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

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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

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

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Chairman: Ahmad Husni bin Monhd. Hanif, PhD
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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^{o}C and 275^{o}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
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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 pandas 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^{o}C dalam relau selama 3 jam. Manakala, tunggul nenas dikumpulkan dari Ladang Peninsula, Simpang Renggam, Malaysia dan dihasilkan pada 250^{o}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 kanduangan 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 kajiaan diperlukan untuk meningkatkan prestasi kaedah simulasi ini.

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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 committe recommends that the student be awarded the Doctorate of Philosophy.

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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 Commitee were as follows:

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