

Kiatkamjon Intani

**Sustainable postharvest
processing of maize residues
(*Zea mays* L.) into biochar for
agricultural and environmental
applications**

***Sustainable postharvest processing of maize residues
(Zea mays L.) into biochar for agricultural
and environmental applications***

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

Faculty of Agricultural Sciences

University of Hohenheim

Institute of Agricultural Engineering 440e
Tropics and Subtropics Group

submitted by
Kiatkamjon Intani

from Chiang Mai, Thailand

2019

This thesis was accepted as a doctoral dissertation to obtain the doctoral degree of Agricultural Sciences (Dr. sc. agr.) at the Faculty of Agricultural Sciences in the University of Hohenheim on 12.08.2019.

Date of oral examination: 16.09.2020

Examination committee

Prof. Dr.-Ing. Stefan Böttinger	(Head of examination committee)
Prof. Dr. Joachim Müller	(1 st examiner)
Prof. Dr. Stefan Pelz	(2 nd examiner)
Prof. Dr. Jens Wünsche	(3 rd examiner)

This work was accomplished within the framework of Bundesministerium für Bildung und Forschung (BMBF) project No. 031A258F “BiomassWeb – Improving food security in Africa through increased system productivity of biomass-based value webs” during my occupation at the Institute of Agricultural Engineering in the University of Hohenheim.

Schriftenreihe des Lehrstuhls für Agrartechnik in den Tropen und
Subtropen der Universität Hohenheim
herausgegeben von Prof. Dr. Joachim Müller

Band 21/2021

Kiatkamjon Intani

**Sustainable postharvest processing of maize
residues (*Zea mays* L.) into biochar for agricultural
and environmental applications**

D 100 (Diss. Universität Hohenheim)

Shaker Verlag
Düren 2021

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

Zugl.: Hohenheim, Univ., Diss., 2020

Copyright Shaker Verlag 2021

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publishers.

Printed in Germany.

ISBN 978-3-8440-7720-9

ISSN 1867-4631

Shaker Verlag GmbH • Am Langen Graben 15a • 52353 Düren

Phone: 0049/2421/99011-0 • Telefax: 0049/2421/99011-9

Internet: www.shaker.de • e-mail: info@shaker.de

Acknowledgements

This doctoral research was funded by the Food Security Center of the University of Hohenheim, the foundation fiat panis, the German Academic Exchange Service (DAAD), the Federal Ministry for Economic Cooperation and Development (BMZ) and the German Federal Ministry of Education and Research (BMBF). This research is the result of the project BiomassWeb WP 5.1 (Project No. 031A258F). I am very thankful to all financial supporters mentioned above.

I would like to express my great gratitude to my supervisor, Prof. Dr. Joachim Müller for giving me the opportunity to conduct my doctoral research and thesis at the Institute of Agricultural Engineering, Tropics and Subtropics Group (440e). I am very grateful for his supervision and support. I would also like to sincerely thank Dr. Sajid Latif for his guidance and support. Many thanks to my students A.K.M. Rafayatul Kabir, Zebin Cao, Md. Shafiqul Islam, Md. Arifur Rahaman and Christian Fink for their support with the laboratory work and data collection.

Special thanks to my friends and office mates Dr. Sebastian Romuli, Ana Alejandra Salvatierra-Rojas and Dr. Simon Munder for their support and the good working atmosphere.

I gratefully thank Ute Waldeck, Olga Gotra, Sarah Fleischmann, Dorothea Hirschbach-Müller, Dr. Catalina Rodriguez Correa, Dominik Wüst and Alice-Jaqueline Reineke for their technical support and their recommendations. Special thanks to Sabine Nugent for proofreading my manuscripts and dissertation.

Many thanks also go to my colleagues Dr. Marcus Nagle, Dr. Wolfram Spreer, Dr. Shkelqim Karaj, Dr. Victor Torres Toledo, Dr. Patchimaporn Udomkun, Dr. Parika Rungpichayapichet, Steffen Schock, Ute Kayser, Dr. Klaus Meissner, Sebastian Awiszus, Sebastian Reyer, Ziba Barati, Prinya Wongsas, Supaporn Klaykruayat, Sawittree Chai Areekitwat, Iris Ramaj and Bilhate Chala.

The additional advice on the design and construction of prototypes provided by Uwe Mauch was highly appreciated. I am also thankful for the support of Siegfried Kömpf to collect the biomass for the experiments. Special thanks to Helmut Gehrung and his farm in Stuttgart-Plieningen and KWS SAAT AG in Gondelsheim for providing biomass residues for the experiments. Mr. Gianluca Bersi is acknowledged for his support on electronic

devices. I also enjoyed conversations with the colleagues mentioned above and Ulrike Werner about daily life.

My special gratitude to H  l  ne and Udo Stauss, Angelika and Uwe Mauch, Ingrid Hadam, Anne and Jan Mosel, Henrike and Robert Kellermann, Rotraud and Willi Mosel, Gudrun and Klaus Weber, Gisela and Olaf Marienhagen, Ingo and Anne-Katrin Quilitz, Dr. Sebastian Romuli, Ana Alejandra Salvatierra-Rojas, Ployapat and Herbert Reinderhoff, Nemia Schmissrauter, Julian Wald, Panida Garaboon, Dr. Arm Tungnirun and Uthaiwan Leelanawakun for their great support during the most difficult time in my life.

I also would like to thank my teachers Siree Yauwapaksoyon, Prapasri Herunya, Issaraporn Jetapai, Duangruedee Ratanawongsa, Panida Garaboon, Montien Suthamma, Sirirat Asana, Pimsawat Suwanpairaj, Ratana Petklai, Renu Khantawong, Kanda Amornpetchkul, Woranuch Wongsakul, Nawarat Kalapapen, Pattama Iemsuwan, Ampan Vongsuvan, Nantana Sasootorn, Wiangjan Janngam and others who guided me on the right path for my education. Thanks to my Thai friends Sasipha Kaewkham, Wanngam Kaewkham, Sathaporn Kaewkham, Dr. Kirati Sriamorn, Suphacha Sriratanaban, Saknarin Maifuei and Wanwisa Prasertsri.

Special thanks go to my family members in Thailand for their continuous support. These special persons are Patcharee and Dang Intani, Emon and Somboon Thepkham, Suriyotin Intani, Prommin Intani, Junya Charnwattanakit and Apatsara Intani. Thanks to Sarah Crestin-Billet for her support and giving birth to our wonderful son (Nathan Intani). I am grateful to my son, who is always the light in the darkness of my days. Without his love, laughs, smiles and motivation, I could not imagine how I could have endured the pressure and difficulties in life during my doctoral studies.

Hohenheim, 08.08.2019

Place, Date

Kiatkamjon Intani

Table of contents

1	General introduction.....	1
1.1	Maize (<i>Zea mays</i> L.)	1
1.2	Potential and use of maize residues	2
1.3	Biochar production from maize residue via pyrolysis process	6
1.4	Problem statement.....	8
1.5	Objectives and outline of the studies	10
1.6	References.....	12
2	Part I: Effect of self-purging pyrolysis on yield of biochar from maize cobs, husks and leaves.....	18
2.1	Abstract	18
2.2	Introduction.....	18
2.3	Material and methods.....	20
2.3.1	Maize residues	20
2.3.2	Pyrolysis reactor and procedure	20
2.3.3	Characterisation of biomass and biochar	22
2.3.4	Design of experiments	24
2.3.5	Statistical analysis	24
2.4	Results and discussion	25
2.4.1	Characteristics of maize biomass and biochar	25
2.4.2	Effect of pyrolysis conditions on biochar yield	30
2.4.3	Biochar yield from maize cobs.....	34
2.4.4	Biochar yield from maize husks.....	36
2.4.5	Biochar yield from maize leaves	38
2.4.6	Comparison of biochar yield from cobs, husks and leaves	41
2.4.7	Biochar yield from self-purging and nitrogen purging pyrolysis.....	44
2.5	Conclusions.....	44
2.6	Appendix A. Supplementary data	46
2.7	References.....	47
3	Part II: Characterisation of biochar from maize residues produced in a self-purging pyrolysis reactor	50
3.1	Abstract	50

3.2	Introduction.....	50
3.3	Material and methods.....	52
3.3.1	Biomass and biochar preparation	52
3.3.2	Characterisation of biochars.....	53
3.3.3	Design of experiments.....	54
3.3.4	Statistical analysis	55
3.4	Results and discussion	55
3.4.1	Characteristics of the maize biomass and biochar samples.....	55
3.4.2	Volatile matter content of biochars	62
3.4.3	Ash content of biochars.....	66
3.4.4	pH and electrical conductivity of biochars.....	69
3.4.5	Optimal pyrolysis conditions	73
3.5	Conclusions.....	77
3.6	Appendix A. Supplementary data	79
3.7	References.....	83
4	Part III: Phytotoxicity of corncob biochar before and after heat treatment and washing	87
4.1	Abstract.....	87
4.2	Introduction.....	87
4.3	Material and methods.....	90
4.3.1	Biomass and biochar preparation	90
4.3.2	Characterisation of corncob biochar	91
4.3.3	Treatments of corncob biochar.....	92
4.3.4	Germination test	93
4.3.5	Statistical analysis	95
4.4	Results and discussion	95
4.4.1	Characteristics of corncob biochar	95
4.4.2	Effects of corncob biochar on cress seed germination.....	99
4.4.3	Effects of corncob biochar on shoot length.....	101
4.4.4	Effects of corncob biochar on shoot fresh weight.....	103
4.4.5	Effects of corncob biochar on dry matter content of the shoot biomass	105
4.4.6	Phytotoxic compounds in biochar.....	107
4.4.7	Effects of biochar treatments and application rates	107
4.5	Conclusions.....	110
4.6	References.....	112

5	General discussion.....	118
5.1	Self-purging pyrolysis of maize residues.....	118
5.2	Properties of biochars derived from self-purging pyrolysis	120
5.3	Phytotoxic effects of corncob biochar treatments on seed germination	122
5.4	Impact to practise	124
5.5	Further research requirements.....	124
5.6	References.....	125
	Summary	131
	Zusammenfassung	133
	Publications	135

List of tables

Table 1.1	The contribution of maize in crop residue utilisation.	3
Table 2.1	Standard methods used for the analyses of maize biomass and biochar.	23
Table 2.2	Characteristics of the maize biomass and biochar samples produced at 300 °C.	27
Table 2.3	RSM-BBD design matrix and experiment results for pyrolysis of maize residues.	32
Table 2.4	ANOVA for the reduced quadratic model for pyrolysis of maize cobs.	33
Table 2.5	ANOVA for the reduced quadratic model for pyrolysis of maize husks.	33
Table 2.6	ANOVA for the reduced quadratic model for pyrolysis of maize leaves.	34
Table 3.1	Main characteristics of the maize biomass and biochar samples produced at 300, 450 and 600 °C.	57
Table 3.2	Mineral content (mg/kg) and trace element content (mg/kg) of the maize biomass and biochar samples produced at operating temperature of 300, 450 and 600 °C (values based on dry matter).	61
Table 3.3	Experiment results of the volatile matter content (VM), ash content (AC), pH and electrical conductivity (EC) of biochars produced from maize residues. ..	63
Table 3.4	The goodness of fit and accuracy of the mathematical models for volatile matter content (VM), ash content (AC), pH and electrical conductivity (EC) of biochars produced from maize cobs, husks, leaves and stalks (see Eq. 2).	66
Table 3.5	Optimal pyrolysis conditions, corresponding responses and recommended values.	75
Table 3.6	RSM-BBD design matrix and experiment results for the biochar yield of maize stalks.	80
Table 3.7	Regression coefficients of the mathematical models for volatile matter content (VM), ash content (AC), pH and electrical conductivity (EC) of biochars produced from maize cobs, husks, leaves and stalks (see Eq. 2).	81
Table 3.8	<i>p</i> -values of the mathematical models for volatile matter content (VM), ash content (AC), pH and electrical conductivity (EC) of biochars produced from maize cobs, husks, leaves and stalks (see Eq. 2).	82
Table 4.1	Experimental set-up.	94
Table 4.2	Proximate analysis, pH, EC, and particle size distribution of the corncob biochar.	96
Table 4.3	Major mineral content, trace element content and ultimate analysis of corncob biomass and biochar.	98
Table 4.4	Exchangeable cations and effective cation exchange capacity (ECEC) of corncob biochar.	98

List of figures

Figure 1.1	Maize residues a) cobs b) husks c) leaves d) stalks.	1
Figure 1.2	Open-field burning of maize residues.	5
Figure 1.3	Simplified process flow diagram of biomass pyrolysis reactions.	7
Figure 2.1	O/C and H/C ratios of biomass and biochar samples, including maize cobs (MC), husks (MH), leaves (ML) and biochars produced at different temperatures (300, 450 and 600 °C). Dashed line is the upper limit of 0.7 for H/C ratios indicating thermochemically converted materials.	29
Figure 2.2	Biochar yield from maize cobs (a) normal probability plot of the residuals (b) plot of residuals versus predicted values (c) surface plot indicating combined effect of temperature and holding time at constant heating rate of 10 °C/min and (d) sliced plot of the reduced quadratic response surface model.	35
Figure 2.3	Biochar yield from maize husks (a) normal probability plot of the residuals (b) plot of residuals versus predicted values (c) surface plot indicating combined effect of temperature and heating rate at constant holding time of 60 min and (d) sliced plot of the reduced quadratic response surface model.	37
Figure 2.4	Biochar yield from maize leaves (a) normal probability plot of the residuals (b) plot of residuals versus predicted values (c) surface plot indicating combined effect of temperature and holding time at constant heating rate of 10 °C/min and (d) sliced plot of the reduced quadratic response surface model.	40
Figure 2.5	Trends of furnace and reaction temperatures during an experimental run with maize cobs (MC), husks (MH) and leaves (ML) for (a) self-purging and (b) nitrogen purging pyrolysis, the letters A, B, C, D, E and F indicating the points where the reaction temperatures were higher than the heating temperatures in the furnace (set point temperature: 300 °C; heating rate: 5 °C/min for MC and MH, 15 °C/min for ML; holding time: 30 min for MC and ML, 33 min for MH).	43
Figure 2.6	SEM images of (a) cobs, (b) husks and (c) leaves, and (d) cob biochar, (e) husk biochar and (f) leaf biochar produced at 300 °C.	46
Figure 3.1	H/C and O/C ratios of biomass and biochar samples, including maize cobs (MC), husks (MH), leaves (ML) and stalks (MS) and biochars produced at different temperatures (300, 450 and 600 °C). Different letters indicate significant differences in H/C (A-H) and O/C (a-j) ratios at <i>p</i> -value < 0.05. Dashed lines are the upper limit of 0.7 for H/C ratio and 0.2 for O/C ratio, indicating degree of carbonisation in biochar.	58
Figure 3.2	Sliced plot of the quadratic response surface models for the volatile matter content (VM) of biochars produced from maize (a) cobs, (b) husks, (c) leaves and (d) stalks.	64
Figure 3.3	Sliced plot of the quadratic response surface models for the ash content (AC) of biochars produced from maize (a) cobs, (b) husks, (c) leaves and (d) stalks. ...	68
Figure 3.4	Sliced plot of the quadratic response surface models for the pH values of biochars produced from maize (a) cobs, (b) husks, (c) leaves and (d) stalks. ...	70
Figure 3.5	Sliced plot of the quadratic response surface models for the electrical conductivity (EC) of biochars produced from maize (a) cobs, (b) husks, (c) leaves and (d) stalks.	71

Figure 3.6	Three-dimensional plots of the interaction effect of temperature and holding time on (a) volatile matter content (VM), (b) ash content (AC), (c) pH and (d) electrical conductivity (EC) of biochars derived from maize residues.....	76
Figure 3.7	SEM images of (a) cob, (b) cob biochar produced at 300 °C-5 °C/min-60 min, (c) cob biochar produced at 450 °C-10 °C/min-60 min, and (d) cob biochar produced at 600 °C-5 °C/min-60 min.....	79
Figure 4.1	Germination rates (GR) under different biochar application rates (10, 20, and 30 t/ha) and treatments (Control: CON, Fresh biochar: FB, Dried biochar: DB, Washed biochar: WB and Biochar water extract: WE). The first stacked column indicates the germination rate after 24 h (GR ₂₄), while the second stacked column shows the germination rate between 24–48 h. The sum of stacked columns represents the germination rate after 48 h (GR ₄₈). Different capital letters show significant differences in GR ₄₈ between biochar treatments at same application rate ($p < 0.05$), and different small letters show significant differences in GR ₄₈ between biochar application rates of same biochar treatment ($p < 0.05$). Standard errors of GR ₄₈ are represented by the bars ($n = 6$ for the treatments, and $n = 24$ for the CON).....	101
Figure 4.2	Shoot length of cress under different biochar application rates (10, 20, and 30 t/ha) and treatments (Control: CON, Fresh biochar: FB, Dried biochar: DB, Washed biochar: WB and Biochar water extract: WE). Different capital letters show significant differences between biochar treatments at same application rate ($p < 0.05$), and different small letters show significant differences between biochar application rates of same biochar treatment ($p < 0.05$). Standard errors are represented by the bars ($n = 6$ for the treatments, and $n = 24$ for the CON).	102
Figure 4.3	Shoot fresh weight of cress under different biochar application rates (10, 20, and 30 t/ha) and treatments (Control: CON, Fresh biochar: FB, Dried biochar: DB, Washed biochar: WB and Biochar water extract: WE). Different capital letters show significant differences between biochar treatments at same application rate ($p < 0.05$), and different small letters show significant differences between biochar application rates of same biochar treatment ($p < 0.05$). Standard errors are represented by the bars ($n = 6$ for the treatments, and $n = 24$ for the CON).	104
Figure 4.4	Dry matter content of the shoot biomass under different biochar application rates (10, 20, and 30 t/ha) and treatments (Control: CON, Fresh biochar: FB, Dried biochar: DB, Washed biochar: WB and Biochar water extract: WE). Different capital letters show significant differences between biochar treatments at same application rate ($p < 0.05$), and different small letters show significant differences between biochar application rates of same biochar treatment ($p < 0.05$). Standard errors are represented by the bars ($n = 6$ for the treatments, and $n = 24$ for the CON).	106