

**PERFORMANCE TESTING OF CADMIUM TREATMENT IN
SOIL USING BROILER LITTER BY PYROLYSIS
FOR SOYBEAN PLANTING**

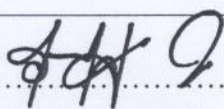
Lt. Col. Chintana Sanvong


**A Dissertation Submitted in Partial
Fulfillment of the Requirements for the Degree of
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(Social Development and Environmental Management)
School of Social and Environmental Development
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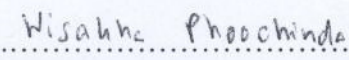
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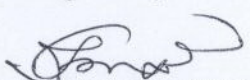
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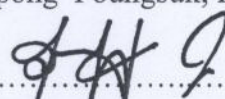
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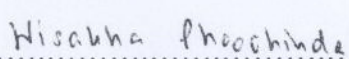
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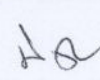
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17 October, 2013

ABSTRACT

| | |
|------------------------------|--|
| Title of Dissertation | Performance Testing of Cadmium Treatment in Soil Using Broiler Litter by Pyrolysis for Soybean Planting |
| Author | Lt. Col. Chintana Sanvong |
| Degree | Doctor of Philosophy (Social and Environmental Development) |
| Year | 2013 |

Cadmium has been identified as a major toxic heavy metal contaminating in our food supply chain. This study want to purpose socio-economic and appropriate technology for ameliorate cadmium contamination in soil by propose broiler litter biochar derived from incinerate pelleted broiler litter in 2 reactor that 1st in lab-scale pyrolysis reactor (PBLBL) and 2nd in 200 liter oil drum (PBLBO) at highest temperature of 500°C. Biochar was subsequently mixed into soil with 4 mixing rate 5.00, 10.0, 15.0 and 20.0 t ha⁻¹. Each mixing rate was added with 5 level of Cd concentrations consisting of 0, 20.0, 40.0, 60.0 and 80.0 mg Cd kg⁻¹soil. Those Cd-contaminated soils were used to cultivate the soybean, Chiang Mai 60 variety, and evaluation of plant growth and productions was performed. PBLBL and PBLBO incinerations with all mixing rate significantly promoted the soybean productivity higher than control. Typically, the harvest soybean seeds (cultivated in 80.0 mg Cd kg⁻¹soil) comparing with as-received soybeans, gained the dry weight of 0, 0, 0, and 142 %, respectively, for PBLBO mixing rates of 5.00, 10.0, 15.0 and 20.0 t ha⁻¹, while PBLBL showed of 98.0, 120, 138, and 126 %, respectively. Moreover PBLBL and PBLBO increased an availability of nutrients (e.g. N, P, K, Ca, Mg) and improved soil properties including % moisture content, pH, OM, C/N, CEC and capably-reduced Cd concentrations in soils. Satisfactory results of residual Cd in biochar-mixed soil were obtained by PBLBO with mixing rate 20.0 t ha⁻¹ and PBLBL with same mixing rate, residual Cd was about 35.0 and 31.4 mg Cd kg⁻¹ soil. Even though

the pretreat Cd-contaminated soils was high to $80.0 \text{ mg Cd kg}^{-1}$ soil, the residual Cd after treatment with biochar was particularly lower than the soil quality standard allowance for habitat and agriculture for cadmium not exceeding 37.0 mg kg^{-1} soil. Furthermore biochar from both reactor reduced Cd in soybean seed which PBLBO helped to reduce Cd in soybean seed to $0.182 \text{ mg Cd kg}^{-1}$ soybean at Cd contamination of 20.0 mg kg^{-1} soil, while PBLBL presented better results than PBLBO. This system reduced Cd in soybean seed to $0.187 \text{ mg Cd kg}^{-1}$ soybean seed at Cd contamination of $60.0 \text{ mg Cd kg}^{-1}$ soil. This met the CCFAC standard that permits Cd in soybean seed not exceeding $0.200 \text{ mg Cd kg}^{-1}$ soybean seed. Results clearly showed that both biochars incinerate in different kilns was similarly in efficiency improving the soil properties and reduce bioavailability and phytotoxicity of cadmium-contaminated soil.

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Lt. Col. Chintana Sanvong

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TABLE OF CONTENTS

| | Page |
|--|-------------|
| ABSTRACT | iii |
| ACKNOWLEDGEMENT | v |
| TABLE OF CONTENTS | vi |
| LIST OF TABLES | viii |
| LIST OF FIGURES | x |
| LIST OF ABBREVIATIONS | xii |
| | |
| CHAPTER 1 INTRODUCTION | 1 |
| 1.1 Background and State of Problem | 1 |
| 1.2 Conceptual Framework of the Study | 7 |
| 1.3 Objectives of the Study | 8 |
| 1.4 Hypothesis of the Study | 8 |
| 1.5 Vocabulary Definition of the Study | 8 |
| 1.6 Scope of the Study | 10 |
| 1.7 Significances and Expected Result of the Study | 11 |
| CHAPTER 2 LITERATURE REVIEW | 12 |
| 2.1 Cadmium: Cd | 12 |
| 2.2 Biochar | 28 |
| 2.3 Pyrolysis | 41 |
| 2.4 Biochar and Poultry Production | 53 |
| 2.5 Relative Literature | 56 |
| CHAPTER 3 MATHERIALS AND METHODS | 64 |
| 3.1 Materials | 64 |
| 3.2 Methods | 65 |
| CHAPTER 4 RESULTS AND DISCUSSION | 69 |
| 4.1 Soil Property before Experiment | 69 |

| | |
|--|-----|
| 4.2 Broiler Litter Property before Pyrolysis | 70 |
| 4.3 Broiler Litter Biochar Property | 71 |
| 4.4 Performance of Broiler Litter Biochar on Soil Properties and Soybean Planting on Soil Polluted with Cadmium | 72 |
| CHAPTER 5 CONCLUSION AND RECOMMENDATIONS | 211 |
| 5.1 Conclusion | 211 |
| 5.2 Recommendations | 214 |
| BIBLIOGRAPHY | 218 |
| BIOGRAPHY | 254 |

LIST OF TABLES

| Tables | Page |
|--|------|
| 2.1 Natural Cadmium Levels in the Environment | 13 |
| 2.2 Two Examples of Estimated Global Emission of Cadmium to the Atmosphere from Natural Sources | 15 |
| 2.3 Daily Intake of Cadmium via Food: Country Examples | 22 |
| 2.4 Codex Alimentarius Maximum Levels for Cadmium | 27 |
| 2.5 Relative Proportion Range of the Four Main Components of Biochar (Weight Percentage) as Commonly Found for a Variety of Source Materials and Pyrolysis Conditions | 31 |
| 2.6 Summary of Total Elemental Composition (C, N, C:N, P, K, Available P and Mineral N) and pH Ranges and Means of Biochars from a Variety of Feed Stocks (Wood, Green Wastes, Crop Residues, Sewage Sludge, Litter, Nut Shells) and Pyrolysis Condition (300-500°C) Used in Various Studies | 31 |
| 2.7 The Pyrolysis Technology Parameters Employed and the Corresponding Product Distribution | 42 |
| 2.8 Scope of Pyrolysis Process Control and Yield Ranges | 43 |
| 2.9 Summary of Pyrolysis Data for Selected Feed Stocks | 46 |
| 2.10 The Comparison of Qualification between General Block and High Efficiency Kiln | 49 |
| 2.11 The Equipment of High Efficiency Kilns | 50 |
| 4.1 Soil Properties before Experiment | 69 |
| 4.2 Pelleted Broiler Litter Properties | 70 |
| 4.3 Broiler Litter Biochar Properties | 71 |
| 4.4 Surface Areas of Biochar | 72 |
| 4.5 Effect of Factor A (Reactor) on Soil Properties, Soybean Growth Stage, and Productive Performance | 82 |

| | | |
|------|--|-----|
| 4.6 | Effect of Factor B (Cd Level) on Soil Properties, Soybean Growth Stage, and Productive Performance | 94 |
| 4.7 | Effect of Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productive Performance | 108 |
| 4.8 | Interaction between Factor A (Reactor) and Factor B (Cd Level) on Soil Properties, Soybean Growth Stage, and Productive Performance | 123 |
| 4.9 | Interaction between Factor A (Reactor) and Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productive Performance | 139 |
| 4.10 | Interaction between Factor B (Cd Level) and Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productive Performance | 150 |
| 4.11 | Interaction Effect between Factor A (Reactor) and Factor B (Cd Level) and Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productive Performance | 191 |

LIST OF FIGURES

| Figures | Page |
|---|------|
| 2.1 Trends in Cadmium Consumption Patterns, 2005 – 2010 A. D. | 16 |
| 2.2 Putative Structure of Charcoal | 30 |
| 2.3 Concept Diagram of Low – Temperature Pyrolysis Biomass | 41 |
| 2.4 Temperature Zones of Pyrolysis | 44 |
| 2.5 30 m ³ Earth Pit – Longitudinal Section | 48 |
| 2.6 JAMICAN 2 – Drum Retort with Tar Condenser | 49 |
| 4.1 Moisture Content | 160 |
| 4.2 pH | 161 |
| 4.3 Electrical Conductivity | 162 |
| 4.4 Organic Matter | 163 |
| 4.5 Nitrogen | 164 |
| 4.6 Phosphorus | 165 |
| 4.7 Potassium | 165 |
| 4.8 Calcium | 166 |
| 4.9 Magnesium | 168 |
| 4.10 C/N Ratio | 169 |
| 4.11 Cation Exchange Capacity | 171 |
| 4.12 % Cd Residual in Soil | 173 |
| 4.13 Planting Date to Stage of Emergence | 174 |
| 4.14 Planting Date to Stage of V4 | 174 |
| 4.15 Planting Date to Stage of Beginning Bloom | 175 |
| 4.16 Planting Date to Stage of Maturity | 177 |
| 4.17 Stem Weight | 178 |
| 4.18 Pod Weight | 179 |
| 4.19 Height | 180 |
| 4.20 100 Seed Dry Weight | 181 |

| | |
|-------------------------------------|-----|
| 4.21 Product per Pot | 182 |
| 4.22 Protein in Soybean Seeds | 184 |
| 4.23 Lipid in Soybean Seeds | 185 |
| 4.24 Leaf Area R1– R7 | 186 |
| 4.25 % Cd Residual in Soybean Root | 187 |
| 4.26 % Cd Residual in Soybean Shoot | 187 |
| 4.27 % Cd Residual in Soybean Leaf | 188 |
| 4.28 % Cd Residual in Soybean Seeds | 190 |

LIST OF ABBREVIATIONS

| Abbreviation | Description |
|--------------------|--|
| % | Percent |
| µg | microgram |
| °C | Degrees Celsius |
| Al | Aluminum |
| ANOVA | Analysis of Variance |
| ATR-FTIR | Attenuated Total Reflection Fourier Transform Infrared |
| Ca | Calcium |
| Cd | Cadmium |
| CdCl ₂ | Cadmium chloride |
| CEC | Cation Exchange Capacity |
| Cl | Chloride |
| Cm | Centimeter |
| Cr | Chromium |
| Cu | Copper |
| dS m ⁻¹ | Deci Siemens per Meter |
| EC | electrical conductivity |
| EPA | Environmental Protection Agency |
| FAO | Food and Agriculture Organization |
| Fe | Iron |
| g | Gram |
| g kg ⁻¹ | Gram per Kilogram |
| ha | Hectare |
| Hg | Mercury |
| HTT | High Treatment Temperature |
| K | Potassium |
| kg | Kilogram |
| m | Meter |

| Abbreviation | Description |
|-----------------------------|--------------------------------------|
| m ² | Square meter |
| m ³ | Cubic Meter |
| Mg | Magnesium |
| mg kg ⁻¹ | Milligram per Kilogram |
| mg Cd kg ⁻¹ soil | Milligram Cadmium per Kilogram Soil |
| N | Nitrogen |
| nd | Not Detectable |
| Ni | Nickel |
| OM | Organic Matter |
| P | Phosphorus |
| PAHs | Polycyclic Aromatic Hydrocarbons |
| Pb | Lead |
| t ha ⁻¹ | Ton per Hectare |
| UNEP | United Nations Environment Programme |
| WHO | World Health Organization |
| Zn | Zinc |

CHAPTER 1

INTRODUCTION

1.1 Background and State of Problem

The contamination of heavy metal residues such as cadmium (Cd) is prominent in our environment (Nriagu, 1979: 409; WHO, 1992). Since Cd has been identified as a major toxic heavy metal contaminating our food supply (Huang, Bazzaz and Vanderhoef, 1974: 122; Witaya Swaddiwudhipong, Limpatanachote, Mahasakpan, Krintratun and Padungtod, 2010: 1217), it has potential health risks directly and indirectly through the uptake of food or via other pathways. The diseases associated with Cd exposure are pulmonary emphysema and the notorious Itai-itai disease which results in painful bone demineralization (osteoporosis), because Cd replaces calcium in the bone. The primary sources of Cd contamination are from industrial activities, especially mining of minerals, metals, and coal in Cd contaminated sites (Narisa Israngkura, 2008: 9; Unhalekhana and Kositanont, 2008: 171), resulting in the drastic increase of Cd contamination in soil through weathering processes. Once the Cd contaminated water seeps through the soil beneath the surface, it can persist in the soil between soil pore; this is possible because Cd is known to be more mobile and soluble than other metals present in the soil. Unlike other metals, Cd does not undergo microbial or chemical degradation, and therefore, persists in soils for longer periods of time after its introduction (Lina Liu, Hansong Chen, Peng Cai, Wei Liang and Qiaoyun Huang 2009: 563).

An example area where Cd residue was found is the Huay Maetao watershed, Mae Sot district, Tak province, Thailand. This is where the rice-based agricultural systems are established in the vicinity of a zinc mine. The prolonged consumption of Cd contaminated rice have potential risks to the public's health and the health impacts of Cd exposed populations in Mae Sot have been demonstrated (Simmons, Pongsakul,

Saiyasitpanich and Klinphoklap, 2005: 501; Swaddiwudhipong et al., 2007: 143; Teeyakasem et al., 2007: 185; Phaenark, Pokethitiyook, Kruatrachue and Ngeransaruay, 2009: 479). Public concerns have been raised over the exposure of inhabitants to high-dosage of Cd through their long-term daily consumption of the rice. By intaking contaminated food, Cd accumulates primarily in the kidney, liver and reproductive organs of both humans and animals (Kirkham, 2006: 19) elevated levels of Cd in humans can cause kidney damage and low levels of Cd in the diet are linked to renal dysfunction. (Simmons et al., 2005: 502; Teeyakasem et al., 2005: 187; Swaddiwudhipong et al., 2007: 145).

Padungtod, Swaddiwudhipong, Nishijo, Ruangyuttikarn And Werawan (2006: 3) showed that Cd levels in 154 soil samples in Mae Sot area ranged from 3.40 – 284 mg Cd kg⁻¹ soil which was 1.13 – 94.0 times higher than the European Economic Community (EEC) maximum permissible criteria of soil cadmium concentration of 3.00 mg Cd kg⁻¹ soil and 1,800 times much higher than the Thai standard of 0.150 mg Cd kg⁻¹ soil. Moreover, rice samples from 90 fields were found to be contaminated with Cd ranging from 0.100 to 4.40 mg kg⁻¹ rice, while the mean Cd concentrations of Thai rice as reported by Pongsakul and Attajarusit (1999: 71) was 0.0430 ± 0.0190 mg kg⁻¹ rice. Based on Thai people's daily rice consumption, this amount of rice Cd contamination can provide an estimation of Cd exposure level for local residents and their exposure level would be 14.0 – 30.0 times higher than the Joint FAO/WHO Expert Committee on Food Additives (JECFA) Provisional Tolerable Weekly Intake (PTWI) standard of 7.00 µg Cd kg⁻¹ body weight (BW) per week, which is related to Teeyakasem et al. (2007: 185).

The study investigated by Teeyakasem et al. (2007: 185) was to find the biological marker for the early detection of renal dysfunction induced by high Cd exposure of the samples from 224 inhabitants (male =104 and female = 114) living in the polluted area. The results showed that Cd concentrations in all subjects were classified into 3 levels; below 5.00 (n=54), 5.00 – 10.0 (n=77), and above 10.0 (n=84) µg g⁻¹ creatinine (Cr), with mean ± S.D. of 3.95 ± 0.96, 7.14 ± 1.37 and 17.81 ± 7.19 µg g⁻¹Cr, respectively. The three average urinary Cd levels exceeded WHO maximum tolerable internal dose for the non-exposed population of 2.00 µg g⁻¹Cr. The evaluation was carried out until the year 2007, where it has been found that Cd levels

excreted by the same sample above ranged between 1.00 and 58.0 $\mu\text{g/g}$ Cr with geometric mean of 8.20 $\mu\text{g g}^{-1}$ Cr, which was 16-fold greater than the average general Thai population of 0.500 $\mu\text{g g}^{-1}$ Cr.

Various in-situ and ex-situ techniques have been employed to remediate the impact of metals in the soil environment including excavation, solidification, stabilization, soil washing, electroremediation, and phytoremediation (Mulligan, Yong and Gibbs, 2001: 193; Tandy, Healey, Nason, Williamson and Jones, 2009: 690). However, excavation and disposal is an expensive procedure due to recent increase in landfill costs and the need to import new soil to replace the removed top soil, this type of method is used for former mining sites where the volumes of contaminated soil are vast. (van Herwijnen, Laverie, Poole, Hodson and Huchings, 2007a: 2422). Other remediation techniques are either expensive or unsuitable for the remediation of large volumes of contaminated soil. Chemical immobilization is an alternative of in-situ remediation method where inexpensive materials such as fertilizer and waste products are added to contaminated soils to reduce the solubility and bioavailability of heavy metals (Liu et al, 2009: 563). Nevertheless, Laird (2010: 443) suggested that the prolonged usage of cultivation could hasten soil acidification and could cause adverse effects in the quality of surface and ground water.

In recent years, biochar have drawn significant attention as a large-scale soil remediation. Biochar acts as a soil conditioner and fertilizer by increasing cation exchange capacity (CEC), pH, and water retention (Lehmann, da silva, Steiner, Nehls, Zech and Glaser, 2003: 343; Uchimiya, Lima, Klasson and Wartelle, 2010a: 935). Biochar is the most common name, however, they are also known as charcoal, chars, black carbon, and agrichar (Verheijen, Jeffery, Bastos, van der Velde and Diafas, 2010: 31). The general application for biochar is to use it as fertilizers; the uptake of biochar as soil conditioner with the combination of regular synthetic fertilizers through plants' root increases the efficiency of the application. Furthermore, biochar plays an important role in retention of nutrients and therefore reduce nutrient leaching, by releasing nutrients at low rates. The content of biochar comprises primarily of organic carbon (up to 90.0 %) and is resistant to chemical/biological degradation, meaning that it can persist in the soil for thousands of years (Lehmann et al., 2008: 832; Yin chan and Xu, 2009).

Biochar can also provide many benefits in the form of broiler litter derived biochar (BLB). Most importantly, BLB can serve as an effective means in dealing with litter management; this is done by using waste and litter from livestock production processes, thus reducing environmental impact. Because broiler production is a prominent livestock industry in Thailand, tremendous amount of waste and litter are produced throughout the process which includes a mixture of manure, bedding material, waste feed, and feathers removed from broiler houses that pose significant effects on the quality of the environment (McCasky et al., 1989: 14-27; Tawadchai Suppadit, 2000: 51-54). If improperly managed, broiler litter can pollute the environment contaminating surface and ground waters. Moreover, the heat produced from biochar production can offset the use of conventional fossil fuels in industrial boilers. (Tawadchai Suppadit, 2003; Laird et al., 2009: 550). In addition to offsetting capabilities, Chan et al. (2008: 437-444) have found that biochar created from poultry litter tends to have more beneficial effects on soil quality and crop production than biochar produced from herbaceous, biomass material. In recent years, studies have shown that biochar is a carbonaceous material that serves as a powerful sorbent to retain organic pollutants, thus plays a crucial role in governing the fate and risk of pollutant (Cornelissen and Gustafsson, 2005: 764-769; Chen et al., 2008: 437-444) and extensive studies have been conducted to determine the sorption mechanisms of organic contaminants on chars (Uchimiya et al., 2010: 935; Tawadchai Suppadit et al., 2012: 244).

Chars sorb organic contaminants such as atrazine via two distinct mechanisms: one, surface adsorption on carbonized fractions and two, partitioning into residual (non-carbonized) organic fraction (Cao et al., 2009: 5222). There are several studies indicating that biochar can reduce the bioavailability of polycyclic aromatic hydrocarbons (PAHs) in soil and sediments (Cornelissen and Gustafsson, 2005: 764; Beesley et al., 2010: 2282). Uchimiya et al. (2010: 935) employed broiler litter manure that underwent various degrees of carbonization for heavy metal Cd^{II} , Cu^{II} , Ni^{II} , and Pb^{II} immobilization in soil and water, results suggested that with higher carbonized fractions and loading of chars, heavy metal immobilization by cation exchange becomes increasingly outweighed by other controlling factors, such as the coordination by π electrons ($\text{C}=\text{C}$) of carbon and precipitation. This coincides with Guo,

Qiu and Song, 2010: 308, which revealed that poultry litter-based activated carbon could remove Cd^{2+} contaminated water.

Considering the mentioned benefits of BLB, we expect to use BLB in the remediation of Cd contaminated soil, which have caused adverse effects on the health of people. In this study, we intend to find an appropriate mean through technology that is small in socio-economic scale, so that local people can improve and improvise the solution to the problems in the near future.

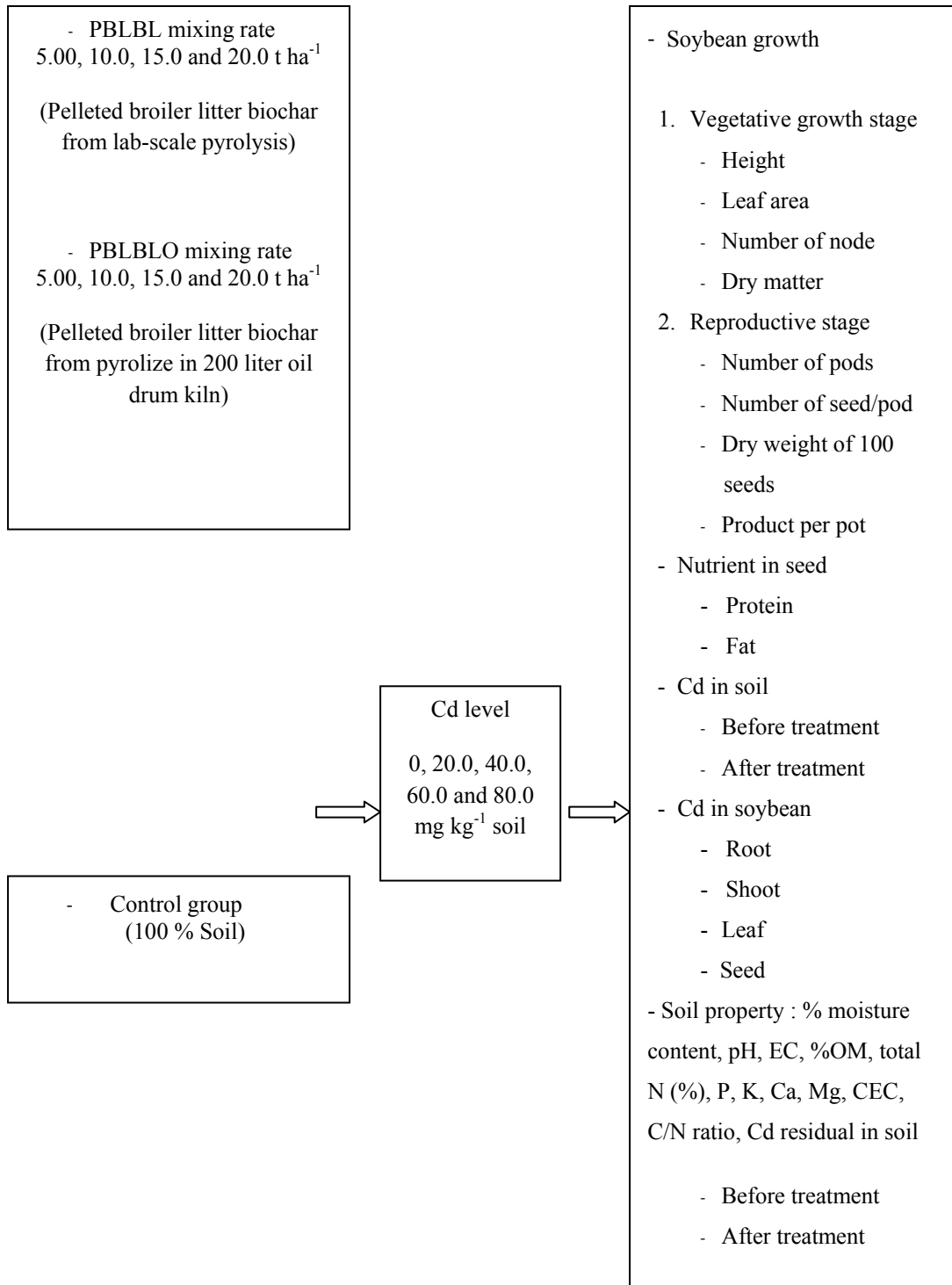
Charcoal making has a long tradition throughout Thailand, which is mostly produced using the earth-mound kiln, an ancient technology dating from the middle ages (Adam, 2009: 1923). During the four-to-seven days of charcoal production using the earth mound kiln, the efficiency is reduced due to heat loss through radiation causing unpredictable fire (Van der Plas, 1995; Adam, 2009: 1924). As the charcoal production becomes environmentally unsustainable, the kilns should be improved to create a more effective carbonization process in an environmental friendly way. Oil tank of 200 litter in size used as a burning tank is considered to be the high efficiency kiln (Appropriate Technology Association, 2003b). It is the most useful type of kiln that could support rural sectors giving its characteristics and suitability (Prawonwan Saipan, 2007). As we know, the quality of biochar depend on varieties of factors, including the source of the materials and the pyrolysis methodology used (Anal and Gronli, 2003: 1619); differences in processing conditions explain differences in the properties of the product (Lima and Marshall, 2005: 699; Chan et al., 2007a: 629).

In most of the literatures, biochar is derived from lab-scale pyrolysis reactor to serve as heavy metal adsorption and the results are as mentioned above. Therefore, this study will compare the potential of Pelleted Broiler Litter-derived Biochar (PBLB) from the two methods; first, PBLB from lab-scale pyrolysis reactor (PBLBL) and second PBLB derived from pyrolyzed PBLB in a 200 liter oil drum kilns (PBLBO). The absorption of Cd added to soil was determined by using soybean (*Glycine max* (L.) Merr.) as indicators. I will examine the correlation between the availability and toxicity of the metals in the soil with plant growth in terms of level of growth, yield, yield component, seed quality, and including nutrient and Cd content of soybean by using PBLBL and PBLBO as Cd-amended soil. The major objective of the research is to compare Cd sorption efficiency of PBLBL and PBLBO in Cd

contaminated soil with assumption that PBLBL and PBLBO can reduce Cd level in soil and have no difference in efficiency.

If the experiment goes according to plan, I will encourage the application which is cost-effective and can be easily re-produced to local people for the remediation of Cd polluted sites.

1.2 Conceptual Framework of the Study



1.3 Objectives of the Study

1.3.1 To determine the potential effect of PBLBL and PBLBO on vegetative and reproductive growth stages of soybean in Cd-amended soils.

1.3.2 To compare the Cd sorption efficiency of PBLBL and PBLBO in Cd contaminated soil.

1.3.3 To evaluate the enhancement of plant growth promotion and Cd uptake in soybean grown in Cd-amended soil with PBLBL and PBLBO.

1.4 Hypothesis of the Study

1.4.1 Cd polluted soil at any level could be reduced by modifying broiler litter as a source of amendment.

1.4.2 PBLBL and PBLBO have not differently in Cd sorption capacity.

1.4.3 Soybean have normal growth rate and have a safety level of Cd in seed production.

1.5 Vocabulary Definition of the Study

1.5.1 Pyrolysis

The process of controlled chemical decomposition of feedstock biomass by heating under limited or no oxygen supply. The process becomes exothermic above a threshold temperature, which is dependent on the source type. Pyrolysis converts feedstocks biomass into energy rich gas and liquid products (syn-gas and bio-oil) and leaves a solid residue rich in carbon content, about 75.0 – 90.0 % carbon on an ash-free basis, which is called biochar (Gryze, Cullen, Durschinger, 2010: 18).

1.5.2 Biochar

Biochar is a fine-grained and porous substance. Its appearance is similar to charcoal and is produced by natural burning. Biochar is produced by the combustion of biomass under oxygen-limited conditions. (Sohi, Lopez-Carpel, Krull and Bol, 2009: 3).

1.5.3 Pelleted Broiler Litter Biochar (PBLB)

A source for biochar production from broiler litter that is already mixed, such as a mixture of spilled feed, feathers, bedding material and excreta, and contains nitrogenous compounds, fiber and minerals, and pressed into pellet form by a die different in sizes, shapes, and thickness depending on the pressure of the pressing screw. The pellets are hard and cylinder (Tawadchai Suppadit, 2000: 136).

1.5.4 Pelleted Broiler Litter Biochar (PBLB) Derived from Lab-Scale Pyrolysis Reactor (PBLBL)

A PBLB that was pyrolyzed in a cubical pyrolysis reactor. The reactor was heated until the PBLB temperature reached 500°C using a lab-pyrolysis reactor with a long residence time (roughly 24 hours). After the PBLBL cooled to room temperature for four-five hours, the reactor was opened and char was collected.

1.5.5 Pelleted Broiler Litter Biochar (PBLB) Derived from 200 Liter Oil Drum Kiln (PBLBO)

A PBLB that was pyrolyzed in a 200 liter oil drum kilns, operated with direct heating for 8 hours in a closed kiln without air. Initial start-up firing was done by firing outside the kiln using hand blower to heat up PBLB until pyrolysis temperature 500°C was reached, then the kiln is closed. The process continued until all stages such as drying, volatile release, carbonization or carbon enrichment has been carried out and cooled for 8-9 hours.

1.5.6 Sorption Potential

The process act like a sponge or filter, soaking up contaminants until they run out of surface area, includes the processes of absorption and adsorption

1.5.7 Soybean Indicator

Identify the growth stage in which potential yield is affected. The system of soybean growth stages is divided into vegetative (V) and reproductive (R) stages. The vegetative stages are numbered according to how many fully-developed trifoliate

leaves are present. The reproductive (R) stages begin at flowering and include pod development, seed development, and plant maturation (Pedersen, 2003).

1.6 Scope of the Study

1.6.1 Broiler Litter

The broiler litter was brought from farms located in Saraburi province that had been produced litters in the same periods of time and has similar surface area ratio and the bedding materials used in broiler house were also used for a source of biochar feedstock. The broiler litter from these sources would be able to represent broiler litter from any provinces in Thailand, since it is very similar in its structure.

1.6.2 Pyrolysis Kilns

- 1) Lab-scale pyrolysis reactor.
- 2) The 200 liter single oil drum kiln as a burning tank.

1.6.3 Pyrolysis Process Types

In this study we use slow pyrolysis as production technology. Slow pyrolysis is the most efficient method to turn biomass into biochar and that is considered to be the most promising technology to generate biochar. Slow pyrolysis needs low to medium temperatures that ranges from 350 to 700°C with a very long residence time (~24 hours) and generates three yields: biochar of 30.0 – 50.0 % from the actual weight of biomass, water, and syngas. The resulting syngas and biochar properties are greatly determined by temperature, source, and residence time.

1.6.4 Soil

A sample (0 to 20.0 cm. layer) of soil were collected randomly from within the Tumbon Promanee, Mueng district, Nakornayok province, Thailand.

1.6.5 Cadmium Preparation

$\text{CdCl}_2 \cdot 2.5\text{-H}_2\text{O}$ was used without further purification.

1.6.6 Soybean (*Glycine max* (L.) Merr.)

Soybean cultivated in Chiang Mai 60 (CM.60) was used for the evaluation.

1.6.7 Experimental Location

Trials were conducted at Mueng District, in Nakhonayok Province from March 2011 to September 2012. The trials were in an artificial greenhouse measuring 6.00 m (in width) x 8.00 m (in length) x 2.00 m (in height) (96.0 m³) with a plastic roof. Corrugate iron and blue net were used as a border around the greenhouse.

1.6.8 Soybean Growth Measurement

Data recorded were planting dates, stage of emergence, number of nodes, height, leaf area, dry matter, number of pods/plant, number of seeds/pod, 100 seeds dry weight, and yield/basin (Tawadchai Suppadit, 2005: 22).

1.7 Significances and Expected Results of the Study

The significances and expected results of the study are as follows:

1.7.1 Soybean have normal growth rate in Cd contaminated soil amended with PBLBL and PBLBO and does not have any Cd residue in soybean.

1.7.2 PBLBL and PBLBO can adsorb Cd contaminated soil at the maximum level of of 80.0 mg Cd/kg soil.

1.7.3 There are no differences in sorption potentials between PBLBL and PBLBO in amended Cd contaminated soil.

CHAPTER 2

LITERATURE REVIEW

2.1 Cadmium: Cd

Cadmium is a non-essential and toxic element for humans mainly affecting kidneys and the skeleton. It is also a carcinogen by inhalation. Cd is accumulated in bone and may serve as a source of exposure later in life (Nriagu, 1980: 71; UNEP, 2008: 34). In environment, Cd is toxic to plants, animals and micro-organisms. Being an element, Cd is persistent, it cannot be broken down into less toxic substances in the environment (UNEP, 2008: 3). The degree of bioavailability and potential for effects varies depending on the form of Cd. Cd bio-accumulates mainly in the kidneys and liver of vertebrates and in aquatic invertebrates and algae (UNEP, 2008: 31).

Cd is released by various natural and anthropogenic sources to the atmosphere, aquatic environments and terrestrial environments. There are fluxes between these compartments (UNEP, 2008: 3). Cd released to the atmosphere can deposit to land and aquatic environments, and some Cd released to soil over time will be washed out to the aquatic environments (UNEP, 2008: 3). The long-term sinks are deep-sea sediments and, to a certain extent, controlled landfills, in cases where, owing to its physicochemical properties, Cd is immobilized and remains undisturbed by anthropogenic or natural activity (UNEP, 2008: 3).

2.1.1 General Characteristics

Cd is a metallic element belonging to group II B of the Periodic Table (atomic number: 48, and relative atomic mass 113.4 g mol^{-1}). Cd in its elemental form is a soft, silver-white metal. It is not usually present in the environment as a pure metal. Cd is most often present in nature as complex oxides, sulphides, and carbonates in

zinc, lead, and copper ores. It is rarely present in large quantities as chloride and sulphates (ATSDR, 1999 quoted in UNEP, 2008: 34).

Cd occurs naturally in the environment from the gradual process of erosion and abrasion of rocks and soils, and from singular events such as forest fires and volcanic eruptions (Rao, Mohapatra, Anand and Venkateswarlu, 2010: 81). It is therefore naturally present everywhere in air, water, soils, and foodstuffs (Table 2.1).

Table 2.1 Natural Cadmium Levels in the Environment

| Natural Cadmium Levels in the Environment | |
|--|--|
| Atmosphere | 0.100 to 5.00 ng m ⁻³ (nanograms per cubic meter) |
| Earth's crust | 0.100 to 0.500 µg g ⁻¹ (micrograms per gram) |
| Marine sediment | ~ 1.00 µg g ⁻¹ (micrograms per gram) |
| Sea-water | ~ 0.100 µg l ⁻¹ (micrograms per liter) |

Higher concentrations – with commercial interest are found in association with zinc, lead and copper ores where Cd is invariably recovered as a by-product, mainly from zinc-containing ores. Cd is not recovered as a principal product of any mine (OSPAR, 2002 quoted in UNEP, 2008: 34) but exclusively as a by-product of other non-ferrous metal extraction. Some rare Cd minerals are, however, known, such as Greenockkite (CdS) and Hawlegite, Cadmoisite (CdSe), Monteponite (CdO) and Otavite (CdCO₃) (OSPAR, 2002 quoted in UNEP, 2008: 34). Sedimentary rocks and marine phosphates contain about 15.0 mg Cd kg⁻¹ (EC, 2001 quoted in UNEP, 2008: 34). Based on data from (ECB, 2005 quoted in UNEP, 2008: 34) the Cd concentrations in fertilizers used in Austria, Belgium, Denmark, Finland, Germany, Norway, Sweden and UK in the period 1984 – 1995 A.D. ranged between 2.50 – 80.0 mg Cd kg⁻¹ P. The current average Cd content in phosphate fertilizers used in European countries is suggested to be 35.0 mg Cd kg⁻¹ P₂O₅ or 79.0 mg Cd kg⁻¹ P (ECB, 2005 quoted in UNEP, 2008: 34).

ATSDR (1999 quoted in UNEP, 2008: 34) has been noted that amount of the Cd compound identified analytically is not necessarily equivalent to the amount that is bio-available. Cd can form a number of salts, and both its mobility in the environment

and the effects on the ecosystem depend to a great extent on the nature of these salts in combination with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulphur (cadmium sulphide) (OSPAR, 2002 quoted in UNEP, 2008: 34). Metallic cadmium and CdO powder are less harmful in the environment than soluble Cd^{2+} (ECB, 2008: 8). However, metallic cadmium and CdO powder transform in the environment to the bioavailable Cd^{2+} (ECB, 2008: 8).

2.1.2 Sources and Releases to the Environment

Cadmium can be released to environment in a number of way, including from natural sources occurring Cd from the earth's crust and mantle, such as volcanic activity and weathering of rock (UNEP, 2008: 4) and anthropogenic (associated with human activity) releases from the mobilization of Cd impurities in raw materials such as phosphate minerals, fossil fuels and other extracted, treated and recycled metals – particularly zinc and copper; current anthropogenic releases of Cd used in products and processes, as a result of use, disposal, recycling, reclamation, open burning or incineration; releases from municipal installations; and the mobilization of historical anthropogenic and natural Cd releases previously deposited in soils, sediments, landfills and waste or tailing piles (ECB, 2008: 11; UNEP, 2008: 4).

2.1.2.1 Natural Sources

Natural sources of Cd to the biosphere include volcanic activity, and the weathering of rocks and minerals. In addition, insignificant amounts of Cd enter the biosphere through meteoritic dust (UNEP, 2010: 68).

Nriagu (1989: 47) estimates Cd from the atmospheric emission from natural sources in 1983 A.D. at 140-1,500 tonnes years⁻¹ while Richardson et al. (2001 quoted in UNEP, 2010: 68) estimated at 150,000 - 88,000 tonnes year.

As Cd is an elements that is naturally present in many minerals, Cd will be present in rocks and soils in low concentrations. Rudnick and Guo (2004: 5) found Cd concentration in the continental crust ranges from 0.00800 to 0.100 mg kg⁻¹ Cd while Cd concentration in common rock types and soils ranges from 0.00100 - 0.600 mg kg⁻¹ for igneous rocks to 0.0500 - 500 mg kg⁻¹ for sedimentary rocks (Adriano, 2001: 175).

Through the weathering of rocks, Cd is released to soils and aquatic systems and made available to the biota. This process plays a significant role in the global Cd cycle, and may locally results in elevated Cd concentrations in soils (UNEP, 2010: 68).

Within the biosphere, Cd is translocated by different processes, e.g. by wind transport of salt spray and soil particles (UNEP, 2010: 69). The major sources for emission to air by natural processes are: volcanoes, airborne soil particles, sea spray, biogenic material and forest fires (UNEP, 2010: 69).

Nriagu (1989: 48) estimates the total emission in 1983 at 150 – 2,600 tonnes year⁻¹. Richardson et al. (2001 quoted in UNEP, 2010: 69.) reported total emissions from natural sources are estimated at 15,000 – 88,000 tonnes year⁻¹. The large difference is mainly due to very different estimates of the significance of the releases of soil particles to the atmosphere and Cd releases from natural fires. The estimates of atmospheric releases due to soil particle flux in Richardson et al. (2001 quoted in UNEP, 2010: 69) are based on data on soil metal flux in scrubland of south-central U.S.A.

Table 2.2 Two Examples of Estimated Global Emission of Cadmium to the Atmosphere from Natural Sources

| Source Category | Cadmium emission in tones year ⁻¹ | | | |
|--|--|-------------------------------|---------------|--------------------|
| | Richardson et al. (2001) | | Niragu (1989) | |
| | Mean | 5-95 th percentile | Mean | Range |
| Release of soil particle during dust storms etc. | 24,000 | 3,000 – 69,000 | 210 | 10.0 – 400 |
| Sea salt spray | 2,000 | 103 – 6,700 | 60.0 | 0 – 110 |
| Volcanic emissions | 1,600 | 380 – 3,800 | 820 | 140 - 1,500 |
| Natural fires | 13,000 | 4,400 – 30,000 | 110 | 0 – 220 |
| Vegetation, pollen and spores | - | - | 190 | 0 – 1,530 |
| Meteoritic dust | 0.000200 | 0.0000400 – 0.000400 | 50.0 | 0 – 100 |
| Total | 41,000 | 15,000 – 88,000 | 1,300 | 150 – 2,600 |

Source: UNEP, 2010: 69.

2.1.2.2 Anthropogenic Sources

Cadmium metal is produced as a by-product from the extraction, smelting and refining of the nonferrous metals zinc, lead and copper. Rather than disposing of it as a waste, engineers have been able to utilize its unique properties for many important industrial application (UNEP, 2008: 5).

Cadmium metal exhibits excellent resistance to corrosion, particularly in alkaline and seawater environments, possesses a low melting temperature and rapid electrical exchange activity, and has both high electrical and thermal conductivity (ICdA, n.d.) Cadmium compounds possess outstanding resistance to high stresses and high temperatures, and deter ultraviolet light degradation of certain plastics. Some cadmium electronic compounds exhibit semi-conducting properties and are utilized in solar cells and many electronic applications (ICdA, n.d.). Cadmium pigments produce intense yellow, orange and red colours, and are widely used in plastic, glasses, ceramics, enamels and artist's colours (ICdA, n.d.). Because of this wide variety of unique properties, cadmium metal and cadmium compounds are used as pigments, stabilizers, coating, specially alloys, electronic compounds, but most of all (more than 80.0 % of its use), in rechargeable nickel-cadmium batteries (ICdA, n.d.). Trends in Western World cadmium consumption patterns from 2005 to 2010 are shown in Figure 2.1

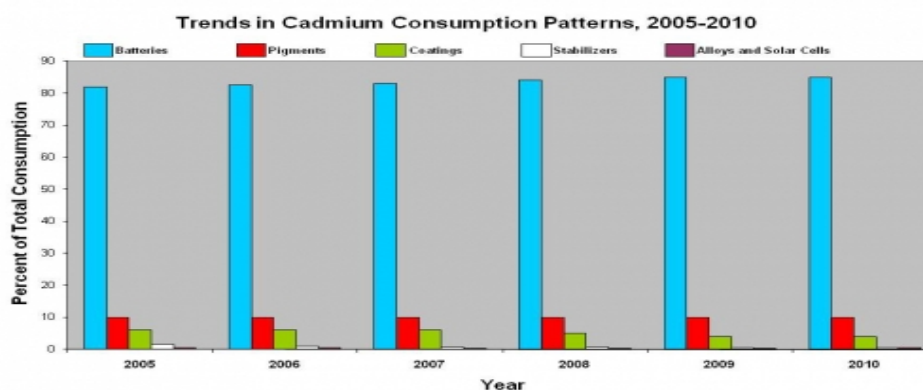


Figure 2.1 Trends in Cadmium Consumption Patterns, 2005-2010 A.D.

Source: ICdA, n.d..

As awareness of the adverse impacts of Cd has increased, many uses have been reduced significantly in industrialized countries. However, some of uses of Cd which have been phased out in industrialized countries have continued in developing countries (UNEP, 2010: 5). In addition, use of Cd has continued or increased in some less developed regions or countries, e.g., in plastic or in paints. Another issue faced by developing countries is the export of new and used products containing Cd, including electronic equipment and batteries, and products containing Cd that may cause exposure through normal use, such as certain toys (UNEP, 2008: 6).

2.1.2.3 Cadmium in Environment

1) Cadmium in the Atmosphere

Most of the Cd in the air is bound to small-size particulate matter (below 1.00 μm) (EC, 2001 quoted in UNEP, 2008: 34). Cd is emitted to the atmosphere from anthropogenic sources as elemental Cd and/or Cd oxide and – from some sources – as sulphide or chloride (EC, 2001 quoted in UNEP, 2008: 34). From atmospheric combustion sources, Cd may be emitted partly as elemental gaseous Cd, but as it is cooled, this Cd is also quickly bound to particulate matter.

In the atmosphere, the particulate matter increases in particle size due to interaction between particles of different sizes, and due to condensation of water vapour and other gases. Cd and many of its compounds have relatively low vapour pressure, and thus are not particularly volatile. However, high heat processes can volatilize Cd and be emitted as a vapour. ASTDR (1999 quoted in UNEP, 2008: 35) and EC (2001 quoted in UNEP, 2008: 35) have note that most of Cd in the atmosphere is in the form of particulate matter emitted from anthropogenic sources as elemental Cd as cadmium sulphide and cadmium oxide be a predominantly species in ambient air which is produced by combustion process.

2) Cadmium in Aquatic Environments

Cadmium sulphate and cadmium chloride are quite soluble in water, whereas elemental cadmium, cadmium oxide and cadmium sulphide are almost insoluble (EC, 2001 quoted in UNEP, 2008: 35). ATSDR (1999 quoted in UNEP, 2008: 35) reported that Cd complexation with chloride ion increases with salinity until, in normal seawater, Cd exists almost entirely as chloride species (CdCl^+ , CdCl_2 , CdCl_3^-) with a minor portion as Cd^{2+} . The complexation of Cd with chloride in

seawater has been shown to greatly influence its bioavailability and hence toxicity to marine organisms. In aquatic systems, Cd is most readily absorbed by organisms directly from the water in its free ionic form (AMAP, 1998 quoted in UNEP, 2008: 35).

3) Cadmium in Soil

Anong Paijitprapapon; Kittapong Udomtanateera, Orapin Udomtanateera; Vanruedee Chariyapisuthi and Trakool Chengsuksawat (2006: 253) elevated Cd concentrations in paddy soil in the Mae Sot District, Tak Province, Thailand reported in 2003 A.D. the result showed 50.0 % and 20.0 % of soil samples from downstream colluvium and alluvial plains respectively of mining sites were highly contaminated with cadmium exceeding 37.0 mg kg^{-1} , the maximum allowable level for residential and agricultural soils (Notification of National Environment Board NO. 25, 2004: 172). Similarly to the discovered of Chetsada Phaenark; Prayad Pokethitiyook; Maleeya Kruatrachue; Chatchai Ngernsansaruay (2009: 479) found a significant Cd contamination in soil and rice five sampling sites at Padaeng Zinc mine, Tak province, Thailand, found total Cd and Zn concentrations in sediments or soils were approximately 596 and $20,673 \text{ mg kg}^{-1}$ in tailing pond area, 543 and $20,272 \text{ mg kg}^{-1}$ in open pit area, 894 and $31,319 \text{ mg kg}^{-1}$ in stockpile area, 1,458 and $57,012 \text{ mg kg}^{-1}$ in forest area and 64.0 and $2,733 \text{ mg kg}^{-1}$ in Cd contaminated rice field. Among a total of 36 plant species from 16 families, four species (*Chromolaena odoratum*, *Gynura pseudochina*, *Impatiens violaeiflora* and *Justicia procumbens*) could be considered as Cd hyperaccumulators since their shoot Cd concentrations exceeded $100 \text{ mg Cd kg}^{-1}$ dry mass. According to Pensiri Akkajit and Chartra Tongcumpou (2010: 126) found the high concentration of Cd in soil ranged from 0.730 to $172.70 \text{ mg kg}^{-1}$ that higher more than European Union (EU) maximum permissible total soil Cd concentration for sludge-amended soils which is 3.00 mg kg^{-1} , collected soil samples in march, july and October 2007 from within zoning of Cd levels in flood plains area of Mae Tao and Mae Ku subcatchments, Mae Sot district, Tak province, Thailand.

The U.S. EPA (1999 quoted in UNEP, 2008: 35) reports that “under acidic conditions, Cd solubility increases and very little adsorption of Cd by soil colloids, hydrous oxides, and organic matter takes place. At pH values greater than 6 units, Cd is adsorbed by the soil solid phase or is precipitated, and the concentrations of dissolved Cd are greatly reduced”. Cd forms soluble complexes with inorganic and organic ligands, in particular with chloride ions.

Toxicity and bioavailability of Cd are influenced by soil characteristics (ECB, 2005 quoted in UNEP, 2008: 35). Soil characteristics influence Cd sorption and therefore its bioavailability and toxicity (ECB, 2005 quoted in UNEP, 2008: 35). Cd mobility and bioavailability are higher in noncalcareous than in calcareous soils (Thornton, 1992 quoted in UNEP, 2008: 35). Liming of soil raises the pH, increasing Cd adsorption to the soil and reducing bioavailability (Thornton, 1992 quoted in UNEP, 2008: 35; He and Singh 1994 quoted in UNEP, 2008: 35). A general trend emerges that toxicity increases in soil when mobility of Cd is higher, i.e. soil toxicity increases as soil pH, or soil organic matter decrease. Kirkham (2006: 19) found that the pH of the soil is usually the most important factor that controls uptake, with low pH favoring Cd accumulation, and that phosphate and zinc decrease Cd uptake. The work reveals that the availability of Cd is increased by the application of chloride and reduced by application of silicon.

Miller, Hassett and Koeppel (1976: 157) studied about the accumulation of Cd and its effect on vegetative growth of soybeans (*Glycine max* (L.) Merr.var.Amsoy) in soils with a range in cation exchange capacity (CEC), pH, and available phosphorus (P) were investigated in greenhouse experiments. Cadmium uptake decreased as soil pH and CEC increased, while increasing available soil P was related to increased Cd accumulation. Cadmium extracted from the soil by Bray P₁/reagent, Bray P₂/reagent, 2N MgCl₂, and 0.100 N EDTA was significantly correlated with plant Cd concentrations. The growth of the soybean shoots was generally depressed when tissue concentrations reached 3.00 – 5.00 mg Cd g⁻¹ dry weight. Cadmium uptake by soybeans was correlated with the ratio of added Cd to the Cd sorptive capacity of soil.

Cd may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide, and phosphate (U.S. EPA, 1999 quoted in UNEP, 2008: 36). Evidence suggests that adsorption mechanisms may be the primary source of Cd removal from soils. In soils and sediments polluted with metal wastes, the greatest percentage of total Cd was associated with the exchangeable fraction. Cd concentrations have been shown to be limited by cadmium carbonate in neutral and alkaline soils (U.S. EPA, 1999 quoted in UNEP, 2008: 36).

Increasing soil zinc is known to reduce Cd availability to plants (ECB, 2005 quoted in UNEP, 2008: 36) because Zn inhibits Cd uptake and Cd translocation from roots to shoots of plants (Chaney and Ryan, 1994 quoted in UNEP, 2008: 36). Huang, Bazzaz and Vanderhoef (1974: 122) studied the inhibition of soybean (*Glycine max* L.) metabolism by cadmium and lead the result found that 300 μM and cadmium 18.0 μM inhibit pod fresh weight in soybeans by 35%. Eighteen micro-molar cadmium caused a 30.0 % decline in nitrogenase activity by day 52 (the day on which maximum activity was measured) and a 71.0 % inhibition by day 59. The heavy metals depressed photosynthetic rates; when photosynthesis was depressed by 60.0 %, as measured on the day of peak photosynthesis activity, carbohydrate did not accumulate with the effect of lead and cadmium on several other aspects of plant metabolism (shoot, root, leaf, and nodule dry weight; nodule ammonia, protein and carbohydrate content) also Tawadchai Suppadit, Viroj Kitikoon and Pichit Suwannachote (2008: 86) suggested that physic nut varieties can not be grown as a renewable energy source in areas where Cd residue is present in soils at a level of 100 mg kg^{-1} and above. The trial show significantly ($P > 0.05$) about Cd soil residue at 100 – 300 mg kg^{-1} , caused a decrease in growth potential, in addition to stunted growth, the plants did not produce any yield.

2.1.3 Human Exposure and Health Effects

2.1.3.1 Human Exposure

Food is the main source of exposure to Cd in the general population, providing over 90.0 percent of the total intake in non-smokers (WHO/UNECE, 2006 quoted in UNEP, 2008: 38). Järup, Berglund, Elinder, Nordberg and Vahter (1998a: 240) quoted that the average daily intake varies according to dietary habits: diets rich in fiber and shellfish which are associated with high dietary Cd intake. The concentrations of Cd in most foods range from 0.0100 to 0.0500 mg kg^{-1} , but higher concentrations may be found in nuts and oil seed, mollusks, and offal, especially liver and kidney (WHO, 1988 quoted in UNEP, 2008: 38). Average daily intakes of Cd from food in long normally distributed, with a small fraction of the population ingesting more Cd than the average (UNEP, 2008: 38). Further, within the population, children may have higher average intake per kg of body weight than adults. People

with a high intake of meat and other products from marine mammals may have a particularly high intake of Cd (UNEP, 2008: 38).

2.1.3.2 Occupational Exposure

Workers may be exposed to Cd in the zinc, copper and steel industries, in the manufacture of nickel-cadmium batteries, solar cells, and jewellery, in metal planting, production of plastics and many other industrial activities (UNEP, 2008: 39). Air concentrations of Cd fumes or dust vary considerably between different industries, such as smelters, pigment plants and battery factories (Järup et al., 1998a: 240).

2.1.3.3 Cadmium in the Diet

Cadmium occurs in all food types; in most countries, agricultural crops account for most of the intake of Cd. Daily human intake of Cd from crops is related to the Cd concentration in the agricultural soils which mainly comes from atmospheric deposition, phosphate fertilizers, manure and sewage sludge (UNEP, 2008: 40). Average daily intake of Cd via food in most of the countries are within the range 0.100 – 0.400 µg per kg of body weight (UNEP, 2008: 40). The rate of uptake of Cd from soil varies considerably for different crops (Park, Lee and Kim, 2011: 575). Ali, Baxerafshan, Hazrati and Tavakkoli (2006: 147) determined and estimated of Cd contents in Tarom rice, the resulted showed that average concentration of Cd in rice was $0.410 \pm 0.170 \text{ mg kg}^{-1}$ dry weight upper than the FAO/WHO Guidelines. Cd in rice comes from soil via rice plant roots. Rice may thus be the best indicator for the environmental monitoring of Cd especially in rice eating countries (Rivai, Koyama and Suzuk, 1990: 910). Examples of daily intake of Cd via food in different countries are shown in the Table 2.3

Table 2.3 Daily Intake of Cadmium via Food: Country Examples

| Country | Type of consumption data/Intake study | Average dietary intake (μg of cadmium per kg body weight per day) | Population group | Information source |
|----------------|--|---|---|--|
| Australia | Total diet study by Food Standards Australia – New Zealand 2002 | 0.0800 – 0.240 0.0700 – 0.220 0.110 – 0.290 0.0900 – 0.220 0.180 – 0.570 0.130 – 0.680 | Males 25 – 34 years Females 25 – 34 years Boys 12 years Girls 12 years Toddler 2 years Infant 9 months | Australia's submission, 2005 quoted in UNEP, 2008 |
| Burkina Faso | Total diet study Calculated from average total daily intake assuming an average weight of 60 kg | 0.280 | | Burkina Faso's submission, 2005 quoted in UNEP, 2008 |
| Finland | Calculated from average total daily intake assuming an average weight of 60 kg | 0.170 | | NFA, 2002 (submitted by Finland) quoted in UNEP, 2008 |
| Norway | Not specified | 0.140 | | European Commission, 1996b quoted in WHO, 2004 |
| Greece | Total diet study Not specified | 0.740 0.940 | | Tsoumbaris and Tsoukali-Papadopoulou, 1994 quoted in WHO, 2004 |

Table 2.3 (Continued)

| Country | Type of consumption data/intake study | Average dietary Intake (μg of cadmium per kg body weight per day) | Population group | Information source |
|----------------|--|--|---|--|
| Mexico | Calculated from average total daily intake assuming an average weight of 60 kg | 4.88 | Population of Mezquital Valley in Hidalgo | Mexico's submission, 2005 quoted in UNEP 2008 |
| Austria | Disappearance | 0.150 | | European Commission, 1996b quoted in WHO, 2004 |
| Belgium | Household purchases, 24-h records, FAO food balance sheets | 0.390 | | European Commission, 1996b quoted in WHO, 2004 |
| Canada | Total diet study | 0.220 | | Dabeka and McKenzie, 1995 quoted in WHO, 2004 |
| Sweden | Not specified | 0.120 0.130 | Males Females | European Commission, 1996b quoted in WHO, 2004 |
| Denmark | National consumption survey | 0.280 | | European Commission, 1996b quoted in WHO, 2004 |
| France | Household consumption survey | 0.220 | | European Commission, 1996b quoted in WHO, 2004 |
| Germany | Total diet study National consumption survey | 0.180 0.190 0.160 | Males Females | European Commission, 1996b quoted in WHO, 2004 |

Table 2.3 (Continued)

| Country | Type of consumption data/intake study | Average dietary Intake (μg of cadmium per kg body weight per day) | Population group | Information source |
|----------------|---|---|---|--|
| Italy | National consumption survey | 0.330 | | European Commission, 1996b quoted in WHO, 2004 |
| Japan | Duplicate diet study | 0.360 0.310 | Adult males Adult females | Watanabe et al., 1992 quoted in WHO, 2004 |
| New Zealand | Total diet study | 0.400/0.240 0.330/0.190 0.330/0.160 0.240 | Young males Adult males Females Female vegetarians | Vanoort et al., 2000 quoted in WHO, 2004 |
| United States | Total diet study | 0.140 – 0.150 0.130 – 0.140 | Adult males Adult females | United States Food and Drug Administration quoted in WHO, 2004 |
| United Kingdom | Total diet study National consumption survey | 0.17 0.20 | | Quoted in WHO, 2004 |

Source: UNEP, 2008: 43-44.

2.1.3.4 Health Effects in Humans

Cd is efficiently retained in the human body, in which it accumulates throughout life (Bernard, 2008: 557). The kidney is considered the critical target organ, for both the general population and occupationally exposed populations especially to the proximal tubular cells. Cd can also cause bone demineralization,

either through direct bone damage or indirectly as a result of renal dysfunction (Bernard, 2008: 557). An increased risk of lung cancer has been reported following inhalation exposure in occupational settings, but there is no evidence that Cd is a carcinogen by the oral route of exposure (WHO, 2006 quote in UNEP, 2008: 42).

1) Kidney Effects

The accumulation of Cd in the renal cortex leads to kidney dysfunction with impaired reabsorption of, for instance, proteins, glucose, and amino acids (IPCS, 1992a quoted in UNEP, 2008: 44). The concentration of Cd in the kidneys reflecting cumulative exposure, can be assessed by measuring Cd levels in urine. The first sign of Cd-induced renal lesions is tubular proteinuria, that results from the damage to the proximal tubular cells and is usually detected as an increase in low molecular weight proteins in the urine (Järup et al., 2000: 668). The primary markers of kidney damage are the urinarily excreted β 2-microglobulin, N-acetyl- α -D-glucosaminidase (NAG), and also retinol-binding protein (RBP).

WHO (1992 quoted in UNEP, 2008: 45) estimated that a urinary excretion of 10.0 nmol/mmol of creatinine could constitute a "critical limit", below which kidney damage would not occur. However, Cd-induced kidney dysfunction in the general population was demonstrated at urinary Cd levels around 2.00 – 3.00 nmol/mmol of creatinine, and a negative dose-effect relationship was found between Cd dose and bone mineral density in people at the age of 60 or older (Järup and Alfven, 2004: 505).

2) Bone Damage and the Itai-Itai-Disease

Bhaskar, Chakravarthi, and Kiran (2012: 241) explained the major mechanisms involved in Cd induced bone damage that Cd interferes with Ca and vitamin-D metabolism in bone, kidney and intestine, which Ca absorption is decreased by competition with Cd in the intestine, and more Ca is released from maternal bone and transferred to neonate by lactation...is an important factor contributing to the decrease in bone mineral density and Cd has an additive effect of decreasing bone metabolism of mother animal, although the Cd intake level is relatively low which approximately $3.00 - 14.0 \mu\text{g Cd kg}^{-1}\text{day}^{-1}$ (Bhaskar et al., 2012: 242).

3) Cancer

International Agency for Research on Cancer (IARC, 1993 quoted in Sarkar, Ravindran and Krishnamurthy, 2013: 23) classified Cd as a human carcinogen (group I) on the basis of classified level B1. (evidence level for inhalation route according to EPA Weight-of-Evidence). Joseph (2009: 272) noted that Cd can cause damage to various organs including the lung, breast, liver, kidney, bones, testes and placenta by induced oxidative stress because of its involvement in Cd induced aberrant gene expression, inhibition of DNA damage repair and apoptosis.

The association between environmental exposure to Cd and lung cancer in a population living near zinc smelters has been reported in a Belgian study (Nawrot et al., 2006: 119). Chronic inhalation of Cd causes pulmonary adenocarcinomas (Satarug, Baker and Urbenjapol, 2003: 65). Inhaled metals are not biodegradable, therefore deposited and remain for long periods in various areas of the pulmonary tissue (Strumylaite and Mechosina, 2011: 14).

4) Reproductive Effects

Cadmium adversely affects the reproductive function (Sarkar, Ravindran, Krishnamurthy 2013: 22). Cd damage to the vascular endothelium, Ledig and Sertoli cells, intercellular connections, the induction of oxidative stress, impaired antioxidant defense mechanisms and the severity of the inflammatory response, which results in their morphologic and functional changes like inhibition of testosterone synthesis and spermatogenesis impairment (Sarkar et al., 2013: 23). Maternal exposure to Cd is associated with low birth weight and spontaneous abortion (Frery et al., 1993: 109; Shiverick and Salafia, 1999: 265).

5) Sensitive Subgroups

The population at highest risk consist on women with low iron stores or nutritional deficiencies, people with kidney disorders and fetuses and children (UNEP, 2008: 47). Smokers, people eating a Cd – rich diet, and those living in the vicinity of industrial plants that emit Cd (e.g. nonferrous metal extraction plants) represent population groups at high risk of exposure (WHO/UNECE, 2006 quoted in UNEP, 2008: 47).

2.1.4 Reference Levels

2.1.4.1 Provisional Tolerable Weekly Intake

The Joint FAO/WHO Expert Committee on Food Additives has established a provisional tolerable weekly intake (PTWI) of $7.00 \mu\text{g kg}^{-1}$ of body weight, corresponding to $1.00 \mu\text{g kg}^{-1}$ of body weight per day. Thus, for a 70.0 kg person, the tolerable daily intake is $70.0 \mu\text{g}$ of cadmium (WHO, 2004a quoted in UNEP, 2008: 47). Although there is some indication that a proportion of the general population might be at an increased risk of tubular dysfunction at the current PTWI, the Joint Expert Committee, at its fifty-fifth meeting, maintained the PTWI at this value because of precision in the risk estimates (WHO, 2004a quoted in UNEP, 2008: 47).

The U.S. EPA has established reference doses (or RfDs) for Cd of $0.000500 \text{ mg kg}^{-1}\text{day}^{-1}$ for exposure through water, and $0.00300 \text{ mg kg}^{-1}\text{day}^{-1}$ for exposure through food. The RfD is defined as an estimate of a daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime (U.S. EPA, 1992 quoted in UNEP, 2008: 47).

2.1.4.2 Codex Alimentarius Maximum Levels

Table 2.4 summarizes the Codex Alimentarius maximum levels for cadmium.

Table 2.4 Codex Alimentarius Maximum Levels for Cadmium

| Code no. | Food | Maximum level (mg kg^{-1}) | Remarks |
|----------|------------------|---------------------------------------|-------------------------------|
| GC 0654 | Wheat grain | 0.200 | |
| VR 0589 | Potato | 0.100 | Peeled |
| VR 0075 | Stem and root | 0.100 | Excluding celeriac and potato |
| VS 0078 | vegetables | | |
| VL 0053 | Leafy vegetables | 0.200 | |
| VA 0035 | Other vegetables | 0.0500 | Excluding fungi and tomatoes |
| VA 0040 | | | |
| VA 0045 | | | |
| VA 0050 | | | |

Source: Codex Alimentarius, 2005 quoted in UNEP, 2008: 48.

2.1.4.3 Drinking Water Guideline

A drinking water guideline value for Cd of $0.00300 \text{ mg l}^{-1}$ has been established by WHO, based on an allocation of 10.0 percent of the PTWI to drinking water and an average water consumption of $2 \text{ l}^{-1} \text{ day}^{-1}$ (WHO, 2004b quoted in UNEP, 2008: 48).

The EPA regulation for drinking water (also known as the Maximum Contaminant Level) limits Cd in drinking water to $0.00500 \text{ mg L}^{-1}$, and the EPA MCL Goal is also $0.00500 \text{ mg L}^{-1}$ (U.S. EPA, 2008b quoted in UNEP, 2008: 48).

2.1.4.4 Cadmium in Soil

In order to prevent any further increase of Cd in agricultural soils likely to increase the dietary intake of future generations, a guideline of 5.00 ng m^{-3} in ambient air has been established by WHO (WHO, 2000 quoted in UNEP, 2008: 48).

2.2 Biochar

A concept biochar is defined as ‘charcoal made from biomass that has been pyrolysed in a zero or low oxygen environment (Lehmann, 2007a: 143, 2007b: 381). Biochar has a relatively structured carbon matrix with a medium-to high surface area, suggesting that it may act as a surface sorbent which is similar in some aspects to activated carbon. It has been proven that BC is effective in adsorbing organic pollutants from wastewater (Lehmann, Gaunt and Randon, 2006: 403). For which, owing to its inherent properties, scientific consensus exists that application of biochar to soil was recently proposed as a novel approach to establish a significant, long-term, sink for atmospheric CO_2 in terrestrial ecosystems (Lehmann, 2007b: 381; Renner, 2007: 5932), and concurrently improve soil functions (Liang et al., 2006: 1719; Lehmann, 2007a: 143), while avoiding short- and long- term detrimental effects to the wider environment as well as created Terra Preta soils (Hortic Anthrosols) in Amazonia where charred organic material plus other (organic and minerals) materials appear to have been added purposefully to soil to increase its agronomic quality. Ancient Anthrosols have been found in Europe as well, where organic matter (peat, manure, ‘plaggen’) was added to soil, but where charcoal additions appear to have been limited or non-existent. Furthermore, charcoal from wildfires (pyrogenic black

carbon) has been found in many soils around the world, including European soils where pyrogenic black carbon can make up a large proportion of total soil organic carbon (Verheijen, Jeffery, Bastos, van der Velde and Diafas, 2010: 36).

Biochar can be produced from a wide range of organic source under different pyrolysis conditions and at a range of scales (Verheijen et al., 2010: 50). Many different materials have been proposed as biomass source for biochar (Sparkes and Stoutjesdijk, 2011: 7; Verheijen et al., 2010: 50). The suitability of each biomass type for such an application is dependent on a number of chemical, physical, environmental, as well as economic and logistical factors (Verheijen et al., 2010: 50). The original feedstock used, combined with the pyrolysis conditions will determine the properties, both physical and chemical, of the biochar product (Verheijen et al., 2010: 50). It is these differences in physicochemical properties that govern the specific interactions which will occur with the endemic soil biota upon addition of biochar to soil, and hence how soil dependent ecosystem functions and services are affected (Verheijen et al., 2010: 50).

2.2.1 Physicochemical Properties of Biochar

The combined heterogeneity of the feedstock and the wide range of chemical reactions which occur during processing, give rise to a biochar product with a unique set of structural and chemical characteristics (Demirbas, 2004: 243).

2.2.1.1 Structural Composition

Thermal degradation of cellulose between 250 and 350 °C results in considerable mass loss in the form of volatiles, leaving behind a rigid amorphous C matrix (Verheijen et al., 2010: 51). As the pyrolysis temperature increases, so thus the proportion of aromatic carbon in the biochar, due to the relative increase in the loss of volatile matter (initially water, followed by hydrocarbons, tarry vapours, H₂, CO and CO₂), and the conversion of alkyl and O-alkyl C to aryl C (Demirbas, 2004: 244). Around 330°C, polyaromatic grapheme sheets begin to grow laterally, at the expense of the amorphous C phase, and eventually coalesce. Above 600 °C, carbonization becomes the dominant process (Verheijen et al., 2010: 51). Carbonization is marked by the removal of most remaining non-C atoms and consequent relative increase of

the C content, which can be up to 90% (by weight) in biochars from woody feedstocks (Demirbas, 2004: 246).

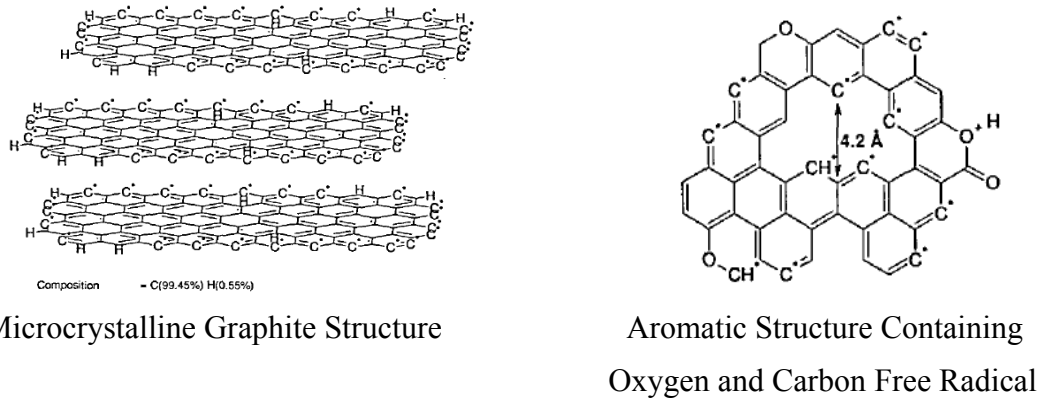


Figure 2.2 Putative Structure of Charcoal

Source: Bourke, quoted in Verheijen et al., 2010: 50.

It is commonly accepted that each biochar particle comprises of two main structural fractions: stacked crystalline grapheme sheets and randomly ordered amorphous aromatic structures. Hydrogen, O, N, P and S are found predominantly incorporated within the aromatic rings as heteroatoms (Bourke et al., 2007 quoted in Verheijen et al., 2010: 52). The presence of heteroatoms is thought to be a great contribution to the highly heterogenous surface chemistry and reactivity of biochar (Verheijen et al., 2010: 52).

2.2.1.2 Chemical Composition and Surface Chemistry

Biochar composition is highly heterogeneous, containing both stable and labile components (Sohi et al., 2009: 2). Carbon, volatile matter, mineral matter (ash) and moisture are generally regarded as its major constituents (Antal and Gronli, 2003 quoted in Verheijen et al., 2010: 52). Table 2.5 summarizes their relative proportion ranges in biochar as commonly found for a variety of source materials and pyrolysis conditions (Antal and Gronli, 2003; Brown, 2009 quoted in Verheijen et al., 2010: 52).

Table 2.5 Relative Proportion Range of the Four Main Components of Biochar (Weight Percentage) as Commonly Found for a Variety of Source Materials and Pyrolysis Conditions

| Component | Proportion (w w ⁻¹) |
|----------------------------|---------------------------------|
| Fixed carbon | 50.0 – 90.0 |
| Volatile matter (e.g.tars) | 0 – 40.0 |
| Moisture | 1.00 – 15.0 |
| Ash (mineral matter) | 0.500 – 5.00 |

Source: Antal and Gronli, 2003; Brown, 2009 quoted in Verheijen et al., 2010: 52.

The relative proportion of biochar components determines the chemical and physical behavior and function of biochar as a whole (Brown, 2009 quoted in Verheijen et al., 2010: 52), which in turn determines its suitability for a site specific application, as well as transport and fate in the environment (Downie, Crosky and Monroe, 2009 quoted in Verheijen et al., 2010: 52).

Biochar can produced from a wide range of sources under different pyrolysis conditions (Table 2.6), its high carbon content and strongly aromatic structure are constant features (Sohi et al., 2009: 11)

Table 2.6 Summary of Total Elemental Composition (C, N, C:N, P, K, available P and Mineral N) and pH Ranges and Means of Biochars from a Variety of Feed Stocks (Wood, Green Wastes, Crop Residues, Sewage Sludge, Litter, Nut Shells) and Pyrolysis Conditions (350-500°C) Used in Various Studies

| | pH | C (g kg ⁻¹) | N (g kg ⁻¹) | N (NO ₃ ⁻ +NH ₄ ⁺) (mg kg ⁻¹) | C:N | P (g kg ⁻¹) | Pa (g kg ⁻¹) | K (g kg ⁻¹) | |
|--------------|------|----------------------------|----------------------------|---|------|----------------------------|-----------------------------|----------------------------|------|
| Range | From | 6.20 | 172 | 1.70 | 0.00 | 7.00 | 0.200 | 0.015 | 1.00 |
| | To | 9.60 | 905 | 78.2 | 2.00 | 500 | 73.0 | 11.6 | 58.0 |
| Mean | | 8.10 | 543 | 22.3 | - | 61.0 | 23.7 | - | 24.3 |

Source: Chan and Xu, 2009 quoted in Verheijen et al., 2010: 53.

The composition and properties of these elements vary with the biomass type (Antal and Gronli, 2003: 1624; Duku, Gu and Hagen, 2011: 3540). Verheijen et al. (2010: 52) reported that biomass with high lignin content produces high biochar yields as a result of the stability of thermal degradation which biochar produced from crop residue and manures are generally finer and less robust which is rich in nutrient and more readily degradable by micro communities in the environment (Sohi et al., 2009: 6). Total carbon content in biochar was various considerably depending on feedstock and may range from 400 g kg⁻¹ up to 500 g kg⁻¹ (Antal and Gronli, 2003: 1625) and from 172 to 905 g kg⁻¹ (Chan and Xu, 2009 quoted in Verheijen et al., 2010: 53). Total N varied between 1.80 and 56.40 g kg⁻¹, depending on the feedstock (Chan and Xu, 2009 quoted in Verheijen et al., 2010: 53). However, biochar total N content seems not necessarily beneficial to crops because mostly present in unavailable form (mineral N contents < 2.00 mg kg⁻¹, Chan and Xu, 2009 quoted in Verheijen et al., 2010: 53). N content and S were richer in biochar produced at lower temperature than higher temperature (Bridle and Pritchard, 2004 quoted in Kookana, Sarmah, Van Zwieten, Krull and Singh, 2011: 107). C:N (carbon to nitrogen) ratio in biochar has been found to vary widely between 7.00 and 500 (Chan and Xu, 2009 quoted in Verheijen et al., 2010: 53). Kookana et al. (2011: 108) report that “most wood and nut based biochars have extremely high C/P and C/N ratios, while manure, crop, food-waste biochar have much lower ratios with manure derived biochar being the most nutrient-rich biochar”.

Total P and total K in biochar were found to range broadly according to feedstock, with values between 2.70 – 480 and 1.00 – 58.0 g kg⁻¹, respectively (Chan and Xu, 2009; Verheijen et al., 2010: 53). DeLuca et al. (2009 quoted in Kookana et al., 2011: 108) reported that “high-temperature biochars (800°C) tend to have a higher pH, electrical conductivity, and extractable NO₃⁻, while low-temperature biochars (350°C) have greater amounts of extractable P, NH₄⁺, and phenols”.

The composition, quality and characteristics of biochar such as density, particle size distribution, ash content, moisture content and pH depend on the type, nature and origin of the feed stocks and pyrolysis reaction conditions (Zheng, Sharma

and Rajagopalan, 2010: 8). Amonette and Joseph (2009 quoted in Duku et al., 2011: 3544) reported that “during pyrolysis of biomass potassium, chlorine and nitrogen vaporized relatively low temperatures, while calcium, magnesium, phosphorus and sulphur increased stability vaporize at high temperature”. Duku et al. (2011: 3544) quoted that slow biomass pyrolysis is reported to high quantities of K, Cl, Si, Mg, P and S in biochars and biochar yield.

2.2.2 Particle Size Distribution

The particle size distribution in biochar is influence mainly by the nature of the biomass source and the pyrolysis conditions (Cetin et al., 2004 quoted in Verheijen et al., 2010: 54). Shrinkage and attrition of the organic material occur during processing, thereby generating a range of particle sizes of the final product (Cetin et al., 2004 quoted in Downie Crosky and Munroe, 2009: 26). The intensity of such processes is dependent on the pyrolysis technology (Cetin et al., 2004 quoted in Downie et al., 2009: 26). Particle size distribution in biochar also has implications for determining the suitability of each biochar product for a specific application (Downie et al., 2009: quoted in Verheijen et al., 2010: 53).

Sohi et al. (2009: 12) discussed about the influence of the type of feedstock on particle size distribution that wood-based feedstocks generate biochars that are coarser and predominantly xylemic in nature, whereas biochars from crop residues and manures offer a finer and more brittle structure. Downie et al. (2009: 26) observed that biochar derived from sawdust and wood chips prepared under different pre-treatments was produced contrasting particle sizes. They found that “as pyrolysis highest heating rate increased from 450°C to 700°C, the particle size tended to decreased due to reduction on the biomass material resistance to attrition during processing”.

2.2.3 Surface Area and Pore Size Distribution

Process temperature greatly affects the surface area of pyrolysis product. Day (2005 quoted in Sohi et al., 2009: 13) found that surface area increase from 120 m²g⁻¹ at 400°C to 460 m²g⁻¹ at 900°C. As HTT increase more structured regular spacing between the molecule, which result is larger surface area per volume (Downie et al.,

2009: 22). Elevated temperatures provide the activation energies and longer retentions allow the time for the reactions to reach completion leading to greater degrees of order in the structure (Downie et al., 2009: 23).

Downie et al. (2009: 22) classified biochar pores into three categories: “macropores which pores of internal width greater than 50.0 nm, mesopores which pore size internal width between 2.00 nm to 50.0 nm, and micropore which pores of internal diameter less than 2.00 nm”. They mentioned that “the surface area of biochars generally increases with increasing HTT until reaches the temperature at which deformation occurs, resulting in subsequent decreases in surface area”. According to Lua, Yang and Guo (2004: 279) found that “increasing pyrolysis temperature from 250 to 500°C enhanced the development of micropores in chars derived from pistachio-nut shells due to increased evolution of volatiles, however, when increase temperature > 800°C, surface area of chars was reduced”.

2.2.4 Biochar Density

The density of the biochars depends upon the nature of the starting material and the pyrolysis process (Pandolfo et al., 1994 quoted in Downie et al., 2009; 28). Downie et al. (2009: 27) classified density of biochar into two types of the C structure “one is accompanied by a decrease in apparent densities as porosity develops during pyrolysis and second type is bulk density consist of multiple particle and includes the macro-porosity within each particle and the inter-particle voids”. Solid density of biochar increase with increasing process temperature and longer heating residence times (Downie et al., 2009: 28). While Brown et al. (2006 quoted in Downie et al., 2009: 28) showed that the density is independent of heating rate, and found a simple and direct dependency of density upon final pyrolysis temperature. Verheijen et al. (2010: 55) concluded that “the operating conditions during pyrolysis e.g. heating rate, high treatment temperature-HTT, residence time, pressure, flow rate of the inert gas, reactor type and shape and pre- (e.g. drying, chemical activation) and post- (e.g. sieving, activation) treatments can greatly affect biochar physical structure”.

2.2.5 Cation Exchange Capacity (CEC) and pH

CEC variation in biochars ranges from negligible to around 40.0 cmol g^{-1} and has been reported to change following incorporation into soils (Lehmann, 2007 quoted in Verheijen et al., 2010: 58). Aged biochar has a high CEC due to high concentrations of negative charge on biochar surfaces (Liang et al., 2006; 1719). While fresh biochar absorb cations CEC and anion exchange capacity vary with overall soil pH and age and weathering environment of biochar (Cheng, Lehmann and Engelhard, 2008: 1598).

The pyrolysis process converts biomass acids into the bio-oil component and the alkalinity is inherited by the solid biochar (Laird et al., 2010: 443). Inorganic carbonates and organic anions are alkaline components in biochar (Yuan, Xu and Zhang, 2011c: 3488). When biochar is produced at different temperatures, their alkalinity increase with increasing charring temperature (Mukherjee, Zimmerman and Harris, 2011: 247; Yuan et al., 2011: 3488). Yuan et al. (2011: 3488) indicated that biochar contain functional groups such as -COO^- (-COOH) and -O^- (-OH) which contributed greatly to the alkalinity of the biochar. Chan and Xu (2009 quoted in Verheijen et al., 2010: 58) reviewed that “biochar pH values from a wide variety of feedstocks and found a mean of pH 8.1 in a total range of pH 6.20 - 9.60 which the lower end of this range seems to be from green waste and tree bark feedstock, with the higher end from poultry litter feedstocks”.

2.2.6 Effects of Biochar Application on Soil Properties

Application of biochar to soils is currently gaining considerable interest due to its potential to improve soil nutrient retention capacity, water holding capacity, sustainably store carbon and reducing greenhouse gas emission (Verheijen et al., 2010: 61). Feedstock type and pyrolysis conditions affect the physico-chemical characteristics of biochar. This variability has significant implications for nutrient content of the biochar and nutrient availability to plants when biochar is applied to soil (Downie et al., 2009: 24).

2.2.6.1 Soil Structure

Atkinson, Fitzgerald and Hipps (2010: 1); Downie et al. (2009: 13) reviewed that “the incorporation in soils influences soil structure, texture, porosity,

particle size distribution and density due to their highly porous structure and large surface area, consequently increase soils aeration, water holding capacity, and plant growth". Biochar has a bulk density much lower than that of mineral soils and, therefore, application of biochar can reduce the overall bulk density of soil (Verheijen et al., 2010: 63). Bruun (2011: 21) review that incorporate of larger biochar particles > 0.50 mm could increased aeration of the soil and reduce anoxic micro-sites. In addition, soil hydrology and soil compaction may be affected by partial or total blockage of soil pores by fine biochar particle incorporated in soil (Verheijen et al., 2010: 63; Bruun, 2011: 21).

2.2.6.2 Soil pH

Many authors measured rises in soil pH when biochar was applied to soil (Chan, Dorahy, Tyler, Well, Miham and Barehia, 2007: 139; Tawadchai Suppadit, Nittaya Phumkokrak and Pakkapong Pongsuk, 2012: 244). For example, Hass, Gonzalez, Lima, Godwin, Halvorson and Boyer (2012: 1096) found that chicken-manure biochar increased soil pH from 4.8 to 6.6 at application rate of 40.0 g kg⁻¹. According to Nigussie, Kissi, Misganaw and Ambow (2012: 371) used maize stalk biochar produced at 500°C pyrolysis temperature increase chromium polluted soil pH from 5.23 to 5.72 at application rate 10.0 t ha⁻¹. Arise in pH can provide a wide range of benefits on soil quality by improving the availability of plant nutrients due to the alkaline substance in biochar are more easily released into the soil (Yuan, Xu, Zhang and Li, 2011: 302). However, applying a biochar with lower pH than the targeted soils might have the potential to decrease soil pH in alkaline soil (Liu and Zhang, 2012: 749), which can aggravate micronutrient deficiencies and reduce crop yields (Kishimoto and Sugiura, 1985: 12).

2.2.6.3 Soil Hydrological Properties

In a study by Tyron (1948: 83) found that "wood-based charcoal increased the moisture content of a sandy soil with 18.0 % after addition of 45.0 vol % biochar, while the moisture content decreased after the addition to clay' soil". Basso, Miguez, Laird, Horton and Westgate (2012: 132) suggested that biochar added to sandy loam soil increases water-holding capacity and might increase water available for crop used.

The direct of biochar application is related to the large inner surface area of biochar, however depend on the initial texture of the soil which effective on coarse-textured soils or soil with large amounts of macro-pores (Verheijen et al., 2010: 64). They also reported that biochar incorporated in the soil will determine long term effects on water retention and soil structure relative on the proportion of micro, meso, and macro pores in the root zone (Verheijen et al., 2010: 64). In sandy soils, the additional volume of water and soluble nutrients stored in the biochar micro-pores may become available as the soil dries and matrix potential increase, may be lead to increased plant water availability during dry periods (Verheijen et al., 2010: 65).

2.2.6.4 Soil Cation Exchange Capacity

The Cation Exchange Capacity (CEC) of soil is a measure for how good cation e.g. ammonium, potassium, calcium etc. are bound in the soil (Bruun, 2011: 25), therefore, available for plants uptake and prevented from leaching to ground and surface waters (Verheijen et al., 2010: 68). Cations are bound by ion-and covalent binding to negatively charged sited on the reactive surface of biochar (Bruun, 2011: 25). Cheng, Lehmann, Thies, Burton and Engelhard (2006: 1477) found that “the formation of carboxylic functional groups was the reason for the enhanced CEC during oxidation which initiated on the surface are of black carbon”. Liang et al. (2006: 1719) found that Anthrosols from Brazilian Amazon with high contents of biomass derived black carbon (BC) had greater potentials CEC per unit organic C than adjacent soils with low BC content.

2.2.6.5 Nutrient Retention in Soil

The pyrolysis operating conditions and biomass feedstock affect physico-chemical structure of biochar cause variability in the availability of nutrients within each biochar to plants (Spakes and Stoutiesdijk, 2011: 18). Biochar derived from manure and animal product feedstocks are relatively rich in nutrients when compared with those derived from plant materials (Chan, Van Zwieten, Meszaros, Downie and Joseph, 2007: 629).

The capacity of biochar to retain nutrient due to great surface area providing adsorption sites for inorganic nutrients (Bruun, 2011: 23). Moreover, biochar may lead to decreased nutrient leaching particularly nitrates and contaminant transport below the root zone which related to increased nutrient use efficiency by

increased water and nutrient retention and availability (Verheijen et al., 2010: 76). Major, Steiner, Downie and Lehmann (2009: 275) suggested that “biochar must be produced at temperature or above 500°C or be activated to increased surface area of the biochar for direct sorption of nutrients”.

Surface of fresh biochars are generally hydrophobic and have relatively low surface charges (Lehmann, Lan, Hyland, Sato, Solomon and Ketterings, 2005: 143). However, after exposure to water and oxygen in the soil, the biochars surfaces oxidizes and forms more carboxylic and phenolic groups (Cheng, Lehmann and Engelhard, 2008: 1598), which more hydrophilic with time and increase its capacity to hold cations (Bruun, 2011: 25). Van Zwieten et al. (2010: 235) observed that after biochar application, “total C, organic C, total N, available P, and exchangeable cations Ca, Mg, Na, and K increase and available Al decreased in soil”.

Chan, Van Zwieten, Meszaros, Downie and Joseph (2007: 629) found that “application poultry litter biochar had increase N uptake by plants. Furthermore, application biochar to soil also promote microbial growth, which is responsible for mineralization of soil N”.

2.2.6.6 Soil Biota

Major (n.d.) hypothesized that the large porosity of biochar provides surface for soil microbes to colonize and grow which larger organisms cannot enter to prey them. Klob, Fermanich and Dornbush (2009: 118) demonstrate that while charcoal additions affects microbial biomass and microbial activity as well as nutrient availability differences in the magnitude of the microbial response was depend on the differences in base nutrients availability in the soils studied.

Biochar has macr-molecular structure dominated by aromatic C, biochar is more recalcitrant to microbial decomposition than uncharred organic matter (Baldock and Smernik, 2002: 1093). The structure of biochar provides a refuge for small beneficial soil organisms such as symbiotic mycorrhical fungi which can penetrate deeply into the pore space of biochar and extra radical fungi hyphae which sporulate in the micropores of biochar where there is lower competition from saprophytes (Satio and Marumoto, 2002: quoted in Verheijen et al., 2010: 87). Warnock, Lehmann, Kuyper and Rillig (2007: 14) hypothesized four mechanism that

biochar can lead to altered total abundance and activity of mycorrhizal fungi in soils and plant roots:

(1) Biochar additions to soil altered levels of nutrient availability and other alternations in soil physic-chemical parameters that have effects on both plant and mycorrhizal fungi. (2) Biochar are beneficial or detrimental to other soil microbes for instance mycorrhization helper bacteria or phosphate solubilizing bacteria. (3) Biochar in soil alters plant-mycorrhizal fungi signaling process or detoxifies allelochemicals leading to altered root colonization by mycorrhizal fungi. (4) Biochar serves as a refuge from hyphal grazers.

However, they have suggest that these mechanism need more future research for testing the occurance and relative important of these mechanism in soil.

2.2.6.7 Sorption

Bioavailable metal concentration in contaminated soils can be minimized through biological immobilization and stabilization methods using a range of organic compounds such as biochar which is a form of environmental black carbon produced using the pyrolysis of C-based biomass (Verheijen et al., 2010 quoted in Trakal, Momarek, Szakova, Zemamova and Tlustos, 2011: 372). Similar to activated carbon, biochar can serve as a sorbent due to greater sorption ability than natural soil organic matter which biochar have greater surface area, negative surface charge, and charge density (Liang et al., 2006: 1719). Addition of biochar to soil expected to enhance the sorption properties of the soil and have a strong influence on the fate and behavior of non-polar organic compounds in soil (Smernik, 2009: 289). Yang and Sheng (2003, quoted in Smernik, 2009: 290) found that biochar has much higher affinity and exhibits non-linear sorption isotherms (adsorption to external or internal surface) than fresh plant material and soil which both exhibit linear sorption isotherms. Wang, Sato and Xing (2006 quoted in Verheijen et al., 2010: 73) demonstrated that adsorption to charcoals is mainly influenced by the structural and properties of the contaminant as well as pore size distribution, surface area and functionality of the

charcoal. Furthermore, Smernik (2009: 296) reported that added biochar to soil is expected to slowly oxidize produces carboxyl groups which contribute CEC to soil which is the most important long-term benefits of biochar in soil and associated with OM and mineral soil components is an important process that turnover of both biochar C and the natural organic matter C (NOM), affecting the C storage benefits of biochar amendment which generally hold up to 10.0 – 1,000 times higher sorption affinities towards such compounds higher than NOM (Chiou and Kile, 1998 quoted in Verheijen et al., 2010: 73) and up to > 2,000 times more effective than soil in sorbing pesticides (Kookana, 2010: 627). Moreover, biochar mediated inhibited of PAH by mineralization in biochar is a consequence of increased sorption and reduced bioavailability (Quilliam, Rangelcroft, Emmett, Deluca and Jones, 2012: 96). Biochar can not only efficiency remove many cationic chemicals including a variety of metal ions but also sorb anionic nutrients such as P ions (Lehmann, 2007a: 381).

2.2.6.8 Biochar on Soil Fertility and Crop Production

There are several evidence that charcoal plays an important role in soil fertility. Anthropogenic enriched dark soil (Terra Preta) which have higher soil fertility than adjacent soil. One studied from Major, Rondon, Molina, Riha and Lehmann (2010: 117) which applied wood-biochar on a Colombian Savanna Oxisol for four years (2003 – 2006 A.D.) under a maize – soybean rotation. They found that maize grain yield increase 28, 30, and 40 % for 2004, 2005, and 2006, respectively with mixing rate 20.0 t ha⁻¹plot⁻¹ over the control. Furthermore, they also found that Ca and Mg was greater with biochar application. Moreover soil pH was increased and exchangeable acidity was decreased due to biochar application. According to Verheijen et al. (2010: 69) reported that the liming effect of biochar apply in acidic soils improved crop yields. Chan, et al., 2007: 629) mentioned that increased nutrient retention by biochar may be the most important for increased crop yield on infertile sandy soils and which was positively to tropical soils too (Steiner et al., 2007: 275).

The beneficial effects appear to be related to alterations in soil physical, chemical, and biological properties such as reduced acidity (Major et al., 2010: 117), increased CEC (Liang et al. 2006: 1719; Lehmann and Engelhard, 2008: 1598), increased microbiological activity (Thies and Rillig, 2009: 85), increased mycorrhizal associations (Warnock et al., 2007: 9), and enhanced nitrogen retention (Lehmann, Da Silva, Steiner, Nehls, Zech and Glaser, 2003: 343).

2.3 Pyrolysis

Pyrolysis is a thermo-chemical decomposition process in which organic material is converted into a carbon-rich solid and volatile matter by heating in the absence of oxygen at temperatures around 350–500°C (Demirbas and Arin, 2002: 471, Meyer, 2009: 2). Pyrolysis has been used to produce biochar for thousands of years (Laird, Brown, Amonette and Lehmann, 2009: 548). The process has endothermic and exothermic phases, the quantity and quality of pyrolysis products, i.e. biochar, tars, oils, and non-condensable vapors depends mainly on the maximum temperature, and the heating rate, but also on pressure and gas flow (Meyer, 2009: 2).

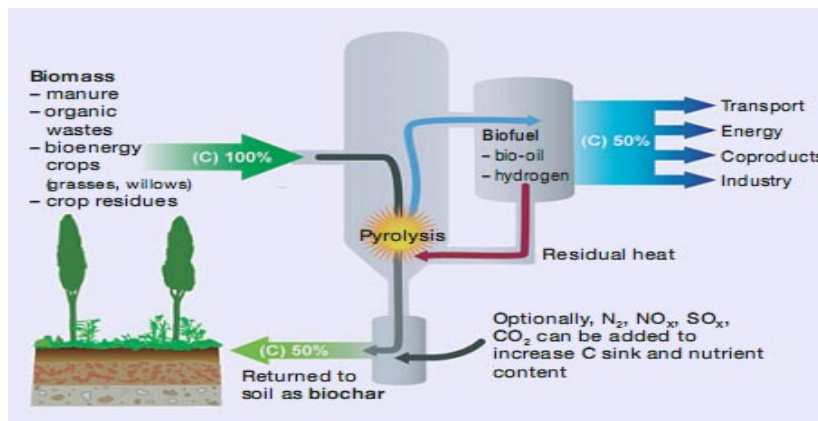


Figure 2.3 Concept Diagram of Low-Temperature Pyrolysis Biomass

Source: CSIRO, n.d.

2.3.1 Pyrolysis Characteristic

Pyrolysis is a thermo-chemical process that can be used to transform low-density biomass and other organic materials into a high-energy-density liquid known as bio-oil, a high-energy-density solid known as biochar, and a relatively low-energy-density gas known as syngas (Bridgwater, Meier and Radlein, 1999: 1479). Pyrolysis occurs spontaneously at high temperatures generally above 300 °C, at its most extreme, pyrolysis leaves only carbon as the residue and is called carbonization (Verheijen et al., 2010: 42).

2.3.2 Pyrolysis Process Types

On the basis of operating condition, the pyrolysis process can be divided as shown in Table 2.7 and Table 2.8

Table 2.7 The Pyrolysis Technology, Parameters Employed and the Corresponding Product Distribution

| Pyrolysis Technology | Process conditions | | | Products | | |
|----------------------|--------------------|--------------|-------------|----------|----------|----------|
| | Residence time | Heating rate | Temperature | Char | Bio-oil | Gases |
| Conventional | 5.00 – 30.0 min | < 50.0°C/min | 400 - 600°C | < 35.0 % | < 30.0 % | < 40.0 % |
| Fast Pyrolysis | < 5.00 sec | ~ 1000°C/s | 400 - 600°C | < 25.0 % | < 75.0 % | < 20.0 % |
| Flash Pyrolysis | < 0.100 sec | ~ 1000°C/s | 650 - 900°C | < 20.0 % | < 20.0 % | < 70.0 % |

Source: Patwardhan, 2010: 7.

2.3.2.1 Conventional Pyrolysis or Slow Pyrolysis

It is defined as the pyrolysis which occurs under slow heating rate, low temperature and, length gas and solids residence times. Depending on the system, heating rates are about 0.100 to 2.00°C per second and prevailing temperature are around 500°C. Gas residence time may be greater than five seconds while the biomass can be range from minutes to day Sadaka (2012) The target product is often the char. Moisture content and particle size are not critical for charcoal kilns while continuous systems do specify some size reduction and drying for optimal results. Product yields from slow pyrolysis are approximately 35.0 % biochar, 30.0 % bio-oil, and 35.0 % syngas by mass (Goyal, Seal and Saxena, 2008: 504).

2.3.2.2 Fast Pyrolysis

Fast pyrolysis is characterized by high heating rates and short vapour residence times. Biomass must first be dried and ground to < 2.00 mm particle size before entering a fast pyrolyzer. Within the pyrolyzer, the biomass is heated rapidly in the absence of oxygen typically to temperatures around 500°C in less than 1 second. (Brownsort, 2009: 10).

2.3.2.3 Flash Pyrolysis

Flash pyrolysis, or very fast pyrolysis usually in the context of laboratory studies involving rapid movement of substrate through a heated tube under gravity or in a gas flow. Higher temperatures and shorter residence times than fast pyrolysis are used. Yields from flash pyrolysis are typically 60.0 % biochar and 40.0 % volatiles (bio-oil and syngas) (Demirbas and Arin, 2002: 471).

Table 2.8 Scope of Pyrolysis Process Control and Yield Ranges

| | | Slow Pyrolysis | Intermediate Pyrolysis | Fast Pyrolysis |
|----------------------------|---------|---------------------------------|------------------------|----------------|
| Feed | | Scores of feeds reported | | |
| Temperature (°C) | Range | 250 – 750 | 320 – 500 | 400 – 750 |
| | Typical | 350 – 400 | 350 – 450 | 450 – 550 |
| Time | Range | Mins – days | 1.00 – 15.0 mins | ms – s |
| | Typical | 30.0 mins – 2.00 days | 4.00 mins | 1.00 – 5.00 s |
| Yields, % wt on dry | | | | |
| Char | Range | 2.00 – 60.0 | 19.0 – 73.0 | 0 – 50.0 |
| | Typical | 25.0 – 35.0 | 30.0 – 40.0 | 10.0 – 25.0 |
| Liquid | Range | 0 – 60.0 | 18.0 – 60.0 | 10.0 – 80.0 |
| | Typical | 20.0 – 50.0 | 35.0 – 45.0 | 50.0 – 70.0 |
| Gas | Range | 0 – 60.0 | 9.00 – 32.0 | 5.00 – 60.0 |
| | Typical | 20.0 – 50.0 | 20.0 – 30.0 | 10.0 – 30.0 |

Source: Brownsort, 2009: 22.

2.3.3 Effects of Pyrolysis on Biochar Properties

Different parameters of the pyrolysis process affect quantity and quality of its products (Meyer, 2009: 10). While the focus lies on biochar, the effects on co-products have to be mentioned too, because they may be of important for energetic and socio-economic evaluations of biochar production systems (Meyer, 2009: 10).

The peak temperature controls a wide range of properties of biochar, like volatile matter content, pore structure, surface area and adsorption capabilities (Antal and Gronli, 2003: 1619). In Figure 2.4, it is shown at which temperature zones different pyrolysis processes occur, and whether they are endo - or exothermic. These zones are not fixed, but can shift a little depending on different parameters, like pressure and heating rate (Lehmann and Joseph, 2009 quoted in Meyer, 2009: 11).

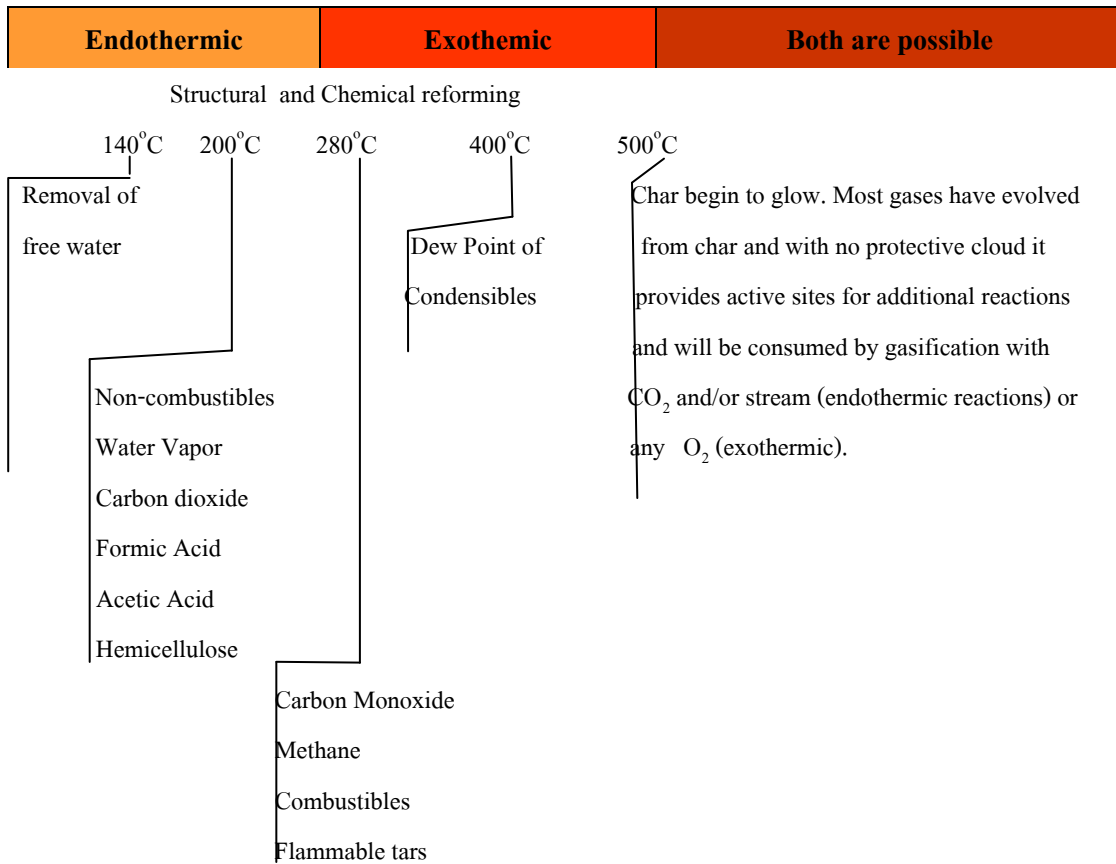


Figure 2.4 Temperature Zones of Pyrolysis

Source: Day, 2005: 2563.

Pyrolysis of biomass is a process of primary and secondary pyrolytic reactions. Primary reactions proceed in solid-phase, while secondary reactions proceed in a liquid phase. In the latter, organic vapors (tar-like) decompose onto the carbonaceous solid to secondary charcoal, which is as reactive as primary charcoal. Low gas flow provides more time for organic vapors to react with the carbonaceous solid and thus increases charcoal yields, while reducing oil and gas yields. Elevated pressures also promote secondary reactions, under higher pressure the tarry vapors have a smaller volume and can remain longer between the solid particles, and thus, have a longer time to decompose to secondary charcoal. Additionally the higher partial pressure of the tarry vapors is

increasing their reaction rate (Antal and Gronli, 2003 quoted in Meyer, 2009: 11).

Through pyrolysis most chemical bonds of the biomass are broken. Since the primary phase involves no liquefaction, these broken bonds remain in a dangling state. These dangling bonds are responsible for the chemi-sorption properties of biochar. Through the chemical absorption of oxygen, which leads to oxides and peroxides at the surface, the charcoal becomes hydrophilic. In addition, a higher oxygen content increase the electrical resistivity of carbon (Antal and Gronli, 2003 quoted in Meyer, 2009: 11).

The amount and volume of pores in biochar is increased through volatilization, which is supported by high temperature, heating rate, and gas flow, as well as by low pressure. The decrease of pore volume and amount occurs through closing of pores, through sintering and melting, which is supported by very high temperatures, high pressure, and low gas flow (Lehmann and Joseph, 2009 quoted in Meyer, 2009: 12).

A high content of inorganic materials in the biomass feedstock can block micropores in the biochar. De-ashing of the biomass can reduce this effect, and therefore increase the surface area. Steam pyrolysis removing highly reactive carbon, and thus, allows a larger pore volume (Antal and Gronli, 2003 quoted in Meyer, 2009: 12).

The density of the feedstock is proportional to the biochars density, resins can increase the density when they are coked during pyrolysis. Additionally, the biochar yield from coniferous woods can be sometimes considerably higher than from deciduous woods (Table 2.9). Also, biomass with higher lignin content allows a higher biochar yield, because lignin preferentially forms char through pyrolysis (Antal and Gronli, 2003 quoted in Meyer, 2009: 12). After pyrolysis, biochar has to cool down before it can come in contact with oxygen, or it would ignite and burn off.

Table 2.9 Summary of Pyrolysis Data for Selected Feed Stocks

| Feed | Process Type and Reference | Feed | Feed | Pyrolysis | Char | Char | Char | Gas | Gas | Gas | Liquid | Liquid | Liquid |
|------------|---|-----------|--------|-------------|-------------|-------------|---------------|-------------|--------|---------------|-------------|--------|---------------|
| | | Moisture | energy | Temperature | Yield | Energy | Energy | Yield | Energy | Energy | Yield | Energy | Energy |
| | | % wt | MJ/Kg | °C | %wt | MJ/Kg | % feed energy | % wt | MJ/Kg | % feed energy | % wt | MJ/Kg | % feed energy |
| Spruce | Fast pyrolysis, waterloo process, continuous shallow fluidized bed (Scott et al., 1999) | 7.00 | | 500 | 12.0 | | | 8.00 | | | 78.0 | | |
| Spruce | Fash pyrolysis, Lurgi-Ruhrgas twin-screw pyrolyser (Henrich, 2007) | 9.00 | 16.0 | 500 | 17.0 | | | 13.0 | | | 70.0 | | |
| Spruce | Fast vacuum pyrolysis, Pyrovac process, agitate vacuum tube (Bridgwater and Peacocke, 2000) | 15.0 | | 450 | 24.0 | | | 12.0 | | | 64.0 | | |
| Spruce | Slow pyrolysis, laboratory, sealed tube (Demiras, 2001) | | 19.770 | 377 | 32.60 | 29.340 | 48.0 | 20.20 | | | 47.20 | | |
| Miscanthus | Fast pyrolysis with partial combustion, fluidized bed (Rocha et al., 2002) | 10.0–12.0 | 17.70 | 450-500 | 12.0 - 15.0 | 20.0 - 25.0 | 17.0 | 10.0 – 12.0 | | | 70.0 - 75.0 | | |
| Miscanthus | Slow pyrolysis, laboratory, rotary kiln (Michel et al., 2006) | 9.60 | | 500 | 23.0, 28.0 | 29.0 | | 46.0, 51.0 | | | 26.0 | | |
| Miscanthus | Slow pyrolysis with steam activation, laboratory, vertical tube packed bed (Zenzi et al., 2001) | 6.60 | | 550 | 24.0 | | | 10.0 | | | 66.0 | | |

Table 2.9 (Continued)

| Feed | Process Type and Reference | Feed | Feed | Pyrolysis | Char | Char | Char | Gas | Gas | Goas | Liquid | Liquid | Liquid |
|---------------------------|---|----------------|---------------|-------------|----------------|--------|----------------|----------------|--------|----------------|----------------|---------------|----------------|
| | | Moisture | energy | Temperature | Yield | Energy | Energy | Yield | Energy | Energy | Yield | Energy | Energy |
| | | % wt | MJ/Kg | °C | %wt | MJ/Kg | % feed energy | % wt | MJ/Kg | % feed energy | % wt | MJ/Kg | % feed energy |
| Wheat Straw | Fast pyrolysis, Biotherm process, deep fluidized bed (Scott et al., 1999; Radlein and Kingston, 2007) | 1.80 | | 440-550 | 18.0 - 30.0 | | | 18.0 - 24.0 | | | 49.0 - 58.0 | | |
| Wheat Straw | Intermediate pyrolysis, Haloclean process, rotary kiln with screw (Hornung et al., 2006) | | 15.90 | 400 | 33.0 - 35.0 | 25.0 | 52.0 – 55.0 | 20.0 - 32.0 | 11.0 | 14.0 – 22.0 | 35.0- 45.0 | 12.0 | 26.0 – 34.0 |
| Wheat Straw pellets | Slow pyrolysis with steam activation, laboratory, vertical tube packed bed (Zanzi et al., 2001) | 6.90 | | 550 | 25.0 | | | 12.0 | | | 63.0 | | |
| Willow | Slow pyrolysis, laboratory, horizontal tube with silica (Leivens et al., 2009) | 10.0, 12.0 | 16.0, 14.0 | 350 | 61.0,55 .0 | | | <1.00 | | | 38.0, 45.0 | 23.0 | 55.0, 74.0 |
| Willow | Slow pyrolysis with steam activation, laboratory, vertical tube packed bed (Zanzi et al., 2001) | 7.30 | | 650 | 12.0 | | | 49.0 | | | 39.0 | | |
| Chicken Litter | Fast pyrolysis, bench scale fluidized bed (Kim et al., 2009; Mante, 2008) | 8.00 – 10.0 | 15.0 | 450,470 | 41.0,43 .0 | | | 36.0, 13.0 | | | 23.0, 43.0 | 27.0, 30.0 | 41.0, 86.0 |

Source: Brownsort, 2009: 25.

2.3.4 Production Methods

The pyrolysis of biomass is a very old technology, which is still relevant within energy production and conversion of biomass (Antal and Gronli, 2003: 1619). Traditional processes, using pits, mounds or kilns, generally involve some direct combustion of the biomass, usually wood, as heat source in the kiln (Brownsort, 2009: 10). Using earth as a shield against oxygen and to insulate the carbonizing wood against loss of heat is the oldest system of carbonization (FAO, 1987) which charcoal (biochar) can be made at places where suitable raw material was abundant (Meyer, 2009: 12) like in Figure 2.5 shows a large pit of about 30 m³ gross volume earth kiln.

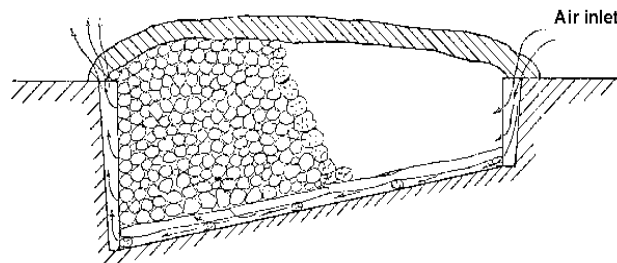


Figure 2.5 30 m³ Charcoal Pit - Longitudinal Section

Source: FAO Forestry Department, 1987.

The earth forms the necessary gas-tight insulating barrier behind which carbonization can take place without leakage of air, which would allow the charcoal to burn away to ashes (FAO, 1987). However, this kiln has a problem while maintaining over the whole period of the burn effective sealing against air, and good circulation which is difficult to detect leaks in the covering, moreover, the earth covering the pit slowly sinks during the carbonization making a danger of fatal burning to any person or animal falling or walking on the pit (FAO 1987).

On more permanent production sites, also brick kilns were developed. These kilns were better insulated, and allowed a better airflow control, which allowed higher charcoal (biochar) yields (FAO, 1987).

In the 1930's, transportable, cylindrical metal kilns were developed in Europe and became popular in the 1960's, in developing countries. They are often made out of oil drums and are more easily to handle than traditional pits. The sealed container allows a high control of airflow, and the biochar can be recovered easier (FAO, 1987).

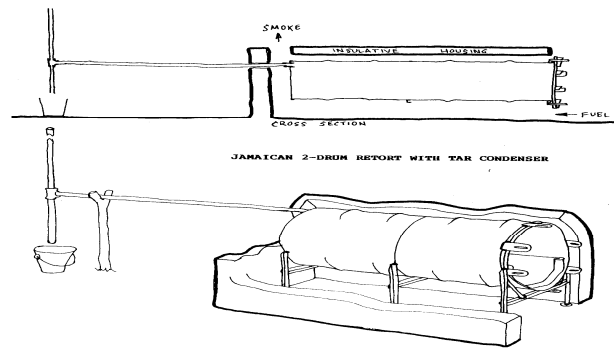


Figure 2.6 JAMICAN 2-drum Retort with Tar Condenser

Source: FAO Forestry Department, 1987.

2.3.4.1 Thailand Traditional Kiln.

Thailand is a developing country which counts on fuel wood and charcoal as a source of energy especially in rural sector. The most people who use this type of energy is lives in rural area and they have low income. This is the important energy source for their life because low price and replenishable (Prawonwan Saipan, 2004: 20) Charcoal is produced from carbonization of solid fuel such as wood. In Thailand there have many type of kiln to produce charcoal for usage in rural sector. Table 2.10 show the comparison of qualification between general block and high efficiency kiln.

Table 2.10 The Comparison of Qualification between General Block and High Efficiency Kiln

| Item | Digestion Block | Dome Block | 200 liter kilns | Unit |
|-----------------------------|-----------------|------------|-----------------|--------|
| Material price (estimation) | 50.0 | 250 | 400 | baht |
| Labors | 1.00 | 2.00 | 1.00 | capita |
| Stipend | 120 | 240 | 120 | baht |
| Wood weight (almost dry) | 500 | 500 | 80.0 | kg |
| Fuel | - | - | - | - |
| Charcoal | 70.0 | 90.0 | 16.0 | kg |
| Life time | 1.00 | 1.00 | 2.00 – 3.00 | year |
| Efficiency | 14.0 | 18.0 | 20.0 | % |

Source: Appropriate Technology Association (ATA), 2003: 99.

2.3.4.2 Qualifications of high efficiency kiln.

The high efficiency kilns was use 200 liter capacity as a burning tank. Its use heat to evaporate moisture in wood to become a charcoal. This process called “Carbonization”. The tightly seal tank can control excess air and has not be in flame. So, the burned product is good qualification and low ash and obtains the wood vinegar as by product for agricultural utilization. The major characteristics of this kilns are summarized as below (ATA, 2003 quoted in Prawonwan Saipan, 2004: 22).

1) Raw Material and Equipment

The fuel wood is most available. It can use small size wood and not require fuel wood too much. Besides, the burned tank is easily maintenance and long life. The composition of equipment is available in general construction equipment shop as shown in table 2.11

Table 2.11 The Equipment of High Efficiency Kilns

| Item | Size | Material | Amount | Price (Baht) |
|-------------------------------|--------------------------------|---------------------------------|--------------------|--------------|
| Burned tank | 200 liter | Oil tank 200 liter size | 1 tank | 250 |
| Front wall tank | 1.2 x 1.2 m ² | Tile, galvanized iron, wood* | 3 sheet | - |
| Post | Diameter 3 inch, Length 1.2 m. | Tile, galvanized iron, wood* | 1 sheet | - |
| Insulator | 0.7 m ³ | Soil or sand* | 0.7 m ³ | - |
| Stack | Diameter 4 inch, Length 1 m. | Rock wool pipe | 1 piece | 60 |
| Stack bend | 90 Bend, Diameter 4 inch | Rock wool pipe | 1 piece | 25 |
| Brick | 40 cm. x 19 cm. x 7 cm. | Stone flake mixed with concrete | 5 piece | 25 |
| Wood vinegar - collected pipe | Diameter 4 inch, Length 5 m. | Bamboo* | 1 piece | - |

Note: *Materials which available in local area (have no price)

Source: Prawonwan Saipan, 2004: 23.

2) Production Process

The burning process of high efficiency kiln is spend time for 1 day. It can control level of air and produce low ash. The processing is consists of composition and installation, wood loading, front kilns composition, and burning charcoal. All processes are using only one labor. The burning process is compose of 4 phase as described below (Adapted from Prawonwan Saipan, 2004: 23-25).

(1) First Phase: Dehydration

(1.1) Initial set on fire in front of burned tank

(1.2) Load fuel carefully. Heat will disperse in fuel tank to drive cool air and dehydrate. The temperature of stack and burned tank are 55.0 – 60.0°C and 150°C respectively. The smoke is white and smells of Methanol acid in wood.

(1.3) Continuous load fuel carefully. The Temperature of stack and burned tank are 70.0 – 75.0°C and 200 – 250°C respectively. The white smoke will increase and odor (spend 2.00 – 3.00 hours).

(2) Second Phase: Exothermic Reaction

(2.1) When continuous burning for a while, the white smoke will become gray. The temperature of stack and burned tank are 80.0 – 85.0°C and 300 – 400°C respectively. Wood will have an exothermal reaction and temperature in burned tank will increase. In this phase, reduce fuel loading.

(2.2) After stop fuel loading, it has to control the air by reduce front tank area to 20.0 – 30.0 m² for temperature level keeping and extend time to collect wood vinegar. The most suitable time for wood vinegar collecting, stack temperature is 82.0 – 120°C. After that, the gray smoke will become dark blue. The temperature of stack and burned tank are 400 – 450°C respectively. The suitable time for wood vinegar collecting can taste by use white glazed tile place near the stack ending. If it has brown clear drop at glazed tile, this can collect wood vinegar immediately and continue collect for 4 hours.

(3) Third Phase: Refinement

(3.1) This phase needs exclusive careful because it is concern to amount of ash. Wood will become completely charcoal. It needs to increase temperature rapidly by open one-third of front area for 30.0 minutes.

(3.2) Observe the end of stack. If dark blue smoke became light blue, it means wood has become completely charcoal. The light blue smoke will will fade away and adhering rubble inner stack will dry. Temperature is about 500°C. Finally, the light blue smoke will become clear.

(3.3) When the smoke is clear, close the front area by use clay filling the hole. Then, close the stack and do not let the air leak into kilns.

(4) Forth Phase: Cooling

Spread out the soil on kilns for release the heat. Live it 1 night or 8.00 hours at least for complete burning. Then, open the kilns and pick up the charcoal, dry in sun for 1.00 hour, and packing.

2.3.5 Relative Literature about Pyrolysis Biomass

In the studied of Novak et al. (2009: 195) about characterization of designer biochar produced at different temperatures and their effects on a loamy sand. They produced biochars from peanut hulls, pecan shells, poultry litter, and switchgrass at temperatures ranging from 250°C to 700°C, mixed at 2.00 % w w⁻¹ with a Norfolk loamy sand and were laboratory incubated to examine changes in the Norfolk's soil properties. They found that "higher pyrolysis temperatures results in lower biochar mass recovery, greater surface areas, elevated pH, higher ash contents, and minimal total surface charge". Furthermore, the studied found that "removal of volatile compounds at the higher pyrolysis temperatures also caused biochars to have higher percentages of carbon but much lower hydrogen and oxygen contents". ¹³C NMR spectral analyses confirmed that aliphatic structure losses occurred at the higher pyrolysis temperatures, causing the remaining structures to be composed mostly of poly-condensed aromatic moieties. Biochars produced at higher pyrolysis temperatures increased soil pH values, while biochar made from poultry litter feedstock grossly increased Meclich-1 extractable phosphorus and sodium concentrations. Water-holding capacity varied after biochar incorporation. They suggested that biochars produced from different feedstocks and under different pyrolysis conditions influenced soil physical and chemical properties in different ways; consequently, biochars may be designed to selectively improve soil chemical and physical properties by altering feedstocks and pyrolysis conditions.

Chen and Chen (2009: 127) evaluated and compared sorption of naphthalene and 1- naphthol in water by biochars derived from pyrolysis orange peels at 150 – 700°C (150 – 700°C referred to OP150 – OP700) characterized via elemental analysis, BET-N₂ surface area, and Fourier transform infrared spectroscopy. Sorption isotherms varied from linear to Freundlich with increasing pyrolysis temperature. The respective

contributions of adsorption and partition to total sorption were correlated with biochar's structural parameters. For OP 150 – OP600, sorption of 1– naphthol with high concentrations, the OP200 exhibited the maximal sorption capacity due to its largest partition and high adsorption among nine biochars. For 1– naphthol with low concentrations and naphthalene, the OP700 displayed the maximal sorption capacity. These observations provide a reference to the use of biochars as engineered sorbents for environmental applications.

Cao and Harris (2010: 5222) studied about the properties of dairy – manure – derived biochar pertinent to its potential use in remediation. In this studied, produced BC from dairy manures by heating at low temperatures ($\leq 500^{\circ}\text{C}$) and under abundant air condition. The resultant BC was characterized for physical, chemical, and mineralogical properties specifically related to its potential use in remediation. The BC was rich in mineral elements such as N, Ca, Mg, and P in addition to C, and concentrations of C and N decreased with increasing temperature as a result of combustion and volatilization; while P, Ca, and Mg increased as temperature increased. For example, C significantly decreased from 36.8 % at 100°C to 1.67 % at 500°C ; whereas P increased from 0.910 % to 2.66 %. Water soluble P, Ca, and Mg increased when heated to 200°C but decreased at higher temperatures likely due to increased crystallization of Ca – Mg – P, as supported by the formation of whitlockite $(\text{Ca,Mg})_3(\text{PO}_4)_2$ following 500°C treatment. The presence of whitlockite was evidenced by X-ray diffraction analysis. Quartz and calcite were present in all BC produced. The BC showed appreciable capability of adsorption for Pb and atrazine from aqueous solution, with Pb and atrazine removal by as high as 100 % and 77.0 %, respectively. The resulted indicated that dairy manure can be converted into biochars as an effective adsorbent for application in environmental remediation.

2.4 Biochar and Poultry Production

With the intensification of poultry farming of chicken excreta is continuously produced and accumulated in the environment. Unless, it is properly disposed of, or utilized, it poses a potential pollution hazard. But if properly managed and utilized, chicken manure could be a valuable agricultural resource as a fertilizer by virtue of its

easily degradable compounds and low C/N ratio (Abdel-Magid, Al-Abdel, Rabie and Sabrah, 1995: 413). It is readily biodegraded when added to soils under conducive conditions of temperature and soil moisture. Abdel Magid et al. (1995: 413) used chicken manure as a bio-fertilizer for wheat in the sandy soils of Saudi Arabia during the winter seasons of 1990/91 and 1991/92 examine the yield and quality responses of wheat. The results showed the profitable grain yield corresponded to the manure rate of 8.25 t ha⁻¹. According to Moss et al. (2001: 43) found comparable between broiler litter used as fertilizer (BLF) to commercial fertilizer (CF) on corn silage and grain yield in corn hybrids. The results showed prolong efficiency of BLF than CF in long term used. Also, Tawadchai Suppadit et al. (2006) used pelleted broiler litter (PBL) with chemical fertilizer (CF) formula 12 – 24 – 12 at substitution levels of 0, 25.0, 50.0, 75.0 and 100 % by weight, following suggested PBL (175.0 g basin⁻¹) and CF (10.0 g basin⁻¹) rates. The results showed that CF can be replaced with PBL in soybean production. Higher percentages of PBL resulted in higher nutrients left in the soil. The substitution level of 75.0 percent by weight was the best to harness the potential productivity of soybeans and performed better than CF alone. However, they not advisable to substitute PBL at levels higher than 75.0 % by weight.

Furthermore, chicken manure still have properly in ameliorate the soil acidity. Such studied belong to Materechera and Mkhabela (2002: 9) applied chicken manure as a acidic soil amendment compare with lime and leaf litter ash. The resulted showed all the three amendments caused significant increases in soil pH and reduced the exchangeable acidity. The liming effectiveness of the amendments varied with rate and type of amendment and were in the order: lime > chicken manure > ash. Other workers have also shown that poultry manure could increase soil pH due its high CaCO₃ content (Mokolobate and Haynes, 2002: 79). Another mechanism that could also have contributed to the increase in soil pH in the chicken manure amended soil could be related to ligand exchange between hydroxyl groups on Al and Fe hydrous oxides and the low molecular weight organic acids/humic substances produced during the decomposition of manure (Hue and Amien, 1989: 1499). Organic amendments contain humic substances with functional groups such as carboxyl and phenolic groups that from during decomposition.

Recently studied of Liu, Chen, Cai, Liang and Huang (2009: 563) found an efficiency in remediate metal contaminate soil by chicken manure composted. They conducted the experiment to evaluate the effect of compost application on immobilization and biotoxicity of cadmium in winter wheat (*Triticum aestivum* L.) potted soils. Soils treated with various levels of Cd (0 – 50.0 mg Cd kg⁻¹ soil) were amended with 0, 30.0, 60.0 and 120 g compost kg⁻¹ soil. The result showed an effectiveness of chicken manure compost in reducing the phytotoxicity of Cd by decreasing more than 70.0 % uptake by wheat tissue and improving wheat growth. Alleviation of Cd phytotoxicity by compost was attributed primary to the increase of soil pH, complexation of Cd by organic matter and co-precipitation with P content.

As we known that Biochars refer to the carbon-rich materials produced from the pyrolysis (heating in the absence of oxygen) of biomass. Recently, there has been much interest in biochars as soil amendments to improve and maintain soil fertility and to increase soil carbon sequestration (Glaser et al., 2002a: 219, 2002b: 421; Lehmann et al., 2003: 343). The latter can be attributed to the relative stable nature and, hence, long turnover time of biochar in soil is of particular relevance to the solution of climate change (Lehmann et al., 2006: 403).

Biochars can be produced from a range of organic materials and under different conditions in products of varying properties (Nguyen, Brown and Ball, 2004: 217; Guerrero, Ruiz, Alzueta, Bilbao and Millera, 2005: 307) and, therefore, of different soil amendment values. Biochars from plant materials are often low in nutrient content, particularly N, compared with other organic fertilizers (Chan, Van Zwieten, Meszaros, Downie and Joseph, 2007b: 629). Due to the generally higher nutrient content of animal wastes than plant wastes (Shinogi, 2004), biochars produced from animal origins may have higher nutrient content.

Poultry litter refers to the mixture of poultry manure and bedding material from poultry farms. In Thailand and elsewhere, it has been widely used by farmers, e.g. vegetable growers, as a source of plant nutrients. However, there are food safety and environmental concerns about it's application on agricultural land in unmodified forms (Wilkinson, 2003: 35; Chan, Dorahy, Tyler, Wells, Miham and Barehia, 2007a: 139). Wilkinson (2003: 37) recommended only composted poultry litter should be used for side-dressing of vegetable crops because of possible pathogen contamination. Several recent studies (Vories, Costello and Glover, 2001: 1495; Chan et al., 2007a: 629) have

associated land applications of poultry litter with a higher potential risk of phosphorus contamination to surface waters. Conversion of poultry litter to biochar using pyrolysis could be a safer and more effective alternative to utilize this resource in agriculture and soil contaminated remediation.

2.5 Relative Literature

Mulan and Farrant (1998: 445) examined the effect of cadmium and nickel on soybean seed development, they found that both metals markedly reduced plant biomass and seed production. Accumulation was mostly in the roots. Nickel was more mobile than Cd, reaching higher levels in all plant parts, especially seeds, moreover Cd reduced mature seed mass, decreased yields of lipids, protein and carbohydrates.

Sheirdill, Bashir, Hayat and Akhtar (2012: 1886) studied the effect of cadmium on soybean growth and nitrogen fixation, they found that application of Cd adversely affected soybean growth, nodulation and N₂ fixation as a function of time and increase in Cd concentration. Maximum reduction in the root and shoot length was found with higher Cd level at 16.0 mg kg⁻¹ sand after 10 weeks of the growth nodulation and the proportion of plant N derived from N₂ fixation decreased sharply as Cd concentrations increased during the whole growth stages and the maximum reduction was observed in the Cd level of 16.0 mg kg⁻¹ sand followed by 8.00 and 4.00 mg kg⁻¹ sand, respectively.

Dobroviczka, Piršelová and Matušgiková (2012) evaluated the morphological and physiological aspects of defense responses in the leaves of two soybean varieties *Glycine max* (L) Merr.cv. Bólyi 44 and cv. Cordoba upon exposure to cadmium ions 50.0 mg kg⁻¹ of soil substrate. They confirmed the negative effect of applied dose of cadmium on the morphological and physiological of epidermal cells of soybean in different developmental stages of leaves, epidermal cells responses to metal included closure and reduction of the size of stomata and increase of their number. They found that Cordoba variety had more tolerant to the tested metal.

Khan, Srivastava, Abdin, Manzoor and Zafar (2013: 707) studied the effect of soil exposure to cadmium and mercury on soybean seed oil quality, they found that heavy metals significantly reduces the oil content when applied separately, while the interactive effect of heavy metal showed less decrease in oil content and showed antagonistic impact of heavy metal on oil content. They also revealed considerable

changes in major and minor fatty acids of the soybean seeds, amounts of fatty acid such as oleic acid, linoleic acid was decreased while the fatty acids such as palmitic acid, stearic acid and linoleic acid were increased due to increasing concentration of heavy metals.

Chen, He, Yang, Yu, Zheng, Tian, Luo, and Wong (2003: 781) reveal that nodulation of soybean roots was greatly inhibited by the addition of Cd, especially at the addition level of 10.0 and 20.0 mg Cd kg⁻¹soil. The inhibition of plant growth especially the root growth increased as the cadmium concentration increased. The weight ratio of soybean root/leaf decreased as the Cd concentration increased. The results reveal that the content of Cd in different parts of the plants was as follows: roots >> stems >> seeds, indicating that the accumulation of Cd by roots is much larger than that any other part of the soybean plant, and might cause deleterious effects to root systems.

Abdo, Nassar, Gomaa and Nassa (2012: 24) obtained results that all concentrations of Cd induced significantly decrease in all characters of vegetative growth (plant height, number of branches, leaves, total leaf area/plant, and shoot dry weight part⁻¹) and in all studied yield characters (number of pods and seeds plant⁻¹, specific seed weight and seed yield plant⁻¹) of soybean 'Giza 35'. Moreover, the significant decrease in morphological and yield characters got higher as the concentration of Cd increased in irrigation water.

Biochar, a form of environmental black carbon resulting from incomplete burning of biomass, can immobilize organic contaminants by both surface adsorption and partitioning mechanisms. The predominance of each sorption mechanism depends upon the proportion of organic to carbonized fractions comprising the sorbent.

Lima and Marshall (2005: 699) pyrolyzed broiler litter and cake at 700°C followed by steam activation in an inert atmosphere, producing 18.0 – 28.0 % AC with surface area ranging from 253 to 548 m² g⁻¹. The broiler cake-based AC with surface area ranging from 253 to 548 m² g⁻¹. The broiler cake-based AC exhibited a high affinity for Cu (adsorption capacity of up to 1.92 mmol g⁻¹ C⁻¹). Further work indicated that turkey manure derived AC has similar yield and surface area to the AC produced from broiler waste and showed a considerable potential to remove Cu from water (Lima and Marshall, 2005b). In another experiment, the poultry manure-based AC was shown to adsorb Cd and Zn in addition to Cu (Lima and Marshall, 2005b).

Mohan et al. (2007: 57) investigated the adsorbents for the removal of toxic metal arsenic (As^{3+}), cadmium (Cd^{2+}) and lead (Pb^{2+}) from water used oak bark, pine bark, oak wood and pine wood chars derived from fast pyrolysis at 400 – 500°C in auger – fed reactor compare with commercial activated carbon. The result reveal that maximum adsorption occurred over a pH range 3.00 – 4.00 for arsenic and 4.00 – 5.00 for lead and cadmium. An optimum equilibrium time of 24 h with and adsorbent dose of 10.0 g L⁻¹ and concentration approximately 100 mg L⁻¹ for Pb and Cd. Oak bark out-performed the other chars and removed similar amounts of Pb and Cd from solution as did a commercial Ac material. Oak bark 10.0 g L⁻¹ also removed about 70.0 % of As and 50.0 % of Cd from aqueous solutions. The oak bark char's ability to remove Pb and Cd in terms of amount of metal adsorbed per unit surface area 0.516 mg m² for Pb and 0.213 mg m² for Cd versus that of commercial activated carbon.

Cao, Ma, Gao and Harris (2009: 3285) evaluated the ability of dairy-manure derived biochar prepare by heating at low temperature of 200°C (BC200) and 350°C (BC300) to sorb heavy metal Pb and organic contaminant atrazine. The untreated manure (BC25) and a commercial activated carbon (AC) were the controls. Chemical speciation, X-ray diffraction, and infrared spectroscopy indicated that Pb was precipitated as $\beta\text{-Pb}_9(\text{PO}_4)_6$ in BC25 and BC200 treatment, and as $\text{Pb}_3(\text{CO}_3)_2$ in BC350. The biochar was 6 times more effective in Pb sorption than AC. BC200 being the most effective up to 680 mmol Pb kg⁻¹. The biochar also effectively sorbed atrazine where atrazine was partitioned into its organic phase, whereas atrazine uptake by AC occurred via surface sorption. The researcher concluded that dairy manure can be converted into value-added biochar as effective sorbent for metal and/or organic contaminants.

Guo, Qiu and Song (2010: 308) revealed that poultry litter-based activated carbon possessed significantly higher adsorption affinity and capacity for heavy metals than commercial activated carbons derived from bituminous coal and coconut shell. The poultry litter was palletized used hydrated chicken fat as a binding agent. The pelleted were 0.500 cm diameter by 0.400 - 4.00 cm length in size and contained 28.5 % incombustible ash and 71.5 % organic matter. Total N, P, and K contents in the pelleted were 30.7, 15.1, and 41.8 g kg⁻¹, respectively. The contents of Cu, Zn, Pb, and Cd were 611, 628, 8.00, and 0.200 mg kg⁻¹, respectively. The poultry litter pelleted

were converted into AC followed the procedure reported by Lima and Marshall (2005b) with slight optimization: after dehydration at 170°C for 1.00 h, the material was pyrolyzed at 700°C for 45.0 min under a N₂ atmosphere and then activated at the same temperature for 45.0 min with steam flow of 2.50 ml min⁻¹. The product was washed with 0.100 M HCl, rinsed with water, and oven-dried at 105°C. The final product yield was 31.3 %. The poultry litter-derived AC contained 5.80 g kg⁻¹ total N and 29.3 g kg⁻¹ total P. Its Cu, Zn, Pb, Cd, and As contents were 2027, 1371, 11.0, 0.500, and 57.0 mg kg⁻¹, respectively. Adsorption of metal ions onto poultry litter-based carbon was rapid and followed Sigmoidal Chapman patterns as a function of contact time. Potentially 404 mmol of Cu²⁺, 945 mmol of Pb²⁺, 236 mmol of Zn²⁺, and 250 - 300 mmol of Cd²⁺ would be adsorbed per kg of poultry litter-derived activated carbon. Releases of nutrients and metal ions from litter-derived carbon did not pose secondary water contamination risks. The studied suggested that poultry litter can be utilized as a precursor material for economically manufacturing granular activated carbon that is to be used in wastewater treatment for removing heavy metals.

Hossain, Strezov, Chan and Nelson (2010: 1167) had investigated and quantify of biochar derived from pyrolysis wastewater sludge at a temperature of 550°C used 10.0 t ha⁻¹ on soil quality, growth, yield and bioavailability of metals in cherry tomatoes. The results showed that the application of biochar improves the production of cherry tomatoes by 64.0% above the control soil conditions. The ability of biochar to increase the yield was attributed to the combined effect of increased P and N and improved soil chemical conditions and also increase EC upon amendment. The yield of cherry tomato production was found to be at its maximum when biochar was applied in combination with the fertilizer. Bioavailability of metals present in the biochar was found to be below the Australian maximum permitted concentrations for food.

Major, Rondon, Molina, Riha and Lehmann (2010: 117) studied the effect of biomass derived biochar 0, 8.00 and 20.0 t ha⁻¹ to Colombian savanna Oxisol for 4 years (2003 – 2006 A.D.) under a maize-soybean rotation. Soil sampling to 30.0 cm was carried out after maize harvest in all years but 2005 A.D., maize tissue samples were collected and crop biomass was measured at harvest. They found that maize

grain yield did not significantly increase in the first year, but increase in the 20.0 t ha⁻¹ plots over the control were 28.0, 30.0 and 140 % for 2004, 2005 and 2006 A.D., respectively. The availability of nutrients such as Ca and Mg was greater with biochar, and crop tissue analyses showed that Ca and Mg were limiting in this system. Soil pH increased, and exchangeable acidity showed a decreasing trend with biochar application. The attributed that the greater crop yield and nutrient uptake primarily to the 77.0 – 320% greater available Ca and Mg in soil where biochar was applied.

Uchimiya, Lima, Klasson, Chang, Wartelle and Rodgers (2010b: 5538) employed broiler litter manure that underwent pyrolysis at 350°C and 700°C as a sorbents for heavy metal (Cd^{II}, Cu^{II}, Ni^{II}, and Pb^{II}) immobilization in water and soil. ATR-FTIR, ¹H NMR, and Boehm titration results suggested that higher pyrolysis temperature and activation lead to the disappearance (e.g. aliphatic- CH₂ and CH₃) and the formation (e.g. C – O) of certain surface functional groups, portions of which are leachable. Both in water and in soil, pH increase by the addition of basic char enhanced the immobilization of heavy metals. Heavy metal immobilization resulted in nonstoichiometric release of protons, that is, several orders of magnitude greater total metal concentration immobilized than protons released. The results suggested that with higher carbonized fractions and loading of chars, heavy metal immobilization by cation exchange become increased outweighed by other controlling factors such as the coordination by π electrons (C=C) of carbon and precipitation.

Beesley and Marmiroli (2011: 474) was explored the capability of biochar to immobilize and retain As, Cd and Zn from the column leaching experiment and scanning electron microanalysis on a multi-element contaminated sediment derived soil. They found that “sorption of Cd and Zn to biochar’s surfaces assisted a 300 and 45-fold reduction in their leachate concentrations, respectively. They concluded that biochar can rapidly reduce the mobility of selected contaminants in polluted soil system, especially encouraging results for Cd”.

Fellet, Marchiol, Delle Vedove and Peressotti (2011: 1262) proposed biochar derived from pyrolysed prune residues at 500°C at four dosages 0 %, 1.00 %, 5.00 % and 10.0 % mixing with mine tailing from dumping site in Cave del Predil, Italy. The result reveal that pH, CEC and the water-holding capacity increased as the biochar

content increased in the substrates and the bio-availability of Cd, Pb, Tl and Zn of the mine tailings decreased.

Trakal, Komárek, Száková, Zemanová and Tlustoš (2011: 372) used biochar derived from stem of willow pyrolyzed at 400°C apply in 1.00 % and 2.00 % w/w to Cd, Cu, Pb, and Zn contaminated soil. The obtained results proved the different sorption behavior of metals in the single-metal solution compared to the multi-metal ones due to competition effect. Moreover, during multi-element sorption, Zn was significantly desorbed. The applied biochar enhance Cu and Pb sorption and no changes were observed when contaminated and uncomtaminated biochar was used. Furthermore, the application rate had no effect as well.

Uzoma, Inoue, Fujimaki, Zahoor and Nishihara (2011: 1) investigated the effect of biochar derived from dry cow manure pyrolysed at 500°C on maize yield, nutrient uptake and physic-chemical properties of a dry land sandy soil at mixing rate 0, 10.0, 15.0 and 20.0 t ha⁻¹, found that 15.0 and 20.0 t ha⁻¹ mixing rate significantly increased maize grain yield by 150 and 98.0 % as compared with control, respectively. Nutrient uptake by maize grain was significantly increased with higher biochar applications.

Uchimiya, Chang and Klasson (2011: 432) had screening biochars derive from cottonseed hull and Broiler litter, they found that biochar increasing Oxygen-containing carboxyl, hydroxyl, and phenolic surface functional groups of soil organic and mineral components play central roles in binding metal ions. Positive Matrix Factorization (PMF) analysis indicated that effective heavy metal stabilization occurred concurrently with the release of Na, Ca, S, K, and Mg originating from soil and biochar, in weathered acidic soil, the heavy metal (Cu, Ni, Cd, Pb) stabilization ability of biochar directly correlated with the amount of oxygen functional groups.

Nigussie, Kissi, Misganaw and Ambaw (2012: 369) had investigated the effect of maize stalk biochar produced at 500°C pyrolysis temperature applied at rate 0, 5.00 and 10.0 t ha⁻¹ on soil soil artificially polluted with chromium at the level of 0, 10.0 and 20.0 ppm. They found that pH, EC, organic carbon, total nitrogen, available phosphorous, CEC and exchangeable based were increase significantly ($p < 0.01$). Moreover, uptake of nitrogen, phosphorous and potassium were increased too. Chromium reduced significantly ($p < 0.01$) due to application of biochar. They concluded that application biochar increase soil fertility, enhance nutrient uptake,

ameliorate chromium polluted soil and reduce amount of carbon produced due to biomass burning.

Schimmelpfennig and Glaser (2012: 1001) used 16 different feedstock materials to create 66 biochars produced from five different pyrolytic processes (traditional charcoal stack, rotary kiln, Pyreg reactor, wood gasifier, and hydrothermal carbonization) to derive a minimum analytical dataset for assessing the potential use of biochar as a soil amendment and for carbon sequestration. On the basis of their results, the authors suggest that biochars containing the following will be effective C sequestration agents when applied to soils: O:C ratio < 0.400 , H:C ratio < 0.600 (O:C:H ratios serve as an indicator for the degree of carbonization that influences the stability of biochar in soil environments); black carbon content $> 15.0\%$ C, Brunauer-Emmett-Teller surface area $> 100 \text{ m}^2\text{g}^{-1}$ and recommend that biochar PAHs be less than background levels in soils for its utilization as a soil amendment.

Hass et al., 2012: 1096) suggestion about using a slow pyrolysis chicken manure biochars produced at 350 and 700°C with and without subsequent steam activation, evaluated in an incubation study as soil amendments for a representative acid and highly weathered soil mixed at 5.00, 10.0, 20.0, and 40.0 g kg⁻¹ into a fine-loamy soil incubated in a climate-controlled chamber for 8 weeks. The results showed biochar increased soil pH from 4.80 to 6.60 at the high application rate, biochar produced at 350°C without activation had the least effect on soil pH. Biochar increased soil micro- and macronutrients. Increase in pyrolysis temperature and biochar activation decreased availability of K, P, and S compared to nonactivated biochar produced at 350°C furthermore biochar increased dissolved organic carbon, total N and P, PO, SO, and K at high application rate (40.0 g kg⁻¹).

Tawadchai Suppadit, Viroj Kitikoon, Anucha Phubphol and Penthip Neumnoi (2012: 244) used quail litter biochar (QLB) at rate 0, 24.6, 49.2, 73.8, 98.4 and 123 g per pot mixture provided to soybean cv. Chiang Mai 60. The results showed QLB could be used as a soil fertility improvement and amendment for soybean production with an optimum rate of 98.4 g per pot mixture, which gave the best performance in terms of number of nodes, height, dry matter accumulation, total yield, and seed quality. QLB at higher than 98.4 g per pot mixture is not advisable to be used because QLB is alkaline in nature, which may affect soil pH.

Tawadchai Suppadit, et al., (2012: 125) investigated the effects of quail litter biochar (QLB) on the availability of Cd to physic nut (*Jatropha curcas* L.) plants. QLB was applied to the soil in which four new physic nut varieties (Takfa, Doi Saket, Lao, and Ranong) in factorial combinations at four levels (0, 5.00, 10.0, and 15.0 g kg⁻¹soil) to soil that contain 60.8 mg Cd kg⁻¹. They found that addition of QLB to soil caused a significant increase in the soil' growth potential and physic nut yield components ($p < 0.05$), a significant decrease in the Cd residue in the plant ($p < 0.05$), and a significant increase in the chemical characteristics, nutrients, and Cd residue in soil ($p < 0.05$). They conclude that QLB application can significantly decrease the bioavailability of Cd to physic nut plants, increase plant growth potential and yield, and has potential to remediate Cd contaminated soil. However, QBL levels higher than 15.0 g kg⁻¹ soil mixture were not advisable because QLB is alkaline in nature, and this can affect soil pH.

Zhang, Solaiman, Meney, Murphy and Rengel (2012: 140) purposed biochars on soil Cd immobilization and phytoavailability, growth of plants, and Cd concentration, accumulation, and translocation, in plant tissues in Cd contaminated soils under water logged conditions. They found that after 3 weeks of soil incubation, pH increased and CaCl-extractable Cd decreased significantly with biochar additions. After 9 weeks of plant growth, biochar additions significantly increased soil pH and electrical conductivity and reduced CaCl-extractable Cd. EDTA extractable soil Cd significantly decreased with biochar additions, in the high Cd treatment, but not in the low Cd treatment. Growth and biomass significantly decreased with Cd additions and biochar additions did not significantly improve plant growth regardless of biochar type or application rate. They concluded that addition of biochars reduced Cd accumulation, but less on Cd translocation in plants, at least in the low contaminated soils.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The materials of the study are listed as follow:

3.1.1 Experimental Apparatuses

3.1.1.1 Fresh broiler litter used were bought from broiler farms located in Saraburi Province.

3.1.1.2 A sample of (0 to 20.0 cm. layer) soil was collected randomly within Tumbon Promanee, Mueng district, Nakornnayok province, Thailand.

3.1.1.3 $\text{CdCl}_2 - 2.5 - \text{H}_2\text{O}$ was used without further purification. Stock solutions of Cd were prepared in distilled water at desired concentrations prior to sowing. Stock solutions were diluted with distilled water to obtain suitable concentrations of test chemicals. Cd was added to the soil (in the solution) before sowing.

3.1.2 Experimental Instruments

3.1.2.1 The pelleting machine from the Siriwan Company Limited located in Ta Tum sub-district, KaengKhoi District, Saraburi Province.

3.1.2.2 The 200-liter-oil-drum-kiln from Wihandang Chacoal Small and Medium Enterprises, Wihandang District, Saraburi Province.

3.1.2.3 The laboratory-scale pyrolysis located in the Land Development Regional Office 1, PathumThani Province.

3.1.3 Places and Experimental House

3.1.3.1 A shed for air-dried broiler litter before and after pelleting was conducted at Siriwan Company Limited located in Ta Tum sub-district, KaengKhoi district, Saraburi province.

3.1.3.2 The pyrolysis process conducted in Nakornayok Province.

3.1.3.3 The sheds used in the experiment of mixing the soil with PBLBL and PBLBO and inoculated with Cd was conducted in Mueng District, Nakhonayok Province.

3.2 Methods

The sequences and methods of the study are described as follow:

3.2.1 Research Design

The experiments were carried out under laboratory conditions. Set up in a 2 x 5 x 4 factorial arrangements plus the control group with 4 replications in a completely randomized design. The first factor being the Pelleted Broiler Litter Biochar derived from laboratory-scale pyrolysis reactor (PBLBL) and Pelleted Broiler Litter Biochar derived from 200 liter oil drum kiln (PBLBO). The second factor is the ratios of PBLBL and PBLBO in soil mixed with Cd inoculation at 0, 20.0, 40.0, 60.0 and 80.0 mg Cd kg⁻¹ soil. The third factor is the mixing rate of PBLBL and PBLBO and soil with mixing rate 5.00, 10.0, 15.0 and 20.0 t ha⁻¹, plus the control group.

3.2.2 Soil Preparation and Analysis

Soil samples were collected from the surface layer (0 to 20.0 cm in depth) using an auger 75.0 mm in diameter during February 2011. The soils were collected randomly from within the Tumbon Promanee, Mueng district, Nakornayok province, Thailand. Samples were thoroughly mixed, air-dried, and passed through a 2.00 mm sieve prior to laboratory analyses. The physical and chemical characteristics of the soils were analyzed at Agricultural Chemistry Division, Bangkok, Thailand. The soils characteristics include: % moisture, pH, electric conductivity (EC), organic matter (OM), total nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium

(Mg), carbon nitrogen ratio (C/N ratio), cation exchange capacity (CEC) and cadmium (Cd) residual in soils. Soil that was used was mixed with PBLBL and PBLBO in 4 mixing rate: 5.00, 10.00, 15.0 and 20.0 t ha⁻¹, plus a control group that was 100% soil per pot. The total soil weight/pot is 10.0 kg.

3.2.3 Broiler Litter Random Sampling

Six broiler farms were randomly selected; by having broilers of the same domesticated age, from the same periods of time, and have similar area ratio. From each broiler farm, 1,000 kilograms of broiler litter was collected for the study.

3.2.4 Pelleting Operation

After air-dried, broiler litter were pelleted by the pelleting machine. The pelleting operation produced heat up to 85.0 – 95.0 °C at the die and the pellet size was 6.00 mm in diameter and 2.00 cm in length according to the method of Suppadit and Panomsri (2010: 441).

3.2.5 Mixing and Cd Inoculation Method

CdCl₂ – 2.5 – H₂O was used without further purification. Stock solutions of Cd were prepared in distilled water at desired concentrations prior to sowing.

Stock solutions were diluted with distilled water to obtain suitable concentrations of test chemicals. Cd at various mixing rate 0, 20.0, 40.0, 60.0 and 80.0 mg kg⁻¹ soil was added into the solution and to the soil before sowing.

3.2.6 Mixing and Pyrolysis Method

Pelleted broiler litter (PBL) were randomized and separated into 2 groups. Group 1 was PBLBL that was pyrolyzed PBL in the lab-scale pyrolysis reactor. Group 2 was PBLBO that pyrolyzed in 200-liter-oil-drum-kiln. Both kilns was heated until the PBL temperature reached 500°C with a residence time of 24 hours. After four-to-five hours, the PBLBL and PBLBO cooled down to room temperature and the reactor was opened to collect char. Afterwards, group 1 was mixed with soil at various mixing rate 5.00, 10.0, 15.0 and 20.0 t ha⁻¹. Group 2 was mixed with soil at various mixing rate similarly to group 1.

3.2.7 Soybean Plant Preparation

The soybean cultivar Chiang Mai 60 (CM.60) seeds were planted in each plastic pot then thinned one week after emergence, leaving four seedlings per pot. These were watered until the R7 stage (beginning maturity).

3.2.8 Pot Experiment

The pot experiment was carried out to study the effects of PBLBL and PBLBO on soybean growth and Cd sorption. Each pot contained 4 seedlings per pot.

3.2.9 Water Management

Watered every three day or when the top layer soil was dry. Watered until the R7 stage (beginning maturity)

3.2.10 Weed Management

The entire pot area was weeded by hand.

3.2.11 Pest Management

Tobacco was used for insect control.

3.2.12 Soybean Growth Measurement

Data that were recorded are planting dates, stage of emergence, number of nodes, height, leaf area, dry matter, yield ($4 \text{ plants pot}^{-1} \times \text{pods plant}^{-1} \times \text{seed pod}^{-1} \times 1 \text{ seed weight}$), number of pods plant^{-1} , number of seeds pod^{-1} , and dry weight of 100 seeds. Proteins and lipids were measured using the Kjeldahl method with a Kjel-Foss Automatic (Model 16210) and by Soxhlet Extraction method, respectively.

3.2.13 Heavy Metals Measurement

Heavy metals were measured using the methods of atomic-direct aspiration for Cd. Heavy metals, Oslen-P, Total C, Total N, exchangeable cations K, Ca, and Mg in the PBLBL, PBLBO, and soil were measured using the method of inductively coupled plasma atomic emission with and Inductively Coupled Plasma Emission Spectrophotometer.

3.2.14 Statistical Analysis

Data were analyzed through analysis of variance (ANOVA). When there are significant differences, the Duncan's New Multiple Range Test (DNMRT) of the Statistical Analysis System (SAS version 6.12) was applied to test for differences among the treatment; the mean at a significance level of $p < 0.05$.

CHAPTER 4

RESULTS AND DISCUSSION

The study aim to testing performance of broiler biochar for soybean planting on soil polluted with cadmium. The experiments were carried out under laboratory conditions. Set up in a 2 x 5 x 4 factorial arrangement plus control group with 4 replications in a completely randomized design with the first factor being the biochar as PBLBL that the PBLB derived from laboratory-scale pyrolysis reactor and PBLBO that the PBLB derived from pyrolyzed PBL in 200 liter oil drum kiln. The second factor being the ratios of PBLBL, PBLBO in soil mixed with Cd inoculation at 0, 20.0, 40.0, 60.0 and 80.0 mg kg⁻¹ Cd. The third factor being the mixing rate of PBLBO and PBLBL and soil with 5.00, 10.0, 15.0 and 20.0 t ha⁻¹ plus control group that was soil without anything. The results are show below:

4.1 Soil Property before Experiment

A sandy loam soil contain sand 60.0 – 70.0 percent, silt 20.0 – 30.0 percent and clay 5.00 – 10.0 percent.

Table 4.1 Soil Properties before Experiment

| Parameter | Soil Property |
|-----------|---------------|
| Moisture | 4.00 |
| pH | 4.50 |
| EC (dS/m) | 0.0898 |
| OM (%) | 1.07 |
| N (%) | 0.0830 |
| P (%) | 3.00 |

Table 4.1 (Continued)

| Parameter | Soil property |
|------------------|----------------------|
| K (%) | 35.0 |
| Ca (%) | 135 |
| Mg (%) | 24.0 |
| C/N Ratio | 7.00 |
| CEC (me/100 g) | 2.87 |
| Cadmium (mg/kg) | nd |

Note: nd = not detected

4.2 Broiler Litter Property before Pyrolysis

Broiler litter that is already mixed, such as a mixture of spilled feed, feathers, bedding material and excreta, and contains nitrogenous compounds, fiber and minerals, and pressed into pellet form. The pellet size was 6.00 mm in diameter and 2.00 cm in length according to the method of Tawadchai Suppadit and Siriwan Panomsri (2010: 441).

Table 4.2 Pelleted Broiler Litter Properties

| Parameter | Pelleted Broiler Litter Properties |
|------------------|---|
| % Moisture | 4.99 |
| pH | 6.00 |
| EC (dS/m) | 7.87 |
| OM (%) | 3.97 |
| N (%) | 3.52 |
| P (%) | 2.53 |
| K (%) | 2.71 |
| Ca (%) | 2.37 |
| Mg (%) | 1.22 |

Table 4.2 (Continued)

| Parameter | Pelleted Broiler Litter Properties |
|--------------------------------|------------------------------------|
| C/N Ratio | 11.0 |
| CEC (me/100 g) | 10.3 |
| Cadmium (mg kg ⁻¹) | nd |

Note: nd = not detected

4.3 Broiler Litter Biochar Property

Pelleted broiler litter (PBL) were separated into two group. Group 1 pyrolysis in the lab – scale pyrolysis reactor (PBLBL) and group 2 pyrolysis in 200 liter oil drum kiln (PBLBO). Both kilns was heated until the PBL temperature reached 500°C with a residence time of 24 hours. After four – to – five hours, the PBLBL and PBLBO cooled down to room temperature and the reactor was opened to collect char.

Table 4.3 Broiler Litter Biochar Properties

| Parameter | PBLBL | PBLBO |
|--------------------------------|-------|-------|
| % Moisture | 5.80 | 5.25 |
| pH | 9.40 | 9.90 |
| EC (dS/m) | 10.2 | 10.9 |
| OM (%) | 3.30 | 3.37 |
| N (%) | 2.97 | 2.86 |
| P (%) | 4.25 | 5.33 |
| K (%) | 5.07 | 5.26 |
| Ca(%) | 5.27 | 7.38 |
| Mg (%) | 2.27 | 2.17 |
| C/N ratio | 9.00 | 8.00 |
| CEC (me/100 g) | 17.6 | 18.2 |
| Cadmium (mg kg ⁻¹) | nd | nd |

Note: nd = not detected

Table 4.4 Surface Areas of Biochar

| Parameter | PBLBL | PBLBO |
|--|--------------|--------------|
| BET Surface Area (m ² g ⁻¹) | 5.20 | 6.41 |
| Total Pore Volume (cm ³ g ⁻¹) | 0.00253 | 0.00315 |
| Average Pore Diameter (nm) | 1.95 | 1.96 |

4.4 Performance of Broiler Litter Biochar on Soil Properties and Soybean Planting on Soil Polluted with Cadmium

The physical and chemical characteristics of the soils were analyzed after amended with PBLBL and PBLBO. The soils characteristics include: % moisture, pH, electric conductivity (EC), organic matter (OM), total nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), carbon nitrogen ratio (C/N ratio), cation exchange capacity (CEC) and cadmium (Cd) residual in soils. Soybean growth measurement were recorded are planting dates, stage of emergence, number of nodes, height, leaf area, dry matter, yield (4 plants pot⁻¹ x pods plant⁻¹ x seed pod⁻¹ x 1 seed weight), number of pods plant⁻¹, number of seeds pod⁻¹, protein and lipid in soybean' seeds and measure for cadmium residual in soybean' part: root, shoot, leaf and seed.

4.4.1 The Effect of Factor A (Reactor) on Soil Properties, Soybean Growth Stage, and Productive Performance.

4.4.1.1 Soil Property

1) % moisture

L kiln showed % moisture higher than O kiln (5.85 and 5.23 respectively) significantly different ($p < 0.05$), while O kiln not significantly different to control group (5.00) ($p > 0.05$).

2) pH

The result showed a significantly different among group ($p < 0.05$), L kiln showed highest pH, following with result from L kiln and the last was control group (5.09, 4.80 and 4.20, respectively).

3) EC

O kiln showed EC amount higher than L kiln significantly different ($p < 0.05$), while L kiln not significantly different to control group ($p > 0.05$).

4) OM

The result showed a significantly different among group ($p < 0.05$), O kiln showed highest result, following with result from L kiln and the last was control group (1.48, 1.42 and 1.07 %, respectively).

5) N

The result showed a significantly different among group ($p < 0.05$), O kiln showed highest N result, following with result from L kiln and the last was control group (0.106, 0.0978 and 0.0830 %, respectively).

6) P

The result showed a significantly different among group ($p < 0.05$), O kiln showed highest P result, following with result from L kiln and the last was control group (51.5, 28.6 and 3.00 %, respectively).

7) K

The result showed a significantly different among group ($p < 0.05$), O kiln showed highest result, following with result from L kiln and the last was control group (184, 174 and 35.0 %, respectively).

8) Ca

The result showed a significantly different among group ($p < 0.05$), O kiln showed highest result, following with result from L kiln and the last was control group (255, 235 and 135 %, respectively).

9) Mg

The result showed a significantly different among group ($p < 0.05$), O kiln showed highest result, following with result from L kiln and the last was control group (64.6, 62.6 and 24.0 %, respectively).

10) C/N ratio

The result of O kiln and L kiln not significantly different among group ($p > 0.05$), but higher more than control group significantly different ($p < 0.05$).

11) CEC

The result showed a significantly different among group ($p < 0.05$), O kiln showed highest result, following with result from L kiln and the last was control group (3.65, 3.10 and 2.87 me/100g, respectively).

12) Cd Residual in Soil

The result of O kiln and L kiln was not significantly different among group ($p > 0.05$), but higher than control group significantly different ($p < 0.05$).

O kiln show the highest result on parameter EC, OM, N, P, K, Ca, Mg and CEC while L kiln show highest in % moisture content and pH, these parameter obviously much higher than control group significantly. This mean that biochar produced in different type of kilns albeit same feedstock had different effect to soil properties. Antal and Gronli (2003: 1619) reported that the peak temperature controls a wide range of properties of biochar, like volatile matter content, pore structure, surface area and absorption capability. Major (2010) has claim about biochar property that “differences pyrolysis type, temperature and time over pyrolysis occur can be varied and have an impact on the characteristics of the results biochar” also with Verheijen et al. (2010: 38) had reported that “in pyrolysis oven, the pyrolysis can be selected and controlled, including maximum temperature and duration but also the rate of temperature increase, and inclusion of steam, activation and oxygen conditions”. Benzanson (2008) presented that during the pyrolysis process heat is transferred to the particles primarily through radiation and convection, though some heating techniques use condition, three mechanism included conduction inside the particle, convection inside the particle pores, and convection and radiation from the particle’s surface. This mean that heat transfer are especially important in the design of the pyrolyzer as heating rate plays a large role in the determination of the final product. Furthermore, Amonette and Joseph (2009: 33) had reported that carboxylic acids and phenolic groups are especially important for the biochar’s capacity to remain nutrient, the concentration increases slightly with increasing pyrolysis temperature (Bruun, 2011: 17).

In this study, both 2 kilns used same type of pyrolysis as slow pyrolysis at maximum temperature of 500°C, duration time from start process to

ending about 1 day, L kiln reload feedstock by put (pelleted broiler litter) in a closed vessel then prevent the inflow of oxygen while O kiln reload feedstock used a principle of making biochar like charcoal making in rural sector of Thailand so while heating methods O and L kilns that uses indirecting heating from outside and strictly excludes oxygen from the inside, transmits the heat for pyrolysis through its walls, since the heat transfer inside the biomass bed is relatively slow, large reactors cannot depend solely of this heating method (Gacia-Perez, Lewis and Kruger, 2010: 28), because of L kiln combustion chamber had a large size so heating not pass through all feedstock, while O kiln made from 200-litter-oil-drum-tank that had a small size so heating inner chamber be well more than L kiln by increasing surface area of biochar more than L kiln so the result about nutrient in soil after treatment with biochar derived from O kilns showed higher than L kilns significantly different (biochar derived from O kiln that call PBLBO had BET surface area $6.41 \text{ m}^2 \text{ g}^{-1}$ while PBLBL that a biochar derived from L kiln had BET surface area $5.20 \text{ m}^2 \text{ g}^{-1}$).

However, L kiln showed % moisture higher than O kilns significantly different ($p < 0.05$), while O kiln not significantly different to control (5.00).

Tyron (1948: 83) had demonstrated that water retention increases in sandy soils treated with biochar supplements. Novak et al. (2009: 204) found among two switchgrass biochars (250 and 500°C) more water was retained by the Norfolk loamy sand after mixing in the biochar produced at the higher temperature (500°C). They concluded that more polar and more micropores in biochar retaining water, or improved aggregation that created pore space for water storage. For this study may be from heating rate that even if these 2 kilns have reached the same highest temperature but L kiln that got heating from LPG which stable more than heating from wooden burning of O kiln so the inner polar of biochar production may be different.

Interestingly in C/N and Cd residue in soil' results. Both two kilns showed not significantly different ($p > 0.05$) but higher than control group significantly different ($p < 0.05$).

As mention above that process parameter such as temperature, pressure, particale size, heating rate, pyrolysis time and nature of feedstock (ash

content, lignocellulosic composition, etc.) have a substantial effect on pyrolysis products (Antal and Grønli, 2003: 1619). The biochar elemental composition was influenced by increasing pyrolysis temperatures (Antal and Gronli, 2003: 1619). As temperature increased, the O and H content decreased, leaving behind a more condensed biochar with a large C fraction, while the N content stayed rather constant (Bruun, 2011: 49), moreover Chen et al. (2004) has claimed that “with increasing pyrolysis temperature, these polar groups largely diminish, which results in the surface of biochar becoming more hydrophobic, thereby affect their sorption capacities for NH_4^+ and PO_4^{3-} . The active surface and porous properties of biochar develop during the producing process enable it to retain nutrient (Lehmann et al., 2003: 343; Liang et al., 2006: 1719) and hold water, thereby increasing soil productivity. Biochar caused an increase in soil pH, cation exchange capacity, organic matter, clay, and CaCO_3 contents, which is turn caused metal sorption to increase as the biochar amendment (Novak et al., 2009: 105). About Cd residual in soil after treatment found that biochar from O and L kiln can removed Cd that polluted in soil 72.5 and 72.4 %, respectively. Adsorption properties of biochar depend on the porous structure and surface chemical properties which are, inturn, a function of the feedstock and pyrolysis condition (Han, Boateng, Qi, Lima and Jainmin, 2013: 196). As the pyrolysis peak temperature increases, produced biochars exhibits a greater surface area and a greater micropore volume and a lower O/C ratio (Manyà, 2012: 20). The micropores of biochar have been shown to contribute the most surface area to biochars which accounts for the high adsorption capacity of high temperature biochars. Adsorptive nature related to surface area is an important physical property of biochars because of strong environmental influence in the uptake and binding effect of materials from their surroundings (Mukherjee and Lah, 2013: 316). The porous nature and surface chemical properties determine the adsorptive capabilities of biochar. Biochars may adsorb polyaromatic compounds, polyaromatic and polyaliphatic hydrocarbons, other toxic chemicals, metals and elements or pollutants in soils, sediments, aerosols and water bodies (Pignatello, Kwon and Lu, 2006: 7757). In this study control the same source of feedstock and pyrolysis condition that was slow pyrolysis at highest temperature of 500°C in both two kilns so the C/N ratio and Cd residual in soil’ results from both two kilns not significantly different, however can

removed Cd in soil lower than previous treatment which as much highest at 80.0 mg Cd kg⁻¹ soil.

4.4.1.2 Soybean Growth Stage

1) Vegetative Growth Stage

(1) Planting Date to Stage of Emergence (VE)

O kiln present this stage faster than L kilns and control significantly different ($p < 0.05$) while L kiln not different to control ($p > 0.05$).

(2) Planting Date to Stage of V4

This stage was the last stage of vegetative growth of soybean in this study. There were significantly different among group ($p < 0.05$). The result from L kiln was developed fastest from planting date to V4 following with O kiln and the last was control group that take longest day.

(3) Planting Date to Beginning Bloom (R1)

There were not significantly among O and L kiln ($p > 0.05$) develop to R1 stage faster than control group significantly different ($p > 0.05$), that was take longest day.

(4) Planting Date to Stage of Maturity (R8)

There were significantly different among group ($p < 0.05$) developed to R8 stage that L kiln developed fastest following with O kiln and the last one was control group.

As we known that characteristic of biochar depend on type of feedstock, preparation of the feedstock for biochar production, temperature, residence time, heating rate and oxygen level during production and as mention above that this study control most of factor that can be effect to the biochar production except the burning tank so the result of soybean development that show L kiln can developed faster than O kiln may be from L kiln had % moisture content higher more than O kiln, which can hold water and accelerate plant growth faster.

4.4.1.3 Soybean Productive Performance

1) Stem Weight

There were significantly different among group ($p < 0.05$). L kilns showed the heaviest following with result from O kiln and the last was result control group.

2) Pod Weight

There were significantly different among group ($p < 0.05$). L kilns showed the heaviest pod weight following with result from O kiln and the last was control group.

3) Height

There were significantly different among group ($p < 0.05$). O kilns showed the highest following with result from L kiln and the last was control group.

4) Number of Node

There were significantly different among group ($p < 0.05$). L kilns showed the highest following with result from O kiln and the last was control group.

5) Number of Pod

There were significantly different among group ($p < 0.05$). L kilns showed the highest following with result from O kiln and the last was control group.

6) Number of Seed per Pod

There were significantly different among group ($p < 0.05$). L kilns showed the highest following with result from O kiln and the last was control group.

7) 100 Seeds Dry Weight

There were significantly different among group ($p < 0.05$). O kilns showed the heaviest weight following with result from L kiln and the last was control group.

8) Product per Pot

There were significantly different among group ($p < 0.05$). L kilns showed the heaviest weight following with result from O kiln and the last was control group.

9) Protein in Soybean's Seeds

The results showed not significantly different among L kiln and O kiln ($p > 0.05$), but significantly different to control group ($p < 0.05$).

10) Lipid in Soybean's Seeds

The results showed not significantly different among L kiln and O kiln ($p>0.05$), but significantly different to control group ($p<0.05$).

11) Leaf Area R1

There were significantly different among group ($p<0.05$). O kilns showed the widest following with result from L kiln and the last was control group.

12) Leaf Area R3

There were significantly different among group ($p<0.05$). O kilns showed the widest following with result from L kiln and the last was control group.

13) Leaf Area R5

There were significantly different among group ($p<0.05$). O kilns showed the widest following with result from L kiln and the last was control group.

14) Leaf Area R7

There were significantly different among group ($p<0.05$). O kilns showed the widest following with result from L kiln and the last was control group.

Biochar soil amendment contributes to improved soil fertility and crop productivity (Tawadchai Suppadit et al., 2012: 244). The positive effects of biochar on crop productivity attributed to direct effects of biochar-supplied nutrients and several other indirect effects, including increase water and nutrient retention (Glaser et al., 2002: 219; Steiner et al., 2007: 275), improvements in soil pH, increased soil cation exchange capacity, effects on P and S transformations and turnover, neutralization of phytotoxic compounds in the soil, improved soil physical properties, promotion of mycorrhiza fungi, and alteration of soil microbial populations and functions.

Biochars produced at relatively low temperatures (below about 500°C) have substantially different characteristics than those produced at high temperatures (above about 500°C) (Elad, Cytryn, Harel, Lew and Graber, 2011: 335). Compared with high Highest Treatment Temperature (HTT) biochars, low HTT biochars have

lower pH values (neutral to mildly alkaline), lower ash contents, lower specific surface areas, and higher cation exchange capacities per unit surface area (Elad et al., 2011: 337). Furthermore, consider about the term of residence time refers to the time a feedstock is held within a constant temperature range and a given carbonization process. The combination of high temperature and longer residence times allows carbonization reactions to be completed. International Biochar Initiative (2012b).

For the result that showed above insisted the effective of biochar derived from pyrolysis pelleted broiler litter in two different kilns improve soybean productive performance. L kilns increase stem, pod, number of node, number of pod number of seed per pot and production per pot higher than O kiln, while O kilns increased the height, leaf area R1 – R7 and 100 seeds dry weight better than L kiln, however the productivity of soybean of both kiln higher than control significantly.

Feedstock, HTT, heating method, heating duration had covered biochar production, which different factor will influence to surface area and physiochemical of biochar even though derieved from the same feedstock. Feedstocks transmits the heat for pyrolysis through its walls, since the heat transfer inside the biomass bed is relatively slow, large reactors cannot depend solely of this heating method (Gacia-Perez, Lewis and Kruger, 2010: 28). May be from these factors that effected to biochar production of O and L kiln that performed differently in many parameter of soybean productive performance, even though this study had control same feedstock, same type of pyrolysis and same highest temperature at 500°C. Furthermore, pressure can be other one factor that effected to pyrolysis process, while operation under high pressures results due to the production differently (Garcia et al.,2010: 42). In this study, O kiln operated in atmospheric pressure due to its simplicity, while L kiln process under vacuum pyrolysis for avoiding air leak so may govern differently derived biochar. Moreover, Garcia et al. (2010: 34) had illustrated more about the reactor position: horizontal or vertical pyrolysis reactor is important because it has significant consequences for how feedstock is loaded and how the pyrolysis unit is operated. O kiln reactor line on horizontal, while L kiln posited vertical.

4.4.1.4 Cd Residue in Soybean Part

1) Cd Residue in Soybean Root

The result showed a significantly different among group ($p < 0.05$). Control group show the best result following with result from O kilns and the last was L kiln that have the amount of Cd residue in soybean root highest among group.

2) Cd Residue in Soybean Shoot

The result showed a significantly different among group ($p < 0.05$). Control group show the best result following with result from O kilns and the last was L kiln that have the amount of Cd residue in soybean shoot highest among group.

3) Cd Residue in Soybean Leaf

The result showed a significantly different among group ($p < 0.05$). Control group show the best result following with result from O kilns and the last was L kiln that have the amount of Cd residue in soybean leaf highest among group.

4) Cd Residue in Soybean Seed

The result showed not significantly different among result from L kiln and O kiln ($p > 0.05$), but significantly different to control group ($p < 0.05$).

This study, biochar was derived from the same feedstock that was pelleted broiler litter. Biochar derived from O kiln (PBLBO) have higher BET surface area ($6.41 \text{ m}^2 \text{ g}^{-1}$) more than biochar derived from L kiln (PBLBL) have BET surface area about $5.20 \text{ m}^2 \text{ g}^{-1}$, so the result of Cd residue in soybean root, shoot and leaf of O kilns exhibited lower than L kiln. However, considering on soybean seed, the result from both kiln not significantly different. The Cd residue in soybean part slightly decrease range from root \gg shoot \gg leaf \gg seed.

The types of feedstocks (Pastor-Villegas, Pastor-Vallegas, Rodriguez and Garcia, 2006: 103) and production conditions have a major impact on the properties and composition of biochar (Zheng, Shama and Rajagopalan, 2010: 8). Sorption to high temperature chars appear to be exclusively by surface adsorption, while that to low temperature chars derived from both surface adsorption and absorption to residual organic matter (Verhijen et al., 2010: 54). Chen, Zhou, Zhu and

Shen (2008: 464) had explained that higher pyrolysis temperatures is attributed to the removal of – OH, aliphatic C – O, and ester C = O groups from outer surfaces of the feedstock. Furthermore, Zheng et al. (2012: 8) found highest surface area of biochar produced at the highest temperature that may possess some fine structures. They concluded that temperatures have a great impact on biochar’s sorption capacity because surface area is a key indicator of uptake ability

The influence of micro – pore distribution on sorption to biochars has been clearly demonstrated by Wang, Sato and Xing (2006: 3267); Zhu, Kwon and Pignatello (2005: 3990) that diminished O functionality on the edges of biochar’s grapheme sheets due to heat treatment, resulted in enhanced hydrophobicity and affinity for both polar and apolar compounds, by reducing competitive adsorption by water molecules The treated char also revealed a consistent increase in micro-pore volume and pore surface area, resulting in better accessibility of solute molecules and an increase in sorption sites. It is generally accepted that much anions leading to an increase in surface area and/or hydrophobicity of the char, reflected in an enhanced sorption affinity and capacity towards trace contaminants, as demonstrated for other forms of biochar (Jonker and Koelmans, 2002: 3725; Noort et al, 2004; Tsui and Ray, 2008: 5673).

Table 4.5 Effect of Factor A (Reactor) on Soil Properties, Soybean Growth Stage, and Productive Performance

| Parameter | Control | 200 Litter Oil Drum Kiln | Lab – scale Pyrolysis Reactor | CV |
|------------------|---------------------|---------------------------------|--------------------------------------|-----------|
| Soil | | | | |
| Moisture (%) | 5.00 ^b | 5.23 ^b | 5.85 ^a | 2.76 |
| pH | 4.20 ^c | 4.80 ^b | 5.09 ^a | 1.82 |
| EC (dS/m) | 0.0898 ^b | 0.102 ^a | 0.0866 ^b | 3.68 |
| OM (%) | 1.07 ^c | 1.48 ^a | 1.42 ^b | 1.96 |
| N (%) | 0.0830 ^c | 0.106 ^a | 0.0978 ^b | 3.82 |
| P (%) | 3.00 ^c | 51.5 ^a | 28.6 ^b | 1.50 |
| K (%) | 35.0 ^c | 184 ^a | 174 ^b | 0.766 |

Table 4.5 (Continued)

| Parameter | Control | 200 Litter Oil Drum Kiln | Lab – scale Pyrolysis Reactor | CV |
|-----------------------------------|--------------------|-------------------------------------|--|-----------|
| Mg (%) | 24.0 ^c | 64.6 ^a | 62.6 ^b | 0.701 |
| C/N (%) | 7.00 ^b | 8.73 ^a | 8.69 ^a | 0.579 |
| CEC (me/100 g) | 2.87 ^c | 3.65 ^a | 3.10 ^b | 1.03 |
| Cd in soil (mg kg ⁻¹) | 0 ^b | 22.0 ^a | 22.1 ^a | 1.92 |
| Soybean | | | | |
| Planting Date – V4 | 33.0 ^a | 31.1 ^b | 30.2 ^c | 0.592 |
| Planting Date – VE | 4.00 ^a | 3.62 ^b | 3.87 ^a | 3.07 |
| VE – VC | 4.00 ^a | 2.87 ^c | 3.62 ^b | 3.36 |
| VC – V1 | 5.00 ^a | 3.87 ^b | 3.87 ^b | 2.77 |
| V1 – V2 | 6.00 ^b | 6.12 ^{ab} | 6.31 ^a | 2.62 |
| V2 – V3 | 6.00 ^b | 6.87 ^a | 6.12 ^b | 1.87 |
| V3 – V4 | 8.00 ^a | 7.00 ^b | 6.18 ^c | 3.49 |
| Planting Date – R1 | 39.0 ^a | 36.0 ^b | 36.0 ^b | 1.80 |
| R1 – R2 | 2.00 ^b | 2.00 ^b | 2.25 ^a | 5.65 |
| R2 – R3 | 3.00 ^a | 3.00 ^a | 2.75 ^b | 4.04 |
| R3 – R4 | 2.00 ^b | 2.18 ^a | 1.43 ^c | 5.44 |
| R4 – R5 | 3.00 ^a | 2.75 ^b | 2.00 ^c | 4.56 |
| R5 – R6 | 10.7 ^b | 12.2 ^a | 12.5 ^a | 5.63 |
| R6 – R7 | 10.5 ^b | 10.7 ^b | 12.2 ^a | 4.22 |
| R7 – R8 | 21.0 ^a | 20.0 ^a | 18.0 ^b | 3.38 |
| Planting Date – R8 | 90.0 ^a | 89.0 ^b | 86.8 ^c | 0.488 |
| Stem Weight | 0.305 ^c | 0.630 ^b | 0.732 ^a | 3.14 |
| Pod Weight | 1.01 ^c | 2.30 ^b | 2.96 ^a | 2.10 |
| Height | 30.6 ^c | 40.4 ^a | 39.7 ^b | 0.504 |
| Number of Node | 5.05 ^c | 5.67 ^b | 6.26 ^a | 0.633 |
| Number of Pod | 3.50 ^c | 6.97 ^b | 8.78 ^a | 2.25 |
| Number of Seed per Pod | 1.26 ^c | 1.99 ^b | 2.08 ^a | 0.888 |

Table 4.5 (Continued)

| Parameter | Control | 200 Litter Oil Drum Kiln | Lab – scale Pyrolysis Reactor | CV |
|------------------|---------------------|-------------------------------------|--|-----------|
| Dry Weight 100 | 10.7 ^c | 17.5 ^a | 17.3 ^a | 0.310 |
| Seeds | | | | |
| Product per Pot | 2.08 ^c | 6.98 ^b | 8.57 ^a | 0.408 |
| Protein in Seed | 35.1 ^b | 36.6 ^a | 36.5 ^a | 1.16 |
| Lipid in Seed | 18.4 ^b | 19.8 ^a | 19.9 ^a | 1.18 |
| Leaf Area R1 | 6.69 ^c | 29.9 ^a | 29.4 ^b | 0.515 |
| Leaf Area R3 | 11.8 ^c | 36.4 ^a | 34.4 ^b | 0.286 |
| Leaf Area R5 | 16.2 ^c | 60.8 ^a | 43.5 ^b | 0.836 |
| Leaf Area R7 | 18.4 ^c | 72.8 ^a | 60.2 ^b | 0.624 |
| Pod Weight R3 | 0.0242 ^c | 0.0694 ^b | 0.156 ^a | 2.79 |
| Pod Weight R5 | 0.0608 ^c | 0.106 ^b | 0.285 ^a | 2.64 |
| Pod Weight R6 | 1.08 ^c | 2.89 ^b | 3.26 ^a | 1.14 |
| Pod Weight R7 | 1.28 ^c | 3.16 ^b | 3.59 ^a | 1.06 |
| Pod Weight R8 | 0.870 ^c | 2.28 ^b | 2.96 ^a | 1.30 |
| Stem Weight R1 | 0.312 ^c | 0.925 ^b | 0.980 ^a | 2.84 |
| Stem Weight R3 | 0.477 ^c | 1.09 ^b | 1.57 ^a | 2.15 |
| Stem Weight R5 | 0.589 ^c | 1.25 ^b | 1.67 ^a | 3.24 |
| Stem Weight R6 | 0.814 ^c | 2.08 ^b | 3.08 ^a | 0.778 |
| Stem Weight R7 | 0.407 ^c | 1.25 ^b | 1.67 ^a | 3.24 |
| Stem Weight R8 | 0.253 ^c | 0.631 ^b | 0.731 ^a | 3.33 |
| Cd in Root | 0 ^c | 6.25 ^b | 10.0 ^a | 11.0 |
| Cd in Shoot | 0 ^c | 2.11 ^b | 3.13 ^a | 11.2 |
| Cd in Leaf | 0 ^c | 1.01 ^b | 1.56 ^a | 9.68 |
| Cd in Seed | 0 ^b | 0.289 ^a | 0.239 ^a | 33.3 |

Note: Means in the Same Row with Different Letters are Significantly Different at P < 0.05.

4.4.2 Effect of Factor B (Cd Level) on Soil Properties, Soybean Growth Stage, and Productive Performance

4.4.2.1 Soil Property

1) % moisture

The result showed a significantly different among group ($p < 0.05$). Cd20.0 had highest % moisture in soil, following with Cd40.0, Cd0, control, Cd60.0 and the last was Cd80.0. This mean that Cd had effected to % moisture in soil by increasing moisture content in soil every level of Cd treatment.

2) pH

The result showed a significantly different among control group and 5 groups of treatment ($p < 0.05$) but not significantly different when compare among each treatment ($p > 0.05$). This mean that Cd in every level had effected to pH by increase pH in soil.

3) EC

The result showed a significantly different among group ($p < 0.05$) but group 1 (Cd0) not significantly with control ($p > 0.05$). Group 5 (Cd80.0) showed the highest EC following with Group 4 (Cd60.0), then Group 3 (Cd40.0), Group 2 (Cd20.0). This mean that Cd had raise up EC in soil and when Cd increase EC in soil had increased too.

4) OM

The result showed the same like pH that among 5 group of treatment not significantly different ($p > 0.05$) but when compare all these group to control was significantly different ($p < 0.05$). This mean that Cd in every level had effected to OM by increased OM in soil.

5) N

The result showed a significantly different among group ($p < 0.05$). But group 2 (Cd20.0), group 3 (Cd40.0), group 4 (Cd60.0) and group 5 (Cd80.0) not significantly different ($p > 0.05$). This mean that Cd had effected to N by increased N in soil but level of Cd not effected to N in each group of Cd treatment. Notification on group 1 (Cd0) had highest N in soil following with group of Cd treatment (group 2, 3, 4, 5) and the last one was control group. Do to these results, N in soil after treatment had increased more than control significantly different.

6) P

The result showed a significantly different among group ($p < 0.05$). This mean that Cd had effected to P by increase P in soil higher than control significantly after treatment. Focus on the detail of each group, group 2 (Cd20.0) showed highest P in soil following with group 3 (Cd40.0), group 4 (Cd60.0), group 5 (Cd80.0), group 1 (Cd0) and the last one was control.

7) K

The result showed a significantly different among group ($p < 0.05$). This mean that Cd had effected to K by increase K in soil higher than control group significantly after treatment. Focus on the detail of each group, group 5 (Cd80.0) showed highest K in soil following with group 4 (Cd60.0), group 3 (Cd40.0), group 2 (Cd20.0), group 1 (Cd0) and the last one was control.

8) Ca

The result showed a significantly different among group ($p < 0.05$). This mean that Cd had effected to Ca by increased Ca in soil higher than control significantly after treatment. Focus on the detailed of each group, group 1 (Cd0) showed highest Ca in soil following with group 5 (Cd80.0), group 4 (Cd60.0), group 3 (Cd40.0), group 2 (Cd20.0) and the last one was control group.

9) Mg

The result showed a significantly different among group ($p < 0.05$). This mean that Cd had effected to Mg by increase Mg in soil higher than control group significantly after treatment. Focus on the detail of each group, group 5 (Cd80.0) showed the highest Mg in soil following with group 4 (Cd60.0), group 3 (Cd40.0), group 2 (Cd20.0), group 1 (Cd0) and the last one was control.

10) C/N ratio

The result showed a significantly different among group of treatment and control group ($p < 0.05$), but group 1 (Cd0) is not significantly different ($p > 0.05$) to group 2 (Cd20.0), group 3 (Cd40.0) and group 4 (Cd60.0) while these group (group 2, 3, 4) not significantly different ($p > 0.05$) to group 5 (Cd80.0). This mean that Cd had effected to C/N ratio by increased C/N ratio in soil significantly different but level of Cd not effect to C/N ratio in each of Cd treatment.

11) CEC

The result showed a significantly different among group ($p < 0.05$), but group 4 (Cd60.0) and group 5 (Cd80.0) were not significantly different ($p > 0.05$). This mean that Cd had effected to CEC by increase CEC in soil higher than control group significantly after treatment. Focus on the detail of each group, group 2 (Cd20.0) shows the highest CEC in soil following with group3 (Cd40) and group4 (Cd40) that equally with group5 (Cd80) then group1 (Cd0) and the last one was control group.

12) Cd Residue in Soil

The result showed a significantly different among group ($p < 0.05$) but group 1 (Cd0) not significantly with control group ($p > 0.05$). Group 5 (Cd80.0) showed the highest Cd residue in soil following with Group 4 (Cd60.0), then Group 3 (Cd40.0), Group 2 (Cd20.0) and the last one was Group 1 (Cd0) equally with control group. This mean that Cd had effected to Cd residue in soil. When Cd increased Cd residual in soil had increased too.

Cadmium concentrations of uncontaminated soils are usually below 0.500 mg kg^{-1} , but can reach up to 3.00 mg kg^{-1} depending on the soil parent materials (Vahter et al., 1991: 78). In soil-plant relationship, Cd may influence physiological process and biological mechanisms primarily by affecting concentration and functions of mineral nutrients (Nazar, 2012: 1476). The toxic effect of Cd is determined more by its form than by its concentrations (Kongkeat Jamasri, 2010: 12). The free ion Cd^{2+} is more likely to be adsorbed on the surfaces of soil solids (Alloway, 1995 quoted in Kongkeat Jamasri, 2010: 12). In soil, metals are associated with several fraction: (1) in soil solutions, as free metal ions and soluble metal complexes, (2) absorbed to inorganic soil constituents at ion exchange sites, (3) bound to soil organic matter, (4) precipitated such as oxides, hydroxides, carbonates, and (5) embedded in structure of the silicate minerals (Kongkeat Jamasri, 2010: 12). In plants, Cd can be taken up by roots through the same plasma membrane transporters as those used for other cations such as Ca, Fe, and Zn (Nakanishi, Ogawa, Ishimaru, Mori and Nishizawa, 2006: 464). Cd solubility was generally low at pH 7 to 8, but the solubility is substantially higher when the soil pH is lower than pH 6 (Brümmer and Herms, 1983 quoted in Akahane, Makino and Maejima, 2012: 101) and this process had explained by

Cornelis, Gestel and Mol (2003: 393) that the decrease of soil pH with increasing Cd concentration by “excess Cd^{2+} ions, added to the soils at high concentrations causing a release of H^+ ions from the sorption sites on the soil”. In this studied soil properties were sandy and acidic soil pH 4.20 so CdCl_2 can soluble and more available in this sandy soil.

4.4.2.2 Soybean Growth Stage

1) Vegetative Growth Stage

(1) Planting Date to Stage of Emergence (VE)

There were significantly different among group ($p < 0.05$). Group 1 (Cd0) take a shortest day similar to group 2 (Cd20.0) and control group developed from planting date to VE stage following with group 3 (Cd40.0) take similar day like group 4 (Cd60.0) and the last was group 5 (Cd80.0) take longest day developed to VE.

(2) Planting Date to Stage of V4

There were significantly different among group ($p < 0.05$). Control group take a shortest day developed from planting date to V4 stage, following with group 1 (Cd0) take similar day like group 2 (Cd20.0) then group 3 (Cd40.0) which take similar day like group 4 (Cd60.0) and the last was group 5 (Cd80.0) take longest day developed to V4.

(3) Planting Date to Beginning Bloom (R1)

There were significantly different among group ($p < 0.05$). Group 1 (Cd0) take a shortest day developed from planting date to R1 stage, following with group 2 (Cd20.0) take similar day like control group and the longest day were group 3 (Cd40.0) take similar day like group 4 (Cd60.0) and group 5 (Cd80.0) developed to R1.

(4) Planting Date to Stage of Maturity (R8)

There were significantly different among group ($p < 0.05$). Group 1 (Cd0) take a shortest day developed from planting date to R8 stage, following with control group then group 2 (Cd20.0) take similar day like group 3 (Cd40.0) but group 3 not significantly different to group 4 (Cd60.0) and the longest day was group 5 (Cd80.0) that not significantly different to group 4 (Cd60.0) developed to R8.

Cd had adverse affected to soybean growth stage that take prolong day developing from planting date to stage of maturity, while the worse affect rely on Cd amount that highest Cd level (80.0 mg kg^{-1}) take longest day.

Cadmium was recognized as one of the most hazardous elements which is not essential for plant growth (Huang, Bazzaz and Vanderhoef, 1974: 122; Tawadchai Suppadit et al., 2008: 86; Beesley and Marmiroli, 2011: 474; Fellet et al., 2011; Jin Hee Park et al., 2011: 239; Uchimiya et al., 2011: 423; Kabata-Pendias and Pendias, 1992 quoted in Addo, Nassar, Gomaa and Nassar, 2012: 25). Shukla, Singh, Joshi and Kakkar (2003: 257) studied the effect of Cd^{2+} on the wheat (*Triticum aestivum* L.) plant, they found that plants treated with 0.500, 1.00, 2.50 and 5.00 mg L^{-1} Cd^{2+} showed symptoms of heavy metal toxicity observed by root, shoot – leaf length, shoot – leaf biomass progressively decreased with increasing Cd^{2+} concentration. According to Abdo et al. (2012: 25) revealed characters of vegetative growth and yield of soybean planting on Cd concentration was decreased in morphological and yield and also with Shierdil et al. (2012: 1886) had concluded that application of Cd adversely affected soybean growth, nodulation and N_2 fixation as a function of time and increase in Cd concentration.

4.4.2.3 Soybean Productive Performance

1) Stem Weight

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed heaviest weight following with group 2 (Cd20.0), group 3 (Cd40.0), control group, group 4 (Cd60.0) and the least was group 5 (Cd80.0).

2) Pod Weight

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed heaviest weight following with control group that heavy similar to group 2 (Cd20.0) then group 3 (Cd40.0), group 4 (Cd60.0) and the least was group 5 (Cd80.0).

3) Height

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed the highest following with control group that

similar to group 2 (Cd20.0) then group 3 (Cd40.0) equally with group 4 (Cd60.0) and the shortest was group 5 (Cd80.0).

4) Number of Node

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displays the most number of soybean's node following with group 2 (Cd20.0) similar to group 3 (Cd40.0) then group 4 (Cd60.0) similar to group 5 (Cd80.0) and the least was control group.

5) Number of Pod

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed the most number of soybean's pod following with control group then group 2 (Cd20.0) similar to group 3 (Cd40.0) then group 4 (Cd60.0) and the least was group 5 (Cd80.0).

6) Number of Seed per Pod

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed the most number of seed per pod, following with group 2 (Cd20.0) then group 3 (Cd40.0) equally with group 4 (Cd60.0) then group 5 (Cd80.0) and the least was control group.

7) 100 Seeds Dry Weight

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed heaviest weight of 100 seeds dry weight, following with group 2 (Cd20.0) then group 3 (Cd40.0), control group, then group 4 (Cd60.0) and the least was group 5 (Cd80.0).

8) Product per Pot

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displays heaviest weight of product per pot, following with group 2 (Cd20.0) then group 3 (Cd40.0), control group and the least is group 5 (Cd80.0) that equally with group 4 (Cd60.0).

9) Protein in Soybean's Seeds

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed the highest amount of protein in soybean's seeds similar to group 2 (Cd20.0) and group 3 (Cd40.0), following with group 4 (Cd60.0) equally with group 5 (Cd80.0) and the least was control group.

10) Lipid in Soybean's Seeds

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed the highest amount of Lipid in soybean's seeds similar to group 2 (Cd20.0) and group 3 (Cd40.0), following with group 4 (Cd60.0) that equally with group 3 (Cd40.0) and group 5 (Cd80.0) and the least was control group.

11) Leaf Area R1

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed the widest of soybean's leaf area R1, following with group 2 (Cd20.0), group 3 (Cd40.0) similar with group 4 (Cd60.0), then group 5 (Cd80.0) and the narrowest was control group.

12) Leaf Area R3

There were significantly different among group ($p < 0.05$). In this parameter, group1 (Cd0) displayed the widest of soybean's leaf area R3, following with group 2 (Cd20.0), then control group, then group 3 (Cd40.0) and the narrowest was group 4 (Cd60.0) equally with group 5 (Cd80.0).

13) Leaf Area R5

There are significantly different among group ($p < 0.05$). In this parameter, group1 (Cd0) displayed the widest of soybean's leaf area R5, following with group 2 (Cd20.0), then control group, then group 3 (Cd40.0), group 4 (Cd60.0) and the narrowest is group 5 (Cd80.0).

14) Leaf Area R7

There are significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed the widest of soybean's leaf area R7, following with control group that similar to group 2 (Cd20.0), then group 3 (Cd40.0) that not significantly different to group 4 (Cd60.0) and the narrowest was group 5 (Cd80.0).

4.4.2.4 Cd Residue in Soybean Part

1) Cd Residue in Soybean Root

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed non Cd residue in soybean's root similar to control group, while the highest amount Cd residue in soybean's root showed by

group 5 (Cd80.0), the 2nd is group 4 (Cd60.0), the 3rd is group 3 (Cd40.0) and the least is group 2 (Cd20.0).

2) Cd Residue in Soybean Shoot

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed non Cd residue in soybean's shoot similar to control group, while the highest amount Cd residue in soybean's shoot showed by group 5 (Cd80.0), the 2nd is group 4 (Cd60.0), the 3rd was group 3 (Cd40.0) not significantly different to group 2 (Cd20.0).

3) Cd Residue in Soybean Leaf

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed non Cd residue in soybean's leaf similar to control group, while the highest amount Cd residue in soybean's leaf showed by group 5 (Cd80.0), the 2nd was group 4 (Cd60.0), the 3rd was group 3 (Cd40.0) and the least was group 2 (Cd20.0).

4) Cd Residue in Soybean Seed

There were significantly different among group ($p < 0.05$). In this parameter, group 1 (Cd0) displayed non Cd residue in soybean's seed similar to control group, while the highest amount Cd residue in soybean's seed shows by group 5 (Cd80.0), the 2nd was group 4 (Cd60.0), the 3rd was group 3 (Cd40.0) and the least was group 2 (Cd20.0).

The result presented the effect of Cd had decreased soybean yield and productive performance due to the toxicity to plant as mentioned above and Cd residue in soybean part slightly reduced from root > shoot > leaf > seed and when compare among group, Cd residue in soybean part slightly decreased from highest to lowest by Cd 80.0 > Cd 60.0 > Cd 40.0 > Cd 20.0 > Cd 0 = control group, respectively.

As we known the dramatically of this heavy metals have negative effect to plants, animals and/or humans (Adriano, 2001: 175; Tawadchai Suppadit, 2008: 86; Uchimiya et al., 2010b). Cd toxicity is 2.00 to 20.0 times greater than any other heavy metals (Pendias and Pendias, 2001 quoted in Sheirdil, Bashir, Hayat and Akhtar, 2012: 1886). Cd inhibits nutrients uptake of plants (Obata, Inoue and Umebayshi, 1996: 361). Higher Cd concentrations caused reduction in plant biomass

(Sheirdil et al., 2012: 1889). Many studied the effect of Cd to soybean, one from Sheirdil et al. (2012: 1886) studied the effect of Cd at 0, 4.00, 8.00 and 16.0 mg kg⁻¹ on soybean growth and nitrogen (N₂) fixation, the results showed an adversely affected soybean growth, nodulation and N₂ fixation as a function of time and increase in Cd concentration in root and shoot part increased with the highest Cd level and similar to Chen et al. (2004: 781) revealed that the nodulation of soybean roots was greatly inhibited by the addition of Cd, especially at the addition level of 10.0 and 20.0 mg kg⁻¹ soil. The inhibition of plant growth, especially the root growth, increased as the Cd concentration increased, with deleterious effects observed for the roots. According to Ghani (2010: 26) found the decreased in seed yield per plant, reduced number of seeds per pod and number of seeds per plant in mungbean variety under Cd toxicity. Cd in the roots as a first barrier to restrict its transport to the shoot (Das, et al., 1997 quoted in Sheirdil et al., 2012: 1886). Sheirdil et al. (2012: 1887) concluded about effected of cadmium on soybean growth and nitrogen fixation that “soybean shoots and root growth reduced with increase in Cd and the different increased with time”. Moreover, addition Cd treated plants display the reduction of height and formation of primary leaves, and fresh and dry weight (Çotuk, Belivermiş and Kiliç, 2010: 3).

Table 4.6 Effect of Factor B (Cd Level) on Soil Properties, Soybean Growth Stage, and Productive Performance

| Parameter | Control | Cadmium Level (mg Cd kg ⁻¹ of Soil) | | | | | CV |
|-----------------------------------|---------------------|--|---------------------|---------------------|---------------------|---------------------|-------|
| | | 0 | 20.0 | 40.0 | 60.0 | 80.0 | |
| Soil | | | | | | | |
| % Moisture | 5.00 ^d | 5.38 ^c | 7.37 ^a | 7.29 ^b | 4.70 ^f | 4.79 ^e | 0.32 |
| pH | 4.20 ^b | 5.20 ^a | 5.20 ^a | 4.96 ^a | 5.01 ^a | 4.99 ^a | 3.71 |
| EC (ds/m) | 0.0898 ^e | 0.0936 ^e | 0.115 ^d | 0.153 ^c | 0.250 ^b | 0.263 ^a | 3.17 |
| OM (%) | 1.07 ^b | 1.42 ^a | 1.40 ^a | 1.41 ^a | 1.41 ^a | 1.38 ^a | 2.81 |
| N (%) | 0.0830 ^c | 0.113 ^a | 0.0998 ^b | 0.0997 ^b | 0.0996 ^b | 0.0995 ^b | 4.17 |
| P (%) | 3.00 ^f | 40.1 ^e | 45.9 ^a | 42.8 ^b | 41.8 ^c | 40.9 ^d | 0.853 |
| K (%) | 35.0 ^f | 185 ^e | 203 ^d | 246 ^c | 293 ^b | 297 ^a | 0.174 |
| Ca (%) | 135 ^f | 192 ^a | 157 ^e | 184 ^d | 188 ^c | 191 ^b | 0.200 |
| Mg (%) | 24.0 ^f | 63.6 ^e | 67.7 ^c | 66.8 ^d | 70.6 ^b | 72.9 ^a | 0.536 |
| C/N Ratio | 7.00 ^c | 8.52 ^a | 8.08 ^{ab} | 8.27 ^{ab} | 8.38 ^{ab} | 8.06 ^b | 3.49 |
| CEC (me/100 g) | 2.87 ^d | 3.09 ^c | 3.89 ^a | 3.26 ^b | 3.28 ^b | 3.28 ^b | 0.765 |
| Cd in soil (mg kg ⁻¹) | 0 ^e | 0 ^e | 9.53 ^d | 19.6 ^c | 34.1 ^b | 39.6 ^a | 2.38 |
| Soy bean | | | | | | | |
| Planting Date – V4 | 33.0 ^d | 33.2 ^c | 33.2 ^c | 39.4 ^b | 40.0 ^b | 42.2 ^a | 3.33 |
| Planting Date – VE | 4.00 ^c | 4.00 ^c | 4.06 ^c | 5.13 ^b | 5.25 ^b | 5.68 ^a | 3.36 |

Table 4.6 (Continued)

| Parameter | Control | Cadmium Level (mg Cd kg ⁻¹ of Soil) | | | | | CV |
|--------------------|--------------------|--|--------------------|--------------------|--------------------|--------------------|------|
| | | 0 | 20.0 | 40.0 | 60.0 | 80.0 | |
| VE – VC | 4.00 ^c | 3.06 ^e | 3.68 ^d | 4.62 ^b | 4.62 ^b | 5.03 ^a | 3.21 |
| VC – V1 | 5.00 ^c | 4.00 ^d | 4.68 ^c | 6.12 ^b | 7.00 ^a | 6.81 ^a | 4.13 |
| V1 – V2 | 6.00 ^d | 6.18 ^c | 6.06 ^{cd} | 6.62 ^b | 7.06 ^a | 7.06 ^a | 1.81 |
| V2 – V3 | 6.00 ^c | 6.43 ^c | 6.87 ^b | 7.12 ^b | 7.62 ^a | 7.62 ^a | 3.87 |
| V3 – V4 | 8.00 ^c | 6.79 ^e | 7.46 ^d | 8.06 ^c | 8.62 ^b | 9.25 ^a | 2.78 |
| Planting Date – R1 | 39.0 ^b | 36.0 ^c | 38.0 ^b | 44.0 ^a | 44.5 ^a | 45.1 ^a | 2.24 |
| R1 – R2 | 2.00 ^{bc} | 2.06 ^c | 2.93 ^{ab} | 2.96 ^{ab} | 2.74 ^b | 3.33 ^a | 11.4 |
| R2 – R3 | 3.00 ^a | 2.12 ^d | 2.62 ^c | 2.86 ^b | 2.86 ^b | 3.02 ^a | 2.53 |
| R3 – R4 | 2.00 ^{ab} | 1.85 ^c | 2.03 ^{bc} | 2.21 ^{ab} | 2.23 ^{ab} | 2.45 ^a | 7.21 |
| R4 – R5 | 3.00 ^a | 2.41 ^c | 2.43 ^c | 2.66 ^b | 2.76 ^b | 3.05 ^a | 4.94 |
| R5 – R6 | 10.8 ^c | 8.81 ^e | 9.66 ^d | 10.1 ^c | 11.2 ^b | 12.6 ^a | 2.91 |
| R6 – R7 | 10.5 ^b | 9.78 ^c | 10.4 ^{bc} | 10.8 ^b | 11.8 ^b | 12.5 ^a | 4.10 |
| R7 – R8 | 21.0 ^b | 18.7 ^c | 21.4 ^b | 23.5 ^a | 24.0 ^a | 25.6 ^a | 5.90 |
| Planting Date – R8 | 90.0 ^d | 86.8 ^e | 93.2 ^c | 96.1 ^{bc} | 99.1 ^{ab} | 101 ^a | 2.22 |
| Stem Weight (g) | 0.306 ^d | 0.675 ^a | 0.397 ^b | 0.368 ^c | 0.297 ^d | 0.189 ^e | 2.59 |
| Pod Weight (g) | 1.00 ^b | 2.62 ^a | 1.01 ^b | 0.638 ^c | 0.399 ^d | 0.356 ^e | 1.38 |

Table 4.6 (Continued)

| Parameter | Control | Cadmium Level (mg Cd kg ⁻¹ of Soil) | | | | | CV |
|---------------------------------|---------------------|--|----------------------|----------------------|---------------------|---------------------|-------|
| | | 0 | 20.0 | 40.0 | 60.0 | 80.0 | |
| Height (cm) | 30.6 ^b | 40.6 ^a | 30.5 ^b | 24.8 ^c | 24.2 ^c | 22.2 ^d | 3.42 |
| Number of Node | 5.05 ^d | 5.96 ^a | 5.45 ^b | 5.40 ^b | 5.29 ^c | 4.95 ^e | 0.737 |
| Number of Pod | 3.50 ^b | 7.85 ^a | 3.32 ^c | 3.25 ^c | 2.49 ^d | 1.83 ^e | 2.82 |
| Number of Seed per Pod | 1.26 ^e | 2.05 ^a | 1.90 ^b | 1.66 ^c | 1.60 ^c | 1.40 ^d | 4.56 |
| Dry Weight 100 Seeds (g) | 10.6 ^d | 17.5 ^a | 12.5 ^b | 12.4 ^c | 9.87 ^e | 9.70 ^f | 0.583 |
| Product per Pot (g) | 2.08 ^d | 7.31 ^a | 3.21 ^b | 2.49 ^c | 1.19 ^e | 1.18 ^e | 3.47 |
| Protein in Seed (%) | 35.1 ^c | 36.2 ^a | 36.3 ^a | 36.1 ^a | 35.6 ^b | 35.3 ^{bc} | 0.702 |
| Lipid in Seed (%) | 18.4 ^d | 19.7 ^a | 19.7 ^{ab} | 19.5 ^{abc} | 19.3 ^{bc} | 19.2 ^c | 1.41 |
| Leaf Area R1 (cm ²) | 6.69 ^e | 25.2 ^a | 11.1 ^b | 7.53 ^c | 7.47 ^c | 7.05 ^d | 0.541 |
| Leaf Area R3 (cm ²) | 11.8 ^c | 35.4 ^a | 15.3 ^b | 9.16 ^d | 8.50 ^e | 8.41 ^e | 0.458 |
| Leaf Area R5 (cm ²) | 16.2 ^c | 51.9 ^a | 18.9 ^b | 11.1 ^d | 10.9 ^e | 10.3 ^f | 0.702 |
| Leaf Area R7 (cm ²) | 18.4 ^b | 66.4 ^a | 21.2 ^b | 12.6 ^c | 11.5 ^c | 8.69 ^d | 8.69 |
| Pod Weight R3 (g) | 0.0242 ^b | 0.117 ^a | 0.0242 ^b | 0.0177 ^c | 0.0174 ^c | 0.0107 ^d | 8.22 |
| Pod Weight R5 (g) | 0.0608 ^b | 0.196 ^a | 0.0530 ^{bc} | 0.0464 ^{cd} | 0.0436 ^d | 0.0411 ^d | 6.90 |

Table 4.6 (Continued)

| Parameter | Control | Cadmium Level (mg Cd kg ⁻¹ of Soil) | | | | | CV |
|------------------------------------|--------------------|--|--------------------|--------------------|--------------------|--------------------|------|
| | | 0 | 20.0 | 40.0 | 60.0 | 80.0 | |
| Pod Weight R6 (g) | 1.08 ^c | 3.09 ^a | 1.15 ^b | 0.956 ^d | 0.693 ^e | 0.656 ^e | 2.33 |
| Pod Weight R7 (g) | 1.28 ^b | 3.38 ^a | 1.24 ^b | 0.975 ^c | 0.950 ^c | 0.716 ^d | 2.79 |
| Pod Weight R8 (g) | 0.87 ^c | 2.64 ^a | 1.09 ^b | 1.06 ^b | 0.678 ^d | 0.578 ^e | 3.56 |
| Stem Weight R1 (g) | 0.312 ^c | 0.887 ^a | 0.420 ^b | 0.321 ^c | 0.295 ^c | 0.249 ^d | 6.41 |
| Stem Weight R3 (g) | 0.477 ^b | 1.172 ^a | 0.471 ^b | 0.406 ^c | 0.364 ^d | 0.300 ^e | 3.96 |
| Stem Weight R5 (g) | 0.589 ^c | 1.26 ^a | 0.681 ^b | 0.592 ^c | 0.574 ^c | 0.430 ^d | 4.70 |
| Stem Weight R6 (g) | 0.814 ^c | 2.60 ^a | 1.14 ^b | 0.807 ^c | 0.789 ^c | 0.644 ^d | 2.67 |
| Stem Weight R7 (g) | 0.407 ^d | 0.836 ^a | 0.672 ^b | 0.650 ^b | 0.553 ^c | 0.330 ^e | 2.65 |
| Stem Weight R8 (g) | 0.253 ^d | 0.681 ^a | 0.388 ^b | 0.387 ^b | 0.298 ^c | 0.210 ^e | 3.78 |
| Cd in Root (mg kg ⁻¹) | 0 ^e | 0 ^e | 4.85 ^d | 5.72 ^c | 5.98 ^b | 12.1 ^a | 1.61 |
| Cd in Shoot (mg kg ⁻¹) | 0 ^d | 0 ^d | 2.71 ^c | 2.79 ^c | 3.01 ^b | 5.07 ^a | 2.57 |
| Cd in Leaf (mg kg ⁻¹) | 0 ^e | 0 ^e | 2.20 ^d | 3.12 ^c | 3.46 ^b | 3.66 ^a | 2.89 |
| Cd in Seed (mg kg ⁻¹) | 0 ^e | 0 ^e | 0.378 ^d | 0.431 ^c | 0.455 ^b | 0.623 ^a | 2.03 |

Note: Means in the Same Row with Different Letters are Significantly Different at P < 0.05.

4.4.3 Effect of Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productive Performance

4.4.3.1 Soil Property

1) % Moisture

The result showed a significantly different among group ($p < 0.05$). Group 3 (B15.0) displayed highest % moisture in soil, following with group 2 (B10.0) that not significantly different to group 1 (B5.00), then group 4 (B20.0) and lowest was control group. This mean that factor C (Biochar mixing rate) had effected to % moisture in soil by increasing % moisture content in every mixing rate of biochar treatment.

2) pH

The result showed a significantly different among group ($p < 0.05$). Group 3 (B15.0) displayed highest pH in soil, following with group 4 (B20.0), group 2 (B10.0), then group 1 (B5.00) and lowest was control group. This mean that factor C (Biochar mixing rate) had effected to pH in soil by increasing pH in soil after treatment with different mixing rate of biochar.

3) EC

The result showed a significantly different among group ($p < 0.05$). Group 4 (B20.0) displayed highest EC in soil, following with group 3 (B15.0), group 2 (B10.0), then group 1 (B5.00) and lowest was control group respectively. This mean that factor C (Biochar mixing rate) had effected to EC in soil, that highest biochar mixing rate had increased highest EC in soil after treatment.

4) OM

The result showed a significantly different when compare group of biochar treatment to control group ($p < 0.05$), but when compare among group of biochar treatment, group 3 (B15.0), group 4 (B20.0) and group 2 (B10.0) are not significantly different ($p > 0.05$) and group 4 (B20.0) not significantly different to group 1 (B5.00). However, group 1 (B5.00) was significantly different to group 3 (B15.0) and control group significantly different ($p < 0.05$). The result of biochar treatment in every mixing rate showed a quantity of OM in soil after treatment higher more than control group clearly.

5) N

The result showed a slightly significant different among group ($p < 0.05$). Group 3 (B15.0), group 2 (B10.0) showed a highest N in soil higher than

group 1 (B5.00) and control group significantly different ($p < 0.05$). However, when compare group 3 (B15.0) and group 2 (B10.0) to group 4 (B20.0) the result showed not significantly different ($p > 0.05$). Beside, group 4 (B20.0) not significantly different to group 1 (B5.00) and control group ($p > 0.05$). This mean that biochar mixing rate 10.0 and 15.0 t ha⁻¹ had increased N in soil clearly, while at mixing rate 20.0 and 5.00 t ha⁻¹ are not improve N in soil after treatment.

6) P

This soil property parameter showed a trend of the result like parameter EC in soil. That show a significantly different among group ($p < 0.05$), where group 4 (B20.0) displays highest P in soil, following with group 3 (B15.0), group 2 (B10.0), then group 1 (B5.00) and lowest was control group. This mean that factor C (Biochar mixing rate) had effected to P in soil which highest biochar mixing rate had increased highest P in soil after treatment.

7) K

This soil property parameter showed a trend of the result like parameter EC and P in soil. That showed a significantly different among group ($p < 0.05$), where group 4 (B20.0) displayed highest K in soil, following with group 3 (B15.0), group 2 (B10.0), then group 1 (B5.00) and lowest was control group. This mean that factor C (Biochar mixing rate) had effected to K in soil which highest biochar mixing rate had increased highest K in soil after treatment.

8) Ca

The results showed a significantly different among group ($p < 0.05$). Group 4 (B20.0) displayed highest Ca in soil, following with group 3 (B15.0) that not significantly different to group 2 (B10.0), then group 1 (B5.00) and lowest was control group. This mean that factor C (Biochar mixing rate) had effected to Ca in soil by increased Ca in soil in every mixing rate of biochar treatment.

9) Mg

This soil property parameter showed a trend of the result like parameter EC and P and K in soil. That showed a significantly different among group ($p < 0.05$), where group 4 (B20.0) displayed highest Mg in soil, following with group 3 (B15.0), group 2 (B10.0), then group 1 (B5.00) and lowest was control group. This mean that factor C (Biochar mixing rate) had effected to Mg in soil which highest biochar mixing rate had increased highest Mg in soil after treatment.

10) C/N Ratio

The results showed a significantly different when compare group of biochar treatment to control group ($p < 0.05$). Group 4 (B20.0) displayed highest C/N ratio in soil following with group 3 (B15.0) showed a result not significantly different to group 2 (B10.0) and group 1 (B5.00) ($p > 0.05$), the lowest was control group. The results of biochar treatment in every mixing rate had increased C/N ratio in soil after treatment higher more than control group clearly.

11) CEC

The results showed a significantly different when compare group of biochar treatment to control group ($p < 0.05$). Group 4 (B20.0) displayed highest CEC in soil following with group 3 (B15.0), then group 2 (B10.0) showed a result not significantly different to group 1 (B5.00) ($p > 0.05$), the lowest was control group respectively. The results of biochar treatment in every mixing rate had increased CEC in soil after treatment higher more than control group clearly.

The results of this studied showed clearly that factor C (biochar mixing rate) had strongly effected to soil properties by improved soil quality e.g. % moisture, pH, OM, N, P, K, Ca, Mg, C/N, and CEC.

Biochar is a charred carbon – enriched material intended to be used as a soil amendment to sequester carbon and enhance soil quality (Zheng, Sharma and Rajagopalan, 2010: 1). Biochar has been reported to boost soil fertility and improve soil quality by raising soil pH, increasing moisture holding capacity, attracting more beneficial fungi and microbes, improving CEC, and retaining nutrients in soil (Lehmann, Gaunt and Rondon, 2006: 403; Lehmann, 2007: 381). Biochar is considered as effective than other organic matter in retaining and making nutrients available to plants due to surface area and complex pore structure are hospitable to bacteria and fungi that plants need to absorb nutrients from the soil (Zheng et al., 2010: 2). Zheng et al. (2010: 19) had clarify the mechanism of biochar sorption on NH_4^+ as a cation while biochar has a greater negative surface charge and charge density, the primary removal mechanism via an electrostatic attraction process, while biochar retain PO_4^{3-} by precipitate reaction. Moreover, Hossain et al. (2010: 1167) and Uchimiya et al. (2010b: 5538) found the applied biochar to acidic soils increased the soil pH, and thus improved the immobilization of heavy metals and nutrient availability. Rison (1979 quoted in Nigussie et al., 2012: 371) elucidated the increase

in soil pH and EC due to application of biochar was generally attributed to ash accretion as ash residues are generally dominated by carbonates of alkali and alkaline earth metals, variable amounts of silica, heavy metals, sesquioxides, phosphates and small amounts of organic and inorganic Nigussie et al. (2012: 371) reported that increase in soil pH due to application of biochar could be because of high surface area and porous nature of biochar that increases the CEC of the soil, their studied found the relationship between soil pH and CEC and concluded that biochar could be used as a substitution for lime materials to increase the pH of acidic soils. Dr. David Laird, of the USDA National Tilth Laboratory had described about biochar as “a fantastic adsorbent and when present in soils it increase the soil’s capacity to adsorb plant nutrients”. This insisted by many studied and one from Chan, Van Zwieten, Meszaros, Downie and Joseph (2008: 437) had found that biochars created from poultry litter tend to have more beneficial affects on soil quality and crop production than biochars produced from herbaceous, biomass material, related to Lehmann, da silva Steiner, Nehls, Zech and Glaser (2003: 346) had reported that biochars created from plant materials tend to be lower in nutrient content than biochar created from poultry litter or other manure products. Considered in detail in each parameter, applied bichar at mixing rate 15.0 t ha^{-1} (group 3) show highest performance improved % moisture and pH more than other groups, while at rate 20.0 t ha^{-1} enhanced on P, K, Ca, Mg and CEC higher than other mixing rate. These 2 mixing rate of biochar’s application increased OM and N equally and highest than others significantly different ($P < 0.05$). Glaser, Lehmann and Zech (2002a: 219) had concluded that “charcoal may contribute to an increase in ion retention of soil and to a decrease in leaching of dissolved OM and organic nutrient” their studied found higher nutrient retention and nutrient availability after charcoal additions to tropical soil. Rondon, Lehmann, Ramirez and Hurtodo (2007: 699) also found that biological N fixation by common beans was increased with biochar additions of 50.0 g kg^{-1} soil while Laird et al. (2010) had proposed biochar amendments in the soils at the rates of 0, 5.00, 10.0, and $20.0 \text{ g - biochar kg}^{-1}$ soil) showed greater water retention, larger surface areas, higher cation exchange capacities, and higher pH values relative to the un-amended controls.

12) Cd Residue in Soil

The results showed a significantly different among group ($p < 0.05$), where group 1 (B5.00) displayed highest Cd residue in soil, following with

group 2 (B10.0), group 3 (B15.0), then group 4 (B20.0) and lowest was control group, respectively. This mean that factor C (biochar mixing rate) had effected to Cd residue in soil. Cd residue in soil decreased due to increase biochar mixing rate. The tendency of Cd residual in soil slightly decreased from highest mixing rate to lowest as biochar $20.0 \text{ t ha}^{-1} > 15.0 > 10.0 > 5.00 \text{ t ha}^{-1} > \text{control group}$, respectively. Even though the results from the studied still have Cd residual in soil after treatment but when considered on initial Cd level in soil as much as high at $80.0 \text{ mg Cd kg}^{-1}$ of soil, these performance give a delightful number that in every mixing rate have lower than soil quality standards for habitat and agriculture of Thailand at not exceed $37.0 \text{ mg Cd kg}^{-1}$ soil (Notification of National Environmental Board No. 25, B.E., 2004).

Biochar has greater potential to beneficially reduce bioavailability of both organic and inorganic contaminants than greenwaste compost in multi-element contaminated soil and supported by Lehmann and Joseph (2009) replied the benefits of biochar had longevity in soil reduced the possibility of heavy metal accumulation associated with repeated applications of other amendments (Uchimiya et al., 2010: 935; Fellet et al., 2011: 1; Uchimiya et al., 2011: 423). Agree with Liang et al. (2006: 1719) had illustrated that biochar usually has a greater sorption ability do to its greater surface area, negative surface charge, and charge density. Beesley, Moreno-Jimenez and Gomez-Eyles (2010: 2282) applied hardwood-derived biochar and greenwaste compost diminished water-soluble Cd and Zn in soil, significantly reducing their phytotoxic effect and can usefully reduce polycyclic aromatic hydrocarbons (PAHS) concentrations (Hongwen Sun and Zunlong Zhou, 2008: 2113). Moreover, Uchimiya et al. (2011: 432) had screening biochars derived from cottonseed hull and broiler litter, they found that biochar increasing oxygen – containing carboxyl, hydroxyl, and phenolic surface functional groups of soil organic and mineral components play central roles in binding metal ions. Positive Matrix Factorization (PMF) analysis indicated that effective heavy metal stabilization occurred concurrently with the release of Na, Ca, S, K, and Mg originating from soil and biochar, in weathered acidic soil, the heavy metal (Cu, Ni, Cd, Pb) stabilization ability of biochar directly correlated with the amount of oxygen functional groups.

4.4.3.2 Soybean Growth Stage

1) Vegetative Growth Stage

(1) Planting Date to Stage of Emergence (VE)

There were a slightly significant different among group ($p < 0.05$). Group 1 (B5.00) and Group 2 (B10.0) take a longest day developed from planting date to VE stage following with group 3 (B15.0) take similar day like group 4 (B20.0) and the fastest was control group.

(2) Planting Date to Stage of V4

There were a slightly significant different among group ($p < 0.05$). Group 1 (B5.00) and Group 2 (B10.0) and group 4 (B20.0) not significantly different ($p > 0.05$) take a longest day developed from planting date to V4 stage, following with group 3 (B15.0) take faster than group 1 (B5.00) and group 2 (B10.0) significantly different ($p < 0.05$), however not significantly different ($p > 0.05$) to group 4 (B20.0) and the fastest was control group.

(3) Planting Date to Beginning Bloom (R1)

There were not significantly different among group ($p > 0.05$) developed from planting date to R1 stage.

(4) Planting Date to Stage of Maturity (R8)

There were significantly different among group 1 ($p < 0.05$) and control group developed from planting date to R8 stage, while other group (2,3,4) were not significantly different among group and control group develop to R8 stage.

4.4.3.3 Soybean Productive Performance

1) Stem Weight

There were significantly different among group ($p < 0.05$). In this parameter group 3 (B15.0) displayed heaviest weight following with group 4 (B20.0), group 2 (B10.0) and the least was group 1 (B5.00) that not significantly different with control group.

2) Pod Weight

There were significantly different among group ($p < 0.05$). The result showed the same trend like Stem weight that group 3 (B15.0) displayed heaviest pod weight following with group 4 (B20.0), group 2 (B10.0) and the least was group 1 (B5.00) that not significantly different with control group.

3) Height

There were a slightly significant different among group ($p < 0.05$). In this parameter group 4 (B20.0) displayed the heightest significantly

different ($p < 0.05$) to control group and group 1 (B5.00) but not significantly different ($p > 0.05$) to group 3 (B15.0) and group 2 (B10.0).

4) Number of Node

There were a slightly significant different among group ($p < 0.05$). In this parameter group 4 (B20.0) displayed the most number following with group 3 (B15.0) which the result not significantly different ($p > 0.05$) to group 2 (B10.0) and group 1 (B5.00) and the least was control group.

5) Number of Pod

There were a slightly significant different among group ($p < 0.05$). In this parameter group 3 (B15.0) displayed the most number following with group 4 (B20.0) and the least were group 2 (B10.0) that the results not significantly different ($p > 0.05$) to group 1 (B5.00) and control group.

6) Number of Seed per Pod

There were a slightly significantly different among group, however much more control group significantly different ($p < 0.05$). In this parameter group 3 (B15.0) displayed the most number following with group 2 (B10.0) that not significantly different ($p > 0.05$) to group 1 (B5.00) and the result of group 1 (B5.00) not significantly different ($p > 0.05$) to group 4 (B20.0) and the least was control group.

7) 100 Seeds Dry Weight

There were a slightly significantly different among group, however much more control group significantly different ($p < 0.05$). In this parameter group 3 (B15.0) displayed heaviest weight following with group 2 (B10.0) that not significantly different ($p > 0.05$) to group 4 (B20.0) then group 1 (B5.00) and the least was control group.

8) Product per Pot

The results displayed like the result of 100 seeds dry weight.

9) Protein in Soybean's Seeds

There were a slightly significantly different among group, however much more control group significantly different ($p < 0.05$). In this parameter, group 1 (B5.00) displayed the highest amount of protein in soybean's seeds following with group 2 (B10.0) then group 3 (B15.0) that not significantly different ($p > 0.05$) to group 4 (B20.0) and the least was control group.

10) Lipid in Soybean's Seeds

There were a slightly significantly different among group, however much more control group significantly different ($p < 0.05$). In this parameter group 3 (B15.0) displayed the highest amount of lipid in soybean's seeds following with group 4 (B20.0) that not significantly different ($p > 0.05$) to group 2 (B10.0) then group 1 (B10.0) and the least was control group.

11) Leaf Area R1

There were significantly different among group ($p < 0.05$). In this parameter group 3 (B15.0) displayed the widest following with group 4 (B20.0), group 2 (B10.0), group 1 (B5.00) and the narrowest was control group respectively.

12) Leaf Area R3

The results show as leaf area R1

13) Leaf Area R5

The results show as leaf area R1

14) Leaf Area R7

The results show as leaf area R1

The varying effects on crop yield appear to depend on such factors as biochar quality, biochar quantities added, soil type, and crop tested (Zheng et al., 2010:2). The paper "Biochar impact on development and productivity of pepper and tomato grown in fertigated soilless media" by Graber et al. (2010: 481) found that when biochar – treated pots were compared against controls, plant development was enhanced. The researcher team found two alternatives to explain the improved plant performance under biochar treatment "first, biochar stimulated shifts in microbial populations towards beneficial plant growth promoting rhizobacteria or fungi, due to either chemical or physical attributes of the biochar and seconds, low doses of biochar chemicals, many of which are phytotoxic or biocidal at high concentrations, stimulated plant growth at low doses".

Many studied point to $50.0 - 60.0 \text{ t ha}^{-1}$ ($20.0 - 25.0 \text{ t ac}^{-1}$) as being an optimal rate of biochar production, however this is a very large amount of material to apply. (Quoted from Laird, of the USDA National Tilth Laboratory (2008) used mixtures of wood biochar, manure, minerals and clay heated to between 180°C and 220°C these mixtures have been characterized using a range of microscopic, chromatographic and spectroscopic technique and set an experiment as pot and field

trial in Western Australia, the studied indicated that significant increase in plant yields may be achieved at low application rates of biochar but not shown in detail how much biochar mixture rate was the best. Furthermore, field trials with biochar application have also shown increased yields of many plants; especially where they are added with mineral fertilizers or with organic fertilizers, such as manure (Blackwell et al., 2009: 207). In an experiment with different planting densities and mineral fertilizers application, biochar applications at 1.50, 3.00 and 6.00 t ha⁻¹ resulted in significantly greater yields than when biochar was not added (Solaiman et al., 2010: 546). The yield increases in all biochar treatments was approximately 45.0 per cent compared with the control. Furthermore, Uzoma et al. (2011: 1) investigation on the effect of cow manure biochar derived from dry cow manure pyrolysed at 500°C, mixed with sandy soil at rate equivalent to 0, 10.0, 15.0 and 20.0 t ha⁻¹ on maize yield, nutrient uptake and physic – chemical properties of a dry land sandy soil, the results showed that applied biochar 15.0 and 20.0 t ha⁻¹ mixing rate significantly increased maize grain yield by 150 to 90.0% as compared with control respectively, nutrient uptake by maize gain was significantly increased with higher biochar applications also like had found that broiler chicken litter biochar improved the germination of lettuce seeds in the sandy loam at the 0.200, 0.500 and 1.00 % rate but not significantly increase the germination of lettece in the silt loam, they also observed that the fine biochar particles coated the lettuce seeds in the coarse textured sandy loam but did not have as many fine particles as the silt loam so suspected that this may have hold water close to the lettuce seed, which led to the increase in germination at low biochar rates in the sandy loam.

4.4.3.4 Cd Residue in Soybean Part

1) Cd Residue in Soybean Root

There were a slightly significant different among group ($p < 0.05$) while control group performed the best result that not have Cd residue in soybean root. In this parameter group 1 (B5.00) displayed highest Cd residue in soybean's root following with group 4 (B20.0) that not significantly different ($p > 0.05$) to group 3 (B15.0) and group 2 (B10.0) and the last was control group that not have Cd residue in soybean root.

2) Cd Residue in Soybean Shoot

There were a slightly significant different among group ($p < 0.05$) while control group performed the best result that not have Cd residue in

soybean shoot. In this parameter, group 1 (B5.00) displayed highest Cd residue in soybean's shoot following with group 2 (B10.0) that not significantly different ($p>0.05$) to group 4 (B20.0) then group 3 (B15.0) that the result not significantly different ($p>0.05$) to group 4 (B20.0) but significantly different ($p>0.05$) to group 2 and group 1, and the last was control group that not have Cd residue in soybean shoot.

3) Cd Residue in Soybean Leaf

There were a slightly significant different among group ($p<0.05$) while control group performed the best result that not have Cd residue in soybean leaf. In this parameter group 1 (B5.00) displayed highest Cd residue in soybean's leaf following with group 2 (B10.0) that the result not significantly different ($p>0.05$) to group 3 (B15.0), then group 4 (B20.0) and the last was control group that not have Cd residue in soybean leaf.

4) Cd Residue in Soybean Seed

There were a slightly significant different among group ($p<0.05$) while control group performed the best result that not have Cd residue in soybean seed. In this parameter group 1 (B5.00) displayed highest Cd residue in soybean's seeds following with group 2 (B10.0) that the result not significantly different ($p>0.05$) to group 3 (B15.0), then group 4 (B20.0) that the result not significantly different ($p>0.05$) to group 3 (B15.0) but significantly different to group 1 (B5.00), group 2 (B10.0) and control group significantly different ($p<0.05$) and the last was control group that not have Cd residue in soybean seed.

The results showed a tendency of Cd in different parts of the plants was as follow: roots \gg stems $>$ leaf $>$ seeds. Chen et al. (2004: 781) indicated that the accumulation of Cd by roots is much larger than other part of the soybean plant, and might cause deleterious effects to root systems. The bio-available fraction of heavy metals is reduced in the presence of biochar (Uchimiya et al., 2010: 935; Tawadchai Suppadit, Viroj Kitikoon, Anucha Phubphol and Penthip Neumnoi, 2012: 128). The strong binding of Cd to the surface functional group of biochar makes it less available to the plants (Namgay, Singh and Sing, 2010: 78). Biochars application reduced the extractability of heavy metals in soil and caused significantly changes in the extractability and metal sequential fractions, indicating that the available form of heavy metals in soil can be transformed into unexchangeable form (Qiu and Guo, 2010: 379)

Table 4.7 Effect of Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productive Performance

| Parameter | Control | Biochar Mixing Rate | | | | CV |
|--------------------------------------|---------------------|---------------------|--------------------|---------------------|---------------------|-------|
| | | 5.00 | 10.0 | 15.0 | 20.0 | |
| Soil | | | | | | |
| % Moisture | 5.00 ^d | 5.91 ^b | 5.88 ^b | 6.05 ^a | 5.81 ^c | 0.463 |
| pH | 4.20 ^e | 4.58 ^d | 4.87 ^c | 5.72 ^a | 5.25 ^b | 3.53 |
| EC (ds/m) | 0.0898 ^e | 0.120 ^d | 0.141 ^c | 0.189 ^b | 0.241 ^a | 4.47 |
| OM (%) | 1.07 ^c | 1.29 ^b | 1.33 ^{ab} | 1.43 ^a | 1.36 ^{ab} | 5.39 |
| N (%) | 0.0830 ^b | 0.0992 ^b | 0.197 ^a | 0.199 ^a | 0.145 ^{ab} | 29.8 |
| P (%) | 3.00 ^e | 17.9 ^d | 35.4 ^c | 48.2 ^b | 63.8 ^a | 1.21 |
| K (%) | 35.0 ^e | 134 ^d | 183 ^c | 298 ^b | 358 ^a | 2.08 |
| Ca (%) | 135 ^d | 166 ^c | 184 ^b | 186 ^b | 195 ^a | 1.36 |
| Mg (%) | 24.0 ^e | 45.0 ^d | 62.5 ^c | 77.9 ^b | 91 ^a | 2.13 |
| C/N Ratio | 7.00 ^c | 7.91 ^b | 7.94 ^b | 7.99 ^b | 8.62 ^a | 3.11 |
| CEC (%) | 2.87 ^d | 3.11 ^c | 3.08 ^c | 3.27 ^b | 3.91 ^a | 1.25 |
| Cd in soil (mg kg ⁻¹) | 0.000 ^e | 22.5 ^a | 21.7 ^b | 20.4 ^c | 17.3 ^d | 0.618 |
| Soy bean | | | | | | |
| Planting | 33.0 ^c | 38.2 ^a | 38.2 ^a | 36.3 ^b | 35.8 ^b | 1.22 |
| Date – V4 | | | | | | |
| Planting | 4.00 ^c | 5.05 ^a | 5.05 ^a | 4.65 ^b | 4.76 ^{ab} | 4.83 |
| Date – VE | | | | | | |
| VE – VC | 4.00 ^b | 4.55 ^a | 4.45 ^a | 4.26 ^{ab} | 4.03 ^b | 5.30 |
| VC – V1 | 5.00 ^C | 5.86 ^a | 5.76 ^{ab} | 5.55 ^{abc} | 5.45 ^{bc} | 4.10 |
| V1 – V2 | 6.00 ^a | 6.61 ^a | 6.62 ^a | 6.46 ^a | 6.61 ^a | 4.11 |
| V2 – V3 | 6.00 ^b | 7.62 ^a | 7.42 ^a | 6.82 ^b | 6.82 ^b | 3.86 |
| V3 – V4 | 8.00 ^a | 8.30 ^a | 7.15 ^b | 7.35 ^b | 8.15 ^a | 3.52 |

Table 4.7 (Continued)

| Parameter | Control | Biochar Mixing Rate | | | | CV |
|------------|--------------------|---------------------|--------------------|--------------------|--------------------|------|
| | | 5.00 | 10.0 | 15.0 | 20.0 | |
| Planting | 39.0 ^a | 40.1 ^a | 41.5 ^a | 40.2 ^a | 39.9 ^a | 5.73 |
| Date – R1 | | | | | | |
| R1 – R2 | 2.00 ^b | 2.88 ^a | 2.82 ^{ab} | 2.67 ^{ab} | 2.79 ^{ab} | 5.25 |
| R2 – R3 | 3.00 ^a | 2.93 ^a | 2.77 ^b | 2.55 ^d | 2.65 ^c | 1.83 |
| R3 – R4 | 2.00 ^b | 2.15 ^a | 2.08 ^a | 1.95 ^b | 2.08 ^a | 2.59 |
| R4 – R5 | 3.00 ^a | 2.46 ^b | 2.29 ^c | 2.12 ^d | 2.05 ^d | 2.77 |
| R5 – R6 | 10.7 ^a | 10.2 ^b | 7.75 ^c | 10.5 ^{ab} | 10.3 ^b | 2.74 |
| R6 – R7 | 10.5 ^b | 13.3 ^a | 10.8 ^b | 10.6 ^b | 10.7 ^b | 2.71 |
| R7 – R8 | 21.0 ^c | 23.2 ^a | 22.4 ^b | 22.3 ^b | 21.3 ^c | 1.64 |
| Planting | 90.0 ^b | 94.7 ^a | 94.0 ^{ab} | 91.3 ^{ab} | 93.3 ^{ab} | 2.73 |
| Date – R8 | | | | | | |
| Stem | 0.305 ^d | 0.303 ^d | 0.372 ^c | 0.469 ^a | 0.399 ^b | 1.58 |
| Weight | | | | | | |
| Pod Weight | 1.00 ^d | 1.01 ^d | 1.09 ^c | 1.39 ^a | 1.29 ^b | 2.84 |
| Height | 30.6 ^{bc} | 28.6 ^c | 30.7 ^{ab} | 31.6 ^a | 32.0 ^a | 3.13 |
| Number of | 5.05 ^c | 5.42 ^b | 5.49 ^b | 5.40 ^b | 6.01 ^a | 1.18 |
| Node | | | | | | |
| Number of | 3.50 ^c | 3.12 ^c | 3.48 ^c | 4.73 ^a | 3.88 ^b | 5.16 |
| Pod | | | | | | |
| Number of | 1.26 ^d | 1.62 ^{bc} | 1.71 ^b | 1.89 ^a | 1.60 ^c | 3.62 |
| Seed per | | | | | | |
| Pod | | | | | | |
| Dry weight | 10.6 ^d | 12.4 ^c | 13.2 ^b | 15.3 ^a | 13.2 ^b | 1.18 |
| 100 Seeds | | | | | | |

Table 4.7 (Continued)

| Parameter | Control | Biochar mixing rate | | | | CV |
|-----------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------|
| | | 5.00 | 10.0 | 15.0 | 20.0 | |
| Product per Pot | 2.08 ^d | 2.82 ^c | 3.20 ^b | 4.62 ^a | 3.14 ^b | 6.17 |
| Protein | 35.1 ^d | 36.4 ^a | 35.9 ^b | 35.8 ^c | 35.8 ^c | 0.114 |
| Lipid | 18.4 ^d | 19.3 ^c | 19.6 ^b | 19.9 ^a | 19.6 ^b | 0.223 |
| Leaf Area R1 | 6.69 ^e | 8.84 ^c | 8.82 ^d | 13.8 ^a | 13.5 ^b | 0.0380 |
| Leaf Area R3 | 11.8 ^e | 13.3 ^d | 14.1 ^c | 18.2 ^a | 16.2 ^b | 0.0159 |
| Leaf Area R5 | 16.2 ^d | 18.5 ^c | 18.5 ^c | 23.4 ^a | 22.0 ^b | 0.0289 |
| Leaf Area R7 | 18.4 ^e | 19.0 ^d | 22.1 ^c | 30.5 ^a | 29.0 ^b | 0.0301 |
| Pod Weight R3 | 0.0242 ^c | 0.0253 ^c | 0.0260 ^c | 0.0888 ^a | 0.0296 ^b | 3.26 |
| Pod Weight R5 | 0.0608 ^d | 0.0618 ^c | 0.0687 ^b | 0.161 ^a | 0.0692 ^b | 0.541 |
| Pod Weight R6 | 1.08 ^c | 1.33 ^b | 1.39 ^b | 1.58 ^a | 1.41 ^b | 4.78 |
| Pod Weight R7 | 1.28 ^d | 1.31 ^c | 1.66 ^b | 1.79 ^a | 1.39 ^c | 3.82 |
| Pod Weight R8 | 0.870 ^d | 1.27 ^b | 0.856 ^c | 1.51 ^a | 1.22 ^c | 0.138 |
| Stem Weight R1 | 0.312 ^c | 0.408 ^b | 0.447 ^a | 0.460 ^a | 0.422 ^b | 2.92 |
| Stem Weight R3 | 0.477 ^c | 0.478 ^c | 0.581 ^b | 0.681 ^a | 0.565 ^b | 4.89 |
| Stem Weight R5 | 0.589 ^d | 0.651 ^c | 0.772 ^b | 0.871 ^a | 0.768 ^b | 4.20 |

Table 4.7 (Continued)

| Parameter | Control | Biochar Mixing Rate | | | | |
|-------------|--------------------|---------------------|--------------------|---------------------|--------------------|------|
| | | CV | | | | |
| | | 5.00 | 10.0 | 15.0 | 20.0 | |
| Stem | 0.814 ^c | 0.852 ^d | 1.42 ^b | 1.56 ^a | 1.28 ^c | 5.28 |
| Weight R6 | | | | | | |
| Stem | 0.407 ^c | 0.515 ^b | 0.704 ^a | 0.715 ^a | 0.674 ^a | 8.71 |
| Weight R7 | | | | | | |
| Stem | 0.253 ^d | 0.324 ^c | 0.424 ^b | 0.507 ^a | 0.420 ^b | 13.2 |
| Weight R8 | | | | | | |
| Cd in Root | 0 ^c | 18.9 ^a | 7.25 ^b | 7.61 ^b | 8.82 ^b | 13.3 |
| Cd in Shoot | 0 ^d | 6.53 ^a | 3.54 ^b | 2.77 ^c | 3.10 ^{bc} | 14.6 |
| Cd in Leaf | 0 ^d | 3.53 ^a | 2.26 ^b | 2.23 ^b | 1.55 ^c | 21.8 |
| Cd in Seed | 0 ^d | 0.652 ^a | 0.482 ^b | 0.362 ^{bc} | 0.263 ^c | 29.5 |

Note: Means in the Same Row with Different Letters are Significantly Different at $P < 0.05$.

4.4.4 Interaction between Factor A (Reactor) and Factor B (Cd Level) on Soil Properties, Soybean Growth Stage, and Productive Performance

4.4.4.1 Soil Property

Factor A (kilns) and Factor B (Cd level) showed an interaction result in every parameter of soil properties. Interaction between this two factor had increased every parameter except % moisture content in soil significantly different to control group.

1) % moisture

The results showed a significantly different among group ($p < 0.05$), almost every group performed higher more than control group except group 4 (OCd60.0), group 5 (OCd80.0) and group 9 (PCd60.0) showed lower than control

group while group 1 (OCd0) and group 10 (PCd80.0) were not significantly different ($p < 0.05$) to control group. Group 2 (OCd20.0) displayed the highest results.

2) pH

Every group of treatment performed pH in soil higher more than control group significantly different. Group 6 (PCd0) and group 7 (PCd20.0) displayed the highest results. Observed that L kiln interacted with Cd level had increased pH in soil higher more than O kiln interact with Cd level.

3) EC

Every group of treatment performed EC in soil higher more than control group significantly different. Group 5 (OCd80.0) displayed the highest results. Observed that EC increased due to Cd level increased and when compare between same Cd level but different kiln. O kiln showed EC in soil higher than L kiln.

4) OM

Every group of treatment performed OM in soil higher more than control group significantly different. Group 8 (PCd40.0) and group 4 (OCd60.0) displayed the highest results.

5) N

The result showed non interaction between Factor A and Factor B on this parameter.

6) P

Every group of treatment performed P in soil higher more than control group significantly different. Group 1 (OCd0) displayed the highest results. Observed that resulted from interaction between O kiln and Cd level showed P in soil higher more than L kiln and Cd level.

7) K

Every group of treatment performed K in soil higher more than control group significantly different. Group 9 (PCd60.0) displayed the highest results.

8) Ca

Every group of treatment performed Ca in soil higher more than control group significantly different. Group 5 (OCd80.0) displayed the highest results.

9) Mg

Every group of treatment performed Mg in soil higher more than control group significantly different. Group 10 (PCd80.0) displayed the highest results.

10) C/N ratio

Every group of treatment performed C/N in soil higher more than control group significantly different. Group 4 (OCd60.0) and Group 6 (PCd0) displayed the highest results.

11) CEC

Every group of treatment performed CEC in soil higher more than control group significantly different. Group 2 (OCd20.0) displayed the highest results.

12) Cd Residue in Soil

Almost every group of treatment performed Cd residual in soil higher more than control group significantly different except group 1 (OCd0) and group 6 (PCd0) not significant different to control group. Group 10 (PCd80.0) displayed the highest results.

Considering in the result of two kilns that interact with same Cd level, L kiln increased up higher in parameter % moisture content, pH, K, Mg, while O kiln perform higher in parameter EC, P, Ca and CEC. For parameter OM, N and C/N ratio results not clearly between this two kiln that which one was higher. Interesting about Cd residue results reveal that at Cd level ≤ 40.0 mg Cd kg⁻¹soil, L kilns showed % Cd removal better more than O kiln, but when Cd level up higher ≥ 60.0 mg Cd kg⁻¹soil, O kilns performed better results.

Pyrolysis reactor characteristics, peak process temperature, heating rate, and feedstock quality (e.q. particle size and water content) strongly influence the proportion and quality of the pyrolysis products. In general, higher pyrolysis temperatures result in lower biochar yields with less original structures and chemical components remaining. Biochar characteristics such as elemental composition, porosity, particle and pore sizes, and fractions of easily degradable hydrocarbons are also highly influenced by the above parameters (Antal and Gronli, 2003: 1619; Downie, Crosky, Manroe, 2009: 13).

It is generally accepted that mechanisms leading to an increase in surface area and/or hydrophobicity of the char, reflected in an enhance sorption affinity and capacity toward trace element (Tsui and Roy, 2008: 5673). The influence of pyrolysis temperatures do to high temperature chars appear to be exclusively by surface adsorption, while that to low temperature chars derived from both surface adsorption and absorption to residual organic matter (Chun, Sheng, Chiou and Xing, 2004: 4649). Evidence from several laboratory and field studies suggest that the application of biochar may lead to decreased nutrient leaching and contaminant transport below the root zone (Verheijen et al., 2010: 76). Several mechanisms contribute to the decrease in nutrient leaching which are related to increased nutrient use efficiency by increase water and nutrient retention and availability, related to an increased internal reactive surface area of the soil – biochar matrix, decreased water percolation below the root zone related to increased plant water use, and increase plant nutrient use through enhanced crop growth. Higher retention times also permit a better decomposition of organic material and promote breakdown of agrichemicals (Verheijen et al., 2010: 76). Biochar directly contributes to nutrient adsorption through charge or covalent interactions on a high surface area. Major et al., 2002 (Quoted in Verheijen et al., 2010: 76) showed that biochar must be produced at temperature above 500 °C or be activated to results in increased surface area of the biochar and thus increase direct sorption of nutrient while Hossain, Strezov and Nelson (2007 quoted in Verheijen et al. 2010: 78) had reported that slow pyrolysis at temperature below 500 °C is known to favour the accumulation of readily available micronutrients. For this study had control same feedstock, pyrolysis type and peak temperature at 500 °C which differently only kiln that be used as pyrolysis reactor. Due to the result showed a differently in many parameter of soil properties that may be from a variation that not control such as position of the kiln where O kiln line in horizontal while L kiln post in vertical position, a heating rate that at highest temperature 500 °C L kiln get heating from burning LPG which can hold a stable heating rate more than O kiln which get heating from wooden burning as a traditional charcoal making principle, may be effect differently to production properties.

4.4.4.2 Soybean Growth Stage

The result showed an interaction between Factor A (kilns) and Factor B (Cadmium level) in every parameter of soybean growth stage. This mean that an interaction between this two factor had effected to soybean growth stage significantly.

1) Vegetative Growth Stage

(1) Planting Date to Stage of Emergence (VE)

Group 1 (OCd0), group 2(OCd20), group 6 (PCd0) and group 7 (PCd20.0), take shortest day not significantly different ($p>0.05$) to control group developed from planting date to VE stage. Except these 4 groups take longer day more than control group significantly different ($p<0.05$).

(2) Planting Date to Stage of V4

Group 1 (OCd0) and group 6 (PCd0) take shortest day developed from planting date to V4 stage significantly different ($p<0.05$) to control group, while group2 (OCd20.0) and group7 (PCd20.0) not significantly different ($p>0.05$) to control group, except these 4 groups take longer day more than control group significantly different ($p<0.05$), especially group 10 (PCd80.0) take longest day.

(3) Planting Date to Beginning Bloom (R1)

Group 1(OCd0) and group6 (PCd0) take shortest day developed from planting date to R1 stage significantly different ($p<0.05$) to control group, while group 2 (OCd20.0) and group 7 (PCd20.0) not significantly different ($p>0.05$) to control group. Except these 4 groups take longer day more than control group significantly different ($p<0.05$), especially group 5 (OCd80.0) and group 10 (PCd80.0) take longest day.

(4) Planting Date to Stage of Maturity (R8)

Group 6 (PCd0) take shortest day developed from planting date to R8 stage significantly different ($p<0.05$) to control group, while group 1 (OCd0) not significantly different ($p>0.05$) to control group. Except these 2 groups take longer day more than control group significantly different ($p<0.05$), especially group 10 (PCd80.0) take longest day.

4.4.4.3 Soybean Productive Performance

Factor A (kilns) and Factor B (Cadmium level) showed an interaction result in every parameter of soybean productive performance. This mean that between this two factors had effected to soybean productive performance significantly.

1) Stem Weight

Group 6 (PCd0) displayed the heaviest weight of soybean stem, following with group 1 (OCd0), then group 7 (PCd20.0), group 2 (OCd20.0) similary with group 8 (PCd40.0), then group 9 (PCd60.0), following with control group, then group 3 (OCd40.0), group 4 (OCd60.0), group 10 (PCd80.0) and the lowest was group 5 (OCd80.0).

2) Pod Weight

Group 6 (PCd0) displayed the heaviest weight of soybean pod, following with group 1 (OCd0), then group 7 (PCd20.0) that similary to group 2 (OCd20.0), then control group that equally to group 8 (PCd40.0), then group 9 (PCd60.0) similary to group 3 (OCd40.0), then group 4 (OCd60.0) that similary to group 10 (PCd80.0) and the lowest was group 5 (OCd80.0) that not significantly different to group 10 (PCd80.0).

3) Height

Group 1 (OCd0) displayed the highest of soybean height, following with group 6 (PCd0), then group 2 (OCd20.0), then control group, group 7 (PCd20.0), group 8 (PCd40.0) that similary to group 9 (PCd60.0), then group 3 (OCd40.0), group 4 (OCd60.0), group 10 (PCd80.0) and the shortest was group 5 (OCd80.0).

4) Number of Node

Group 6 (PCd0) displayed the most of number of soybean node, following with group 1 (OCd0) that similary to group 7 (PCd20.0), then group 2 (OCd20.0) that equally to group 8 (PCd40.0) and group 9 (PCd60.0), then group 3 (OCd40.0) that the result showed not significantly different to group 4 (OCd60.0) and control group, then group 10 (PCd80.0) and the least was group 5 (OCd80.0).

5) Number of Pod

Group 6 (PCd0) displayed the most of number of soybean pod, following with group 1 (OCd0), then group 7 (PCd20.0), control group, group 8

(PCd40.0), group 2 (OCd20.0), group 3 (OCd40.0), group 4 (OCd80.0) that equally to group 9 (PCd60.0) and group 9 (PCd60.0), then group 10 (PCd80.0) and the least was group 5 (OCd80.0).

6) Number of Seed per Pod

Group 6 (PCd0) displayed the most of number of soybean seed per pod, following with group 7 (PCd20.0) that similar to group 1 (OCd0), then group 2 (OCd20.0) that equally to group 8 (PCd40.0), following with group 9 (PCd60.0), group 3 (OCd40.0) that the result showed not significantly different to group 10 (PCd80.0), group 4 (OCd60.0) that similar to control group and group 5 (OCd80.0) presented the least of number of seed per pod.

7) 100 Seeds Dry Weight

Group 1 (OCd0) displayed the heaviest of 100 seeds dry weight, following with group 6 (PCd0), then group 7 (PCd20.0) that similar to group 2 (OCd20.0), then group 8 (PCd40.0), group 9 (PCd60.0), control group, group 3 (OCd40.0), group 4 (OCd60.0), group 10 (PCd80.0) and the lowest was group 5 (OCd80.0).

8) Product per Pot

Group 6 (PCd0) displayed the heaviest of product per pot, following with group 1 (OCd0), then group 2 (OCd20.0), group 7 (PCd20.0) that similar with group 8 (PCd40.0), then control group, group 9 (PCd60.0), group 3 (OCd40.0) that equally to group 4 (OCd60.0) and group 10 (PCd80.0) and the lowest was group 5 (OCd80.0).

9) Protein in Soybean's seeds

Group 1 (OCd0) displayed the most of protein amount, however not significantly to group 6 (PCd0) and group 2 (OCd20.0), following with group 3 (OCd40.0) while this group not significantly different to group 2 (OCd20.0) and group 6 (PCd0), then group 7 (PCd20.0) that similar to group 8 (PCd40.0), then group 4 (OCd60.0) equally with group 9 (PCd60.0), however not significantly different to group 7 (PCd20.0), and group 8 (PCd40.0), then group 10 (PCd80.0) that not significantly different group 4 (OCd60.0) and group 9 (PCd60.0), then control group that was not significantly different to group 5 (OCd80.0).

10) Lipid in Soybean's Seeds

Group 6 (PCd0) displayed the heaviest of product per pot, following with group 7 (PCd20.0), then group 1 (OCd0), group 2 (OCd20.0), group 3 (OCd40.0), group 4 (OCd60.0) that not significantly different to group 8 (PCd40.0), then group 9 (PCd60.0) that not significantly to group 8 (PCd40.0), then group 10 (PCd80.0), group 5 (OCd80.0), and the lowest was control group.

11) Leaf Area R1

Group 6 (PCd0) displayed the highest of leaf area R1, following with group 1 (OCd0), then group 7 (PCd20.0), group 2 (OCd20.0), group 8 (PCd40.0), group 3 (OCd40.0), group 9 (PCd60.0), then group 4 (OCd60.0), group 10 (PCd80.0), then group 5 (OCd80.0), and the lowest was control group.

12) Leaf Area R3

Group 6 (PCd0) displayed the highest of leaf area R3, following with group 1 (OCd0), then group 2 (OCd20.0), group 7 (PCd20.0), control group, group 3 (OCd40), group 4 (OCd60.0), group 8 (PCd40.0), group 5 (OCd80.0), group 9 (PCd60.0), and the lowest was group 10 (PCd80.0).

13) Leaf Area R5

Group 1 (OCd0) displayed the highest of leaf area R5, following with group 6 (PCd0), then group 7 (PCd20.0), group 2 (OCd20.0), control group, group 3 (OCd40.0), group 8 (PCd40.0), group 9 (PCd60.0), group 4 (OCd60.0), group 5 (OCd80.0), and the lowest was group 10 (PCd80.0).

14) Leaf Area R7

Group 1 (OCd0) displayed the highest of leaf area R7, following with group 6 (PCd0), then group 7 (PCd20.0), group 2 (OCd20.0), control group, group 3 (OCd40.0), group 8 (PCd40.0), group 9 (PCd60.0), then group 4 (OCd60.0), group 5 (OCd80.0), and the lowest was group 10 (PCd80.0).

Consider for the result of soybean productive performance L kiln perform better more than O kiln in almost every parameter accept height, protein and leaf area R1 – R7 which O kiln displayed better. Interesting that albeit pre – treat soil had polluted with Cd which we know that Cd had negative effect to plant development and decreased the production, however the result in this study still showed better more than control group which not polluted Cd especially the results

from interaction between O or L kiln with Cd level 20.0 mg Cd kg⁻¹soil. Surprisingly in the result of L kiln which interact with Cd level 40.0 mg Cd kg⁻¹soil perform better more than control group in parameter 100 seeds dry weight and production per pot.

4.4.4.4 Cd Residue in Soybean Part

The result showed an interaction between Factor A (kilns) and Factor B (Cadmium level) in every parameter of Cd residue in soybean part. This mean that an interaction between this two factor had effected to Cd residue in soybean part significantly.

1) Cd Residue in Soybean Root

Control group performed the best result do like Group 1 (OCd0) and group 6 (PCd0) that not have Cd residue in soybean root after treatment. In this parameter group 10 (PCd80.0) had highest Cd residue in soybean root following with group 5 (OCd80.0) that similary to group 9 (PCd60.0), then group 4 (OCd60.0), group 8 (PCd40.0), then group 7 (PCd20.0), group 2 (OCd20.0) respectively.

2) Cd Residue in Soybean Shoot

The result of Cd residue in soybean shoot had shown the trend like the result that displayed on Cd residue in soybean root.

3) Cd Residue in Soybean Leaf

The result of Cd residue in soybean leaf had shown the trend like the result that displayed on Cd residue in soybean root and shoot.

4) Cd Residue in Soybean Seed

The result of Cd residue in soybean seed had shown the trend like the result that displayed on Cd residue in soybean root, shoot and leaf.

The results showed a tendency of Cd in different parts of the soybean was as follow: roots >> stems > leaf > seeds. Furthermore, the trend of Cd that remain in each part of soybean after treatment, obviously clarify that when compare between O and L kiln in the same Cd level, O kiln had shown the result of Cd residue in each part lower than L kiln significantly different and the trend slightly lower from highest Cd level 80.0 mg kg⁻¹ had Cd residue in soybean part higher more than Cd level 60.0 > Cd level 40.0 > Cd level 20.0 > Cd 0 that not have Cd residue in soybean part like control. This mean that an interaction between O kiln with Cd level had effected to

the process of the uptake of Cd the polluted in soil by soybean effective more than L kiln. This studied use pelleted broiler litter biochar derieved from one condition that was slow pyrolysis, less O₂, highest temperature of 500°C and duration 8.00 hrs to 1 day but different in the burning tank that one was lab–scale pyrolysis reator (PBLBL) that used LPG for the heating source, the other one was 200 liter oil drum kiln (PBLB0) using wooden burning as a heating source that had been done in locally sector as charcoal production. The two purpose using biochar of this studied were: 1st for the soil fertilizer and conditioner and 2nd a sorptive agent for Cd contaminated soil remediation. As known that the sorptive mechanism do to the porous and surface of adsorption agent, our two biochar PBLBL and PBLBO had BET surface area about 5.20 and 6.41 m² g⁻¹, respectively, moreover had pH about 9.40 and 9.90, respectively that may be suspected that PBLBO had powerful being a sorptive agent and absorp Cd effectively than PBLBL. Furthermore chicken manure was a source of organic materials so when this study used as an OM in Cd soil can reduce Cd uptake by plants, enhanced OM and CEC in soil and promote growth quality of plant. Kasmaei and Fekri (2012: 2209) had concluded about the effect of organic matter on the release behavior and extractability of copper and cadmium in soil by used poultry manure and pistachio at the rate 300 g kg⁻¹, results showed that Cd decreased with both pistachio compost and poultry manure treatments as compared to the control soil. Haghiri (1974: 180) conclude that “The retaining power of organic matter for Cd is predominately through CEC property rather than chelating ability”. Uptake and accumulation of trace elements by plants were effected by several soil factors, including pH, clay content, organic matter content, cation exchange capacity, nutrient balance, concentration of other trace elements in soil, and soil moisture and temperature (Efremova and Izosimova (2013) Increased acidity also leads to desorption of Cd from soil organic matter (Zachara, Smith, Resch and Cowan, 1992: 1074). Also with Qadir, Ghafoor, Murtaza and Murtaza (2000: 13) quoted that soil Cd concentration was significantly correlated with soil clay content, pH, electrical conductivity, and cation exchange capacity. Soil pH was a major factor influence Cd solubility and mobility in soils (Carrillo-Gonzalez, Simunek, Sauve and Adrino, 2006: 111). In the soil, increasing pH from 5.5 to 7.0 has significantly decreased Cd concentrations in clover, lettuce, carrot, rye grass and to a lesser extent in wheat (Gray, McLaren, Roberts and Condrón, 1999(b): 169).

Cations are held more strongly when pH increases from 5 to 7. Cu, Zn, Ni, Cd and other metals become significantly less soluble and less exchangeable when pH increases. Retention of metals in soil can occur through several processes: (1) cation exchange (non-specific adsorption), (2) specific adsorption, (3) organic complexation and (4) co-precipitation. In a given situation most, if not all, of these processes contribute to metal retention in soils...Specific adsorption is pH dependent and related to the hydrolysis of the heavy metal ion. In specific adsorption partly covalent bonds are formed with the lattice ions. Partly covalent bonds are inherently stronger than electrostatic binding involved in the non-specific electrostatic binding involved in the non-specific cation exchange...Metals most able to form hydroxyl complexes are specifically adsorbed to the greatest extent: $Hg > Pb > Cu > Zn > Co > Ni > Cd$. Specific adsorption may also include diffusion of metals into mineral interlayer spaces and their fixation. Such diffusion increases with an increase in pH...In chemical terms, pH represents a measure of H^+ activity in a soil solution which is in a dynamic equilibrium with a negatively charged solid phase. H^+ ions are strongly attracted to these negative sites and have sufficient power to replace other cations from them. A diffuse layer in the vicinity of a negatively charged surface has higher H^+ activity than the bulk soil solution.

According to the studies of Miller et al. (1976: 157) had concluded that “cadmium uptake decreased as soil pH and CEC increasing” and according to Hinesly, Redberg, Ziegler and Alexander (1982: 490) that “an increase in CEC

decreases uptake of metals by plants". Moreover, Sarwar et al. (2010: 925) have shown the interaction of mineral nutrients in reducing Cd accumulation, and elucidate the roles of essential and beneficial plant elements in Cd stress alleviation. Pankovic, et al., (2000: 841) have shown that optimal N supply decreased the inhibitory effects of Cd on photosynthesis of sunflower plants by increasing ribulose 1, 5 – biphosphate carboxylase activity or by increase in soluble protein content. Wang, Zhao, Liu, Zhou and Jin (2009: 277) revealed that application of phosphate fertilizers decreased the mobility of Cd in soil by changing mobile forms of Cd to the immobile form of Cd phosphate. The form of K applied has differential effect on Cd accumulation and Cd stress (Nazar, et al., 2012: 1483). Availability of K protects mustard plants from Cd toxicity by reducing its availability thereby depressing H₂O₂ content and lipid peroxidation, and increasing the activity of antioxidative enzymes (Umar, Diva, Anjum and Iqbal, 2008 quoted in Nazar, et al., 2012: 1483). The increasing concentration of Cd in the external medium replaces Ca at the binding site by other heavy metal cations at the exterior surface of the plasma membrane, thereby increasing Ca requirement (Nazar, et al., 2012: 1483). Ca reduces the Cd toxicity mainly by reducing its uptake and competing at the transport site and through influencing various physiological processs (Nazar, et al., 2012: 1483). Herman, Chen, Coppens, Inzé and Verbruggen (2011: 428) had concluded the protective effect of Mg against Cd toxicity could be "attributable partly to the maintenance of Fe status but also to the increase in antioxidative capacity, detoxification and/or protection of the photosynthetic apparatus". Wang, Ji, Yang, Chen, Browne and Yu (2012: 264) had identified the effects of soil properties on the transfer of Cd from soil to wheat under field conditions, they found that Cd showed a strong correlation with Fe, S, and P present in the grain and the soil, whereas there was no significant corration in the straw or root and found that soil pH, Ca, Mg, Mn, P, and slowly available K restricted Cd transfer from soil to wheat, whereas soil S, N, Zn, DTPA-Fe, and total organic carbon enhance Cd uptake by wheat.

Table 4.8 Interaction between Factor A (Reactor) and Factor B (Cd Level) on Soil Properties, Soybean Growth Stage, and Productive Performance

| Para meter | Control | Inter Action | 200 Liter Oil Drum Kiln (PBLBO) | | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | | | CV |
|-----------------|---------------------|-----------------|---------------------------------|----------------------|----------------------|----------------------|----------------------|---------------------------------------|---------------------|---------------------|----------------------|----------------------|-------|
| | | | Cd0 | Cd20.0 | Cd40.0 | Cd60.0 | Cd80.0 | Cd0 | Cd20.0 | Cd40.0 | Cd60.0 | Cd80.0 | |
| Soil | | | | | | | | | | | | | |
| Moisture | 5.00 ^f | I | 4.95 ^{fg} | 8.82 ^a | 8.40 ^b | 4.88 ^g | 4.62 ^h | 5.88 ^e | 5.98 ^d | 6.28 ^c | 4.60 ^h | 5.01 ^f | 1.21 |
| pH | 4.20 ^e | I | 4.69 ^d | 4.83 ^b | 4.75 ^c | 4.65 ^d | 4.68 ^d | 5.08 ^a | 5.06 ^a | 4.78 ^c | 4.87 ^b | 4.87 ^b | 0.729 |
| EC | 0.0898 ^j | I | 0.107 ⁱ | 0.108 ^h | 0.127 ^f | 0.193 ^d | 0.318 ^a | 0.0871 ^k | 0.115 ^g | 0.189 ^e | 0.217 ^c | 0.315 ^b | 0.145 |
| OM | 1.07 ^f | I | 1.36 ^c | 1.36 ^e | 1.37 ^c | 1.41 ^{ab} | 1.14 ^d | 1.09 ^e | 1.37 ^{bc} | 1.43 ^a | 1.38 ^{bc} | 1.37 ^c | 2.14 |
| N | 0.0830 ^b | NI | 0.129 ^a | 0.0986 ^{ab} | 0.0987 ^{ab} | 0.0987 ^{ab} | 0.0991 ^{ab} | 0.0968 ^{ab} | 0.129 ^a | 0.100 ^{ab} | 0.0995 ^{ab} | 0.0987 ^{ab} | 19.5 |
| P | 3.00 ⁱ | I | 50.8 ^a | 47.8 ^b | 43.7 ^d | 46.8 ^c | 42.0 ^e | 28.5 ^h | 43.9 ^d | 39.8 ^f | 38.8 ^g | 39.6 ^f | 0.774 |
| K | 35.0 ^k | I | 183 ^j | 189 ^b | 205 ^g | 256 ^e | 318 ^b | 186 ⁱ | 217 ^f | 286 ^c | 357 ^a | 275 ^d | 0.350 |
| Ca | 135 ^k | I | 179 ^e | 176 ^f | 153 ^j | 170 ^g | 206 ^a | 204 ^b | 192 ^d | 160 ⁱ | 164 ^h | 201 ^c | 0.237 |
| Mg | 24.0 ^h | I | 64.3 ^f | 64.3 ^f | 61.8 ^g | 65.8 ^e | 75.8 ^c | 62.4 ^g | 71.0 ^d | 71.5 ^d | 82.0 ^b | 141 ^a | 0.719 |
| C/N | 7.00 ^d | I | 7.78 ^{bc} | 8.02 ^{abc} | 8.04 ^{abc} | 8.35 ^a | 8.04 ^{abc} | 8.29 ^a | 7.73 ^c | 8.18 ^{ab} | 7.98 ^{abc} | 7.95 ^{abc} | 3.11 |
| CEC | 2.87 ^g | I | 3.24 ^{cd} | 4.66 ^a | 3.13 ^e | 3.36 ^b | 3.27 ^c | 2.95 ^f | 3.10 ^e | 3.35 ^b | 3.19 ^d | 3.26 ^c | 1.13 |
| Cd in soil | 0.000 ^j | I | 0.000 ^j | 10.3 ^g | 21.0 ^e | 27.2 ^d | 40.6 ^b | 0.000 ^j | 8.84 ^h | 18.9 ^f | 39.8 ^c | 41.8 ^a | 0.767 |
| Soy bean | | | | | | | | | | | | | |
| Planting | 33.0 ^e | I | 31.2 ^f | 33.5 ^e | 39.2 ^d | 40.7 ^{bc} | 41.0 ^b | 30.5 ^f | 33.7 ^e | 40.0 ^{cd} | 39.9 ^{cd} | 42.9 ^a | 1.45 |
| Date –V4 | | | | | | | | | | | | | |
| Planting | 4.00 ^d | I | 3.75 ^d | 4.25 ^{cd} | 5.00 ^{bc} | 5.50 ^{ab} | 5.75 ^{ab} | 4.00 ^d | 4.00 ^d | 5.50 ^{ab} | 5.50 ^{ab} | 6.00 ^a | 12.4 |
| Date-VE | | | | | | | | | | | | | |
| VE – VC | 4.00 ^{ef} | I | 3.00 ^g | 4.00 ^{ef} | 4.50 ^{de} | 4.75 ^{cde} | 5.75 ^{ab} | 3.25 ^{fg} | 4.00 ^{ef} | 5.00 ^{bcd} | 5.50 ^{abc} | 6.00 ^a | 12.2 |
| VC – V1 | 5.00 ^{de} | I | 4.00 ^f | 4.50 ^{ef} | 6.18 ^{abc} | 7.00 ^a | 6.25 ^{ab} | 4.00 ^f | 5.25 ^{cde} | 5.75 ^{bcd} | 7.00 ^a | 7.00 ^a | 11.2 |
| V1 – V2 | 6.00 ^c | I | 6.25 ^{bc} | 6.25 ^{bc} | 6.50 ^{abc} | 7.25 ^a | 7.00 ^{ab} | 6.50 ^{abc} | 6.00 ^C | 7.00 ^{ab} | 7.25 ^a | 7.25 ^a | 8.89 |

Table 4.8 (Continued)

| Parameter | Control | Inter action | 200 Liter Oil Drum Kiln (PBLBO) | | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | | | CV |
|-------------------|--------------------|-----------------|---------------------------------|--------------------|--------------------|--------------------|---------------------|---------------------------------------|--------------------|--------------------|--------------------|---------------------|-------|
| | | | Cd0 | Cd20.0 | Cd40.0 | Cd60.0 | Cd80.0 | Cd0 | Cd20.0 | Cd40.0 | Cd60.0 | Cd80.0 | |
| | | | V2 – V3 | 6.00 ^d | I | 7.00 ^{bc} | 6.75 ^{bcd} | 6.00 ^d | 7.25 ^{ab} | 7.25 ^{ab} | 6.25 ^{cd} | 7.25 ^{ab} | |
| V3 – V4 | 8.00 ^b | I | 7.50 ^b | 8.00 ^b | 9.00 ^a | 8.25 ^b | 9.50 ^a | 6.50 ^c | 8.25 ^b | 9.25 ^a | 9.25 ^a | 9.50 ^a | 6.00 |
| Planting | 39.0 ^c | I | 36.0 ^d | 38.2 ^c | 43.6 ^b | 44.0 ^b | 46.2 ^a | 36.0 ^d | 38.5 ^c | 43.7 ^b | 44.2 ^b | 45.7 ^a | 1.27 |
| Date – R1 | | | | | | | | | | | | | |
| R1 – R2 | 2.00 ^b | I | 2.00 ^b | 2.50 ^b | 3.00 ^b | 3.00 ^b | 3.00 ^b | 2.25 ^b | 3.00 ^b | 3.00 ^b | 3.00 ^b | 4.25 ^a | 25.2 |
| R2 – R3 | 3.00 ^a | NI | 3.00 ^a | 2.50 ^a | 2.50 ^a | 2.66 ^a | 3.00 ^a | 2.75 ^a | 3.00 ^a | 2.50 ^a | 2.75 ^a | 3.25 ^a | 19.4 |
| R3 – R4 | 2.00 ^b | NI | 2.00 ^b | 2.50 ^{ab} | 2.50 ^{ab} | 3.00 ^a | 3.00 ^a | 2.00 ^b | 2.75 ^{ab} | 2.75 ^{ab} | 2.75 ^{ab} | 3.25 ^a | 23.3 |
| R4 – R5 | 3.00 ^a | I | 1.25 ^c | 2.00 ^b | 2.25 ^b | 2.36 ^{ab} | 2.75 ^{ab} | 2.00 ^b | 2.25 ^b | 2.25 ^b | 2.75 ^{ab} | 2.75 ^{ab} | 19.6 |
| R5 – R6 | 10.7 ^{de} | I | 7.50 ^g | 10.0 ^{de} | 10.9 ^c | 12.5 ^b | 12.5 ^b | 8.63 ^f | 9.75 ^e | 9.75 ^e | 10.5 ^d | 13.0 ^a | 3.23 |
| R6 – R7 | 10.5 ^c | I | 10.0 ^d | 10.03 ^d | 10.5 ^{bc} | 11.0 ^b | 12.5 ^a | 9.25 ^d | 10.2 ^c | 10.5 ^{bc} | 12.2 ^a | 12.5 ^a | 4.08 |
| R7 – R8 | 21.0 ^d | I | 20.0 ^e | 20.5 ^{de} | 23.2 ^c | 24.0 ^{bc} | 24.6 ^b | 18.0 ^f | 21.2 ^d | 24.0 ^{bc} | 24.0 ^{bc} | 25.7 ^a | 2.59 |
| Planting | 90.0 ^g | I | 89.5 ^g | 91.5 ^f | 96.5 ^d | 99.0 ^c | 100 ^b | 87.0 ^h | 94.7 ^e | 96.5 ^d | 99.0 ^c | 103 ^a | 0.640 |
| Date – R8 | | | | | | | | | | | | | |
| Stem | 0.305 ^f | I | 0.615 ^b | 0.359 ^d | 0.279 ^g | 0.245 ^h | 0.154 ^j | 0.716 ^a | 0.433 ^c | 0.358 ^d | 0.313 ^e | 0.206 ⁱ | 0.870 |
| Weight | | | | | | | | | | | | | |
| Pod | 1.00 ^{de} | I | 2.27 ^b | 1.14 ^{cd} | 0.613 ^f | 0.449 ^g | 0.285 ^h | 2.77 ^a | 1.24 ^c | 0.976 ^e | 0.655 ^f | 0.420 ^{gh} | 8.92 |
| Weight | | | | | | | | | | | | | |
| Height | 30.6 ^d | I | 40.3 ^a | 30.9 ^c | 23.4 ^g | 21.8 ^h | 21.4 ^j | 39.5 ^b | 29.4 ^e | 25.2 ^f | 25.2 ^f | 21.6 ⁱ | 0.143 |
| Number of Node | 5.05 ^e | I | 5.65 ^b | 5.44 ^c | 5.16 ^d | 5.06 ^{de} | 4.70 ^f | 6.23 ^a | 5.55 ^b | 5.36 ^c | 5.35 ^c | 5.03 ^e | 1.35 |

Table 4.8 (Continued)

| Parameter | Control | Inter action | 200 Liter Oil Drum Kiln (PBLBO) | | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | | | CV |
|---------------------------|---------------------|-----------------|---------------------------------|----------------------|----------------------|----------------------|---------------------|---------------------------------------|---------------------|---------------------|----------------------|----------------------|--------|
| | | | Cd0 | Cd20.0 | Cd40.0 | Cd60.0 | Cd80.0 | Cd0 | Cd20.0 | Cd40.0 | Cd60.0 | Cd80.0 | |
| | | | Number of Pod | 3.50 ^d | I | 6.95 ^b | 2.88 ^f | 2.50 ^g | 2.15 ^h | 1.43 ^j | 8.55 ^a | 3.63 ^c | |
| Number of Seed per Pod | 1.26 ^f | I | 1.99 ^b | 1.65 ^c | 1.47 ^e | 1.28 ^f | 1.26 ^f | 2.07 ^a | 2.01 ^b | 1.65 ^c | 1.51 ^d | 1.44 ^e | 1.30 |
| Dry Weight 100 Seeds | 10.6 ^f | I | 17.5 ^a | 12.9 ^c | 10.4 ^g | 9.97 ^h | 7.58 ^j | 17.3 ^b | 13.0 ^c | 12.0 ^d | 11.8 ^e | 9.19 ⁱ | 0.383 |
| Product per Pot | 2.08 ^e | I | 6.36 ^b | 3.51 ^c | 1.43 ^g | 1.28 ^g | 0.798 ^h | 8.69 ^a | 3.12 ^d | 3.02 ^d | 1.76 ^f | 1.28 ^g | 5.46 |
| Protein | 35.1 ^{de} | I | 36.6 ^a | 36.2 ^{ab} | 36.1 ^b | 35.6 ^{cd} | 34.8 ^e | 36.2 ^{ab} | 36.0 ^{bc} | 35.9 ^{bc} | 35.6 ^{cd} | 35.3 ^d | 0.848 |
| Lipid | 18.4 ⁱ | I | 19.6 ^c | 19.5 ^d | 19.3 ^e | 19.2 ^f | 19.0 ^h | 19.8 ^a | 19.7 ^b | 19.2 ^f | 19.1 ^g | 19.1 ^g | 0.0828 |
| Leaf Area R1 | 6.69 ^k | I | 24.9 ^b | 11.0 ^d | 7.59 ^f | 7.24 ^h | 6.99 ^j | 25.4 ^a | 22.4 ^c | 7.75 ^e | 7.36 ^g | 7.04 ⁱ | 0.245 |
| Leaf Area R3 | 11.8 ^e | I | 34.4 ^b | 16.4 ^c | 9.71 ^f | 8.90 ^g | 8.53 ⁱ | 36.4 ^a | 14.1 ^d | 8.68 ^h | 8.24 ^j | 7.76 ^k | 0.487 |
| Leaf Area R5 | 16.2 ^e | I | 60.7 ^a | 17.6 ^d | 11.5 ^f | 10.5 ⁱ | 10.39 ^j | 43.1 ^b | 20.1 ^c | 10.7 ^g | 10.6 ^h | 9.86 ^k | 0.178 |
| Leaf Area R7 | 18.4 ^e | I | 72.7 ^a | 19.8 ^d | 12.7 ^f | 11.8 ^g | 10.9 ^{hi} | 59.6 ^b | 21.0 ^c | 12.6 ^f | 11.2 ^h | 10.6 ⁱ | 1.44 |
| Pod Weight R3 | 0.0242 ^e | I | 0.0694 ^c | 0.0281 ^d | 0.0167 ^{gh} | 0.0127 ^{ij} | 0.0106 ^j | 0.155 ^a | 0.0970 ^b | 0.0212 ^f | 0.0186 ^{fg} | 0.0147 ^{hi} | 4.38 |
| Pod Weight R5 | 0.0608 ^c | I | 0.104 ^b | 0.0484 ^{de} | 0.0447 ^{ef} | 0.0349 ^h | 0.0298 ⁱ | 0.290 ^a | 0.0497 ^d | 0.0488 ^d | 0.0418 ^{fg} | 0.0382 ^{gh} | 3.65 |
| Pod Weight R6 | 1.08 ^d | I | 3.22 ^a | 1.03 ^e | 0.847 ^g | 0.670 ⁱ | 0.569 ^j | 2.920 ^b | 1.27 ^c | 0.973 ^f | 0.726 ^h | 0.658 ⁱ | 1.36 |
| Pod Weight R7 | 1.28 ^d | I | 3.12 ^b | 1.10 ^e | 0.978 ^g | 0.627 ^j | 0.588 ^k | 3.58 ^a | 1.33 ^c | 1.06 ^f | 0.930 ^h | 0.744 ⁱ | 1.04 |
| Pod Weight R8 | 0.870 ^f | I | 2.27 ^b | 1.12 ^d | 0.628 ⁱ | 0.450 ^j | 0.285 ^k | 2.93 ^a | 1.24 ^c | 0.976 ^e | 0.779 ^g | 0.654 ^h | 0.666 |
| Stem Weight R1 | 0.312 ^{de} | I | 0.928 ^a | 0.319 ^{de} | 0.309 ^{de} | 0.286 ^e | 0.176 ^f | 0.800 ^b | 0.518 ^c | 0.358 ^d | 0.288 ^e | 0.288 ^e | 8.06 |

Table 4.8 (Continued)

| Parameter | Control | Inter Action | 200 Liter Oil Drum Kiln (PBLBO) | | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | | | CV |
|-------------|--------------------|-----------------|---------------------------------|--------------------|--------------------|--------------------|--------------------|---------------------------------------|--------------------|--------------------|--------------------|--------------------|-------|
| | | | Cd0 | Cd20.0 | Cd40.0 | Cd60.0 | Cd80.0 | Cd0 | Cd20.0 | Cd40.0 | Cd60.0 | Cd80.0 | |
| Stem | 0.477 ^e | I | 1.10 ^b | 0.447 ^f | 0.340 ⁱ | 0.310 ^l | 0.258 ^k | 1.51 ^a | 0.846 ^c | 0.578 ^d | 0.377 ^g | 0.349 ^h | 0.423 |
| Weight R3 | | | | | | | | | | | | | |
| Stem | 0.589 ^f | I | 0.939 ^b | 0.710 ^d | 0.617 ^e | 0.535 ^h | 0.379 ^j | 1.65 ^a | 0.825 ^c | 0.565 ^g | 0.536 ^h | 0.459 ⁱ | 1.35 |
| Weight R5 | | | | | | | | | | | | | |
| Stem | 0.814 ^g | I | 2.59 ^b | 0.868 ^e | 0.855 ^f | 0.676 ⁱ | 0.527 ^j | 3.07 ^a | 1.39 ^c | 1.25 ^d | 0.855 ^f | 0.705 ^h | 0.281 |
| Weight R6 | | | | | | | | | | | | | |
| Stem | 0.407 ⁱ | I | 0.856 ^a | 0.768 ^c | 0.580 ^g | 0.479 ^h | 0.299 ^k | 0.795 ^b | 0.744 ^d | 0.620 ^e | 0.600 ^f | 0.348 ^j | 0.619 |
| Weight R7 | | | | | | | | | | | | | |
| Stem | 0.253 ^h | I | 0.616 ^b | 0.359 ^f | 0.280 ^g | 0.245 ⁱ | 0.156 ^j | 0.716 ^a | 0.548 ^c | 0.488 ^d | 0.396 ^e | 0.257 ^h | 0.803 |
| Weight R8 | | | | | | | | | | | | | |
| Cd in Root | 0 ^g | I | 0 ^g | 2.29 ^f | 5.6 ^d | 7.45 ^c | 9.22 ^b | 0 ^g | 3.30 ^e | 6.01 ^d | 9.35 ^b | 12.8 ^a | 10.9 |
| Cd in Shoot | 0 ^g | I | 0 ^g | 2.87 ^f | 3.87 ^d | 4.06 ^d | 7.36 ^b | 0 ^g | 3.30 ^e | 4.11 ^d | 5.36 ^c | 9.20 ^a | 6.36 |
| Cd in Leaf | 0 ^f | I | 0 ^f | 1.59 ^e | 4.00 ^d | 4.95 ^c | 5.89 ^a | 0 ^f | 1.71 ^e | 4.02 ^d | 5.55 ^b | 6.06 ^a | 4.74 |
| Cd in Seed | 0 ^e | I | 0 ^e | 0.187 ^d | 0.295 ^c | 0.442 ^b | 0.680 ^a | 0 ^e | 0.187 ^d | 0.267 ^c | 0.417 ^b | 0.645 ^a | 10.6 |

Note: Means in the Same Row with Different Letters are Significantly Different at P < 0.05.

4.4.5 Interaction between Factor A (Reactor) and Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productive Performance

4.4.5.1 Soil Property

Factor A (kilns) and Factor C (Biochar mixing rate) showed an interaction result in every parameter of soil properties. Interaction between these two factors had increased almost every parameter, except % moisture content in soil significantly different to control group.

1) % Moisture

The results showed a slightly significantly different among groups ($p < 0.05$), where group 1 (PBLBO5.00) performed highest % moisture content in soil similarly to group 4 (PBLBO20.0), following with group 5 (PBLBL5.00) similar with group 8 (PBLBL20.0), then group 7 (PBLBL15.0) not significantly with group 6 (PBLBL10.0) and group 3 (PBLBO15.0) and group 2 (PBLBO10.0), all these groups not significantly different to control group.

2) pH

Every group of treatment performed pH in soil higher more than control group significantly different. Group 8 (PBLBL20.0) displayed the highest results. Observed that PBLBL interact with biochar at high mixing rate had increased pH in soil higher more than the result from PBLBO at same mixing rate and pH slightly decreased due to biochar mixing rate decreased.

3) EC

Every group of treatment performed EC in soil higher more than control group significantly different. Group 8 (PBLBL20.0) displayed the highest results. Observed that PBLBL interact with biochar at high mixing rate had increased EC in soil higher more than the result from PBLBO, and EC slightly decreased due to biochar mixing rate decreased.

4) OM

Every group of treatment performed OM in soil higher more than control group significantly different. Group 3 (PBLBO15.0) displayed the highest results following with group 5 (PBLBO20.0) that similarly to group 7 (PBLBL15.0), then group 2 (PBLBO10.0), group 8 (PBLBL20.0) and group 2 (PBLBO10.0)

all these group had similarly result and not significantly different to previous group, then group 1 (PBLBO5.00), and the lowest was control group. PBLBO seem showed better result more than PBLBL when compared at same biochar mixing rate.

5) N

Every group of treatment performed N in soil higher than control group significantly different. Group 3 (PBLBO15.0), group 4 (PBLBO20.0), group 7 (PBLBL15.0), group 8 (PBLBL20.0) showed the highest N, following with group 1 (PBLBO5.00), group 2 (PBLBO10.0), group 5 (PBLBL5.00) and group 6 (PBLBL10.0) and the lowest were control group. Obviously seen that the result from PBLBL or PBLBO with biochar mixing rate 15.0 – 20.0 t ha⁻¹ had increased N in soil higher more than control group, while at mixing rate 10.0 and 5.00 t ha⁻¹ not significantly different increased N in soil.

6) P

Every group of treatment performed P in soil higher more than control group significantly different. Group 4 (PBLBO20.0) displayed the highest results following with group 3 (PBLBO15.0), then group 8 (PBLBL20.0), then group 7 (PBLBL15.0), group 6 (PBLBL10.0), group 2 (PBLBO10.0), group 1 (PBLBO5.00), and the lowest was control group. When compare at same biochar mixing rate PBLBO performed P in soil better than PBLBL.

7) K

Every group of treatment performed K in soil higher than control group significantly different. Group 8 (PBLBL20.0) displayed the highest results following with group 4 (PBLBO20.0), then group 3 (PBLBO15.0), then group 7 (PBLBL15.0), group 6 (PBLBL10.0), group 2 (PBLBO10.0), group 5 (PBLBL5.00), group 1 (PBLBO5.00), and the lowest was control group. When compare at same biochar mixing rate PBLBL performed K in soil better than PBLBO.

8) Ca

Every group of treatment performed Ca in soil higher more than control group significantly different. Group 8 (PBLBL20.0) displayed the highest results, following with group 7 (PBLBL15.0), then group 6 (PBLBL10.0), then group 4 (PBLBO20.0) similarly with group 3 (PBLBO15.0) and group 2 (PBLBO10.0), then group 5 (PBLBL5.00), group 1 (PBLBO5.00), and the lowest was control group.

When compare at same biochar mixing rate PBLBL performed K in soil better than PBLBO.

9) Mg

Every group of treatment performed Mg in soil higher than control group significantly different. Group 8 (PBLBL20.0) displayed the highest results following with group 4 (PBLBO20.0), then group 3 (PBLBO15.0) similarly to group 7 (PBLBL15.0), then group 6 (PBLBL10.0), group 2 (PBLBO10.0) equally with group 1 (PBLBO5.00), then group 5 (PBLBL5.00), and the lowest was control group. When compare at same biochar mixing rate PBLBL performed K in soil better than PBLBO.

10) C/N Ratio

Every group of treatment performed C/N ratio in soil higher than control group significantly different. Group 3 (PBLBO15.0) displayed the highest result.

11) CEC

Every group of treatment performed CEC in soil higher than control group significantly different. Group 3 (PBLBO15.0) and group 7 (PBLBL15.0) displayed the highest result and this not significantly different to group 4 (PBLBO20.0) and group 8 (PBLBL20.0). Observing that the higher CEC result were from PBLBO and PBLBL at biochar mixing rate 15.0 and 20.0 t ha⁻¹ which not different and slightly decrease at lower mixing rate, however higher than control group.

The original feedstock used, combined with the pyrolysis conditions will determine the properties, both physical and chemical, of the biochar product (Verheijen et al., 2010: 50). This physic – chemical properties govern the specific interactions which will occur with the endemic soil biota upon addition of biochar to soil (Verheijen et al., 2010: 50). Pyrolysis is a thermal conversion process in which organic material is converted into carbon rich solids and volatile matter in an oxygen depleted atmosphere (Bridgwater, Meier and Radlein, 1999: 1479). Pyrolysis reactor characteristics, peak process temperature, heating rate, and feedstock quality strongly influence the proportion and quality of the pyrolysis products (Bruun, 2011: 10). During thermal degradation of the feedstock, potassium, chlorine, and N vaporize at relatively low temperature, while calcium, magnesium, phosphorus and

sulphur due to increased stability, vaporize at temperatures that are considerably higher (Amonette and Joseph, 2009: 33). The pyrolysis temperature range also affects how the biochar will interact with the soil community, lower pyrolysis temperatures retains an interior layer of bio-oil which is equal to glucose in its effect on microbial growth (Steiner, 2004). When pyrolysed at higher temperatures, this internal layer of bio – oil is lost and so it is likely that the biochar will have less impact with regard to promoting soil fertility when compared to biochar which does have the internal layer of bio – oil. During pyrolysis, the mineral content of the feedstock is concentrated in the biochar product, which ends up containing a considerably higher proportion of ash (Bruun, 2011: 18) that may supply important macro- and micronutrients beneficial for the plant and soil microbial community (Bruun, 2011: 21). Brodowski, Amelung, Haumaier, Abetz and Zech (2005: 116) have analysis of biochar by using X-ray spectrometry and scanning electron microscopy showed that biochar particles in soil occur either as discrete particles or as particles embedded and bound to minerals in the enriched agricultural soil. Soil with a high cation exchange capacity has the ability to hold or bind cationic plant nutrients on the surface of biochar particles, humus and clay, so nutrients are available for uptake by plants. CEC result of this study displayed higher than control group significantly different in every biochar mixing rate, especially mixing rate 15.0 and 20.0 t h⁻¹ do the same result even though from other different kilns. May be due to the same process of both kiln that was the same condition that was slow pyrolysis. A high CEC means applied nutrients are held in soils rather than leached to ground and surface water by rainfall (Verheijen et al., 2010: 68; Sparkas and Stoutjesdijk, 2011: 12). Cheng et al. (2008: 1598) found that CEC can be increased as biochar gets oxidized and develops carboxyl functional groups, according to Amonette and Joseph (2009: 33) had reported that carboxylic acids and phenolic groups are especially important for the biochar's capacity to retain nutrients. Furthermore, this study revealed that the increasing trend of pH in soil do the same like CEC results. The liming effect has been discussed in the literature as one of the most likely mechanisms behind increases in plant productivity after biochar applications (Glaser et al., 2001: 37; Glaser et al., 2002: 212; Laird et al., 2010: 436). In this study PBLBL showed pH in soil after treatment much higher than PBLBO which interact at same biochar mixing rate, PBLBL also present K, Ca, Mg higher than

PBLBO too. Lower pH values in soils (greater acidity) often reduce the CEC and thereby the nutrient availability (Verheijen et al., 2010: 69). It is usual practice to amend acidic soils by adding agricultural lime to raise the pH, which allows plants to grow at their maximum potential. Although high pH biochars can be produced, they may not have a big impact on the pH of soils to which they are added; this effect is related to biochar's acid neutralizing capacity (Sparkas and Stoutjesdijk, 2011: 17). Hass et al. (2012: 1096) had suggested about using a slow pyrolysis chicken manure biochars produced at 350 and 700°C with and without subsequent steam activation, evaluated in an incubation study as soil amendments for a representative acid and highly weathered soil mixed at 5.00, 10.0, 20.0, and 40.0 g kg⁻¹ into a fine – loamy soil incubated in a climate controlled chamber for 8 weeks. The results showed biochar increasing soil pH from 4.80 to 6.60 at the high application rate, biochar produced at 350°C without activation had the least effect on soil pH. Biochar increased soil micro – and macro – nutrients. Increase in pyrolysis temperature and biochar activation decreased availability of K, P, and S compared to nonactivated biochar produced at 350°C furthermore, biochar increasing dissolved organic carbon, total N and P, PO, SO, and K at high application rate (40.0 g kg⁻¹).

When look at N, the results from both kilns interacted with biochar at mixing rate 15.0 and 20.0 t ha⁻¹, raised up to the highest N in soil after treatment (table 4.9) and become lower at biochar mixing rate 5.00 and 10.0 t ha⁻¹ but higher than control group significantly different (p<0.05). A possible contributing mechanism to increased N retention in soils amended with biochar is the stimulation of microbial immobilization of N and increased nitrates recycling due to higher availability of carbon (Verheijen et al., 2010: 88). According to Rondon et al. (2007: 699) reported that adding biochar at 50.0 g kg⁻¹ soil increased the biological N fixation by common beans and also increase C/N.

12) Cd Residue in Soil

Almost every group of treatment performed Cd residue in soil higher than control group significantly different. An interaction between L kiln and biochar at mixing rate 20.0 t ha⁻¹ showed Cd residual in soil at 14.8 mg kg⁻¹, which was the best results (not included control group). However the result from O kiln with biochar mixing rate 5.00 and 10.0 t ha⁻¹ showed lower Cd residual while L kiln must

use at high mixing rate. All results from every interaction between kilns and biochar at any mixing rate performed a admirable number, lower than soil quality standards for habitat and agriculture of Thailand at not exceed $37.0 \text{ mg Cd kg}^{-1}\text{soil}$ (Notification of National Environmental Board No. 25, B.E., 2004). Biochars are a form of environmental black carbon, a ubiquitous geosorbent found in soils and sediments as a result of incompleting burning of carbon-rich biomass (Cornelissen, Gustafsson, 2005: 549). Amonette and Joseph (2009: 33) reported that the functional groups of biochar influence the sorption process depending on the nature of their surface charge so that both transition metals and non-transition metals can be sorbed onto the surface of biochar particles. Biochars are known to have a highly porous structure, contain various functional groups and shown to be effective in the adsorption of heavy metals, especially in aquatic systems (Liu and Zhang, 2009: 933; Uchimiya et al., 2010a,b). According to Jin et al. (2011: 439) concluded that chicken manure-derived biochar produced at a temperature of 550°C in a low temperature pyrolysis plant have the potential of in situ remediation by immobilizing metals, thereby reducing metal availability to the plants. Ahmad et al. (2012: 536) compared biochars developed from soybean stover at 300 and 700°C and peanut shells at same temperature, they found that high adsorption capacity of biochars produced at 700°C was attributed to their high aromaticity and low polarity. The efficacy of soybean stover biochar at 700°C and peanut shells biochar at 700°C for removing trichloroethylene from water was comparable to that of activated carbon. They conclude that pyrolysis temperature influencing the BC properties was a critical factor to assess the removal efficiency of trichloroethylene from water.

4.4.5.2 Soybean Growth Stage

1) Vegetative Growth Stage

(1) Planting Date to Stage of Emergence (VE)

Factor A (kilns) and Factor C (Biochar mixing rate) showed no interaction result in this soybean growth stage. This mean that interaction between this two factors not effected to VE stage, while compare among group of treatment were not significantly different.

(2) Planting Date to Stage of V4

Factor A (kilns) and Factor C (Biochar mixing rate) showed interaction result in this soybean growth stage. This mean that interaction between this two factors had effected to this stage. Every group of treatment take longer day more than control group significantly different while the result from both 2 kilns that interact with biochar mixing rate 5.00 and 10.0 t ha⁻¹ take longest day, following with biochar mixing rate 15.0 and 20.0 t ha⁻¹.

(3) Planting Date to Beginning Bloom (R1)

Factor A (kilns) and Factor C (Biochar mixing rate) showed interaction result in this soybean growth stage. This mean that interaction between this two factors had effected to this stage. Every group of treatment take prolong day than control group significantly different. While the result from both 2 kilns which interact with biochar mixing rate 5.00 and 10.0 t ha⁻¹ take longest day slightly significant different to the group that being the result from biochar mixing rate 15.0 and 20.0 t ha⁻¹ interacted with PBLBL or PBLBO, take shorter day but longer than control group.

(4) Planting Date to Stage of Maturity (R8)

Factor A (kilns) and Factor C (Biochar mixing rate) showed interaction result in this soybean growth stage. This mean that interaction between this two factors had effected to this stage. Every group of treatment take prolong day than control group significantly different and PBLBL take longer than PBLBO.

4.4.5.3 Soybean Productive Performance

Factor A (kilns) and Factor C (Biochar mixing rate) showed an interaction result in every parameter of soybean productive performance. Interaction between these two factors had increased almost every parameter significantly different to control group, except height, number of node, number of pod, product per pot, and leaf area at R 3 stage.

1) Stem Weight

Every groups of treatment performed soybean stem weight heavier than control group significantly different. At biochar mixing rate 15.0 t ha⁻¹, PBLBL showed a weight of soybean stem higher more than PBLBO, but at other biochar mixing rate, PBLBL and PBLBO showed similar result, anyway higher than control group.

2) Pod Weight

Every group of treatment performed soybean pod weight heavier than control group significantly different. Compare to same biochar mixing rate at 15.0 t ha⁻¹ which presented the heaviest pod weight present by PBLBL, following with PBLBO at same rate, however at biochar lower rate 10.0 and 5.00 t ha⁻¹, PBLBO showed better than PBLBL.

3) Height

L kiln interact with biochar mixing rate 15.0 t ha⁻¹ present the highest result, However, at other biochar mixing rate, O or L Kiln compare by same biochar mixing rate, performed similar result.

4) Number of Node

L kiln interact with biochar mixing rate 5.00 t ha⁻¹ present the most amount of this parameter, and L kiln interact with other biochar mixing rate showed better result of number of node than O kilns.

5) Number of Pod

L kiln interact with biochar mixing rate 15.0 t ha⁻¹ present the most amount of this parameter, and L kiln interact with other biochar mixing rate showed number of pod much than O kiln, except at lowest biochar mixing rate 5.00 t ha⁻¹, present lower than O kiln interact with biochar mixing rate 15.0 t ha⁻¹.

6) Number of Seed per Pod

L kiln interact with biochar mixing rate 15.0 t ha⁻¹ present the most amount of this parameter, following with O kiln at same mixing rate, L kiln at other mixing rate slightly showed better than O kiln. However, result from O kiln was better than control group significantly.

7) 100 Seeds Dry Weight

L kiln interact with biochar mixing rate 15.0 t ha⁻¹ present the heaviest weight, L kiln at other mixing rate still showed better result than O kiln but at highest mixing rate at 20.0 t ha⁻¹, result from L kiln slightly decrease lower than O kiln at same mixing rate. However, result from O kiln was better than control group significantly.

8) Product per Pot

L kiln interact with biochar mixing rate 15.0 t ha⁻¹ present the heaviest weight following with O kiln at same biochar mixing rate, at other biochar mixing rate whether L or O kiln showed not different result higher than control group significantly.

9) Protein in Soybean's Seeds

O kiln interact with biochar mixing rate 5.00 t ha⁻¹ showed the the highest percent protein, following with same kiln and biochar mixing rate 10.0 t ha⁻¹, while L kiln at every biochar mixing rate presented similar result as O kiln at mixing rate 15.0 and 20.0 t ha⁻¹. However, higher than control group significantly.

10) Lipid in Soybean's seeds

L kiln interact with biochar mixing rate 15.0 t ha⁻¹ displayed highest percent lipid, following with same kiln and biochar mixing rate 10.0 t ha⁻¹ and 20.0 t ha⁻¹ and similar to O kiln interact with biochar mixing rate 15.0 t ha⁻¹ and slightly decreased in other treatment, however, higher than control group significantly.

11) Leaf Area R1- Leaf Area R5

O kiln interact with biochar mixing rate 20.0 t ha⁻¹ showed the widest result, following with L kiln at mixing rate 15.0 t ha⁻¹ and slightly decreased at mixing rate 10.0 t ha⁻¹, then 5.00 t ha⁻¹ which interact whether O or L kiln.

12) Leaf area R7

L kiln interact with biochar mixing rate 15.0 t ha⁻¹ show widest result, following with mixing rate 20.0 t ha⁻¹, then O kiln interact with biochar mixing rate 20.0 t ha⁻¹ and slightly decreased at mixing rate 10.0 t ha⁻¹ which wider than mixing rate 5.00 t ha⁻¹. Compare among same biochar mixing rate, O kiln presented wider than L kiln.

Biochar can be used as soil amendments for improving soil properties and crop yield (Suppadit et al., 2012: 244). According to Uzoma et al. (2011: 1) used biochar derived from cow manure at 10.0, 15.0 and 20.0 t ha⁻¹ mixing rate for investigate the effect on maize yield, the results showed that application biochar at mixing rate 15.0 and 20.0 t ha⁻¹ significantly increased maize grain yield by 150 and 98.0 % as compared with the control group, respectively. Spokas, Baker and Reicosky (2010: 443) had observed soil added with biochar had increased root density, crop

growth and productivity. Verheijen et al. (2010: 50) summarized about biochar as an organic material produced via the pyrolysis of C – based feedstocks (biomass) and was best described as a soil conditioner. Biochar can be produced from a wide range of organic feedstocks under different pyrolysis conditions and at a range of scales. Many different materials have been proposed as biomass feedstocks for biochar. The suitability of each biomass type for such an application was dependent on a number of chemical, physical, environmental, as well as economic and logistical factors. The original feedstock used, combined with the pyrolysis conditions will determine the properties, both physical and chemical, of the biochar product. These differences in physicochemical properties that govern the specific interactions which will occur with the endemic soil biota upon addition of biochar to soil, and hence how soil dependent ecosystem functions and services are affected. The application strategy used to apply biochars to soils is an important factor to consider when evaluating the effects of biochar on soil properties and processes. According to Uchimiya et al., (2010a: 935) reported that “the source materials of biochar may affect their performance in terms of carbon sequestration and soil conditioning. Whereas plant – derived biochars are considered to be a soil conditioner rather than fertilizer, manure – derived biochar can release nutrients and be used as both soil fertilizer and conditioner”.

4.4.5.4 Cd Residue in Soybean Part

1) Cd Residue in Soybean Root

O kiln interact with biochar mixing rate 15.0 t ha⁻¹ showed lowest Cd residue in this part and slightly increased at mixing rate 10.0 and 20.0 t ha⁻¹ equally with result from L kiln interact with biochar mixing rate 15.0 t ha⁻¹. Biochar at mixing rate 5.00 t ha⁻¹ in both kiln showed the highest Cd residue in soybean root.

2) Cd Residue in Soybean Shoot

O kiln interact with biochar mixing rate 15.0 t ha⁻¹ showed lowest Cd residue in this part of soybean, following with at mixing rate 20.0 t ha⁻¹ which showed similiary with L kiln at mixing rate 15.0 t ha⁻¹. Compare between O kiln and L kiln at same biochar mixing rate, O Kiln show Cd residue in soybean shoot lower than L kiln.

3) Cd Residue in Soybean Leaf

L kiln interact with biochar mixing rate 15.0 and 20.0 t ha⁻¹ showed lowest Cd residue in this part of soybean, following with O kiln interact with biochar mixing rate 10.0 and 15.0 t ha⁻¹ which similar to a result from L kiln interact with biochar mixing rate 10.0 t ha⁻¹.

4) Cd Residue in Soybean Seed

O kiln interact with biochar mixing rate 15.0 t ha⁻¹ showed the best result at 0.200 mg Cd kg⁻¹ soybean seed, which line on the safety range of the standard acceptable Cd in soybean seed by Codex Committee on Food Additives and Contaminants that specify Cd in soybean seed not over 0.200 mg Cd kg⁻¹ soybean seed. Moreover, rely on statistically this number were not significantly different ($p > 0.05$) to the result by O kiln interact with biochar mixing rate 20.0 t ha⁻¹ (0.245 mg Cd kg⁻¹ soybean seed) and also similar to L kiln interact with biochar mixing rate 15.0 (0.212 mg Cd kg⁻¹ soybean seed) and 20.0 t ha⁻¹ (0.212 mg Cd kg⁻¹ soybean seed).

Factor A (kilns) and Factor C (Biochar mixing rate) showed an interaction result in every parameter of Cd residue in soybean part. Interaction between this two factors had showed the result of Cd residue in soybean part higher more than control group significantly different. However, previous treatment soybean planting in soil polluted with Cd at level 20.0, 40.0, 60.0 and 80.0 mg kg⁻¹soil, so after treatment still have Cd residue in each part of soybean. The result showed an apparently decreasing tendency of Cd residue in all part of soybean line on seeds < leaf < shoot < root, respectively due to biochar mixing rate which used as Cd's soil amendment.

Similar to activated carbon, biochar can serve as a sorbent in some respects (Revell, 2010: 1). Biochar usually has a greater sorption ability than natural soil organic matter due to it greater surface area, negative surface charge, and charge density (Liang et al., 2006: 1719). Biochar can not only efficiently remove many cationic chemicals including a variety of metal ions, but also sorb anionic nutrient such as phosphate ions, though the removal mechanism for this process is not fully understood (Lehmann, 2007 quoted in Revell, 2010: 1). Haghiri (1974: 180) determined Cd concentration in oat shoots (*Avena sativa L.*) was decreased by increasing the cation exchange capacity (CEC) of the soil. Except for its CEC affect, organic matter did not influence the concentration of Cd in oat shoots, the result indicated that the retaining

power of organic matter for Cd is predominantly through its CEC property rather than chelating ability. Insisted with the discovery by Uchimiya et al. (2010a: 935) that broiler litter derived char formed at low pyrolysis temperature (350°C) improved the immobilization of all heavy metals (Cu, Cd, and Ni). Schimmelpfennig and Glaser (2012: 1001) used 16 different feedstock materials to create 66 biochars produced from five different pyrolytic processes (traditional charcoal stack, rotary kiln, Pyreg reactor, wood gasifier, and hydrothermal carbonization) to derive a minimum analytical dataset for assessing the potential use of biochar as soil amendment and for carbon sequestration. On the basis of their results, the authors suggest that biochars containing the following will be effective C sequestration agents when applies to soils: O : C ratio < 0.400, H : C ratio < 0.600 (O : C : H ratios serve as an indicator for the degree of carbonization that influences the stability of biochar in soil environments); black carbon content > 15.0% C, Brunauer – Emmett – Teller surface area > 100 m²g⁻¹ and recommend that biochar PAHs be less than background levels in soils for its utilization as a soil amendment. Furthermore, Rovell (2010: 8) had evaluated biochar's properties, they revealed the carbon content of biochar generated from corn cob increased while the oxygen and hydrogen contents decreased with increasing temperature the indicated degree of carbonization. By increasing pyrolysis temperature from 250 to 550°C, the H/C ratio of biochar produce from corn cob decrease greatly. Chen, Zhou, Zhu and Shen (2008: 464) had amplified about the degree of carbonization by H/C ratio, because H is primarily associated with plant organic matter, The low value of H/C ratio indicate that the biochar is highly carbonized, by contrast, a high H/C ratio suggests that the sample contains a good amount of original organic residues, such as polymeric CH₂ and fatty acid, lignin and some cellulose, furthermore had explained that the decrease of the polarity index O/C with the pyrolysis temperature indicate a reduction in the content of polar functional groups.

Table 4.9 Interaction between Factor A (Reactor) and Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productive Performance

| Parameter | Control | Interaction | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | | CV |
|----------------|---------------------|-------------|---------------------------------|---------------------|--------------------|--------------------|---------------------------------------|---------------------|--------------------|---------------------|--------|
| | | | Biochar5.00 | Biochar10.0 | Biochar15.0 | Biochar20.0 | Biochar5.00 | Biochar10.0 | Biochar15.0 | Biochar20.0 | |
| Soil | | | | | | | | | | | |
| Moisture | 5.00 ^c | I | 6.27 ^a | 4.82 ^c | 4.83 ^c | 6.23 ^a | 5.61 ^b | 5.02 ^c | 5.05 ^c | 5.55 ^b | 4.09 |
| pH | 4.20 ^g | I | 4.46 ^f | 4.58 ^e | 4.99 ^c | 5.11 ^b | 4.59 ^e | 4.81 ^d | 5.10 ^b | 5.33 ^a | 1.42 |
| EC | 0.0898 ⁱ | I | 0.134 ^g | 0.136 ^f | 0.196 ^c | 0.217 ^b | 0.110 ^h | 0.161 ^e | 0.190 ^d | 0.277 ^a | 0.0903 |
| OM | 1.07 ^e | I | 1.31 ^d | 1.39 ^{bc} | 1.44 ^a | 1.40 ^b | 1.37 ^{bc} | 1.37 ^c | 1.40 ^b | 1.39 ^{bc} | 1.39 |
| N | 0.0830 ^c | I | 0.0971 ^b | 0.0991 ^b | 0.104 ^a | 0.106 ^a | 0.0965 ^b | 0.0975 ^b | 0.106 ^a | 0.107 ^a | 3.08 |
| P | 3.00 ^h | I | 17.5 ^g | 32.5 ^f | 58.4 ^b | 76.6 ^a | 17.6 ^g | 37.6 ^e | 46.4 ^d | 50.6 ^c | 1.27 |
| K | 35.0 ⁱ | I | 82.0 ^h | 182 ^f | 298 ^c | 310 ^b | 129 ^g | 235 ^e | 295 ^d | 396 ^a | 0.292 |
| Ca | 135 ^g | I | 152 ^f | 178 ^d | 178 ^d | 178 ^d | 170 ^e | 188 ^c | 199 ^b | 211 ^a | 0.295 |
| Mg | 24.0 ^g | I | 54.0 ^e | 54.02 ^e | 79.1 ^c | 86.0 ^b | 44.3 ^f | 70.1 ^d | 78.6 ^c | 92.9 ^a | 0.978 |
| C/N | 7.00 ^e | I | 7.77 ^d | 7.92 ^{cd} | 8.54 ^a | 8.24 ^b | 7.90 ^d | 8.12 ^b | 8.18 ^b | 8.08 ^{bc} | 1.41 |
| CEC | 2.87 ^d | I | 3.10 ^c | 3.18 ^{bc} | 3.42 ^a | 3.40 ^{ab} | 3.02 ^c | 3.11 ^c | 3.42 ^a | 3.21 ^{abc} | 4.61 |
| Cd in Soil | 0 ^h | I | 18.1 ^e | 17.5 ^f | 22.8 ^b | 19.3 ^d | 21.7 ^c | 26.8 ^a | 22.1 ^{bc} | 14.8 ^g | 4.64 |
| Soybean | | | | | | | | | | | |
| Planting | 33.0 ^d | I | 38.0 ^a | 38.0 ^a | 36.9 ^b | 35.5 ^c | 38.5 ^a | 38.5 ^a | 36.6 ^b | 36.6 ^b | 1.59 |
| Date – V4 | | | | | | | | | | | |
| Planting | 4.00 ^b | NI | 5.20 ^a | 5.00 ^a | 4.55 ^{ab} | 4.55 ^{ab} | 5.00 ^a | 4.55 ^{ab} | 4.55 ^{ab} | 4.55 ^{ab} | 12.1 |
| Date – VE | | | | | | | | | | | |
| VE – VC | 4.00 ^b | NI | 4.40 ^{ab} | 4.20 ^{ab} | 4.20 ^{ab} | 4.00 ^b | 4.55 ^{ab} | 5.00 ^a | 4.40 ^{ab} | 3.78 ^b | 12.2 |
| VC – V1 | 5.00 ^b | NI | 5.55 ^{ab} | 5.65 ^{ab} | 5.55 ^{ab} | 5.40 ^{ab} | 6.00 ^a | 6.00 ^a | 5.55 ^{ab} | 5.55 ^{ab} | 10.3 |
| V1 – V2 | 6.00 ^b | NI | 6.80 ^a | 6.80 ^a | 6.40 ^{ab} | 6.60 ^{ab} | 6.60 ^{ab} | 6.60 ^{ab} | 6.70 ^a | 7.00 ^a | 6.40 |

Table 4.9 (Continued)

| Parameter | Control | Interaction | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | | CV |
|----------------|--------------------|-------------|---------------------------------|---------------------|--------------------|---------------------|---------------------------------------|--------------------|---------------------|---------------------|-------|
| | | | Biochar5.00 | Biochar10.0 | Biochar15.0 | Biochar20.0 | Biochar5.00 | Biochar10.0 | Biochar15.0 | Biochar20.0 | |
| V2 – V3 | 6.00 ^b | I | 7.65 ^a | 6.95 ^a | 7.00 ^a | 7.00 ^a | 7.55 ^a | 7.55 ^a | 7.00 ^a | 6.80 ^a | 7.77 |
| V3 – V4 | 8.00 ^a | NI | 8.05 ^a | 8.55 ^a | 8.20 ^a | 8.15 ^a | 8.80 ^a | 9.00 ^a | 8.00 ^a | 8.00 ^a | 7.47 |
| Planting | 39.0 ^e | I | 42.0 ^{ab} | 41.6 ^{abc} | 40.0 ^d | 40.6 ^{cd} | 42.5 ^a | 42.2 ^a | 41.0 ^{bcd} | 40.1 ^d | 1.62 |
| Date – R1 | | | | | | | | | | | |
| R1 – R2 | 2.00 ^c | NI | 2.58 ^{abc} | 2.62 ^{abc} | 2.50 ^{bc} | 2.55 ^{bc} | 2.65 ^{abc} | 3.00 ^{ab} | 3.40 ^a | 3.15 ^{ab} | 18.6 |
| R2 – R3 | 3.00 ^a | NI | 2.32 ^a | 2.75 ^a | 3.00 ^a | 2.55 ^a | 2.70 ^a | 2.70 ^a | 3.00 ^a | 2.80 ^a | 19.2 |
| R3 – R4 | 2.00 ^b | I | 2.00 ^b | 2.00 ^b | 2.00 ^b | 2.10 ^b | 2.00 ^b | 2.10 ^b | 2.10 ^b | 2.25 ^a | 4.47 |
| R4 – R5 | 3.00 ^a | I | 2.58 ^b | 2.32 ^{cd} | 2.27 ^{cd} | 2.22 ^d | 2.35 ^c | 2.55 ^b | 2.35 ^c | 2.12 ^e | 2.67 |
| R5 – R6 | 10.7 ^b | I | 10.5 ^b | 10.50 ^b | 10.5 ^b | 10.9 ^{ab} | 10.3 ^b | 10.3 ^b | 10.6 ^b | 11.4 ^a | 3.39 |
| R6 – R7 | 10.5 ^b | NI | 10.50 ^b | 10.50 ^b | 10.4 ^b | 10.6 ^b | 10.3 ^b | 10.3 ^b | 10.5 ^b | 11.4 ^a | 4.60 |
| R7 – R8 | 21.0 ^{cd} | I | 22.2 ^b | 22.2 ^b | 21.3 ^c | 21.4 ^c | 24.3 ^a | 22.4 ^b | 20.2 ^e | 20.6 ^{de} | 1.83 |
| Planting | 90.0 ^e | I | 93.9 ^c | 94.0 ^c | 93.3 ^{cd} | 94.0 ^c | 98.0 ^a | 95.1 ^b | 92.8 ^d | 93.3 ^{cd} | 0.633 |
| Date – R8 | | | | | | | | | | | |
| Stem | 1.00 ^e | I | 0.378 ^{ef} | 0.427 ^{cd} | 0.532 ^b | 0.386 ^{ef} | 0.358 ^f | 0.455 ^c | 0.576 ^a | 0.409 ^{de} | 5.68 |
| Weight | | | | | | | | | | | |
| Pod | 30.6 ^b | I | 1.35 ^b | 1.21 ^c | 1.36 ^b | 1.15 ^{cd} | 1.07 ^{de} | 1.07 ^{de} | 1.75 ^a | 1.19 ^e | 6.16 |
| Weight | 5.05 ^f | | | | | | | | | | |
| Height | | I | 30.5 ^b | 28.9 ^d | 30.0 ^{bc} | 28.1 ^d | 26.7 ^e | 29.0 ^{cd} | 31.9 ^a | 28.5 ^d | 2.24 |
| Number of Node | | I | 4.97 ^g | 5.48 ^c | 5.13 ^e | 5.19 ^d | 5.69 ^a | 5.20 ^d | 5.60 ^b | 5.48 ^c | 0.568 |

Table 4.9 (Continued)

| Parameter | Control | Interaction | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | | CV |
|------------------------|-------------------|-------------|---------------------------------|--------------------|-------------------|--------------------|---------------------------------------|--------------------|-------------------|--------------------|-------|
| | | | Biochar5.00 | Biochar10.0 | Biochar15.0 | Biochar20.0 | Biochar5.00 | Biochar10.0 | Biochar15.0 | Biochar20.0 | |
| Number of Pod | 3.50 ^l | I | 2.75 ^l | 3.19 ^h | 4.09 ^d | 3.33 ^g | 3.56 ^e | 4.49 ^c | 5.26 ^a | 4.80 ^b | 0.689 |
| Number of Seed per Pod | 1.26 ^g | I | 1.67 ^c | 1.35 ^f | 1.77 ^b | 1.59 ^e | 1.69 ^c | 1.63 ^d | 1.96 ^a | 1.57 ^e | 1.76 |
| Dry Weight 100 Seeds | 10.6 ^h | I | 12.8 ^d | 12.8 ^d | 13.5 ^b | 12.3 ^e | 13.3 ^c | 11.0 ^g | 14.8 ^a | 11.9 ^f | 0.630 |
| Product per Pot | 2.08 ^e | I | 2.20 ^e | 2.92 ^{cd} | 3.59 ^b | 2.79 ^{cd} | 3.02 ^{cd} | 2.58 ^{de} | 5.40 ^a | 3.31 ^{bc} | 10.8 |
| Protein | | | | | | | | | | | |
| Lipid | 35.1 ^d | I | 37.8 ^a | 36.1 ^b | 35.9 ^c | 35.9 ^c | 35.9 ^c | 35.9 ^c | 35.9 ^c | 35.9 ^c | 0.224 |
| Leaf Area R1 | 18.4 ^e | I | 19.3 ^d | 19.4 ^d | 19.8 ^b | 19.6 ^c | 19.4 ^d | 19.9 ^b | 20.0 ^a | 19.8 ^b | 0.447 |
| Leaf Area R3 | 6.69 ^h | I | 8.28 ^f | 7.80 ^g | 13.4 ^c | 17.1 ^a | 9.39 ^e | 10.1 ^d | 14.2 ^b | 13.5 ^c | 0.645 |
| Leaf Area R5 | 11.8 ^d | I | 14.2 ^c | 14.6 ^c | 15.3 ^c | 19.2 ^a | 12.6 ^d | 15.0 ^c | 17.2 ^b | 17.2 ^b | 5.56 |
| Leaf Area R5 | 16.2 ^h | I | 19.7 ^e | 20.6 ^d | 24.4 ^b | 27.9 ^a | 17.8 ^f | 16.6 ^g | 19.8 ^e | 20.9 ^c | 0.476 |

Table 4.9 (Continued)

| Parameter | Control | Interac Tion | 200 Liter Oil Drum Kiln (PBLBO) | | | | Labscale – scale Pyrolysis Reactor (PBLBL) | | | | CV |
|----------------|-----------------------|-----------------|---------------------------------|---------------------|-----------------------|---------------------|--|----------------------|-----------------------|----------------------|-------|
| | | | Biochar | Biochar | Biochar | Biochar | Biochar | Biochar | Biochar | Biochar | |
| | | | 5.00 | 10.0 | 15.0 | 20.0 | 5.00 | 10.0 | 15.0 | 20.0 | |
| Leaf Area R7 | 18.4 ^h | I | 20.0 ^g | 21.5 ^f | 30.7 ^b | 37.6 ^a | 18.2 ⁱ | 22.8 ^c | 24.9 ^d | 28.4 ^c | 0.412 |
| Pod Weight R3 | 0.0242 ^{de} | I | 0.0422 ^a | 0.0443 ^a | 0.0257 ^{bc} | 0.0197 ^f | 0.0198 ^f | 0.0204 ^{ef} | 0.0246 ^{cd} | 0.0277 ^b | 6.50 |
| Pod Weight R5 | 0.0608 ^{cde} | I | 0.0685 ^{bcd} | 0.0765 ^b | 0.0566 ^{def} | 0.0442 ^f | 0.219 ^a | 0.0500 ^{ef} | 0.0651 ^{bcd} | 0.0716 ^{bc} | 11.4 |
| Pod Weight R6 | 1.08 ^f | I | 1.36 ^c | 1.50 ^b | 1.51 ^b | 1.36 ^c | 1.27 ^d | 1.58 ^a | 1.60 ^a | 1.17 ^c | 2.94 |
| PodWeight R7 | 1.29 ^e | I | 1.23 ^e | 1.50 ^d | 1.62 ^c | 1.61 ^c | 1.41 ^d | 1.77 ^b | 1.98 ^a | 1.30 ^e | 4.90 |
| Pod Weight R8 | 0.870 ^c | I | 0.704 ^d | 1.27 ^b | 1.45 ^a | 1.15 ^b | 0.993 ^c | 1.46 ^a | 1.55 ^a | 1.57 ^a | 8.20 |
| Stem Weight R1 | 0.313 ^h | I | 0.332 ^g | 0.349 ^f | 0.541 ^a | 0.5263 ^b | 0.538 ^a | 0.449 ^c | 0.422 ^d | 0.361 ^e | 1.35 |
| Stem Weight R3 | 0.477 ^f | I | 0.581 ^d | 0.571 ^d | 0.510 ^e | 0.506 ^e | 0.738 ^a | 0.628 ^b | 0.376 ^g | 0.611 ^c | 1.34 |
| Stem Weight R5 | 0.589 ^e | I | 0.602 ^{de} | 0.591 ^c | 0.649 ^c | 0.668 ^c | 0.995 ^a | 0.815 ^b | 0.637 ^{cd} | 0.852 ^b | 3.78 |
| Stem Weight R6 | 0.814 ^f | I | 0.840 ^f | 1.19 ^d | 1.07 ^e | 1.07 ^e | 0.640 ^g | 1.58 ^b | 1.99 ^a | 1.46 ^c | 1.85 |
| Stem Weight R7 | 0.407 ⁱ | I | 0.419 ^h | 0.505 ^g | 0.599 ^d | 0.701 ^b | 0.525 ^f | 0.688 ^c | 0.727 ^a | 0.583 ^e | 0.900 |
| Stem Weight R8 | 0.253 ^g | I | 0.259 ^g | 0.360 ^e | 0.412 ^d | 0.355 ^e | 0.326 ^f | 0.436 ^b | 0.527 ^a | 0.429 ^c | 1.17 |
| Cd in Root | 0 ^g | I | 22.1 ^a | 10.0 ^c | 7.58 ^f | 10.1 ^e | 21.4 ^b | 12.3 ^c | 10.2 ^c | 11.4 ^d | 2.93 |
| Cd in Shoot | 0 ^g | I | 7.36 ^b | 3.94 ^d | 2.37 ^f | 3.37 ^e | 9.08 ^a | 5.36 ^c | 3.30 ^e | 4.07 ^d | 8.26 |
| Cd in Leaf | 0 ^f | I | 4.29 ^a | 1.69 ^d | 1.75 ^d | 2.68 ^c | 3.74 ^b | 1.84 ^d | 1.31 ^e | 1.27 ^e | 10.9 |
| Cd in Seed | 0 ^d | I | 0.420 ^b | 0.395 ^b | 0.200 ^e | 0.245 ^c | 0.550 ^a | 0.460 ^b | 0.212 ^c | 0.212 ^c | 18.7 |

Note: Means in the Same Row with Different Letters are Significantly Different at P < 0.05.

4.4.6 Interaction between Factor B (Cd Level) and Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productivity Performance

4.4.6.1 Soil Property

Factor B (Cd level) and Factor C (Biochar mixing rate) showed an interaction result in every parameter of soil properties. Interaction between this two factor had increased almost every parameter, except % moisture content and EC in soil significantly different to control group.

1) % Moisture

Almost every treatment presented higher more than control group significantly different. Observed that at Cd level 20.0 and 40.0 mg kg⁻¹ interacted with Factor C had increase % moisture in soil higher than other group.

2) pH

The result of every group of treatment were increased higher more than control group significantly different, especially the result from interaction between Cd and biochar mixing rate $\geq 15.0 \text{ t ha}^{-1}$ had raised up pH in soil higher than the result from an interaction between Cd and biochar mixing rate $< 15.0 \text{ t ha}^{-1}$. Tendency of pH increase due to biochar mixing rate increase.

3) EC

The result of EC trend to increased rely on 2 order by 2 factors that 1st Cd level: Cd level up higher, EC in soil raise up too, 2nd Biochar mixing rate: Biochar mixing rate increased, EC in soil increased too.

4) OM

The result showed the same like pH.

5) N

The result of every group of treatment higher more than control group significantly different while among group not different.

6) P

The result showed the same like pH.

7) K

The result showed the same like EC and every group of treatment showed higher more than control group significantly.

8) Ca

The result showed the same like pH.

9) Mg

The result showed the same like EC and every group of treatment showed higher than control group significantly.

10) C/N Ratio

The result of every group of treatment higher than control group significantly. Obviously seen that interacton between Factor B and Factor C, at Factor C being biochar mixing rate 15.0 t ha^{-1} interact with any level of Factor B had displayed highest C/N in soil.

11) CEC

The result showed the same like EC and every group of treatment showed higher than control group significantly.

12) Cd Residue in Soil

The result of Cd residue in soil showed higher than control group significantly different. However when considered to Factor B before treatment, the result of each Cd level showed lower than the previously. The most satisfy result showed an interaction between Cd level 60.0 mg kg^{-1} and biochar mixing rate at 15.0 t ha^{-1} (32.0 mg kg^{-1}), following with Cd level 80.0 mg kg^{-1} and biochar mixing rate at 20.0 t ha^{-1} (30.7 mg kg^{-1}) and become lower, line in this order Cd60.0 >> Cd 40.0 >> Cd 20.0 >> Cd 0 interaction with biochar mixing rate 20.0 t ha^{-1} reduced Cd residue in soil better than $15.0 >> 10.0 >> 5.00 \text{ t ha}^{-1}$ respectively, and the results in these groups be in the line for Thailand Soil Quality Standards for Habitat and Agriculture permit for Cadmium in soil not exceed 37.0 mg kg^{-1} .

Factor B (Cd level) and Factor C (Biochar mixing rate) showed an interaction resulted in almost every parameter. This mean that interacted between these 2 factors had effected to soil properties. When compared among group in each parameter, showed a strongly significant different ($p < 0.05$) and the number in soil's parameter display a positive trend improving soil quality.

Biochars has ability to retain cations in an exchangeable and plant available form better than other soil organic matter to adsorb cations per unit carbon (Lehmann et al., 2003: 343) due to its greater charge density (Liang et al.,

2006: 1719). Biochar also appears to be able to strongly adsorb phosphate, even though it is an anion (Lehmann, 2007b: 143). These properties make biochar a unique substance, retaining exchangeable and therefore plant available nutrients in the soil, and offering the possibility of improving crop yields while decreasing environmental pollution by nutrients (Lehmann, 2007b: 144). Steiner et al. (2007: 275) postulated biochar as a soil conditioner and fertilizer by increasing cation exchange capacity (CEC), pH, and water retention, and by sequestering toxic heavy metals and gradually releasing limiting nutrients. In addition, manure derived char can release its phosphorus, potassium and nitrogen content and function both as soil fertilizer and conditioner (Chan et al., 2008: 437). In this studied about N in soil, the results indicated not significantly different ($p > 0.05$) when compare between any Cd level or Biochar mixing rate, but significantly different when compare all that to control group ($p < 0.05$). Harns et al. n.d. hull biochar (PN) and pine chip biochar (PC) produced at 400°C, stream carrier gas for increase C mineralization in loamy sand soils, found that C mineralization tended to increase with biochar application rates, anyway biochar application rate did not affect N mineralization, although in the longer incubation. There was a trend for higher N mineralization with the PN biochar, but it does not appear to be easily. Further potential benefits of adding biochar to soil have also been reported (Lehmann, 2007a,b; Chan and Xu, 2009: 67; Ippolito et al., 2012: 967; Sohi et al., 2010: 16; Verheijen et al., 2009: 61; Thawadchai Suppadit et al., 2012: 244) these include the adsorption of dissolved organic carbon (Pietikainen et al., 2000: 231; Song-Yung Wang et al., 2008; Beesley et al., 2009: 2282; Jin et al., 2011: 439), increase in soil pH and macro – elements, and reductions in trace metals in leachates (Novak et al., 2009: 105). Furthermore, biochar was longevity in soil reduces the possibility of heavy metal accumulation associated with repeated applications of others amendments (Lehmann and Joseph, 2009).

From all of these results on soil properties, showed a positive trend of an interaction between Factor B and Factor C, increase the liming effect, cation exchange capacity, C/N ratio and all of plant necessary element higher than control group significantly different even if had a Cd binding in soil.

4.4.6.2 Soybean Growth Stage

Factor B (Cd level) and Factor C (Biochar mixing rate) showed an interaction result in every parameter of soybean growth stage. Higher Cd binding in soil affected to soybean development taked prolong day developing from planting date to next growth stage.

1) Vegetative Growth Stage

(1) Planting Date to Stage of Emergence (VE)

When Cd binding at higher level, soybean take longer day run to VE stage. The trend of the result showed in this study performed in 2 line: 1st Cd level 80.0 mg kg⁻¹ take prolong day than Cd 60.0 > Cd 40.0 > Cd 20.0 > control > Cd 0 mg kg⁻¹ and 2nd Biochar mixing rate 5.00 t ha⁻¹ take prolong day than > 10.0 > 15.0 ≥ 20.0 t ha⁻¹.

(2) Planting Date to Stage of V4

When Cd binding at higher level, soybean take longer day run to next stage. However, it was too gladly in the results on an interaction between Factor B and Factor C that at biochar mixing rate 10.0, 15.0, and 20.0 t ha⁻¹ take shorter time than control group albeit combine with Cd binding at 20.0 mg kg⁻¹.

(3) Planting Date to Beginning Bloom (R1)

The results display like stage V4 but this time an interaction between Cd level 20.0 mg kg⁻¹ and Biochar mixing lowest rate 5.00 t ha⁻¹ take a shorter day than control group developed from first plant to R1.

(4) Planting Date to Stage of Maturity (R8)

The shortest day were an interaction between Cd level 0 mg kg⁻¹ and Biochar at mixing rate 15.0 and 20.0 t ha⁻¹ (85.2 and 85.8 day, respectively) following with Biochar mixing rate at 10.0 equally with rate 5.00 t ha⁻¹ (88.2 and 89.0 day, respectively) significantly different ($p < 0.05$) compare these groups with control group (91.0 day).

Zhang et al. (2012: 140) investigated the impact of biochars on soil Cd immobilization and phytoavailability, growth of plants, and Cd concentration, accumulation, and transportation in plant tissues in Cd contaminated soils under waterlogged conditions. After 3 week of soil incubation, pH increased and CaCl₂ –

extractable Cd decreased significantly with biochar additions, after 9 weeks of plant growth, biochar additions significantly increase soil pH and Electrical Conductivity and reduced CaCl_2 -extractable Cd. EDTA-extractable soil Cd significantly decreased with biochar additions. Growth and biomass significantly decreased with Cd additions, and biochar additions did not significantly improve plant growth regardless of biochar type or application rate.

4.4.6.3 Soybean Productive Performance

Factor B (Cd level) and Factor C (Biochar mixing rate) showed an interaction result in every parameter of soybean growth stage. Higher Cd binding in soil affected to soybean productive performance but the result from and interaction between this two factors especially at interaction with biochar $\geq 15.0 \text{ t ha}^{-1}$ had improved soybean productive performance up higher than control group.

An interaction between Factor B and Factor C at Cd level 0 mg kg^{-1} and Biochar mixing rate 15.00 t ha^{-1} showed a highest productivity in every parameter significantly different among group ($p < 0.05$). Furthermore, the results showed a gladly on quality of soybean' seeds that every treatment of an interaction between Cd level and biochar mixing rate raise up amount of protein and lipid higher than control group significantly different ($p < 0.05$). According to Uzoma et al. (2011:1) indicated that maize yield and nutrient uptake in sandy soil were significantly improved by cow manure derived biochar at 15.0 and 20.0 t ha^{-1} mixing rate significantly increase maize grain yield by 150 and 98.0% as compared with the control and nutrient uptake by maize grain was significantly increased with higher biochar application. In tropical soils, above ground biomass was shown to increase by 189% when 23.0 t ha^{-1} was added to Columbian soils (Major et al., 2010: 117). Major (2010b) had studied in a field trials, the maize yield over the four years following biochar application was higher in all but the year of application. In that year biochar addition showed no effect. In the second, third and fourth years after 20.0 t ha^{-1} biochar application, maize yield increased by 28.0 , 30.0 and 140% , respectively. At an application rate of 8.00 t ha^{-1} , maize yields also increased in these years by 9.00 , 15.0 , and 71.0% , respectively.

Even though, biochar at mixing rate 15.0 t ha^{-1} present a positive effected to soybean production significantly different but when look in detail on parameter 100 seeds dry weight, at Cd binding raise up to 60.0 mg kg^{-1} and upon, this amount of biochar and much more (20.0 t ha^{-1}) seem not appropriated enough for relieve Cd toxicity. The results suggested a lower biochar mixing rate (10.0 and 5.00 t ha^{-1}) showed a proper rate for raise up 100 seeds dry weight at this Cd level and heaviest than control group significantly different ($p < 0.05$). Nigussie et al. (2012: 369) elucidated that biochar increased pH and EC values due to addition of biochar. In chromium polluted and unpolluted soils, the highest mean values of pH and EC were observed in soils treated with 10.0 t ha^{-1} biochar (maize stalk derived biochar), while the lowest values were recorded at the control group. The increase in soil pH and EC due to application of biochar was generally attributed to ash accretion as ash residues are generally dominated by carbonates of alkali and alkaline earth metals, variable amounts of silica, heavy metals, sesquioxides, phosphates and small amounts of organic and inorganic N (Raison, 1979: 73). Due to Nigussie et al. (2012: 373), EC increase related to biochar added in soil and this may be affected to plant that too salty condition for uptake nutrients in soil. According to Thawadchai Suppadit et al. (2012: 125) investigated the effects of quail litter biochar (QLB) on the availability of Cd to physic nut (*Jatropha curcas* L.) plants. QLB was applied to the soil in which four new physic nut varieties (Takfa, Doi Saket, Lao, and Ranong) in factorial combinations at four levels ($0, 5.00, 10.0,$ and 15.0 g kg^{-1} soil) to soil that contain $60.8 \text{ mg Cd kg}^{-1}$. They found that addition of QLB to soil caused a significant increase in the soil growth potential and physic nut yield components ($p < 0.05$), a significant decrease in the Cd residue in the plant ($p < 0.05$), and a significant increase in the chemical characteristics, nutrients, and Cd residue in soil ($p < 0.05$). They had concluded QLB application can significantly decrease the bioavailability of Cd to physic nut plants, increase plant growth potential and yield, and has potential to remediate Cd contaminated soil. However, QLB levels higher than 15.0 g kg^{-1} soil mixture were not advisable because QLB is alkaline in nature, and this can affect soil. Furthermore, Jin, et al. (2012: 439) had evaluated the metal immobilizing impact of chicken manure and green waste derived biochar and their effectiveness in promoting plant growth. The results showed chicken manure derived biochar increased plant dry biomass by 353

and 572 % for shoot and root, respectively with 1.00 % of biochar addition and found that both of biochar significantly increased shoot and root biomass of Indian mustard, which may be attributed to reduced metal toxicity through immobilization and supply for nutrients.

4.4.6.4 Cd Residue in Soybean Part

Factor B (Cd level) and Factor C (Biochar mixing rate) showed an interaction result in every parameter of Cd residue in soybean part. Interaction between this two factors had showed the result of Cd residue in soybean part higher more than control group significantly different.

Cd residue slightly decrease in part of soybean from root > shoot > leaf > seeds, obviously seen on an interaction between Cd level 20.0 mg kg⁻¹ and Biochar mixing rate 20.0 t ha⁻¹ from root to seeds line in this order: 5.58 > 1.25 > 1.08 > 0.252 mg kg⁻¹. This trend cover all groups albeit at highest Cd level. This mean that interaction between Factor B and Factor C have a potential reduced Cd in soil.

In the soil environment, biochar has already been shown to be effective in mitigating mobility and toxicity of heavy metals (Cao et al., 2009: 3285; Mohan et al., 2007: 57). Uchimiaya et al. (2010a: 935) found that adding broiler litter biochar to soil enhanced the immobilization of a mixture of Pb, Cd and Ni, and the authors attributed this effect mostly to the raise in pH brought about by biochar and also with Beesley et al. (2010: 2282) found that biochar was much more efficient than compost in reducing the bioavailability of Cd and Zn, mostly due to the fact that biochar raised the soil pH than compost did. The availability of metals such as these in soil decrease as pH rises.

Table 4.10 Interaction between Factor B (Cd Level) and Factor C (Biochar Mixing Rate) on Soil Properties, Soybean Growth Stage, and Productivity Performance

| Parameter | Control | Interac Tion | CV | Cd 0 | | | | Cd 20.0 | | | |
|-------------------|----------------------|-----------------|-------|---------------------|----------------------|----------------------|---------------------|-----------------------|-----------------------|---------------------|---------------------|
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Soil | | | | | | | | | | | |
| Moisture | 5.00 ^{fg} | I | 6.89 | 5.80 ^{cd} | 5.23 ^{cdef} | 5.71 ^{cde} | 5.71 ^{cde} | 8.18 ^a | 7.36 ^b | 7.34 ^b | 6.86 ^b |
| pH | 4.20 ⁱ | I | 2.61 | 4.56 ^h | 4.76 ^{fgh} | 5.25 ^{abc} | 5.45 ^a | 4.71 ^{gh} | 4.90 ^{efg} | 5.35 ^{ab} | 5.40 ^a |
| EC | 0.0898 ^{mn} | I | 5.52 | 0.0643 ^o | 0.0825 ⁿ | 0.0884 ^{mn} | 0.127 ^j | 0.0838 ⁿ | 0.100 ^{lm} | 0.118 ^{jk} | 0.123 ^{jk} |
| OM | 1.07 ^e | I | 3.25 | 1.36 ^d | 1.39 ^{cd} | 1.40 ^{bcd} | 1.39 ^{cd} | 1.37 ^d | 1.38 ^d | 1.39 ^d | 1.47 ^a |
| N | 0.0830 ^b | I | 8.36 | 0.107 ^a | 0.106 ^a | 0.109 ^a | 0.109 ^a | 0.103 ^a | 0.107 ^a | 0.107 ^a | 0.116 ^a |
| P | 3.00 ^q | I | 1.67 | 16.0 ^p | 25.5 ⁿ | 46.5 ⁱ | 70.5 ^b | 22.0 ^o | 43.5 ^j | 48.5 ^h | 69.0 ^c |
| K | 35.0 ^t | I | 0.276 | 95.0 ^s | 158 ^o | 223 ^k | 261 ^g | 116 ^r | 184 ^m | 232 ⁱ | 279 ^f |
| Ca | 135 ^m | I | 1.37 | 157 ^l | 180 ^{hi} | 189 ^g | 247 ^a | 158 ^l | 188 ^g | 198 ^{de} | 199 ^{cd} |
| Mg | 24.0 ^o | I | 1.08 | 46.5 ^l | 46.5 ^l | 73.0 ^{fg} | 87.0 ^{cd} | 45.0 ^m | 67.0 ^{hi} | 72.0 ^g | 86.5 ^{cd} |
| C/N Ratio | 7.00 ^g | I | 2.75 | 7.74 ^f | 8.56 ^{bc} | 8.71 ^{ab} | 7.84 ^{ef} | 8.12 ^{de} | 8.13 ^{de} | 8.24 ^{cd} | 7.71 ^f |
| CEC | 2.87 ⁱ | I | 1.05 | 2.97 ^h | 3.06 ^g | 3.17 ^f | 3.46 ^c | 3.37 ^d | 3.07 ^g | 3.19 ^f | 3.09 ^g |
| Cd in Soil | 0 ^q | I | 1.19 | 2.00 ^p | 2.00 ^p | 3.00 ^o | 3.00 ^o | 10.0 ^l | 9.14 ⁿ | 9.53 ^m | 9.35 ^{mn} |
| Soybean | | | | | | | | | | | |
| Planting Date -V4 | 33.0 ^f | I | 1.94 | 31.0 ^g | 31.0 ^g | 30.5 ^g | 30.0 ^g | 35.0 ^e | 33.5 ^f | 33.0 ^f | 33.0 ^f |
| Planting Date-VE | 4.00 ^{cd} | I | 15.2 | 4.00 ^{cd} | 4.00 ^{cd} | 3.50 ^d | 4.00 ^{cd} | 4.50 ^{bcd} | 4.00 ^{cd} | 4.00 ^{cd} | 4.00 ^{cd} |
| VE – VC | 4.00 ^{bcd} | I | 14.8 | 3.00 ^d | 3.50 ^{cd} | 3.00 ^d | 3.00 ^d | 4.00 ^{bcd} | 4.50 ^{abc} | 3.50 ^{cd} | 4.50 ^{abc} |
| VC – V1 | 5.00 ^{de} | I | 12.2 | 4.50 ^{def} | 4.00 ^{ef} | 3.50 ^f | 4.00 ^{ef} | 5.00 ^{de} | 5.00 ^{de} | 5.00 ^{de} | 4.50 ^{def} |
| V1 – V2 | 6.00 ^a | I | 11.9 | 5.00 ^b | 5.00 ^b | 5.75 ^{ab} | 5.87 ^{ab} | 5.00 ^b | 5.62 ^{ab} | 5.00 ^b | 5.00 ^b |
| V2 – V3 | 6.00 ^{cde} | I | 11.4 | 5.62 ^e | 5.62 ^e | 6.12 ^{bcd} | 5.87 ^{de} | 6.50 ^{abcde} | 6.50 ^{abcde} | 5.87 ^{de} | 5.87 ^{de} |

Table 4.10 (Continued)

| Parameter | Control | Interac Tion | CV | Cd 40.0 | | | | Cd 60.0 | | | |
|-------------------|----------------------|-----------------|-------|---------------------|----------------------|-----------------------|-----------------------|--------------------|---------------------|----------------------|----------------------|
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Soil | | | | | | | | | | | |
| Moisture | 5.00 ^{fg} | I | 6.89 | 7.29 ^b | 8.04 ^a | 7.10 ^b | 6.91 ^b | 4.47 ^g | 4.85 ^{fg} | 5.18 ^{def} | 5.90 ^c |
| pH | 4.20 ⁱ | I | 2.61 | 4.66 ^h | 4.92 ^{ef} | 5.35 ^{ab} | 5.33 ^{ab} | 4.66 ^h | 4.65 ^h | 4.98 ^{de} | 5.26 ^{ab} |
| EC | 0.0898 ^{mn} | I | 5.52 | 0.110 ^{kl} | 0.127 ^j | 0.158 ^h | 0.207 ^f | 0.141 ⁱ | 0.163 ^h | 0.295 ^c | 0.367 ^a |
| OM | 1.07 ^c | I | 3.25 | 1.37 ^d | 1.40 ^{bcd} | 1.46 ^{abc} | 1.39 ^{cd} | 1.36 ^d | 1.47 ^{ab} | 1.46 ^{abc} | 1.41 ^{abcd} |
| N | 0.0830 ^b | I | 8.36 | 0.105 ^a | 0.108 ^a | 0.108 ^a | 0.107 ^a | 0.101 ^a | 0.109 ^a | 0.109 ^a | 0.109 ^a |
| P | 3.00 ^q | I | 1.67 | 16.0 ^p | 41.5 ^k | 50.0 ^g | 59.0 ^e | 17.0 ^p | 30.0 ^m | 51.0 ^f | 72.5 ^a |
| K | 35.0 ^t | I | 0.276 | 131 ^q | 220 ^l | 280 ^f | 351 ^c | 137 ^p | 235 ⁱ | 378 ^e | 477 ^a |
| Ca | 135 ^m | I | 1.37 | 160 ^l | 164 ^k | 161 ^{kl} | 171 ^j | 178 ⁱ | 177 ⁱ | 219 ^b | 183 ^h |
| Mg | 24.0 ^o | I | 1.08 | 41.0 ⁿ | 66.5 ⁱ | 74.0 ^f | 85.0 ^e | 46.0 ^{lm} | 62.5 ^j | 86.0 ^{de} | 101 ^a |
| C/N Ratio | 7.00 ^g | I | 2.75 | 8.29 ^{cd} | 8.30 ^{cd} | 8.37 ^{cd} | 8.29 ^{cd} | 7.59 ^f | 8.31 ^{cd} | 8.71 ^{ab} | 8.26 ^{cd} |
| CEC | 2.87 ⁱ | I | 1.04 | 3.00 ^h | 3.09 ^g | 3.09 ^g | 3.88 ^a | 3.18 ^f | 3.26 ^e | 3.59 ^b | 3.17 ^f |
| Cd in Soil | 0 ^q | I | 1.19 | 17.7 ^j | 18.2 ⁱ | 27.0 ^h | 16.5 ^k | 37.0 ^d | 38.2 ^c | 32.0 ^e | 30.1 ^g |
| Soybean | | | | | | | | | | | |
| Planting Date -V4 | 33.0 ^f | I | 1.94 | 41.0 ^c | 41.0 ^c | 38.5 ^d | 38.0 ^d | 42.5 ^{ab} | 42.0 ^{bc} | 39.0 ^d | 38.0 ^d |
| Planting Date -VE | 4.00 ^{cd} | I | 15.1 | 5.00 ^{abc} | 5.50 ^{ab} | 5.00 ^{abc} | 5.50 ^{ab} | 6.00 ^a | 6.00 ^a | 5.00 ^{abc} | 5.00 ^{abc} |
| VE – VC | 4.00 ^{bcd} | I | 14.8 | 5.50 ^a | 5.00 ^{ab} | 5.00 ^{ab} | 4.00 ^{bcd} | 5.00 ^{ab} | 5.50 ^a | 4.50 ^{abc} | 4.00 ^{bcd} |
| VC – V1 | 5.00 ^{cde} | I | 12.1 | 6.00 ^{abc} | 6.50 ^{ab} | 6.00 ^{abc} | 5.50 ^{bcd} | 7.00 ^a | 7.00 ^a | 7.00 ^a | 7.00 ^a |
| V1 – V2 | 6.00 ^a | I | 11.9 | 5.75 ^{ab} | 5.75 ^{ab} | 5.75 ^{ab} | 5.75 ^{ab} | 6.50 ^a | 6.37 ^a | 6.50 ^a | 6.50 ^a |
| V2 – V3 | 6.00 ^{cde} | I | 11.4 | 7.12 ^{abc} | 7.00 ^{abcd} | 6.50 ^{abcde} | 6.50 ^{abcde} | 7.25 ^{ab} | 6.00 ^{cde} | 6.12 ^{bcde} | 6.00 ^{cde} |

Table 4.10 (Continued)

| Parameter | Control | Interaction | CV | Cd 80.0 | | | |
|-------------------|----------------------|-------------|-------|---------------------|---------------------|-----------------------|-----------------------|
| | | | | B5.00 | B10.0 | B15.0 | B20.0 |
| Soil | | | | | | | |
| Moisture | 5.00 ^{fg} | I | 6.89 | 5.10 ^{efg} | 5.16 ^{def} | 5.87 ^c | 4.83 ^{fg} |
| pH | 4.20 ⁱ | I | 2.61 | 4.66 ^h | 4.66 ^h | 5.15 ^{bcd} | 5.06 ^{cde} |
| EC | 0.0898 ^{mn} | I | 5.52 | 0.182 ^g | 0.223 ^e | 0.264 ^d | 0.352 ^b |
| OM | 1.07 ^e | I | 3.25 | 1.37 ^d | 1.38 ^d | 1.39 ^{cd} | 1.39 ^{cd} |
| N | 0.0830 ^b | I | 8.36 | 0.103 ^a | 0.106 ^a | 0.108 ^a | 0.108 ^a |
| P | 3.00 ^q | I | 1.67 | 16.5 ^p | 34.5 ^l | 65.0 ^d | 47.0 ⁱ |
| K | 35.0 ^t | I | 0.276 | 169 ⁿ | 247 ^h | 371 ^d | 398 ^b |
| Ca | 135 ^m | I | 1.37 | 184 ^h | 202 ^c | 194 ^{ef} | 191 ^{fg} |
| Mg | 24.0 ^o | I | 1.08 | 48.0 ^k | 68.0 ^h | 89.0 ^b | 87.5 ^c |
| C/N Ratio | 7.00 ^g | I | 2.75 | 8.23 ^{cd} | 8.26 ^{cd} | 8.93 ^a | 8.20 ^{cd} |
| CEC | 2.87 ⁱ | I | 1.04 | 3.16 ^f | 3.45 ^c | 3.26 ^c | 3.28 ^c |
| Cd in Soil | 0 ^q | I | 1.19 | 37.1 ^d | 46.7 ^a | 45.5 ^b | 30.7 ^f |
| Soybean | | | | | | | |
| Planting Date-V4 | 33.0 ^f | I | 1.94 | 42.5 ^{ab} | 43.5 ^a | 41.0 ^c | 41.0 ^c |
| Planting Date -VE | 4.00 ^{cd} | I | 15.1 | 6.00 ^a | 6.00 ^a | 6.00 ^a | 5.50 ^{ab} |
| VE – VC | 4.00 ^{bcd} | I | 14.8 | 5.25 ^a | 5.25 ^a | 5.50 ^a | 5.00 ^{ab} |
| VC – V1 | 5.00 ^{cde} | I | 12.1 | 6.50 ^{ab} | 7.00 ^a | 6.50 ^{ab} | 6.50 ^{ab} |
| V1 – V2 | 6.00 ^a | I | 11.8 | 6.50 ^a | 6.50 ^a | 6.50 ^a | 6.50 ^a |
| V2 – V3 | 6.00 ^{cde} | I | 11.4 | 7.12 ^{abc} | 7.37 ^a | 6.50 ^{abcde} | 6.75 ^{abcde} |

Table 4.10 (Continued)

| Parameter | Control | Interac Tion | CV | Cd 0 | | | | Cd 20.0 | | | |
|------------------------|--------------------|-----------------|-------|---------------------|--------------------|--------------------|---------------------|----------------------|-----------------------|----------------------|----------------------|
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| V3 – V4 | 8.00 ^{ab} | I | 11.2 | 6.50 ^{def} | 6.25 ^{ef} | 5.88 ^f | 5.88 ^f | 7.38 ^{bcde} | 7.12 ^{bcdef} | 6.87 ^{cdef} | 6.88 ^{cdef} |
| Planting Date – R1 | 39.0 ^c | I | 1.66 | 36.0 ^h | 36.0 ^h | 36.0 ^h | 36.0 ^h | 38.5 ^f | 37.2 ^g | 37.2 ^g | 37.2 ^g |
| R1 – R2 | 2.00 ^b | NI | 28.5 | 2.00 ^b | 2.50 ^{ab} | 2.00 ^b | 2.00 ^b | 2.00 ^b | 2.00 ^b | 3.00 ^{ab} | 2.75 ^{ab} |
| R2 – R3 | 3.00 ^a | NI | 26.5 | 2.00 ^a | 2.50 ^a | 3.00 ^a | 2.50 ^a | 2.50 ^a | 2.50 ^a | 3.00 ^a | 2.50 ^a |
| R3 – R4 | 2.00 ^{ab} | NI | 34.6 | 2.00 ^{ab} | 2.50 ^{ab} | 1.50 ^b | 1.50 ^b | 2.00 ^{ab} | 2.00 ^{ab} | 1.50 ^b | 2.50 ^{ab} |
| R4 – R5 | 3.00 ^{ab} | I | 27.2 | 3.12 ^a | 2.00 ^{bc} | 2.00 ^{bc} | 2.00 ^{bc} | 2.00 ^{bc} | 2.00 ^{bc} | 1.50 ^c | 1.50 ^c |
| R5 – R6 | 10.7 ^{bc} | I | 8.39 | 12.0 ^{ab} | 12.2 ^a | 12.2 ^a | 12.0 ^{ab} | 11.0 ^{abc} | 10.2 ^{cd} | 11.0 ^{abc} | 11.2 ^{abc} |
| R6 – R7 | 10.5 ^{bc} | I | 9.61 | 10.0 ^{bc} | 10.5 ^{bc} | 10.5 ^{bc} | 12.5 ^a | 11.5 ^{ab} | 10.5 ^{bc} | 11.5 ^{ab} | 12.2 ^a |
| R7 – R8 | 21.0 ^c | I | 4.51 | 19.5 ^f | 19.2 ^f | 17.2 ^{gh} | 16.8 ^h | 21.5 ^e | 21.2 ^e | 19.2 ^f | 18.2 ^{fg} |
| Planting Date – R8 | 90.0 ^{hi} | I | 1.22 | 89.0 ^{ij} | 88.2 ^j | 85.2 ^k | 85.8 ^k | 94.2 ^g | 94.3 ^g | 90.5 ^h | 90.5 ^h |
| Stem Weight | 0.305 ^k | I | 0.874 | 0.540 ^d | 0.669 ^b | 0.808 ^a | 0.649 ^c | 0.279 ^m | 0.498 ^f | 0.509 ^e | 0.349 ^j |
| Pod Weight | 1.00 ^{fg} | I | 15.5 | 2.21 ^c | 3.01 ^{ab} | 3.12 ^a | 2.81 ^b | 0.819 ^{ghi} | 1.66 ^d | 1.44 ^{de} | 1.20 ^f |
| Height | 30.6 ^g | I | 0.469 | 40.5 ^b | 40.1 ^c | 42.3 ^a | 36.6 ^d | 28.6 ⁱ | 31.8 ^f | 32.3 ^e | 28.9 ^h |
| Number of Node | 5.05 ^{ij} | I | 3.26 | 6.15 ^{abc} | 6.18 ^{ab} | 6.39 ^a | 6.08 ^{bcd} | 5.90 ^{cde} | 5.47 ^{fg} | 5.66 ^{ef} | 5.65 ^{ef} |
| Number of Pod | 3.50 ^g | I | 3.19 | 6.63 ^d | 8.23 ^b | 8.45 ^a | 8.01 ^c | 3.10 ^h | 2.71 ^{ij} | 4.62 ^e | 3.92 ^f |
| Number of Seed per Pod | 1.26 ^k | I | 1.98 | 1.99 ^d | 2.07 ^b | 2.54 ^a | 2.04 ^{bc} | 1.79 ^f | 1.99 ^d | 2.01 ^{cd} | 1.80 ^f |
| Dry Weight 100 Seeds | 10.6 ⁿ | I | 0.240 | 16.7 ^d | 18.0 ^a | 17.8 ^b | 17.0 ^c | 11.7 ^k | 12.3 ^g | 14.2 ^e | 12.0 ^j |
| Product per Pot | 2.08 ⁱ | I | 5.67 | 6.37 ^c | 7.86 ^b | 8.76 ^a | 4.51 ^c | 1.97 ^{ij} | 2.84 ^g | 5.06 ^d | 3.59 ^f |

Table 4.10 (Continued)

| Parameter | Control | Interac tion | CV | Cd 40.0 | | | | Cd 60.0 | | | |
|------------------------|--------------------|-----------------|-------|----------------------|----------------------|-----------------------|---------------------|----------------------|----------------------|----------------------|----------------------|
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| V3 – V4 | 8.00 ^{ab} | I | 11.2 | 7.88 ^{abcd} | 7.88 ^{abcd} | 7.50 ^{abcde} | 8.00 ^{abc} | 7.75 ^{abcd} | 8.37 ^{ab} | 7.37 ^{bcde} | 7.25 ^{bcde} |
| Planting Date –R1 | 39.0 ^c | I | 1.66 | 46.4 ^a | 45.7 ^{ab} | 41.8 ^d | 42.6 ^d | 45.3 ^{ab} | 44.7 ^{bc} | 42.3 ^d | 41.7 ^d |
| R1 – R2 | 2.00 | NI | 28.5 | 3.00 ^{ab} | 3.00 ^{ab} | 3.00 ^{ab} | 3.00 ^{ab} | 3.00 ^{ab} | 3.00 ^{ab} | 3.50 ^a | 2.87 ^{ab} |
| R2 – R3 | 3.00 ^a | NI | 26.5 | 2.50 ^a | 2.50 ^a | 3.00 ^a | 2.50 ^a | 3.00 ^a | 3.00 ^a | 3.00 ^a | 3.00 ^a |
| R3 – R4 | 2.00 ^{ab} | NI | 34.6 | 2.00 ^{ab} | 2.00 ^{ab} | 2.50 ^{ab} | 2.50 ^{ab} | 2.00 ^{ab} | 2.50 ^{ab} | 2.50 ^{ab} | 2.50 ^{ab} |
| R4 – R5 | 3.00 ^{ab} | I | 27.2 | 2.00 ^{bc} | 2.00 ^{bc} | 2.50 ^{abc} | 2.50 ^{abc} | 2.00 ^{bc} | 2.50 ^{abc} | 3.00 ^{ab} | 2.50 ^{abc} |
| R5 – R6 | 10.7 ^{bc} | I | 8.39 | 7.00 ^f | 8.00 ^{ef} | 8.250 ^e | 9.00 ^{de} | 9.25 ^{de} | 8.25 ^e | 9.25 ^{de} | 9.00 ^{de} |
| R6 – R7 | 10.5 ^{bc} | I | 9.61 | 9.00 ^c | 9.00 ^c | 9.00 ^c | 9.25 ^c | 10.2 ^{bc} | 9.25 ^c | 10.2 ^{bc} | 10.2 ^{bc} |
| R7 – R8 | 21.0 ^c | I | 4.51 | 23.5 ^{cd} | 22.2 ^{de} | 22.2 ^{de} | 21.5 ^e | 24.2 ^{bc} | 23.2 ^{cd} | 24.2 ^{bc} | 23.7 ^{bcd} |
| Planting Date – R8 | 90.0 ^{hi} | I | 1.22 | 97.0 ^{de} | 95.0 ^{fg} | 94.0 ^g | 98.0 ^{cde} | 99.3 ^c | 99.2 ^c | 98.3 ^{cd} | 96.5 ^{ef} |
| Stem Weight | 0.305 ^k | I | 0.874 | 0.219 ^o | 0.368 ⁱ | 0.460 ^g | 0.399 ^h | 0.280 ^m | 0.298 ^l | 0.308 ^k | 0.309 ^k |
| Pod Weight | 1.00 ^{fg} | I | 15.5 | 0.807 ^{ghi} | 1.20 ^{ef} | 1.72 ^d | 1.41 ^{de} | 0.611 ^{hi} | 0.914 ^{fgh} | 1.04 ^{fg} | 0.606 ^{hi} |
| Height | 30.6 ^g | I | 0.469 | 21.5 ^r | 25.4 ^l | 22.8 ^o | 23.5 ⁿ | 20.2 ^s | 22.5 ^p | 23.8 ^m | 22.3 ^q |
| Number of Node | 5.05 ^{ij} | I | 3.26 | 5.86 ^{de} | 5.47 ^{fg} | 5.15 ^{hi} | 5.65 ^{ef} | 5.15 ^{hi} | 5.36 ^{gh} | 5.15 ^{hi} | 4.88 ^{ij} |
| Number of Pod | 3.50 ^g | I | 3.19 | 2.42 ^k | 2.60 ^j | 3.38 ^g | 2.83 ⁱ | 2.18 ^{lm} | 2.35 ^{kl} | 2.73 ^{ij} | 2.13 ^m |
| Number of Seed per Pod | 1.26 ^k | I | 1.98 | 1.54 ^h | 1.68 ^g | 1.88 ^e | 1.68 ^g | 1.538 ^h | 1.17 ^l | 1.88 ^e | 1.40 ^j |
| Dry Weight 100 seeds | 10.6 ⁿ | I | 0.240 | 11.4 ^l | 12.1 ⁱ | 12.2 ^h | 11.7 ^k | 10.9 ^m | 12.5 ^f | 9.98 ^o | 9.68 ^p |
| Product per Pot | 2.08 ⁱ | I | 5.67 | 1.91 ^{ij} | 1.81 ^j | 3.79 ^f | 3.04 ^g | 1.79 ^j | 1.23 ^k | 2.39 ^h | 1.26 ^k |

Table 4.10 (Continued)

| Parameter | Control | Interaction | CV | Cd 80 | | | |
|------------------------|--------------------|-------------|-------|--------------------|---------------------|---------------------|---------------------|
| | | | | B5 | B10 | B15 | B20 |
| V3 – V4 | 8.00 ^{ab} | I | 11.2 | 8.87 ^a | 8.88 ^a | 8.37 ^{ab} | 8.37 ^{ab} |
| Planting Date –R1 | 39.0 ^c | I | 1.66 | 46.3 ^a | 45.3 ^{ab} | 43.8 ^c | 44.0 ^c |
| R1 – R2 | 2.00 ^b | NI | 28.5 | 3.00 ^{ab} | 3.00 ^{ab} | 3.00 ^{ab} | 3.00 ^{ab} |
| R2 – R3 | 3.00 ^a | NI | 26.5 | 3.00 ^a | 3.00 ^a | 3.00 ^a | 3.00 ^a |
| R3 – R4 | 2.00 ^{ab} | NI | 34.6 | 2.00 ^{ab} | 2.00 ^{ab} | 3.00 ^a | 2.50 ^{ab} |
| R4 – R5 | 3.00 ^{ab} | I | 27.2 | 3.00 ^{ab} | 3.00 ^{ab} | 3.00 ^{ab} | 2.00 ^{bc} |
| R5 – R6 | 10.7 ^{bc} | I | 8.39 | 10.2 ^{cd} | 10.2 ^{cd} | 8.25 ^c | 9.00 ^{de} |
| R6 – R7 | 10.5 ^{bc} | I | 9.61 | 9.25 ^c | 10.2 ^{bc} | 9.25 ^c | 9.25 ^c |
| R7 – R8 | 21.0 ^c | I | 4.51 | 27.2 ^a | 25.2 ^b | 23.2 ^{cd} | 23.5 ^{cd} |
| Planting Date – R8 | 90.0 ^{hi} | I | 1.22 | 105 ^a | 103 ^b | 98.3 ^{cd} | 97.8 ^{cde} |
| StemWeight | 0.305 ^k | I | 0.874 | 0.149 ^r | 0.228 ⁿ | 0.198 ^p | 0.159 ^q |
| Pod Weight | 1.00 ^{fg} | I | 15.5 | 0.518 ⁱ | 0.616 ^{hi} | 0.636 ^{hi} | 0.530 ⁱ |
| Height | 30.6 ^g | I | 0.469 | 19.4 ^t | 22.8 ^o | 26.8 ^k | 27.9 ^j |
| Number of Node | 5.05 ^{ij} | I | 0.362 | 4.55 ^k | 5.15 ^{hi} | 4.78 ^{ik} | 4.99 ^{ij} |
| Number of Pod | 3.50 ^g | I | 3.19 | 1.35 ⁿ | 2.20 ^{lm} | 2.76 ^{ij} | 1.14 ^o |
| Number of Seed per Pod | 1.264 ^k | I | 1.98 | 1.49 ⁱ | 1.10 ^m | 1.55 ^h | 1.01 ⁿ |
| Dry Weight 100 Seeds | 10.6 ⁿ | I | 0.240 | 0.613 ^t | 9.06 ^q | 8.70 ^r | 8.47 ^s |
| Product per Pot | 2.081 ⁱ | I | 5.67 | 1.12 ^k | 1.11 ^k | 0.978 ^k | 0.686 ^l |

Table 4.10 (Continued)

| Parameter | Control | Interac tion | CV | Cd 0 | | | | Cd 20.0 | | | |
|----------------|-----------------------|-----------------|-------|----------------------|----------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Protein | 35.1 ^l | I | 0.109 | 36.3 ^e | 35.8 ⁱ | 36.0 ^g | 36.4 ^d | 36.3 ^e | 36.1 ^f | 35.9 ^h | 36.6 ^b |
| Lipid | 18.4 ^j | I | 0.181 | 19.4 ^f | 19.4 ^f | 19.8 ^c | 19.9 ^{ab} | 19.3 ^g | 19.9 ^b | 20.0 ^a | 19.5 ^e |
| Leaf Area R1 | 6.69 ⁿ | I | 0.365 | 16.8 ^c | 16.9 ^d | 33.2 ^b | 33.9 ^a | 7.67 ^k | 7.52 ^l | 11.9 ^f | 17.4 ^c |
| Leaf Area R3 | 11.8 ^h | I | 0.266 | 29.7 ^d | 31.9 ^c | 34.8 ^b | 45.0 ^a | 11.2 ⁱ | 13.4 ^g | 18.9 ^e | 17.0 ^f |
| Leaf Area R5 | 16.2 ^g | I | 0.226 | 47.2 ^d | 50.0 ^c | 53.2 ^b | 57.1 ^a | 12.7 ⁱ | 14.0 ^h | 24.4 ^f | 25.2 ^e |
| Leaf Area R7 | 18.4 ^g | I | 0.411 | 46.5 ^d | 61.9 ^c | 78.7 ^a | 78.5 ^b | 13.7 ^k | 15.8 ^h | 27.3 ^f | 28.0 ^e |
| Pod Weight R3 | 0.0242 ^{ef} | I | 29.3 | 0.297 ^a | 0.0675 ^b | 0.0534 ^{bc} | 0.0492 ^{bcd} | 0.0380 ^{cde} | 0.0324 ^{def} | 0.0376 ^{cde} | 0.0308 ^{def} |
| Pod Weight R5 | 0.0608 ^b | I | 32.0 | 0.587 ^a | 0.0938 ^b | 0.0925 ^b | 0.0873 ^b | 0.0805 ^b | 0.0734 ^b | 0.0760 ^b | 0.0724 ^b |
| Pod Weight R6 | 1.08 ^{defg} | I | 15.0 | 2.61 ^b | 3.53 ^a | 3.33 ^a | 3.42 ^a | 1.51 ^c | 1.25 ^{cdef} | 1.42 ^{cd} | 1.27 ^{cde} |
| Pod Weight R7 | 1.28 ^{de} | I | 17.3 | 2.62 ^b | 3.83 ^a | 3.83 ^a | 3.81 ^a | 1.20 ^{de} | 1.20 ^{de} | 1.94 ^c | 1.51 ^d |
| Pod Weight R8 | 0.870 ^{fgh} | I | 16.3 | 2.21 ^b | 3.01 ^a | 3.12 ^a | 2.80 ^a | 0.819 ^{gh} | 0.818 ^{gh} | 1.74 ^c | 1.40 ^{cde} |
| Stem Weight R1 | 0.312 ^{fg} | I | 21.5 | 1.04 ^a | 0.741 ^b | 1.03 ^a | 0.942 ^a | 0.511 ^{cde} | 0.511 ^{cde} | 0.467 ^{cdef} | 0.532 ^{cd} |
| Stem Weight R3 | 0.477 ^{efg} | I | 17.7 | 1.68 ^a | 1.46 ^b | 0.906 ^c | 1.05 ^c | 0.586 ^{de} | 0.586 ^{de} | 0.573 ^{de} | 0.685 ^d |
| Stem Weight R5 | 0.589 ^{fgh} | I | 14.1 | 1.93 ^a | 1.30 ^b | 1.21 ^{bc} | 1.08 ^{cd} | 0.720 ^{efgh} | 0.720 ^{efgh} | 0.744 ^{ef} | 1.00 ^d |
| Stem Weight R6 | 0.814 ^{ijkl} | I | 9.04 | 1.10 ^{ef} | 3.59 ^a | 3.10 ^b | 2.79 ^c | 0.854 ^{hijk} | 0.854 ^{hijk} | 1.16 ^{de} | 1.29 ^d |
| Stem Weight R7 | 0.407 ^{hi} | I | 16.0 | 0.695 ^{def} | 0.824 ^{bcd} | 1.18 ^a | 0.994 ^b | 0.697 ^{def} | 0.697 ^{def} | 0.961 ^b | 1.00 ^b |
| Stem Weight R8 | 0.253 ^{gh} | I | 20.3 | 0.608 ^{bc} | 0.738 ^b | 0.876 ^a | 0.717 ^b | 0.348 ^{fgh} | 0.348 ^{fgh} | 0.577 ^{cd} | 0.516 ^{cde} |
| Cd in Root | 0 ⁱ | I | 9.31 | 0 ⁱ | 0 ⁱ | 0 ⁱ | 0 ⁱ | 5.74 ^{fg} | 6.01 ^{fg} | 2.35 ^h | 5.58 ^{fg} |
| Cd in Shoot | 0 ⁿ | I | 8.09 | 0 ⁿ | 0 ⁿ | 0 ⁿ | 0 ⁿ | 4.20 ^d | 2.51 ^{jk} | 2.34 ^k | 1.25 ^m |
| Cd in Leaf | 0 ^j | I | 21.2 | 0 ^j | 0 ^j | 0 ^j | 0 ^j | 3.17 ^{ef} | 1.84 ^{ghi} | 1.62 ^{hi} | 1.08 ⁱ |
| Cd in Seed | 0 ⁱ | I | 8.00 | 0 ⁱ | 0 ⁱ | 0 ⁱ | 0 ⁱ | 0.525 ^d | 0.467 ^c | 0.218 ^h | 0.252 ^h |

Table 4.10 (Continued)

| Parameter | Control | Interac Tion | CV | Cd 40.0 | | | | Cd 60.0 | | | |
|----------------|-----------------------|-----------------|-------|-----------------------|------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Protein | 35.1 ^l | I | 0.109 | 37.3 ^a | 36.5 ^c | 35.8 ^l | 35.5 ^l | 36.0 ^f | 35.5 ^j | 36.0 ^g | 35.5 ^j |
| Lipid | 18.4 ^j | I | 0.181 | 19.3 ^g | 19.27 ^g | 19.61 ^d | 19.9 ^b | 19.1 ⁱ | 19.3 ^g | 19.5 ^e | 19.8 ^c |
| Leaf Area R1 | 6.69 ⁿ | I | 0.368 | 6.27 ^q | 6.59 ^o | 8.51 ^h | 8.73 ^g | 6.38 ^p | 6.77 ^m | 7.98 ^j | 8.29 ⁱ |
| Leaf Area R3 | 11.8 ^h | I | 0.266 | 7.77 ^r | 8.62 ^o | 9.97 ^k | 10.3 ^j | 7.49 ^s | 7.98 ^q | 8.61 ^o | 9.42 ^l |
| Leaf Area R5 | 16.2 ^g | I | 0.226 | 10.2 ^o | 10.0 ^p | 11.9 ^k | 12.4 ⁱ | 8.78 ^t | 9.60 ^r | 10.4 ⁿ | 11.5 ^l |
| Leaf Area R7 | 18.4 ^g | I | 0.411 | 10.5 ^p | 11.4 ⁿ | 13.9 ^j | 14.6 ⁱ | 10.3 ^q | 10.9 ^o | 12.3 ^l | 12.4 ^l |
| Pod Weight R3 | 0.0242 ^{ef} | I | 29.3 | 0.0291 ^{ef} | 0.0322 ^{def} | 0.0248 ^{ef} | 0.0206 ^{ef} | 0.0234 ^{ef} | 0.0186 ^{ef} | 0.0218 ^{ef} | 0.0202 ^{ef} |
| Pod Weight R5 | 0.0608 ^b | I | 32.0 | 0.0703 ^b | 0.0730 ^b | 0.0724 ^b | 0.0674 ^b | 0.0640 ^b | 0.0574 ^b | 0.0724 ^b | 0.0730 ^b |
| Pod Weight R6 | 1.08 ^{defg} | I | 15.0 | 1.19 ^{cdefg} | 1.17 ^{cdefg} | 1.07 ^{defg} | 1.16 ^{cdefg} | 0.983 ^{efg} | 0.916 ^{efg} | 1.02 ^{efg} | 0.890 ^{fgh} |
| Pod Weight R7 | 1.28 ^{de} | I | 17.3 | 1.09 ^{de} | 1.20 ^{de} | 1.29 ^{de} | 1.07 ^{de} | 0.988 ^c | 1.13 ^{de} | 1.19 ^{de} | 1.02 ^c |
| Pod Weight R8 | 0.870 ^{fgh} | I | 16.3 | 0.807 ^{gh} | 1.20 ^{def} | 1.49 ^{cd} | 1.20 ^{def} | 0.621 ^h | 0.914 ^{fgh} | 1.07 ^{efg} | 1.08 ^{efg} |
| Stem Weight R1 | 0.312 ^{fg} | I | 21.5 | 0.463 ^{cdef} | 0.414 ^{defg} | 0.393 ^{defg} | 0.454 ^{cdef} | 0.331 ^{fg} | 0.344 ^{efg} | 0.334 ^{efg} | 0.415 ^{defg} |
| Stem Weight R3 | 0.477 ^{efg} | I | 17.7 | 0.444 ^{efg} | 0.513 ^{defg} | 0.479 ^{efg} | 0.564 ^{de} | 0.444 ^{efg} | 0.457 ^{efg} | 0.337 ^{fgh} | 0.522 ^{def} |
| Stem Weight R5 | 0.589 ^{fghi} | I | 14.1 | 0.698 ^{efgh} | 0.652 ^{efghi} | 0.630 ^{fghi} | 0.822 ^c | 0.586 ^{fghi} | 0.597 ^{fghi} | 0.581 ^{fghi} | 0.765 ^{ef} |
| Stem Weight R6 | 0.814 ^{ijkl} | I | 9.04 | 0.812 ^{ijkl} | 0.953 ^{fghij} | 1.02 ^{efgh} | 1.05 ^{efg} | 0.688 ^{klm} | 0.852 ^{hijk} | 0.907 ^{ghij} | 0.823 ^{ijkl} |
| Stem Weight R7 | 0.407 ^{hi} | I | 16.0 | 0.550 ^{fgh} | 0.731 ^{cdef} | 0.740 ^{cde} | 0.964 ^b | 0.500 ^{ghi} | 0.641 ^{efg} | 0.660 ^{defg} | 0.625 ^{efg} |
| Stem Weight R8 | 0.253 ^{gh} | I | 20.3 | 0.346 ^{fgh} | 0.436 ^{def} | 0.550 ^{cd} | 0.378 ^{efg} | 0.309 ^{fgh} | 0.366 ^{fgh} | 0.380 ^{efg} | 0.367 ^{fg} |
| Cd in Root | 0 ⁱ | I | 9.31 | 11.62 ^c | 5.39 ^{fg} | 5.34 ^g | 6.37 ^f | 14.6 ^b | 10.2 ^d | 8.27 ^c | 9.83 ^d |
| Cd in Shoot | 0 ⁿ | I | 8.09 | 3.77 ^{ef} | 2.86 ⁱ | 2.79 ^{ij} | 1.83 ^l | 5.48 ^b | 3.50 ^{fg} | 3.11 ^{hi} | 3.27 ^{gh} |
| Cd in Leaf | 0 ^j | I | 21.2 | 3.42 ^{de} | 1.65 ^{hi} | 1.63 ^{hi} | 2.17 ^{gh} | 4.00 ^{cd} | 3.97 ^{cd} | 4.68 ^{bc} | 2.21 ^{gh} |
| Cd in Seed | 0 ⁱ | I | 8.00 | 0.563 ^{cd} | 0.587 ^c | 0.586 ^c | 0.317 ^g | 0.587 ^c | 0.517 ^d | 0.676 ^b | 0.367 ^f |

Table 4.10 (Continued)

| Parameter | Control | Interaction | CV | Cd 80.0 | | | |
|----------------|-----------------------|-------------|-------|----------------------|----------------------|----------------------|-----------------------|
| | | | | B5.00 | B10.0 | B15.0 | B20.0 |
| Protein | 35.1 ^l | I | 0.109 | 35.4 ^j | 35.3 ^k | 35.3 ^k | 35.3 ^k |
| Lipid | 18.4 ^j | I | 0.181 | 19.2 ^h | 19.2 ^h | 19.3 ^g | 19.3 ^g |
| Leaf Area R1 | 6.691 ⁿ | I | 0.368 | 6.10 ^f | 6.60 ^o | 7.57 ^l | 7.97 ^j |
| Leaf Area R3 | 11.8 ^h | I | 0.266 | 7.40 ^t | 8.20 ^p | 8.79 ⁿ | 9.19 ^m |
| Leaf Area R5 | 16.2 ^g | I | 0.226 | 8.90 ^s | 9.76 ^q | 10.4 ⁿ | 11.0 ^m |
| Leaf Area R7 | 18.4 ^g | I | 0.411 | 9.46 ^r | 10.6 ^p | 11.5 ⁿ | 11.7 ^m |
| Pod Weight R3 | 0.0242 ^{ef} | I | 29.3 | 0.0176 ^{ef} | 0.0148 ^f | 0.0118 ^f | 0.0193 ^{ef} |
| Pod Weight R5 | 0.0608 ^b | I | 30.0 | 0.0565 ^b | 0.0683 ^b | 0.0683 ^b | 0.0641 ^b |
| Pod Weight R6 | 1.08 ^{defg} | I | 15.0 | 0.914 ^{efg} | 0.835 ^{gh} | 0.892 ^{fgh} | 0.564 ^h |
| Pod Weight R7 | 1.28 ^{dc} | I | 17.3 | 0.967 ^e | 1.12 ^{de} | 0.833 ^e | 1.12 ^{dc} |
| Pod Weight R8 | 0.870 ^{fgh} | I | 16.3 | 0.550 ^h | 0.631 ^h | 0.670 ^h | 0.606 ^h |
| Stem Weight R1 | 0.312 ^{fg} | I | 21.5 | 0.330 ^{fg} | 0.313 ^{fg} | 0.292 ^{fg} | 0.244 ^g |
| Stem Weight R3 | 0.477 ^{efg} | I | 17.7 | 0.441 ^{efg} | 0.331 ^{gh} | 0.229 ^h | 0.426 ^{efg} |
| Stem Weight R5 | 0.589 ^{fghi} | I | 14.1 | 0.541 ^{hij} | 0.510 ^{ij} | 0.393 ^j | 0.551 ^{ghij} |
| Stem Weight R6 | 0.814 ^{ijkl} | I | 9.04 | 0.604 ^m | 0.779 ^{kl} | 0.670 ^{lm} | 0.651 ^{lm} |
| Stem Weight R7 | 0.407 ^{hi} | I | 16.0 | 0.412 ^{hi} | 0.492 ^{ghi} | 0.430 ^{hi} | 0.345 ⁱ |
| Stem Weight R8 | 0.253 ^{gh} | I | 20.3 | 0.217 ^h | 0.297 ^{fgh} | 0.265 ^{gh} | 0.278 ^{gh} |
| Cd in Root | 0 ⁱ | I | 9.31 | 20.6 ^a | 10.7 ^d | 8.60 ^e | 10.5 ^d |
| Cd in Shoot | 0 ⁿ | I | 8.09 | 8.42 ^a | 4.69 ^c | 3.12 ^{hi} | 3.86 ^e |
| Cd in Leaf | 0 ^j | I | 21.2 | 5.09 ^{ab} | 3.04 ^{ef} | 5.64 ^a | 2.57 ^{fg} |
| Cd in Seed | 0 ⁱ | I | 8.00 | 0.699 ^{ab} | 0.671 ^b | 0.725 ^a | 0.387 ^f |

Note: Means in the Same Row with Different Letters are Significantly Different at P < 0.05.

4.4.7 Interaction between Factor A (Reactor) and Factor B (Cadmium Level) and Factor C (Biochar Mixing Rate) on Soil Property, Soybean Growth Stage, and Productive Performance

4.4.7.1 Soil Property

1) Moisture Content

The results on the table above showed an increasing trend of moisture content in soil which an interaction between Kilns x Cd level x Biochar mixing rate significantly different ($p < 0.05$). Consider to an interaction between Pelleted Broiler Litter Biochar derived from 200 liter oil drum kiln (PBLBO) interact with Cd level $\geq 20.0 \text{ mg kg}^{-1}$ and up high to 60.0 mg kg^{-1} interact with any mixing rate of biochar (5.00, 10.0, 15.0, and 20.0 t ha^{-1}) PBLBO raise up highest moisture content than an interaction between Pelleted Broiler Litter Biochar derived from Lab – scale Pyrolysis Reactor (PBLBL) interact with same Cd level and biochar mixing rate. However, when Cd level raise up high more than 60.0 mg kg^{-1} , PBLBL can elevated moisture content in soil better than PBLBO and higher than control group significantly different ($p < 0.05$). The direct effect of biochar application is related to the large inner surface area of biochar. Biochars with a range in porous structures will result from feedstocks and pyrolysis conditions (Verheijen et al., 2010: 45). Kishimoto and Sugiura, (1985: 12) estimated the inner surface area of charcoal formed between 400 and $1,000^\circ\text{C}$ to range from 200 to $300 \text{ m}^2\text{g}^{-1}$. Van Zwieten et al. (2010: 235) measured the surface area of biochar derived from papermill waste with slow pyrolysis at $115 \text{ m}^2\text{g}^{-1}$. For this studied biochar derived from broiler litter pyrolyzed type as slow pyrolysis at $400 - 500^\circ\text{C}$ in 200 liter oil drum kiln have BET surface area $6.41 \text{ m}^2\text{g}^{-1}$, slightly higher than same source and pyrolysis condition in lab –scale pyrolysis reactor which has BET surface area at $5.19 \text{ m}^2\text{g}^{-1}$, this may be caused to a different moisture content in soil after treatments. Tryon (1948: 83) studied the effect of charcoal on the percentage of available moisture in soils of different textures. In sandy soil the addition of charcoal increased the available moisture by 18.0 % after adding 45.0% of charcoal by volume, while no changes were observed in loamy soil additions. Biochar's high surface area can thus lead to increased water retention, although the effect seems to depend on the initial texture in soil (Verheijen et al., 2010: 64) conform to Downie et al. (2009) and Sohi et al. (2010:

35) reported that the surface area and porosity of biochar under different pyrolysis temperatures has potentially significant effects on water holding capacity, adsorption capacity and nutrient retention ability.

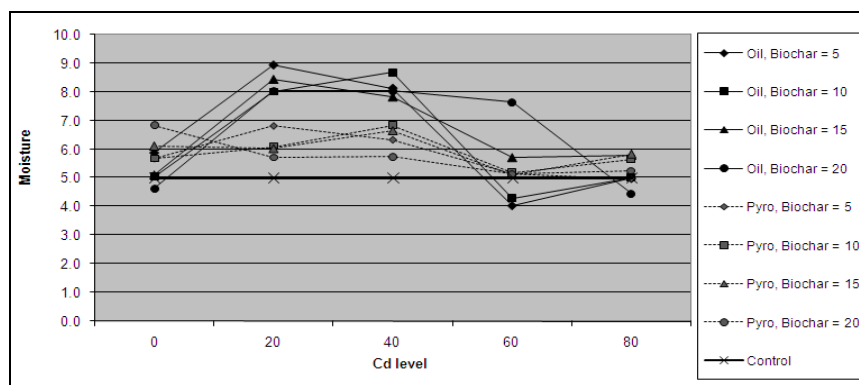


Figure 4.1 Moisture Content

2) pH

For pH, an interaction between kiln x Cd level x Biochar mixing rate showed a slightly significantly different among group ($p < 0.05$). When look in detail, the result showed obviously that an influence of Factor C (biochar at high mixing rate $\geq 10.0 \text{ t ha}^{-1}$) have strongly effect, raise up pH in soil than other Factor (kiln or Cd level). However, at lower biochar mixing rate at 5.00 t ha^{-1} interact with other factor showed pH not different among group include control group and at this biochar mixing rate, PBLBL slightly lift up pH higher than PBLBO but line in statistically not significantly different ($p > 0.05$). Biochar is comprised of stable carbon compounds created when biomass is heated to temperature between 300 to $1,000^\circ\text{C}$ under low oxygen concentrations (Lehmann and Joseph, 2009). The structural and chemical composition of biochar is highly heterogeneous, with the exception of pH, which is typically > 7.00 (Verheijen et al., 2010: 58). In this studied choose a feedstock for biochar was a pelleted broiler litter that have pH at 6.00 before pyrolyze. After pyrolyzed at temperature $400 - 500^\circ\text{C}$ in 2 types of kilns, 1st 200 liter oil drum kiln and 2nd was Lab – scale pyrolysis reactor, pH raise up high to 10.9 and 10.2 , respectively. According to Chan and Xu (2009: 67) reviewed biochar pH values from a wide variety of feedstocks and found a mean of pH 8.10 in a total range of pH 6.20

– 9.60. The lower end of this range seems to be from green waste and tree bark feedstock, with the higher end from poultry litter feedstock.

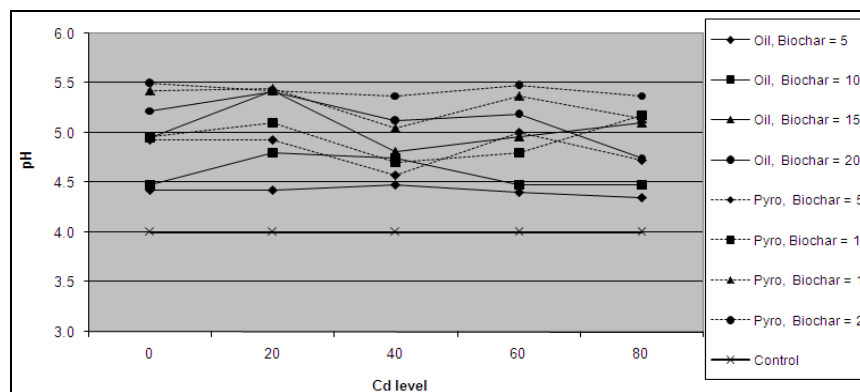


Figure 4.2 pH

3) EC

On the parameter EC in soil after treatment displayed an elevated trend when Factor B interact with factor C in any kind of kilns. The results showed a significantly different among group ($p < 0.05$) obviously on an interaction between Cd at high level $\geq 40.0 \text{ mg kg}^{-1}$ and Biochar mixing rate $\geq 15.0 \text{ t ha}^{-1}$ increase EC in soil higher than control group significantly different ($p < 0.05$). Furthermore, at low biochar mixing rate (5.00 t ha^{-1}) interact with Cd at high level $\geq 60.0 \text{ mg kg}^{-1}$ the results showed an increasing trend lift up EC than control group too, but lower than using high biochar mixing rate significantly different ($p < 0.05$). Temperature, the time a material is held at a given temperature and the heating rate directly influence the chemical properties of biochar (DeLuca et al., 2009 quoted in Lehmann and Joseph, 2009: 251). Individual elements are potentially lost to the atmosphere, fixed into recalcitrant forms or liberated as soluble oxides during the heating process. Electrical conductivity provides an indication of the amount of neutral soluble salts in the material or its salinity. High soil salinity often impedes the growth of most agricultural plants. Adding amendments that increase soil salinity, even though other beneficial properties such as water holding capacity would increase, would be counterproductive (Clay and Malo, n.d.. According to Thawadchai

Suppadit et al. (2012: 125) had suggested that do not used quail litter biochar (QLB) higher than 15.0 g kg⁻¹ because QLB is alkaline in nature.

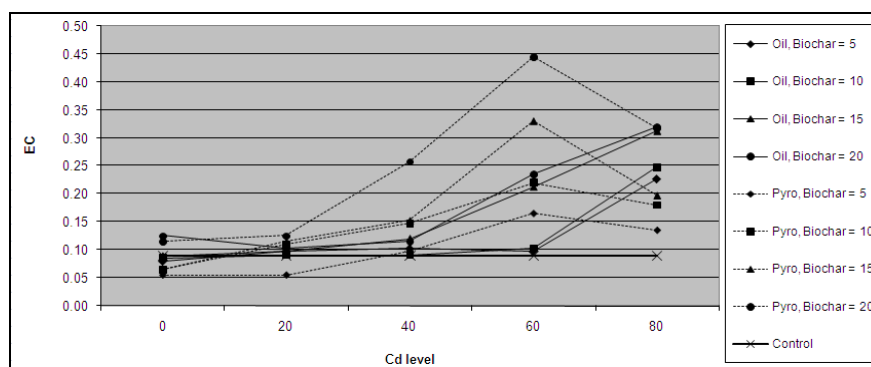


Figure 4.3 Electrical Conductivity

4) OM

Parameter OM in soil, showed an interaction between Factor A and Factor B and Factor C had a positive effect improved OM in soil significantly different when compare with control group ($p < 0.05$) but not differently when compare among group ($p > 0.05$). This mean that biochar prepare by the same feedstock, pyrolysis condition even though not the same kilns, can originate organic matter capacity in soil. Lehmann and Joseph (2009: 3) declared a concept of biochar for soil amendment originated from soils particular to the Amazonian Basin, where charcoal from incompletely combusted biomass, such as wood from household fires and in – field burning of crop stubble has, over thousands of years, produced highly fertile terra preta soils. These soils have been found to contain high levels of organic matter and nutrients when compared with adjacent soils. Pyrolysis can occur on many different scales; from simple, low – input traditional kilns to large, highly efficient industrial plants. Humans have used temporary pits and kilns constructed from earth, stones and wood for char production for thousands of years (Pratt and Moran, 2010: 1149). Traditional pit kilns and mound kilns are a low cost method of producing char; particularly in developing countries (Brown, 2009: 127). The composition of the feedstock, temperature and heating rates can be altered to provide different amounts of each product and their inherent properties (Sparkes and Stoutjesdijk, 2011: 5).

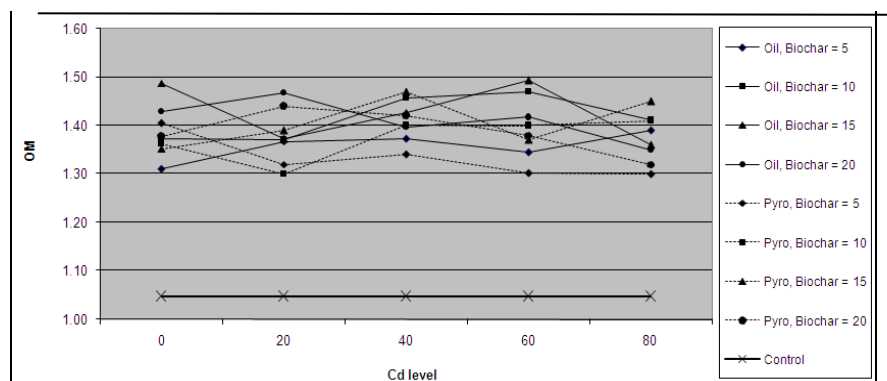


Figure 4.4 Organic Matter

5) N

For parameter N, the results showed a slightly significantly different among group ($p < 0.05$). An interaction between L kiln and Cd level 20.0 mg kg^{-1} and biochar at mixing rate 20.0 t ha^{-1} showed the highest N in soil after treatment significantly different, better than an interaction between O kiln and Cd level and same biochar mixing rate albeit not have Cd binding in soil (0 mg kg^{-1}). The trend increase N in soil display in this studied suggest that as if soil binding with $\text{Cd} \leq 20.0 \text{ mg kg}^{-1}$ should prepare biochar in lab – scale pyrolysis and used biochar at mixing rate 20.0 t ha^{-1} . As if soil not polluted with Cd (0 mg kg^{-1}) both of kilns (O or L kilns) and biochar mixing rate 15.0 and 20.0 t ha^{-1} showed N raise up high than control group strongly significantly different ($p < 0.05$). Nitrogen is the most sensitive of all macronutrients to heating, thus, the N content of high temperature biochar is extremely low (Tyron, 1948: 82). According to Bruun et al. (2012: 73) concluded that pyrolysis method did have a large influence on the mineralization – immobilization of soil N. Day (2005: 2558) also illustrated that at low temperature pyrolysis conditions may produce biochars suitable for use as a nitrogen fertilizer substitute.

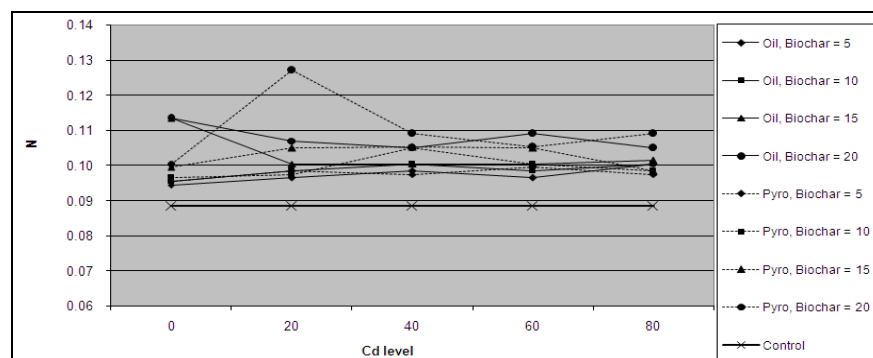


Figure 4.5 Nitrogen

6) P

About P in soil, this studied display a strongly significant different among group especially when compare with control group that Factor C (biochar mixing rate) had high effect increasing P in soil. The trend of an interaction between kilns and Cd level and biochar mixing rate, PBLBO seems raise up P higher better than PBLBL when interact with same Cd level and biochar mixing rate, especially at higher biochar mixing rate ($\geq 15.0 \text{ t ha}^{-1}$) showed a highest P raise up high 34.6 % than control group and become lower when interact with lower biochar mixing rate, but higher than control group 3.34 % significantly different ($p < 0.05$). The release of P from biochar has long been recognized (Tyron, 1948: 82). Combustion or charring of organic materials can greatly enhance P availability from plant tissue by disproportionately volatilizing C and by cleaving organic P bonds, resulting in a residue of soluble P salts associated with the charred material (Lehmann and Joseph, 2009). Gundale and Deluca (2007: 303) demonstrated this as an increased extractable PO_4^{-3} from biochar made from bark and bole samples of Douglas – fir and ponderosa pine trees from a Montana pine forest. Furthermore, it was found that charring at both low and high temperature (350°C and 800°C) resulted in a significant extractable PO_4^{-3} pool from all substrates, but that extractable P declined in biochar produced at high relative to low temperatures, where the volatilization threshold for P had been reached. Increased extractable P in soils amended with a variety of charred materials has been observed for tropical soils (Glaser et al., 2002a, 2002b: 219; Lehmann et al., 2003: 343).

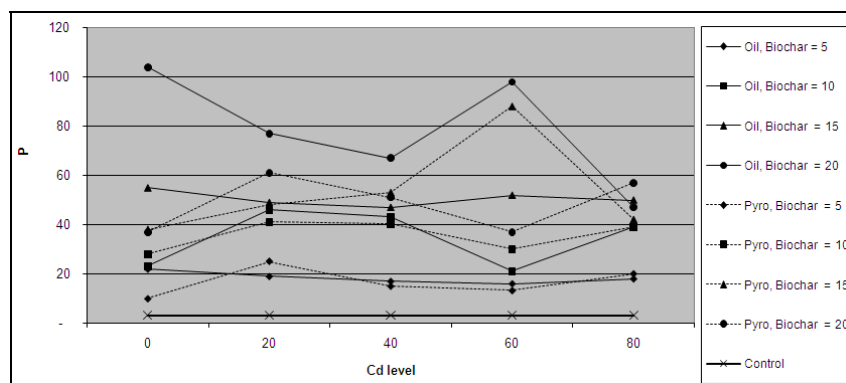


Figure 4.6 Phosphorus

7) K

For parameter K, The results of K in every treatment had increase K higher than control group strongly significant different ($p < 0.05$) especially K raise up highest than control group 554 percent in PBLBL interact with Cd level 80.0 mg kg⁻¹ interact with biochar mixing rate at 20 t ha⁻¹, following with 464 percent in PBLBO interact at same Cd and biochar condition. This trend of K amount in soil after treatment become lower line on this order Cd 80.0 mg kg⁻¹ raise up highest K that interact with highest biochar mixing rate (20.0 t ha⁻¹) > Cd60 > Cd40 > Cd20 > Cd0 > control group and K descend from biochar at highest mixing rate to lowest mixing rate (20.0 > 15.0 > 10.0 > 5.00 t ha⁻¹, respectively). In this parameter Factor A (kilns) seems have slightly effect to K results less than Factor B (Cd level) or Factor C (biochar mixing rate).

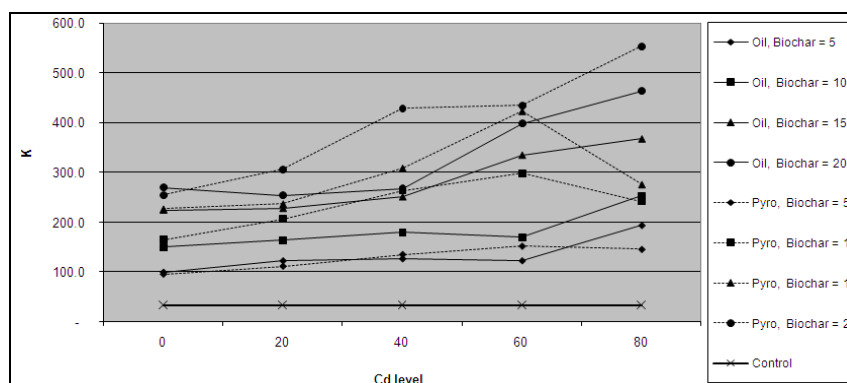


Figure 4.7 Potassium

8) Ca

Due to the results of Ca in soil after treatments, an interaction between PBLBO and Cd level 0 mg kg^{-1} and biochar at highest mixing rate (20.0 t ha^{-1}) showed the highest Ca amount in soil (260 mg) and following with an interaction between PBLBL at the same Cd level and biochar mixing rate and slightly become lower related to Factor C (biochar mixing rate) that become lower too. Nevertheless, when Factor B raise up $\geq 20.0 \text{ mg kg}^{-1}$, interact at same biochar mixing rate, whether PBLBO or PBLBL showed not difference elevated Ca in soil, however raise up Ca than control group slightly different.

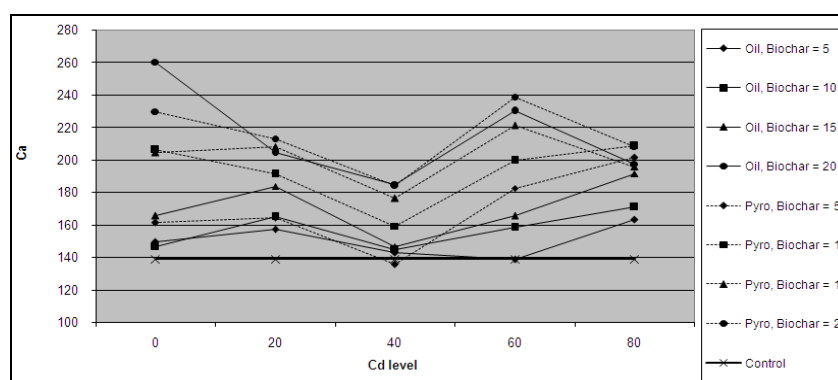


Figure 4.8 Calcium

9) Mg

About Mg results, showed the trend like Ca, that up higher when Factor C is the highest biochar mixing rate in none Cd condition ($\text{Cd } 0 \text{ mg kg}^{-1}$), whether PBLBO or PBLBL, this significantly different among group ($p < 0.05$). Interestingly on the number of Mg in treatment that belong to an interaction between PBLBO and Cd level 0 mg kg^{-1} and biochar level at lowest mixing rate (5.00 t ha^{-1}) compared with PBLBL in same Cd and biochar condition, the result of Mg from PBLBO showed a desirable Mg higher than PBLBL and also higher than control group significantly different ($p < 0.05$), furthermore, even though Cd level raise up higher but the effective of this interaction between Factor A x Factor B x Factor C have potential lift up Mg in soils higher than control group dramatically different ($p < 0.05$).

Uchimiya et al. (2012: 5035) used a phosphorus – rich broiler litter biochars produced at 350 and 650°C were employed to understand how biochar's elemental composition (P, K, Ca, Mg, Na, Cu, Pb, Sb, and Zn) affected the extent of heavy metal stabilization, their concluded that lower pyrolysis temperature was favorable for stabilization Pb and releasing P, K, Ca, and other plant nutrient in a sandy acidic soil. Chan and Xu (2009: 67) reported about total P and total K in biochar that were found broadly according to feedstock, with values between 2.70 – 480 and 1.00 – 58.0 g kg⁻¹, respectively. Interestingly, total ranges of N, P and K in biochar are wider than those reported in the literature for typical organic fertilizers (Verheijen et al., 2010: 76). Most minerals within the ash fraction of biochar are thought to occur as discrete associations independent of the carbon matrix, with the exception of K and Ca (Amonette and Joseph, 2009). Typically, each mineral association comprises more than one type of mineral. There is experimental evidence that demonstrates the composition, distribution, relative proportion and reactivity of functional groups within biochar are dependent on a variety factors, including the source material and the pyrolysis methodology used (Antal and Gronli, 2003: 1619). Different processing conditions explained differences in N contents between three biochars from poultry litter (Lima and Marshall, 2005: 699; Chan et al., 2007a: 139). As the pyrolysis temperature rises, so does the proportion of aromatic carbon in the biochar, while N contents peak at around 300°C (Baldock and Smernik, 2002: 1093). In contrast, low processing temperatures (<500°C) favor the relative accumulation of a large proportion of available K, Cl (Yu et al., 2005: 1435), Si, Mg, P and S (Bourke et al., 2007: 5954; Schnitzer et al., 2007: 71). Therefore, processing temperature <500°C favor nutrient retention in biochar (Chan and Xu, 2009: 67), while being equally advantageous in respect to yield (Gaskin et al., 2008: 2061). Nevertheless, it is important to stress that different permutations of those processing conditions, including temperature, may effect differently each source material (Verheijen et al., 2010: 50).

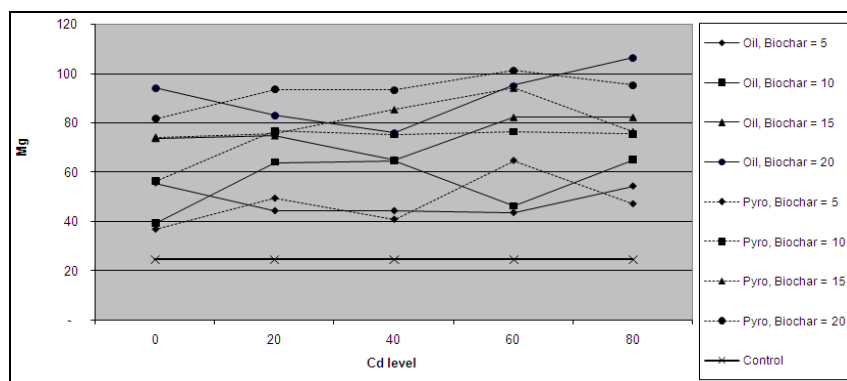


Figure 4.9 Magnesium

10) C/N Ratio

For parameter C/N, an interaction between kiln x Cd level x biochar mixing rate, increase C/N ratio significantly different when compare with control group, but when compare among group, seem slightly different and can't defined what factor have the most effect to the results. An interaction between PBLBO and Cd level 0 mg kg⁻¹ and Biochar mixing rate at 15.0 t ha⁻¹ showed the highest C/N ratio (9.28) but not strongly different when compare with PBLBL at the same conditions (8.83). Observed specific on none Cd condition, interesting on an interaction between PBLBO interact with whether highest biochar mixing rate at 20.0 t ha⁻¹ (7.52) or lowest at 5.00 t ha⁻¹ (7.75) showed as similar results not different among group and not different to control group (7.00) too, however the desirable number of C/N on this condition showed at biochar mixing rate 15.0 and 10.0 t ha⁻¹ (9.28 and 8.66 respectively). This mean that it not necessary used much or less amount of biochar for raise up C/N ratio at non Cd polluted soil but should use only 15.0 or 10.0 t ha⁻¹ that were enough for this conditions. Contrary to the results by an interaction between PBLBL at Cd level 0 mg kg⁻¹ with biochar mixing rate 5.00 t ha⁻¹, this conditions display number of C/N (8.83) not different whether 10.0 (8.69), 15.0 (8.26), or 20.0 t ha⁻¹ (8.38) (p>0.05). This can be concluded that within as above condition should use PBLBL at biochar mixing rate only 5.00 t ha⁻¹ was sufficient for improving C/N. In the situation of Cd binding in soil, at same Cd binding level that interact with same biochar mixing rate, PBLBO showed a slightly raise up C/N ratio in soil better than PBLBL. C/N ratio often used as an indicator of the ability of

organic substrates to mineralize and release inorganic N when applied to soils (Lehmann and Joseph, 2009: 70). The C/N ratio of biochars vary widely between 7.00 to 400, with a mean of 67.0 (In this study the C/N ratio of biochar derive form pyrolyzed broiler litter at 400 – 500°C in 2 kilns: O kiln and L kiln give the C/N 8.00 and 9.00, respectively). Most of the biochars are expected to cause N immobilization and possibly induce N deficiency of plant when applied to soil. Pereira et al. (n.d.) had reported that soils amended with high C : N plant materials generally have a greater incidence of fungal feeding nematodes, therefore the addition of biochar with high C : N ration to soil could lead to a shift in decomposition to a more fungal based channel. Therefore, biochar has the potential to promote a more intact, healthy soil food web with more effective nutrient cycling which in turn can result in a reduction in green house gas emissions.

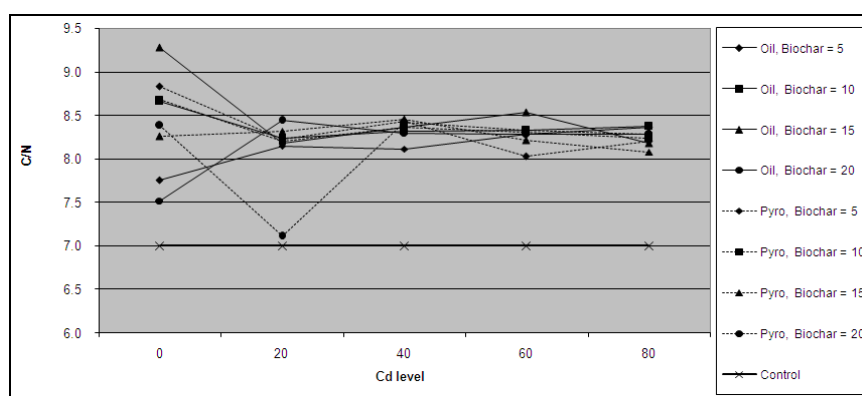


Figure 4.10 C/N Ratio

11) CEC

CEC in soil after treatment showed a significantly different among group ($p < 0.05$). At Cd level in soil at 0 mg kg^{-1} , the result showed a significantly efficiency of PBLBO interact with biochar mixing rate 20.0 t ha^{-1} (3.80) raise up CEC better than PBLBL (3.17) at same biochar mixing rate, even though interact with biochar mixing rate 15.0 t ha^{-1} (3.55), PBLBO lift up CEC higher than PBLBL that interact with biochar mixing rate 20.0 t ha^{-1} and higher than control group (2.92) significantly different ($p < 0.05$). However, at lower biochar mixing rate (10.0 and 5.00 t ha^{-1}) interact with whether PBLBO or PBLBL, display CEC not

different among group ($p > 0.05$). At Cd level 20.0 mg kg^{-1} , PBLBO interact with biochar mixing rate $\geq 10.0 \text{ t ha}^{-1}$ increased CEC up higher than control group and higher than PBLBL significantly different ($p < 0.05$) but at biochar mixing rate 5.00 t ha^{-1} PBLBO and PBLBL show a similarly CEC result and slightly higher than control group (3.15, 3.00, and 2.92, respectively). At Cd level $\geq 40.0 \text{ mg kg}^{-1}$ which activated with biochar 20.0 t ha^{-1} showed an increasing of CEC higher than control group and other group of treatments significantly different, and at this condition PBLBO show an efficiency up higher CEC than PBLBL significantly different, however at biochar mixing rate lower than 20.0 t ha^{-1} whether PBLBO or PBLBL display CEC in soil not different ($p > 0.05$) lower than 20.0 t ha^{-1} but higher than control group significantly different ($p < 0.05$). Cation Exchange Capacity determines the soil's ability to hold cations. Plant mineral nutrients such as Ca, P, K and N are present in soil water (soil solution), predominantly as cations and in some case anions, the higher the cation exchange capacity, the more fertile soil (Sparkas and Stoutjesdijk, 2011: 12). Chan et al. (2007: 629) and Lehmann (2007a: 143) have shown that biochar produced at low temperature have a high CEC, while those produced at high temperature (greater than 600°C) have a limited or no CEC. This finding suggest that biochar for soil amendment should not be produced at high temperature. Additionally, freshly produced biochar have a little CEC, (Liarg et al., 2006: 1719) while their anion exchange capacity is substantial. As biochar ages or matures in the soil, its cation exchange capacity increased (Cheng, Lehmann, Thies, Burton and Engelhard, 2006: 1477). Furthermore, additions of biochar to soil have shown definite increase in cation exchange capacity (CEC) and pH (Tyron et al., 2002; Topoliontz et al., 2002). Example by the result by Nigussie et al. (2012: 369) that applied maize stalk – derived biochar at rate 0, 5.00 and 10.0 t ha^{-1} on soils artificially polluted with chromium at the levels of 0, 10.0, and 20.0 ppm, showed a significantly ($p < 0.01$), increase in pH, electrical conductivity (EC), organic carbon, total N, available P, CEC and moreover uptake on N, P and K increased by addition of biochar.

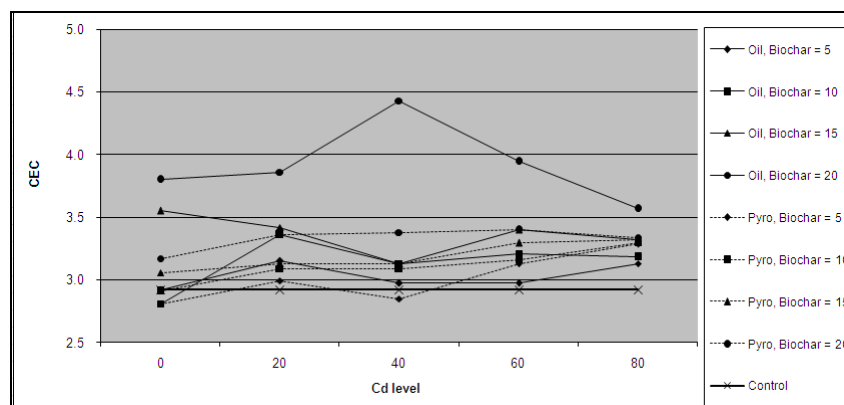


Figure 4.11 Cation Exchange Capacity

12) % Cd Residual in Soil

For Cd residual in soil, the results showed a decreasing trend lower than the pre-treatment obviously seen. The decreasing trend arrange from 2 factors 1st from Cd level that Cd 0 mg kg⁻¹ had Cd residual < Cd20 < Cd40 < Cd60 < Cd 80.0 mg kg⁻¹ respectively and 2nd from biochar mixing rate that highest biochar mixing rate 20.0 t ha⁻¹ perform Cd residual < 15 t ha⁻¹ < 10 t ha⁻¹ < 5.00 t ha⁻¹, respectively. The result from non Cd polluted soil, PBLBO and/or PBLBL with every biochar mixing rate showed not different ($p>0.05$) among group that not had Cd residual in soil but when Cd raise up to 20.0 mg kg⁻¹, PBLBL mixing rate 20.0 t ha⁻¹ showed the best efficiency more than other group, removed Cd in soil 70.5 % from pre – treatment, following with the result from PBLBO in the same conditions can removed Cd in soil 58.1 % and Cd residual slightly increase belong to lower biochar mixing rate. At Cd level 40.0 mg kg⁻¹, PBLBL interact with biochar mixing rate 20.0 t ha⁻¹ still showed the best potential reduced Cd lower than PBLBO in same condition, interesting that every results from this Cd level not more than the soil quality standard for habitat and agriculture for cadmium not more than 37.0 mg kg⁻¹(Ministry of Natural and Environment, Thailand) but higher than non Cd polluted soil and Cd level 20.0 mg kg⁻¹. At Cd 60 mg kg⁻¹, PBLBO and PBLBL still showed the results in each group of treatment lower than the Cd in soil quality standard except PBLBL at mixing rate 5.00 and 10.0 t ha⁻¹ showed higher than the Cd in soil quality standard. Finally at Cd 80.0 mg kg⁻¹, PBLBL and PBLBO at mixing rate 20 t ha⁻¹ showed Cd residual in

soil at 31.4 mg kg^{-1} (60.8 % removal efficiency) and 35.0 mg kg^{-1} (56.3 % removal efficiency) lower than the soil quality standard for habitat and agriculture for cadmium not more than 37.0 mg kg^{-1} (Ministry of Natural and Environment, Thailand), except this groups showed higher than the standard. Considered that at same biochar mixing rate PBLBO showed lower Cd residual in soil than PBLBL that may be due to the former CEC level in PBLBO had CEC at $18.2 \text{ me}/100\text{g}$ which higher PBLBL that had CEC in soil at $17.6 \text{ me}/100 \text{ g}$. As we known that high CEC capacity, biochars have the ability absorbing heavy metals and organic contaminants such as pesticides and herbicides from the environment (Navia and Cowley, 2010: 479). According to Zhang et al. (2012: 140) proposed biochars on soil Cd immobilization and phytoavailability, growth of plants, and Cd concentration, accumulation, and translocation, in plant tissues in Cd contaminated soils under water logged conditions. They found that after 3 weeks of soil incubation, pH increased and CaCl-extractable Cd decreased significantly with biochar additions. After 9 weeks of plant growth, biochar additions significantly increased soil pH and electrical conductivity and reduced CaCl-extractable Cd. EDTA extractable soil Cd significantly decreased with biochar additions, in the high Cd treatment, but not in the low Cd treatment. Trakal et al. (2011: 372) used biochar derived from stem of willow pyrolyzed at 400°C apply in 1.00 % and 2.00 % w/w to Cd, Cu, Pb, and Zn contaminated soil. The obtained results proved the different sorption behavior of metals in the single-metal solution compared to the multi-metal ones due to competition effect. Moreover, during multi-element sorption, Zn was significantly desorbed. The applied biochar enhance Cu and Pb sorption and no changes were observed when contaminated and uncontaminated biochar was used. Furthermore, the application rate had no effect as well.

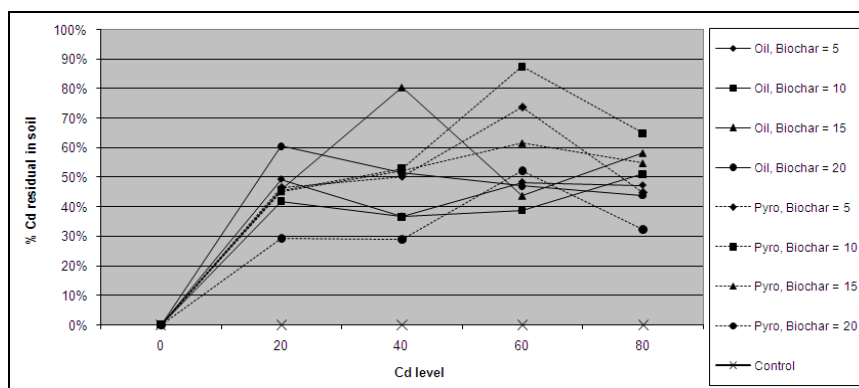


Figure 4.12 % Cd Residual in Soil

4.4.7.2 Soybean Growth Stage

1) Stage of Emergence

An interaction between PBLBO and biochar mixing rate at 15.0 t ha⁻¹ interact with Cd level 0 mg kg⁻¹ showed a shortest day (2.25) from date of planting to the emergence stage and significantly different among group while control group take longer day (4.00). Belong to statistical the results from control group and others treatment were not different ($p > 0.05$), even though the longest day at 5.25 that been the results from the soybean plant in soil polluted with Cd up high more than 40 mg kg⁻¹. This mean that an interaction between Factor A x Factor B x Factor C had ability develop soybean to the next stage albeit had Cd binding in soil. However Cd toxicity had affected to soybean growth, obviously seen on the last stage of vegetative growth stage that take prolong day rely on the level of Cd in soil from the shortest day at Cd level 0 mg kg⁻¹ (29.5 day) to the longest day at Cd level 80.0 mg kg⁻¹ (43.5 day). Interesting on Cd level 20.0 mg kg⁻¹, an interaction between PBLBO and biochar mixing rate ≥ 15.0 t ha⁻¹ take shorter day (31.5 day) than control group (33.0 day) significantly different ($p < 0.05$) and shorter than PBLBL that interact with same Cd level and biochar mixing rate (33.5 day). However, at same Cd level at low rate of biochar (5.00 and 10.0 t ha⁻¹), the results showed an efficiency less than higher biochar mixing rate while PBLBO display a slightly effective more than PBLBL.

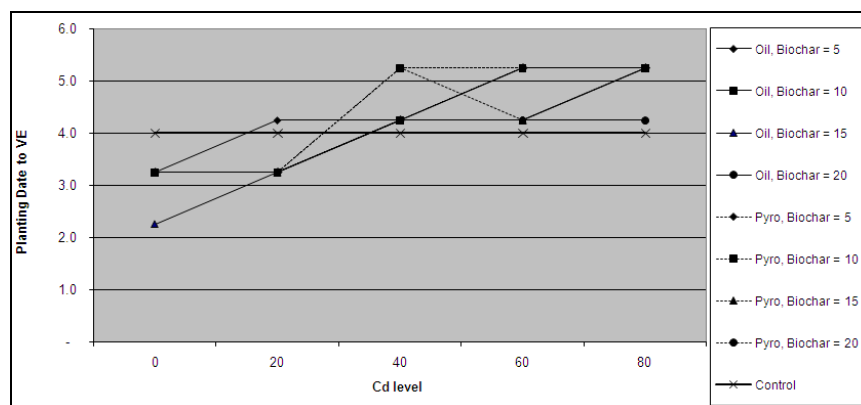


Figure 4.13 Planting Date to Stage of Emergence

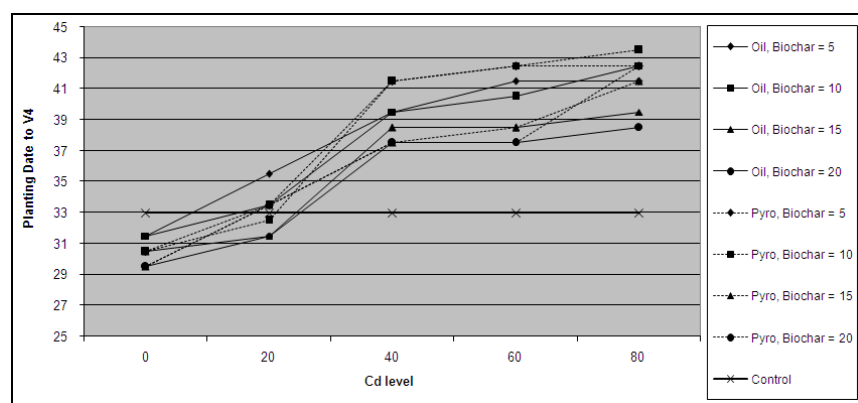


Figure 4.14 Planting Date to Stage of V4

2) Planting Date to Stage of beginning bloom

For the stage of planting date to beginning bloom (R1), the results showed a significantly different among group ($p < 0.05$) especially on Cd level 0 mg kg^{-1} interact between kiln x Cd level x biochar any mixing rate significantly different take shorter day than control group but when compare in group, results showed not different. Interesting on an interaction between PBLBO and biochar at mixing rate $\geq 15.0 \text{ t ha}^{-1}$ at Cd level 20.0 mg kg^{-1} , albeit this group polluted with Cd, the results still perform an accelerate soybean develop to beginning bloom faster than control group significantly and faster than PBLBL in the same condition too (36.5, 39.0 and 38.5 day, respectively). However, this trend not cover to Cd $\geq 40.0 \text{ mg kg}^{-1}$ cause when soil polluted with this Cd level results from an interaction between PBLBL and biochar mixing rate $\geq 15.0 \text{ t ha}^{-1}$ showed shorter time than PBLBO in

same condition and in descending order by biochar mixing rate that at higher rate showed shorter time than lower rate, obviously seen on an interaction between 4 groups OCd80B15, OCd80B10, OCd80B5, and OCd60B5, these groups all died at this stage, this indicated that soybean planting in Cd polluted soil $\geq 60.0 \text{ mg kg}^{-1}$ amend with biochar derived from pyrolysis broiler litter biochar at temperature $400 - 500^\circ\text{C}$ in 200 liter oil drum kiln used at rate $< 20.0 \text{ t/ha}$ can not tolerated to Cd toxicity.

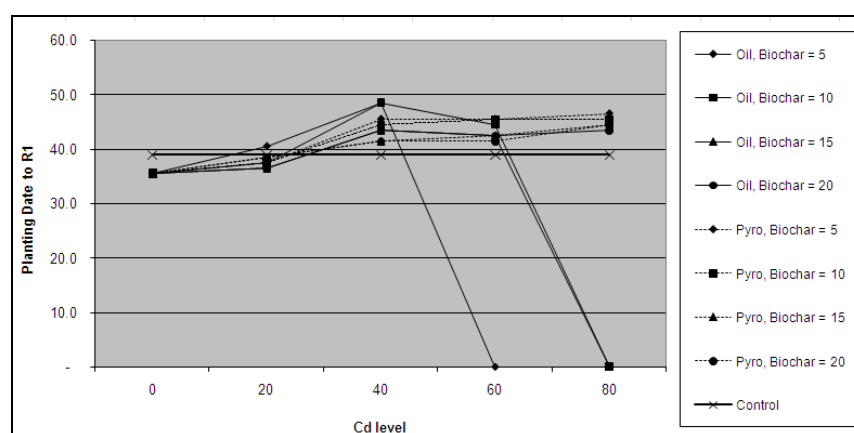


Figure 4.15 Planting Date to Stage of Beginning Bloom

3) Planting Date to Stage of Maturity (R8)

Go to the stage of maturity (R8) as last results at stage R1 that at Cd level 0 mg kg^{-1} were not different in groups but for coming to this stage was showed a significantly different among groups and control groups, obviously seen on an interaction between PBLBL and Cd level 0 mg kg^{-1} and biochar mixing rate 15.0 t ha^{-1} showed a shortest day run from date of planting to R8, the second was an interaction between PBLBL and Cd level 0 mg kg^{-1} and biochar mixing rate 20.0 t ha^{-1} , then interaction between PBLBL and Cd level 0 mg kg^{-1} and biochar mixing rate 10.0 t ha^{-1} that take time as same as OCd0B15 and OCd0B20 respectively (84.2, 85.2, 88.7, 88.7, and 88.7 day, respectively). From the trend we can indicated that when soil not polluted with Cd should use biochar at mixing rate 15.0 t ha^{-1} derived from lab-scale pyrolysis reactor for a shortest day accelerated soybean growth to maturity, shorter than control group (90.0 day) strongly significant different, anyway PBLBO

with same biochar mixing rate quite well developed to R8 even though take more time than the best but also faster than control group significantly different. When we considered at Cd level 20.0 mg kg^{-1} , the results showed an interesting point that PBLBO interact with biochar $\geq 10.0 \text{ t ha}^{-1}$ (90.0 day) take same period like control group go to R8 stage and take shorter day better than results from PBLBL significantly different. However when Cd raise up high more than 20.0 mg kg^{-1} , the results show PBLBL interact with biochar mixing rate $\geq 15.0 \text{ t ha}^{-1}$ take shorter day than PBLBO in the same conditions. Confirm that PBLBL sound better than PBLBO by the dead of 4 groups that died at stage of R1.

Chen et al. (2004: 781) reveal that nodulation of soybean roots was greatly inhibited by the addition of Cd, especially at the addition level of 10.0 and 20.0 mg kg^{-1} soil. The inhibition of plant growth especially the root growth increased as the cadmium concentration increased. The weight ratio of soybean root/leaf decreased as the Cd concentration increased, the results reveal that the content of Cd in different parts of the plants was as follows: roots >> stems >> leaf >> seeds, indicating that the accumulation of Cd by roots is much larger than that any other part of the soybean plant, and might cause deleterious effects to root systems and also with Sheirdill et al. (2012: 1886) studied the effect of cadmium on soybean growth and nitrogen fixation, they found that application of Cd adversely affected soybean growth, nodulation and N_2 fixation as a function of time and increase in Cd concentration. Maximum reduction in the root and shoot length was found with higher Cd level at 16.0 mg kg^{-1} sand after 10 weeks of the growth nodulation and the proportion of plant N derived from N_2 fixation decreased sharply as Cd concentrations increased during the whole growth stages and the maximum reduction was observed in the Cd level of 16.0 mg kg^{-1} sand followed by 8.00 and 4.00 mg kg^{-1} sand, respectively. Teixeira et al. (2010: 1959) suggested that the effects caused by Cd may be due to excessive production of monolignols forming lignin, which solidifiers the cell wall and restrict root growth. Moreover, Dobroviczka et al. (n.d.) have confirmed the negative effected of applied dose of Cd on the morphological and physiological parameters of the epidermal cells of soybean in different developmental stages of leaves. The general features of the epidermal cells responses to metal included closure and reduction of the size of stoma and increase of their number. Also with Oliveira et al.

(2012) found that total Cd content increased with plant age, although no statistical difference in the root to shoot per cent destructions, a large increase in the concentration and in the amount of Cd accumulated was also observe with time of treatment.

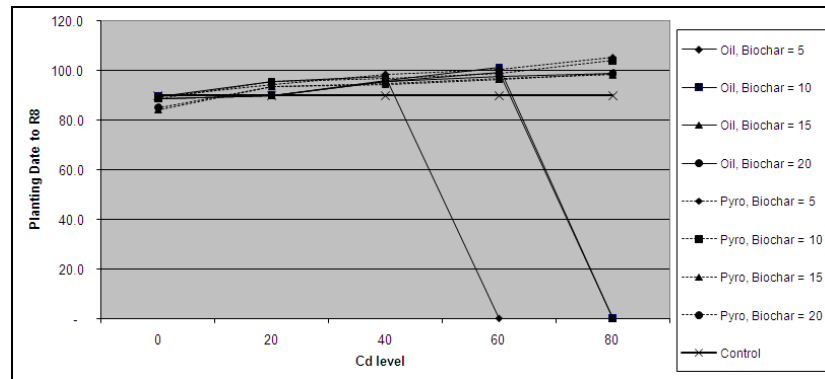


Figure 4.16 Planting Date to Stage of Maturity

4.4.7.3 Soybean Productive Performance

1) Stem Weight

Related to soybean stage of maturity (R8), product performance of soybean showed about stem weight develop rely on results of stage R8 that at Cd 0 mg kg⁻¹, interaction between PBLBL and biochar mixing rate 15.0 t ha⁻¹ display heaviest (0.730 g) than others and significantly different among groups (p<0.05). Stem weight slightly decrease depend on biochars level 20.0 > 10.0 > 5.00 t ha⁻¹, respectively. When Cd level raise up, the influence of biochar mixing rate strongly effected to stem weight in every groups of treatment, in order that when Cd raise up high, biochars at rate 15.0 t ha⁻¹ following with 20.0, 10.0 and last 5.00 t ha⁻¹, play role increase stem weight. When compare between only kiln factor in same Cd level and same biochar mixing rate, PBLBL present better result than PBLBO significantly different insists by the dead of 4 groups.

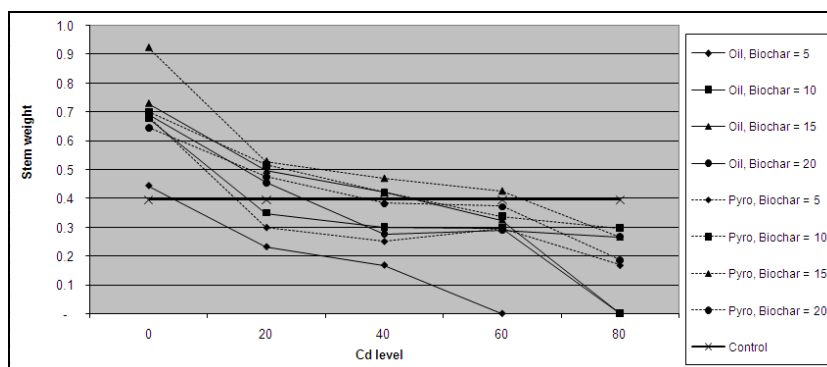


Figure 4.17 Stem Weight

2) Pod Weight

An interaction of 3 factors showed a significantly different among group. The results of pod weight rely on this order from the heaviest to light weight, considered by Factor B (Cd level): $0 > 20.0 > 40.0 > 60.0 > 80.0 \text{ mg kg}^{-1}$ respectively. An interaction between PBLBL and Cd 0 mg kg^{-1} and biochar at mixing rate 15.0 t ha^{-1} show the heaviest weight than other groups strongly significant different ($p < 0.05$) and slightly decreased in order $15.0, 10.0, 5.00$ and 20.0 t ha^{-1} . This results seem contrary to an interaction between PBLBO and biochar at the same condition, that pod weight of soybean grow in soil added with PBLBO with high mixing rate display a slightly heavy weight than lower biochar mixing rate, line in this order: $20.0 > 15.0 > 10.0 > 5.00 \text{ t ha}^{-1}$ respectively. At Cd level 20.0 mg kg^{-1} an interaction between PBLBO and biochar mixing rate 15.0 t ha^{-1} present a heavy weight (1.76 g) than others at this Cd level included control group (1.00 g) and also higher than the results from an interaction between PBLBL and biochar at Cd higher level respectively, anyway by statistical clearing that not different when compared with PBLBL interact with Cd level 20.0 mg kg^{-1} and biochar mixing rate 20.0 t ha^{-1} (1.66 g). Observing on biochar mixing rate at 5.00 t ha^{-1} whether any kiln interact with any Cd level (not include Cd 0 mg kg^{-1}), performed the lowest pod weight than other biochar mixing rate significantly different insist by the result of the dead of 4 groups as last mentioned. Abdo et al. (2012: 24) obtained results that all concentrations of Cd induced significantly decrease in all characters of vegetative growth (plant height, number of branches, leaves, total leaf area/plant, and shoot dry weight/part) and in all studied yield characters (number of pods and seeds/plant,

specific seed weight and seed yield/plant) of soybean ‘Giza 35’. Moreover, the significant decrease in morphological and yield characters got higher as the concentration of Cd increased in irrigation water. According to the conclusion of Srivastava, Khan and Manzoor (2011: 125) found the ill effects generated by Cd toxicity impaired the growth of the plants as evident by the shoot and root lengths, shoot fresh and dry weights. Their noted that Cd block the mechanism of cell division and as a result of this root become shunted and damage.

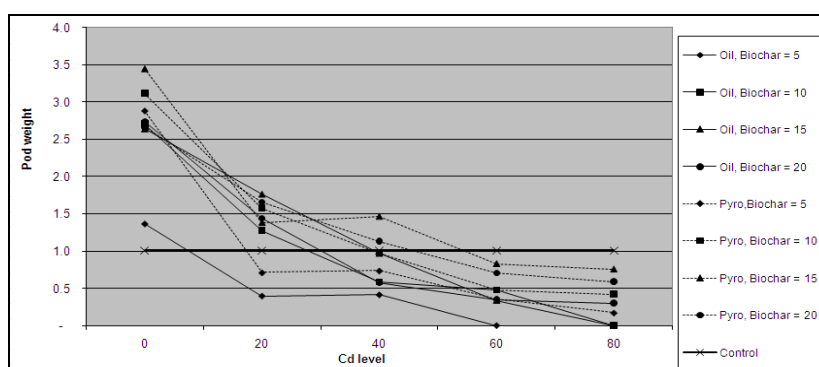


Figure 4.18 Pod Weight

3) Height

The interaction in this parameter showed significantly different among groups ($p < 0.05$). Consider at Cd level 0 mg kg^{-1} , the series from tallest to shortest run in this order: PBLBO mixing rate 15.0 t ha^{-1} (43.3 cm.) > PBLBL mixing rate 15.0 t ha^{-1} > PBLBO mixing rate 5.00 t ha^{-1} > PBLBL mixing rate 10.0 t ha^{-1} > PBLBL mixing rate 5.00 t ha^{-1} > PBLBO mixing rate 10.0 t ha^{-1} > PBLBO mixing rate 20.0 t ha^{-1} > PBLBL mixing rate 20.0 t ha^{-1} > control group (30.6 cm.), respectively. From the results imply that at soil site which not polluted with Cd, PBLBO used at mixing rate $5.00 - 15.0 \text{ t ha}^{-1}$ raise up the height of soybean significantly higher than control group. Surprisingly that biochar mixing rate 10.0 t ha^{-1} (31.7 cm.), and 15.0 t ha^{-1} (31.8 cm.) interact with PBLBO can increase the height of soybean even though planting in the soil contaminate with Cd 20.0 mg kg^{-1} and significantly taller than control group. However, when Cd raise up high than 20.0 mg kg^{-1} biochar mixing rate $\geq 15.0 \text{ t ha}^{-1}$ interact with PBLBL showed a good results of the height better than

PBLBO slightly significantly different ($p < 0.05$), nevertheless, shorter than control group.

Srivastava et al. (2011: 125) reported that increasing concentrations of Cd reduced the height and also fresh and dry weight of soybean *Glycine max L.* Furthermore the observed lower values for fresh and dry weight of the plant upon Cd treatments are in agreement with many researcher (Balestrasse et al., 2003: 57; Dell'Amico, Cavalca, Andreoni, 2008: 74).

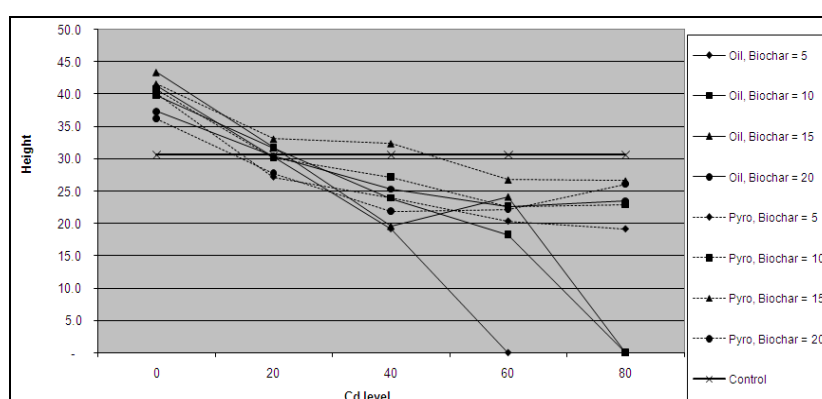


Figure 4.19 Height

4) 100 Seeds Dry Weight

An interaction between 3 factors strongly increase 100 seeds dry weight significantly, especially at Cd level 0 mg kg⁻¹ at any mixing rate of biochar lower or higher derived from PBLBO or PBLBL induced 100 seeds dry weight up high than control group and others Cd level significantly different ($p < 0.05$). The weight increasing up high rely on 2 orders, 1st line rely on Cd level from heaviest to light weight: Cd 0 > Cd 20 > Cd40 > Cd60 > Cd 80.0 mg kg⁻¹ and 2nd line rely on biochar mixing rate: 15.0 ≥ 20.0 > 10.0 > 5.00 t ha⁻¹. The optimizing rate of biochar in this study was 15.0 t ha⁻¹ also with Uzoma et al. (2011: 1) investigated the effect of cow manure biochar on maize yield, nutrient uptake and physicochemical properties of a dry land sandy soil at mixing rate 0, 10.0, 15.0 and 20.0 t ha⁻¹, found that 15.0 and 20.0 t ha⁻¹ mixing rate significantly increased maize grain yield by 150 and 98.0 % as compared with control, respectively. According to the studied of Thawadchai Suppadit et al. (2012: 244) used quail litter biochar (QLB) at rate 0, 24.6, 49.2, 73.8, 98.4 and 123 g per pot mixture provided to soybean cv. Chiang Mai 60. The results

showed QLB improved soybean production with an optimum rate at 98.4 g per pot mixture, but at higher QLB mixing rate than 98.4 g per pot is not advisable be used because QLB is alkaline in nature, which may affect soil pH.

Surprisingly on an interaction between PBLBL and Cd level 60.0 mg kg⁻¹ and biochar mixing rate 15.0 t ha⁻¹ (12.7 g) showed 100 seeds dry weight heavy than control group significantly (p<0.05). Although the weight of 100 seeds dry weight from PBLBL showed heavy than PBLBO in Cd level up high \geq 60.0 mg kg⁻¹ but at lower level of Cd as at 20.0 mg kg⁻¹ interact with PBLBO only 5.00 t ha⁻¹ (12.6g) can increased weight up higher than control group (10.7 g) significantly different (p<0.05). However, when Cd raise up upon 20.0 mg kg⁻¹, necessitated using higher quantity of biochar (\geq 15.0 t ha⁻¹) whether PBLBL or PBLBO.

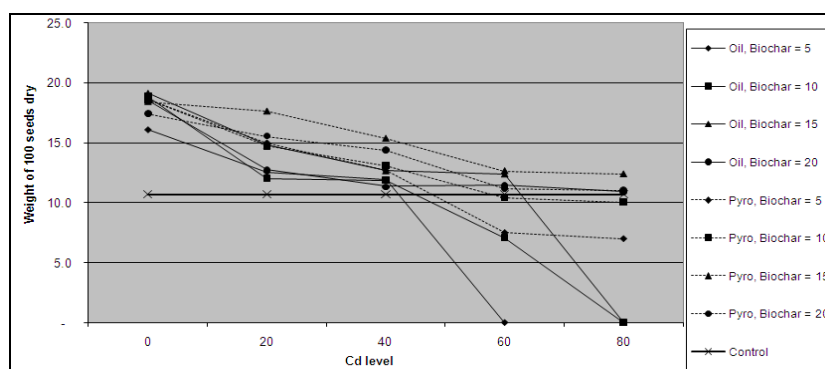


Figure 4.20 100 Seeds Dry Weight

5) Product Per Pot

The result displayed according to presentation of 100 seeds dry weight that increasing higher than control group rely on 2 orders, 1st line rely on Cd level from heaviest to light weight: Cd 0 > Cd 20 > Cd40 > Cd60 > Cd 80.0 mg kg⁻¹, and 2nd line rely on biochar mixing rate: 15.0 \geq 20.0 > 10.0 > 5.00 t ha⁻¹. One example that perform a satisfy result was an interaction between PBLBO and biochar mixing rate \geq 10.0 t ha⁻¹ lift up production per pot weight heavy than control group significantly different even though have planting on Cd polluted soil 40.0 mg kg⁻¹. However, when Cd level raise up upon 40.0 mg kg⁻¹, reply from the result that must used biochar higher mixing rate 15.0 – 20.0 t ha⁻¹ interact with PBLBL showed a better number of production per pot higher than PBLBO and many time higher than

control group, obviously seen at highest level of Cd at 80.0 mg kg⁻¹, PBLBO interact with biochar level ≤ 15.0 t ha⁻¹ all be dead. Contrary to the results of Namgay et al. (n.d.) used activated wood biochar at three rate 0, 5.00 and 15.0 g kg⁻¹ plant maize on soil polluted with As an Cd at 0, 10.0 and 50.0 mg kg⁻¹, reveal that the addition of wood biochar to soil did not have any significant influence on the dry matter yield of maize, shoot, even at the highest application rate. However, Laird et al. (2010: 436) reported that biochar amended soils retained more water and greater pH values relative to the un-amended control. The biochar amendments significantly increased total N, organic carbon and Mehlich III extractable phosphorus, potassium, magnesium and calcium but had no effect on Mehlich III extractable sulfur, copper, and zinc. They summit that biochar amendments have the potential to substantially improve the quality and fertility status of Midwestern agriculture soils, according to Suppadit et al. (2012: 247) revealed that quail litter biochar (QLB) released nutrients which beneficial and positive influence on soybean growth and yield.

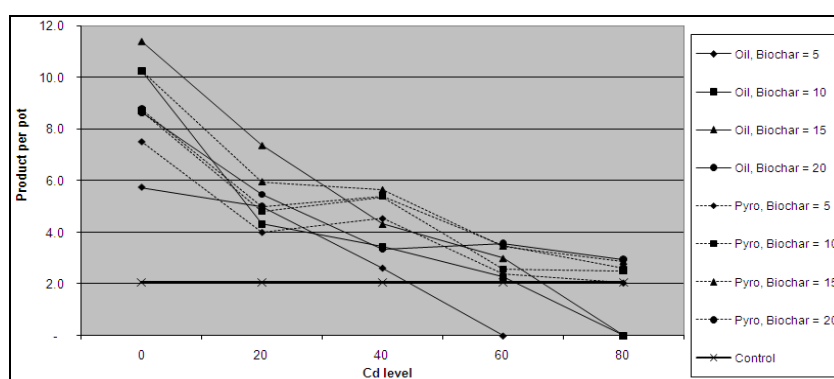


Figure 4.21 Product Per Pot

6) Protein in Soybean Seeds

About protein in soybean seeds showed a significantly different among groups ($p < 0.05$). Almost every treatment display high amount of this parameter higher than control group significantly, except at Cd level higher than 80.0 mg kg⁻¹. At Cd level ≤ 40.0 mg kg⁻¹ an interaction between PBLBO and biochar mixing rate 5.00 t ha⁻¹ showed the best quantity of protein than others when compare among groups as same Cd level, and biochar mixing rate, while PBLBL must used

higher amount of biochar up high to 20.0 t ha⁻¹. However, when Cd raise up high to ≥ 60.0 mg kg⁻¹, PBLBL sound perform a better number of protein higher than PBLBO significantly different ($p < 0.05$). Protein quantity in soybean seeds showed in this studied (38.2 % – 35.3%) be in the line for Quality Standards for U.S. Soybeans and Soy products that suggest protein could be as low as 25.0% and a high as 50.0% and a range of 30.0% to 40.0% was common in commodity – type soybeans. This founding insist that Factor biochar had strongly effect increase protein in soybean seeds insist by the trial of Blackwell, Reithmuller and Collins, (2009: 80) that biochar application have also shown increased yields of many plants; especially where they are added with mineral fertilizers or with organic fertilizers, such as manure and also with Thawadchai Suppadit et al. (2012: 248) used quail litter biochar (QLB) planting soybean in sandy soil, they found that increased the content of QLB caused an increase in seed protein or seed N contents, which suggested that QLB had the ability to release available N one applied to the soil via mineralization. Even if biochar had influence raise up protein but at high level of Cd binding in soil affect negative to productivity of plant and for this studied we found that at Cd level 80.0 mg kg⁻¹ had decrease protein in soybean seeds more than others, anyway not different to control group. Protein content may be considered as important indicators to assess growth performance of plants under stress conditions. The reduction in the amount of protein could be due to decrease in protein synthesis or an increase in the rate of protein degradation (Balestrasse et al., 2003: 57). Srivastava et al. (2011: 20) found that Cd treatments significantly decrease in total protein content lower than control group. They assumed that decrease in protein content could be a consequence of increased protein degradation and/or a decrease in protein synthesis and also with Balestrasse et al. (2003: 57) have shown that under Cd stress, decrease in protein content was related with increased protease activity in soybean.

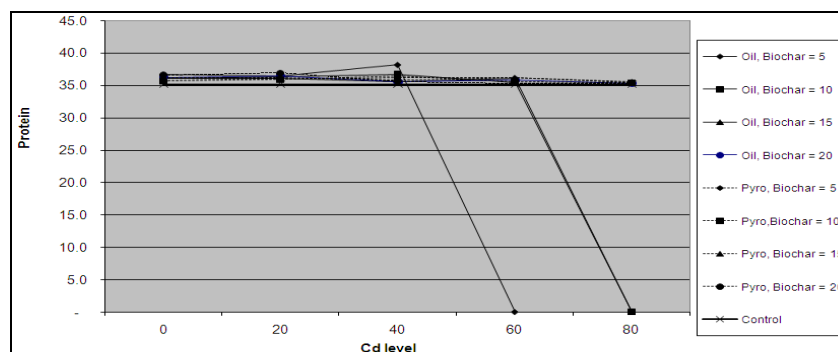


Figure 4.22 Protein in Soybean Seeds

7) Lipid in Soybean Seeds

Interaction between PBLBO and biochar mixing rate ≥ 15.0 t ha^{-1} showed amount of lipid in soybean seed higher than others significantly different among group, even though have or not have Cd binding in soil. However, lipid in soybean seeds decrease when biochar mixing rate decrease, anyway at least biochar mixing rate 5.00 t ha^{-1} can raise up high lipid in soybean production higher than control group significantly different. This can be imply that biochar had strongly influence to quantity of lipid in soybean seeds. This amount of lipid that showed in this studied (19.0–20.2 %) be in the line of Quality Standards for U.S. Soybeans and Soy products that suggest oil content could range from 13.0% to 25.0%, with a commodity–range of 16.0 % to 23.0 %. According to the resulted of Malan and Farrant (1998 :445) concluded that cadmium reduced mature soybean seed mass and decreased yields of lipids, protein and carbohydrates and also with Khan et al. (2013 :707) had suggested that Cd and Hg exposures adversely affected the soybean seed oil content and changes in the fatty acid composition of oil. Contrary to the founding of Thawadchai Suppadit et al. (2012: 248) that increasing amount of quail litter biochar corresponded to a decrease in soybean' seed lipid content. One of the suggested mechanism of Cd toxicity is that it causes lipid peroxidation (Liu et al., 2007: 443; Cuyper et al., 2002: 869) that was the oxidative stress damaging factor in plants.

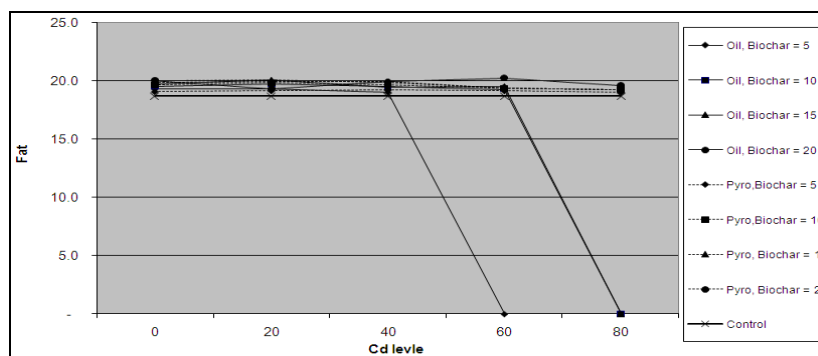


Figure 4.23 Lipid in Soybean Seeds

8) Leaf Area R1 – R7

The differences in the soybean leaf areas were significant for all treatments ($p < 0.05$). The highest leaf area (R7 stage) values were obtained from an interaction between PBLBL and Cd level 0 mg kg^{-1} and biochar mixing rate 15.0 t ha^{-1} showed at $96.2 \text{ cm}^2 \text{ 2 plants}^{-1}$ and continued to decrease when Cd level increased. Considered on Cd level 20.0 mg kg^{-1} an interaction between biochar $\geq 15.0 \text{ t ha}^{-1}$ and PBLBL or PBLBO display a higher area of the leaf more than control significantly different ($p < 0.05$). However when Cd level increased higher or biochar mixing rate $\leq 10.0 \text{ t ha}^{-1}$, had affected and decreased leaf area, obviously seen on Cd level 80.0 mg kg^{-1} interact with PBLBO and biochar mixing rate $\leq 15.0 \text{ t ha}^{-1}$, showed the death situation at this treatment. As we know that Cd has influence on the plants as an abiotic stress factor causing changes in the physiological, morphological and biochemical level (Ozdener and Kutbay, 2011: 1521). The most frequently reported symptoms of Cd toxicity include browning of root hairs on young leaves (Adriano, 2001) and growth reduction (Stoeva et al., 2005). Dobroviczka et al. 2012 confirmed the negative effect of applied dose of Cd on the morphological and physiological parameters of the epidermal cells of soybean in different developmental stages of leaves that the epidermal cells respond to toxic metals is closure and minimizing of stomata and increase their number.

Obviously seen that at Cd level 0 mg kg^{-1} , whether PBLBL or PBLBO showed not differently increase overall of soybean productive performance higher than control group significantly different. PBLBL and PBLBO mixing rate 15.0 and 20.0 t ha^{-1} still increased soybean productive performance albeit planting on Cd polluted soil

especially at Cd level 20.0 mg kg^{-1} but when Cd raise up higher $\geq 40.0 \text{ mg kg}^{-1}$, PBLBL showed the better result than PBLBO especially at mixing rate $\geq 15.0 \text{ t ha}^{-1}$, while the optimized mixing rate of both biochar should used at 15.0 t ha^{-1} . May be do to biochar properties that produced under different pyrolysis reactor effected to physical and chemical of biochar properties which influenced soil physical and chemical and promote soybean growth and productive performance. PBLBO had showed the efficiency removed Cd in soil better than PBLBL due to high pH, CEC and high surface area higher than PBLBL, however the efficiency slightly decreased, albeit the nutrient content whether PBLBL and PBLBO do not differently but soybean performance of PBLBL showed higher than PBLBO, may be from PBLBL released nutrient from biochar particle longevity and efficiency more than PBLBO due to the continuous and stable at high heating rate of 500°C while pyrolysis in reactor.

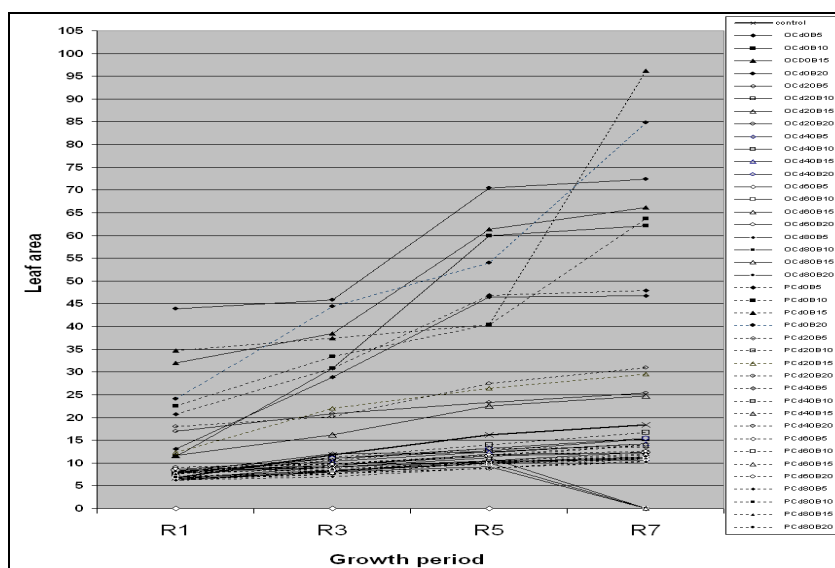


Figure 4.24 Leaf Area R1 – R7

9) % Cd Residual in Soybean Root

The results showed a tendency of Cd residue in soybean' root from none to highest rely on the order: Cd level $0 < 20 < 40 < 60$ and highest at Cd level 80.0 mg kg^{-1} , further more depend on biochar mixing rate from lowest Cd residue to highest Cd residue due to biochar mixing rate $20.0 \text{ t ha}^{-1} < 15.0 < 10.0$ and highest at biochar mixing rate 5.00 t ha^{-1} respectively. When this 3 factors, A x B X C

had interact in the same Cd level and same biochar mixing rate, PBLBL or PBLBO not performed difference ($p>0.05$).

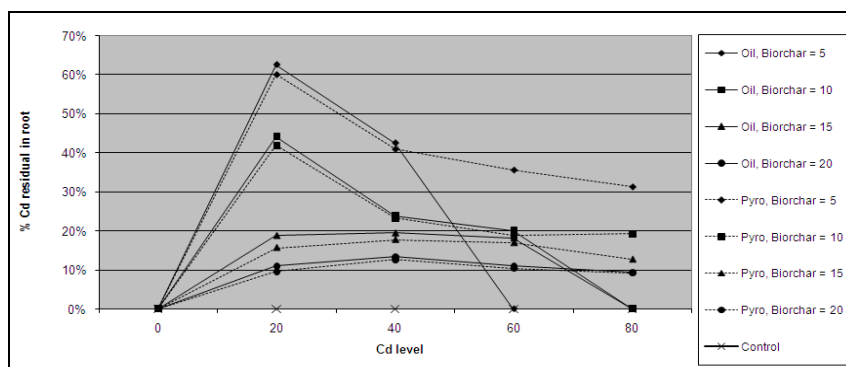


Figure 4.25 % Cd Residual in Soybean Root

10) % Cd Residual in Soybean Shoot

In Cd polluted soil $\geq 20.0 \text{ mg kg}^{-1}$ an interaction between PBLBL and biochar mixing rate $\geq 15.0 \text{ t ha}^{-1}$ showed capability reduced Cd in shoot than PBLBO significantly different ($p<0.05$). However, at Cd 0 mg kg^{-1} whether PBLBL or PBLBO at any level of biochar showed same number as control group that was the best number of had none Cd in soil.

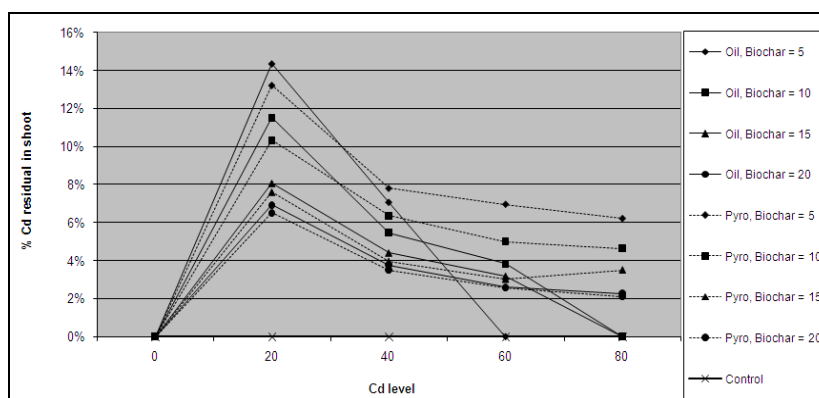


Figure 4.26 % Cd Residual in Soybean Shoot

11) % Cd Residual in Soybean Leaf

Considered on Cd level 0 mg kg^{-1} the results show not different among group ($p>0.05$) even though had interact with biochar at high mixing rate or

whether PBLBL or PBLBO but when Cd increase up to 20.0 mg kg⁻¹ PBLBL interact with biochar mixing rate 20.0 t ha⁻¹ show the best result reduced Cd in soybean leaf lowest at 1.05 mg kg⁻¹, following with 1.20 mg kg⁻¹ that been result from PBLBO interact with same biochar mixing rate. Cd residue in soybean leaf slightly increase due to two factors: 1st from decrease biochar mixing rate and 2nd from higher level of Cd in soil before treatment.

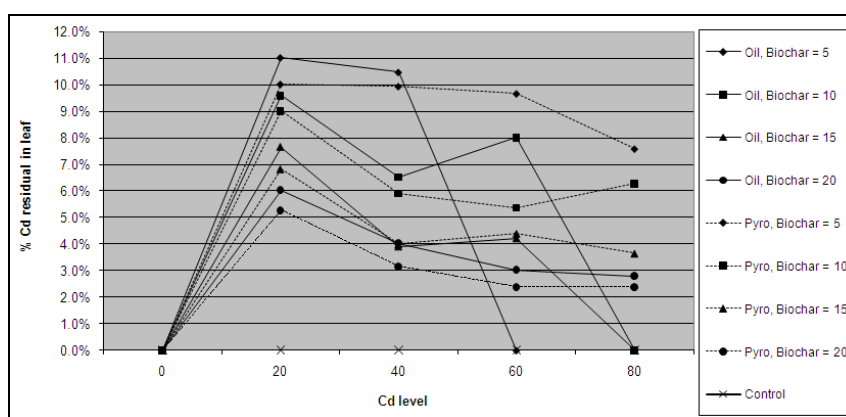


Figure 4.27 % Cd Residual in Soybean Leaf

12) % Cd Residual in Soybean Seed

There were not difference results for Cd residue in soybean seed whether PBLBL or PBLBO or control group at Cd level 0 mg kg⁻¹ ($p > 0.05$). However, when Cd raise up high the results display a significantly different among groups ($p < 0.05$). Cd residue in soybean seed slightly decrease from lowest to highest due to two factors: 1st was factor Cd level before treatment, that Cd 0 mg kg⁻¹ had Cd residue $< \text{Cd}20.0 < \text{Cd}40.0 < \text{Cd} 60.0 < \text{Cd} 80.0$ mg kg⁻¹, respectively and 2nd, was factor biochar mixing rate, that biochar mixing rate 20.0 t ha⁻¹ had Cd residue $\leq 15.0 < 10.0 < 5.00$ t ha⁻¹, respectively. Focus on Cd level 20.0 mg kg⁻¹, PBLBL or PBLBO interact with biochar 15.0 t ha⁻¹ perform the best result reduced Cd and present Cd remained in soybean seed only 0.125 and 0.137 mg, respectively, due to statistically not significantly different among this two groups, following with the result of PBLBL and/or PBLBO mixing rate 20 t ha⁻¹. Furthermore, PBLBL mixing rate 10.0 t ha⁻¹ interact with Cd level 20.0 mg kg⁻¹ had reduce Cd to 0.192 mg in soybean seed not different to the result of PBLBO interact with same Cd level but must used higher

amount of biochar up to 20.0 t ha⁻¹ (0.182 mg) and obviously seen that PBLBL had an efficiency reduced Cd better more than PBLBO, displayed by an interaction between PBLBL and biochar mixing rate 20.0 t ha⁻¹ and Cd level 60.0 mg kg⁻¹ (0.187 mg) remain Cd residue in soybean seed not difference to interaction between PBLBO and same biochar mixing rate, while Cd level only 20.0 mg kg⁻¹ (0.182 mg). These results were safe for edible because not exceed than the standard of CCFAC (Codex Committee on Food Additive and Contaminants, 2002) that permit Cd in soybean seed not over 0.200 mg kg⁻¹ soybean seeds. These may be the effect of biochar which increase pH in soil. As well known that pH was the most important factor controlling Cd solubility in the soil solution (Impellitteri et al., 2001: 101). Cd solubility is generally low at pH 7 to 8, but the solubility is substantially higher when the soil pH is lower than pH 6 (Brümmer and Herms, 1983). Ionic strength also affects the release of Cd from soils. Some of the Cd adsorbed in exchangeable form on soil colloids equilibrates with Cd in the soil solution. This exchangeable Cd becomes solubilized as the ionic strength of the solution increases (Salardini et al., 1993: 101; Grant et al., 1996: 153). pH and ionic strength are therefore the primary factors controlling the release of Cd from soils. Biochar had employ for this purpose e.g. on the studied of Fellet et al. (2011: 1262) apply prune residue derived biochar produced at highest temperature 500 °C for ameliorated the mine tailings, the result found that pH, CEC and the water holding capacity increased as the biochar content increased in the substrates and the bioavailability of Cd, Pb, Tl and Zn of the mine tailing decreased. They concluded that biochar can be in favor on mine wastes to help the establishment of a green cover in a phytostabilization process. Further explanation for heavy metal stabilization by biochar occurred with a concurrent release of various elements such as Na, Ca, K, Mg, P, and S originating from soil and biochar. Both soil and biochar possess buffering capacity and can serve as the source and sink of all elements (Uchimiya et al., 2011: 423). These may be from the properties of biochar that have high CEC as many researcher (Haghiri, 1974: 180; Miller et al., 1976: 157) had claim that CEC had ability control the availability of trace elements, increase in CEC means decrease uptake of metals by plant. Macronutrients interfere antagonistically with uptake of trace elements (Efremova and Izosimova, Phosphate ions reduce the uptake of Cd and Zn in plants (Haghiri, 1974: 180; Smilde, Van and van Driel, 1992: 233). Calcium controls the absorption of metals, e.g. Cd, as a result

of competition for available absorption sites at the root surface (Cataldo, Garland and Wildung, 1983: 844).

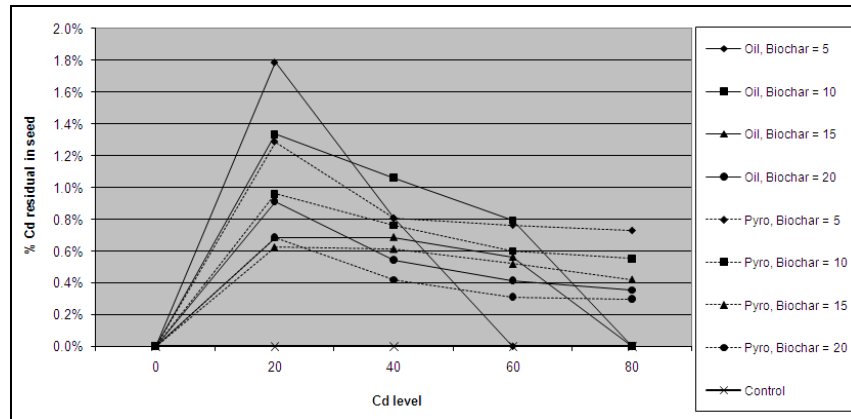


Figure 4.28 % Cd Residual in Soybean Seeds

Table 4.11 Interaction between Factor A (Reactor) and Factor B (Cd Level) and Factor C (Biochar Mixing Rate) on Soil Properties, and Productive Performance

| Parameter | Control | Interac Tion | CV | Cd0 | | | | | | | |
|--------------------|------------------------|-----------------|------|----------------------------------|------------------------|-------------------------|-----------------------|---------------------------------------|-------------------------|------------------------|------------------------|
| | | | | 200 Litter Oil Drum Kiln (PBLBO) | | | | Lab - scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Soil | | | | | | | | | | | |
| Moisture | 5.00 ^{klmn} | I | 7.15 | 5.87 ^{gh} | 5.06 ^{jklmn} | 5.10 ^{jklmn} | 4.63 ^{mno} | 5.68 ^{ghijkl} | 5.67 ^{ghijkl} | 6.12 ^{fg} | 6.84 ^e |
| pH | 4.20 ^h | I | 8.84 | 4.43 ^{efgh} | 4.48 ^{defgh} | 4.95 ^{abcdefg} | 5.23 ^{abcd} | 4.93 ^{abcdefg} | 4.96 ^{abcdefg} | 5.45 ^{abc} | 5.50 ^a |
| EC | 0.0898 ^{mnpq} | I | 13.8 | 0.0800 ^{opq} | 0.0850 ^{mnpq} | 0.0888 ^{mnpq} | 0.125 ^{jklm} | 0.0550 ^q | 0.0650 ^{pg} | 0.0650 ^{pg} | 0.115 ^{klmno} |
| OM | 1.07 ^b | I | 8.30 | 1.31 ^a | 1.37 ^a | 1.49 ^a | 1.43 ^a | 1.41 ^a | 1.36 ^a | 1.35 ^a | 1.38 ^a |
| N | 0.0830 ^f | I | 6.60 | 0.0945 ^{ef} | 0.0955 ^{def} | 0.113 ^b | 0.114 ^b | 0.0955 ^{def} | 0.0965 ^{def} | 0.0995 ^{cdef} | 0.100 ^{cde} |
| P | 3.00 ^D | I | 5.60 | 22.0 ^{uvw} | 23.0 ^{uv} | 55.0 ^{gh} | 104 ^a | 10.0 ^C | 28.0 st | 38.0 ^{qr} | 37.0 ^r |
| K | 35.0 ^z | I | 2.99 | 99.5 ^y | 150 ^{ij} | 224 ^p | 269 ^{ij} | 96.5 ^y | 166 ^t | 228 ^{op} | 255 ^{kl} |
| Ca | 135 ^q | I | 5.82 | 150 ^{mnpq} | 147 ^{nopq} | 166 ^{klm} | 260 ^a | 161 ^{klmno} | 206 ^{def} | 205 ^{def} | 230 ^{bc} |
| Mg | 24.0 ⁱ | I | 11.9 | 55.5 ^{ef} | 39.3 ^h | 73.8 ^{cd} | 94.0 ^{ab} | 36.8 ^h | 56.2 ^{ef} | 74.0 ^{cd} | 81.5 ^{bc} |
| C/N | 7.00 ⁱ | I | 4.15 | 7.75 ^{fg} | 8.66 ^{bcd} | 9.28 ^a | 7.52 ^{gh} | 8.83 ^{ab} | 8.69 ^{bc} | 8.26 ^{bcd} | 8.38 ^{bcde} |
| CEC | 2.87 ^{mno} | I | 3.17 | 2.92 ^{mno} | 2.81 ^o | 3.55 ^{cd} | 3.80 ^b | 2.81 ^o | 2.91 ^{mno} | 3.17 ^{hij} | 3.80 ^b |
| Cd in Soil | 0 ^r | I | 4.42 | 0 ^r | 0 ^r | 0 ^r | 0 ^r | 0 ^r | 0 ^r | 0 ^r | 0 ^r |
| Soybean | | | | | | | | | | | |
| Planting Date – V4 | 33.0 ^h | I | 2.69 | 31.5 ^{ij} | 31.5 ^{ij} | 30.5 ^{jk} | 29.5 ^k | 30.5 ^{jk} | 30.5 ^{jk} | 29.5 ^k | 29.5 ^k |
| Planting Date – VE | 4.00 ^{ab} | I | 22.6 | 3.25 ^{bc} | 3.25 ^{bc} | 2.25 ^c | 3.25 ^{bc} | 3.25 ^{bc} | 3.25 ^{bc} | 3.25 ^{bc} | 3.25 ^{bc} |
| VE – VC | 4.00 ^{bc} | I | 12.4 | 2.75 ^d | 2.75 ^d | 2.75 ^d | 2.75 ^d | 2.75 ^d | 3.75 ^c | 2.75 ^d | 2.75 ^d |
| VC – V1 | 5.00 ^{bc} | I | 9.08 | 3.75 ^d | 3.75 ^d | 3.75 ^d | 3.75 ^d | 4.75 ^c | 3.75 ^d | 2.75 ^e | 3.75 ^d |

Table 4.11 (Continued)

| Parameter | Control | Interact Tion | CV | Cd20.0 | | | | | | | |
|----------------|-----------------------|------------------|------|----------------------------------|-------------------------|-----------------------|-----------------------|---------------------------------------|-------------------------|------------------------|------------------------|
| | | | | 200 Liter Oil drum kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Soil | | | | | | | | | | | |
| Moisture | 5.00 ^{klmn} | I | 7.15 | 8.93 ^a | 8.02 ^{bcd} | 8.44 ^{abc} | 8.02 ^{bcd} | 6.83 ^c | 6.10 ^{fg} | 6.03 ^{fg} | 5.72 ^{ghijkl} |
| pH | 4.20 ^h | I | 8.84 | 4.42 ^{efgh} | 4.80 ^{abcdefg} | 5.43 ^{ABC} | 5.41 ^{abc} | 4.93 ^{abcdefg} | 5.10 ^{abcdefg} | 5.45 ^{abc} | 5.43 ^{ABC} |
| EC | 0.0898 ^{mnp} | I | 13.8 | 0.0975 ^{mnp} | 0.0900 ^{mnp} | 0.0975 ^{mnp} | 0.103 ^{lmno} | 0.0550 ^q | 0.110 ^{lmno} | 0.115 ^{klmno} | 0.125 ^{iklm} |
| OM | 1.07 ^b | I | 8.30 | 1.37 ^a | 1.37 ^a | 1.37 ^a | 1.47 ^a | 1.32 ^a | 1.36 ^a | 1.39 ^a | 1.44 ^a |
| N | 0.0830 ^f | I | 6.60 | 0.0985 ^{cdef} | 0.0985 ^{cdef} | 0.100 ^{cde} | 0.107 ^{bcd} | 0.0965 ^{def} | 0.0975 ^{cdef} | 0.105 ^{bcde} | 0.127 ^a |
| P | 3.00 ^D | I | 5.60 | 19.0 ^{wxyz} | 46.0 ^{mn} | 49.0 ^{klm} | 77.0 ^d | 25.0 ^u | 41.0 ^{opq} | 48.0 ^{klm} | 61.0 ^f |
| K | 35.0 ^z | I | 2.99 | 123 ^{wx} | 165 ^t | 228 ^{op} | 254 ^{lm} | 113 ^x | 207 ^q | 238 ^{no} | 306 ^h |
| Ca | 135 ^q | I | 5.82 | 157 ^{lmnop} | 165 ^{klm} | 184 ^{hij} | 205 ^{def} | 164 ^{klm} | 191 ^{fghi} | 208 ^{def} | 213 ^{de} |
| Mg | 24.0 ⁱ | I | 11.9 | 44.3 ^{fgh} | 64.0 ^{de} | 74.8 ^{cd} | 83.0 ^{bc} | 49.3 ^{fgh} | 76.8 ^{cd} | 75.8 ^{cd} | 93.5 ^{ab} |
| C/N | 7.00 ⁱ | I | 4.15 | 8.15 ^{cdef} | 8.24 ^{cdef} | 8.18 ^{cdef} | 8.44 ^{bcde} | 8.23 ^{cdef} | 8.21 ^{cdef} | 8.32 ^{bcdef} | 7.11 ^{hi} |
| CEC | 2.87 ^{mno} | I | 3.17 | 3.15 ^{hijk} | 3.36 ^{ef} | 3.42 ^{cde} | 3.86 ^b | 3.00 ^{klmn} | 3.09 ^{ijkl} | 3.13 ^{ijkl} | 3.36 ^{ef} |
| Cd in Soil | 0 ^f | I | 4.22 | 12.1 ⁿ | 9.87 ^o | 9.14 ^{op} | 8.38 ^p | 9.30 ^{op} | 9.12 ^{op} | 9.06 ^{op} | 5.90 ^q |
| Soybean | | | | | | | | | | | |
| Planting | 33.0 ^h | I | 2.69 | 35.5 ^g | 33.5 ^h | 31.5 ^{ij} | 31.5 ^{ij} | 33.5 ^h | 32.5 ^{hi} | 33.5 ^h | 33.5 ^h |
| Date – V4 | | | | | | | | | | | |
| Planting | 4.00 ^{ab} | I | 22.6 | 4.25 ^{ab} | 3.25 ^{bc} | 3.25 ^{bc} | 3.25 ^{bc} | 3.25 ^{bc} | 3.25 ^{bc} | 3.25 ^{bc} | 3.25 ^{bc} |
| Date – VE | | | | | | | | | | | |
| VE – VC | 4.00 ^{bc} | I | 12.4 | 3.75 ^c | 3.75 ^c | 2.75 ^d | 3.50 ^c | 3.75 ^c | 4.75 ^b | 3.75 ^c | 4.75 ^b |
| VC – V1 | 5.00 ^{bc} | I | 9.08 | 4.75 ^c | 3.75 ^d | 4.75 ^c | 3.75 ^d | 4.75 ^c | 4.75 ^c | 5.75 ^b | 4.75 ^c |

Table 4.11 (Continued)

| Parameter | Control | Interac Tion | CV | Cd40.0 | | | | | | | |
|----------------|-----------------------|-----------------|-------|---------------------------------|-------------------------|-------------------------|------------------------|---------------------------------------|------------------------|-------------------------|-----------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab - scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Soil | | | | | | | | | | | |
| Moisture | 5.00 ^{klmn} | I | 7.15 | 8.13 ^{bcd} | 8.69 ^{ab} | 7.82 ^{cd} | 8.04 ^{bcd} | 6.34 ^{efg} | 6.85 ^e | 6.66 ^{ef} | 5.74 ^{ghijk} |
| pH | 4.20 | I | 8.84 | 4.35 ^{gh} | 4.75 ^{abcdefg} | 4.81 ^{abcdefg} | 5.13 ^{abcdef} | 4.58 ^{defgh} | 4.70 ^{cdefgh} | 5.05 ^{abcdefg} | 5.38 ^{ABC} |
| EC | 0.0898 ^{mnp} | I | 13.8 | 0.103 ^{lmno} | 0.0900 ^{mnp} | 0.120 ^{ijklmn} | 0.115 ^{klmno} | 0.0975 ^{mnp} | 0.148 ^{hijk} | 0.153 ^{hij} | 0.258 ^c |
| OM | 1.07 ^b | I | 8.30 | 1.37 ^a | 1.46 ^a | 1.43 ^a | 1.40 ^a | 1.34 ^a | 1.40 ^a | 1.47 ^a | 1.42 ^a |
| N | 0.0830 ^f | I | 6.60 | 0.0985 ^{cdef} | 0.105 ^{cde} | 0.101 ^{cde} | 0.105 ^{bcde} | 0.0975 ^{cdef} | 0.105 ^{bcde} | 0.105 ^{bcde} | 0.109 ^{bc} |
| P | 3.00 ^D | I | 5.60 | 17.0 ^{yzA} | 43.0 ^{no} | 47.0 ^{lm} | 67.0 ^e | 15.0 ^{AB} | 40.0 ^{opqr} | 53.0 ^{hi} | 51.0 ^{ijk} |
| K | 35.0 ^z | I | 2.99 | 127 ^{vw} | 180 ^s | 251 ^{lm} | 267 ^{ij} | 136 ^v | 265 ^{jk} | 309 ^h | 429 ^{cd} |
| Ca | 135 ^q | I | 5.82 | 143 ^{pq} | 145 ^{opq} | 147 ^{nopq} | 185 ^{ghij} | 136 ^q | 159 ^{klmnop} | 176 ^{ijk} | 184 ^{ghij} |
| Mg | 24.0 ⁱ | I | 11.9 | 44.3 ^{fgh} | 64.5 ^{de} | 65.0 ^{de} | 75.8 ^{cd} | 40.8 ^{gh} | 75.3 ^{cd} | 85.3 ^{bc} | 93.3 ^{ab} |
| C/N | 7.00 ⁱ | I | 4.15 | 8.12 ^{cdef} | 8.32 ^{bcdef} | 8.36 ^{bcde} | 8.30 ^{bcdef} | 8.44 ^{bcde} | 8.37 ^{bcde} | 8.45 ^{bcde} | 8.42 ^{bcde} |
| CEC | 2.87 ^{mno} | I | 3.17 | 2.98 ^{lmn} | 3.13 ^{ijkl} | 3.13 ^{ijkl} | 4.43 ^a | 2.85 ^{no} | 3.09 ^{ijkl} | 3.13 ^{ijkl} | 3.38 ^{ef} |
| Cd in Soil | 0 ^r | I | 4.22 | 32.2 ^h | 20.6 ^l | 14.7 ^m | 14.6 ^m | 21.1 ^l | 20.9 ^l | 20.1 ^l | 11.6 ⁿ |
| Soybean | | | | | | | | | | | |
| Planting | 33.0 ^h | I | 2.69 | 39.5 ^{de} | 39.5 ^{de} | 38.5 ^{ef} | 37.5 ^f | 41.5 ^{bc} | 41.5 ^{bc} | 37.5 ^f | 37.5 ^f |
| Date – V4 | | | | | | | | | | | |
| Planting | 4.00 ^{ab} | I | 22.6 | 5.25 ^a | 4.25 ^{ab} | 4.25 ^{ab} | 4.25 ^{ab} | 4.25 ^{ab} | 5.25 ^a | 4.25 ^{ab} | 5.25 ^a |
| Date – VE | | | | | | | | | | | |
| VE – VC | 4.00 ^{bc} | I | 12.44 | 4.75 ^b | 3.75 ^c | 4.75 ^b | 3.75 ^c | 5.75 ^a | 4.75 ^b | 4.75 ^b | 3.75 ^c |
| VC – V1 | 5.00 ^{bc} | I | 9.08 | 5.75 ^b | 6.75 ^a | 5.75 ^b | 5.75 ^b | 5.75 ^b | 5.75 ^b | 5.75 ^b | 4.75 ^c |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd60.0 | | | | | | | |
|----------------|-----------------------|-------------|------|---------------------------------|------------------------|-------------------------|-----------------------|---------------------------------------|-------------------------|-----------------------|------------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Soil | | | | | | | | | | | |
| Moisture | 5.00 ^{klmn} | I | 7.15 | 4.02 ^o | 4.30 ^o | 5.70 ^{ghijkl} | 7.64 ^d | 5.15 ^{hijklmn} | 5.18 ^{hijklmn} | 5.10 ^{JLMN} | 5.14 ^{ijklmn} |
| pH | 4.20 ^h | I | 8.84 | 4.40 ^{fgh} | 4.48 ^{defgh} | 4.96 ^{abcdefg} | 5.19 ^{ABCD} | 5.00 ^{abcdefg} | 4.80 ^{abcdefg} | 5.37 ^{ABC} | 5.48 ^{ab} |
| EC | 0.0898 ^{mnp} | I | 13.8 | 0.0975 ^{mnp} | 0.103 ^{lmno} | 0.213 ^{ef} | 0.235 ^{cde} | 0.165 ^{hi} | 0.220 ^{def} | 0.330 ^b | 0.445 ^a |
| OM | 1.07 ^b | I | 8.30 | 1.35 ^a | 1.47 ^a | 1.49 ^a | 1.42 ^a | 1.30 ^a | 1.40 ^a | 1.37 ^a | 1.38 ^a |
| N | 0.0830 ^f | I | 6.60 | 0.0965 ^{def} | 0.0985 ^{cdef} | 0.101 ^{cde} | 0.109 ^{bc} | 0.0995 ^{cdef} | 0.101 ^{cde} | 0.105 ^{bcde} | 0.105 ^{bcde} |
| P | 3.00 ^D | I | 5.60 | 16.0 ^{zAB} | 21.0 ^{vwx} | 52.0 ^{hij} | 98.0 ^b | 13.3 ^B | 30.0 ^s | 88.0 ^c | 37.0 ^r |
| K | 35.0 ^z | I | 2.99 | 123 ^{wx} | 171 st | 335 ^g | 399 ^e | 153 ^{ij} | 299 ^h | 423 ^d | 436 ^c |
| Ca | 135 ^q | I | 5.82 | 183 ^{hij} | 158 ^{lmnop} | 166 ^{klm} | 230 ^{bc} | 139 ^q | 200 ^{efgh} | 221 ^{cd} | 239 ^b |
| Mg | 24.0 ⁱ | I | 11.9 | 43.5 ^{fgh} | 46.3 ^{fgh} | 82.3 ^{bc} | 95.0 ^{ab} | 64.5 ^{de} | 76.5 ^{cd} | 94.0 ^{ab} | 101 ^a |
| C/N | 7.00 ⁱ | I | 4.15 | 8.29 ^{bcdef} | 8.33 ^{bcdef} | 8.54 ^{bcde} | 8.28 ^{bcdef} | 8.03 ^{ef} | 8.31 ^{bcdef} | 8.21 ^{cdef} | 8.33 ^{bcdef} |
| CEC | 2.87 ^{mno} | I | 3.17 | 2.98 ^{lmn} | 3.21 ^{fghij} | 3.40 ^{de} | 3.94 ^b | 3.13 ^{ijkl} | 3.16 ^{hijk} | 3.30 ^{efghi} | 3.40 ^{de} |
| Cd in Soil | 0 ^f | I | 4.22 | 29.0 ⁱ | 28.2 ⁱ | 26.2 ^j | 23.2 ^k | 51.9 ^a | 35.9 ^{fg} | 37.0 ^{ef} | 25.8 ^j |
| Soybean | | | | | | | | | | | |
| Planting | 33.0 ^h | I | 2.69 | 41.5 ^{bc} | 40.5 ^{cd} | 38.5 ^{ef} | 37.5 ^f | 42.5 ^{ab} | 42.5 ^{ab} | 38.5 ^{ef} | 37.5 ^f |
| Date – V4 | | | | | | | | | | | |
| Planting | 4.00 ^{ab} | I | 22.6 | 5.25 ^a | 5.25 ^a | 4.25 ^{ab} | 4.25 ^{ab} | 5.25 ^a | 5.25 ^a | 4.25 ^{ab} | 4.25 ^{ab} |
| Date – VE | | | | | | | | | | | |
| VE – VC | 4.00 ^{bc} | I | 12.4 | 4.75 ^b | 4.75 ^b | 4.75 ^b | 3.75 ^c | 4.75 ^b | 5.75 ^a | 3.75 ^c | 3.75 ^c |
| VC – V1 | 5.00 ^{bc} | I | 9.08 | 6.75 ^a | 6.75 ^a | 6.75 ^a | 6.75 ^a | 6.75 ^a | 6.75 ^a | 6.75 ^a | 6.75 ^a |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd80.0 | | | | | | | |
|----------------|-----------------------|-------------|------|---------------------------------|-----------------------|-------------------------|-------------------------|---------------------------------------|------------------------|------------------------|------------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Soil | | | | | | | | | | | |
| Moisture | 5.00 ^{klmn} | I | 7.15 | 4.97 ^{lmn} | 5.01 ^{klmn} | 5.78 ^{ghij} | 4.45 ^{no} | 4.98 ^{lmn} | 5.65 ^{ghijkl} | 5.84 ^{ghi} | 5.26 ^{hijklm} |
| pH | 4.20 ^h | I | 8.84 | 4.57 ^{defgh} | 4.48 ^{defgh} | 5.10 ^{abcdefg} | 4.75 ^{abcdefg} | 4.73 ^{bcdefgh} | 5.18 ^{abcde} | 5.15 ^{abcdef} | 5.38 ^{ABC} |
| EC | 0.0898 ^{mnp} | I | 13.8 | 0.228 ^{cdef} | 0.248 ^{cd} | 0.313 ^b | 0.320 ^b | 0.135 ^{ijkl} | 0.180 ^{gh} | 0.1975 ^{fg} | 0.318 ^b |
| OM | 1.07 ^b | I | 8.30 | 1.39 ^a | 1.41 ^a | 1.36 ^a | 1.35 ^a | 1.30 ^a | 1.41 ^a | 1.45 ^a | 1.32 ^a |
| N | 0.0830 ^f | I | 6.60 | 0.101 ^{cde} | 0.101 ^{cde} | 0.102 ^{cde} | 0.105 ^{bcde} | 0.0975 ^{cdef} | 0.0985 ^{cdef} | 0.0985 ^{cdef} | 0.109 ^{bc} |
| P | 3.00 ^D | I | 5.50 | 18.0 ^{xyza} | 39.0 ^{pqr} | 39.0 ^{pqr} | 47.0 ^{lm} | 20.0 ^{vwxy} | 39.0 ^{pqr} | 50.0 ^{ijkl} | 57.0 ^g |
| K | 35.0 ^r | I | 2.99 | 194 ^r | 253 ^{lm} | 368 ^f | 464 ^b | 146 ^{ij} | 243 ^{mn} | 277 ⁱ | 554 ^a |
| Ca | 135 ^q | I | 5.82 | 163 ^{klmn} | 171 ^{ijkl} | 192 ^{fghi} | 198 ^{fgh} | 202 ^{efg} | 209 ^{def} | 196 ^{efgh} | 208 ^{def} |
| Mg | 24.0 ⁱ | I | 11.9 | 54.3 ^{efg} | 65.0 ^{de} | 82.3 ^{bc} | 106 ^a | 47.0 ^{fgh} | 75.5 ^{cd} | 76.3 ^{cd} | 95.3 ^{ab} |
| C/N | 7.00 ⁱ | I | 4.15 | 8.36 ^{bcde} | 8.37 ^{bcde} | 8.18 ^{cdef} | 8.28 ^{bcdef} | 8.21 ^{cdef} | 8.24 ^{cdef} | 8.08 ^{def} | 8.29 ^{bcdef} |
| CEC | 2.87 ^{mno} | I | 3.17 | 3.13 ^{ijkl} | 3.19 ^{ghij} | 3.32 ^{efgh} | 3.57 ^c | 3.29 ^{efghi} | 3.30 ^{efgh} | 3.32 ^{efgh} | 3.34 ^{efg} |
| Cd in Soil | 0 ^r | I | 4.22 | 46.6 ^b | 40.9 ^d | 37.8 ^e | 35.0 ^g | 52.6 ^a | 42.2 ^c | 43.9 ^c | 31.4 ^h |
| Soybean | | | | | | | | | | | |
| Planting | 33.0 ^h | I | 2.69 | 41.5 ^{bc} | 42.5 ^{ab} | 39.5 ^{de} | 38.5 ^{ef} | 42.5 ^{ab} | 43.5 ^a | 41.5 ^{bc} | 42.5 ^{ab} |
| Date – V4 | | | | | | | | | | | |
| Planting | 4.00 ^{ab} | I | 22.6 | 5.25 ^a | 5.25 ^a | 5.25 ^a | 4.25 ^{ab} | 5.25 ^a | 5.25 ^a | 5.25 ^a | 5.25 ^a |
| Date – VE | | | | | | | | | | | |
| VE – VC | 4.00 ^{bc} | I | 12.4 | 4.75 ^b | 4.75 ^b | 4.75 ^b | 4.75 ^b | 4.75 ^b | 4.75 ^b | 5.75 ^a | 4.75 ^b |
| VC – V1 | 5.00 ^{bc} | I | 9.08 | 5.75 ^b | 6.75 ^a | 5.75 ^b | 5.75 ^b | 6.75 ^a | 6.75 ^a | 6.75 ^a | 6.75 ^a |

Table 4.11 (Continued)

| Parameter | Control | Interac tion | CV | Cd0 | | | | | | | |
|---------------------------|-------------------------|-----------------|-------|---------------------------------|-----------------------|-----------------------|-----------------------|---------------------------------------|-----------------------|-----------------------|-----------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| V1 – V2 | 6.00 ^{bc} | I | 9.20 | 5.50 ^c | 5.50 ^c | 6.50 ^b | 5.50 ^c | 5.50 ^c | 5.50 ^c | 6.50 ^b | 6.50 ^b |
| V2 – V3 | 6.00 ^e | I | 6.77 | 6.25 ^{de} | 6.25 ^{de} | 6.25 ^{de} | 6.25 ^{de} | 6.00 ^e | 6.00 ^e | 6.75 ^{cde} | 6.00 ^e |
| V3 – V4 | 8.00 ^{bc} | I | 6.82 | 7.50 ^c | 7.50 ^c | 6.50 ^{de} | 6.50 ^{de} | 7.25 ^{cd} | 7.25 ^{cd} | 6.00 ^e | 6.00 ^e |
| Planting Date – R1 | 39.0 ⁱ | I | 1.46 | 35.5 ^l | 35.5 ^l | 35.5 ^l | 35.5 ^l | 35.5 ^l | 35.5 ^l | 35.5 ^l | 35.5 ^l |
| R1 – R2 | 2.00 ^{cd} | I | 22.4 | 1.75 ^d | 1.75 ^d | 1.75 ^d | 1.75 ^d | 1.75 ^d | 2.75 ^c | 1.75 ^d | 1.75 ^d |
| R2 – R3 | 3.00 ^a | I | 19.0 | 2.50 ^{ab} | 2.50 ^{ab} | 2.50 ^{ab} | 2.50 ^{ab} | 2.50 ^{ab} | 2.25 ^{ab} | 2.50 ^{ab} | 2.50 ^{ab} |
| R3 – R4 | 2.00 ^a | I | 24.1 | 2.13 ^a | 2.50 ^a | 2.25 ^a | 2.13 ^a | 2.50 ^a | 2.25 ^a | 2.00 ^a | 2.00 ^a |
| R4 – R5 | 3.00 ^a | I | 24.2 | 1.50 ^d | 1.50 ^d | 1.75 ^{cd} | 1.50 ^d | 2.50 ^{abc} | 2.25 ^{abcd} | 2.25 ^{abcd} | 2.25 ^{abcd} |
| R5 – R6 | 10.8 ^{abc} | I | 11.2 | 11.5 ^{abc} | 11.8 ^{abc} | 11.8 ^{abc} | 11.5 ^{abc} | 11.5 ^{abc} | 11.5 ^{abc} | 11.5 ^{abc} | 11.5 ^{abc} |
| R6 – R7 | 10.5 ^{cde} | I | 11.1 | 11.0 ^{bcde} | 11.3 ^{abcde} | 11.3 ^{abcde} | 11.3 ^{abcde} | 10.8 ^{cde} | 11.3 ^{abcde} | 11.3 ^{abcde} | 11.3 ^{abcde} |
| R7 – R8 | 21.0 ^{hi} | I | 3.22 | 19.8 ^{jk} | 19.8 ^{jk} | 19.8 ^{jk} | 19.8 ^{jk} | 20.5 ^{ij} | 19.8 ^{jk} | 15.8 ^l | 15.0 ^l |
| Planting Date – R8 | 90.0 ^k | I | 0.632 | 89.8 ^k | 89.8 ^k | 88.7 ^l | 88.8 ^l | 89.8 ^k | 88.8 ^l | 84.3 ⁿ | 85.3 ^m |
| Stem Weight | 0.305 ^{ijklmn} | I | 12.4 | 0.444 ^{cdefg} | 0.679 ^b | 0.730 ^b | 0.691 ^b | 0.684 ^b | 0.702 ^b | 0.924 ^a | 0.648 ^b |
| Pod Weight | 1.00 ^{jk} | I | 8.77 | 1.37 ^{hi} | 2.71 ^d | 2.639 ^d | 2.74 ^d | 2.89 ^c | 3.12 ^b | 3.45 ^a | 2.67 ^d |
| Height | 30.6 ^l | I | 0.733 | 41.3 ^c | 39.8 ^f | 43.3 ^a | 37.4 ^g | 40.1 ^e | 40.8 ^d | 41.6 ^b | 36.2 ^h |
| Number of Node | 5.05 ^h | I | 1.66 | 5.32 ^g | 5.71 ^e | 6.55 ^b | 5.97 ^d | 6.19 ^c | 5.99 ^d | 6.79 ^a | 6.09 ^{cd} |
| Numbe of Pod | 3.50 ^k | I | 3.15 | 4.89 ^h | 7.89 ^d | 7.74 ^{de} | 7.68 ^e | 8.44 ^c | 8.62 ^b | 9.27 ^a | 8.34 ^c |
| Number of Seed per Pod | 1.26 ⁿ | I | 6.07 | 2.02 ^{cde} | 2.05 ^{cde} | 2.16 ^{bc} | 2.13 ^{bc} | 2.13 ^{bc} | 2.15 ^{bc} | 2.60 ^a | 2.10 ^{bcd} |

Table 4.11 (Continued)

| Parameter | Control | Interac tion | CV | Cd20.0 | | | | | | | |
|------------------------|-------------------------|-----------------|-------|---------------------------------|--------------------------|-----------------------|-----------------------|---------------------------------------|---------------------|----------------------|-----------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab - scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| V1 – V2 | 6.00 ^{bc} | I | 9.20 | 5.50 ^c | 6.50 ^b | 5.50 ^c | 5.50 ^c | 5.50 ^c | 5.50 ^c | 5.50 ^c | 5.50 ^c |
| V2 – V3 | 6.00 ^e | I | 6.77 | 7.25 ^{bc} | 6.25 ^{de} | 6.00 ^e | 6.00 ^e | 6.75 ^{cde} | 7.50 ^b | 6.75 ^{cde} | 6.75 ^{cde} |
| V3 – V4 | 8.00 ^{bc} | I | 6.82 | 7.50 ^c | 7.50 ^c | 7.50 ^c | 7.50 ^c | 7.50 ^c | 7.50 ^c | 7.50 ^c | 8.50 ^b |
| Planting Date – R1 | 39.0 ⁱ | I | 1.46 | 40.5 ^h | 37.5 ^j | 36.5 ^k | 36.5 ^k | 37.5 ^j | 37.5 ^j | 38.5 ⁱ | 38.5 ⁱ |
| R1 – R2 | 2.00 ^{cd} | I | 22.4 | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 4.50 ^a | 3.75 ^b |
| R2 – R3 | 3.00 ^a | I | 19.0 | 2.00 ^b | 2.75 ^{ab} | 2.75 ^{ab} | 2.50 ^{ab} | 2.75 ^{ab} | 2.50 ^{ab} | 2.75 ^{ab} | 2.75 ^{ab} |
| R3 – R4 | 2.00 ^a | I | 24.1 | 2.25 ^a | 2.00 ^a | 2.00 ^a | 2.25 ^a | 2.75 ^a | 2.75 ^a | 2.25 ^a | 2.75 ^a |
| R4 – R5 | 3.00 ^a | I | 24.2 | 1.75 ^{cd} | 2.00 ^{bcd} | 1.75 ^{cd} | 1.75 ^{cd} | 2.50 ^{abc} | 2.75 ^{ab} | 2.25 ^{abcd} | 2.50 ^{abc} |
| R5 – R6 | 10.8 ^{abc} | I | 11.2 | 12.5 ^a | 12.0 ^{abc} | 12.2 ^{ab} | 12.2 ^{ab} | 10.3 ^{bc} | 12.7 ^a | 10.0 ^c | 12.7 ^a |
| R6 – R7 | 10.5 ^{cde} | I | 11.1 | 12.5 ^{abc} | 12.3 ^{abcd} | 12.0 ^{abcde} | 12.0 ^{abcd} | 10.3 ^{de} | 12.7 ^{abc} | 10.0 ^e | 12.7 ^{abc} |
| R7 – R8 | 21.0 ^{hi} | I | 3.22 | 20.8 ^{hi} | 21.7 ^{gh} | 21.7 ^{gh} | 21.2 ^{hi} | 24.5 ^{cd} | 23.2 ^{ef} | 19.7 ^{jk} | 19.2 ^k |
| Planting Date – R8 | 90.0 ^k | I | 0.632 | 95.7 ^h | 90.0 ^k | 90.0 ^k | 90.0 ^k | 94.7 ⁱ | 95.7 ^h | 93.7 ^j | 93.7 ^j |
| Stem Weight | 0.305 ^{ijklmn} | I | 12.4 | 0.232 ^{nop} | 0.350 ^{ghijklm} | 0.498 ^{cd} | 0.455 ^{cdef} | 0.301 ^{ijklmn} | 0.517 ^{cd} | 0.530 ^c | 0.478 ^{ocde} |
| Pod Weight | 1.00 ^{jk} | I | 8.77 | 0.398 ^{op} | 1.27 ⁱ | 1.76 ^e | 1.44 ^{gh} | 0.713 ^{lm} | 1.58 ^{fg} | 1.39 ^{hi} | 1.66 ^{ef} |
| Height | 30.6 ^l | I | 0.733 | 30.2 ^m | 31.7 ^k | 31.8 ^k | 30.4 ^{lm} | 27.2 ^o | 30.2 ^m | 33.0 ⁱ | 27.8 ⁿ |
| Number of Node | 5.05 ^h | I | 1.66 | 5.08 ^h | 5.38 ^g | 5.79 ^e | 5.28 ^g | 6.08 ^{cd} | 5.68 ^{ef} | 5.71 ^e | 6.07 ^{cd} |
| Number of Pod | 3.50 ^k | I | 3.15 | 2.00 ^{rs} | 1.94 ^{rs} | 4.10 ⁱ | 3.82 ^j | 3.10 ^l | 3.49 ^k | 5.85 ^f | 5.20 ^g |
| Number of Seed per Pod | 1.26 ⁿ | I | 6.07 | 1.89 ^{efgh} | 1.81 ^{fghi} | 1.89 ^{efgh} | 1.96 ^{def} | 2.05 ^{cde} | 2.05 ^{cde} | 2.26 ^b | 2.08 ^{cd} |

Table 4.11 (Continued)

| Parameter | Control | Interac tion | CV | Cd40.0 | | | | | | | |
|---------------------------|-------------------------|-----------------|-------|---------------------------------|-------------------------|-------------------------|-----------------------|---------------------------------------|-------------------------|-----------------------|--------------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab - scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| V1 – V2 | 6.00 ^{bc} | I | 9.20 | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 5.50 ^c | 5.50 ^c |
| V2 – V3 | 6.00 ^e | I | 6.77 | 7.50 ^b | 7.50 ^b | 7.50 ^b | 7.50 ^b | 7.75 ^b | 7.75 ^b | 6.75 ^{cde} | 6.75 ^{cde} |
| V3 – V4 | 8.00 ^{bc} | I | 6.82 | 8.50 ^b | 8.50 ^b | 8.50 ^b | 8.75 ^{ab} | 9.50 ^a | 9.50 ^a | 7.50 ^c | 8.50 ^b |
| Planting Date – R1 | 39.0 ⁱ | I | 1.46 | 48.5 ^a | 48.5 ^a | 43.5 ^e | 43.5 ^e | 45.5 ^c | 44.5 ^d | 41.5 ^g | 41.5 ^g |
| R1 – R2 | 2.00 ^{cd} | I | 22.5 | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c |
| R2 – R3 | 3.00 ^a | I | 19.1 | 2.50 ^{ab} | 2.50 ^{ab} | 2.5 ^{ab} | 2.50 ^{ab} | 2.75 ^{ab} | 2.75 ^{ab} | 2.75 ^{ab} | 2.50 ^{ab} |
| R3 – R4 | 2.00 ^a | I | 24.2 | 2.25 ^a | 2.00 ^a | 2.25 ^a | 2.25 ^a | 2.75 ^a | 2.50 ^a | 2.75 ^a | 2.75 ^a |
| R4 – R5 | 3.00 ^a | I | 24.2 | 1.75 ^{cd} | 2.25 ^{abcd} | 2.75 ^{ab} | 2.75 ^{ab} | 3.00 ^a | 2.50 ^{abc} | 2.50 ^{abc} | 2.50 ^{abc} |
| R5 – R6 | 10.7 | I | 11.2 | 12.2 ^{ab} | 12.5 ^a | 12.7 ^a | 12.7 ^a | 13.0 ^a | 12.7 ^a | 12.7 ^a | 12.7 ^a |
| R6 – R7 | 10.5 ^{cde} | I | 11.1 | 12.5 ^{abc} | 12.5 ^{abc} | 12.7 ^{abc} | 12.7 ^{abc} | 13.0 ^{ab} | 12.7 ^{abc} | 12.7 ^{abc} | 12.7 ^{abc} |
| R7 – R8 | 21.0 ^{hi} | I | 3.22 | 24.7 ^{cd} | 23.2 ^{ef} | 23.2 ^{ef} | 22.5 ^{fg} | 24.2 ^d | 23.2 ^{ef} | 23.2 ^{ef} | 23.2 ^{ef} |
| Planting Date – R8 | 90.0 ^k | I | 0.632 | 97.7 ^f | 95.7 ^h | 95.7 ^h | 95.7 ^h | 98.7 ^{de} | 96.7 ^g | 94.7 ⁱ | 94.7 ⁱ |
| Stem Weight | 0.305 ^{ijklmn} | I | 12.4 | 0.168 ^p | 0.300 ^{ijklmn} | 0.422 ^{defghi} | 0.277 ^{lmno} | 0.253 ^{mnop} | 0.422 ^{defghi} | 0.470 ^{cdef} | 0.383 ^{efghijk} |
| Pod Weight | 1.00 ^k | I | 8.77 | 0.414 ^{op} | 0.585 ^{mn} | 0.970 ^k | 0.578 ^{mn} | 0.738 ^l | 0.970 ^k | 1.47 ^{gh} | 1.13 ^j |
| Height | 30.6 ^l | I | 0.733 | 19.2 ^a | 23.9 ^s | 19.6 ^z | 25.3 ^f | 24.0 ^s | 27.2 ^o | 32.4 ^j | 21.9 ^x |
| Number of Node | 5.05 ^h | I | 1.66 | 4.58 ⁱ | 4.50 ^{ij} | 5.11 ^h | 5.08 ^h | 5.08 ^h | 5.38 ^g | 5.08 ^h | 5.58 ^f |
| Number of Pod | 3.50 ^k | I | 3.15 | 1.60 ^t | 2.10 ^{qr} | 2.77 ^m | 2.60 ⁿ | 2.43 ^o | 3.10 ^l | 4.05 ⁱ | 3.43 ^k |
| Number of Seed per Pod | 1.26 ⁿ | I | 6.07 | 1.60 ^{jk} | 1.43 ^{lm} | 1.93 ^{defg} | 1.60 ^{ik} | 1.60 ^{jk} | 1.85 ^{fghi} | 2.10 ^{bcd} | 2.10 ^{bcd} |

Table 4.11 (Continued)

| Parameter | Control | Interac tion | CV | Cd60.0 | | | | | | | |
|---------------------------|-------------------------|-----------------|-------|---------------------------------|-------------------------|-------------------------|-----------------------|---------------------------------------|-------------------------|------------------------|--------------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| V1 – V2 | 6.00 ^{bc} | I | 9.20 | 7.50 ^a | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b |
| V2 – V3 | 6.00 ^c | I | 6.77 | 7.50 ^b | 6.75 ^{cde} | 6.75 ^{cde} | 6.75 ^{cde} | 8.50 ^a | 6.75 ^{cde} | 6.75 ^{cde} | 6.00 ^c |
| V3 – V4 | 8.00 ^{bc} | I | 6.82 | 7.50 ^c | 8.50 ^b | 7.50 ^c | 7.50 ^c | 8.50 ^b | 9.50 ^a | 8.50 ^b | 8.50 ^b |
| Planting Date – R1 | 39.0 ⁱ | I | 1.46 | Dead | 44.5 ^d | 42.5 ^f | 42.5 ^f | 45.5 ^c | 45.5 ^c | 42.5 ^f | 41.5 ^g |
| R1 – R2 | 2.00 ^{cd} | I | 22.4 | Dead | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c |
| R2 – R3 | 3.00 ^a | I | 19.0 | Dead | 2.75 ^{ab} | 2.75 ^{ab} | 2.50 ^{ab} | 2.75 ^{ab} | 2.50 ^{ab} | 3.00 ^a | 3.00 ^a |
| R3 – R4 | 2.00 ^a | I | 24.1 | Dead | 2.75 ^a | 2.75 ^a | 2.75 ^a | 2.25 ^a | 2.25 ^a | 2.75 ^a | 2.75 ^a |
| R4 – R5 | 3.00 ^a | I | 24.2 | Dead | 2.25 ^{abcd} | 2.75 ^{ab} | 2.50 ^{abc} | 2.25 ^{abcd} | 2.50 ^{abc} | 2.75 ^{ab} | 3.00 ^a |
| R5 – R6 | 10.7 ^{bc} | I | 12.2 | Dead | 12.5 ^a | 13.2 ^a | 13.0 ^a | 13.0 ^a | 12.5 ^a | 12.7 ^a | 13.0 ^a |
| R6 – R7 | 10.5 ^{cde} | I | 11.1 | Dead | 12.5 ^{abc} | 13.2 ^a | 13.0 ^{ab} | 13.0 ^{ab} | 12.5 ^{abc} | 12.7 ^{abc} | 13.0 ^{ab} |
| R7 – R8 | 21.0 ^{hi} | I | 3.22 | Dead | 25.7 ^b | 24.7 ^{cd} | 23.2 ^{ef} | 24.7 ^{cd} | 22.7 ^{ef} | 23.7 ^{de} | 24.7 ^{cd} |
| Planting Date – R8 | 90.0 ^k | I | 0.632 | Dead | 101 ^c | 99.5 ^d | 97.7 ^f | 101 ^c | 98.7 ^{de} | 96.7 ^g | 96.7 ^g |
| Stem Weight | 0.305 ^{ijklmn} | I | 12.4 | Dead | 0.297 ^{ijklmn} | 0.326 ^{ijklmn} | 0.289 ^{klmn} | 0.297 ^{ijklmn} | 0.339 ^{hijklm} | 0.426 ^{defgh} | 0.373 ^{fghijkl} |
| Pod Weight | 1.00 ^{jk} | I | 8.78 | Dead | 0.477 ^{no} | 0.339 ^{op} | 0.349 ^{op} | 0.356 ^{op} | 0.480 ^{no} | 0.833 ^l | 0.704 ^{lm} |
| Height | 30.6 ^l | I | 0.733 | Dead | 18.3 ^B | 24.1 ^s | 22.7 ^v | 20.4 ^y | 22.7 ^v | 26.8 ^p | 22.2 ^w |
| Number of Node | 5.05 ^h | I | 1.67 | Dead | 4.50 ^{ij} | 4.39 ^j | 5.08 ^h | 5.08 ^h | 6.08 ^{cd} | 5.08 ^h | 6.08 ^{cd} |
| Number of Pod | 3.50 ^k | I | 3.15 | Dead | 1.21 ^u | 2.10 ^{qr} | 1.85 ^s | 2.20 ^{pq} | 3.10 ^l | 3.10 ^l | 2.10 ^{qr} |
| Number of Seed per Pod | 1.26 ⁿ | I | 6.07 | Dead | 1.38 ^{mn} | 1.43 ^{lm} | 1.35 ^{mn} | 1.41 ^{mn} | 1.70 ^{ij} | 2.03 ^{cde} | 2.10 ^{bed} |

Table 4.11 (Continued)

| Parameter | Control | Interac tion | CV | Cd80.0 | | | | | | | |
|---------------------------|-------------------------|-----------------|-------|---------------------------------|-------------------|---------------------|----------------------|---------------------------------------|-------------------------|----------------------|----------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5 | B10 | B15 | B20 | B5 | B10 | B15 | B20 |
| V1 – V2 | 6.00 ^{bc} | I | 9.20 | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 6.50 ^b | 7.50 ^a |
| V2 – V3 | 6.00 ^c | I | 6.77 | 7.75 ^b | 7.75 ^b | 6.75 ^{cde} | 6.75 ^{cde} | 7.50 ^b | 8.50 ^a | 7.00 ^{bcd} | 7.50 ^b |
| V3 – V4 | 8.00 ^{bc} | I | 6.82 | 9.50 ^a | 9.50 ^a | 8.50 ^b | 8.50 ^b | 9.50 ^a | 9.50 ^a | 8.50 ^b | 8.50 ^b |
| Planting Date – R1 | 39.0 ⁱ | I | 1.46 | Dead | Dead | Dead | 43.5 ^e | 46.5 ^b | 45.5 ^c | 44.5 ^d | 44.5 ^d |
| R1 – R2 | 2.00 | I | 22.4 | Dead | Dead | Dead | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c | 2.75 ^c |
| R2 – R3 | 3.00 ^a | I | 19.0 | Dead | Dead | Dead | 2.75 ^{ab} | 3.00 ^a | 3.00 ^a | 3.00 ^a | 3.00 ^a |
| R3 – R4 | 2.00 ^a | I | 24.1 | Dead | Dead | Dead | 2.50 ^a | 2.25 ^a | 2.50 ^a | 2.75 ^a | 2.75 ^a |
| R4 – R5 | 3.00 ^a | I | 24.2 | Dead | Dead | Dead | 2.50 ^{abc} | 2.50 ^{abc} | 2.75 ^{ab} | 2.75 ^{ab} | 2.50 ^{abc} |
| R5 – R6 | 10.7 ^{abc} | I | 11.2 | Dead | Dead | Dead | 12.7 ^a | 12.5 ^a | 12.7 ^a | 12.7 ^a | 12.7 ^a |
| R6 – R7 | 10.5 ^{cde} | I | 11.1 | Dead | Dead | Dead | 12.7 ^{abc} | 12.5 ^{abc} | 12.7 ^{abc} | 12.7 ^{abc} | 12.7 ^{abc} |
| R7 – R8 | 21.0 ^{hi} | I | 3.22 | Dead | Dead | Dead | 24.2 ^d | 27.2 ^a | 25.5 ^{bc} | 23.7 ^{de} | 24.2 ^d |
| Planting Date – R8 | 90.0 ^k | I | 0.632 | Dead | Dead | Dead | 99.0 ^{de} | 105 ^a | 104 ^b | 98.5 ^{ef} | 99.0 ^{de} |
| Stem Weight | 0.305 ^{ijklmn} | I | 12.4 | Dead | Dead | Dead | 0.266 ^{mno} | 0.170 ^p | 0.297 ^{ijklmn} | 0.267 ^{mno} | 0.187 ^{op} |
| Pod Weight | 1.00 ^k | I | 8.77 | Dead | Dead | Dead | 0.297 ^{pq} | 0.174 ^q | 0.422 ^{op} | 0.759 ^l | 0.588 ^{mn} |
| Height | 30.6 ^l | I | 0.733 | Dead | Dead | Dead | 23.5 ^t | 19.2 ^A | 22.9 ^u | 26.7 ^p | 26.2 ^q |
| Number of Node | 5.05 ^h | I | 1.66 | Dead | Dead | Dead | 5.08 ^h | 5.08 ^b | 6.08 ^{cd} | 5.08 ^h | 4.58 ⁱ |
| Number of Pod | 3.50 ^k | I | 3.15 | Dead | Dead | Dead | 1.10 ^u | 1.10 ^u | 2.35 ^{op} | 3.06 ^l | 1.14 ^u |
| Number of Seed per Pod | 1.26 ⁿ | I | 6.07 | Dead | Dead | Dead | 1.10 ^o | 1.50 ^{klm} | 1.57 ^{kl} | 1.77 ^{hi} | 1.83 ^{fghi} |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd0 | | | | | | | |
|-----------------|-------------------------|-------------|-------|---------------------------------|----------------------|----------------------|-----------------------|---------------------------------------|------------------------|------------------------|------------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Dry Weight | 10.6 ^{hij} | I | 8.75 | 16.1 ^{bc} | 18.89 ^a | 19.1 ^a | 18.6 ^a | 18.6 ^a | 18.6 ^a | 18.42 ^a | 17.45 ^{ab} |
| 100 Seeds | | | | | | | | | | | |
| Product per Pot | 2.08 ^p | I | 15.2 | 5.74 ^{ef} | 10.3 ^b | 11.4 ^a | 8.65 ^c | 7.50 ^d | 8.70 ^c | 10.3 ^b | 8.78 ^c |
| Protein | 35.1 ^o | I | 0.665 | 36.6 ^{bcd} | 36.1 ^{ghij} | 36.0 ^{hij} | 36.3 ^{efghi} | 36.2 ^{ghij} | 35.6 ^{klmn} | 36.1 ^{hij} | 36.6 ^{bcd} |
| Lipid | 18.4 ^o | I | 0.532 | 19.3 ^{klm} | 19.5 ^{gh} | 19.7 ^f | 20.1 ^{bc} | 19.1 ⁿ | 19.6 ^{fg} | 19.9 ^{bcd} | 19.9 ^{de} |
| Leaf Area R1 | 6.69 ^{wx} | I | 1.58 | 13.1 ⁱ | 11.3 ^l | 31.9 ^e | 43.9 ^a | 20.7 ^f | 22.6 ^e | 34.7 ^b | 24.1 ^d |
| Leaf Area R3 | 11.8 ⁿ | I | 1.11 | 28.8 ^g | 30.8 ^f | 32.4 ^e | 45.8 ^a | 30.8 ^f | 33.4 ^d | 37.5 ^c | 44.5 ^b |
| Leaf Area R5 | 16.2 ^l | I | 0.850 | 46.7 ^e | 59.9 ^c | 66.2 ^b | 70.4 ^a | 47.9 ^d | 40.4 ^g | 40.5 ^g | 44.1 ^f |
| Leaf Area R7 | 18.4 ^m | I | 0.695 | 46.5 ^h | 60.2 ^f | 61.4 ^e | 72.4 ^c | 46.8 ^g | 63.7 ^d | 96.2 ^a | 84.8 ^b |
| Pod Weight R3 | 0.0242 ^{ijkl} | I | 30.4 | 0.115 ^b | 0.097 ^{bc} | 0.0679 ^{de} | 0.102 ^{bc} | 0.502 ^a | 0.0530 ^{efgh} | 0.0579 ^{defg} | 0.0596 ^{def} |
| Pod Weight R5 | 0.0608 ^{ghij} | I | 14.9 | 0.158 ^b | 0.120 ^c | 0.104 ^d | 0.0830 ^{ef} | 0.894 ^a | 0.0749 ^{efgh} | 0.0905 ^{de} | 0.0910 ^{de} |
| Pod Weight R6 | 1.08 ^{jk} | I | 3.82 | 2.88 ^f | 3.12 ^d | 3.40 ^c | 3.57 ^b | 2.04 ^g | 3.69 ^a | 2.98 ^e | 2.98 ^e |
| Pod Weight R7 | 1.28 ^h | I | 4.08 | 1.88 ^g | 3.04 ^e | 3.73 ^c | 4.11 ^b | 3.11 ^e | 4.43 ^a | 3.68 ^c | 3.27 ^d |
| Pod Weight R8 | 0.870 ^k | I | 4.81 | 1.32 ^h | 2.66 ^{de} | 2.59 ^e | 2.69 ^d | 2.84 ^c | 3.07 ^b | 3.40 ^a | 2.62 ^{de} |
| Stem Weight | 0.313 ^{ijklmn} | I | 11.2 | 0.587 ^f | 0.662 ^{de} | 1.06 ^b | 1.40 ^a | 1.42 ^a | 0.673 ^{de} | 0.867 ^c | 0.338 ^{hijkl} |
| R1 | | | | | | | | | | | |
| Stem Weight | 0.477 ^{ijkl} | I | 9.90 | 1.18 ^c | 1.22 ^c | 1.21 ^c | 0.959 ^e | 2.09 ^a | 1.60 ^b | 0.509 ^{hijk} | 1.06 ^d |
| R3 | | | | | | | | | | | |
| Stem Weight | 0.589 ^{lm} | I | 7.76 | 1.09 ^d | 0.789 ^{ghi} | 1.25 ^c | 0.820 ^{gh} | 2.74 ^a | 1.70 ^b | 1.08 ^d | 1.23 ^c |
| R5 | | | | | | | | | | | |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd20.0 | | | | | | | |
|-----------------|-------------------------|-------------|-------|---------------------------------|--------------------------|------------------------|------------------------|---------------------------------------|--------------------------|--------------------------|------------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBO) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Dry Weight | 10.6 ^{hij} | I | 8.75 | 12.6 ^{efg} | 12.0 ^{efghi} | 14.79 ^c | 12.7 ^{ef} | 15.0 ^c | 14.7 ^c | 17.6 ^{ab} | 15.6 ^c |
| 100 Seeds | | | | | | | | | | | |
| Product per Pot | 2.08 ^p | I | 15.2 | 5.00 ^{efghi} | 4.32 ^{hijk} | 7.37 ^d | 5.47 ^{efg} | 4.01 ^{ijkl} | 4.80 ^{fghi} | 5.96 ^e | 5.00 ^{efghi} |
| Protein | 35.1 ^o | I | 0.665 | 36.2 ^{fghij} | 36.4 ^{defgh} | 36.4 ^{cdefg} | 36.5 ^{cdef} | 36.2 ^{fghij} | 36.0 ^{ijk} | 35.9 ^{ijkl} | 36.9 ^b |
| Lipid | 18.4 ^o | I | 0.532 | 19.3 ^{klm} | 19.8 ^{ef} | 19.9 ^{cd} | 19.3 ^{ijkl} | 19.1 ^{mn} | 19.8 ^{de} | 20.1 ^{bc} | 19.9 ^{de} |
| Leaf Area R1 | 6.69 ^{wx} | I | 1.58 | 7.90 ^{qrs} | 7.75 ^{rstu} | 11.7 ^k | 17.0 ^h | 7.65 ^{stu} | 7.48 ^u | 12.3 ^j | 18.0 ^g |
| Leaf Area R3 | 11.8 ⁿ | I | 1.11 | 12.0 ^m | 17.0 ^j | 16.2 ^k | 20.9 ⁱ | 10.6 ^p | 11.2 ^o | 22.0 ^h | 13.3 ^l |
| Leaf Area R5 | 16.2 ^l | I | 0.850 | 12.4 ^p | 12.7 ^o | 22.6 ^k | 23.3 ^j | 13.2 ⁿ | 14.0 ^m | 26.4 ⁱ | 27.4 ^h |
| Leaf Area R7 | 18.4 ^m | I | 0.696 | 14.3 ^p | 15.3 ^o | 24.8 ^l | 25.4 ^k | 13.4 ^r | 16.7 ⁿ | 29.5 ^j | 30.9 ⁱ |
| Pod Weight R3 | 0.0242 ^{ijkl} | I | 30.4 | 0.0257 ^{ijkl} | 0.0306 ^{hijk} | 0.0820 ^{cd} | 0.0550 ^{efgh} | 0.0244 ^{ijkl} | 0.0223 ^{ijkl} | 0.0478 ^{efghij} | 0.0551 ^{efgh} |
| Pod Weight R5 | 0.0608 ^{fghij} | I | 14.9 | 0.0412 ^{lmno} | 0.0518 ^{ijklmn} | 0.0301 ^{op} | 0.0340 ^{nop} | 0.0710 ^{fghi} | 0.0512 ^{ijklmn} | 0.0770 ^{efgh} | 0.0813 ^{efg} |
| Pod Weight R6 | 1.09 ^{ik} | I | 3.82 | 1.01 ^l | 1.04 ^{kl} | 1.04 ^{kl} | 1.13 ^j | 1.70 ^h | 0.896 ^{mn} | 1.50 ⁱ | 1.05 ^{kl} |
| Pod Weight R7 | 1.29 ^h | I | 4.08 | 0.644 ^p | 1.02 ^{klm} | 1.07 ^{ijkl} | 1.84 ^g | 1.04 ^{klm} | 1.06 ^{ijkl} | 2.54 ^f | 1.17 ⁱ |
| Pod Weight R8 | 0.870 ^k | I | 4.81 | 0.439 ^{pq} | 1.22 ⁱ | 1.66 ^f | 1.34 ^h | 0.688 ^{lm} | 1.53 ^g | 1.34 ^h | 1.61 ^f |
| Stem Weight | | | | | | | | | | | |
| R1 | 0.313 ^{ijklmn} | I | 11.2 | 0.260 ^{lmno} | 0.277 ^{lmno} | 0.331 ^{ijklm} | 0.363 ^{hij} | 0.615 ^{ef} | 0.707 ^d | 0.438 ^g | 0.554 ^f |
| Stem Weight | | | | | | | | | | | |
| R3 | 0.477 ^{ijkl} | I | 9.90 | 0.341 ^{nop} | 0.357 ^{mno} | 0.358 ^{mno} | 0.495 ^{hijk} | 0.455 ^{ijkl} | 0.574 ^h | 0.693 ^g | 0.784 ^f |
| Stem Weight | | | | | | | | | | | |
| R5 | 0.589 ^{lm} | I | 7.76 | 0.387 ^{pq} | 0.517 ^{mn} | 0.455 ^{nop} | 0.967 ^e | 0.747 ^{hij} | 0.853 ^g | 0.941 ^{ef} | 0.951 ^e |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd40.0 | | | | | | | |
|-----------------|--------------------------|-------------|-------|---------------------------------|--------------------------|-------------------------|-------------------------|---------------------------------------|--------------------------|-------------------------|-------------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Dry Weight | 10.6 ^{hij} | I | 8.75 | 12.0 ^{efghi} | 11.90 ^{efghi} | 12.67 ^{efg} | 11.36 ^{efghij} | 12.70 ^{efg} | 13.1067 ^{de} | 15.36 ^c | 14.41 ^{cd} |
| 100 Seeds | | | | | | | | | | | |
| Product per Pot | 2.08 ^p | I | 15.2 | 2.62 ^{mnp} | 3.44 ^{ijklmn} | 4.42 ^{hijk} | 3.36 ^{klmno} | 4.54 ^{ghij} | 5.38 ^{efgh} | 5.65 ^{efg} | 5.40 ^{efgh} |
| Protein | 35.1 ^o | I | 0.665 | 38.2 ^a | 36.8 ^{bc} | 35.6 ^{mn} | 35.6 ^{lmn} | 35.8 ^{ijklm} | 36.4 ^{cdefg} | 36.2 ^{efghij} | 35.6 ^{mn} |
| Lipid | 18.4 ^o | I | 0.532 | 19.0 ⁿ | 19.5 ^{gh} | 19.4 ^{hi} | 19.9 ^{bcd} | 19.2 ^{lm} | 19.6 ^g | 19.8 ^{de} | 19.9 ^d |
| Leaf Area R1 | 6.69 ^{wx} | I | 1.58 | 6.27 ^{yzA} | 6.48 ^{xyz} | 8.18 ^{pq} | 8.51 ^{no} | 6.40 ^{yzA} | 6.96 ^{vw} | 9.02 ^m | 9.11 ^m |
| Leaf Area R3 | 11.8 ⁿ | I | 1.11 | 8.26 ^{uv} | 9.15 ^s | 10.4 ^p | 11.0 ^o | 7.46 ^x | 8.23 ^{uv} | 9.75 ^q | 9.89 ^q |
| Leaf Area R5 | 16.2 ^l | I | 0.850 | 10.4 ^t | 10.3 ^{tu} | 12.5 ^p | 13.2 ⁿ | 10.1 ^{uv} | 10.0 ^v | 11.5 ^r | 11.8 ^{qr} |
| Leaf Area R7 | 18.4 ^m | I | 0.695 | 10.2 ^b | 11.3 ^{wx} | 14.3 ^p | 15.4 ^o | 11.3 ^{wxy} | 11.8 ^v | 13.8 ^q | 14.0 ^q |
| Pod Weight R3 | 0.0242 ^{ijkl} | I | 30.4 | 0.0305 ^{hijk} | 0.0528 ^{efgh} | 0.105 ^{bc} | 0.0256 ^{ijkl} | 0.0512 ^{efghi} | 0.0246 ^{ijkl} | 0.0175 ^{kl} | 0.0316 ^{ghijk} |
| Pod Weight R5 | 0.0608 ^{efghij} | I | 14.8 | 0.0338 ^{nop} | 0.0660 ^{efghij} | 0.0346 ^{mnp} | 0.0442 ^{klmno} | 0.0642 ^{ghij} | 0.0500 ^{ijklmn} | 0.0535 ^{ijkl} | 0.0526 ^{ijklm} |
| Pod Weight R6 | 1.08 ^{ik} | I | 3.82 | 0.678 ^p | 0.587 ^q | 0.687 ^p | 0.423 ^f | 1.00 ^l | 1.02 ^{kl} | 0.909 ^m | 1.01 ^{kl} |
| Pod Weight R7 | 1.28 | I | 4.08 | 0.451 ^r | 0.951 ^{mn} | 0.637 ^p | 0.654 ^p | 1.01 ^{lm} | 1.26 ^h | 1.03 ^{klm} | 1.11 ^{ijk} |
| Pod Weight R8 | 0.870 ^k | I | 4.81 | 0.365 ^{qr} | 0.535 ⁿ | 0.920 ^k | 0.528 ^{no} | 0.663 ^m | 1.02 ^j | 1.52 ^g | 1.53 ^g |
| Stem Weight | 0.312 ^{ijklmn} | I | 11.2 | 0.213 ^o | 0.280 ^{klmno} | 0.293 ^{ijklmn} | 0.453 ^g | 0.390 ^{ghi} | 0.411 ^{gh} | 0.310 ^{ijklmn} | 0.328 ^{ijklm} |
| R1 | | | | | | | | | | | |
| Stem Weight | 0.477 ^{ijkl} | I | 9.90 | 0.343 ^{nop} | 0.465 ^{ijkl} | 0.488 ^{hijk} | 0.575 ^h | 0.445 ^{ijkl} | 0.392 ^{lmn} | 0.432 ^{klm} | 0.543 ^{hi} |
| R3 | | | | | | | | | | | |
| Stem Weight | 0.589 ^{lm} | I | 7.76 | 0.462 ^{nop} | 0.687 ^{jk} | 0.831 ^{gh} | 0.751 ^{hij} | 0.671 ^{jk} | 0.725 ^{ij} | 0.527 ^{mn} | 0.867 ^{fg} |
| R5 | | | | | | | | | | | |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd60.0 | | | | | | | |
|-----------------|-------------------------|-------------|-------|---------------------------------|-------------------------|--------------------------|-------------------------|---------------------------------------|------------------------|------------------------|-------------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Dry Weight | 10.6 ^{hij} | I | 8.75 | Dead | 7.10 ^k | 12.4 ^{efgh} | 11.49 ^{efghij} | 7.52 ^k | 10.46 ^{ij} | 12.66 ^{efg} | 11.2 ^{lghij} |
| 100 Seeds | | | | | | | | | | | |
| Product per Pot | 2.08 ^p | I | 15.2 | Dead | 2.27 ^{op} | 2.99 ^{lmnop} | 3.58 ^{ijklm} | 2.40 ^{nop} | 2.56 ^{mnop} | 3.48 ^{ijklmn} | 3.51 ^{ijklmn} |
| Protein | 35.1 ^o | I | 0.665 | Dead | 35.6 ^{mn} | 36.0 ^{hij} | 35.8 ^{ijklm} | 36.2 ^{fghij} | 35.6 ^{lmn} | 36.1 ^{fghij} | 35.4 ^{no} |
| Lipid | 18.4 ^o | I | 0.532 | Dead | 19.3 ^{ijklm} | 19.5 ^{gh} | 20.2 ^a | 19.1 ^{mn} | 19.3 ^{ijkl} | 19.4 ^{hijk} | 19.4 ^{hij} |
| Leaf Area R1 | 6.69 ^{wx} | I | 1.58 | Dead | 6.71 ^{wx} | 8.10 ^q | 8.40 ^{op} | 6.49 ^{xyz} | 7.02 ^v | 8.02 ^{qr} | 8.71 ⁿ |
| Leaf Area R3 | 11.8 ⁿ | I | 1.11 | Dead | 8.44 ^u | 9.02 st | 9.42 ^r | 7.60 ^{wx} | 7.73 ^w | 8.43 ^u | 9.68 ^q |
| Leaf Area R5 | 16.2 ^l | I | 0.850 | Dead | 10.0 ^{wv} | 10.5 ^t | 11.5 ^r | 8.85 ^y | 8.83 ^y | 10.4 ^t | 11.8 ^{qr} |
| Leaf Area R7 | 18.4 ^m | I | 0.695 | Dead | 11.0 ^{yz} | 12.4 ^s | 12.4 st | 10.5 ^A | 11.1 ^{xyz} | 12.1 ^u | 12.6 ^s |
| Pod Weight R3 | 0.0242 ^{ijkl} | I | 30.4 | Dead | 0.0534 ^{efgh} | 0.0459 ^{efghij} | 0.0210 ^{ijkl} | 0.0457 ^{efghi} | 0.0296 ^{hijk} | 0.0170 ^{kl} | 0.0322 ^{ghijk} |
| Pod Weight R5 | 0.0608 ^{fghij} | I | 14.8 | Dead | 0.0665 ^{fghij} | 0.0620 ^{hijk} | 0.0447 ^{klmno} | 0.0557 ^{ijkl} | 0.0428 ^{lmno} | 0.0310 ^{op} | 0.0534 ^{ijkl} |
| Pod Weight R6 | 1.08 ^{jk} | I | 3.82 | Dead | 0.657 ^p | 0.709 ^p | 0.717 ^p | 0.826 ^{no} | 0.803 ^o | 1.02 ^{kl} | 0.353 ^s |
| Pod Weight R7 | 1.28 ^h | I | 4.08 | Dead | 1.03 ^{klm} | 1.14 ^{ij} | 0.910 ⁿ | 0.920 ⁿ | 1.03 ^{klm} | 0.964 ^{mn} | 0.905 ⁿ |
| Pod Weight R8 | 0.870 ^k | I | 4.81 | Dead | 0.427 ^{pq} | 0.289 ^r | 0.499 ^{nop} | 0.506 ^{nop} | 0.883 ^k | 0.913 ^k | 1.184 ⁱ |
| Stem Weight | 0.312 ^{ijklmn} | I | 11.2 | Dead | 0.273 ^{lmno} | 0.144 ^p | 0.454 ^g | 0.300 ^{ijklmn} | 0.265 ^{lmno} | 0.356 ^{hijk} | 0.311 ^{ijklmn} |
| R1 | | | | | | | | | | | |
| Stem Weight | 0.477 ^{ijkl} | I | 9.90 | Dead | 0.420 ^{klmn} | 0.162 ^r | 0.445 ^{ijkl} | 0.352 ^{mno} | 0.285 ^{opq} | 0.501 ^{hijk} | 0.522 ^{hij} |
| R3 | | | | | | | | | | | |
| Stem Weight | 0.589 ^{lm} | I | 7.76 | Dead | 0.481 ^{no} | 0.632 ^{kl} | 0.682 ^{jk} | 0.523 ^{mn} | 0.460 ^{nop} | 0.521 ^{mn} | 0.671 ^{jk} |
| R5 | | | | | | | | | | | |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd80.0 | | | | | | | |
|-----------------|-------------------------|-------------|-------|---------------------------------|--------------------|---------------------|-------------------------|---------------------------------------|------------------------|------------------------|-------------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Dry Weight | 10.6 ^{hij} | I | 8.75 | Dead | Dead | Dead | 10.9 ^{ghij} | 7.02 ^k | 10.0 ^l | 12.4 ^{efgh} | 11.0 ^{fghij} |
| 100 Seeds | | | | | | | | | | | |
| Product per Pot | 2.08 ^p | I | 15.3 | Dead | Dead | Dead | 2.96 ^{lmnop} | 2.05 ^p | 2.50 ^{mnop} | 2.88 ^{lmnop} | 2.62 ^{mnop} |
| Protein | 35.1 ^o | I | 0.665 | Dead | Dead | Dead | 35.3 ^{no} | 35.6 ^{mn} | 35.4 ^{no} | 35.4 ^{no} | 35.3 ^{no} |
| Lipid | 18.4 ^o | I | 0.532 | Dead | Dead | Dead | 19.6 ^{fg} | 19.0 ⁿ | 19.2 ^{lm} | 19.3 ^{klm} | 19.3 ^{klm} |
| Leaf Area R1 | 6.69 ^{wx} | I | 1.58 | 6.16 ^A | 6.53 ^{xy} | 7.80 ^{rst} | 8.02 ^{qr} | 6.23 ^{zA} | 6.84 ^w | 7.58 ^{tu} | 8.10 ^q |
| Leaf Area R3 | 11.8 ⁿ | I | 1.11 | 8.01 ^v | 8.16 ^v | 9.02 st | 9.40 ^r | 7.06 ^y | 8.45 ^u | 8.83 ^t | 9.23 ^{rs} |
| Leaf Area R5 | 16.2 ^l | I | 0.850 | 9.15 ^x | 10.0 ^{uv} | 11.1 ^s | 11.9 ^q | 8.88 ^y | 9.69 ^w | 10.0 ^{uv} | 10.3 ^{tu} |
| Leaf Area R7 | 18.4 ^m | I | 0.695 | Dead | Dead | Dead | 12.2 ^{tu} | 10.3 ^{AB} | 10.9 ^z | 11.2 ^{wxy} | 11.4 ^w |
| Pod Weight R3 | 0.0242 ^{ijkl} | I | 30.3 | Dead | Dead | Dead | 0.0250 ^{ijkl} | 0.0329 ^{fghijk} | 0.0247 ^{ijkl} | 0.0308 ^{hijk} | 0.0297 ^{hijk} |
| Pod Weight R5 | 0.0608 ^{fghij} | I | 14.8 | Dead | Dead | Dead | 0.0528 ^{ijklm} | 0.0425 ^{lmno} | 0.0310 ^{op} | 0.0215 ^p | 0.0526 ^{ijklm} |
| Pod Weight R6 | 1.08 ^{jk} | I | 3.82 | Dead | Dead | Dead | 0.869 ^{mno} | 0.816 ^o | 0.859 ^{mno} | 0.930 ^m | 0.333 ^s |
| Pod Weight R7 | 1.28 ^h | I | 4.08 | Dead | Dead | Dead | 0.634 ^p | 0.532 ^q | 0.734 ^o | 0.923 ⁿ | 0.631 ^p |
| Pod Weight R8 | 0.870 ^k | I | 4.81 | Dead | Dead | Dead | 0.444 ^{opq} | 0.406 ^q | 0.538 ⁿ | 0.751 ^l | 0.574 ⁿ |
| Stem Weight | 0.312 ^{ijklmn} | I | 11.2 | Dead | Dead | Dead | 0.333 ^{ijklm} | 0.256 ^{mno} | 0.235 ^{no} | 0.264 ^{lmno} | 0.356 ^{hikj} |
| R1 | | | | | | | | | | | |
| Stem Weight | 0.477 ^{ijkl} | I | 9.90 | Dead | Dead | Dead | 0.253 ^q | 0.282 ^{opq} | 0.264 ^{pq} | 0.360 ^{mno} | 0.501 ^{hijk} |
| R3 | | | | | | | | | | | |
| Stem Weight | 0.589 ^{lm} | I | 7.76 | Dead | Dead | Dead | 0.332 ^q | 0.401 ^{opq} | 0.331 ^q | 0.471 ^{nop} | 0.439 ^{nop} |
| R5 | | | | | | | | | | | |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd0 | | | | | | | |
|-------------------|-----------------------|-------------|------|---------------------------------|---------------------|--------------------|---------------------|---------------------------------------|---------------------|--------------------|--------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Stem Weight R6 | 0.814 ^{nop} | I | 4.76 | 1.29 ^{gh} | 2.76 ^c | 2.44 ^e | 1.97 ^l | 0.8240 ^{mno} | 4.30 ^a | 3.67 ^b | 3.67 ^b |
| Stem Weight R7 | 0.407 ^{klmn} | I | 9.29 | 0.582 ⁱ | 0.784 ^{fg} | 1.25 ^a | 1.00 ^c | 0.831 ^{def} | 0.804 ^{fg} | 1.00 ^c | 0.912 ^d |
| Stem Weight R8 | 0.253 ^m | I | 10.2 | 0.455 ^{ef} | 0.679 ^c | 0.743 ^b | 0.699 ^{bc} | 0.674 ^c | 0.697 ^{bc} | 0.930 ^a | 0.673 ^c |
| Cd in Root | 0 ^t | I | 6.27 | 0 ^t | 0 ^t | 0 ^t | 0 ^t | 0 ^t | 0 ^t | 0 ^t | 0 ^t |
| Cd in Shoot | 0 ^s | I | 3.20 | 0 ^s | 0 ^s | 0 ^s | 0 ^s | 0 ^s | 0 ^s | 0 ^s | 0 ^s |
| Cd in Leaf | 0 ^v | I | 2.78 | 0 ^v | 0 ^v | 0 ^v | 0 ^v | 0 ^v | 0 ^v | 0 ^v | 0 ^v |
| Cd in Seed | 0 ^m | I | 17.3 | 0 ^m | 0 ^m | 0 ^m | 0 ^m | 0 ^m | 0 ^m | 0 ^m | 0 ^m |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd20.0 | | | | | | | |
|-------------------|-----------------------|-------------|------|---------------------------------|-----------------------|-----------------------|---------------------|---------------------------------------|----------------------|----------------------|---------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Stem Weight R6 | 0.814 ^{nop} | I | 4.76 | 0.734 ^p | 0.811 ^{nop} | 0.770 ^{op} | 1.35 ^g | 0.881 ^{klmn} | 1.15 ⁱ | 2.54 ^d | 1.12 ⁱ |
| Stem Weight R7 | 0.407 ^{klmn} | I | 9.29 | 0.455 ^{ikl} | 0.558 ⁱ | 0.394 ^{klmn} | 1.11 ^b | 0.697 ^h | 0.773 ^{fgh} | 0.830 ^{def} | 0.896 ^{de} |
| Stem Weight R8 | 0.253 ^m | I | 10.2 | 0.245 ^m | 0.357 ^{hij} | 0.500 ^{de} | 0.463 ^{ef} | 0.304 ^{iklm} | 0.515 ^{de} | 0.532 ^d | 0.388 ^{gh} |
| Cd in Root | 0 ^t | I | 6.27 | 12.5 ^f | 8.83 ^{jk} | 3.77 ^q | 2.19 ^s | 12.0 ^f | 8.40 ^k | 3.14 ^r | 1.92 ^s |
| Cd in Shoot | 0 ^s | I | 3.20 | 2.87 ^f | 2.30 ⁱ | 1.61 ^o | 1.39 ^q | 2.64 ^g | 2.06 ^k | 1.52 ^p | 1.30 ^f |
| Cd in Leaf | 0 ^v | I | 2.78 | 2.20 ^l | 1.91 ⁿ | 1.53 ^q | 1.20 ^t | 2.00 ^m | 1.80 ^o | 1.36 ^s | 1.05 ^u |
| Cd in Seed | 0 ^m | I | 17.3 | 0.357 ^c | 0.267 ^{efgh} | 0.137 ^{kl} | 0.182 ^{jk} | 0.257 ^{fgh} | 0.192 ^{ij} | 0.125 ^l | 0.137 ^{kl} |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd40.0 | | | | | | | |
|-------------------|-----------------------|-------------|------|---------------------------------|----------------------|-----------------------|----------------------|---------------------------------------|-----------------------|----------------------|----------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Stem Weight R6 | 0.814 ^{nop} | I | 4.76 | 0.629 ^{qr} | 0.840 ^{mno} | 0.863 ^{lmn} | 0.903 ^{klm} | 0.763 ^{op} | 0.907 ^{klm} | 0.971 ^j | 1.26 ^h |
| Stem Weight R7 | 0.407 ^{klmn} | I | 9.29 | 0.356 ^{mno} | 0.451 ^{jkl} | 0.690 ^h | 0.812 ^{efg} | 0.500 ^{ij} | 0.513 ^{ij} | 0.836 ^{def} | 0.824 ^{ef} |
| Stem Weight R8 | 0.253 ^m | I | 10.2 | 0.173 ⁿ | 0.287 ^{klm} | 0.326 ^{ijkl} | 0.284 ^{klm} | 0.299 ^{ijklm} | 0.346 ^{hijk} | 0.483 ^{def} | 0.483 ^{def} |
| Cd in Root | 0 ^t | I | 6.27 | 17.0 ^c | 9.54 ⁱ | 7.79 ^l | 5.34 ^p | 16.3 ^d | 9.31 ^{ij} | 7.11 ^{mn} | 5.09 ^p |
| Cd in Shoot | 0 ^s | I | 3.20 | 2.83 ^f | 2.18 ^j | 1.76 ^{mn} | 1.51 ^p | 3.12 ^d | 2.54 ^h | 1.58 ^{op} | 1.40 ^q |
| Cd in Leaf | 0 ^v | I | 2.78 | 4.19 ^e | 2.61 ⁱ | 1.56 ^{pq} | 1.61 ^p | 3.97 ^f | 2.36 ^k | 1.59 ^{pq} | 1.26 ^t |
| Cd in Seed | 0 ^m | I | 17.3 | 0.322 ^{cde} | 0.425 ^b | 0.275 ^{efg} | 0.217 ^{hij} | 0.322 ^{cde} | 0.305 ^{cdef} | 0.245 ^{gh} | 0.167 ^{jkl} |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd60.0 | | | | | | | |
|-------------------|-----------------------|-------------|------|---------------------------------|--------------------|-----------------------|-----------------------|---------------------------------------|-----------------------|-----------------------|----------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Stem Weight R6 | 0.814 ^{nop} | I | 4.76 | Dead | 0.278 ^s | 0.552 ^f | 0.863 ^{lmn} | 0.650 ^q | 0.650 ^q | 0.886 ^{klmn} | 0.944 ^{kl} |
| Stem Weight R7 | 0.407 ^{klmn} | I | 9.29 | Dead | 0.251 ^p | 0.408 ^{klmn} | 0.440 ^{iklm} | 0.347 ^{no} | 0.728 ^{gh} | 0.733 ^{gh} | 0.753 ^{fgh} |
| Stem Weight R8 | 0.253 ^m | I | 10.2 | Dead | 0.175 ⁿ | 0.290 ^{klm} | 0.273 ^{lm} | 0.264 ^{lm} | 0.304 ^{iklm} | 0.381 ^{ghi} | 0.424 ^{fg} |
| Cd in Root | 0 ^l | I | 6.27 | Dead | 12.0 ^f | 10.9 ^g | 6.56 ^{no} | 21.3 ^b | 11.2 ^g | 10.1 ^h | 6.26 ^o |
| Cd in Shoot | 0 ^s | I | 3.20 | Dead | 2.30 ⁱ | 1.91 ^l | 1.56 ^{op} | 4.17 ^b | 2.99 ^e | 1.81 ^m | 1.54 ^{op} |
| Cd in Leaf | 0 ^v | I | 2.78 | Dead | 4.80 ^d | 2.53 ^j | 1.81 ^o | 5.79 ^b | 3.22 ^g | 2.63 ⁱ | 1.43 ^r |
| Cd in Seed | 0 ^m | I | 17.3 | Dead | 0.477 ^b | 0.337 ^{cd} | 0.247 ^{gh} | 0.457 ^b | 0.361 ^c | 0.311 ^{edef} | 0.187 ^{ijk} |

Table 4.11 (Continued)

| Parameter | Control | Interaction | CV | Cd80.0 | | | | | | | |
|-------------------|-----------------------|-------------|------|---------------------------------|-------|-------|-----------------------|---------------------------------------|----------------------|------------------------|----------------------|
| | | | | 200 Liter Oil Drum Kiln (PBLBO) | | | | Lab – scale Pyrolysis Reactor (PBLBL) | | | |
| | | | | B5.00 | B10.0 | B15.0 | B20.0 | B5.00 | B10.0 | B15.0 | B20.0 |
| Stem Weight R6 | 0.814 ^{nop} | I | 4.76 | Dead | Dead | Dead | 0.560 ^r | 0.559 ^r | 0.642 ^q | 0.768 ^{op} | 0.951 ^{jk} |
| Stem Weight R7 | 0.407 ^{klmn} | I | 9.29 | Dead | Dead | Dead | 0.369 ^{lmno} | 0.302 ^{op} | 0.352 ^{no} | 0.371 ^{klmno} | 0.502 ^{ij} |
| Stem Weight R8 | 0.253 ^m | I | 10.2 | Dead | Dead | Dead | 0.182 ⁿ | 0.177 ⁿ | 0.304 ^{klm} | 0.372 ^{ghi} | 0.381 ^{ghi} |
| Cd in Root | 0 ^t | I | 6.27 | Dead | Dead | Dead | 7.51 ^{lm} | 24.9 ^a | 15.3 ^e | 10.1 ^h | 7.39 ^{lm} |
| Cd in Shoot | 0 ^s | I | 3.20 | Dead | Dead | Dead | 1.82 ^m | 4.97 ^a | 3.71 ^c | 2.81 ^f | 1.69 ⁿ |
| Cd in Leaf | 0 ^v | I | 2.78 | Dead | Dead | Dead | 2.23 ^l | 6.06 ^a | 5.01 ^c | 2.91 ^h | 1.90 ⁿ |
| Cd in Seed | 0 ^m | I | 17.3 | Dead | Dead | Dead | 0.282 ^{defg} | 0.582 ^a | 0.442 ^b | 0.337 ^{cd} | 0.237 ^{ghi} |

Note: Means in the Same Row with Different Letters are Significantly Different at P < 0.05

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

This study was conducted to determine the potential effect of broiler litter derived biochar that been produced by pyrolyzed pelleted broiler litter of highest temperature 500°C in two types of kilns that one, was Lab – scale Pyrolysis Reactor (PBLBL: L kiln) and second was 200 Liter Oil Drum Kilns (PBLBO: O kiln). To determine, compare, and evaluate the efficiency of these two types of biochar at 4 mixing rate: 5.00, 10.0, 15.0, and 20.0 t ha⁻¹ on soil property and soybean productive performance planting in soil polluted with Cd at 0, 20.0, 40.0, 60.0, and 80.0 mg kg⁻¹. The conclusion and recommendation of this study are describes as follows:

5.1 Conclusion

5.1.1 Soil Properties before Experimentation

The soil texture was sandy soil. Soil pH was very strongly acid. The organic matter and cation exchange capacity (CEC) were lower than the recommended reference values. The concentrations of essential nutrients were low.

5.1.2 Total Cd in Soil Background

The background level of Cd in soil was not detected.

5.1.3 The Hypothesis of the Study

5.1.3.1 The studied revealed Factor A (Lab – scale Pyrolysis Reactor and 200 Liter Oil Drum Kiln), Factor B (Cadmium level), Factor C (Biochar mixing rate), interaction between Factor A and Factor B, interaction between Factor A and Factor C, interaction between Factor B and Factor C, interaction between Factor A, and Factor B and Factor C had effected to almost every parameter of soil properties,

soybean growth stage, soybean productive performance and Cd residue in soybean' root, shoot, leaf and seed. Almost results showed a significantly different between PBLBL and PBLBO.

5.1.4 Conclusion of the Effect of PBLBL and PBLBO to Soil Properties, and Soybean Growth Stage, and Productive Performance.

5.1.4.1 Soil Properties

1) Non Cd Polluted Soil

(1) The result showed not significantly different among PBLBL and PBLBO: OM, and Cd residual in soil.

(2) The result showed significantly different among group, where PBLBL showed better result than PBLBO: % moisture, pH, EC, and C/N.

(3) The result showed significantly different among group, where PBLBO showed better result than PBLBL: N, P, K, Ca, Mg, and CEC

2) Cd Polluted Soil

(1) The result showed not significantly different PBLBL and PBLBO: EC, OM, pH, N, K, Ca

(2) The result showed significantly different among group, where PBLBL showed better result more than PBLBO : Cd residual in soil.

(3) The result showed significantly different among group, where PBLBO showed better result more than PBLBL : % moisture content, P, Mg, C/N, CEC.

5.1.4.2 Soybean Growth Stage

1) Non Cd Polluted Soil

(1) The result showed not significantly different among PBLBL and PBLBO: Planting Date to VE, Planting Date to V4, Planting Date to R1.

(2) The result showed significantly different among group, where PBLBL showed shorter day developed to R8 faster than PBLBO.

2) Cd Polluted Soil

(1) The result showed not significantly different PBLBL and PBLBO: Planting Date to VE.

(2) The result showed significantly different among group, where PBLBO developed faster than PBLBL : Planting Date to V4, Planting Date to R1, Planting Date to R8.

5.1.4.3 Soybean Productive Performance

1) Non Cd Polluted Soil

(1) The result showed not significantly different among PBLBL and PBLBO: Number of Seed per Pod, Dry Weight 100 Seeds, Product per Pot, Protein in Soybean's Seeds, Lipid in Soybean's Seeds.

(2) The result showed significantly different among group, where PBLBL showed better result than PBLBO: Stem Weight, Pod Weight, Number of Node, Number of Pod, and Leaf Area R7.

(3) The result showed significantly different among group, where PBLBO showed better result than PBLBL: Height, and Leaf Area R1 – R5.

2) Cd Polluted Soil

(1) The result showed significantly different among group, where PBLBL showed better result more than PBLBO: Stem Weight, Pod Weight, Height, Node Number, Number of Pod, Seed per Pod, 100 Seeds Dry Weight, Product per Pot, Protein, Lipid, Leaf Area R1, Leaf Area R3, and Leaf Area R7.

(2) The result showed significantly different among group, where PBLBO showed better result more than PBLBL : Leaf Area R5.

5.1.4.4 Cd Residue in Soybean's Part

1) Non Cd Polluted Soil

(1) The result showed not significantly different among PBLBL and PBLBO, that not have Cd Residual in Soybean' Root, Shoot, Leaf nor Seeds.

2) Cd Polluted Soil

PBLBO had Cd Residue in Soybean Root, Shoot, Leaf and Seed, higher than PBLBL significantly.

5.2 Recommendations

5.2.1 Factor for Improve Soil Quality

5.2.1.1 The result from the study obviously seen that PBLBL and PBLBO at mixing rate $\geq 15.0 \text{ t ha}^{-1}$ improving over all of soil properties especially in non Cd polluted soil, PBLBO had performed better than PBLBL and slightly decrease the efficiency lower than PBLBL when $\text{Cd} > 20.0 \text{ mg kg}^{-1}$, so in non Cd polluted soil and even if had Cd binding but not higher than 20.0 mg kg^{-1} , local people can make their own biochar prepare from simple kilns like 200 Liter Oil Drum Kiln, do as charcoal making process that was too easy and low capital costs.

5.2.1.2 At Cd polluted soil range from $20.0 - 80.0 \text{ mg kg}^{-1}$ should use PBLBL at mixing rate $\geq 15.0 \text{ t ha}^{-1}$ for improving soil properties.

5.2.1.3 At dry soil land that not have Cd polluted or polluted but lower than 60.0 mg kg^{-1} should use PBLBO for enhance moisture content in soil but when Cd polluted up to 80.0 mg kg^{-1} should use PBLBL for this purpose.

5.2.1.4 Obviously seen from the studied that PBLBL and PBLBO can raise up pH in soil, so these biochar can be use as a liming substance like limestone, marl, bentonite, or vermiculite etc., but PBLBL and PBLBO had more ability not just only liming effect but had present higher plant nutrient that can be use as a fertilizer and improving soil structure.

5.2.1.5 In soil that had low soil organic matter, PBLBL and PBLBO albeit at lowest mixing rate 5.00 t ha^{-1} can raise OM in soil up higher significantly, moreover at mixing rate 15.0 t ha^{-1} had the most efficiency increase OM in soil.

5.2.1.6 In non Cd polluted soil PBLBL or PBLBO had similar result but in soil polluted with Cd, PBLBO at mixing rate $\geq 10.0 \text{ t ha}^{-1}$ had perform the efficiency decrease Cd in soil higher than PBLBL, so this must distribute and promote to be the most efficiency alternation for Cd polluted soil remediation.

5.2.2 Short Cut from Planting Date to Stage of Maturity of Plant

5.2.2.1 In non Cd polluted soil condition, concern on economic feasibility, PBLBO at mixing rate 15.0 t ha^{-1} , offer the best accelerator develop plant growing faster than normal growth time.

5.2.2.2 In low Cd polluted soil, PBLBO $\geq 10.0 \text{ t ha}^{-1}$ can be an interesting volunteer adding to soil for planting, however at higher Cd amount contaminated soil, PBLBL mixing rate 15.0 t ha^{-1} should be the best choice for this condition.

5.2.3 Essential for Promote Plant Productive Performance

5.2.3.1 In non Cd polluted soil, PBLBL mixing rate $\geq 15.0 \text{ t ha}^{-1}$ and PBLBO 20.0 t ha^{-1} drastically enhance leaf area, stem weight, pod weight, height, 100 seeds dry weight, yield of soybean including enhance protein and lipid in soybean seed, albeit use at lower mixing rate still confirm positive to all over that parameter.

5.2.3.2 In Cd polluted soil, at low level $\leq 40.0 \text{ mg kg}^{-1}$, PBLBL or PBLBO mixing rate $\geq 10.0 \text{ t ha}^{-1}$ can increase all of soybean productivity, however when Cd raise up higher should use high biochar mixing rate $\geq 15.0 \text{ t ha}^{-1}$, nevertheless properly should use PBLBL for this situation.

5.2.4 Fighting for Sustain Food Scarcity and Security

5.2.4.1 In non Cd polluted soil, PBLBL or PBLBO at any mixing rate especially at rate 15.0 t ha^{-1} had raise up yield and nutrient in soybean seed higher than control strongly significant different. Moreover many research had confirm the biochar benefit not only improve soil quality and productivity but can reduced CO_2 and CH_4 that affect to global temperature. This must be confirm the utility of biochar for agricultural purpose.

5.2.4.2 In Cd polluted soil, PBLBO mixing rate $\geq 15.0 \text{ t ha}^{-1}$ should be useful in low Cd polluted soil not higher than 20 mg kg^{-1} but when Cd raise up higher shall be chose PBLBL mixing rate $\geq 15.0 \text{ t ha}^{-1}$ for planting edible plant but when Cd raise up to 80 mg kg^{-1} , albeit used at highest mixing rate of PBLBL (20.0 t ha^{-1}) can not tolerate to Cd toxicity that present Cd residual in soybean seed higher than CCFAC permit Cd in soybean seed standard not over 0.200 mg/kg soybean seed. This must be concern and make a plan for planting edible plant on Cd polluted soil which higher than 60.0 mg kg^{-1} .

5.2.5 Issue that Must be Concern

5.2.5.1 PBLBL and PBLBO had raise up EC in soil that may be increase the salty affect.

5.2.5.2 Although simple kilns are easy to use and incur low capital costs, but in the process producing excess heats or carbon monoxide or carbon dioxide (Brown, 2009: 127) so modification of kilns used in rural areas of developing nations must concern that process excess and design a burning tank that more efficient, emits less pollution and improves the health of users (Pratt and Moran, 2010: 1149).

5.2.5.3 Availability of large quantities of biomass feedstock and the transportation distance to a pyrolysis and plant are essential considerations for an efficient and economically viable biochar production system (Roberts et al., 2010: 827).

5.2.5.4 Cd and Zn, two metals chemically close similarity in electronic configuration and reactivity with organic ligands, interact in the soil – plant system, causing well – known Cd/ZN antagonism (Smilde et al., 1992: 233). Zn depresses Cd uptake (Cataldo et al., 1983). On the other hand, at low concentrations the interaction is synergistic and the input of Zn increase Cd uptake (Haghiri, 1974: 180). For these point, even though PBLBL and PBLBO have demonstrated clear potential for the Cd remediation as present in this study and others but in some cases this may require their combination with other amendment such as using mycorrhizal fungi or biosurfactant bacteria, for example of Krupa and Piotrowska – Seget (2003: 723) evaluated the protective role of ectomycorrhizal fungi against contamination of plants growing in soil treated with cadmium at a dose of 150 μg Cd/g soil. An alginate immobilized inoculum of mycorrhizal fungi was used to introduce the fungi to the soil. The impact of fungi was examined in terms of changes in cadmium levels in inoculated and non-inoculated seedlings of *Pinussylvestris* L. It was found that the concentration of cadmium in plants inoculated with fungi was significantly lower than in non-inoculated seedlings and also found that the total concentration of cadmium in contaminated soil inoculated with fungi was lower than in non – inoculated soil, resemble to the revealed by Charoon Sarin and Siripun Sarin (2010) assessed biosurfactant bacteria produced from *Bacillus subtilis* TP8 and *Pseudomonas fluorescens* G7 for survival in heavy metal contaminated soil and for their ability to remove

cadmium and zinc from contaminated soil. The results of soil remediation showed that approximately 19.0% of Zn and 16.7% of Cd could be removed by biosurfactant produced from this bacteria after incubation for 2 weeks. *P.fluorescens* G7 was considered to be a good candidate for bioremediation of heavy metals because of its high minimum inhibitory concentrations for each heavy metal and because of the obviously increased numbers of cell surviving after incubation in the heavy metal contaminated soil up to 4 weeks.

5.2.5.5 This study produce biochar at highest temperature in both 2 kiln at 500°C, under oxygen – limited conditions, had improve sandy soil properties, soybean productivity and reduce Cd in soil and root, shoot, leaf and seeds of soybean significantly but many researcher e.g. Major et al., 2002; Sohi et al., 2009, had claim that biochar must be produce at temperatures above 500°C or be activated to results in increased surface area of the biochar and thus increased direct sorption of nutrient.

5.2.5.6 As we known that biochar is a very fine textured that may be dustiness cause the negative property during transport, from storage heaps and application of biochar to soil (Major, 2010: 7) that easily moved by light winds that may be poses unacceptable pollution in neighbouring residential zones. Covering biochar heaps with sheets or spraying solutions to stabilize the surface may be required to minimize the risk of dust formation during storage. On – site application of water to assist spreading may be a feasible solution. For this study we concern for this point so we had pelleted our feedstock before run the pyrolysis process according to the method of Tawadchai Suppadit and Siriwan Panomsri (2010: 239), insist the positive effect using pelleted biochar before application by the study of Dumrose, Heiskanen, Englund, and Tervahauta. (2011: 2018) added biochar-based pellets to pure peat, they discover that high ratios of pellets to peat 75.0 % peat and 25.0 % pellets had enhanced hydraulic conductivity and greater water availability.

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