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DISSERTATION

Sustainable Conversion of Biomass to Nitrogen-Functionalized Carbon Materials via the Hydrothermal Carbonization with the Potential of Nitrogen Recovery

Muhammad-Jamal Alhnidi

Band 6

***Sustainable Conversion of Biomass to
Nitrogen-Functionalized Carbon Materials via
the Hydrothermal Carbonization with the
Potential of Nitrogen Recovery***

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Faculty of Agricultural Sciences

University of Hohenheim

Institute of Agricultural Engineering

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submitted by

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رسالة الى أمي *To my mother Rima Alkilarijy*

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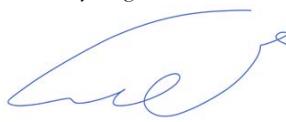
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Abstract

Combating climate change and reducing greenhouse gas emissions are the main aims of the Paris Agreement. Responding to the accelerated global demand for food, animal feed, and energy following a sustainable strategy is a real challenge. The concept of considering biowaste as a valuable material is known and applied wildly e.g. in Biogas or Biofuel production. However, sustainability requires persistent optimization of the available conversion strategies and continuous search for novel technologies for a better valorization of biowaste. Hydrothermal carbonization (HTC) is a promising technology to convert biomass to functionalized carbon materials. However, the achievement of sustainable conversion of N-rich biowaste via HTC is unattainable without influencing the N profile in its products; the hydrochar (HC) or the process water (PW).

This dissertation aimed to improve the understanding of the reactions of N-containing compounds during HTC, the synthesis of target-oriented N-hydrochar (N-HC), and the potential of N recovery in HTC. To achieve this aim, model compounds (Fructose and glucose) and biomass (spent coffee grounds and Miscanthus) were used as the C precursor in HTC. Amino acids (alanine, asparagine), urea, ammonium chloride, sodium nitrate, and sodium nitrite were used as N-containing compounds in HTC.

The results of this work showed that recovery of N to the HC during HTC mainly depends on the composition of the feedstock before HTC. Inorganic-N is recovered to the HC via sorption, except for NH_4^+ -N which can be also chemically incorporated into the structure of the HC. Moreover, the availability of the carbon network in the HC is a key factor for N recovery to the HC.

It transpires that N-containing compounds have a significant influence on the formation of HC via the solved-intermediates pathway during HTC. The pH value of the reaction environment during HTC can guide the Maillard reaction (MR) toward the formation of N-HC or oil-like materials. N-containing compounds showed a notable influence on the morphology and composition of N-HC, this influence included the formation of heterocyclic N in the HC, reducing the O content on the surface of HC, and affecting the formation of spherical HC.

The results exhibited a promising performance of HTC for the synthesis of N-enriched carbon materials (NCM) as electrode materials in electrochemical double-layer capacitors (EDLCs). HTC enabled the incorporation of N to the bulk of the NCM and improved the overall capacitance of the produced NCM.

The outcome of this dissertation helps to support further research toward a sustainable conversion of biomass to a target-oriented N-HC for previously identified applications.

Zusammenfassung

Die Bewältigung des Klimawandels und die Verminderung der Treibhausgasemissionen sind die Hauptziele des Pariser Abkommens. Es ist eine Herausforderung, die gestiegene globale Nachfrage nach Lebensmitteln, Tierfutter und Energie mit einer nachhaltigen Strategie entgegenzuwirken. Das Konzept, Bioabfälle als Wertschöpfungsprodukt zu betrachten, ist bekannt und wird z.B. in der Biogas- oder Biokraftstoffproduktion in großem Ausmaß angewendet. Nachhaltigkeit erfordert jedoch eine ständige Optimierung der verfügbaren Konversionsstrategien und eine kontinuierliche Suche nach neuen Technologien für eine bessere Verwertung von Bioabfällen. Die hydrothermale Carbonisierung (HTC) ist eine vielversprechende Technologie zur Umwandlung von Biomasse in funktionalisierte Kohlenstoffmaterialien. Eine nachhaltige Umwandlung von N-reichem Bioabfall mittels HTC ist allerdings nur durch Beeinflussung des N-Profs in den Produkten, d.h. der Hydrokohle (HC) oder dem Prozesswasser (PW) möglich.

Ziel dieser Arbeit ist es, das Verständnis für die Reaktionen N-haltiger Verbindungen während der HTC, die Synthese zielgerichteter N-Hydrokohle (N-HC) und das Potential der N-Rückgewinnung in der HTC zu verbessern. Um dieses Ziel zu erreichen, wurden Modellverbindungen (Fructose und Glucose) und Biomasse (Kaffeesatz und Miscanthus) als C-Vorläufermaterialien in der HTC verwendet. Aminosäuren (Alanin, Asparagin), Harnstoff, Ammoniumchlorid, Natriumnitrat und Natriumnitrit wurden als N-haltige Verbindungen in der HTC verwendet. Die Ergebnisse dieser Arbeit zeigen, dass die Rückgewinnung von N zur HC während der HTC hauptsächlich von der Zusammensetzung der Biomasse, d.h. dem Ausgangsmaterial, vor der HTC abhängt. Anorganisches N wird über Sorption in die HC zurückgewonnen, mit Ausnahme von NH_4^+ -N, das auch chemisch in die Struktur der HC eingebaut werden kann. Darüber hinaus ist die Verfügbarkeit des Kohlenstoffnetzwerks in der HC ein Schlüsselfaktor für die N-Rückgewinnung in die HC.

Es stellt sich heraus, dass N-haltige Verbindungen einen bedeutenden Einfluss auf die Bildung von HC über den Weg der gelösten Zwischenprodukte während der HTC haben. Der pH-Wert der Reaktionslösung während der HTC kann die Maillard-Reaktion (MR) in Richtung der Bildung von N-HC oder ölartigen Materialien lenken. N-haltige Verbindungen weisen einen bemerkenswerten Einfluss auf die Morphologie und Zusammensetzung der N-HC auf. Dieser Einfluss beinhaltete die Bildung von heterocyclischem N im HC, die Herabsenkung des O-Gehalts auf der Oberfläche des HC, und die Beeinflussung der Bildung von sphärischem HC.

Die Ergebnisse zeigen, dass eine Anwendung von N-angereicherten Kohlenstoffmaterialien (NCM) als Elektrodenmaterialien in elektrochemischen Doppelschichtkondensatoren (EDLCs)

vielversprechend erscheinen. HTC ermöglicht die Einbindung von N in die Masse des NCM und verbesserte die Gesamtkapazität des hergestellten NCM.

Das Ergebnis dieser Dissertation trägt dazu bei, die weitere Forschung in Richtung einer nachhaltigen Umwandlung von Biomasse zu einem zielgerichteten N-HC für EDLC-Anwendungen voranzutreiben.

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List of Abbreviations

ADF	Acid detergent fiber
ADL	Acid detergent lignin
AC	Activated Carbon
Al	Alanine
As	Asparagine
CV	Cyclic voltammetry
DW	Distilled water
EC	Electrical conductivity
EDLCs	Electrochemical double-layer capacitors
SEM	Field emission scanning electron microscopy
GC	Gas chromatography
HPLC	High-Performance Liquid Chromatography
HC	Hydrochar
HTC	Hydrothermal carbonization
HMF	Hydroxymethylfurfural
MR	Maillard reaction
NCM	N-enriched carbon materials
N-HC	Nitrogen-containing hydrochar
NMR	Nuclear Magnetic Resonance Spectroscopy
PTFE	Polytetrafluoroethylene
PSD	Pore size distributions
PW	Process water
SSA	Specific surface areas
SCG	Spent coffee grounds
BET	The Brunner-Emmett-Teller theory
TCD	Thermal conductivity detector
TC	Total carbon
TIC	Total inorganic carbon
TNb	Total nitrogen
TOC	Total organic carbon
U	Urea
XPS	X-ray Photoelectron Spectroscopy