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Kinetic Studies about the Hydrothermal Carbonization of Fructose

Dennis Jung

Band 8

Kinetic Studies about the Hydrothermal Carbonization of Fructose

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(Dr. sc. agr)**

Faculty of Agricultural Sciences

University of Hohenheim

Institute of Agricultural Engineering

submitted by
Dennis Jung

from Filderstadt
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Annex 3

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1. The dissertation submitted on the topic

Kinetic Studies about the Hydrothermal Carbonization of Fructose

is work done independently by me.

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Place, Date

Signature

Curriculum Vitae

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List of publications

A. Scientific publications within the dissertation

1. Jung, D.; Körner, P. and Kruse, A. Calculating the Reaction Order and Activation Energy for the Hydrothermal Carbonization of Fructose. *Chemie Ingenieur. Technik*. 2020, 92 (6), 692–700.
2. Jung, D.; Körner, P. and Kruse A. Kinetic Study on the Impact of Acidity and Acid Concentration on the Formation of 5-Hydroxymethylfurfural (HMF), Humins, and Levulinic Acid in the Hydrothermal Conversion of Fructose. *Biomass Conversion and Biorefinery*. 2019. (Article in Press)
3. Jung, D.; Zimmermann, M. and Kruse, A. Hydrothermal Carbonization of Fructose: Growth Mechanism and Kinetic Model. *ACS Sustainable Chemistry and Engineering*. 2018, 6 (11), 13877–13887.
4. Jung, D.; Duman, G.; Zimmermann, M.; Kruse, A. and Yanik, J. Hydrothermal carbonization of fructose – effect of salts and reactor stirring on the growth and formation of carbon spheres. (Submitted to *Biomass Conversion and Biorefinery*)

B. Scientific publications not within the dissertation

1. Konnerth, P.; Jung, D.; Straten, J. W.; Raffelt, K. and Kruse, A. Metal Oxide-Doped Activated Carbons from Bakery Waste and Coffee Grounds for Application in Supercapacitors. *Mater. Sci. Energy Technol.* 2021, 4, 69–80.
2. Hoffmann, V.; Jung, D.; Alhnidi, M. J.; Mackle, L. and Kruse, A. Bio-Based Carbon Materials from Potato Waste as Electrode Materials in Supercapacitors. *Energies*. 2020, 13 (9), 2406.
3. Paksung, N.; Pfersich, J.; Arauzo, P. J.; Jung, D. and Kruse, A. Structural Effects of Cellulose on Hydrolysis and Carbonization Behavior during Hydrothermal Treatment. *ACS Omega*. 2020, 5 (21), 12210–12223.
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6. Hoffmann, V.; Jung, D.; Zimmermann, J.; Rodriguez Correa, C.; Elleuch, A.; Halouani, K. and Kruse, A. Conductive Carbon Materials from the Hydrothermal Carbonization of Vineyard Residues for the Application in Electrochemical Double-Layer Capacitors (EDLCs) and Direct Carbon Fuel Cells (DCFCs). *Materials*. 2019, 12 (10).
7. Körner, P.; Jung, D. and Kruse, A. Influence of the pH Value on the Hydrothermal Degradation of Fructose. *ChemistryOpen*. 2019, 8 (8), 1121–1132.

8. Cao, Z.; Jung, D.; Olszewski, M. P.; Arauzo, P. J. and Kruse, A. Hydrothermal Carbonization of Biogas Digestate: Effect of Digestate Origin and Process Conditions. *Waste Manag.* 2019, 100, 138–150.
9. Körner, P.; Jung, D. and Kruse, A. The Effect of Different Brønsted Acids on the Hydrothermal Conversion of Fructose to HMF. *Green Chem.* 2018, 20 (10), 2231–2241.
10. Jung, D. and Kruse, A. Evaluation of Arrhenius-type overall kinetic equations for hydrothermal carbonization. *Journal of Analytical and Applied Pyrolysis* 2017.127, 286–291.

C. Conference contributions - Presentations

1. Jung, D.; Straten, J.W. and Kruse, A. "Biobased carbon materials from municipal organic wastes as anodes for supercapacitors". Conference: Bioeconomy Congress Baden-Württemberg, Stuttgart 2020.
2. Jung, D. and Kruse, A. "Kinetische Modellierung der Hydrothermalen Karbonisierung". Conference: Jahrestreffen der ProcessNet-Fachgruppen Adsorption und Hochdruckverfahrenstechnik, Freiberg 2019.

D. Conference contributions - Posters

1. Jung, D. and Kruse, A. "Hydrothermale Karbonisierung von Fructose". Conference: Jahrestreffen der ProcessNet-Fachgruppen Hochdruckverfahrenstechnik, Erlangen 2018.
2. Jung, D.; Wüst, D. and Kruse, A. "Phytotoxic effects of phenolic substances in hydrothermal carbonized sewage sludge". Conference: HTP-Fachforum "Biobasierte hydrothermale Prozesse – Technologien zur stofflichen und energetischen Nutzung", Leipzig 2014.

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Summary

This present dissertation has been written at the chair of Prof. Andrea Kruse at the University of Hohenheim at the Department of Conversion Technologies of Biobased Resources in the period from 2017 to 2021. The cumulative dissertation consists of 4 articles, from which 3 have already been published and the last one has been submitted.

1. Jung, D.; Körner, P.; Kruse, A. Calculating the Reaction Order and Activation Energy for the Hydrothermal Carbonization of Fructose. *Chemie Ing. Tech.* 2020, 92 (6), 692–700. <https://doi.org/10.1002/cite.201900093>.
2. Jung, D.; Körner, P.; Kruse, A. Kinetic Study on the Impact of Acidity and Acid Concentration on the Formation of 5-Hydroxymethylfurfural (HMF), Humins, and Levulinic Acid in the Hydrothermal Conversion of Fructose. *Biomass Convers. Biorefinery* 2019. <https://doi.org/10.1007/s13399-019-00507-0>.
3. Jung, D.; Zimmermann, M.; Kruse, A. Hydrothermal Carbonization of Fructose: Growth Mechanism and Kinetic Model. *ACS Sustain. Chem. Eng.* 2018, 6 (11), 13877–13887. <https://doi.org/10.1021/acssuschemeng.8b02118>.
4. Jung, D.; Duman, G.; Zimmermann, M.; Kruse, A.; Yanik, J.; Hydrothermal carbonization of fructose – effect of salts and reactor stirring on the growth and formation of carbon spheres. Submitted (09.03.2021) to *Biomass Conversion and Biorefinery*

In the following an English and German summary of the work is presented.

English summary

The present work deals with the kinetic modeling of hydrothermal carbonization (HTC). HTC is a chemical process for the conversion of biomass into a carbon-rich material. In this process, the reactions take place in an aqueous environment under the influence of temperature (180-250 °C) and high pressures. HTC is a process for the technical utilization of wet biogenic residues, in particular, for the production of energy or renewable resources. For the construction of a technical production plant, an understanding of the chemical reactions during the process is necessary. The reaction rates can be determined by a kinetic model and provide an information basis for the design of reactors. The evaluation of kinetic models is also a method to understand the reaction mechanism. Against this background, this work deals with the formulation of a kinetic model for HTC. Fructose is used as a model substance since it is an important intermediate in the HTC of carbohydrate-containing biomasses. During the process, the formation of carbon particles, so-called hydrochar, takes place due to the polymerization of dissolved intermediates. This results in the formation of a new solid phase that must be considered in the kinetic modeling. Evaluation of the concentration curve of the individual substances shows that the decrease in hydroxymethylfurfural (HMF) correlates with the increase in hydrochar. Therefore, for the development of the kinetic model, polycondensation of HMF is used as the polymerization mechanism. This reaction results in the formation of higher molecular weight oligomers, which are a precursor to the newly formed hydrochar. The kinetic model takes advantage of the fact that during the polycondensation of HMF, one water molecule is split off for each reaction. For larger amounts of HMF, this leads to a simplified stoichiometric equation that is used for formulating a rate equation in the kinetic model. Upon validation, it is found that the experimentally determined concentration profiles of HMF and hydrochar are in agreement with the model. Furthermore, the elemental composition of the hydrochar is also in agreement with the model.

Based on the kinetic model, several research questions were answered in this work. The reaction order for the global reaction HMF to hydrochar was determined in a temperature range between 190-210 °C. The results show that the reaction order does not take a constant value, but varies between 1 and 2 depending on the reaction time, initial concentration and temperature. This finding confirms the hypothesis that the global reaction HMF to hydrochar follows a polymerization mechanism. Another aspect considered by the kinetic model was the reaction order

with respect to protons during the catalysis by Brønsted acids. As an approach, the relationship between proton concentration and the rate constant of the kinetic model was investigated. It was found that the rate constant for the reaction HMF to hydrochar increases linearly with increasing proton concentration, while the parallel reaction HMF to levulinic acid and formic acid increases quadratically accordingly. It was possible to work out that the yields shift in favor of levulinic acid and formic acid at a pH lower approx. 2. In addition to the investigations of the reaction mechanism, another focus of this work was on the particle growth and morphology of the hydrochar. Several results indicate that the growth of the particles proceeds by coagulation and thus the state of matter of the particles has a similarity to viscous pitch or tar during this process. The addition of salts causes a shielding of the surface charge and thus reduces repulsive forces during the collision of two hydrochar particles, consequently the coagulation rate increases. To improve the model, further research is needed. This concerns the development of a method to determine the oligomers by means of suitable standards. Following this, it must be clarified at which size or concentration of the oligomers the nucleation takes place. The latter can be used as a basis for the formulation of a nucleation mechanism. Following the nucleation, the growth of the particles can be modeled with the Smoluchowski equation, taking into account the DLVO (Derjaguin, Landau, Verwey, Overbeek) theory. In addition, the incorporation of diffusion processes, if they are rate-determining, must be considered. Furthermore, a validation of the model for further carbohydrates is necessary as well as the integration into HTC models with biomass as starting material.

German summary

Die vorliegende Arbeit beschäftigt sich mit der kinetischen Modellierung der hydrothermalen Karbonisierung (HTC). Bei der HTC handelt es sich um ein chemisches Verfahren zur Umwandlung von Biomasse in ein kohlenstoffreiches Material. Der Prozess findet dabei in einer wässrigen Umgebung unter dem Einfluss von Temperatur (180-250 °C) und hohen Drücken statt. Die HTC ist ein Verfahren, um insbesondere nasse biogene Reststoffe technisch im Rahmen einer energetischen oder stofflichen Nutzung zu verwerten. Für den Bau einer technischen Produktionsanlage ist ein Verständnis über die chemischen Reaktionen während des Prozesses notwendig. Die Reaktionsgeschwindigkeiten können dabei durch ein kinetisches Modell bestimmt werden und liefern eine Informationsgrundlage für die Auslegung von Reaktoren. Die Auswertung von kinetischen Modellen stellt

zudem eine Methode dar um den Reaktionsmechanismus zu verstehen. Vor diesem Hintergrund beschäftigt sich diese Arbeit mit der Erstellung eines kinetischen Modells für die HTC. Als Modellsubstanz wird Fruktose verwendet, da es sich hierbei um ein wichtiges Zwischenprodukt bei der HTC von kohlenhydrathaltigen Biomassen handelt. Während des Prozesses kommt es zur Bildung von Kohlepartikel, sogenannte HTC-Kohle, die durch die Polymerisierung von gelösten Substanzen entsteht. Dies hat die Entstehung einer neuen Feststoffphase zur Folge, die bei der kinetischen Modellierung berücksichtigt werden muss. Die Auswertung des Konzentrationsverlaufs der einzelnen Substanzen zeigt, dass die Abnahme von Hydroxymethylfurfural (HMF) mit der Zunahme von HTC-Kohle korreliert. Für die Entwicklung des kinetischen Modells wird daher die Polykondensierung von HMF als Polymerisationsmechanismus verwendet. Diese Reaktion hat die Bildung von höher molekularen Oligomeren zur Folge, welche eine Vorstufe der neu gebildeten HTC-Kohle darstellen. Das kinetische Modell nutzt dabei die Tatsache, dass bei der Polykondensierung von HMF ein Wasser Molekül für jede Reaktion abgespalten wird. Für größere Mengen an HMF führt dies zu einer vereinfachten stöchiometrischen Gleichung, die als Grundlage für die Formulierung einer Ratengleichung im kinetischen Modell verwendet wird. Bei der Validierung zeigt sich, dass die experimentell ermittelten Konzentrationsverläufe von HMF und der HTC-Kohle im Einklang mit dem Modell sind. Des Weiteren stimmt auch die elementare Zusammensetzung der HTC-Kohle mit dem Modell überein. Auf der Grundlage des kinetischen Modells wurden in dieser Arbeit verschiedene Forschungsfragen beantwortet. Die Reaktionsordnung für die globale Reaktion HMF zu HTC-Kohle wurde in einem Temperaturbereich zwischen 190-210 °C bestimmt. Die Ergebnisse zeigen, dass die Reaktionsordnung keinen konstanten Wert einnimmt, sondern abhängig von der Reaktionszeit, der Anfangskonzentration und der Temperatur zwischen 1 und 2 variiert. Dieser Befund bestätigt die Hypothese, dass die globale Reaktion HMF zu HTC-Kohle tatsächlich einem Polymerisationsmechanismus folgt. Ein weiterer Aspekt, der durch das kinetische Modell betrachtet wurde, war die Reaktionsordnung in Bezug auf die Protonen während der Katalyse durch Brønsted-Säuren. Als Herangehensweise wurde der Zusammenhang zwischen der Protonenkonzentration und der Geschwindigkeitskonstanten des kinetischen Modells untersucht. Dabei stellte sich heraus, dass die Geschwindigkeitskonstante für die Reaktion HMF zu HTC-Kohle mit steigender Protonenkonzentration linear zunimmt, während die Parallelreaktion HMF zu Lävulinsäure und Ameisensäure entsprechend quadratisch zunimmt. Es konnte herausgearbeitet werden, dass die

Ausbeuten ab einem pH-Wert kleiner als ca. 2 sich zugunsten der Lävulinsäure und Ameisensäure verschieben. Neben den Untersuchungen zum Reaktionsmechanismus bestand ein weiterer Fokus dieser Arbeit auf dem Wachstum und der Morphologie der HTC-Kohle-Partikel. Dabei deuten mehrere Ergebnisse daraufhin, dass das Wachstum der Partikel durch Koagulation voranschreitet und somit der Aggregatzustand der HTC-Kohle Ähnlichkeit mit zähflüssigem Pech oder Teer hat. Die Hinzugabe von Salzen bewirkt eine Abschirmung der Oberflächenladung und reduziert somit repulsive Kräfte bei der Kollision zweier HTC-Kohle Partikel, folglich erhöht sich die Koagulationsrate. Um das Modell zu verbessern, besteht weiterer Forschungsbedarf. Dies betrifft die Entwicklung einer Methode zur Bestimmung der Oligomere mittels geeigneter Standards. Daran angeschlossen muss geklärt werden bei welcher Größe bzw. Konzentration der Oligomere die Keimbildung stattfindet. Letzteres kann als Grundlage für die Formulierung eines Keimbildungsmechanismus verwendet werden. Im Anschluss an die Keimbildung kann das Wachstum der Partikel mit der Smoluchowski Gleichung, unter Berücksichtigung der DLVO (Derjaguin, Landau, Verwey, Overbeek) Theorie modelliert werden. Zusätzlich muss die Einbindung von Diffusionsvorgängen, sofern diese geschwindigkeitsbestimmend sind, berücksichtigt werden. Darüber hinaus ist eine Validierung des Modells für weitere Kohlenhydrate notwendig sowie die Integration in HTC-Modelle mit Biomasse als Ausgangsmaterial.

"All models are wrong but some are useful"

George E. P. Box

Contents

List of Figures	XIV
List of Tables	XIX
Abbreviations	XXI
1 Introduction	1
1.1 Motivation	1
1.2 Fructose as a starting material	3
1.3 Kinetic model	7
1.4 Research objectives	11
Bibliography	12
2 Hydrothermal carbonization of fructose: growth mechanism and kinetic model	15
2.1 Introduction	16
2.2 Materials and Methods	20
2.3 Results	22
2.4 Discussion	27
2.5 Conclusions	34
Bibliography	36
3 Calculating the reaction order and activation energy for the hydrothermal carbonization of fructose	41
3.1 Introduction	42
3.2 Materials and Methods	44
3.3 Results	49
3.4 Discussion	53
3.5 Conclusion	56

Bibliography	57
4 Kinetic Study on the Impact of Acidity and Acid Concentration on the Formation of 5-Hydroxymethylfurfural (HMF), Humins, and Levulinic Acid in the Hydrothermal Conversion of Fructose	61
4.1 Introduction	62
4.2 Materials and Methods	64
4.3 Results	68
4.4 Discussion	79
4.5 Conclusion	88
Bibliography	90
5 Hydrothermal carbonization of fructose – effect of salts and reactor stirring on the growth and formation of carbon spheres	95
5.1 Introduction	96
5.2 Material and Methods	98
5.3 Results	104
5.4 Discussion	116
5.5 Conclusions	120
Bibliography	121
6 Conclusion	125
6.1 Outlook	126