum Beispiel landwirtschaftliche Reststoffe, welche noch ein stoffliches Potential enthalten, das zur Herstellung wertvoller Produkte verwendet werden kann. In diesen Produkten ist das Ziel, die erdölbasierte Komponente durch eine biobasierte Komponente zu ersetzen. Die Produkte sollen somit konkurrenzfähig oder, im besten Falle, besser sein als die herkömmlichen Produkte. 5-Hydroxymethylfurfural (HMF) kann als Plattformchemikalie ein Wegbereiter für die Produktion biobasierter Kunststoffe sein. Gewonnen wird diese Plattformchemikalie aus Kohlenhydraten. Die Thematik lässt sich in den Forschungsbereich der zirkulären Bioökonomie einordnen, deren wichtigstes Ziel die Substitution erdölbasierter Produkte durch biobasierte Produkte darstellt. Außerdem stellt die Kreislaufwirtschaft einen wichtigen Schritt in der Entwicklung einer nachhaltigeren Wirtschaft dar. Chicorée-Wurzeln sind ein landwirtschaftlicher Reststoff aus der Salatproduktion. Ohne in die Nahrungsmittelproduktionskette einzugreifen, kann dieser Reststoff in einer Bioraffinerie für die Produktion von HMF verwendet werden. Die dafür erforderlichen Zucker finden sich in Form von Inulin, einer Polyfructose, als Speicherkohlenhydrat in den Wurzeln und können mit heißem Wasser extrahiert werden.

In dieser Dissertation werden die Bedingungen und die Kinetik dieser Zuckerextraktion genauer betrachtet. Das Ziel lag hier in der Festlegung der besten Reaktionsbedingungen für eine maximal mögliche Ausbeute der Zucker. Für die Herstellung von für die HMF-Produktion optimal geeigneten Extrakten wurde zudem die Säurehydrolyse dieser Extrakte untersucht, um den Fructose-Gehalt dieser zu steigern. In einem weiteren Schritt wurden diese Extraktionsexperimente in einem Bioraffineriekonzept mit den herkömmlichen Methoden zur Verwertung von Chicorée-Wurzeln verglichen und evaluiert.

Diese Arbeit zeigt am Beispiel der Chicorée-Wurzel, dass aus einem Reststoff über verschiedene Routen wertvolle Produkte gewonnen werden können. Anhand zusätzlich implementierter

Prozessschritte kann das Potential eines Reststoffes ausreichend genutzt werden. Hierbei ist es außerdem nicht notwendig, in die Nahrungsmittelproduktionskette einzugreifen, um den Teller-Tank-Konflikt zu vermeiden.

Preface

In almost all areas of modern life, progress is constantly taking place. However, in many cases, this progress is associated with an increasing use of fossil resources. The use of these products, especially for energetic purpose, promotes climate change by increasing the concentration of CO_2 in the atmosphere. Besides, it is well known that these resources are finite, even though there are currently sufficient fossil resources available for the next few years - which may give the impression that the time for action has not yet been reached. On the other hand, already existing bio-based products are mostly expensive niche products. An exception is the use of renewables energies, such as solar energy and wind energy, which have been well established in the recent years.

Moreover, most of the time the general public ignores for which products fossil resources are used and that we use most of them in our everyday life. In addition, the relevance of these products is not always entirely clear. For example, it is not enough to ban plastic bags and straws, as plastics are an essential part of today's world. It clearly makes sense to drastically reduce disposable products, but an alternative must be found for the plastics that are actually needed, as it happens in many fields, such as medicine, construction, housing and electronics, where plastics are currently indispensable and irreplaceable. In addition, plastics will still play an important role in the future and they will gain more attention in industries that are currently still developing, like, for example, 3D-printing.

Based on the above-mentioned points, a different plan of action is needed, which originates in the manufacturing process of these products. The goal must be to replace the fossil-based component in these products with a bio-based component. As a consequence, regenerative carbon sources would help reduce CO_2 emissions to the atmosphere. The challenge is to make these products not only competitive, but even better in their properties than conventional fossil-based products. However, the bio-based step in this chain also requires caution, because the world's population is also growing and in some parts of the world, agricultural areas for food production are becoming scarce. Conflicts have already sparked over the biogas sector, and is referred to as the "corn war", which aims at using agricultural land for the actual production of food through energy corn.

The plate-tank conflict must be avoided for two reasons: on the one hand, the production of bio-based materials should not interfere with the food industry and raise conflicts. Enough materials are probably available to enable the production of biobased products without growing extra biomass. This concerns various waste streams from the agricultural and food industry, and it already begins with the organic waste in households. These waste streams are mostly used e.g. in biogas plants, whereby a large part of their respective residual potential is lost, which can be counteracted in so-called biorefineries. Value chains are extended in these and cycles are closed. The umbrella term for this process is Circular Bioeconomy and allows, on the one hand, a complete use of the product and a return of the material flows, but also gives the possibility of gaining valuable products from residual materials. It goes along with the important principle of "reduce, reuse, recycle".

The goal of the bioeconomy is to complete the transformation from a fossil-based to a bio-based economy. For this purpose, it is important from the beginning to identify the previously mentioned material flows and to recognize potentials. Furthermore, unit operations must be developed to extract substances from the biomass or to transform it in such a way that it can be fed into the production cycles of conventional products.

An example of a waste stream with such a potential are the roots of chicory. Chicory lettuce is produced in dark forcing rooms; the roots are a waste product. Due to their high bitterness, they cannot be used neither as a food product nor as animal fodder. Since the lettuce is produced all year round, its waste product is generated throughout the whole year, which is one of the requirements for a biorefinery. The roots contain the storage carbohydrate inulin, which consists of fructose units. Once extracted from the biomass using hot water, a perfect material for the production of the platform chemical HMF is obtained, which is the starting material for the production of a wide range of substances for the manufacturing of biobased plastics. Since the chicory roots are used for biorefinery only after the forcing process, there is no interference in the food production chain. There are even advantages in the use of by-products and waste streams: first of all, the more food is produced, the better - because more products are produced for use in biorefineries. Secondly, in the process of storage and forcing, long-chained sugars in the chicory roots are broken down into monosaccharides, and in this way, HMF yields and selectivities can be improved. In other words, the roots represent a first reactor in the production chain to HMF. Concerning the circular bioeconomy aspect using chicory roots, the resulting product could be a plastic foil that will be used to wrap the salad in the supermarket, exemplifying how circles can be perfectly closed.

This is just an example of how to use a biomass or a biomass component in a circular bioeconomy concept or in a biorefinery, but it also represents the challenge in developing biorefinery concepts, looking for potential, finding recycling and upcycling routes followed by an evaluation. This challenge led to the research questions answered in this dissertation:

1) Chicory root inulin can be easily extracted using hot water at elevated temperatures without applying any pressure or pretreatment, but how does this work with roots that were forced and contain, therefore, a higher amount of monosaccharides instead of long-chained inulin? **How are the extraction kinetics of sugar extraction from forced chicory roots and what are the optimal conditions?**
2) Hydrolysis of inulin is a first step in the reaction to HMF. Chicory roots after forcing contain only low amounts of inulin. However, if in the future, the postharvest losses will also be taken into consideration for utilization in the biorefinery, higher inulin content in the extracts might be resulting. **Is acid hydrolysis a promising process step to increase the monosaccharide content in the extract to obtain fructose-enriched extracts?**
3) The extraction of sugars from chicory roots is very promising and extracts with satisfactory yields of sugar can be obtained. At this point, it is important to investigate a biorefinery concept to optimize the whole process chain. **Is it possible to develop a biorefinery concept for chicory roots to extend the value chain in the direction of additional products?**

These questions were addressed in the publications included in this dissertation. Therefore, the thesis is divided into four chapters. The first one represents a general introduction on the topic. The other chapters are summarized as follows:

in **Chapter 2,** *"Extraction of sugars from forced chicory roots"* (Katrin Stökle, Andrea Kruse; *Biomass Conv. Bioref.,* 2019 (9), 699-708), the sugar extraction kinetics of forced chicory roots were investigated. It was found that it is possible to achieve high extraction yields of more than 90% at 80 °C extraction temperature, 1:10 solid-to-liquid ratio and with chicory roots cut in julienne shape. The important findings of this article were the following: the accumulation of monosaccharides after the forcing process leads to high extraction yields. Besides, the resulting extracts had a sufficient concentration of sugars to be a starting material for the production of HMF.

Chapter 3, *"Acid-assisted extraction and hydrolysis of inulin from chicory roots to obtain fructose-enriched extracts"* (Katrin Stökle, Dennis Jung, Andrea Kruse; *Biomass Conv. Bioref.,* 2020, accepted and published online while this dissertation was finalized), deals with the hydrolysis of chicory extracts. This paper gave an interesting outlook on increasing the monosaccharide content in the extract which is more suitable for subsequent HMF production. Applying a two-step approach in terms of a hydrolysis step after the biomass extraction results in a fructose-enriched extract. It was confirmed that this can be achieved using a pH below 2.5.

Chapter 4, *"A biorefinery concept using forced chicory roots for the production of biogas, hydrochar, and platform chemicals"* (Katrin Stökle, Benedikt Hülsemann, David Steinbach, Zebin Cao, Hans Oechsner, Andrea Kruse; *Biomass Conv. Bioref.,* 2019, accepted and published online while this dissertation was finalized), investigates a biorefinery concept for chicory roots. The basic scenario of disposing forced roots in a biogas plant was compared with two biorefinery scenarios using sugar extraction, hydrothermal carbonization and anaerobic digestion. It was found that a combination of these three processes results in a carbon efficiency of 96%, which is promising regarding the complete utilization of an agricultural residue.

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List of Abbreviations

ADF	Acid detergent fiber
ADL	Acid detergent lignin
CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical oxygen demand
D_{eff}	Effective diffusion coefficient
DM	Dry matter
DP	Degree of polymerization
DP_a	Average degree of polymerization
dTG	Derivative thermogravimetry
F	Fructose
FDCA	Furan dicarboxylic acid
FEH	Fructanexohydrolase
FFT	Fructan:fructan fructosyl transferase
G	Glucose
H_2SO_4	Sulfuric acid
HBT	Hohenheim biogas yield test
HCl	Hydrochloric acid
HMF	5-Hydroxymethylfurfural
HNO_3	Nitric acid
HTC	Hydrothermal carbonization
NaOH	Sodium hydroxide
NDF	Neutral detergent fiber
oDM	Organic dry matter
PEF	Polyethylene furanoate
PET	Polyethylene terephthalate
SST	Sucrose:sucrose fructosyl transferase
TGA	Thermogravimetric analysis
TOC	Total organic carbon