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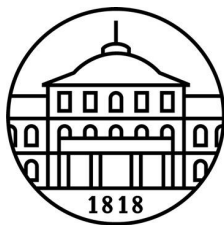
Hrsg. Prof. Dr. Andrea Kruse

DISSERTATION

Phosphate recovery in the processes of hydrothermal treatment of phosphate-rich biomasses

Ekaterina Ovsyannikova

Band 10



***Phosphate recovery in the processes of
hydrothermal treatment of phosphate-rich
biomasses***

**Dissertation to obtain the doctoral degree of Agricultural
Sciences (Dr. sc. agr.)**

Faculty of Agricultural Sciences

University of Hohenheim

Institute of Agricultural Engineering

submitted by

Ekaterina Ovsyannikova

from Tver

2022

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We may be able to substitute nuclear power for coal, and plastics for wood, and yeast for meat, and friendliness for isolation - but for phosphorus there is neither substitute nor replacement.

Isaac Asimov, Professor of Biochemistry,
Boston University School of Medicine, 1974.

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I was incredibly lucky to have the great professional and personal environment that made this achievement possible.

Thank you!

Declaration in lieu of an oath on independent work

The dissertation submitted on the topic

“Phosphate recovery in the processes of hydrothermal treatment of phosphate-rich biomasses”

is work done independently by me.

I only used the sources and aids listed and did not make use of any impermissible assistance from third parties. In particular, I marked all content taken word-for-word or paraphrased from other works.

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Stuttgart, 08.03.2022

Place and date



Signature

Ekaterina Ovsyannikova

Summary

Issues relating to the environment, resource supply, and the economy drive today's developing sustainable circular bioeconomy. The European Union aims to create conditions for economic growth decoupled from resources and to be climate-neutral by 2050. One of the key factors in reaching these targets is the conversion of biomasses into renewable energy carriers, bio-based platform chemicals, and bio-based carbon materials. Hydrothermal processes (HTPs) offer a promising conversion route for wet biomasses. Hydrothermal carbonization (HTC) and hydrothermal liquefaction (HTL) are of particular interest. HTC enables the disposal of organic wastes and the production of a solid coal-like product (hydrochar) that can act as a substitute for the fossil energy carriers. HTL is applied to wet biomasses to obtain an oil-like product (biocrude) that can be upgraded to renewable fuels. Biomasses processed with HTC and HTL also contain many nutrients, which are essential for the biomass production and the food supply chain. Among these is phosphate, which is irreplaceable in agriculture. Moreover, phosphate reserves are limited, and their sustainable management has become a priority. The HTC and HTL of phosphate-rich biomasses, such as sewage sludge, manure, and algae, should include phosphate recovery for reuse in agriculture. Otherwise, a negative environmental impact could occur. However, there are only few studies considering the HTC and HTL of phosphate-rich biomasses from the perspective of phosphate recovery. Phosphate recovery in these processes is at a later stage of development than conversion itself, particularly in the case of HTL. For this reason, this dissertation provides a step toward effective phosphate recovery for agriculture in the processes of HTC and HTL and to enhance the phosphate recovery technology readiness level.

The fate of phosphates after HTC and HTL affects the phosphate recovery approach and its efficiency. To increase the understanding of the fate of phosphates, this work investigated how hydrothermal conditions influence phosphate behavior during HTC of digested sewage sludge (DSS), as one example of phosphate-rich biomass. It was identified that by increasing the treatment temperature, the phosphates initially presented in DSS were homogenized and mainly recovered as acid soluble inorganic phosphates in hydrochar. This is also an important basis for the knowledge of the fate of phosphate during the HTL that takes place at higher temperatures than HTC. Thereafter, the focus was moved to the pilot-scale HTL, which first required general investigations to clarify uncertainty regarding the flow of phosphate and to identify the most appropriate approach for phosphate recovery. For this purpose, a full analysis of nutrient flows between the HTL products for two phosphate-rich biomasses, primary sewage sludge (PSS) and *Spirulina* microalgae (SPR), was provided. From a partial experimentally derived mass balance of nutrient elements, strategies for phosphate recovery were developed, taking into consideration the existing

approaches for HTC. The processing of PSS in the pilot plant HTL produced a phosphate-rich solid byproduct suitable for phosphate recovery as a slow-release fertilizer, such as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ or struvite via an adjusted approach from the field of HTC. This approach includes solubilization of phosphates by means of acid from the HTL solid byproduct and subsequent binding of these phosphates in struvite by adding HTL liquid byproduct, magnesium ions containing salt, and by increasing the pH. For *SPR*, direct isolation of phosphate as struvite from the HTL liquid byproduct proved promising. The last investigation within this work provided a basis for the design of the unit for phosphate recovery in the form of struvite from the HTL- as well as HTC-derived products. The used products were originated from the pilot-scale HTL of sewage sludge and manure. This study evaluated the effects of the solution composed of extract from the HTL solid byproduct and HTL liquid byproduct on struvite precipitation. In addition, the effects of a specially for struvite precipitation designed air-agitated reactor were examined. Struvite-rich product with high potential for agricultural use was recovered from HTL byproducts of manure and sewage sludge. It was found that the application of citric acid benefits the purity of the fertilizing product, in particular from sewage sludge. The study also demonstrated that an air-agitated system can improve the properties of the product, leading to a fertilizer that is ready to use in shape (particle size) and quality (struvite content).

The findings presented in this work support optimization and the upscaling of phosphate recovery in the processes of HTC and HTL of phosphate-rich biomasses. Additionally, these findings can improve further life cycle and techno-economic assessments of HTC and HTL-based biorefineries. This work also indicates gaps and limitations that open opportunities for future research.

Zusammenfassung

Gegenwärtig treiben Umwelt-, Ressourcenversorgungs- und Wirtschaftsfragen die Entwicklung einer nachhaltigen zirkulären Bioökonomie an. Die Europäische Union hat es sich zum Ziel gesetzt, die Voraussetzungen für ein von Ressourcen entkoppeltes Wirtschaftswachstum zu schaffen und bis zum Jahr 2050 klimaneutral zu werden. Einer der Schlüsselfaktoren zur Erreichung dieser Ziele ist die Umwandlung der Biomassen in Bioenergieträger und biogene Kunststoffe oder Kohlenstoffmaterialien. Hydrothermale Prozesse (*hydrothermal processes*, HTPs) sind vielversprechende Methoden zur Umwandlung feuchter Biomassen. Von besonderem Interesse sind hier die hydrothermale Karbonisierung (*hydrothermal carbonization*, HTC) und die hydrothermale Verflüssigung (*hydrothermal liquefaction*, HTL). Erstere ermöglicht es, organische Abfälle zu entsorgen und ein festes, kohleähnliches Produkt (*Hydrochar*) zu erzeugen, mit welchem fossile Energieträger ersetzt werden können. Die HTL dient hingegen der Gewinnung eines ölartigen Produkts (*Biocrude*), welches zu Kraftstoffen weiterverarbeitet werden kann. Die bei der HTC und der HTL verwendeten Biomassen enthalten Nährstoffelemente, die in der landwirtschaftlichen Produktion und der Ernährung von Bedeutung sind. Dazu zählt unter anderem Phosphat, welches als Düngemittel in der Landwirtschaft eingesetzt wird. Für Phosphat gibt es aktuell keinen Ersatz. Die weltweiten Phosphatreserven sind außerdem begrenzt, weshalb eine nachhaltige Rückgewinnung zur Priorität geworden ist. Die hydrothermale Behandlung von phosphatreichen Biomassen wie Klärschlamm, Gülle und Algen sollte zukünftig eine Rückgewinnung von Phosphaten zur Wiederverwendung in der Landwirtschaft beinhalten. Anderenfalls könnte sich dies negativ auf die Umwelt auswirken. Derzeit werden die HTC und die HTL unter dem Gesichtspunkt der Phosphatrückgewinnung jedoch nur eingeschränkt berücksichtigt. Auch befindet sich die Phosphatrückgewinnung in einem niedrigeren Entwicklungsstand als die eigentliche hydrothermale Umwandlung. Insbesondere gilt dies für die HTL. Aus diesem Grund treibt diese Dissertation die effektive Phosphatrückgewinnung für die Landwirtschaft in den Prozessen der hydrothermalen Behandlung von phosphatreichen Biomassen voran und verbessert somit den Entwicklungsstand der Phosphatrückgewinnung.

Der allgemeine Ansatz und die Effizienz der Phosphatrückgewinnung wird dadurch beeinflusst, in welchem Produkt und in welcher Form die Phosphate nach der HTC und der HTL verbleiben. Um das Verständnis für den Verbleib von Phosphat zu erweitern, wurde im Rahmen dieser Arbeit untersucht, wie hydrothermale Bedingungen das Verhalten von Phosphat während der HTC von ausgefaultem Klärschlamm (*digested sewage sludge*, DSS), als Beispiel für phosphatreiche Biomasse, beeinflussen. Durch die Erhöhung der Behandlungstemperatur wurden die ursprünglich im DSS vorhandenen Phosphate homogenisiert und im Wesentlichen als säurelösliche anorganische

Phosphate in der Hydrokohle zurückgewonnen. Dies ist auch eine wichtige Grundlage für die Bestimmung des Verbleibs von Phosphat nach der HTL, die bei höheren Temperaturen als die HTC stattfindet. Bei der Verlagerung der Untersuchungen auf die HTL im Pilotmaßstab wurden zunächst allgemeine Untersuchungen zur Klärung des Nährstoffflusses und zur Ermittlung des am besten geeigneten Ansatzes zur Phosphatrückgewinnung vorgenommen. Zu diesem Zweck wurde eine vollständige Analyse der Nährstoffflüsse zwischen den HTL-Produkten für zwei phosphatreiche Biomassen—Primärklärschlamm (*primary sewage sludge*, PSS) und die Mikroalge *Spirulina* (SPR)—durchgeführt. Basierend auf einer teilweise experimentell abgeleiteten Massenbilanz der Nährstoffelemente wurden die Strategien zur Phosphatrückgewinnung entwickelt. Die HTL von PSS im Pilotmaßstab lieferte ein phosphatreiches, festes Nebenprodukt, das sich für die Phosphatrückgewinnung als Langzeitdünger wie $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ oder Struvit mittels eines angepassten Ansatzes aus dem Bereich der HTC eignet. Dieser Ansatz umfasst die Auflösung von Phosphaten aus dem festen HTL-Nebenprodukt mit Hilfe von Säure und eine anschließende Abtrennung dieser Phosphate in Form von Struvit durch Zugabe von flüssigem HTL-Nebenprodukt, magnesiumionenhaltiges Salz sowie Erhöhung des pH-Werts. Für die SPR erwies sich die direkte Extraktion von Phosphat als Struvit aus dem flüssigen HTL-Nebenprodukt als erfolgversprechend. Die letzte Untersuchung im Rahmen dieser Arbeit lieferte eine Grundlage für die Auslegung der Anlage zur Rückgewinnung von Phosphat in Form von Struvit aus den HTL- sowie HTC-Produkten. Die verwendeten Produkte stammten aus der HTL von Klärschlamm und Gülle im Pilotmaßstab. Untersucht wurden die Auswirkungen der Zusammensetzung der Lösung aus dem Extrakt aus einem festen HTL-Nebenprodukt und einem flüssigen HTL-Nebenprodukt auf den Fällungsprozess von Struvit. Darüber hinaus erfolgte eine Analyse der Auswirkung des speziell für die Struvit-Fällung konzipierten luftgerührten Reaktors. Das struvitreiche Produkt, das als Düngemittel verwendet werden kann, konnte sowohl aus HTL-Nebenprodukten von Gülle als auch aus HTL-Nebenprodukten von Klärschlamm gewonnen werden. Insbesondere bei Klärschlamm wirkte sich die Zugabe von Zitronensäure positiv auf die Qualität des Produkts aus. Die vorliegende Studie zeigt, dass ein luftgerührter Reaktor das Potenzial hat, die Eigenschaften des Produkts zu verbessern, sodass ein in Form (Partikelgröße) und Qualität (Gehalt von Struvit) gebrauchsfertiger Dünger entstehen kann.

Die in dieser Dissertation präsentierten Ergebnisse werden die Optimierung der Phosphatrückgewinnung in den HTC- und HTL-Prozessen von phosphatreichen Biomassen und deren Hochskalierung unterstützen. Außerdem werden sie die weitere Ökobilanz und die techno-ökonomischen Bewertungen von HTC- bzw. HTL-basierten Bioraffinerien verbessern. Darüber hinaus werden in dieser Arbeit Forschungslücken und Grenzen aufgezeigt, welche Ansatzpunkte für zukünftige Untersuchungen bieten.

Preface

This dissertation provides a step toward the effective coupling of phosphate recovery in HTC- and HTL-based biorefineries. I was engaged in researching and writing this dissertation from February 2018 to February 2022 while working at the University of Hohenheim in the group of Conversion Technologies of Biobased Resources (440f) under the supervision of Professor Dr. Andrea Kruse.

Most of this work was conducted within the EU project “Hydrothermal liquefaction: Enhanced performance and feedstock flexibility for efficient biofuel production (HyFlexFuel)¹”, which aim was to develop the entire process chain for producing sustainable liquid fuels through hydrothermal liquefaction of a broad range of biomass feedstocks. The aspects of valorization of residual process streams via nutrient recovery to increase sustainability and add value to the production chain were examined by the research group of Professor Dr. Andrea Kruse.

The path to the finalization of this thesis was challenging, but conducting this investigation has allowed me to answer the identified research questions and to grow professionally and personally.

I hope you enjoy reading my dissertation,

Ekaterina Ovsyannikova

¹ <https://www.hyflexfuel.eu/>

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List of abbreviations

AbfKlärV	Germany sewage sludge regulation (Klärschlammverordnung)
AD	Anaerobic digestion
ATP	Adenosine triphosphate
cHTG	Catalytic hydrothermal gasification
COD	Chemical oxygen demand
CSH	Calcium silica hydrate
DSS	Digested sewage sludge
DüV	Germany fertilizer regulation (Düngeverordnung)
EU	The European Union
EU-27	European Union 27 Member States including: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, United Kingdom
HMF	5-hydroxymethylfurfural
HTC	Hydrothermal carbonization
HTL	Hydrothermal liquefaction
HTP	Hydrothermal process
$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	Struvite or magnesium ammonium phosphate
P	Phosphorus
PSS	Primary sewage sludge
rPeff	Relative phosphorus effectiveness
SPR	<i>Spirulina</i>
TOC	Total organic carbon
TRL	Technology readiness level
UK	The United Kingdom
US	The United States
WWTP	Wastewater treatment plants