



UNIVERSITI PUTRA MALAYSIA

**PHYSICO-CHEMICAL TRANSFORMATION AND STABILITY OF
JATROPHA POD BIOCHAR IN AN ACIDIC MINERAL SOIL AND
PINEAPPLE STUMP BIOCHAR IN TROPICAL PEAT**

CHEAH POH MENG

FP 2014 8



**PHYSICO-CHEMICAL TRANSFORMATION AND STABILITY OF
JATROPHA POD BIOCHAR IN AN ACIDIC MINERAL SOIL AND
PINEAPPLE STUMP BIOCHAR IN TROPICAL PEAT**

By

CHEAH POH MENG

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in
Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

August 2014

COPYRIGHT

All material contained within the thesis, including without limitation text, logos, icons, photographs and all other artwork, is copyright material of Universiti Putra Malaysia unless otherwise stated. Use may be made of any material contained within the thesis for non-commercial purposes from the copyright holder. Commercial use of material may only be made with the express, prior, within permission of Universiti Putra Malaysia.

Copyright © Universiti Putra Malaysia



Dear Dad, Fook Thin,

Beloved Mom, Foong Khew

Brother and Sister, Chooi Ying, Poh Weng

Grandparents, Cheah Wei and Kim Thye

Thank you for all the support and love



Special Thanks to Shir Yih



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

**PHYSICO-CHEMICAL TRANSFORMATION AND STABILITY OF
JATROPHA POD BIOCHAR IN AN ACIDIC MINERAL SOIL AND
PINEAPPLE STUMP BIOCHAR IN TROPICAL PEAT**

By

CHEAH POH MENG

August 2014

Chairman: Ahmad Husni bin Monhd. Hanif, PhD
Faculty: Agriculture

Biochar is classified as stable C sequester that can last hundreds to thousands of years. Though, it is a vague explanation as biochar experienced various transformations resulted from different climatic pattern and soil type. It is safe to assume stability of similar biochar varies depending on environmental factor. Assessing resident time of biochar in soil is a taunting task since current estimation methods are flawed and time consuming. Abiotic and biotic oxidation is the main degradation mechanisms of biochar. Moreover, biochar field decomposition study in Malaysia at acidic mineral soil and tropical peat soil are yet to be conducted. It is hypothesized biochar decomposition in Malaysia is rapid due to high amount of annual rainfall. Besides, accelerating biochar decomposition with oxidation could provide quick estimation of the biochar resident time in soil. Biochar could serve as a mean in managing the high amount of biomass waste produced from Jatropha and pineapple cultivation. The study was undertaken to examine the physico-chemical transformation of Jatropha pod (JP) biochar in an acidic mineral soil and pineapple stump (PS) biochar in tropical peat soil respectively. Furthermore, hydrogen peroxide (H_2O_2) was used to simulate the JP and PS biochars litterbag decomposition model.

The raw Jatropha pod was collected from Universiti Agriculture Park, Plot D, UPM. Meanwhile, raw pineapple stump was collected from Peninsula Plantation, Simpang Renggam, Malaysia. Both PS and JP biochars were produced by partially combusting the dried raw samples for 3 hours at $250^{\circ}C$ and $275^{\circ}C$ respectively in a carbolite furnace. The physico-chemical properties were characterized using surface area analyzer based on Brunauer, Emmet and Teller (BET) theory, Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy (SEM).

Field decomposition of JP and PS biochars was determined using the litterbag method. Furthermore, hydrogen peroxide (H_2O_2) was utilized to replicate biochar litterbag field decomposition.

The BET surface area of JP biochar increased significantly after 16 months buried in acidic mineral soil implying physical fragmentation. Adsorption of organic matter was unlikely due to the increasing BET surface area. Instead, interaction with minerals such as Fe could have contributed to the resident time of JP biochar. Increase of O functionalities (phenolic, carboxylic and hydroxyl) implied JP biochar suffered severe oxidation shown by FTIR and NMR analysis. The JP biochar litterbag field decomposition was fitted into hyperbolic decay model with 3 parameters.

However, the BET surface area of PS biochar decreased significantly after 16 months under tropical peat soil. This could be attributed to adsorption of organic matter but the declining C content indicated contrarily. This also implied PS biochar was less susceptible to physical fragmentation. Instead, increasing Fe in PS biochar overtime suggested interaction between biochar and Fe from peat by ligand bridging. Further study was needed to verify this phenomena and its effect on recalcitrance of biochar. Increasing O functionalities hinted surface oxidation shown in the FTIR spectrum of PS biochar. However, C structure of PS biochar was not oxidized or protected from degradation. This could be attributed to lower microbial activities in peat. The PS biochar litterbag field decomposition was also fitted into hyperbolic decay model with 3 parameters. The forecasted mean resident time of JP and PS biochars were 104 years in acidic mineral soil and 333 years in tropical peat respectively.

Oxidation process played a major role in biochar decomposition. Both JP and PS biochars field decomposition pattern were able to be simulated and accelerated with 30% H_2O_2 . However, the estimated results might be underestimated as the H_2O_2 simulation was unable to replicate the chemisorption on biochar. Further research was needed to improve this simulation method.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**TRANSFORMASI FIZIKAL KIMIA ARANG DALAM TANAH MINERAL
BERACID & GAMBUT TROPIKA DAN ESTIMASI KESTABILAN ARANG
MELALUI SIMULASI MAKMAL**

By

CHEAH POH MENG

Ogos 2014

Pengerusi: Ahmad Husni bin Mohd. Hanif, PhD
Fakulti: Pertanian

Arang diklasifikasikan sebagai sekuestasi karbon yang stabil dan tahan beberapa ratus atau ribu tahun. Walau bagaimanapun, ini adalah penerangan yang lemah kerana melalui pelbagai transformasi akibat perbezaan cuaca dan jenis tanah. Kestabilan arang yang sama bergantung kepada faktor persekitaran. Penilaian masa tinggal arang di tanah adalah tugas yang susah kerana kaedah estimasi semasa mempunyai pelbagai kelemahan dan memakan masa. Pengoksidaan abiotik and biotik adalah mekanisme degradasi arang yang utama. Selain itu, pengajian lapang penguraian arang pada tanah mineral beracid dan gambut tropika di Malaysia belum lagi dijalankan. Penguraian arang di Malaysia adalah dihipotesiskan pesat kerana jumlah hujan tahunan yang tinggi. Simulasi pengoksidaan arang boleh memberi estimasi pantas kepada masa tinggal arang dalam tanah. Arang boleh digunakan untuk menguruskan jumlah sisa biomas yang banyak masa penanaman *Jatropha* dan nenas. Kajian ini dijalankan untuk menguji transformasi fizikal kimia arang buah *Jatropha* (JP) di tanah mineral beracid dan arang tunggul nenas (PS) di gambut tropika. Selain itu, hidrogen peroksida digunakan untuk mensimulasi penguraian arang JP dan PS yang diisi kepada beg nilon yang dijalankan pada jenis tanah masing-masing.

Buah *Jatropha* dikumpul dari Plot D, Taman Pertanian Universiti, UPM and dibakar pada 275°C dalam relau selama 3 jam. Manakala, tunggul nenas dikumpulkan dari Ladang Peninsula, Simpang Renggam, Malaysia dan dihasilkan pada 250°C dalam relau selama 3 jam. Ciri-ciri fiziko kimia kedua-dua arang ditentukan dengan analyzer kawasan permukaan dengan teori Brunauer, Emmet dan Teller (BET), Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Differential Scanning Calorimetry (DSC) dan Scanning Electron Microscopy (SEM). Penguraian lapang arang JP dan PS juga ditentukan dengan kaedah beg nilon

yang diisi dengan arang. Tambahan, hidrogen peroksida digunakan untuk meniru penguraian lapang arang dengan beg nilon.

Kawasan permukaan BET arang JP meningkat dengan ketara selepas 16 bulan dalam tanah mineral beracid dan ini menunjukkan pemecahan fizikal. Kemungkinan penjerapan bahan organik pada arang JP adalah rendah kerana peningkatan kawasan permukaan BET tetapi interaksi arang JP dengan mineral seperti Fe mungkin menyumbang kepada masa tinggalnya dalam tanah. Peningkatan kumpulan berfungsi oksigen seperti fenolik, karboksilik dan hidroksil menunjukkan arang JP mengalami oksidasi yang besar seperti yang ditunjukkan oleh analisis FTIR dan NMR. Penguraian lapang arang JP bersesuaian dengan model pereputan hiperbola tiga-parameter.

Manakala, kawasan permukaan BET arang PS menurun dengan ketara selepas 16 bulan dalam gambut tropikal. Ini mungkin disebabkan of jerapan bahan organik tetapi penurunan kandungan karbon menunjukkan sebaliknya. Sebaliknya, peningkatan kandungan Fe arang PS mencadangkan interaksi arang PS dengan Fe akibat penyambungan ligan. Kajian lanjut diperlukan untuk mengesahkan fenomena ini dan kesannya kepada kestabilan arang. Peningkatan kumpulan berfungsi oksigen menunjukkan oksidasi pada permukaan arang PS seperti ditunjukkan pada spektrum FTIR. Struktur karbon arang PS tidak dioksidasikan atau dilindungi daripada penguraian. Ini mungkin disebabkan aktiviti mikrob yang rendah dalam gambut. Penguraian lapang arang PS juga bersesuaian dengan model pereputan hiperbola tiga-parameter. Arang JP diramalkan tinggal di dalam tanah mineral beracid untuk 104 tahun. Manakala, arang PS diramalkan tinggal di dalam gambut tropikal untuk 333 tahun.

Pengoksidaan main peranan penting dalam penguraian arang. Kedua-dua corak penguraian dapat disimulasikan dan dipercepatkan dengan 30% hidrogen peroksida. Walau bagaimanapun, masa anggaran arang di dalam tanah mungkin lebih rendah kerana tidak dapat meniru penjerapan pada permukaan arang. Lagi banyak kajian diperlukan untuk meningkatkan prestasi kaedah simulasi ini.

ACKNOWLEDGEMENTS

I am grateful to Lord Almighty for His grace, blessings and the strength granted to him to complete his study. I wish to express my gratitude to Assoc. Prof. Dr. Ahmad Husni bin Mohd. Hanif, the Chairman of the Supervisory Committee for the keen interest, valuable contribution and tireless guidance during the preparation of this thesis. His countless support and generosity cannot be over emphasized.

I express my deepest gratitude to Dr. Samsuri Abdul Wahid and Prof. Dr. Luqman Chuah Abdullah, members of the Advisory Committee for their invaluable assistance and guidance at the various stages of the research. Their tolerance and patient throughout the whole study are very much appreciated. Special reference also goes to the management of Peninsula Plantation, Simpang Renggam, Johor for their support and commitment of partnership in this collaborative research. Financial support from the Ministry of Higher Education, Malaysia via Universiti Putra Malaysia (UPM) is acknowledged.

Appreciation goes to my family for their love, understanding, spiritual support and prayers. The author is thankful to the entire technical staff of the Land Management Department for their cooperation that led to the smooth run of all the experiments of the research. Help from my friends is acknowledged.

I certify that a Thesis Examination Committee has met on 6 August 2014 to conduct the final examination of Cheah Poh Meng on his thesis entitled "Physico-chemical Transformation and Stability of Jatropha Pod Biochar in an Acidic Mineral Soil and Pineapple Stump Biochar in Tropical Peat" in accordance with the Universities and University College Act 1971 and the Constitution of Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctorate of Philosophy.

Members of the Thesis Examination Committee were as follows:

Shamshuddin b Jusop, PhD
Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Christopher Teh Boon Sung, PhD
Lecturer
Faculty of Agriculture
Universiti Putra Malaysia
(Internal Examiner)

Hamdan b Jol, PhD
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Internal Examiner)

Sota Tanaka, PhD
Professor
Research and Education Faculty
Kochi University
(External Examiner)

NORITAH OMAR, PhD
Associate Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 25 August 2014

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Ahmad Husni Mohd. Hanif, PhD

Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Samsuri Abdul Wahid, PhD

Senior Lecturer
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

Luqman Chuah Abdullah, PhD

Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 20 October 2014

Declaration by graduate student

I hereby declare that:

- this thesis is original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: _____ Date: _____

Name and Matric No: _____

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: _____
Name of
Chairman of
Supervisory
Committee: _____

Signature: _____
Name of
Member of
Supervisory
Committee: _____

Signature: _____
Name of
Member of
Supervisory
Committee: _____

TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	iii
ACKNOWLEDGEMENTS	v
APPROVAL	vi
DECLARATION	viii
LIST OF TABLES	xiii
LIST OF FIGURES	xiv
LIST OF ABBREVIATIONS	xvi
LIST OF SYMBOLS	xvii
CHAPTER	
1 INTRODUCTION	1
2 LITERATURE REVIEW	3
2.1 Defination of Biochar	3
2.2 Biochar for Environmental Management	3
2.2.1 Biochar Provides Agronomic Benefits	4
2.2.2 Biochar as Waste Management	5
2.2.3 Biochar and Bio-energy	5
2.2.4 Biochar to Mitigate Climate Change	6
2.3 Pyrolysis and Biochar Production	6
2.3.1 Fast Pyrolysis	7
2.3.2 Slow Pyrolysis	7
2.4 Biochar Production Mechanisms During Pyrolysis	7
2.5 Changes of Physico-Chemical Properties Due to Pyrolysis	8
2.5.1 Surface Area and Porosity	8
2.5.2 Elemental Composition	9
2.5.3 Surface Chemistry	10
2.5.4 Chemical Structure	11
2.5.5 Chemical Composition	12
2.6 Assessing Biochar Decomposition	12
2.6.1 Labile Fraction of Biochar	14
2.6.2 Non-labile Fraction of Biochar	15
2.7 Biochar Changes in Soil	15
2.7.1 Biochar Physical Breakdown	15
2.7.2 Organic Matter Adsorption on Biochar	16
2.7.3 Changes of Elemental Composition of Biochar	16
2.7.4 Increase of Oxygen Functionalities on Biochar	17
2.7.5 Biochar Interaction with Minerals and Organic Matter	17
2.7.6 Biotic Degradation of Biochar	18

2.8	Role of Hydrogen Peroxide in Biochar Decomposition	19
2.9	Acidic Mineral and Oligotrophic Peat Soil in Malaysia	19
2.10	Jatropha and Pineapple Industry in Malaysia	19
2.11	Sumarry	20
3	JATHROPA POD (JP) BIOCHAR PRODUCTION, CHARACTERIZATION AND DECOMPOSITION STUDY IN AN ACIDIC MINERAL SOIL	22
3.1	Introduction	22
3.2	Materials and Methods	23
3.2.1	Biochar Production	23
3.2.2	Biochar Characterization	24
3.2.2.1	pH Value	24
3.2.2.2	Elemental Composition	24
3.2.2.3	Brunauer, Emmet and Teller (BET) Surface Area	25
3.2.2.4	Chemical Composition	25
3.2.2.5	Morphology Analysis	26
3.2.2.6	Thermal Analysis	26
3.2.2.7	Surface Chemistry	26
3.2.2.8	Chemical Structure Analysis	27
3.2.2.9	Field Decomposition	27
3.2.3	Statistical Analysis	28
3.3	Results and Discussions	28
3.3.1	Jathropa Pod Biochar Production and Characterization	28
3.3.1.1	Elemental and Chemical Composition	28
3.3.1.2	Surface Chemistry	32
3.3.1.3	Chemical Structure	32
3.3.1.4	Morphology Analysis	32
3.3.1.5	Thermal Analysis	36
3.3.1.6	Carbon Footprint of Jathropa Pod Biochar Production	38
3.3.2	Field Decomposition of Jathropa Pod Biochar	39
3.3.2.1	Site History	39
3.3.2.2	Elemental Composition and Physical Changes	39
3.3.2.3	Surface Chemistry Transformation	41
3.3.2.4	Chemical Structure Alteration	44
3.3.2.5	Decomposition Model	48
3.4	Conclusions	50
4	PINEAPPLE STUMP (PS) BIOCHAR PRODUCTION, CHARACTERIZATION AND DECOMPOSITION STUDY IN A TROPICAL PEAT SOIL	51

4.1	Introduction	51
4.2	Materials and Methods	52
4.2.1	Biochar Production	52
4.2.2	Field Decomposition	52
4.3	Results and Discussions	53
4.3.1	Pineapple Stump Biochar Production and Characterization	53
4.3.1.1	Elemental and Chemical Composition	53
4.3.1.2	Surface Chemistry	58
4.3.2.3	Chemical Structure	58
4.3.2.4	Overestimation of Lignin Content in PS Biochar	59
4.3.2.5	Morphology Analysis	59
4.3.2.6	Thermal Analysis	61
4.3.2.7	Carbon Footprint of Pineapple Stump Biochar Production	63
4.3.2	Field Decomposition of Pineapple Stump Biochar	64
4.3.2.1	Site History	64
4.3.2.2	Elemental Composition and Physical Changes	64
4.3.2.3	Surface Chemistry Transformation	66
4.3.2.4	Chemical Structure Alteration	69
4.3.2.5	Decomposition Model	73
4.4	Conclusions	75
5	ESTIMATING BIOCHAR STABILITY	76
5.1	Introduction	76
5.2	Materials and Methods	77
5.2.1	Biochar Simulated Decomposition	77
5.2.2	Statistical Analysis	78
5.3	Results and Discussions	78
5.3.1	Simulation of Jathropa Pod (JP) Biochar Litterbag Field Decomposition	78
5.3.2	Simulation of Pineapple Stump (PS) Biochar Litterbag Field Decomposition	83
5.4	Conclusions	86
6	SUMMARY, GENERAL CONCLUSION AND RECOMMENDATION FOR FUTURE RESEARCH	87
	REFERENCES	89
	APPENDICES	103
	BIODATA OF STUDENT	105
	LIST OF PUBLICATIONS	106