



Faculty of Resource Science and Technology

**Potential of Biochar to Improve Soil Properties and Growth Performance
of Oil Palm Seedlings**

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Potential of Biochar to Improve Soil Properties and Growth Performance of Oil Palm Seedlings

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

Fertilizers are the costliest input in the oil palm plantation, losses of inorganic fertilizers are not only detrimental to the environment, but also a significant financial loss to the oil palm industry. Empty fruit bunch (EFB) and palm kernel shell (PKS) biochar are potential soil ameliorator to improve nutrient use efficiency in the oil palm plantation. Field studies were carried out to determine the effects of EFB and PKS biochar, respectively on plant growth, soil chemical properties and plant nutrient uptake of oil palm seedlings. Three rates of EFB and PKS biochar (0, 1.5 and 3%) were incorporated into the loamy sand soil for 9 months and 8 months experimental period, respectively under field condition. Oil palm seedlings at 7th month were planted in a polybag containing 15 kg dry soil and incorporated homogenously with 3 rates of EFB and PKS biochar (0, 0.225 and 0.450 kg) respectively. The experiments were arranged in a randomized complete block design (RCBD), with 3 replications. Results of the EFB biochar field study showed that the 3% biochar incorporation rate significantly ($p < 0.05$) improved the plant growth, biomass, soil chemical properties (CEC, available P, total P, exchangeable Ca and Mg) and plant nutrient uptake (P, Mg, Ca and B) whereas these positive effects were not observed in the PKS biochar field study. Isotope nitrogen (^{15}N) tracing method was applied in PKS biochar field study to quantify the nitrogen up-take performance when the seedlings were 9 months old. Measurement of total plant biomass, total N and percentage N derived from fertilizer (%NdFF) were conducted during the study. The seedlings did not demonstrate any difference in nitrogen uptake with and without PKS biochar treatments. Thus, PKS biochar did not have any positive effect on nitrogen uptake.

Keywords: Empty fruit bunch, palm kernel shell, soil chemical properties, nutrient uptake, isotope nitrogen (^{15}N)

Potensi Bio-arang untuk Memperbaiki Sifat-sifat Tanah dan Prestasi Pertumbuhan Anak Pokok Kelapa Sawit

ABSTRAK

Baja merupakan kos yang tertinggi di ladang kelapa sawit, kehilangan baja bukan organik bukan sahaja mengancam alam sekitar, ia juga adalah satu kerugian yang besar dari segi ekonomi kepada industri kelapa sawit. Bio-arang tandan kosong dan bio-arang isirung kelapa sawit merupakan pindaan tanah yang berpotensi untuk meningkatkan kecekapan penggunaan nitrogen di ladang kelapa sawit. Kajian lapangan telah dijalankan untuk menentukan kesan-kesan bio-arang tandan kosong dan isirung kelapa sawit terhadap pertumbuhan, sifat-sifat kimia tanah dan pengambilan nutrien anak pokok kelapa sawit masing-masing. Tiga kadar bio-arang tandan kosong dan isirung kelapa sawit (0, 1.5 dan 3 %) telah dicampur ke dalam tanah pasir berlumpur untuk 9 bulan dan 8 bulan tempoh eksperimen di bawah keadaan lapangan. Anak-anak pokok kelapa sawit yang berumur 7 bulan telah ditanam di dalam beg poli yang mengandungi 15 kg tanah kering yang telah dicampur secara sekata dengan 3 kadar bio-arang tandan kosong dan isirung kelapa sawit (0, 0.225 dan 0.450 kg) masing-masing. Eksperimen ini disusun dalam reka bentuk “randomized complete block design” (RCBD) dengan 3 ulangan. Keputusan kajian lapangan bio-arang tandan kosong kelapa sawit menunjukkan bahawa percampuran bio-arang yang berkadar 3% telah meningkatkan pertumbuhan, biomas, sifat-sifat kimia tanah (keupayaan pertukaran kation, P yang ada, jumlah P, kebolehtukaran Ca dan Mg) dan pengambilan nutrien tumbuhan (P, Mg, Ca dan B) dengan ketara ($p < 0.05$). Namun, kesan-kesan positif tersebut tidak diperhatikan dalam kajian lapangan bio-arang isirung kelapa sawit. Cara pengesanan isotop nitrogen (^{15}N) telah dilaksanakan ke dalam kajian lapangan bio-arang isirung kelapa sawit untuk mengukur prestasi pengambilan nitrogen

ketika anak pokok kelapa sawit berumur 9 bulan. Pengukuran terhadap jumlah biomas tumbuhan, jumlah nitrogen dan peratus nitrogen berasal dari baja (%NdFF) telah dijalankan semasa kajian ini dilakukan. Anak-anak pokok kelapa sawit tersebut tidak menunjukkan sebarang perbezaan yang ketara terhadap pengambilan nitrogen. Oleh sebab itu, arang-bio isirung kelapa sawit tidak ada sebarang kesan positif terhadap pengambilan nitrogen.

Kata kunci: *Tandan kosong kelapa sawit, isirung kelapa sawit, sifat-sifat kimia tanah, pengambilan nutrien, isotop nitrogen (^{15}N)*

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrophotometer
ANCA	Automated nitrogen carbon analyser
ANOVA	Analysis of variance
CEC	Cation Exchangeable Capacity
CS	Coarse sand
EC	Electrical conductivity
EFB	Empty fruit bunch
FTIR	Fourier transform infrared
FS	Fine sand
GHG	Greenhouse gases
GSL	Gases, solids, liquids
IRMS	Isotope ratio mass spectrophotometer
LSD	Least significant different
MM	Mobile matter
MOP	Muriate of potash
NdFF	Nitrogen derived from fertilizer
PAH	Polycyclic aromatic hydrocarbons
PKS	Palm kernel shell
RCBD	Randomized complete block design
RP	Rock phosphate
rpm	Round per minute
SAS	Statistical analysis system
SEM	Scanning electron microscopy

T1	Treatment 1
T2	Treatment 2
T3	Treatment 3
UV	Ultra violet

CHAPTER 1

INTRODUCTION

Malaysia is well-known as the world's second largest oil palm grower and also one of the biggest international exporters of palm oil products (Alam et al., 2015). Most of the oil palms are planted at highly weathered tropical Ultisol and Oxisol soils, which are acidic and infertile naturally (Goh et al., 2003; Shamshuddin & Anda, 2012). Poor soil fertility is one of the most crucial constraints that can restrict the crop productivity (Ayoub, 1999). Hence, intensive inorganic fertilizers application in the oil palm plantation is indispensable for ensuring high crop yield. However, the fertilizer nutrients that are not taken up by the palms could be easily dissolved and lost through surface runoff, leaching, erosion, volatilization and denitrification (Goh et al., 2003), causing health problems and irrecoverable environmental pollution.

Oil palm is a heavy feeder that demands large amount of nutrients for achieving good productivity (Comte et al., 2012). Foster and Goh (1977) estimated that the production of 25 tonnes of fresh fruit bunch per hectare per year will remove a total of approximately 192 kg N (Nitrogen), 11 kg P (Phosphorus), 209 kg K (Potassium), 36 kg Mg (Magnesium) and 71 kg Ca (Calcium) from the soil. Subsequently, growing oil palm at the low fertility soils could cause further soil degradation. Hence, intensive fertilizer applications are required to replenish and sustain the nutrients required by the crop.

Losses of fertilizer nutrients from the haphazard application of inorganic fertilizers particularly nitrogen-based which are used in excess quantities, poses adverse impacts to the environment. It can cause water pollution and nitrogen emission. On the other hand, Goh (2005) reported that an additional cost of about RM117.25 million would be incurred

to the oil palm industry in Malaysia by over application of as much as 0.25 kg ammonium nitrate per palm per year. Conversely, insufficient fertilizer supply would lead to the loss of oil palm yields. Thus, it is essential to maximize nutrient use efficiency in the oil palm plantation, which will in turn, reduce fertilizer wastage.

As reported by MPOB (2019), there are 452 palm oil mills in Malaysia producing large volume of agriculture wastes such as empty fruit bunch (EFB), palm kernel shell (PKS) and mesocarp fiber with about 15 million tonnes of EFB are created per annum (Abdul et al., 2016). Thus, these agricultural wastes could be transformed into biochar as they have the potential to be used for soil amendment in the oil palm plantation to increase nutrient use efficiency.

Biochar is one of the alternatives that is gaining increasing popularity to enhance nutrient use efficiency and promote plant growth in the agricultural world (Bonanomi et al., 2017). Biochar is a charcoal-like substance which is used for soil amendment. It is produced from plant biomass through pyrolysis process at the temperature of below 700 °C (Lehmann et al., 2009). It is highly porous, exhibits large surface area (Lua et al., 2004; Brown et al., 2006) and usually alkaline (Gaskin et al., 2008; Spokas et al., 2012). Cheng et. al. (2008) revealed that oxidation of biochar in the soil facilitates the development of negatively charged functional groups on its surface. There are some evidences to suggest that the incorporation of biochar can reduce the leaching losses of soil nutrients such as nitrogen and phosphorous (Rondon et al., 2007).

Moreover, the porous structure of biochar increases soil water-holding capacity, surface sorption capacity, base saturation and cation exchange capacity (CEC) when it is incorporated into the soil (Glaser et al., 2002; Belanger et al., 2004; Keech et al., 2005; Liang et al., 2006). The application of biochar into soils has great potential in reviving soil

fertility, repairing damaged soil caused by conventional inorganic fertilizer, as well as enhancing plant growth (Beesley et al., 2011). Furthermore, biochar can also alleviate climate change (Lehmann, 2007). Biochar is a source of renewable energy as biochar production generates heat, syngas and bio-oil apart from converting agricultural wastes into valuable soil amendment.

1.1 Problem Statements

Oil palms are usually planted at the soils that have low fertility, consequently inorganic fertilizers are essential to attain and sustain sufficient palm nutritional level and optimum yields (Goh et al., 1999). Excessive inorganic fertilizer application for the intentions of healthy vegetative growth and yield maximization in the oil palm plantation may facilitate the decrease in nutrient use efficiency as a result of nutrients loss.

For instant, plants only utilize up to 50% of the nitrogen fertilizer applied while the rest is discharged to the environment with 2-20% volatilizes to the atmosphere, 15-25% reacts with organic compounds in the clay soil and the remaining 2-10% contaminates the surface and groundwater (Feigin & Halevy, 1989). This is corroborated by the findings of Sukreeyapongse et al. (2001) and Cassman et al. (2002) that half of the nitrogen applied could be lost and only half of the nitrogen fertilizer applied is taken up by the crop at the end of the growing season. It can generate adverse consequences to the environment and human health as the latter is associated with pollution risks including nitrate leaching to the ground and surface water, and nitrous oxide emission to the atmosphere (Corley & Tinker, 2003; Choo et al., 2011; Comte et al., 2012).

As reported by Sabri (2009) and Goh et al. (2003), fertilizers are the costliest input and the major variation expenses in oil palm plantation where they constitute about 25% of

the total production cost and 50–70% of the field operational cost (Goh & Hardter, 2003; Carcasses et al., 2007). Hence, losses of fertilizers are not only harmful to the environment, but they also contribute to significant financial loss in the oil palm industry.

In addition, 452 palm oil mills in Malaysia produce vast amount of palm biomass annually (MPOB, 2019), It is vital to make use of this biomass by transforming it into valuable material such as biochar.

1.2 Significance of the Study

Biochar is a low-cost product recognized worldwide as an influential soil amendment for boosting soil fertility and improving soil quality, which will eventually initiate an increase in crop yields. The incorporation of biochar into the agricultural soil is a potential approach to maintain soil fertility by raising the soil pH, improving cation exchangeable capacity (CEC), retaining soil nutrients, increasing water holding capacity, boosting microbial diversity and altering soil taxonomy (Glaser et al., 2001; Lehmann et al., 2003, Lehmann et al., 2006; Gaskin et al., 2008; Laird et al., 2010; Lehmann et al., 2011; Novak et al., 2012). These are associated with the high surface area and porous structure of biochar that facilitate nutrient retention and water absorption to furnish a suitable environment for beneficial microorganisms (Glaser et al., 2002; Lehmann et al., 2006; Warnock et al., 2007).

There are some evidences which suggested that the addition of biochar could enhance nutrient bioavailability (Shen et al., 2016), reduce nitrate leaching and increase nitrogen retention in soil (Major et al., 2012; Yao et al., 2013; Sun et al., 2017). Biochar incorporation has been observed to suppress soil nitrification and denitrification (reducing aqueous and gaseous N losses) (Taghizadeh-Toosi et al., 2012; Clough et al., 2013) and it

has also been shown to enhance plant nutrient uptake and nutrient-use efficiency, though the mechanism for this effect is still in question.

Lehmann (2007) proposed that a significant amount of anthropogenic carbon dioxide (CO₂) emission could be alleviated if biochar management were espoused globally. This is because biochar has the potential to absorb CO₂ from the atmosphere through carbon sequestration that can help to reduce greenhouse gases (GHG). However, this approach is still under investigation (Geoffrey, 2008). Biochar can establish a carbon sink by slowing down the decaying and mineralization of the biological carbon cycle. As estimated by Woolf et al. (2010), about 12% of the GHG emissions caused by human activities could be reduced through the production of biochar. The utilization of surplus organic matter or biomass to create biochar has gained promising outcomes in the reduction of CO₂ (Krishnakumar et al., 2013).

Conversely, some researchers reported that biochar has insignificant effect on crop production (Jeffrey et al., 2011; Ruyschaert et al., 2016) and it may have undesirable effects on crop yield as nitrogen could be tied up by biochar (Kammann et al., 2015; Hairder et al., 2016), especially in clay-rich soils. Graber and Kookana (2015) suggested that the biochar may inactivate soil applied with pesticides. As biochar has a long half-life, it could not be taken away easily after it has been applied; as such, one should be careful and take small measured steps in the utilisation of biochar before its extensive use.

The application of biochar in improving soil properties and plant growth has been extensively studied. However, the study on the growth of oil palm by the application of biochar made from oil palm biomass is limited (Radin et al., 2017). A total of 90% of oil palm biomass is waste (Awalludin et al., 2015); EFB and PKS are the two most commonly

known oil palm residues that are converted into biochar. Their effects in enhancing soil properties, facilitating nutrient uptake and oil palm growth have yet to be fully explored.

1.3 Research Objectives

The primary objective of this study is to determine the nutrient uptake when biochar is incorporated into mineral soil planted with oil palm seedlings. Biochar were produced from EFB and PKS. They were applied on oil palm seedlings where the soil properties, seedling growth and nutrient uptake were monitored. An isotope (^{15}N) study was conducted to investigate the destination of ^{15}N after its application.

Specifically, the objectives of this study are as follows:

1. to determine the characteristics of biochar produced from EFB and PKS;
2. to evaluate the soil characteristics, growth performance and nutrient uptake of oil palm seedlings treated with and without biochar; and
3. to quantify nitrogen transfer in oil palm seedlings using the ^{15}N isotope Analysis.

CHAPTER 2

LITERATURE REVIEW

2.1.1 Definition of Biochar

The word “biochar” is a combination of “bio” as in biomass and “char” as in charcoal. Essentially, biochar is a charcoal-like substances made from biomass through pyrolysis process (Glaser et al., 2001). It is a stable, insoluble, carbon-rich and highly aromatic solid material (Sohi et al., 2010; Li et al., 2011; Xu et al., 2012) which is used for soil amendment and carbon sequester (Geoffrey, 2008).

2.1.2 History of Biochar as an Ancient Soil Amendment

Biochar exists naturally in soils as a consequence of forest and vegetation fires (Sombroek et al., 2003). Biochar originated in the Amazon Basin of South America 2500 years ago through the burning and smoldering pits as a result of traditional agricultural practices. The most well-known charcoal-rich soil area is *Terra Preta*. It was discovered by a Dutch soil scientist, Wim Sombroek in the Amazon Rainforest in the 1950’s. This place is also called “the Black Earth” because of the black soil and it comprehends about 50 Mg ha⁻¹ carbon in the form of biochar of about 1-meter depth (Verheijen et al., 2009). The high concentrations of biochar in the soils of *Terra Preta* are highly likely initiated from low-heat smoldering fires of which native population used for cooking and heating (Glaser et al., 2001). The soils in this area are high in pH, water retention and nutrients content (Kim et al., 2007; Daniel, 2009). These have made *Terra Preta* one of the most fecund soils in the world which supports productive farming.

2.1.3 Biomass for Biochar Production

Biochar is a carbon rich and solid substances produced from the agricultural biomass through pyrolysis (Lehmann, 2007). Biochar can be made from a variety of biomasses with different chemical and physical properties including agricultural wastes, bioenergy crops, forest residues, organic wastes and sewage wastes (Nartey & Zhao, 2014). Large number of agricultural wastes has been created due to the high demand of food production as a result of the rapid growth of population (Abdelhafez et al., 2014). The agricultural biomass is one of the most copious renewable resources that can be used as a feedstock for biochar production.

For instance, oil palm industry in Malaysia produces approximately 80 million tonnes of dry solid palm biomass annually and these agricultural wastes consist of oil palm frond, oil palm trunk, PKS, EFB and mesocarp fibre (National Innovation Agency of Malaysia, 2013). It is imperative to make use of these agricultural residues efficiently. Producing biochar from agricultural biomass offers an excellent alternative for converting and recycling such wastes into valuable materials.

2.2.1 Pyrolysis

Pyrolysis is a thermal decomposition process of substances in an inert atmosphere at elevated temperatures (Compendium of Chemical Terminology, 2009). It is irreversible as it implicates the alteration of chemical decomposition. Pyrolysis is coined from the Greek language where pyro means “fire” and lysis means “separating”. Pyrolysis can be categorized into three types including slow pyrolysis, fast pyrolysis and flash pyrolysis depending on the temperature, residence time and heat transfer rate in the process (Maschio et al., 1992; Bruun et al., 2012).

The main pyrolysis products are biochar, pyrolytic oil (bio-oil) and synthesis gas (syngas) with dissimilar energy values (Yaman, 2004; Gaunt & Lehmann, 2008). This is corroborated with the findings of several studies that besides generating volatile products, pyrolysis also produces carbon rich solid residue, condensable liquid (tar), and permanent gasses (Jones, 2011; Ramin et al., 2014; Zhou et al., 2014; Morgan et al., 2015). Volatile matters produced during the pyrolysis process can be trapped to supply energy, or upgraded to specific chemical products such as meat browning, food flavouring, wood preservative, adhesives and etc (Czernik & Bridgwater, 2004; Lehmann, 2007).

Table 2.1: Classification of pyrolysis methods

Method	Temperature (°C)	Residence Time	Heating rate (°C/s)	Major products
Conventional/slow pyrolysis	Medium - high 400 - 500	Long 5 - 30 min	Low 10	Gases, char bio-oil (tar)
Fast pyrolysis	Medium - high 400 - 650	Short 0.5 - 2 s	High 100	Bio-oil (thinner) gases, char
Ultra-fast/flash pyrolysis	High 700 - 1000	Very short < 0.5 s	Very high >500	Char, gases, bio-oil

Source information: Boyt, R., (November 2003), Wood Pyrolysis. Retrieved from Bioenergylists.org

2.2.2 Effects of Pyrolysis Temperature

There are three stages of biochar production including pre-pyrolysis, main-pyrolysis and formation of carbonaceous products (Lee et al., 2017). The first stage is involved with the evaporation of moisture and light volatiles when the temperature rises from ambient temperature to 200 °C, resulting in the breakage of bonds and formation of -COOH and -CO groups (Ca'rdenas-Aguilar et al., 2017). The second stage occurs at the temperature from 200 °C to 500 °C where the hemicellulose and cellulose are devolatilized and decomposed (Ding et al., 2014). The last stage ensues at the temperature above 500 °C

where the lignin and other organic matter with stronger chemical bonds are degraded (Ca'rdenas-Aguiar et al., 2017). The changes in the physicochemical properties and structure of biochar are strongly correlated with the pyrolysis temperature (Asadullah et al., 2007; Chen et al., 2008; Mukherjee et al., 2011; Jindo et al., 2014).

2.2.3 Pyrolysis Temperature Affects the Yield and Quality of Biochar

The amounts and properties of biochar, bio-oil and syngas depend on the pyrolysis temperature, pressure and residence time (Lewandowskiet et al., 2010; Brewer, 2012; Cheah et al., 2016). Low temperature, high heating rate, and short gas residence time produce maximum yields of liquid products; High temperature, low heating rate and long gas residence time produce high yields of fuel gas whereas low operational temperatures and low heating rates produce greatest yields of biochar (Demirbas, 2008).

Typically, the higher the temperature, the lower the yield of biochar with more liquid and gas fractions being produced. High pyrolysis temperature produces a better-quality biochar in terms of the nutrients content, porosity and surface area (Putun et al., 2005; Lehmann et al., 2006; Tan et al., 2017; Xu et al., 2017). The yield of biochar and the content of organic compounds decrease when the pyrolysis temperature increases whilst the mineral materials and the syngas yield increase (Al-Wabel et al., 2013; Jin et al., 2016).

High pyrolysis temperature stimulates the transformation of biomass organic constituents into volatiles and gases leaving behind mineral compounds such as P, Mg and Ca which have become concentrated in the biochar (Zhang & Wang, 2016). Meanwhile, the yield of biochar and acidic functional groups decrease when the pyrolysis temperature increases while the yield of ash content, carbon stability and pH increase (Zhang et al., 2015). Organic functional groups such as —COOH and —OH can be destroyed by high

pyrolysis temperature and this could lead to an increase in the pH. Cracking of the organic functional groups usually occurs at a higher temperature (Al-Wabel et al., 2013).

2.2.4 Differences between Biochar and Charcoal

Biochar and charcoal production methods are similar where both materials are derived through pyrolysis process from the carbonaceous feedstock (Aller, 2016). Both biochar and charcoal are black in colour as they have high carbon (C) substances. However, they are technically two different products and they can be differentiated by their starting material and end application as illustrated in Table 2.2:

Table 2.2: Comparisons between biochar and charcoal

Description	Biochar	Charcoal
Definition	Carbonized biomass ^a .	Carbonized wood ^b .
Feedstock	Plant biomass and animal manures.	Wood.
Purposes	Uses for agricultural purposes, e.g., soil amendment and carbon sequestration ^c . Uses as a feed supplement to improve the health and productivity of ruminants or poultry ^d .	Uses as a smokeless fuel for cooking, heating and steel production ^e .
Production	Pyrolyses at the temperature of below 700°C and the gases released from the biomass during heating are captured and combusted. It can used as a form of clean energy ^f .	Produces at low temperature in a smoldering process that is highly polluting ^{g,h,i} .
Morphology	Highly porous.	Cooking charcoal is not very porous because its pores are clogged with condensed soot, tar and oil.
Adsorption and surface area	High.	Low ^{j,k}

Table 2.2: Comparisons between biochar and charcoal

Description	Biochar	Charcoal
Ash content	Less ash content due to incomplete carbonization process ^{b,l} .	0.5% to more than 5% ⁿ .

^a Glaser et al. (2002), ^b Lehmann et al. (2009), ^c Lehmann et al. (2015), ^d Gerlach & Schmidt (2012), ^e Brown et al. (2015), ^f Lehmann, 2007, ^g Mara et al. (2006), ^h Adam (2009), ⁱ Pennise et al. (2001), ^j McClellan et al. (2007), ^k McLaughlin et al. (2009), ^l Abdelhafez et al. (2017), ⁿ Elías et al. (2019)

As charcoal briquettes are typically produced from de-volatilized coal, it cannot be utilized as biochar. Charcoal should not be used in the soil because it contains chemicals that can be toxic to plant growth (McLaughlin et al., 2009). Lumps of charcoal produced from oak or kiawe (mesquite) are specially designed for cooking fuel purpose. Charcoal contains unwanted resins, tars, polycyclic aromatic hydrocarbons (PAH) and charcoal generally has lower adsorption capacities, limiting their capability to enhance soil quality (McClellan et al., 2007; McLaughlin et al., 2009).

The organic part of biochar has a high C content which mostly appears in aromatic compounds characterized by rings of six carbon atoms connected together without hydrogen (H) or oxygen (O). It is different from graphite as the aromatic rings in graphite are arranged on perfectly stacked and aligned sheets. Graphite does not form under the temperatures that are applied for producing biochar because the structures of carbon atoms in the biochar are altered by H and O ions; thus, C atoms are linked and organized in irregular forms depending on the sort of biomass used for the biochar production and the pyrolysis temperature (Lehmann et al., 2009).

2.3.1 Biochar Physicochemical Characteristics

The properties, composition and yield percentage of biochar are determined by various factors. Their physicochemical characteristics are governed by plant feedstock and pyrolysis conditions (Enders et. al., 2012). Biochar produced from relatively low pyrolysis temperature contains high volatile matter that holds easily decomposable substrates, which has the potential to enhance plant growth (Robertson et al., 2012; Mukherjee et al., 2013). Conversely, biochar derived from high pyrolysis temperature is predominated with aromatic carbon possessing large surface area, which may increase the adsorption capacity and recalcitrant characteristic (Lehmann, 2007).

2.3.2 Ash, Mineral Elements and pH of Biochar

During pyrolysis, the organic materials begin to decompose at above 120 °C; hemicellulose decomposes at 200 - 260 °C whilst lignin decomposes at 240 - 350 °C. (Sjostrom, 1993). Heating has led to the volatilization of some nutrients, particularly those at the surface of the materials, whereas other nutrients become concentrated and thus, remain in the biochar (Abdelhafez & Li, 2016). The volatile components of biochar decrease along with the composition of H and O in pace with the increase of temperature; whilst carbon and ash contents gradually increase (Cao & Harris, 2010). Typically, biochar contains more than 60% carbon with other elements including H, O, N and S (Wang et al., 2018). For wood-rich materials, carbon starts to volatilize at 100 °C, N above 200 °C, sulfur (S) above 375 °C, K and P between 700 °C to 800 °C whilst Mg, Ca and manganese (Mn) decompose at a temperature of above 1000 °C (Neary et al., 1999; Knoepp et al., 2005). Xu et al. (2012) and Cao and Harris (2010) verified that majority of biochar are alkaline and the alkalinity increases with the increasing pyrolysis temperature because it

contains a considerable amount of alkali salt, alkali metal ions (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and CaCO_3 , offering liming effect. It can raise the pH of acidic soil, which promotes metal hydroxide precipitation and adsorption of heavy metals (Ahmed et al., 2014).

2.3.3 Aromatic Properties of Biochar (H/C and O/C)

Chun et al. (2004) and Chen et al. (2008) verified that H/C and O/C are the main factors that can affect the aromatization of biochar and their ratios are useful indicators for biochar characterization (Nguyen & Lehmann, 2009). In fact, the aromaticity of biochar depends on the pyrolysis temperature; the pore structure and crystalline structure change significantly with the rise of temperature. Lignin and cellulose in plant residue biochar break down into smaller molecules during the process of dewatering and polymerization, resulting in lower H/C and O/C. The increase of temperature would lead to a greater loss of H and O compared to C (Jindo et al., 2014). The dehydrogenation of CH_3 caused by thermal induction signifies a change in the biochar recalcitrance (Harvey et al., 2012). Biomass substances generally comprise of labile and recalcitrance O fractions; the former vanishes promptly after preliminary heating while the latter is retained in the char of the final product (Rutherford et al., 2012). Chen et al. (2008) suggested the aromaticity structure of biochar can form π bond with pollutants as it can function as a π -electron donor or acceptor, further influencing the adsorption of pollutants on biochar.

2.3.4 Surface Structure and Functional Groups

The surface structure and morphology of biochar are affected by the raw materials and pyrolysis temperature. When the pyrolysis temperature increases to 600 °C, the H- and O- holding functional groups, including phenolic -OH, aromatic -CO, ester C=O and

aliphatic alkyl-CH₂ groups will be obliterated and this will lead to the exposure of aromatic lignin nucleus improving the surface area (Chen et al., 2008). High pyrolysis temperature biochar has a strong aromaticity and its heavy metals adsorption is mostly related to the specific surface area and π -bond; conversely, low pyrolysis temperature biochar contains additional oxygenated functional groups, and its adsorption is associated with the complexation with functional groups (Wang et al., 2018). The presence of functional groups and macropores with an average size of 51-138 m²g⁻¹ (Laine & Yunes, 1992) have been reported to have the ability to remove organic and inorganic pollutants from aqueous solutions (Abdelhafez & Li, 2016).

2.4.1 Biochar Application as a Soil Enhancer

Biochar is commonly used as a soil enhancer as it has marvelous potential in improving soil quality. When biochar is applied to the low fertility soil, it is beneficial to plant growth and biomass production (Lehmann et al., 2003; Zhang et al., 2010). The interactions of biochar with soil, plant roots and microbes facilitate the positive effects of biochar. Adsorption-desorption, acid-base, redox reactions and dissolution-precipitation are the reactions that may occur after the addition of biochar into the soil (Joseph et al., 2010).

Biochar addition can improve the soil water holding capacity as biochar can assist in water retention which is attributed to its high porous texture (Glaser et al., 2002; Belanger et al., 2004; Keech et al., 2005; Liang et al., 2006). Furthermore, the addition of biochar to soil can increase the CEC, reducing the loss of nutrients through leaching (Lehmann 2007). This is corroborated with the findings that certain biochar has the ability to adsorb ammonium (Thomsen et al., 2011; Yao et al., 2012; Spokas et al., 2011) and

reduce leaching of NO_3^- and PO_4^{3-} (Beck et al., 2008; Laird et al., 2010; Yao et al., 2012; Mukherjee & Zimmerman, 2013; Zheng et al., 2013; Sika & Hardie, 2014). As biochar possesses negatively charged surface area, it has the ability to hold nutrients which are positively charged, increasing the nutrient use efficiency that could otherwise be washed away during precipitation.

As most of the high pyrolysis biochar are alkaline (Jiang et al., 2012), Glaser et al. (2002) revealed that biochar has a liming effect on soil as the incorporation of biochar to acidic soil has indicated an increase in soil pH. The increase of soil pH can suppress the activity of enzymes that is involved in the conversions of nitrite to nitrous oxide, which will in turn increase nitrogen availability in soil (Zhang et al., 2009). Biochar has the capability to adsorb inorganic nutrients, soluble organic matter, gases and intricate internal structure which is attributed to its large surface area; it provides a suitable habitat for microorganisms. Consequently, the microorganism's population rises in the biochar amended soil and the effect of biochar fades away over time (Lehmann, 2007; Anderson et al., 2011; Rutigliano et al., 2014).

Scientific studies concluded that the porous structure associated with a large surface area of biochar (Thies & Rillig, 2009; Atkinson et al., 2010; Beck et al., 2011) can enhance plant growth by improving soil physical and chemical properties including pH (Dias et al., 2010; Yuan & Xu, 2011), water holding capacity (Beck et al., 2011; Karhu et al., 2011), CEC (Liang et al., 2006; Yuan & Xu, 2011) and nutrient retention (Dias et al., 2010; Beck et al., 2011). However, soil fertility and fertilizer management are the main factors influencing the outcome of biochar as a soil ameliorator (Asai et al., 2009).

Researches in both tropical and temperate regions verified that biochar has the potential to enhance plant growth, improve water retention, reduce nutrients leaching, and

boost microbial activity. Based on a study done on Columbian Oxisol, the incorporation of 23.2 tons of biochar per hectare has increased the total above-ground biomass by 189 percent (Major et al., 2005). Both biological nitrogen fixation and beneficial mycorrhizal rapports in common beans (*Phaseolus vulgaris*) have been boosted by biochar application (Rondon et al., 2007; Warnock et al., 2007). The plant growth has improved evidently over time after biochar application (Cheng et al., 2006; Cheng et al., 2008; Major et al., 2010). Zheng et al. (2013) reported that N leaching has been reduced and N retention and bioavailability have been increased in the agricultural soils after the addition of 5% slow pyrolysis giant reed grass biochar.

2.4.2 Negative Effects of Biochar on Plant Growth

Some studies indicated that biochar has adverse effects on plant growth. Although biochar possesses some ash such as Ca, K, and Mg that can supply nutrients to plants, these nutrients are usually limited in infertile soils. Provisional levels of pH, mobile matter (MM) and nutrients imbalances associated with fresh biochar could be the reasons of the decreased in plant growth after the incorporation of biochar in most cases (McClellan et al., 2007).

Biochar is usually alkaline and it is suitable to be applied in acidic degraded soils; nevertheless, if the soil pH is too alkaline, plants may suffer nutrient deficiencies. As reported by Sika and Hardy (2014), the application of 2.5 and 10% pine wood slow pyrolysis biochar (450 °C) to sandy soil has facilitated to over-liming causing some doubts regarding the practical use of biochar in improving N fertilizer-use efficiency of plants. Hence, biochar should be selected carefully prior to its application. For example, high temperature or aged biochar are recommended to be used at the sandy soils due to they

have a lower tendency to release sudden pulses of nutrients (Mukherjee & Zimmerman, 2013).

In addition, biochar contains mobile matter that can restrain plant growth. According to McClellan et al. (2007) and McLaughlin et al. (2009), mobile matter refers to resins, tars and other short-lived substances that attach on the surface of biochar after its production. The quantity of mobile matter can be decreased through good production practices. Carbon-rich mobile matter can be decomposed and transformed into nutrient for plants *via* microbial activities. The microorganisms would require nitrogen in this process. This will cause the nitrogen to be unavailable for plants uptake provisionally. Nevertheless, these transitional imbalances can be corrected after the pH is neutralized, the mobile matter is decomposed, and the unavailable nutrients are released (Hunt et al., 2010).

2.4.3 Quality of Biochar

The type of feedstock and the conditions of biochar production determine the quality of biochar for soil amendment (McClellan et al., 2007; McLaughlin et al., 2009). The physical formation of feedstock, particularly its pore size, highly influences water retention capacity, surface area and biological application of the biochar produced (Hunt et al., 2010). High cation exchange capacity and high adsorption capacity with low level of mobile matter (resins, tars and other short-lived compounds) are the most important measurements of biochar quality (Glaser et al., 2002; Liang et al., 2006; McClellan et al., 2007; McLaughlin et al., 2009).

Over time, the adsorption capacity of biochar decreases while its cation exchange capacity increases (Cheng et al., 2008; McLaughlin et al., 2009). The porosity of biochar can be blocked by mobile matter but it is prone to biological decay. Warnock et al. (2007)

suggested that larger proportion of micro-pores may produce a higher surface area which will increase nutrient retention capacity. However, only certain soil microorganisms can gain benefit from the micro-pores as most of them are too large to make use of such small spaces. Therefore, biochar with assorted pore sizes may be the best to improve the chemical, physical and biological characteristics of soil for the benefit of plant growth.

2.4.4 Life Span of Biochar

Cheng et al. (2008) and Liang et al. (2008) proposed that biochar has a mean residence time in soils on the order of 1300-4000 years in accordance with the prediction of laboratory experiment. This is corroborated by the findings on *Terre Preta* soils in Amazon Basin; further, the naturally occurring biochar resulting from forest and vegetation fires has proven that biochar with very little decay can persist for millenia.

2.4.5 Dosage of Biochar

To date, the data available for the determination of the optimal biochar incorporation rates in dissimilar soils and cropping systems is scanty. Thus, there is no specific recommended rate for biochar application as it depends on the soil type and plants (Julie, 2010). Based on the informal observations, the ideal biochar application rate is between 5-20% by volume of soil (Hunt et al., 2010). Some studies revealed that minor application rates have shown affirmative outcomes (Glaser et al., 2002). The rates recommended by the literature are 5-50 tonnes per hectare (Julie, 2010) whilst the percentage reported may range from 2-15% (Dalila et al., 2016; Yang et al., 2016) for positive effects on plants.

2.5.1 Nitrogen Content in Biochar

Nitrogen is the most susceptible macronutrient under temperature, thus biochar produced under high temperature is characterized by its low nitrogen content (Tyron, 1948). During the pyrolysis process, N begins to volatilize at above 200 °C (Neary et al., 2005) and this has led to the depletion of nitrogen relative to other thermally stable nutrients. Gundale and DeLuca (2006) suggested that the increase of pyrolysis temperature will facilitate the decrease in extractable NH_4^+ and PO_4^{3-} as a portion of NH_4^+ will be oxidized to a small exchangeable NO_3^- pool at a higher temperature. Hence, instead of being a primary source of nutrients, biochar is more likely to function as a soil conditioner and driver of nutrient transformation (Glaser et al., 2002; Lehmann et al., 2003).

2.5.2 Influences of Biochar on Soil Nitrogen Transformations

Vitousek and Howarth (1991) reported that nitrogen is the most limiting plant nutrient in the cold and temperate terrestrial ecosystem. Most of N exists in complex organic forms in soil. Before plants uptake, it is essential for the complex organic N to be ammonified to NH_4^+ and subsequently nitrified to NO_3^- (Stevenson & Cole, 1999). Hence, N transformations on ammonification, nitrification, denitrification and N_2 -fixation could be influenced by the incorporation of biochar to mineral soils (DeLuca et al., 2009).

2.5.3 Ammonification and Nitrification

The transformation of organic N into inorganic N through ammonification (where NH_4^+ is formed) and nitrification (where NO_3^- is formed) is termed as nitrogen mineralization. Heterotrophic bacteria and a range of fungi are the primary factors that determine the biotic process of ammonification (Stevenson & Cole, 1999). Meanwhile,

autotrophic organisms such as bacteria and archaea in agricultural, grassland and forest soils mediate the biotic process of nitrification (Stevenson & Cole, 1999; Grenon et al., 2004; Leininger et al., 2006; Islam et al., 2007).

Net nitrification rates have been increased in temperate and boreal forest soils that otherwise show no net nitrification (Berglund et al., 2004; DeLuca et al., 2006). Nevertheless, there is no significant nitrification effect in the agricultural soils (Lehmann et al., 2003; Rondon et al., 2007) and this is corroborated by the findings of DeLuca et al. (2006) in the grassland. As reported by DeLuca et al. (2009), biochar additions to phenol-rich soils has the ability to activate nitrification but this effect was not observed in the agricultural and grassland soils. As a result of NH_4^+ adsorption or enhanced immobilization, it may show a minor decline in net ammonification.

2.5.4 Mineralization

Mineralization is the decomposition (i.e., oxidation) of chemical compounds in organic matter, whereby nutrients are released in soluble inorganic forms that may be available to plants (Beare et al., 1994; White, 2005). It is opposite from immobilization. The bioavailability of nutrients particularly nitrogen, phosphorous and sulfur can be raised by mineralization. The specific element will be mineralized if its concentration surpasses the demands of the decomposer for biosynthesis or storage.

2.5.5 Immobilization

The transformation of inorganic compounds to organic compounds by microorganisms or plants, by which it is prohibited from uptake by plants is termed as immobilization (White, 2005). All living creatures demand N. Hence, there is a

competition for N between the microorganisms in soil and plants. Immobilization refers to the process when inorganic nutrients (nitrate and ammonium) are utilized by soil microorganisms rendering them unavailable to plants. The addition of high carbon to nitrogen ratio materials particularly biochar will raise biological activity and facilitate a higher demand for N, resulting in N immobilization.

Some studies suggested that NH_4^+ and NH_3^- can be absorbed by biochar from soil solution (Lehmann et al., 2006), dropping inorganic N solution provisionally, but possibly concentrating it for microbial use. Zackrisson et al. (1996) and Wardle et al. (1998) proposed that biochar in soil could be occluded with organic matter whereas Brodowski et al. (2006) suggested that biochar could aggregate mineral and organic matter fractions into physically protected pools. As a result, the N in those organic matter pools may persist inaccessible for plant uptake for a period of time.

Biochar is a nitrogen depleted substance and it is exceptionally high in C/N ratio. Schneour (1996) and Liang et al. (2006) anticipated that some decomposition may happen after fresh biochar is incorporated into soil. As a result, net immobilization of inorganic N which has existed in the soil solution could be stimulated. The microbes degraded residue bio-oil (Streiner et al., 2007) and the surface functional groups (Liang et al., 2006) of low temperature biochar tends to induce net immobilization. Leaching of inorganic N in highly weathered soil could be reduced by a temporary organic N reservoir generated by the immobilization process (Streiner et al., 2007).

2.5.6 Volatilization

Ammonia volatilization is a process when ammonia gas is emitted from the soil to the atmosphere. Stevenson and Cole (1999) revealed that alkaline pH may induce ammonia

volatilization in agricultural soils. The pH of acidic soil can be raised by the addition of biochar (Glaser et al., 2002), but would not reach the rate that can increase ammonia volatilization (Stevenson & Cole, 1999). A reduction in NH_4^+ concentration has been found in the agricultural soils and acid forest soils after the incorporation of biochar. It could be either due to NH_3 volatilization or the surface adsorption of biochar (Le Leuch & Bandosz, 2007), reducing soil NH_4^+ concentrations and decreases the potential for NH_3 volatilization (DeLuca et al., 2009).

2.5.7 Denitrification

A biotic dissimilatory process whereby NO_3^- is reduced to N_2 (g) in the absence of oxygen is referred to denitrification. When the situations are not favorable for a complete reduction of NO_3^- during the reductive process, some intermediates (including NO and N_2O) will be formed and they are potentially released into the soil atmosphere. Biochar could induce the reduction of N_2O to N_2 , which indirectly alleviate climate change by reducing N_2O emission (DeLuca et al., 2009).

2.5.8 Carbon to Nitrogen Ratio

Carbon and nitrogen in soils are the main components of organic content where the C:N ratio is an indicator of soil fertility (Kanokporn, 2015) because it could have a significant effect on crop residues decomposition. C:N ratio of the decomposing organic matter determines the mineralization and immobilization of nitrogen in soil (McLaren & Cameron, 1996). The soil organic matter mineralization would happen at the C:N ratio of below 25 (Qi et al., 2013) whereas N immobilization would occur at the C:N ratio of 25 and above.

As reported by United States Department of Agriculture (USDA, 2011), soil microbes have a C:N ratio of 8:1. They must integrate into their cells 8 parts of carbon for every 1 part of N. Soil microbes use carbon as a source of energy. During their respiration, certain amount of carbons is lost as carbon dioxide. Therefore, not all the carbons consumed by a soil microbe remains in its body. To stay alive with attaining sufficient body maintenance and energy, a soil microbe requires about 1 part of N for every 24 parts of C in its diet where 8 parts of C use for maintenance and 16 parts for energy. Thus, the soil is ruled by 24:1 (C:N) ratio (USDA, 2011).

Caley and Jodi (2019) suggested that soil microorganisms will obtain a perfect balance of energy and nutrients from the residues with a C:N of about 25:1. When the C/N ratio of organic matter is about 25:1, soil microbes will have to scavenge the soil solution to gain sufficient N. As a result, plants will undergo N deficiency by the decrease of soil natural N with the addition of high C/N residues. Conversely, when the C/N ratio is lesser than 20, organic matter aids in increase in N content of soil for plants and organisms. This is corroborated with the findings of Kanokporn (2015) that mineral N is released in the early stage of decomposition process if the C:N ratio is below 20.

Eventually, soil organic matter is a mixture of different types of residues, each with different C:N and decomposition speed. The C:N levels of residues are different than those of a soil sample. Soil C:N ratios are typically low (around 12:1), and that reflects the C:N of the mineral, organic and living portions of the soil (Caley & Jodi, 2019). When the C:N ratio is lesser than 25:1, such as manure (20:1) or alfalfa (12:1), microbes can obtain plenty of nutrients from the residues, resulting the release of nitrogen (mineralized) into the soil. The decomposers remain active and decomposition happens rapidly when they are

provided with sufficient nutrients from the residues as per illustrated at Figure 2.1 (Caley & Jodi 2019),

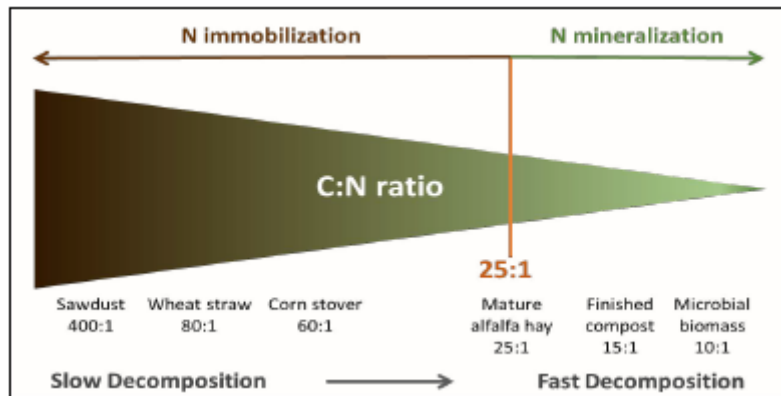


Figure 2.1: C:N ratio of N mineralization and immobilization

2.5.9 ¹⁵N-Pulse-Chase Experiment

¹⁵N-pulse-chase analysis is a technique used to investigate cellular process for a period of time by consecutively disclosing the cells to a labeled compound (pulse) and then to the same compound in an unlabeled form (chase) (Takahashi, 2003). It is a practical method to determine the activity of certain cells over an extended period of time. As reported by Evans (2007) and Pardo et al. (2006), the deployment of nitrogen isotopes technique has increased over the past decade to evaluate N cycling and status, including responses to the disturbance in the plant ecosystem.

Nevertheless, research in large-scale field experiments with ¹⁵N technique is restricted because of the high cost of the labeled product. Furthermore, specialized technical assistance in the elaboration of sampling procedure in mass spectrometry analysis is required. Researchers who use isotopic N typically apply ¹⁵N jointly with N fertilizer treatments at low enrichment rates of about 5% atom ¹⁵N or use ¹⁵N depleted fertilizers in

open or closed systems due to the pricey ^{15}N products (Coelho et al., 1991; Boaretto et al., 2004; Gallais et al., 2006).

In the previous studies, ^{15}N has been used in quantifying nitrogen recovery efficiency of coated urea in potato field (Zvomuya et al., 2003) and nitrogen uptake efficiency of *Arabidopsis* (Chardon et al., 2010). Other than that, ^{15}N has also been utilized as tracers to estimate N_2 fixation (Chalk, 1985; Danso, 1986; Hamilton et al., 1991; Chalk, 1996; Alves et al., 2000), N deposition in field (Böhme & Russow, 2005) and to determine nitrogen leaching from fertilizer (Bergstrom & Kirchmann, 2004).

CHAPTER 3

METHODOLOGY

This study comprises of three parts: 1) Characterization of EFB and PKS biochar; 2) Field study to evaluate the effects of EFB biochar and PKS biochar as a soil amendment on oil palm seedlings; 3) Determination on the transfer of N in oil palm seedlings with and without biochar.

3.1.1 Production of Biochar

The EFB and PKS biochar used in this study were provided by the Malaysian Palm Oil Board (MPOB). The pressed-shredded EFB and raw PKS biochar were obtained from Ulu Kanchong Palm Oil Mill of Negeri Sembilan, Malaysia. The EFB and PKS were sun dried until their moisture content were below 10% prior to the pyrolysis process. After that, the EFB and PKS were heated respectively through a closed-system brick reactor which was built with double walls of clay bricks (1000 mm x 1000 mm external dimension, 220 mm thick). The kiln has been modified with an air suction blower to fix the air flow rate at 36m³/hour for ensuring a uniform circulation and distribution of hot air from top to bottom prior to discharge through a 3 meters chimney (Idris et al., 2015b).

Approximately 30 kg of the EFB or PKS was fed into the reactor. Fire was ignited manually at the top of reactor using a portable propane gas burner. The reactor's cover was closed tightly to avoid the entrance of oxygen and the carbonization temperature was self-sustained by itself using feedstock biomass as a fuel. The feedstock was burnt at the temperature between 300 – 500 °C (Idris et al., 2015a). After that, it was left to cool and collected on the next day.

3.1.2 Characterization of Biochar

The EFB and PKS biochar were subjected to analysis including the loss on evaporation, loss on ignition, pH, conductivity, cation exchangeable (K^+ , Mg^{2+} , Ca^{2+}), cation exchange capacity (CEC) (Malaysian Standard 678: Part VI-IX: 1980; Malaysian Standard, 679: Part I-V: 1980), nitrogen (N), phosphorous (P), potassium (K), magnesium (Mg), calcium (Ca), boron (B), zinc (Zn), copper (Cu) (Malaysian Standard: 677, Part I-VIII, 1980).

The morphological characteristics were evaluated using Scanning Electron Microscope (JOEL JSM-6390LA SEM, Japan) whilst Fourier Transform Infrared (Thermo Nicolet iS10 FTIR, USA) was used for functional group characterization.

3.2.1 Field Study

A total of 108 oil palm seedlings at seven months-old were supplied by the estate of Sarawak Oil Palm Plantation and their progeny are Applied Agricultural Hybrida. The seedlings were subjected to treatments with EFB and PKS biochar at 0% (T1), 1.5% (T2) and 3.0% (T3), each constituted 54 seedlings. They were transplanted into polybags containing 17.38 kg of mineral top soil with or without biochar accordingly. The pretreated soil properties were evaluated prior to the field study; these include pH, conductivity, moisture and ash content, total nitrogen, total phosphorous, available phosphorous, organic carbon, exchangeable cations, CEC and particle size analysis.

Note that the amount of biochar added is calculated in relative to the dry weight of the soil where the average moisture content was determined at 13.61%. As the average moisture content of EFB biochar was determined at 50%, 1.5% refers to the addition of 0.45 kg EFB biochar to each polybag containing soil with dry weight of 15 kg whilst 3.0%

represents 0.90 kg EFB biochar. On the other hand, the average moisture content of PKS biochar was determined at 3.91%. Hence, 1.5% refers to the addition of 0.234 kg PKS biochar to each polybag containing soil with dry weight of 15 kg whilst 3.0% represents 0.468 kg PKS biochar. Biochar was mixed homogeneously with the soil prior to transplanting. After transplanting, every plant height of the seedlings was recorded and the seedlings were set aside for two weeks for acclimatization.

Next, the seedlings were moved to the field and laid out in a randomized complete block design (RCBD). The polybags were placed above some bricks to avoid the root from penetrating the ground. The plant height was measured and recorded every two weeks.

3.2.2 Fertilizer Application

During the field study, urea and commercially available fertilizer were applied in accordance with the estate practice. Granular urea, rock phosphate (RP), Muriate of potash (MOP) and Kieserite were applied in accordance with the manuring programme tabulated in Table 3.1 and 3.2 according to palm age. The granular urea contains 46% of N, RP contains 27% of P_2O_5 whilst MOP and Kieserite both contain 60% of K_2O and 27% of MgO , respectively. At 7th month old, 2.61 g urea N, 4.44 g rock phosphate, 2.83 g potash and 0.74 g of Kieserite were mixed together and applied to each seedling. Note that there was a modification on the fertilizer application from an interval of two months to a month.

3.2.3 Vegetative Growth Measurement and Destructive Sampling

Weeding and irrigation were done manually for all seedlings throughout the experimental study. The oil palm seedlings were left to grow for a period of nine months. The plant height was measured every two weeks to monitor the growth rate of the

seedlings. For the fertilizer application with a two months interval, destructive sampling was carried out after a month whereas with the schedule of a monthly interval, destructive sampling was conducted after a week. The modification was for the purpose of reducing the fertilizers loss over time.

Three seedlings from each treatment were selected randomly for every batch of destructive sampling. Therefore, nine samples will be harvested per sampling. To destruct the sample, firstly, the seedlings was placed in a rectangular plastic tray and the polybag was torn off. The plant was chopped off from the roots and thereafter, the leaves were separated from the shoots and stems. The fresh weight of the leaves and stems were recorded. After that, the leaves and stems samples were placed in an oven at a temperature of 70 °C for three days to obtain a constant weight. Thereafter, the leaves and stems were weighed and recorded.

On the other hand, the roots were removed from the soil. All roots were collected in a tray and they were washed with water to remove the soil; they were left to dry before their weight were recorded. After that, they were placed in an oven at a temperature of 70 °C for three days to obtain a constant weight. The roots samples were weighed and recorded. Total plant biomass was the sum of the dried leaves weight, dried stems weight and dried root weight as per stated in the equation below:

$$\text{Plant biomass} = (\text{dried leaves weight} + \text{dried stems weight} + \text{dried roots weight}) \text{ g}$$

Equation 3.1

The soil sample was mixed homogeneously and a small portion of the soil was collected and dried in the laboratory fan oven (Carbolite, AX120, United Kingdom) at a temperature of 40 °C for three to five days to obtain a constant weight.

Then, the leaves, roots and stems were ground into powder form and analyzed for N, P, K, Mg, Ca, B, Zn and Cu. The soils were also analyzed for pH, EC, loss on evaporation and ignition, total N, organic carbon, total P, available P, exchangeable cations (K, Mg and Ca), CEC and particle size. Note that ^{15}N pulse chase experiment was only conducted in the treatment with PKS biochar with seedlings at 9th month old.

Table 3.1: Fertilizer programme for treatment with EFB biochar

Treatment	Seedling age (month)	Amount of N (g)	Amount of Urea (46%N) per seedling (g)	Amount of P ₂ O ₅ (g)	Amount of RP (27% P ₂ O ₅) per seedling (g)	Amount of K ₂ O (g)	Amount of MOP (60% K ₂ O) per seedling (g)	Amount of MgO (g)	Amount of Kieserite (27% MgO) per seedling (g)
T1 (control)	7 th	1.20	2.61	1.20	4.44	1.70	2.83	0.20	0.74
	9 th	2.40	5.22	2.40	8.89	3.40	5.67	0.40	1.48
	11 th	3.60	7.83	3.60	13.33	5.10	8.50	0.60	2.22
	13 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	14 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	15 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
T2 1.5% biochar	7 th	1.20	2.61	1.20	4.44	1.70	2.83	0.20	0.74
	9 th	2.40	5.22	2.40	8.89	3.40	5.67	0.40	1.48
	11 th	3.60	7.83	3.60	13.33	5.10	8.50	0.60	2.22
	13 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	14 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	15 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
T3 3.0% biochar	7 th	1.20	2.61	1.20	4.44	1.70	2.83	0.20	0.74
	9 th	2.40	5.22	2.40	8.89	3.40	5.67	0.40	1.48
	11 th	3.60	7.83	3.60	13.33	5.10	8.50	0.60	2.22
	13 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	14 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	15 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11

Table 3.2: Fertilizer programme of treatment with PKS biochar

Treatment	Seedling age (month)	Amount of N (g)	Amount of Urea (46%N) per seedling (g)	Amount of P₂O₅ (g)	Amount of RP (27% P₂O₅) per seedling (g)	Amount of K₂O (g)	Amount of MOP (60% K₂O) per seedling (g)	Amount of MgO (g)	Amount of Kieserite (27% MgO) per seedling (g)
T1 (control)	7 th	1.20	2.61	1.20	4.44	1.70	2.83	0.20	0.74
	9 th	2.40	5.22	2.40	8.89	3.40	5.67	0.40	1.48
	11 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	12 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	13 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	14 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
T2 1.5% biochar	7 th	1.20	2.61	1.20	4.44	1.70	2.83	0.20	0.74
	9 th	2.40	5.22	2.40	8.89	3.40	5.67	0.40	1.48
	11 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	12 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	13 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	14 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
T3 3.0% biochar	7 th	1.20	2.61	1.20	4.44	1.70	2.83	0.20	0.74
	9 th	2.40	5.22	2.40	8.89	3.40	5.67	0.40	1.48
	11 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	12 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	13 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11
	14 th	1.80	3.92	1.80	6.67	2.55	4.25	0.30	1.11

3.2.4 ¹⁵N isotope Urea Analysis

Ten grams of the ¹⁵N labeled urea (Sigma-Aldrich, ≥ 99.0% purity) was used for the ¹⁵N-pulse-chase experiment. A 3.72% of the unlabeled urea was substituted with labeled urea to achieve a 4 atomic % enrichment. With 45 oil palm seedlings receiving 5.22 g of urea each, this gave a total application of 234.9 g of urea, 3.72 % of this was 8.74 g of the labeled urea. The remainder was 226.16 g of the unlabelled urea. These two quantities were weighed and dissolved in distilled water to a concentration that allowed aliquots to be taken that contained the desired dosage, 5.22 g of urea. Therefore, 8.74 g of the labeled urea and 226.16 g of the unlabeled urea were dissolved in 1350 mL of distilled water to make up a concentration of 0.174 g/mL for 45 applications with a 30 mL solution per seedling. The vessel containing the dissolved urea was well shaken before each application to ensure that the desired dosage was evenly applied. Destructive sampling was conducted a week after the fertilizer application. The dry and ground plant and soil samples were analyzed using a Sercon 20-20 Isotope Ratio Mass Spectrophotometer (IRMS) coupled with an automated nitrogen carbon analyzer- gases, solids, liquids (ANCA GSL, United Kingdom) at the University of Aberdeen.

3.2.5 Fertilizer N Yield Derived from ¹⁵N-Pulse-Chase Experiment

The unit of the ¹⁵N in plant and soil samples analysis was reported in delta ¹⁵N (δ¹⁵N) and it was expressed in part per thousand (‰). δ¹⁵N can be converted to atomic% when the enrichment is high using the following equation (Rattan and Steward, 2018):

$$\text{Atom\% } ^{15}\text{N in a sample} = \frac{100}{\frac{1}{A} + 1} \quad \text{Equation 3.2}$$

Where,

^{15}N is the nitrogen-15 isotope

A is the $[(\delta^{15}\text{N sample} / 1000) + 1]$ times R standard

R standard is the atom% ^{15}N in a standard divided by atom% ^{14}N in a standard (for atmospheric N_2)

$$\begin{aligned} \text{R standard} &= 0.3663 / (100 - 0.3663) \\ &= 0.0036765 \end{aligned}$$

The percentage of N derived from fertilizer (%NdFF) was calculated based on the isotope dilution technique using the following equation (IAEA, 1983):

$$\% NdFF = \frac{\% \text{ }^{15}\text{N atomic excess in plant sample}}{\% \text{ }^{15}\text{N atomic in fertilizer}} \times 100 \quad \text{Equation 3.3}$$

$$\begin{aligned} N \text{ yield} &= \text{Dry matter (DM) yield of plant} \times 100 \\ &= \text{Total N uptake in plant (g plant}^{-1}\text{)} \end{aligned} \quad \text{Equation 3.4}$$

$$\text{Fertilizer N yield} = \frac{N_{\text{yield}} \times \% Ndff}{100} \quad \text{Equation 3.5}$$

The ability of oil palm seedlings in taking up the N fertilizer was assessed by the total N uptake derived from the labelled fertilizer (Fertilizer N yield).

3.3.1 Preparation of Soil Samples

The dry soil samples were crushed by a mortar and pestle into powder and sieved through a 2 mm sieve and a 150 µm sieve. The sample from the 2 mm sieve was analyzed for pH, conductivity, loss on evaporation, loss on ignition, total P, available P, soil exchangeable (K, Mg, Ca), CEC and soil particle size analysis whereas the sample from the 150 µm sieve was used for total N and soil organic carbon analysis.

3.3.2 Determination of pH and electrical conductivity (EC)

The soil pH was measured with a pH meter (TRANS BP3001, Singapore) in a suspension of soil in water at a ratio of 1:2.5. Ten grams of soil was weighed into a plastic bottle and added with 25 mL of distilled water. It was agitated for one hour and left overnight. The suspension was agitated and read with the calibrated pH meter (Malaysian Standard 678: Part 1: 1980). The soil conductivity was measured with a conductivity meter (Eutech Con 5, Singapore) in the suspension of soil in water at a ratio of 1:5 according to the Malaysian Standard 678: Part VI: 1980.

3.3.3 Determination of Loss on Evaporation and Loss on Ignition

Soil moisture was estimated by loss on evaporation while total soil organic matter was determined based on loss on ignition. Ten grams of air-dried 2 mm soil was weighed into a silica crucible and it was dried in a laboratory fan oven (Carbolite, AX120, United Kingdom) at 105 °C overnight. The crucible was left to cool in a desiccator and weighed.

$$\% \text{ Loss on evaporation} = \frac{\text{Weight of air-dried soil} - \text{Weight of oven-dried soil}}{\text{Weight of air-dried soil}} \times 100\%$$

Equation 3.6

The crucible of the oven-dried sample was transferred to a muffle furnace (Daihan Scientific, CLF-M25, Korea). The sample was combusted in a muffle furnace at 800 °C for one hour. The crucible was left to cool and transferred to a desiccator. After that, the crucibles were weighed to obtain a constant weight.

$$\% \text{ Loss on ignition} = \frac{\text{Weight of air-dried soil} - \text{Weight of ignited soil}}{\text{Weight of air-dried soil}} \times 100\% \quad \text{Equation 3.7}$$

3.3.4 Determination of Soil Organic Carbon

Walkley and Black rapid titration method was used to analyze the organic carbon present in soil. The organic carbon in soil was estimated by oxidizing the soil with potassium dichromate in concentrated sulphuric acid followed by back titration with unutilized dichromate and ferrous ammonium sulphate with diphenylamine as an indicator (Malaysian Standard 678: Part III: 1980).

One gram of ground 100 mesh sieve (150 µm) was weighed into a conical flask. Ten millilitres of 1 normality of potassium dichromate was pipetted into the soil. The flask was swirled gently to disperse the soil in the solution. Twenty millilitres of concentrated H₂SO₄ (98%) was added and swirled gently until the soil and reagents were mixed evenly. The mixture was left for half an hour to allow for the reaction to take place. After that, 100 mL of distilled water and 4 mL of concentrated phosphoric acid (85%) were added. Next, 15-20 drops of 2% diphenylamine indicator were added until the solution turned purple. The sample solution was titrated with 1/3 normality of ferrous ammonium sulphate until the colour changed from purple to dark green. A blank was titrated similarly. The amount of organic carbon oxidized is expressed in percentage in accordance with the mass of soil as follows:

$$\frac{(\text{Volume of } K_2Cr_2O_7 - \text{Volume of } Fe^{2+} \text{ salt}) \times 0.003 \times 100\%}{\text{Weight of soil taken (g)}}$$

Equation 3.8

Where,

$$\text{Volume of } Fe^{2+} \text{ salt} = \frac{\text{Volume of titrate} \times 10}{\text{Volume of blank}}$$

3.3.5 Determination of Soil Total N

Total N in soil was determined according to Kjeldahl digestion method (Malaysian Standard 678: Part II: 1980). A 0.5 g of ground soil was weighed into a Kjeldahl flask. One gram of catalyst mixture (selenium sodium sulphate) and 0.3 g of sodium thiosulphate 5 hydrate were added into the soil. In the fume cupboard, 5 mL of sulphuric–salicylic acid was added into the flask and shaken well. The Kjeldahl flask was heated gently on a digestion rack for about one and a half hours until the solution turned clear suggesting that the digestion was completed.

The digested solution was transferred into a distillation flask. Twenty-five millilitres of the 30% w/v NaOH and 5 mL of distilled water were added. The sample solution was distilled by a distillation unit (BUCHI K-360, Switzerland). The distillate was collected in a conical flask containing 20 mL of 2% boric acid added with 2 drops of screen purple indicator (a mixture of methyl red and methylene blue in ethanol). The indicator would change to green if NH_3 (aqueous) was present. The distillate was titrated against 0.02 N H_2SO_4 . The reading was recorded to obtain %N. A blank was conducted through the same digestion procedure and the titration result was corrected accordingly.

$$\text{Nitrogen, \%} = \frac{V \times 0.014 \times N \times 100}{W}$$

Equation 3.9

Where,

N is the normality of H_2SO_4 used in the titration

V is the volume of H_2SO_4 used in the titration

W is the weight in grams of sample taken for the determination

3.3.6 Determination of Soil Available P (Bray 2 method)

The available P was measured based on Bray's procedure modified by Arnold (1947) using hydrochloric acid and ammonium fluoride. The method is recommended as the most suitable method for Malaysian soil (Owen, 1953).

Two grams of soil (< 2 mm) was weighed into a conical flask. Twenty millilitres of extracting solution (mixture of 0.03 N NH_4F and 0.1 N HCl) was added. The suspension was agitated using an orbit shaker for 1 minute at 200 rpm, left to settle and filtered through a Whatman No. 1 filter paper. Five millilitres of the sample solution was pipetted into a specimen tube followed by 1 mL of acidified ammonium molybdate and 1 mL of 1% ascorbic acid. Then, 5 mL of extracting solution was added into the specimen tube. It was left for 2 hours until the mixture turned blue.

The above steps were repeated for blank and standards. The UV-Vis spectrophotometer (Shimadzu, UV1800, Japan) was corrected to zero with distilled water and the wavelength was set at 660 nm. Phosphorous in the extract, present as molybdenum-blue complex, was measured using colorimetric technique (Bray and Kurtz, 1945).

Readings for standards (0.2 ppm, 0.5 ppm, 1.0 ppm, 2.0 ppm and 4.0ppm) and unknown sample solutions were recorded and they were converted into ppm. If the reading fell outside the range of standards the sample was diluted with distilled water. Soil available

P can be obtained by multiplying the reading of the sample solution with 10 times dilution rate.

$$\text{Available P} = \text{Reading (ppm)} \times 10 \quad \text{Equation 3.10}$$

3.3.7 Determination of Soil Total P

The ground soil (100 mesh) was digested with sulphuric acid-perchloric acid (1:1). Total P in the digested solution was determined by the phosphovanadatemolybdate complex method of Hanson (1950). One grams of soil was weighed into a Kjeldahl flask. Ten millilitres of sulphuric-perchloric acid was added into the flask. The sample was left for digestion for 2 hours. After that, it was agitated and left to cool. The sample solution was filtered with a Whatman filter paper into a 50 mL volumetric flask and made up to volume. It was left for overnight.

Two milliliters of sample solution was pipetted into a glass specimen tube and 4 mL of vanadate-molybdate was added into the specimen tube. The solutions were left for an hour for color development and analyzed using a UV-visible spectrophotometer (Shimadzu, UV1800, Japan) at 425 nm. The spectrophotometer was corrected to zero with distilled water. The reading was recorded and converted to ppm. The procedure was repeated for blank and standards (2 ppm, 4 ppm, 8 ppm, 10 ppm and 20 ppm). Soil total P can be obtained by multiplying the reading of the sample solution with 50 times dilution rate.

$$\text{Total P} = \text{Reading (ppm)} \times 50 \quad \text{Equation 3.11}$$

3.3.8 Determination of Soil cation Exchange Capacity (CEC)

Leaching the soil continuously with neutral ammonium acetate solution is the technique employed to evaluate the soil CEC. Ten grams of soil was weighed and leached

with 100 mL of 1 N ammonium. The mixture was filtered through a Whatman filter paper into a volumetric flask. The ammonium acetate filtrate was collected for the determination of exchangeable K^+ , Mg^{2+} and Ca^{2+} (Malaysian Standard 679: Part IV: 1980).

After that, the soil was washed with 100 mL of denatured alcohol (95%) to remove any excess ammonium ion. The presence of NH_4^+ was tested using Nessler's reagent. The washing was repeated until no red or brown precipitate was observed. The soil was left to dry before leaching with KCl. A total of 100 mL KCl (0.1 N) was added slowly to the soil. The mixture was filtered and collected in a 100 mL volumetric flask.

Twenty-five millilitres of filtrate was distilled with a distillation unit (BUCHI K-360, Switzerland) The distillate was collected in a conical flask containing 20 mL of 2% boric acid added with 2 drops of screen purple indicator (a mixture of methyl red and methylene blue in ethanol). The distillate was titrated against 0.02 N H_2SO_4 . The reading was recorded to obtain CEC (cmol(+)/kg). A blank was conducted and the titration result was corrected accordingly (Malaysian Standard 679: Part V: 1980).

$$CEC = \frac{W \times V \times 100}{25 \times N} \quad \text{Equation 3.12}$$

Where,

W is the weight in grams of sample taken for the determination

V is the volume of H_2SO_4 used in the titration

N is the normality of H_2SO_4 used in the titration

3.3.9 Soil Particle Size Analysis (Pipette Method)

Sand, silt and clay fractions were determined. The international scale defines the particle size of various fractions as follows:

- Particle size greater than 2.0 mm are stones or gravel and is not considered as soil material.
- Coarse sand (0.2 - 2.0 mm)
- Fine sand (0.02 - 0.2 mm)
- Silt (0.002 – 0.02 mm)
- Clays (< 0.002 mm)

When a soil sample was stirred or shaken in a 500 mL cylinder, heavy and large particles such as coarse and fine sand (2.0 - 0.02 mm) would settle to at least 10 cm after 4 minutes at 30 °C whereas the clay and silt particles stay in suspension. A sample that was withdrawn from a depth of 10 cm after 4 minutes contained only silt and clay. After 6 hours 21 minutes at 30 °C, silt size particles would settle to at least 10 cm, and only the clay stays in suspension. A sample that was withdrawn from a depth of 10 cm after 6 hours 21 minutes contained only clay.

Ten grams of soil was weighed and combined with 30 mL of water, a few drops of ammonia and 10 mL of 20% v/v H₂O₂. The solution was allowed to react until the reaction was completed. The soil solution was then heated gently for 15 minutes. The soil solution was allowed to cool. Ten millilitres of sodium hexametaphosphate was added and stirred. It was left to stand overnight. After that the soil solution was stirred at 1000 rpm for 10 minutes. The mixture was transferred into a 500 mL measuring cylinder and made it up to 500 mL with tap water. After that, it was closed with a stopper. The solution in the cylinder was agitated and left to stand overnight.

The soil solution was mixed vigorously by rotating the covered cylinder hand-over-hand for at least 10 minutes. It was allowed to stand for 4 minutes. The petri dish was

weighed. After 4 minutes, the pipette was placed at 10 cm below the surface of the solution and 10 mL of solution was collected and transferred into a petri dish. Likewise, 10 mL of the sample was pipetted into a petri dish after 6 hours 21 minutes to obtain the clay fraction. The petri dishes containing the soil solutions were placed in an oven at 100 °C. They were left to dry overnight and weighed. The silt and clay fractions were calculated as follows,

$$\text{Weight of silt + clay in 500 mL soil solution} = 50 \times [\text{Weight of silt + clay in petri dish, (W)}]$$

Equation 3.13

$$\text{Weight of clay in 500 mL soil solution} = 50 \times \text{Weight of clay in petri dish (W}_{\text{clay}})$$

Equation 3.14

$$\text{Thus, weight of silt} = W - W_{\text{clay}} = W_{\text{silt}}$$

Equation 3.15

The sand fraction would have settled down at the bottom of the cylinder. The suspension was poured away carefully, not to disturb the sand fraction. The sample was transferred into a beaker and water was added to 10 cm. At 30 °C, all sand would settle to the bottom of the beaker in 4 minutes after stirring. The supernatant suspension was decanted to remove silt and clay. The sand fraction was determined after drying in an oven. The sand fraction was categorized into coarse sand (CS) and fine sand (FS). The total weight was first measured; the fraction was then sieved through a 0.2 mm sieve to obtain coarse sand. The distribution of the respective fraction was calculated according to the following:

$$\% \text{ Clay} = \frac{\text{Weight of clay}}{\text{Weight of soil used}} \times 100 \%$$

Equation 3.16

$$\% \text{ Silt} = \frac{\text{Weight of silt}}{\text{weight of soil used}} \times 100 \% \quad \text{Equation 3.17}$$

$$\% \text{ Fine sand} = \frac{\text{Weight of FS}}{\text{weight of soil used}} \times 100 \% \quad \text{Equation 3.18}$$

$$\% \text{ Coarse sand} = \frac{\text{Weight of CS}}{\text{weight of soil used}} \times 100 \% \quad \text{Equation 3.19}$$

3.4.1 Preparation of Leaves, Stems and Roots Samples

Dried leaves, stems and roots sample were ground with a Christy and Turner grinder (United Kingdom) into powder and sieved through a 1 mm sieve. The samples were placed in 25 mm × 75 mm specimen tubes and dried in the Carbolite laboratoty fan oven (AX120, made in England) at 80 °C overnight. After that, they were ready for N, P, K, Mg, Ca, B, Zn and Cu analyses.

3.4.2 Ashing and Sample Solution Preparation

The organic matter in plant sample was destroyed *via* a dry ashing procedure before the ash content was determined. One gram of ground sample was weighed into a silica crucible. The sample was charred in a muffle furnace (Daihan Scientific, CLF-M25, Korea) at 300 °C for 1 hour, followed by a temperature of 500 °C for 5 hours until the carbon free ash was obtained. The crucible was left to cool in a desiccator and weighed (Malaysian Standard 677: Part II: 1980).

For the analyses of P, K, Mg and Ca, 10 mL of 20% HNO₃ was pipetted into a crucible containing ash sample of plant and digested on a water bath for 1 hour. For the analysis of Zn and Cu, 1 mL of concentrated HCl was pipetted into the crucible containing ash sample and was left to evaporate until dry. After that, 5 mL of 6 N HCl was added to the sample and digested on a water bath for 1 hour. The digested sample was then filtered

into a 100 mL volumetric flask and made up to mark before analysis for P, K, Mg and Ca. For Zn and Cu analysis, the sample was filtered into a 25 mL volumetric flask for analysis.

3.4.3 Determination of Nitrogen in Plant

Nitrogen are present in plant material in protein form. Protein-N in leaf is determined by measuring its nitrogen content. Nitrogen in plant was determined according to the wet ashing procedure. Protein nitrogen was converted to ammonium by heating it with concentrated sulphuric acid in the presence of a catalytic mixture of sodium sulphate and selenium. The ammonium content was then determined based on the Kjeldahl method (Malaysian Standard 67: Part III: 1980).

A 0.1 g of the plant sample was weighed into a Kjeldahl flask. A small spoon of catalyst mixture (~ 0.5 g) and 3 mL of concentrated sulphuric acid were added into the flask. The mixture was shaken well and heated gently until the mixture turned clear.

The digested solution was transferred into a distillation flask. Fifteen millilitres of NaOH (30% w/v) and 5 mL of distilled water were added. The samples solution was distilled by a distillation unit (BUCHI K-360, Switzerland). The distillate was collected in a conical flask containing 10 mL of 2% boric acid added with 4 drops of screen purple indicator (a mixture of methyl red and methylene blue in ethanol). The distillation continued for an additional 5 minutes. The indicator would change to green if NH_3 (aqueous) was present. The distillate was titrated against 0.02 N H_2SO_4 until the colour changed from green to purple. A blank was conducted through the same digestion procedure and the titration result was corrected accordingly. The N content was calculated as follows:

1000 mL of 1 N H₂SO₄ is equivalent to 14 g Nitrogen

1 mL of 1 N H₂SO₄ is equivalent to 14 mg Nitrogen

Therefore, nitrogen in sample = 14 × V × N mg

$$\% \text{ Nitrogen} = \frac{14 \times V \times N \text{ mg}}{W \times 1000} \quad \text{Equation 3.20}$$

Where,

N is the normality of H₂SO₄ used in the titration

V is the volume of H₂SO₄ used in the titration

W is the weight in grams of sample taken for the determination

3.4.4 Determination of Phosphorous in Plant

One milliliter of the digested sample solution was pipetted into a glass specimen tube containing 5 mL of ammonium vanadate/molybdate. (Malaysian Standard 677: Part IV: 1980). The mixture was left for 1 hour for yellow colour development. The UV-vis spectrophotometer (Shimadzu, UV1800, Japan) was corrected to zero with a blank solution at 425nm. The absorbance of the sample and a series of standards at the concentrations of 10 ppm, 15 ppm, 20 ppm and 25 ppm at 425 nm were measured with the spectrophotometer. The phosphorous content was calculated according to the following:

If the sample solution concentration is C ppm, then it contains C mg/L.

Therefore, % P in 1 g of plant sample is 0.1 C mg

$$\% \text{ P in 1g plant sample is } 0.1 \text{ C mg} \times 100 / 1000 \text{ mg} = 0.01C \quad \text{Equation 3.21}$$

3.4.5 Determination of Potassium in Plant

A 0.5 mL of the digested sample solution was pipetted into a flat bottom glass specimen tube (25mm x 75mm) with 10 mL of distilled water added. The amount of K of the sample was measured with the flamephotometer (Sherwood, 410, United Kingdom) based on series of standards at concentrations of 50 ppm, 100 ppm and 150 ppm (Malaysian Standard: Part V: 1980). The K content was calculated according to the following:

If the sample solution concentration is C ppm, then it contains C mg/L.

In 100 mL, the amount of K is 0.1 C mg

%K in 1 g plant sample is $0.1 \text{ C mg} \times 100 / 1000 \text{ mg} = 0.01\text{C}$ Equation 3.22

3.4.6 Determination of Calcium, Magnesium, Zink and Copper in Plant

A 0.5 mL of the digested sample solution was pipetted into a flat bottom glass specimen tube (25 mm x 75 mm). Then, 10 mL of 800 ppm strontium nitrate was added into the glass specimen tube and subjected to analysis with the atomic absorption spectrophotometer (Perkin Elmer, PinAAcle 500, Singapore). The amount of Ca of the sample was measured based on series of standards at concentrations of 20 ppm, 50 ppm, 70 ppm and 100 ppm (Malaysian Standard 677: Part VI: 1980).

If the sample solution concentration is C ppm, then it contains C mg/L.

Therefore, %Ca in 1 g of plant sample is 0.1 C mg

%Ca in 1 g plant sample is $0.1 \text{ C mg} \times 100 / 1000 \text{ mg} = 0.01\text{C}$ Equation 3.23

For Mg, 0.1 mL of the digested sample solution was pipetted into a flat bottom glass specimen tube (25 mm × 75 mm). Then, 10 mL of 800 ppm strontium nitrate was

added into the glass specimen tube and subjected to analysis with PinAAcle 500. The amount of Mg of the sample was measured based on series of standards at concentrations of 5 ppm, 10 ppm, 25 ppm and 50 ppm (Malaysian Standard 677: Part VII: 1980).

If the sample solution concentration is C ppm, then it contains C mg/L.

Therefore, %Mg in 1 g of plant sample is 0.1 C mg

$$\% \text{Mg in 1 g plant sample is } 0.1 \text{ C mg} \times 100 / 1000 \text{ mg} = 0.01\text{C} \quad \text{Equation 3.24}$$

For Zn and Cu, the digested samples in the 25 mL volumetric flask were also determined using atomic absorption spectrophotometer. The amount of Zn and Cu of the sample were analyzed with PinAAcle 500 respectively based on series of standards at concentrations of 0.2 ppm, 0.5 ppm and 1.0 ppm. If the sample solution concentration is C ppm, the amount of Zn and Cu in the plant sample can be obtained by multiplying the reading of the sample solution with 25 times dilution rate.

$$\text{Zn or Cu} = \text{C ppm} \times 25 \quad \text{Equation 3.25}$$

3.4.7 Determination of Boron in Plant

Boron is determined using the Azomethine-H method. The method employs azomethine-H reagent to form a yellow complex with B(OH)_3 in aqueous media. The method is sensitive, simple, fast and is subjected to little interference (John et al., 1975).

One gram of the plant sample was ashed and 10 mL of 0.7 N H_2SO_4 was added. The solution was stirred well with a plastic rod and left to stand for 10 minutes. Then, the ash solution was filtered through Whatman No 1 filter paper. 1 mL of standard or sample solution was pipetted into a flat bottom glass specimen tube (25 mm x 75 mm) followed by 0.5 mL of 0.05 M EDTA and 1 mL of ammonium acetate. The solution was mixed well

and allowed to stand for 15 minutes. Thereafter, 1 mL of Azomethine solution was added, swirled and left for the colour to develop.

The absorbance of the standards (0.5 ppm, 1.0 ppm, 1.5 ppm, 2.0 ppm and 3.0 ppm) and the samples at 425 nm were measured with a UV-Vis spectrophotometer (Shimadzu, UV-1800, Japan). The blank solution was prepared and the results were corrected accordingly. The amount of boron was calculated by multiplying the reading of the sample solution with 10 times dilution rate.

If the sample solution concentration is C ppm,

$$B = 10 \times C \text{ ppm} \quad \text{Equation 3.26}$$

3.4.8 Statistical Analysis

All the data have been transformed *via* square-rooting and their normality tests were assessed using SPSS Statistics Software version 25. Effects of biochar treatments on plant growth, soil properties and nutrient contents were evaluated using the Analysis of Variance (ANOVA). Least significant difference (LSD) test was applied to identify the treatment differences at $p < 0.05$. The ANOVA and LSD statistical analysis were done using SAS Statistical Software version 9.0.

CHAPTER 4

RESULTS AND DISCUSSION

4.1.1 Soil Properties

The soil used for the field study belongs to Bekenu series which is equivalent to red-yellow Podzolic according to the USDA system of soil classification. The soil is developed over mixed sedimentary rock and is characterized by its deep and well drained profile with subsoil of brownish yellow to yellow colours. The soil texture is classified as fine sandy clay loam containing 15% clay, 7% silt, 72% fine sand and 6% coarse sand. Table 4.1 summarizes the physical and chemical properties of the soil.

Table 4.1: The physical and chemical properties of soil used for field study

Soil Parameters	Measurements	Optimum range for agricultural soil*
pH-H ₂ O	3.93 ± 0.01	5.5 - 7.0 ^a
Conductivity, µS cm ⁻¹	33.00 ± 0.62	< 2000 ^a
Loss on evaporation (%)	0.11 ± 0.01	n.d.
Loss on ignition (%)	0.97 ± 0.03	5 – 8 ^a
Total N (%)	0.03 ± 0.00	0.2 - 0.5 ^a
Organic carbon (%)	0.06 ± 0.00	4 – 10 ^a
C/N ratio	2.00 ± 0.00	<25 ^d
Total P (mg/kg)	54.68 ± 2.08	250 – 400 ^c
Available P (mg/kg)	5.69 ± 0.13	20 – 40 ^a
Calcium (cmol(+)kg ⁻¹ soil)	0.44 ± 0.09	60 – 80% of soil CEC ^a
Magnesium (cmol(+)kg ⁻¹ soil)	0.05 ± 0.03	10 - 20% of soil CEC ^a
Potassium (cmol(+)kg ⁻¹ soil)	0.07 ± 0.03	2.8 – 4.0% of soil CEC ^a
CEC (cmol(+)kg ⁻¹ soil)	0.80 ± 0.11	15 – 25 ^a
Clay (%)	15.00 ± 0.58	n.d.
Silt (%)	7.00 ± 0.58	n.d.
Fine sand (%)	72.00 ± 0.58	n.d.
Coarse sand (%)	6.00 ± 0.58	n.d.

a Dume et al. (2015)

b Howell, 2005

c Goh, 1997

d USDA, 2011

n.d Not determined

Typically, loamy sand soil is characterized with low pH, K, Mg, Ca, available P and CEC with high sand content. The low pH (3.93) signifies the presence of exchangeable aluminium that can restrain the root development and affect the accessibility of other nutrients and mineralization of organic matter. The value of K, Mg and Ca were very low, which is indicative of a highly weathered soil. The base saturation was also very low, suggesting that the cation exchange sites were possibly occupied by components of H^+ and Al^{3+} (Havlin et al., 1999; Ebeling et al., 2011).

4.1.2 Biochar Properties

Table 4.2 summarizes the physico-chemical properties of EFB and PKS biochar. The pH of EFB and PKS biochar were 7.10 and 6.08, respectively. These biochar were anticipated to be produced under low pyrolysis temperature of below 350 °C as their pH were neutral and acidic. According to studies elsewhere, biochar produced under low pyrolysis temperature can be acidic (Novak et al., 2009; Hagner et al., 2016; Zhang et al., 2017) whereas biochar produced at high temperature is usually alkaline (Jiang et al., 2012) as more acidic functional groups will be removed and destroyed at a higher temperature (Ippolito et al., 2016). Hence, the pH of biochar can range from acidic to alkaline (Chan & Xu, 2009) and it is governed by the pyrolysis temperature during its production.

For example, Hagner et al. (2016) reported that birch (*Betula spp.*) biochar produced at 300 °C and 375 °C were acidic (pH 5.1 and 5.2) while Novak et al. (2009) verified that pekan shell biochar produced at 350 °C and switchgrass biochar produced at 250 °C exhibited pH of 5.9 and 5.4 respectively. The acidic switchgrass biochar was found to lower the soil pH, increasing the nutrient availability at the onset of the application (Ippolito et al., 2012; Ippolito et al., 2016).

EFB consists of 16-28% hemicellulose, 37-59.7% cellulose and 10-32% lignin (Abdullah & Sulaiman, 2013; Baharuddin et al., 2013; Sudiyani et al., 2013) whilst PKS consists of 17.94% hemicellulose, 31.33% cellulose and 48.83% lignin (Yanti et al., 2018). Upon thermochemical degradation, hemicellulose decomposes at 150-350 °C whilst cellulose and lignin degrade at 275-350 °C and 250-500 °C, respectively (Demirbas, 2004).

Hemicellulose degradation produces chemical products which are mostly “wood vinegar” that include a mixture of acetic, propionic, butyric acids along with other low molecular weight organic acids (Spokas et al., 2011; Gale et al., 2016), contributing to a decrease in the pH of biochar. Their nutrient and cation exchange properties vary among biochar. Compare to the biochar reported in the literature, the CEC and nutrient properties of EFB and PKS biochar were relatively lower; this is possibly attributable to the pyrolysis temperature and feedstock used.

Table 4.2: Physicochemical properties of EFB and PKS biochar

Parameters	EFB biochar	PKS biochar	Literature
pH-H ₂ O	7.10 ± 0.15	6.08 ± 0.06	9.1 ^d
Conductivity, $\mu\text{S cm}^{-1}$	467.00 ± 18.72	557.00 ± 15.87	n.d
Ash (%)	6.64 ± 1.10	11.30 ± 0.14	11.6 ^d
Total organic matter (%)	93.36 ± 1.10	88.70 ± 0.14	n.d
Organic carbon (%)	4.13 ± 0.44	3.83 ± 0.25	n.d
Exchangeable Mg (cmol(+)/kg)	4.32 ± 0.63	0.41 ± 0.07	n.d
Exchangeable Ca (cmol(+)/kg)	3.74 ± 0.75	2.28 ± 0.07	n.d
Exchangeable K (cmol(+)/kg)	4.94 ± 1.29	0.85 ± 0.29	n.d
CEC (cmol(+)/kg)	12.16 ± 2.10	2.53 ± 0.21	63.2 ^a 63.93 ^b
N (%)	0.61 ± 0.04	0.62 ± 0.02	1.58 ^a 1.63 ^b 1.10 ^c
P (%)	0.089 ± 0.005	0.033 ± 0.000	0.22 ^a 0.21 ^b 0.026 ^c
K (%)	0.27 ± 0.05	0.19 ± 0.05	4.9 ^a 5.3 ^b 4.12 ^c
Mg (%)	0.24 ± 0.01	0.11 ± 0.02	0.14 ^a 0.13 ^b 0.186 ^c
Ca (%)	0.26 ± 0.02	0.54 ± 0.00	0.11 ^a 0.11 ^b 0.023 ^c
B (ppm)	13.00 ± 0.00	10.67 ± 0.00	n.d
Zn (ppm)	30.02 ± 2.63	17.90 ± 5.40	n.d
Cu (ppm)	19.23 ± 1.35	15.23 ± 0.12	n.d

a Abdulrahman et al. (2016)

b Noraliza et al. (2014)

c Fahmi et al. (2018)

d Kong et al. (2014)

n.d = not determined

4.1.3 FTIR Analysis

Fourier transform infrared (FTIR) is commonly used to characterize the functional group properties of biochar. Figure 4.1 shows the FTIR spectra of EFB and PKS biochar.

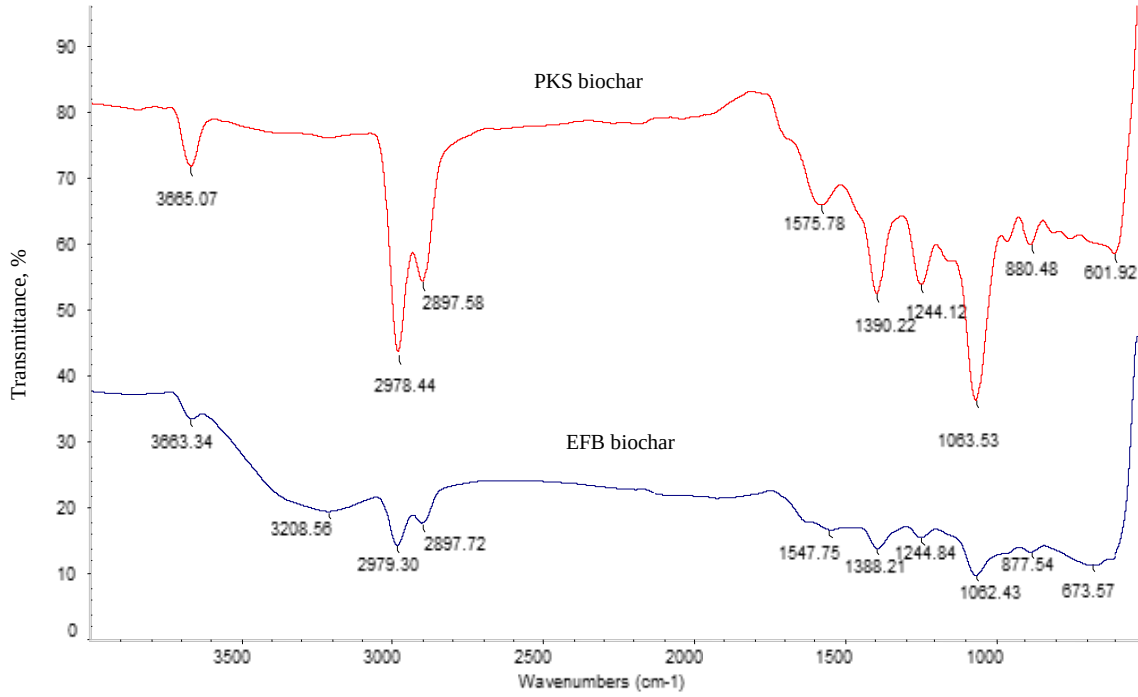


Figure 4.1: FTIR spectra of EFB and PKS biochar

The frequencies between 3600-3200 cm⁻¹ are assigned to the stretching of -OH groups. It signifies H-bonded O-H stretching vibrations of hydroxyl groups from alcohols, phenol and organic acids. The peaks of O-H (3600 cm⁻¹) and C-H (2850-2950 cm⁻¹) stretching are ascribed to the dehydration reaction in biomass (Claoston et al., 2014) where Zhou et al. (2016) reported a decrease in the polar functional groups with an increase in pyrolysis temperature. It is attributed to the loss of moisture in the gasification process which indicates dehydration of cellulose and hemicellulose components (Kim et al., 2012).

A broad band of O-H can be seen in the spectra of EFB biochar and this could be ascribed to the O-H stretching of water molecules, suggesting high moisture content. The peaks between 2978-2898 cm⁻¹ are related to the C-H stretching of hemicellulose and

cellulose (Sheng et al., 2014). The peaks at 1576-1547 cm^{-1} on the other hand, represent the presence of C=C ring stretching. According to Nastri et al. (2013), absorption bands around 850-890 cm^{-1} signify the deformation of C-H bending. The presence of aromatic C, typically the out of plane deformations of aromatic C-H, is indicated by the peaks between 880-674 cm^{-1} (Keiluweit et al., 2010; Ozcimen & Ersoy, 2010).

Other functional groups that exist in the spectra of biochar are COO^- groups at 1576-1548 cm^{-1} , CH_2 - groups at 1390-1388 cm^{-1} (Chun et al., 2004), and C-O of alcohols, carboxylic acid and ester between 1300-1020 cm^{-1} (Stuart 1996; Abdel-Ghani et al., 2007). Most of the chemical interactions between biochar and the environment are directly related to its surface chemistry. The existence of the carboxyl and hydroxyl functional groups suggest that these biochar have the potential to be used as a soil amendment for improving soil cation exchange capacity and as a potential adsorbent (Oh et al., 2012). This can be ascribed to the negative charge on its surfaces that can function to retain nutrients in the soil.

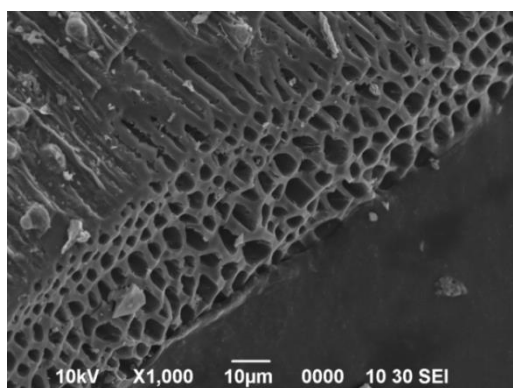
4.1.4 SEM Analysis

Scanning electron microscopy (SEM) is a microscopic technique to determine the physical morphology and macro porosity image of solid substances (Angin, 2013). The macro porous structure of biochar produced from cellulose plant material depends on the intrinsic architecture of the feedstock. It is important for water holding and adsorptive capacity of pollutant in soil and solution system (Angin, 2013; Gao et al., 2013).

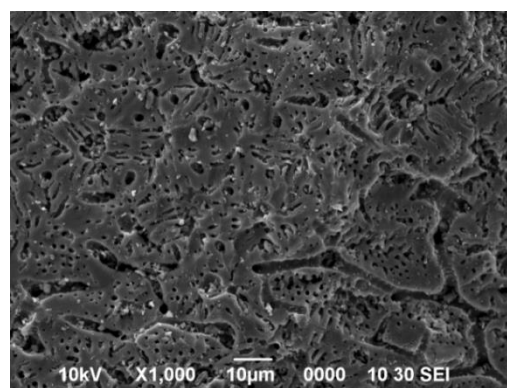
Figure 4.2 (a and b) shows the surface morphology of EFB and PKS biochar. Spongy-like structure of EFB biochar is the effect of the torrefaction process and the formation of pores is observed. The water contained in the biomass along with the

superfluous volatiles are released, and the biopolymers such as hemicellulose, cellulose and lignin are partly decomposed, giving off various types of volatiles during the torrefaction process (Bates & Ghoniem, 2012). Torrefaction of biomass usually starts to occur from the temperature between 200 - 320°C, where the hemicellulose is degraded while cellulose and lignin are remained in the absence of oxygen under atmospheric pressure (Prins, 2005; Tumuluru et al., 2011; Nunes et al., 2018; Ribeiro et al., 2018). Hemicellulose, cellulose and lignin are depleted under certain temperatures of torrefaction (Wen et al., 2014). Hemicellulose decomposes at 200 – 260 °C and will be totally destroyed when the temperature reaches 300 °C (Chen & Kuo, 2011). Cellulose degradation occurs at a temperature of above 250 °C whilst lignin depletes at 240 - 350 °C (Sjostrom, 1993).

Ruptured surface structure can be seen in both EFB and PKS biochar. Breakage of fiber wall is due to the decomposition of hemicellulose and cellulose. Porosity is caused by the degradation of lignocellulose. High porosity signifies extensive degradation of lignocellulose. Lignin is hard to be degraded due to its complex structure which possesses phenolic polymer, making them strong and durable against an enzymatic attack (Gomez et al., 2008). Thus, decomposition of lignin requires a higher temperature and residence time.



(a) EFB biochar



(b) PKS biochar

Figure 4.2: Scanning Electron Micrographs of EFB and PKS biochar at ×1000 magnification.

4.2.1 Plant Growth Performance

The plants treated with and without EFB biochar were monitored for a period of 9 months. Figure 4.3 (a and b) shows the average height and the growth rate of oil palm seedlings treated with and without EFB biochar. The incorporation of 3% EFB biochar (T3) demonstrated the best growth followed by T1 (0% EFB biochar) and T2 (1.5% EFB biochar) during the 9 months observation period. According to Bonanomi et al. (2017), the incorporation of biochar could improve the soil quality and nutrient retention capacity, enhancing plant growth. Other studies likewise reported enhancement in plant growth upon treatment with biochar as a result of the increased nutrient availability and retention, improved cation exchange capacity (CEC), raised of soil pH and promoted positive interactions with soil microorganisms (Iswaran et al., 1980; Glaser et al., 2002; Lehmann & Rondon, 2006; Liang et al., 2006). Carter et al. (2013) reported that treatment with rice-husk biochar produced by the gasification process had led to an increase in final biomass, root biomass, plant height and number of leaves. Furthermore, a combination of mineral fertilizer with biochar would be more effective in improving crop productivity (Chan et al., 2007; Asai et al., 2009; Van et al., 2010; Schulz & Glaser, 2012; Albuquerque et al., 2013; Abbasi & Anwar, 2015; Li & Shangguan, 2018).

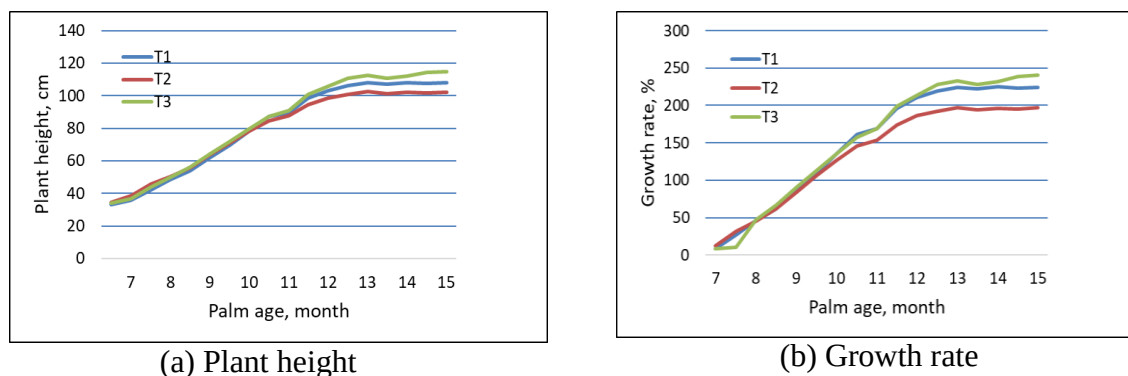


Figure 4.3: Plant height and growth rate of seedlings treated with EFB biochar

Figure 4.4 (a and b) shows the plant height and growth rate of seedlings treated with PKS biochar. The seedlings planted in soil treated with 3% biochar (T3) have grown better than T2 and T1 from the 8th month to the 12th month but starting from the 12th month, the seedlings of T1 outperformed T2 and T3. Jeffrey et al. (2015) suggested that biochar application does not improve the soil hydrological function of sandy soil. It forms a layer that can reduce the infiltration capacity and hydraulic conductivity at the soil surface as a result of the hydrophobic properties of biochar. The reduction in infiltration capacity would increase surface runoff and reduce the plant's available water. On the other hand, the coarse texture of PKS (≥ 2 mm) have increased the porosity of biochar-soil matrix, resulting in high nutrient leaching rate.

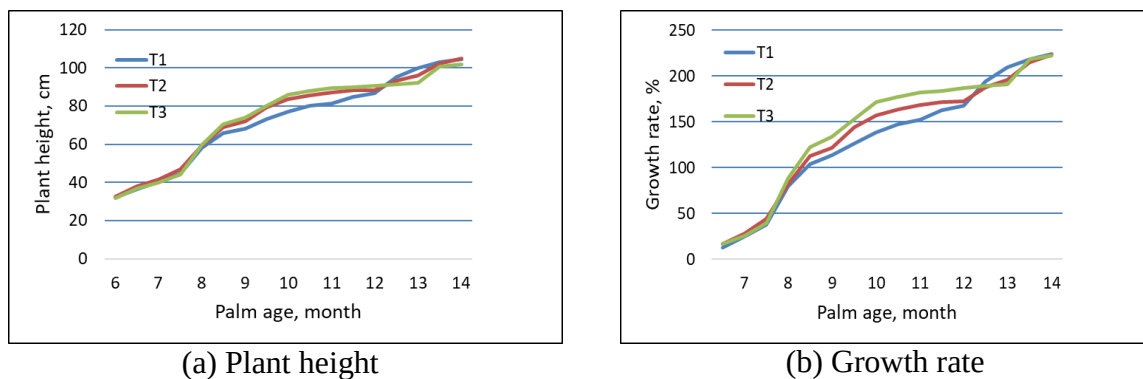


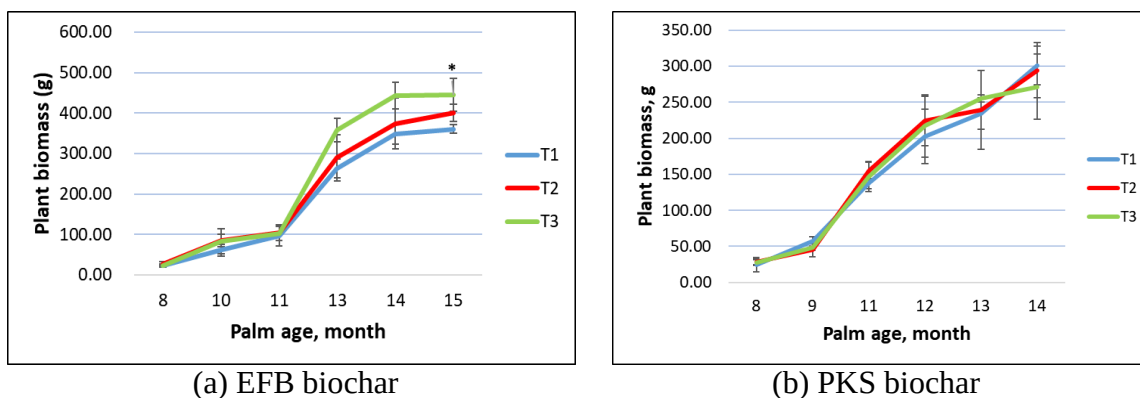
Figure 4.4: Plant height and growth rate of seedlings treated with PKS biochar

Figure 4.5 (a and b) shows the plant biomass of EFB and PKS biochar treatments respectively. Biomass assessment in the EFB biochar field study indicated that the total biomass in oil palm seedlings grown in T1, T2 and T3 have no significant difference in the early stages from the 8th month to the 14th month. However, the biomass of the seedling grown in T3 was significantly higher than T2 and T1 for the 15th month whilst the biomass of T2 was also significantly higher than the untreated soil (T1). It was apparent that the

amount of biomass has increased in relation to the amount of EFB biochar added. The increase of plant biomass may be attributed to the high porosity, surface area, and ion exchange capacity of the biochar (Yooyen et al., 2005; Lehmann et al., 2009; Downie et al., 2009; Lehmann et al., 2011; Chen et al., 2012; Wijitkosum & Kallayasiri, 2015). Moreover, the typically high aromatic nature of biochar has led to a high occasion of oxidation reactions to form oxygenated functional groups. This can attract more anions on its surface area, resulting in high ion exchange capacity (Glaser et al., 2002; Yooyen et al., 2005; Steiner, 2007; Lehmann et al., 2009; Atkinson et al., 2010; Zhang et al., 2015). Biochar is also rich in micropores that can absorb nutrients from the soil solution (Glaser et al., 2002; Downie & Crosky, 2009; Sohi et al., 2009; Atkinson et al., 2010; Chen et al., 2012; Kim et al., 2012; Kloss et al., 2012; Schulz et al., 2013), reducing nutrient leaching whilst providing sustainable nutrient release to the plants. In addition, the presence of Al^{3+} in soil solution is essentially stressful to plant growth, which will eventually damage the root cells and affect nutrient uptake (Elisa et al., 2011). Application of biochar as a soil amendment will react with Al^{3+} , providing a more favourable environment for root growth that will subsequently increase nutrient uptake, which will in turn increase plant biomass.

Conversely, in the experimental study with PKS biochar, the total biomass of oil palm seedlings grown in T1, T2 and T3 was statistically insignificant. This could be due to the low surface area and low absorption capacity of PKS biochar. Mahmood et al. (2015) reported that the surface area, micropore area, micropore volume and adsorption capacity of PKS biochar were 23.73 m²/g, 23.38 m²/g, 0.01 m³/g and 10 m³/g, respectively. The findings verify that PKS biochar has a relatively low surface area compared to other biomass such as switch grass, hardwood and corn stover biochar as reported by Brewer et al. (2009). The authors revealed that the highest surface area was switch grass biochar

(50.2 m²/g) produced from the slow pyrolysis process. The low surface area of PKS biochar indicates that it has a somewhat marginal porous structure and tiny pores, hence a weaker adsorption capacity to attract organic and nutrients for plant use.



* denotes significant different at $p < 0.05$.

Figure 4.5: Plant biomass against palm age for seedlings of EFB and PKS biochar treatments

4.2.2 Soil pH

The pH of treated and untreated soil throughout the experimental study are summarized in Table 4.3 and Table 4.4 respectively. The pH of EFB biochar treated and untreated soil ranged from 4.43 to 5.46 whereas for PKS, the range was between 4.14 and 5.33. There was no significant different in soil pH treated with and without PKS biochar over the 8 months observation period ($p > 0.05$). The initial pH of PKS biochar was slightly acidic, hence its influence in the alteration of soil pH was imperceptible. Nevertheless, there was a significant response to the EFB biochar treatments at the 8th month and 13th month where the pH of soil treated with biochar (4.98 - 5.10) were higher than the untreated soil (4.43 - 4.83).

In the experimental study with EFB and PKS biochar, a significant increase in pH was not observed. This is likely because the biochar applied to the planting medium were acidic and neutral. Hence, they did not have liming effect to increase the soil pH.

Table 4.3: pH of untreated and treated soil with EFB

Palm age (month)	EFB biochar treatments (pH)		
	T1	T2	T3
8	4.43±0.06 ^b	5.10±0.31 ^a	4.83±0.22 ^a
10	4.87±0.10 ^a	5.46±0.59 ^a	5.25±0.19 ^a
11	4.85±0.21 ^a	5.09±0.07 ^a	4.94±0.28 ^a
13	4.83±0.15 ^b	4.98±0.25 ^a	5.01±0.21 ^a
14	4.87±0.13 ^a	5.05±0.33 ^a	4.73±0.09 ^a
15	4.72±0.33 ^a	4.69±0.18 ^a	4.69±0.20 ^a

The values represent the mean ($\pm$ standard deviation) of data obtained in the experiment (n=3). The means in the same row followed by the same letters are not significantly different at $p > 0.05$ based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

Table 4.4: pH of untreated and treated soil with PKS biochar

Palm age (month)	PKS biochar treatments (pH)		
	T1	T2	T3
8	5.33±0.92 ^a	4.33±0.06 ^a	4.56±0.13 ^a
9	4.37±0.09 ^a	4.36±0.16 ^a	4.65±0.18 ^a
11	4.47±0.27 ^a	4.27±0.13 ^a	4.63±0.18 ^a
12	4.47±0.30 ^a	4.29±0.09 ^a	4.34±0.18 ^a
13	4.61±0.61 ^a	4.14±0.25 ^a	4.28±0.15 ^a
14	4.33±0.22 ^a	4.30±0.36 ^a	4.68±0.30 ^a

The values represent the mean ($\pm$ standard deviation) of data obtained in the experiment (n=3). The means in the same row followed by the same letters are not significantly different at $p > 0.05$ based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

4.2.3 Soil Conductivity (EC)

Table 4.5 and Table 4.6 summarize the soil EC treated with and without EFB and PKS biochar over the experimental period respectively. The EFB biochar treated soils (T3 and T2) have demonstrated significant difference compared to the untreated soil at the 8th month over the experimental period (Table 4.5) whilst the addition of PKS biochar did not show significant difference throughout the study ($p > 0.05$) (Table 4.6). Similar to pH, the EC of the biochar samples is also dependent on the type of feedstock and the pyrolysis temperature. Biochar produced at higher temperatures normally have higher EC values (Cantrell et al., 2012; Claoston et al., 2014; Rehrah et al., 2014). This could be ascribed to the increasing concentration of ash and residue caused by the loss of volatile matter during pyrolysis (Cantrell et al., 2012). The effect of biochar on soil EC depends on the soil chemical properties (e.g. soil pH) and biochar properties (type of feedstock and pyrolysis temperature).

Specifically, EC values represent the amount of total dissolved salts or total dissolved ions in the soil solutions (Ding et al., 2010). Chintala et al. (2013) observed an increase in soil EC after the application of biochar and it was attributed to the release of weakly bound nutrients (cations and anions) from biochar into the soil solution. This would take place when alkaline biochar produced at a high pyrolysis temperature is incorporated. Shen et al. (2015) reported an increase in pH when the particle size of biochar was reduced. A similar trend was observed by Fahmi et al. (2018) for the EC values as the authors reported that fine EFB biochar ($<50\ \mu\text{m}$) showed the highest EC followed by medium FFB biochar (0.25-0.5 mm) and coarse EFB biochar ($> 2\ \text{mm}$). This is corroborated by the findings of Yang et al. (2016) that the application of fine biochar of less than 0.25 mm was more effective in raising soil pH, EC and CEC than a coarser biochar of less than 1 mm.

Essentially, the presence of K and other elements are the main reason that contributed to the high EC value of EFB biochar (Fahmi et al., 2018).

Disparities in the EC of biochar produced from different feedstocks have been attributed to the differences in their ash contents (Rehrah et al., 2014). The effect of biochar on soil EC are highly varied (Spokas, 2010). For example, under similar temperature, biochar produced from switchgrass and corn stover have a lower aromatic C and higher ash contents than those produced from woody materials such as red oak and wood wastes (Brewer et al., 2011). The biochar EC values range from 0.04 dS m⁻¹ (Rajkovich et al., 2012) to 54.2 dS m⁻¹ (Smider & Singh, 2014). Singh et al. (2010) and Rajkovich et al. (2012) revealed that wood and paper waste biochar commonly have lower EC value than manure biochar. Variations in EC also exist within the same type of feedstock depending on the pyrolysis temperatures.

Table 4.5: EC of untreated and treated soil with EFB biochar

Palm age (month)	EFB biochar treatments (μS cm ⁻¹)		
	T1	T2	T3
8	44.47±3.41 ^b	54.03±8.79 ^a	61.47±7.15 ^a
10	46.57±20.51 ^a	51.00±20.67 ^a	51.23±19.23 ^a
11	151.20±10.45 ^a	190.30±72.08 ^a	92.67±37.84 ^a
13	72.27±20.72 ^a	92.20±41.83 ^a	72.67±32.42 ^a
14	107.67±5.14 ^a	78.37±29.34 ^a	58.10±19.76 ^a
15	63.57±17.01 ^a	54.50±10.35 ^a	51.17±9.49 ^a

The values represent the mean (± standard deviation) of data obtained in the experiment (n=3). The means in the same row followed by the same letters are not significantly different at p > 0.05 based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

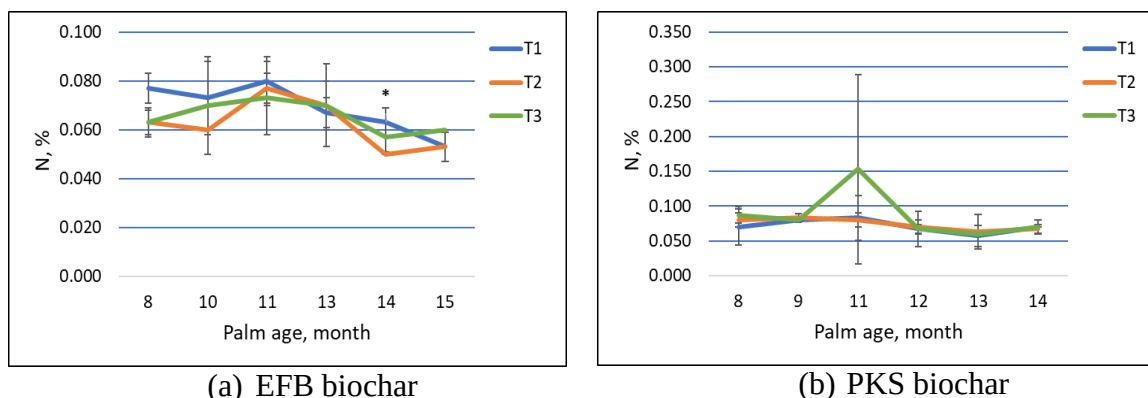
Table 4.6: EC of untreated and treated soil with PKS biochar

Palm age (month)	PKS biochar treatments ($\mu\text{S cm}^{-1}$)		
	T1	T2	T3
8	85.50 $\pm$ 34.18 ^a	98.67 $\pm$ 7.98 ^a	119.50 $\pm$ 38.38 ^a
9	150.17 $\pm$ 24.11 ^a	163.63 $\pm$ 22.49 ^a	161.70 $\pm$ 36.54 ^a
11	118.30 $\pm$ 28.37 ^a	129.63 $\pm$ 33.77 ^a	129.30 $\pm$ 24.22 ^a
12	119.47 $\pm$ 31.57 ^a	89.00 $\pm$ 30.31 ^a	108.27 $\pm$ 38.31 ^a
13	210.27 $\pm$ 242.26 ^a	184.97 $\pm$ 73.35 ^a	199.93 $\pm$ 106.82 ^a
14	132.60 $\pm$ 16.00 ^a	260.00 $\pm$ 107.89 ^a	303.43 $\pm$ 165.26 ^a

The values represent the mean ($\pm$ standard deviation) of data obtained in the experiment (n=3). The means in the same row followed by the same letters are not significantly different at $p > 0.05$ based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

4.2.4 Soil Nitrogen

Figure 4.6 (a and b) shows the nitrogen in the treated and untreated soil of EFB and PKS biochar over the experimental period respectively. Nitrogen in the untreated soil of EFB biochar was significantly higher compared to those in the treated soil at the 14th month. An increase of soil N immobilization after biochar incorporation was observed by Lehmann et al. (2003), Bruun et al. (2012), Tammgeorg et al. (2013) and Zheng et al. (2013). Table 4.7 and Table 4.8 summarize the C/N ratio of soil treated with and without EFB and PKS biochar respectively. It was observed that the C/N ratio has increased with EFB biochar treatment at the 13th month whilst this effect was not observed across the PKS biochar treatments.



*denotes significant different at $p < 0.05$

Figure 4.6: Nitrogen in the treated and untreated soil of EFB and PKS biochar

Table 4.7: C/N ratio of untreated and treated soil with EFB biochar

Palm age (month)	Soil C/N of EFB biochar treatments		
	T1	T2	T3
8	6.25±0.65 ^a	6.75±0.59 ^a	6.61±0.59 ^a
10	5.14±1.01 ^a	5.50±0.33 ^a	5.65±2.25 ^a
11	5.90±1.82 ^a	6.61±2.66 ^a	7.18±1.96 ^a
13	2.87±0.98 ^b	2.67±0.88 ^b	4.07±1.22 ^a
14	4.79±0.80 ^a	7.73±0.61 ^a	8.22±3.34 ^a
15	2.87±0.42 ^a	2.24±1.80 ^a	2.56±1.17 ^a

The values represent the mean ($\pm$ standard deviation) of data obtained in the experiment ($n=3$). The means in the same row followed by the same letters are not significantly different at $p > 0.05$ based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

Table 4.8: C/N ratio of untreated and treated soil with PKS biochar

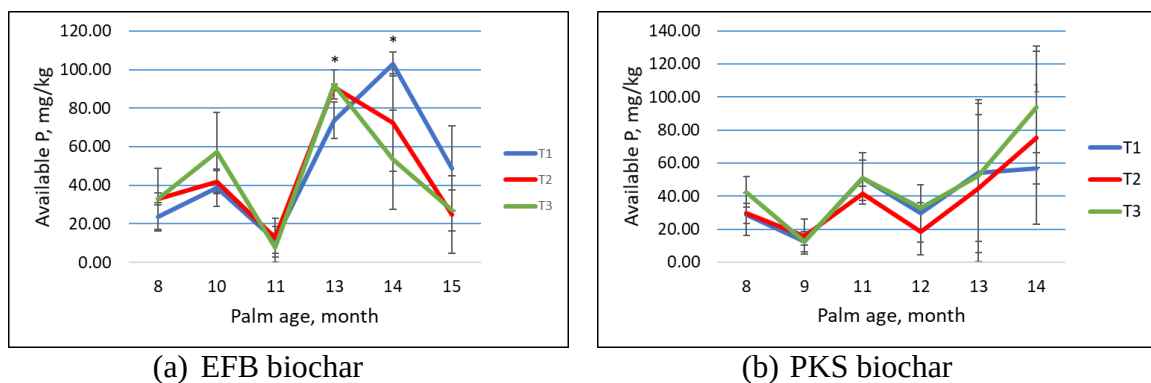
Palm age (month)	Soil C/N of PKS biochar treatments		
	T1	T2	T3
8	5.77±1.44 ^a	6.49±0.94 ^a	6.16±0.58 ^a
9	8.00±1.00 ^a	8.75±0.90 ^a	7.83±0.58 ^a
11	4.17±1.93 ^a	3.26±1.26 ^a	3.74±2.10 ^a
12	6.47±2.09 ^a	8.18±2.72 ^a	9.25±2.64 ^a
13	6.98±0.82 ^a	9.18±4.40 ^a	8.72±0.19 ^a
14	6.10±0.34 ^a	6.82±0.97 ^a	7.24±1.35 ^a

The values represent the mean ($\pm$ standard deviation) of data obtained in the experiment ($n=3$). The means in the same row followed by the same letters are not significantly different at $p > 0.05$ based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

4.2.5 Soil Available P and Total P

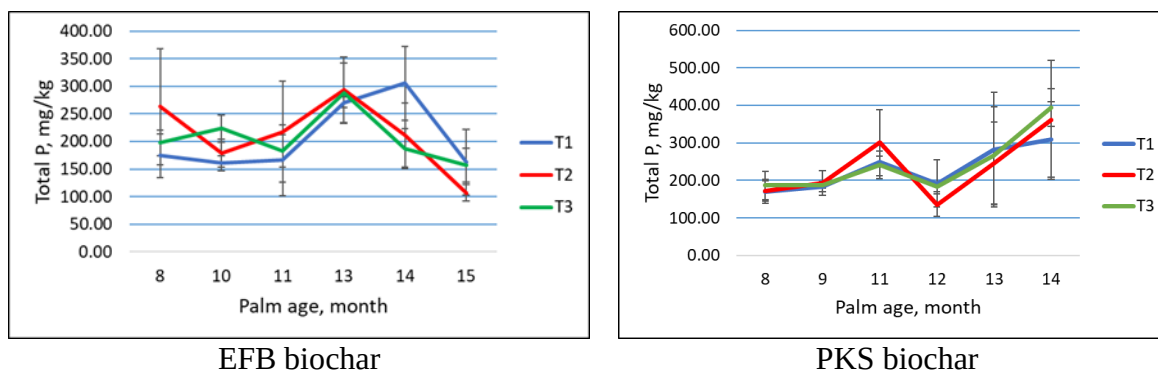
Figure 4.7 (a and b) shows the available P in the treated and untreated soil of EFB and PKS biochar whilst figure 4.8 (a and b) demonstrates the total P in the treated and untreated soil of EFB and PKS biochar. For the experimental study with EFB biochar, soil available P of seedlings in T3 and T2 were significantly higher than the seedlings in the untreated soil (T1) at the 13th month whereas there was insignificant result in the total P of the treated and untreated soil over the experimental period. Nevertheless, soil available P in T1 was detected significantly higher compared to those in T2 and T3 at the 14th month. This could be ascribed to the soil available P has been up taken by the seedlings in T2 and T3, and as a result, low available P was detected in the biochar treated soil. This can be supported by the evidence which shows that P up taken by the seedlings in T3 was significantly higher compared to those in T2 and T1 at the 13th month and 14th month (Figure 4.11a).

For the experimental study with PKS biochar, there were insignificant results in the soil available P (Figure 4.7b), soil total P (Figure 4.8b) and P uptake by the plant (Figure 4.11b) for the biochar treated and untreated soil over the experimental period. This could be attributed to the low adsorption capacity of the hard and coarse texture of PKS biochar.



* denotes significant different at $p < 0.05$

Figure 4.7: Available P in the treated and untreated soil of EFB and PKS biochar



* denotes significant different at $p < 0.05$

Figure 4.8: Total P in the treated and untreated soil of EFB and PKS biochar

4.2.6 Soil Cation Exchangeable Capacity (CEC)

Table 4.9 and Table 4.10 show the CEC of EFB and PKS biochar treated and untreated soils. In the field study of EFB biochar, the CEC of T3 was significantly higher than T2 and T1 ($p < 0.05$). The CEC of T2 did not show any significant difference compared to the untreated soil (T1) for the period of 9 months except for the 10th month where the CEC of T2 was significantly higher than T1. Overall, the CEC of EFB biochar treated soil was higher than the untreated soil; this may be due to the presence of various chemical functional groups in the biochar that render it with active chemical exchange surface (Mukherjee et al., 2013; Zornoza et al., 2016). Generally, biochar burnt at a lower temperature is enriched with carboxylic group that acts to retain cations increasing CEC (Zornoza et al., 2016). Besides, the slow pyrolyzed biochar also tends to release charged humic-like-substances that increases CEC (Kasozzi et al., 2010; Ameloot et al., 2015). Meszaros et al. (2007) suggested that K, Na, Mg and P in the biomass may facilitate the formation of oxygen groups on the surface of biochar at low pyrolysis temperatures. Oxygen groups such as carboxyls, lactones and phenols could contribute to the development of negative surface charges (Boehm, 1994). Oxidized functional group could

lead to high CEC and charge density to retain cations (Liang et al. 2006). Wu et al. (2012) suggested that low pyrolysis temperature (300°C) increases the CEC and decreases pH in the biochar compared to high pyrolysis temperature (700°C). There is evidence to suggest that on mass basis, the intrinsic CEC of biochar is consistently higher than that of whole soil, clays or soil organic matter (Sohi et al., 2009). Hence, it is logical that soil treated with biochar has high CEC. An increase in soil CEC has also been observed by Chan et al. (2008) and Aguslim et al. (2010).

In the trial with PKS biochar, the CEC of biochar soils (treated and untreated) showed no significant difference ($p > 0.05$) (Table 4.10). Normally, biochar possess oxygen-containing functional groups (Bruun et al., 2011; Manya, 2012) that can increase CEC and negative charge of soils (Lehmann, 2007; Maia et al., 2011; Mohamad et al., 2015; Zhang et al., 2017). However, our results suggest that the increase of soil functional groups caused by PKS biochar is insignificant to cause changes to the soil surface charge. This could be attributed to its relatively low adsorption capacity of 10 m³/g (Mahmood et al., 2015), resulting in poor water absorption ability and weak nutrients retention capacity after its incorporation into the loamy sand soil. Moreover, its hard and coarse particle texture of greater than 2 mm has increased the total porosity of the soil. It would also reduce the homogeneity of pore distribution. Biochar particle size can affect the interaction with soil matrix. The greater and/or lesser interaction of biochar with soil matrix may have a direct effect on its chemical, physical and hydrological properties (Barnes et al., 2014). This interaction is dependent on the biochar particle size and can hence, influence the physical and hydraulic properties of soil (Blanco-Canqui, 2017). Glab et al. (2016) verified that the soil total porosity has increased with particle size of biochar from 0.5 mm to 2 mm. He et al. (2019) recorded an increase in the total porosity of soil with the addition of 4 mm

biochar. Consequently, soil nutrients could be easily leached away during heavy rain due to the high porosity and low nutrient holding ability. CEC is the indicator of nutrients retention capacity of soil; the results suggest that PKS biochar does not increase the soil nutrient holding ability. This finding is in corroboration with the study of Slavich et al., (2013) as the authors reported that the application of green waste biochar (10 t/ha) showed no effect on the exchangeable cations and CEC of Ferrosolin in a 36-month field experiment. Schulz and Glaser (2012) also observed that biochar (5%) failed to change the CEC of an infertile sandy soil in a greenhouse experiment.

Table 4.9: CEC of the untreated and treated soil with EFB biochar

Palm age (month)	Soil CEC of EFB biochar treatments (cmol(+)/kg)		
	T1	T2	T3
8	1.81±0.05 ^b	2.05±0.23 ^b	2.76±0.23 ^a
10	1.71±0.18 ^c	2.11±0.23 ^b	2.72±0.17 ^a
11	2.48±0.74 ^b	3.17±0.79 ^a	3.30±0.58 ^a
13	1.95±0.13 ^b	2.08±0.21 ^b	2.75±0.22 ^a
14	1.83±0.02 ^b	2.08±0.04 ^b	2.89±0.24 ^a
15	1.69±0.41 ^a	1.91±0.13 ^a	2.23±0.98 ^a

The values represent the mean ($\pm$ standard deviation) of data obtained in the experiment (n=3). The means in the same row followed by the same letters are not significantly different at $p > 0.05$ based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

Table 4.10: CEC of the untreated and treated soil with PKS biochar

Palm age (month)	Soil CEC of PKS biochar treatments (cmol(+)/kg)		
	T1	T2	T3
8	2.32±0.98 ^a	3.01±0.28 ^a	2.88±0.30 ^a
9	4.38±1.50 ^a	5.52±2.22 ^a	4.36±1.38 ^a
11	4.17±1.14 ^a	4.17±1.52 ^a	3.36±0.48 ^a
12	2.79±0.78 ^a	3.23±0.44 ^a	2.49±0.31 ^a
13	2.44±0.54 ^a	2.93±0.24 ^a	3.15±0.78 ^a
14	2.69±0.57 ^a	2.86±0.10 ^a	2.87±0.38 ^a

The values represent the mean ($\pm$ standard deviation) of data obtained in the experiment (n=3). The means in the same row followed by the same letters are not significantly different at $p > 0.05$ based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

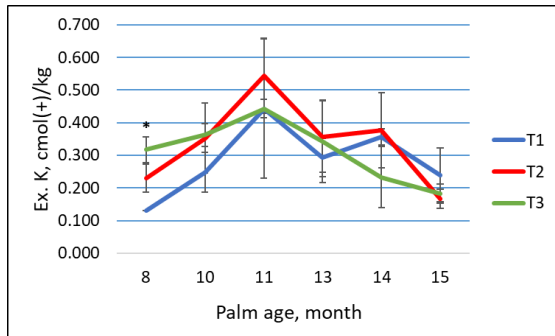
4.2.7 Soil exchangeable (K, Mg and Ca)

The incorporation of EFB biochar showed significant result on soil exchangeable K at the 8th month (Figure 4.9a), exchangeable Mg at the 10th (Figure 4.9c) month and exchangeable Ca at the 11th month (Figure 4.9e), respectively. However, its effect only appeared in the early stages of the experimental study and did not persist over the experimental period. This could be attributed to the biochar being characterized with less recalcitrant carbon. It may contain considerable amount of labile carbon that serves as a substrate for the soil microorganisms. According to Smith et al. (2010), biochar can be served as an energy source caused by providing massive labile C, which is easily available to soil microbes for use in a relatively short period of time. The labile carbon tends to reduce over time due to decomposition resulting in a decrease in the soil functional groups caused by biochar. Another reason of the insignificant result on the exchangeable cations in the treated and untreated soil at the 13th, 14th and 15th month could be attributed to the fact that the nutrients (Mg and Ca) up taken by seedlings in biochar treated soil were significantly higher compared to the seedlings in the untreated soil. This can be supported by the significantly higher biomass of seedlings with biochar treatment compared to the biomass of the seedlings in the untreated soil.

For the experimental study with PKS biochar, there was insignificant result on the soil exchangeable cations (K, Mg and Ca) in the biochar treated and untreated soil over the experimental period as per shown in figure 4.9 (b, d and f) except for the 9th month where soil exchangeable Ca in the biochar treated soil (T3) was notably higher compared to those in T2 and T1 (Figure 4.9f). The insignificant effect of PKS biochar on soil exchangeable cations over the experimental period could be attributed to the low adsorption capacity of the biochar, resulting in poor nutrients retention.

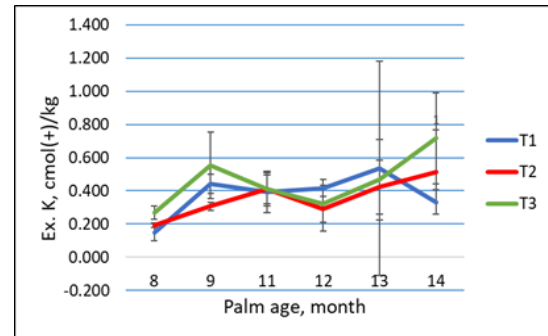
Essentially, available K, Mg and Ca occur in the form of cations (K^+ , Mg^{2+} and Ca^{2+}) in the soil solution. The increase of the cations can be explicated by the increase of CEC in the biochar treated soil. According to Liang et al. (2006), biochar has the ability to adsorb cations due to its high net negative surface charge and adsorption affinity of cations. This will enable cations flush on the surface of the biochar, thus increasing the cationic species in biochar treated soil. According to Mukherjee et al. (2011) and Abdurahman et al. (2016), an increase in CEC and pH of the biochar treated soil may reduce the activity of Fe and Al and thus, enable nutrients retention in soil, resulting in an increase in their bioavailability. Tejada et al. (2006) suggested that biochar has a high surface area and porosity that enable the biochar to retain its nutrients, and also provide a suitable circumstance for beneficial microorganisms to flourish. A similar finding was observed by Abebe (2012) who reported an improvement in soil chemistry through the application of alkaline biochar. On the other hand, the noticeable highest values of exchangeable bases of the soil treated with biochar might also be ascribed to the presence of ash in the biochar. The ash content of biochar has contributed to the direct release of the occluded mineral nutrients such as Ca, K and N for crop uptake (Scheuner et. al., 2004, Niemeyer et. al., 2005). This is corroborated by the studies of Lehmann et al. (2003), Rondon et al. (2007) and Chan et al. (2008) who reported the highest exchangeable bases in biochar treated soils.

Treatment with EFB biochar

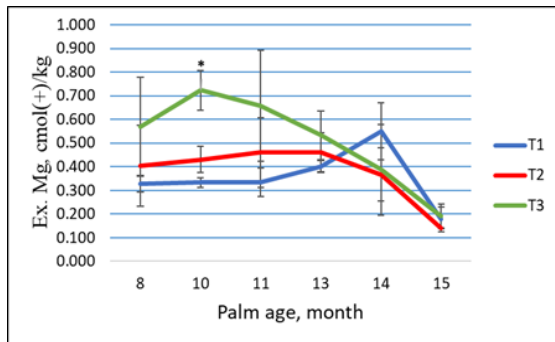


(a) Exchangeable K

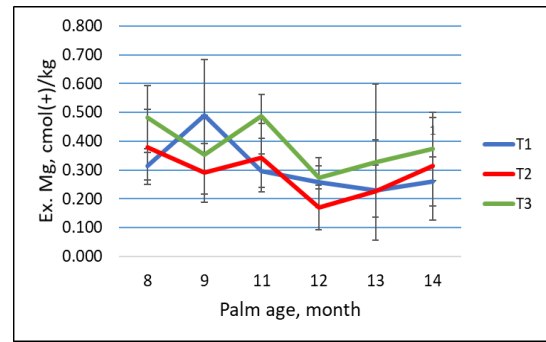
Treatment with PKS biochar



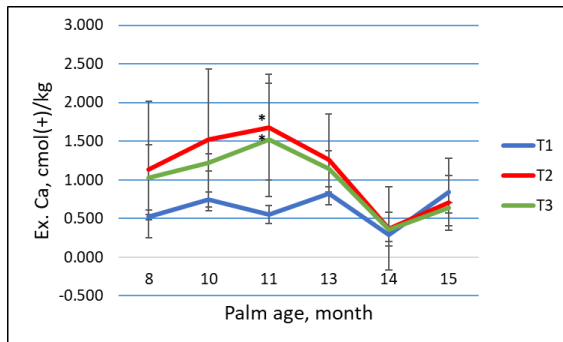
(b) Exchangeable K



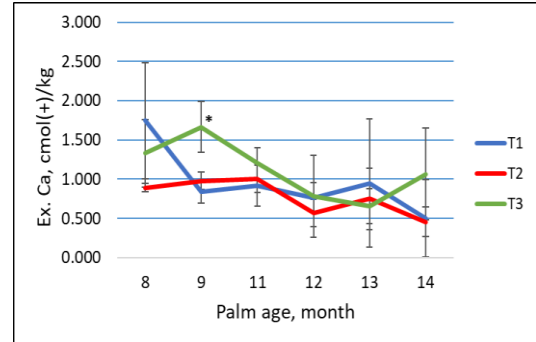
(c) Exchangeable Mg



(d) Exchangeable Mg



(e) Exchangeable Ca



(f) Exchangeable Ca

* denotes significant different at $p < 0.05$

Figure 4.9: Exchangeable cations in the treated and untreated soil of EFB and PKS biochar

4.3.1 Nutrient Contents in Seedlings

The total N stored in the seedlings are obtained by summing the N in leaves, stems and roots and it is expressed as mg plant⁻¹. Figure 4.10 (a and b) shows the average total N up taken by seedlings treated with EFB and PKS biochar. There was no significant difference in the total nitrogen up taken by plant for both biochar treatments over the experimental period.

The non-stimulatory effect of the PKS biochar could be ascribed to its low surface area and adsorption capacity (Mahmood et al., 2015) whereas the non-stimulatory effect of the EFB biochar could be attributed to the considerable amount of labile carbon as a result of low pyrolysis production temperatures (Nelissen et al., 2012). The labile carbon could serve as a microbial substrate, leading to an increase in microbial demand for inorganic N, which will in turn immobilize the nitrogen through abiotic process (Lehmann et al., 2003; Nelissen et al., 2012 and 2014; Zheng et al., 2013). Microbial immobilization and sorption effect as a result of high total organic carbon to nitrogen ratio in the biochar treated soil suggests the non-availability of nitrogen which could possibly induce N deficiency in plants (Ippolito et al., 2012). Likewise, Lehmann et al. (2003a) and Asai et al. (2009) revealed that high C/N ratio of biochar might cause negative effects on N immobilization. An increase of soil N immobilization after biochar incorporation was also observed by Bruun et al. (2012), Lehmann et al. (2013), Tammeorg et al. (2013), Zheng et al. (2013) and Lehmann et al. (2014). Correspondingly, Masto et al. (2013) and Dai et al. (2015) reported a decrease in N mineralization in their studies. The authors have suggested that the high C/N ratio of the biochar may hinder the potential of N mineralization, which is likely dependant on the biochar feedstock. Biochar derived from wood or N-limited

feedstock may be prone to the immobilization of nitrogen, converting inorganic nitrogen to organic (Lentz & Ippolito, 2012).

Conversely, the recalcitrant carbon in biochar may also limit N immobilization (Chan & Xu, 2009). Bruun et al. (2012) recorded in their incubation study that there was a huge influence of biochar pyrolysis method on the immobilization of N. Kerer et al. (2013) suggested that biochar produced with fast pyrolysis and low temperature may possess bio-available carbon for microbial activity but biochar produced with slow pyrolysis would hold less bio-available carbon. Similarly, Rajkovich et al. (2012) revealed that high pyrolysis temperature at 500 - 600 °C might minimize N-immobilisation.

Another reason for the insignificant effect of biochar on N uptake could be due the high adsorption capacity of biochar, which restricts soil N availability for plant uptake. Albuquerque et al. (2013) reported a decrease in N plant uptake after the incorporation of biochar and the authors suggested that it could be related to the ability of biochar to adsorb N and limit its availability. The biochar surface area and microporosity increase with increasing pyrolysis temperature, resulting in higher physical sorption capacity (Kookana et al., 2011, Nguyen et al., 2017) that restricts plant N uptake. Nevertheless, Novak et al. (2010) revealed that there was a stimulation of N mineralization after biochar amendment to a forest soil in their laboratory incubation study. Majority of the studies are short-term and N immobilization could be associated with labile carbon in the biochar. Therefore, Clough et al. (2013) proposed long-term studies to provide better insights into the effect of biochar on N immobilization.

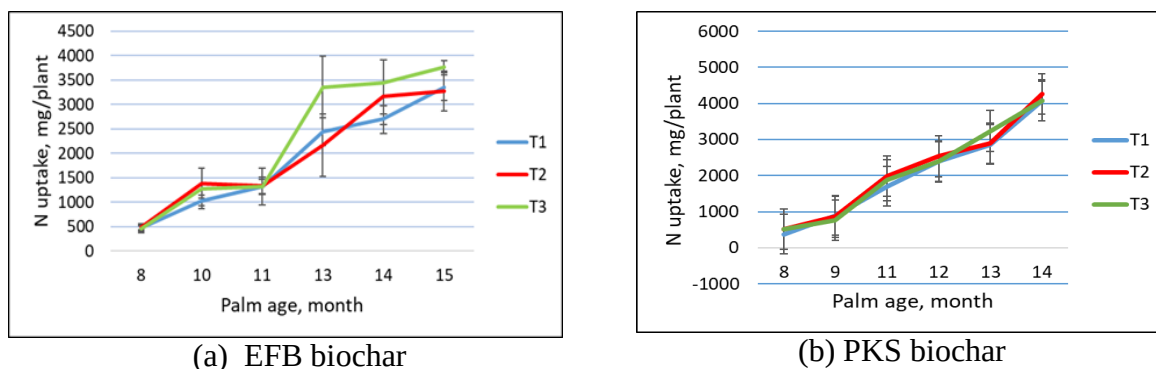
The sandy loam soil used in this study is characteristically low in clay and organic matter, contributing to low water holding capacity and low fertility. Essentially, nitrogen leaching from sandy soils is more profound than other agricultural soils (Wang et al.,

2015), leading to low nitrogen use efficiency. Some losses of N are inevitable as urea is susceptible to volatilization and evaporation. This is favourable in humid environment in oil palm nurseries (Bouwmeester et al., 1985; Foster et al., 1988). Liu et al. (2017) reported that $\text{NH}_3\text{-N}$ loss *via* volatilization from biochar-amended loamy soil and sandy soil was greater than the untreated soil and the amount of volatilized $\text{NH}_3\text{-N}$ was found to increase with the increasing rate of biochar. The incorporation of alkaline biochar may potentially promote NH_3 volatilization as the increase in soil pH tends to volatilize NH_3 . Conversely, some studies reported that biochar could adsorb NH_3 where the mechanism involves the acidic functional groups in biochar (Asada et al., 2002; Kastner et al., 2009; Taghizadeh-Toosi et al., 2012) and these could be neutralized by bases such as OH^- other than NH_3 . Besides, nitrogen deficiency in loamy sand soil could be due to leaching. The leaching of N or losses in the form of gaseous N in agriculture fields after fertilizer application has become a major challenge (Yanai et al., 2007; Ding et al., 2010).

Note that the total N up taken by the seedlings in T3 of EFB biochar was apparently higher compared to those in T2 and T1 from the 13th month to the 15th month although it was statistically insignificant (Figure 4.10a). This could be ascribed to aged biochar in influencing N availability in a different manner than fresh biochar. Zheng et al. (2013) suggested that aged biochar contains oxygenated functional groups (e.g., carboxyl and hydroxyl) that have greater capacity to absorb NH_4^+ than fresh biochar. Biochar could adsorb ammonia through its acidic functional groups (Asada et al., 2002) or through its high CEC (Taghizadehtoosi et al., 2012). Sohi et al. (2010) proposed that the increase in N uptake might be due to the high CEC of biochar and its potential to retain NH_4^+ in the soil. An increase in N uptake by plants that were grown in biochar amended soils was also reported by Nigussie et al. (2012). Similarly, Lehmann et al. (2006) recorded an

improvement in the total N availability after the addition of biochar. Rubab et al. (2017) suggested that high CEC of biochar might be the reason for the increase in soil N retention capacity and the decrease in N losses *via* ammonia volatilization and denitrification from the calcareous soils.

Although biochar is unable to supply N directly, it serves as a habitat for N fixing microbes, reducing N leaching and increasing nitrogen use efficiency (DeLuca et al., 2009; Clough et al., 2013). Several studies likewise reported that addition of biochar could increase nitrogen use efficiency (Chan et al., 2007; Steiner et al., 2008; Van Zwieten et al., 2010; Huang et al., 2014). Biochar has a potential to act as a soil conditioner through its adsorption effect, increasing N retention in soil (Van Zwieten et al., 2010). The decrease in N losses can also be explained as a result of electrostatic adsorption to exchange sites or their acidic functional groups in biochar facilitating retention of NH_4^+ (Steiner et al., 2008; Clough et al., 2013). Apart from the potential to increase crop yield, the amount of nitrogen fertilizer applied to the soil could be reduced with an improved effectiveness of nitrogen uptake. However, in some cases, N availability may decrease (Lehmann et al., 2003). The above discussion demonstrates that the incorporation of biochar may result in varying effects on nitrogen use efficiency, possibly reducing or increasing plant nitrogen uptake or showing no noticeable effect. In this study, the effect of biochar on N uptake was not observed in both of the EFB and PKS biochar treatments.



* denotes significant different at $p < 0.05$

Figure 4.10: Total nitrogen up taken by plant of EFB and PKS biochar in field study

Figure 4.11 (a to h) shows the total P, K, Mg and Ca up taken by plant in EFB and PKS biochar experimental study, respectively. Statistically, total P, K, Mg and Ca were insignificant from the 8th to 11th month in the EFB biochar treated and untreated seedlings. Those nutrients may have been adsorbed on the macropores and micropores of EFB biochar and they have yet to be released for plant uptake. However, the effect of EFB biochar on nutrients uptake (P, Mg and Ca) was observed when the seedlings were at the 13th, 14th and 15th month.

The total P in the seedlings of T3 was significantly higher compared to those in T2 and T1 at the 13th and 14th month (Figure 4.11a). The biochar is enriched with P, which contributes to a higher concentration of extractable P (Kwabiah et al., 2003) that could serve as a short-term P supply for plants. According to studies, biochar is a potential source of P for crops, (Lehmann et al., 2003; Asai et al., 2009) promoting root growth. Nelson and Sommers (1982) reported that the increase application of biochar can increase the available P. Similarly, Cao and Harris (2010) verified that the addition of biochar can alter P availability in soil. The presence of charged functional groups on the surface of biochar

further enhance P retention, increase microbial activities and improve soil quality. The improvement of root growth in biochar treated plants are associated with increased P uptake (Spokas et al. 2010). Peng et al. (2012) and Yao et al. (2013) suggested that biochar is a potential P source and some biochar can retain P. Lehmann et al. (2003) also observed an increase in P concentration in plants with increasing biochar application. The mechanisms of P uptake upon biochar addition was reviewed by Atkinson et al. (2010). It acts as a source of soluble and exchangeable P, preventing P precipitation by modifying soil pH (bonding or sorbing elements that precipitate P). However, Chintala et al. (2014) and Zhang et al. (2016a) revealed that the ability of biochar to increase P retention in soils may vary depending on the concentration of P in soil solution. The effect of biochar on P retention in soil is scanty (Zhang et al. 2016b) and requires continuous investigation.

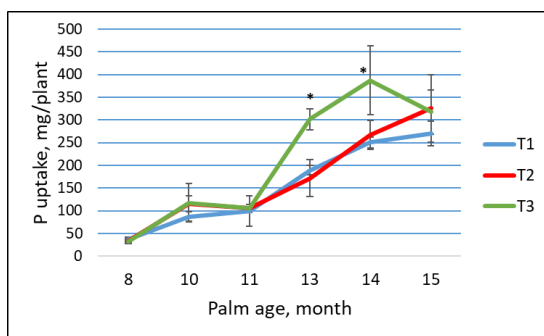
Even though total K in the seedlings of T3 was apparently higher at the 13th, 14th and 15th month compared to those in T2 and T1, the K uptake in seedlings treated with and without EFB biochar was insignificant statistically (Figure 4.11c). According to the K availability to plants, soil potassium is ascribed to four different pools such as soil solution, exchangeable K, fixed K and lattice K (Syers, 1998). As plant can only adopt K^+ from solution, its availability is dependent on the nutrient dynamics as well as on the total K content. The exchange of potassium in different pools in soil is strongly dependent on the concentration of other macronutrients in the soil solution such as nitrate (Yanai et al., 1996). The release of exchangeable K is often slower than the rate of K^+ acquisition by plants (Sparks & Huang, 1985), and as a result, the K^+ content in some soils is very low (Pretty & Stangel, 1985; Johnston, 2005). Plant potassium status may further deteriorate in the presence of high levels of Na^+ and NH_4^+ that interfere with potassium uptake (Spalding et al., 1999; Qi & Spalding, 2004; Rus et al., 2004). K^+ uptake can be suppressed or

influenced by the amount of NH_4^+ available (Norman & William, 2008). The antagonism effect between Na^+ , NH_4^+ and K^+ may facilitate the competition between the nutrients for plant uptake, and as a result, the K uptake in the biochar treated and untreated seedlings has no significant effect. Furthermore, the antagonism effect between Mg and K could possibly happen in soils containing various concentrations of Mg and K. According to Mehmet et al. (2015), in the situation of a higher Mg concentration in soil solution, K uptake is not disturbed generally. Naturally, the amount of K in the soil solution is much lower than Mg concentration; therefore, plants have developed specific K-transport systems in the root cells to ensure sufficient K uptake when its concentration in the soil solution is critically low (Horie et al. 2011). These specific K transporters would not be blocked by other nutrients. Conversely, the Mg transporters are non-specific and can be passed by other cations such as K. Therefore, when K concentration in the soil–root interface is high, plant ability to take up sufficient Mg is limited. Seggewiss and Jungk (1988) and Wilkinson et al. (1990) revealed that Mg uptake at the root surface was inhibited by K concentrations $> 20 \text{ mmol L}^{-1}$. Furthermore, ratios of Mg accumulated in shoots to the whole plant Mg content were reported to be negatively correlated with plant K concentrations in roots (Huang et al., 1990). This suggests that excessive K concentration in roots may depress the rate of net Mg translocation from roots to shoots. However, further studies are required to confirm this hypothesis.

Simultaneously, Mg and Ca up taken by the seedlings of T3 were significantly higher compared to those in T2 and T1 at the 13th and 14th month (Figure 4.11e and g). This could be correlated with the increase of CEC in the soil of T3. This supports the findings that biochar has the potential to increase the soil CEC (Liang et al., 2006) and subsequently improve the plant nutrients uptake (Lehmann et al., 2003).

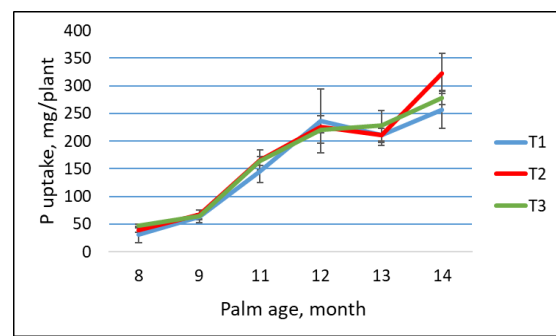
The application of EFB biochar may have contributed to the increase of microbial activity, leading to high nutrient uptake in biochar treated soils. Pietikainen et al. (2000) suggested that biochar could be a favourable habitat for soil microorganism involving N, P or S transformation. Moreover, biochar may have the capacity to support the presence of adsorbed bacteria, which will influence soil processes (Pietikainen et al., 2000).

Treatment with EFB biochar

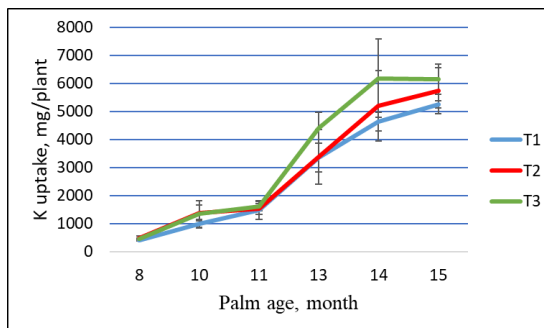


(a) P

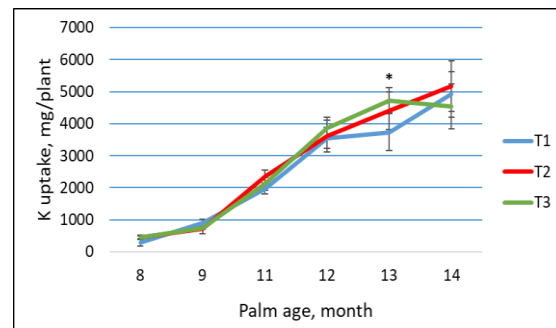
Treatment with PKS biochar



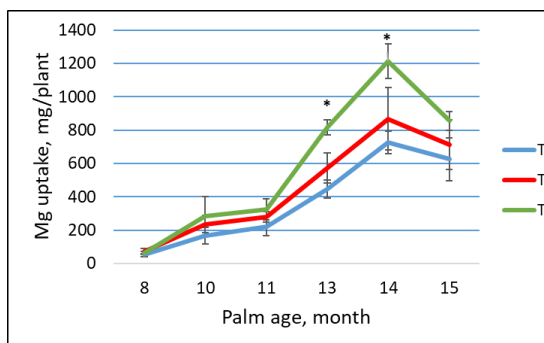
(b) P



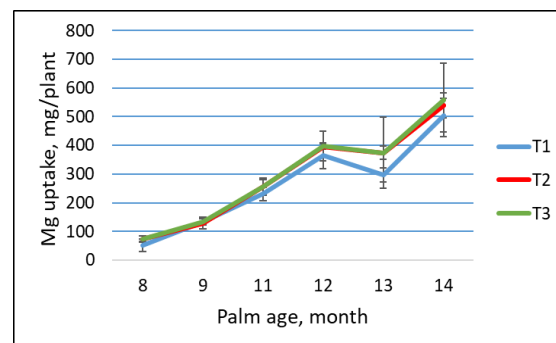
(c) K



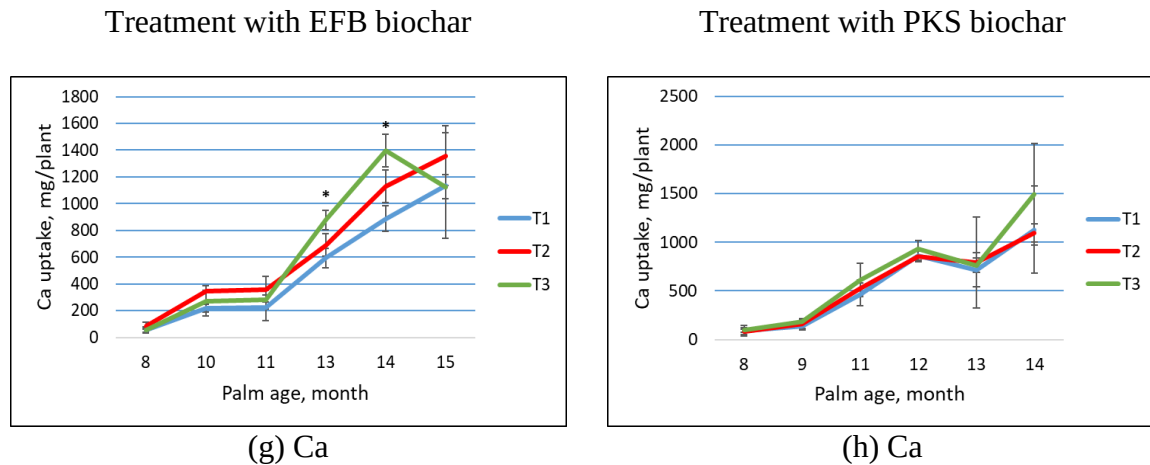
(d) K



(e) Mg



(f) Mg



* denotes significant different at $p < 0.05$

Figure 4.11: Total phosphorous, potassium, magnesium and calcium up taken by plant in EFB and PKS biochar field study

On the other hand, PKS biochar showed insignificant effect on the plant nutrients uptake for P, Mg and Ca (Figure 4.11b, d, f and h). This could be attributed to its coarse and hard texture which is low in adsorption capacity, resulting in poor soil nutrient retention. However, K uptake in the seedlings of PKS biochar treated soils (T3 and T2) have demonstrated significant effect at the 13th month (Figure 4.11d). The increase in K uptake of the biochar amended soil could be attributed to the charged functional groups of biochar may have been retaining some of the soil available K for plant uptake. This result corresponded with Lehmann et al. (2003), as the study reported an increase in K upon charcoal application. The increase of K availability was also observed by Kraska et al. (2016) after the incorporation of wheat straw derived biochar. Positive effect of biochar application on the accumulation of K and P was observed after longer exposure. Chan et al. (2007) also stated an increase uptake of P and K by plants in some of the studies, which signifies high concentration of these nutrients in biochar and their availability for plant

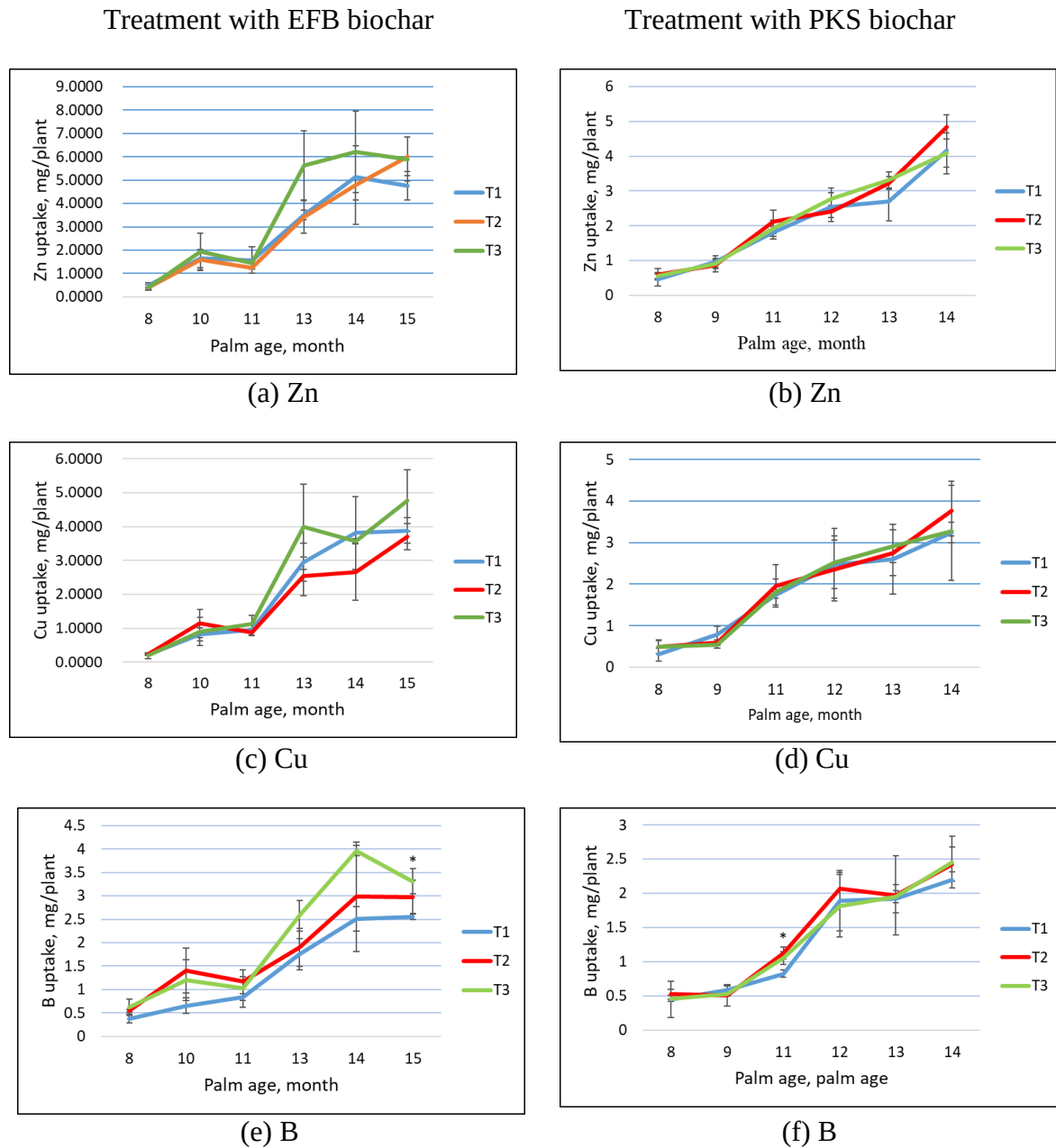
uptake. In addition, Lehmann and Rondon (2006) and Uzoma et al. (2011) also reported an increase nutrient uptake in the tropical environment.

4.3.2 Micronutrients Uptake

Micronutrients such as boron (B), Zinc (Zn), Copper (Cu) can be essential for plant growth (Alloway, 2008). Biochar is a potential amendment for metal retention. The mechanism is ascribed to cation exchange capacity, acid neutralization and high specific surface area of biochar (Asai et al., 2009; Beesley et al. 2010). Over the experimental period, EFB and PKS biochar demonstrated insignificant effect ($P > 0.05$) on plant Zn and Cu uptake (Figure 4.12a, b, c and d). In the literatures, the addition of biochar was found to reduce the availability of Zn in mine-contaminated soil planted with Jack bean (*Canavalia ensiformis*) and *Mucuna aterrima* (Puga et al., 2015). Likewise, Jayawardhana et al. (2016) reported a marginal decrease of exchangeable Zn (from 13 to 10 mg/kg) with increasing biochar application, indicating high Zn sorption capacity. Meanwhile, a reduction of Cu uptake by corn silage after biochar application was observed by Lenzt and Ippolito (2012). Similarly, Park et al. (2011) reported a decrease of Cu availability after biosolid amendments, indicating the formation of inorganic metal complexation leading to the immobilization of available Cu. Some researchers reported that the concentration of Cu was not influenced significantly by the application of pecan shell biochar (Novak et al. 2009).

Conversely, treatment with EFB and PKS biochar showed significant effect on the uptake of B on 15th month (Figure 4.12e) and 11th month (Figure 4.12f), respectively. This suggests an increase in B availability upon biochar treatment that renders enhanced uptake of B. This result contradicts the findings of Kloss et al. (2012) where B and Zn contents in

wheat plant was found to decrease after the biochar addition; this is explained by the high adsorption capacity of biochar and enhanced soil pH that leads to precipitation of Zn, reducing availability of B. The low uptake of micronutrients after the incorporation of biochar suggests low risk of metal accumulation in plants (Gunarathne et al., 2017).



* denotes significant different at $p < 0.05$

Figure 4.12: Total Zn, Cu and B up taken by plant of the EFB and PKS biochar field study

4.3.3 Destination of ^{15}N in Plant Partitions after the Application of Labelled Urea

Figure 4.13 shows the ^{15}N up taken by seedlings in the PKS biochar treated and untreated soil against different plant partitions. The unit of ^{15}N is $\delta^{15}\text{N}$ (delta ^{15}N) and it is expressed in part per thousand (‰). The $\delta^{15}\text{N}$ valued ranged between 1072.88 and 2164.32 for different plant partitions. Statistically, there was insignificant result in the $\delta^{15}\text{N}$ uptake among biochar treated and untreated seedlings. However, the amount of $\delta^{15}\text{N}$ up taken by the seedlings in T3 was higher compared to those in T2 and T1 whereas the uptake of $\delta^{15}\text{N}$ in T2 and T1 were similar. Meanwhile, the $\delta^{15}\text{N}$ that remained in the soil of T3 was the least compared to T2 and T1, suggesting that more ^{15}N have been taken up by T3 than T2 and T1. The distribution of $\delta^{15}\text{N}$ in different parts of the oil palm seedlings a week after the application of labelled urea showed that the highest enrichment was found in the stem and root for the treated and untreated soil and that the enrichment was higher in T3 followed by T1 and T2. This could be attributed to the 3% of PKS biochar treatment, which may have been able to retain more ^{15}N for plant uptake compared to those in T1 (0% PKS biochar) and T2 (1.5% PKS biochar).

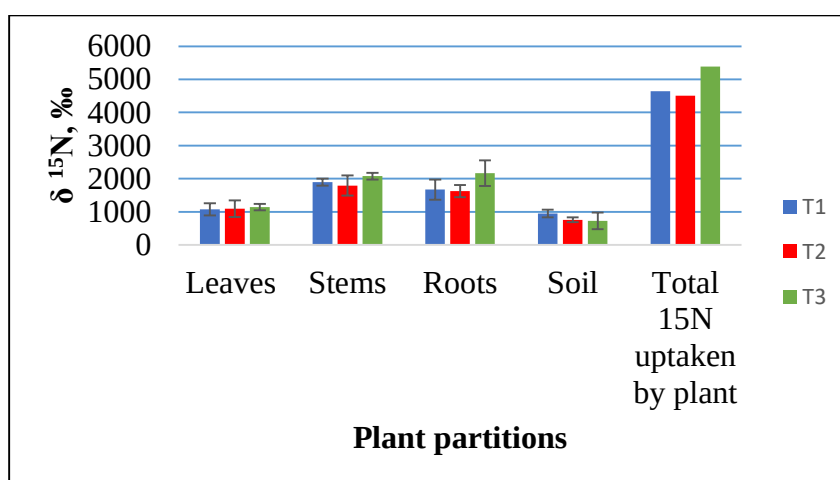


Figure 4.13: $\delta^{15}\text{N}$ in the plant partitions against treatment in the PKS biochar treated seedlings

4.3.4 Nitrogen Derived from Fertilizer (NdFF)

Table 4.11 summarizes the leaves, stems and roots dry matter production of oil palm seedlings grown in the PKS biochar treated and untreated soil. Their corresponding total N yield is tabulated in Table 4.12 where no significant difference was found in the seedlings of T1, T2 and T3.

Table 4.11: Dry matter yield (% of total dry matter) and its distribution in plant parts of the 9th month old seedling

Treatment	Dry matter yield (g part ⁻¹)			Total dry matter yield (g plant ⁻¹)
	Leaves	Stems	Roots	
T1	23.80±3.36 ^a	19.74±1.58 ^a	13.51±3.26 ^a	57.05±6.52 ^a
T2	20.39±3.38 ^a	14.08±3.66 ^a	10.62±2.96 ^a	45.09±9.67 ^a
T3	21.03±2.06 ^a	16.71±2.87 ^a	10.88±3.34 ^a	48.63±4.43 ^a

The values represent the mean ($\pm$ standard deviation) of data obtained in the experiment (n=3). The means in the same row followed by the same letters are not significantly different at $p > 0.05$ based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

Table 4.12: Total N yield (g plant⁻¹) against PKS biochar treated and untreated of 9th month old seedling

Treatment	N (%)			N yield (g part ⁻¹)			Total N yield (g plant ⁻¹)
	Leaves	Stems	Roots	Leaves	Stems	Roots	
T1	2.52	0.88	0.92	0.60±0.05 ^a	0.17±0.02 ^a	0.12±0.02 ^a	0.8943±0.08 ^a
T2	2.81	1.23	1.15	0.57±0.09 ^a	0.17±0.03 ^a	0.12±0.02 ^a	0.8628±0.14 ^a
T3	2.42	0.92	1.00	0.51±0.02 ^a	0.15±0.01 ^a	0.11±0.04 ^a	0.7675±0.03 ^a

The values represent the mean ($\pm$ standard deviation) of data obtained in the experiment (n=3). The means in the same row followed by the same letters are not significantly different at $p > 0.05$ based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

Table 4.12 shows the N yield derived from labelled fertilizer of the 9th month old oil palm seedlings; no significant difference ($p > 0.05$) was found across the treatments. The other parameters, namely total %N_{dff} and N yield derived from ¹⁵N fertilizer of the treated and untreated seedlings were also not significantly different ($p > 0.05$). Generally, there was no difference in the N uptake for the PKS biochar treated and untreated soil.

Meanwhile, the ¹⁵N labelling technique has given an insight into the nitrogen use efficiency (NUE) of the seedlings, whereby T1, T2 and T3 achieved 8.53%, 7.95% and 8.54% respectively. The seedlings of T3 contained 58.05% of ¹⁵N within the plants as compared to the total N of the plant, followed by T1 and T2 which contained 49.78% and 48.12% of ¹⁵N in the total N of plants respectively, which suggests that the 3% PKS biochar treated seedlings (T3) has taken up the highest ¹⁵N labelled urea compared to those 1.5% PKS biochar (T2) and untreated seedling (T1).

This result is corroborated by the findings of Zaharah et al (2012), which stated that genotype A achieved the highest NUE at 6.12% and genotype F at 3.27%, while the others genotypes used less than 2% of the labelled fertilizer. The authors reported that genotype A contained 10.48% of ¹⁵N within the plants as compared to the total N of the plant, followed by genotype F which contained 7.62% of ¹⁵N in total N of the plants.

Table 4.13: The effect of PKS biochar on total %N derived from fertilizer (%N_{dff}) and N yield derived from ¹⁵N

Treatment	Total atom% ¹⁵ N in plant	Total %NdFF	N yield derived from ¹⁵ N fertilizer (g palnt ⁻¹)
T1	2.7711±0.17 ^a	49.5849±5.00 ^a	0.4452±0.08 ^a
T2	2.7342±0.25 ^a	48.4829±7.45 ^a	0.4152±0.08 ^a
T3	3.0500±0.21 ^a	57.9098±6.13 ^a	0.4455 ±0.06 ^a

The values represent the mean (± standard deviation) of data obtained in the experiment (n=3). The means in the same row followed by the same letters are not significantly different at p > 0.05 based on the LSD Test. (T1: 0% biochar; T2: 1.5% biochar and T3: 3% biochar)

It can be summarized that EFB biochar have demonstrated positive effects on the plant growth, biomass, soil chemical properties (CEC, available P, total P, exchangeable Ca and Mg) and plant nutrient uptake (P, Mg, Ca and B) whereas these positive effects were not seen in the PKS biochar field study. For the ¹⁵N tracing experiment, there was no significant difference in the total dry matter, total N and N yield derived from ¹⁵N fertilizer in the 9th month old PKS biochar treated and untreated seedlings.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1.1 Conclusion

The EFB and PKS biochar used in this study are anticipated to be produced under low pyrolysis temperature as both of them are neutral and acidic and there is not much difference in their conductivity value. Nevertheless, the EFB biochar is better in CEC, exchangeable cations, nutrient contents and morphology than the PKS biochar generally.

In this study, a significant increase in pH and EC are not observed in the EFB and PKS biochar treated soil because of their neutral and acidic natures do not have liming effect to increase the soil pH. However, the seedlings treated with the EFB biochar has evidently demonstrated improved plant growth, biomass, soil nutrients retention and plant nutrients uptake, corresponding to the dosage of biochar. The stimulatory effect of EFB biochar on plant is primarily determined by its high surface area, porous nature and cation exchange properties that have significantly increased the soil CEC and nutrient holding capacity.

Conversely, these positive effects are not observed in the PKS biochar treated seedlings over the experimental period. There is also no significant difference in the nitrogen use efficiency in the ^{15}N tracing experiment of the 9th month old seedlings treated with and without PKS biochar. Compared to EFB biochar, PKS biochar is coarser with a larger and harder texture. The incorporation of PKS biochar into the loamy sand soil has increased the porosity of soil. High soil porosity with high infiltration have increased the nutrient leaching rate, limiting available nutrients for plant use. Moreover, PKS biochar has a relatively low adsorption capacity, poor water retention ability and weak nutrient

retention capacity, thus it could not increase the soil CEC and retain the soil nutrient efficiently.

In conclusion, EFB biochar is more suitable to be used for soil amendment compared to PKS biochar in oil palm plantations as it can retain more soil nutrients and hence increasing nutrients use efficiency.

5.1.2 Recommendations

PKS biochar does not demonstrate any significant positive effect on plant growth and nutrients use efficiency of the oil palm seedlings, likely associated with its coarse and less porous structure. Hence, its effectiveness as a soil amendment is negligible. On the other hand, high pyrolysis alkaline EFB biochar is recommended to be used in the experimental study to investigate its effects and the ^{15}N -pulse-chase experiment is recommended to be performed in the EFB biochar. Meanwhile, a long-term field study on the effect of EFB biochar on plant nutrient uptake and acidic soil chemical properties are necessary to confirm the findings.

REFERENCES

- Abebe, N., Endalkachew, K., Mastawesha, M., & Gebermedihin, A. (2012). Effect of biochar application on soil properties and nutrient uptake of Lettuces (*Lactuca sativa*) grown in chromium polluted soils. *American-Eurasian Journal of Agricultural & Environmental Science*, 12(3), 369-376.
- Abbasi, M. K., & Anwar, A. A. (2015). Ameliorating effects of biochar derived from poultry manure and white clover residues on soil nutrient status and plant growth promotion-greenhouse experiments. *PLoS ONE*, 10(6), e0131592.
- Abdel-Ghani, N. T., Hefny, M., & El-Chaghaby, G. A. F. (2007). Removal of lead from aqueous solution using low cost abundantly available adsorbents. *International Journal of Environmental Science and Technology*, 4, 67–73.
- Abdelhafez, A. A., Li, J., & Abbas, M. H. H. (2014). Feasibility of biochar manufactured from organic wastes on the stabilization of heavy metals in a metal smelter contaminated soil. *Chemosphere*, 117, 66-71.
- Abdelhafez, A. A., & Li, J. (2016). Removal of Pb (II) from aqueous solution by using biochars derived from sugarcane bagasse and orange peel. *Journal of Taiwan Institute of Chemical Engineers*, 61, 367-375.
- Abdelhafez, A. A., Abbas, M. H., & Li, J. (2017). Biochar: The black diamond for soil sustainability, contamination control and agricultural production. In: Huang WJ, editor. *Engineering Applications of Biochar*. Croatia: Intech Open, pp. 7-27.
- Abdul, P. M., Jahim, J. M., Harun, S., Markom, M., Lutpi, N. A., Hassan, O., Balan, V., Dale, B. E., & Nor, M. T. M. (2016). Effects of changes in chemical and structural characteristic of ammonia fibre expansion (AFEX) pretreated oil palm empty fruit

- bunch fibre on enzymatic saccharification and fermentability for biohydrogen. *Bioresource Technology*, 211, 200-208.
- Abdullah, N., & Sulaiman, F. (2013). The properties of the washed empty fruit bunches of oil palm. *Journal of Physical Science*, 24(2), 117–137.
- Abdulrahman, D. K., Radziah, O., & Halimi, M. S. (2016). Effect of empty bunch biochar and nitrogen-fixing bacteria on soil properties and growth of sweet corn. *Malaysian Journal of Soil Science*, 20, 177-194.
- Adam, J.C. (2009). Improved and more environmentally friendly charcoal production system using a low-cost retort-kiln (Eco-charcoal). *Renewable Energy*, 34, 1923-1925.
- Agusalim, M., Wani, H. U., & Syechfani, M. S. (2010). Rice husk biochar for rice based cropping system in acid soil: The characteristics of rice husk biochar and its influence on the properties of acid sulfate soils and rice growth in west Kalimantan. Indonesia. *Journal of Agriculture Science*, 2(1), 39-47.
- Ahmed, M., Lee, S. S., & Lim, J. E. (2014). Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS Spectroscopy and Chemical Extractions. *Chemosphere*, 95, 433-441.
- Alam, A. S. A. F., Er, A. C., & Begum, H. (2015). Malaysian oil palm industry: Prospect and problem. *Journal of Food Agriculture and Environment*, 13(22), 143-148.
- Alburquerque, J. A., Salazar, P., Barrón, V., José Torrent, J., Campillo M. C., Gallardo A., & Villar, R. (2013). Enhanced wheat yield by biochar addition under different mineral fertilization levels. *Agronomy for Sustainable Development*, 33, 475–484.

- Aller, M. F. (2016). Biochar properties: Transport, fate, and impact. *Critical Reviews in Environmental Science and Technology*, 46, 1183-1296.
- Alves, B. J. R., Resende, A. S., Urquiaga, S., & Boddey, R. M. (2000). Biological nitrogen fixation by two tropical forage legumes assessed from the relative ureide abundance of stem solutes: ¹⁵N calibration of the technique in sand culture. *Nutrient Cycling in Agroecosystems*, 56, 165-176.
- Al-Waber, M. I., Al-Omran, A., El-Naggar, A. H., Nadeem, M., and Usman, A. R. A. (2013). Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. *Bioresource Technology*, 131, 374-379.
- Alloway, B. J. (2008). Micronutrient deficiencies in global crop production. Netherlands: *Springer Science & Business Media*, pp 41-61.
- Ameloot, N., Sleutel, S., Das, K. C., Kanagaratnam, J., & De Neve, S. (2015). Biochar amendment to soils with contrasting organic matter level: Effects on N mineralization and biological soil properties. *Global Change Biology Bioenergy*, 7(1), 135–144.
- Anderson, C. R., Condron, L. M., Clough, T. J., Fiers, M., Steward, A., Hill, R. A., & Sherlock, R. R. (2011). Biochar induced soil microbial community change: implications for biogeochemical cycling of carbon, nitrogen and phosphorous. *Pedobiologia*, 54, 309-320.
- Angin, D. (2013). Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresource Technology*, 128, 593–597.

- Arnold, C. Y. (1947). Analysis of vegetable fertiliser plots with a soil test which measures acid soluble and adsorbed phosphorus. *Soil Science*, 64, 101-109.
- Asada, T., Ishihara, S., Yamane, T., Toba, A., Yamada, A., & Oikawa, K. (2002). Science of bamboo charcoal: Study on carbonizing temperature of bamboo charcoal and removal capability of harmful gases. *Journal of Health Science*, 48(6), 473-479.
- Asadullah, M., Rahman, M. A., Ali, M. M., Rahman, M. S., Motin, M. A., Sultan, M. B., & Alam, M. R. (2007). Production of bio-oil from fixed bed pyrolysis of bagasse. *Fuel*, 86, 2514–2520.
- Asai, H., Samson, B. K., Stephan, H. M., Songyikhangsuthor, K., Homma, K., Kiyono, Y., Inoue, Y., Shiraiwa, T., & Horie, T. (2009). Biochar amendment techniques for upland rice production in northern Laos 1: Soil physical properties, leaf SPAD, and grain yield. *Field Crops Research*, 111, 81–84.
- Atkinson, C., Fitzgerald, J., & Hipps, N. (2010). Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: A review. *Plant and Soil*, 337, 1-18.
- Awalludin, M. F., Sulaiman, O., Hashim, R., & Nadhari, W. N. A. W. (2015). An overview of the oil palm industry in Malaysia and its waste utilization through thermochemical conversion, specifically via liquefaction. *Renewable and Sustainable Energy*, 50, 1469–1484.
- Ayoub, A. T. (1999). Fertilizers and the environment. *Nutrient Cycling in Agroecosystems*, 55, 117-121.
- Baharuddin, A., Sulaiman, A., Hee Kim, D., Mokhtar, M., Hassan, M., Wakisaka, M., Shirai, Y., & Nishida, H. (2013). Selective component degradation of oil palm

- empty fruit bunches (OPEFB) using high-pressure steam. *Biomass and Bioenergy*, 55, 268–275.
- Bonanomi, G., Ippolito, F., Cesarano, G., Nanni, B., Lombardi, N., & Rita, A. (2017). Biochar as plant growth promoter: better off alone or mixed with organic amendment? *Frontiers in Plant Science*, 8, 1-13.
- Bates, R. B., & Ghoniem, A. F. (2012). Biomass Torrefaction: Modeling of volatile and solid product evolution kinetics. *Bioresource Technology*, 124, 460-469.
- Barnes, R. T., Gallagher, M. E., Masiello, C. A., Liu, Z., & Dugan, B. (2014). Biochar-induced changes in soil hydraulic conductivity and dissolved nutrient fluxes constrained by laboratory experiments. *PLoS ONE*, 9, 1-9.
- Beare, M. H., Hendrix, P. F., Cabrera, M. L., & Coleman, D. C. (1994). Aggregate-protected and unprotected organic matter pools in conventional- and no-tillage soils. *Soil Science Society of America Journal*, 58(3), 787-795.
- Beck, D. A., Johnson G. R., & Spolek, G. A. (2011). Amending greenroof soil with biochar to affect runoff water quantity and quality. *Environmental Pollution*, 159, 2111–2118.
- Beesley, L., Moreno-Jiménez, E., & Gomez-Eyles, J. L. (2010). Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environmental Pollution*, 158(6), 2282–2287.
- Beesley, L., Moreno-Jimenez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., & Sizmur, T. (2011). A review of biochars' potential roles in remediation, vegetation and restoration of contaminated soils. *Environmental Pollution*, 159, 3269-3282.

- Belanger, N. I., Cote, B., Fyles, J. W., Chourchesne, F., & Hendershot, W. H. (2004). Forest re-growth as a controlling factor of soil nutrient availability 75 years after fire in a deciduous forest of southern Quebec. *Plant and Soil*, 262, 363-372.
- Berglund, L. M., DeLuca, T. H., & Zackrisson, O. (2004). Activated carbon amendments of soil alters nitrification rates in scots pine forests. *Soil Biology and Biochemistry*, 36, 2067–2073.
- Bergstrom, L., & Kirchmann, H. (2004). Leaching and crop uptake of nitrogen from nitrogen¹⁵-labeled green manures and ammonium nitrate. *Journal of Environment Quality*, 33(5), 1786-1792.
- Blanco-Canqui, H. (2017). Biochar and soil physical properties. *Soil Science Society of America Journal*, 84, 687-711.
- Boaretto, A. E., Trivelin P. C. O., & Muraoka T. (2004). Uso de isotopos como tracadores em fertilidade do solo e nutricao de plantas, (In Portuguese). In Proceedings of the Soil Fertility and Plant Nutrition Conference (FERTBIO), (Lages: Centro de Energia Nuclear na Agricultura, CENA).
- Boehm, H. P. (1994). Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon*, 32(5), 759-769.
- Böhme, F., & Russow, R. (2005). Determination of the total nitrogen deposition by the ¹⁵N isotope dilution method and problems in extrapolating results to field scale. *Geoderma*, 127(1-2), 62-70.
- Bouwmeester, R. J. B., Vlek, P. L. G., & Stumple, J. M. (1985). Effects of environmental factors on ammonia volatilization from urea-fertilized soil. *Soil Science Society of America Journal*, 49, 376-381.

- Bray, R. H., & Kurtz, L. T. (1945). Determination of total, organic and available forms of phosphorous in soils. *Soil Science* 59, 39-45
- Brewer, C. E., Schmidt-Rohr, K., Satrio, J. A., & Brown, R. C. (2009). Characterization of biochar from fast pyrolysis and gasification systems. *Environmental Progress and Sustainable Energy*, 28, 386-396.
- Brewer, C. E., Unger, R., Schmidt-Rohr, K., & Brown, R. C. (2011). Criteria to select biochars for field studies based on biochar chemical properties. *Bioenergy Research*, 4, 312-323.
- Brewer, C.E. (2012). Biochar characterization and enigneering. Paper 12284, Iowa State University.
- Brodowski, S., John, B., Flessa, H., & Amelung, W. (2006). Aggregate-occluded black carbon in soil. *European Journal of Soil Science*, 57, 539–546.
- Brown, R. A., Kercher, A. K., Nguyen, T. H., Nagle, D. C., & Ball, W. P. (2006). Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. *Organic Geochemistrty*, 37, 321-333.
- Brown, R., del Campo, B., Boateng, A. A., Garcia-Perez, M., & Masek, O. (2015). Fundamentals of biochar production. In *Biochar for Environmental Management: Science, Technology and Implementation*; Lehmann, J., Joseph, S., Eds., Routledge: Oxford, UK.
- Bruun, E., Hauggaard-Nielsen, H., Ibrahim, N., Egsgaard, H., Ambus, P., Jensen, P. A., & Dam-Johansen, K. (2011). Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil. *Biomass and Bioenergy*, 35(3), 1182-1189.

- Bruun, E. W., Ambus P., Egsgaard H., & Hauggaard-Nielsen H. (2012). Effects of slow and fast pyrolysis biochar on soil c and n turnover dynamics. *Soil Biology and Biochemistry*, 46, 73–79.
- Caley G., & Jodi D. H. (2019). Soil organic matter does matter. North Dakota State University, Fargo. Extension. Extending knowledge, Changing Lives, SF1942. <https://www.ag.ndsu.edu/publications/crops/soil-organic-matter-does-matter/sf1942.pdf>.
- Caliman, J. P., Carcasses, R., Perel, N., Wohlfahrt, J., Girardin, P., Wahyu, A., Pujianto, Dubos, B., & Verwilghen, A. (2007). Agri-environmental indicators for sustainable palm oil production. *Palmas*, 28, 434–445.
- Cantrell, K. B., Hunt, P. G., Uchimiya, M., Novak, J. M., & Ro, K. S. (2012). Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresource Technology*, 107, 419–428.
- Cao, X. D., & Harris, W. (2010). Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource Technology*, 101(4), 5222–5228.
- Cardenas-Aguiar, E., Gasco, G., Paz-Ferreiro, J., & Méndez, A. (2017). The effect of biochar and compost from urban organic waste on plant biomass and properties of an artificially copper polluted soil. *International Biodeterioration and Biodegradation*, 124, 223–232.
- Caley, G., & Jodi, De J. H. (2019). Soil Organic Matter Does Matter. SF1942, Nov. 2019. North Dakota State University.
- Carter, S., Shackley, S., Sohi, S., Tan, B. S., & Haefele, S. (2013). The impact of biochar application on soil properties and plant growth of pot grown lettuce (*Lactuca sativa*) and cabbage (*Brassica chinensis*). *Agronomy*, 3, 404–418.

- Cassman, K. G., Dobermann, A., & Walters D. T. (2002). Agroecosystems, nitrogen-use efficiency and nitrogen management. *Ambio*, 31, 132-140.
- Chalk, P. M. (1985). Estimation of N₂ fixation by isotope dilution: An appraisal of techniques involving ¹⁵N enrichment and their application. *Soil Biology and Biochemistry*, 17(4), 389-410.
- Chalk, P. M. (1996). Estimation of N₂ fixation by ¹⁵N isotope dilution - the a-value approach. *Soil Biology and Biochemistry*, 28(9), 1123-1130.
- Chan, K. Y., L. Van Zwieten, Meszaros, I., Downie, A., & Joseph, S. (2007). Agronomic values of greenwaste biochar as a soil amendment. *Australian Journal of Soil Research*, 45(8), 629–634.
- Chan, K. Y., L. Van Zwieten, Meszaros, I., Downie, A., & Joseph, S. (2008). Using poultry litter biochars as soil amendments. *Australian Journal of Soil Research*, 46, 437-444.
- Chan, K.Y., & Xu, Z. (2009). Biochar: Nutrient properties and their enhancement. In: Lehmann, J. & Joseph, S. (eds.). Biochar for environmental management: *Science and Technology*. London, UK: Earthscan, pp 67–84.
- Chardon, F., Barthelemy, J., Daniel-Vedele, F., & Masclaux-Daubresse, C. (2010). Natural variation of nitrate uptake and nitrogen use efficiency in arabidopsis thaliana cultivated with limiting and ample nitrogen supply. *Journal of Experimental Botany*, 61(9), 2293-2302.
- Cheah, S., Jablonski, W. S., Olstad, J. L., Carpenter, D. L., Barthelemy, K. D., Robichaud, D. J., Andrews, J. C., Black, S. K., Oddo, M. D., & Westover, T. L. (2016). Effects of thermal pretreatment and catalyst on biomass gasification efficiency and syngas composition. *Green Chemistry*, 18, 6291–6304.

- Chen, B. L., Zhou, D. D., & Zhu, L. Z. (2008). Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperature. *Environmental Science and Technology*, 42(14), 5137-5143.
- Chen, B. L., Zhou, D., & Zhu, L. (2008). Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science and Technology*, 42, 5137–5143.
- Chen, W. H., & Kuo, P. C. (2011). Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis. *Energy*, 36(11), 6451-6460.
- Chen, Y. Q., Yang, H. P., & Wang, X. H. (2012). Biomass-based pyrolytic polygeneration system on cotton stalk pyrolysis: Influence of temperature. *Bioresource Technology*, 107, 411-418.
- Cheng, C. H., Lehmann J., Thies, J. E., Burton, S. D., & Engelhard, M. H. (2006). Oxidation of black carbon by biotic and abiotic processes. *Organic Geochemistry*, 37, 1477-1488.
- Cheng, C. H., Lehmann J., & Engelhard, M. H. (2008). Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. *Geochimica et Cosmochimica Acta*, 72, 1598-1610.
- Chintala, R., Schumacher, T. E., McDonald, L. M., Clay, D. E., Malo, D. D., Papiernik, S. K., Clay, S. A., & Julson, J. L. (2014). Phosphorus sorption and availability from biochars and soil/biochar mixtures. *Clean – Soil, Air, Water*, 42, 626–634.
- Choo, Y. M., Muhammad, H., Hashim, Z., Subramaniam, V., Pua, C. W., & Tan, Y. (2011). Determination of GHG contributions by subsystems in the oil palm supply

- chain using the LCA approach. *International Journal of Life Cycle Assessment*, 16, 669-681.
- Chun, Y., Sheng, G. Y., Chiou, C. T., & Xing, B. S. (2004). Compositions and sorptive properties of crop residue-derived chars. *Environmental Science and Technology*, 38(17), 4649–4655.
- Claoston, N., Samsuri, A. W., Ahmad Husni, M. H., & Mohd Amran, M. S. (2014). Effect of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars. *Waste Management and Research*, 32, 331-339.
- Clough, T. J., Condon, L. M., Kammann, C., & Müller, C. (2013). A review of biochar and soil nitrogen dynamics. *Agronomy* 3, 275-293.
- Coelho, A. M., Franca, G. C., Bahia, A. F. C., & Guedes, G. A. A. (1991). Balanço de nitrogênio ¹⁵N em um Latossolo Vermelho-Escuro, sob vegetação de cerrado, cultivado com milho. *Revista Brasileira de Ciência do Solo*, 15, 187-193.
- Comte, I., Colin, F., Whalen, J.K., Grunberger, O., & Caliman, J. P. (2012). Agricultural practices in oil palm plantations and their impact on hydrological changes, nutrient fluxes and water quality in Indonesia, in: *Advances in Agronomy*, 116, 71-124.
- Compendium of Chemical Terminology. (2009). *International union of pure and applied chemistry*, pp 1824.
- Corley, R. H. V., & Tinker, P. B. H. (2003). *The Oil Palm*. Published by Edition: Oxford, Blackwell.
- Czernik, S., & Bridgwater, T. (2004). Overview of Applications of Biomass Fast Pyrolysis Oil. *Energy & Fuels*, 18(2), 590-598.
- Dalila, T., Claudia, C., Silvia, B., Carla, A., Francesco, P. V., Giuseppe, L., Sara, D. L., Francesca, F., Roberto, T., & Gabriella, S. S. (2017). The Effects of Biochar and Its

- Combination with Compost on Lettuce (*Lactuca sativa* L.) Growth, Soil Properties, and Soil Microbial Activity and Abundance. *Hindawi, International Journal of Agronomy*, 2017, 1-12. <https://doi.org/10.1155/2017/3158207>
- Dai, L., Tan, F., Wu, B., Mingxiong, H., Wang, W., Tang, X., Hu, Q., & Zhang, M. (2015). Immobilization of phosphorus in cow manure during hydrothermal carbonization. *Journal of Environmental Management*, 157, 49–53.
- Daniel, M.K. (2009). Biochar-A survey. Thesis for: ENER-1346 Special Assignment in Energy and Process Engineering. Advisor: Antti Oksanen
- Danso, S. K. A. (1986). Review: Estimation of N₂-fixation by isotope dilution: An appraisal of techniques involving ¹⁵N enrichment and their application-comments. *Soil Biology and Biochemistry*, 18(3), 243-244.
- DeLuca, T. H., MacKenzie, M. D., Gundale, M. J., & Holben, W. E. (2006). Wildfire-produced charcoal directly influences nitrogen cycling in forest ecosystems. *Soil Science Society America Journal*, 70, 448–453.
- DeLuca, T. H., MacKenzie, M. D., & Gundale, M. J. (2009). Biochar effects on soil nutrient transformations. In J. Lehmann, S. Joseph Eds., *Biochar for environmental management: Science and Technology*, Earthscan, London, pp 251-270.
- Demirbas, A. (2004). Combustion characteristics of different biomass fuels. *Progress in Energy and Combustion Science*, 30, 219–230.
- Demirbas, A. (2008). Producing bio-oil from olive cake by fast pyrolysis. *Energy Sources*, 30 (Part A), 38-44.
- Dias, B. O., Silva, C. A., Higashikawa, F. S., Roig, A. & Sánchez-Monedero, M. A. (2010). Use of biochar as bulking agent for the composting of poultry manure:

- effect on organic matter degradation and humification. *Bioresource Technology*, 101, 1239-1246.
- Ding, Y., Liu, Y. X., Wu, W. X., Shi, D. Z., & Yang, M. (2010). Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. *Water Air and Soil Pollution*, 213(1), 47–55.
- Ding, W., Dong, X., Ime, I. M., Gao, B., & Ma, L. Q. (2014). Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars. *Chemosphere*, 105, 68–74.
- Downie, A., Crosky, A., & Munroe, P. (2009). Physical properties of biochar. In: Lehmann J, Joseph S, editors. Biochar for environmental management: *Science and Technology*. London: Earthscan, pp 13-32.
- Dume, B., Brerecha, G., & Tulu, S. (2015). Characterisation of biochar produced at different temperatures and its effect on acidic Nitosol of Jimma, Southwest Ethiopia. *International Journal of Soil Science*, 10, 63-73.
- Ebeling, A. G., L. Anjos, L. H. C., Perez, D.V., Pereira, M. G., & Valladares, G. S. (2011). Relationship between acidity and other chemical attributes of soils with high organic matter content. *Bragantia*, 70, 157-165.
- Elías, R. D. P., Luis, R. O. S., Diego, A. S., João, L. D. B., Gabriela, B. B, Fabio, M. Y., Teófilo M. S., & Cristiane, I. C. (2019). Eucalyptus bark charcoal: the Influence of carbonization temperature in thermal behavior. *Material Research*, 22(suppl.1): e20190371.
- Elisa, A. A., Shamshuddin, J., & Fauziah, C. I. (2011). Root elongation, root surface area and organic acid exudation by rice seedling under Al^{3+} and/or H^{+} stress. *American Journal of Agricultural and Biological Sciences*, 6, 324-331.

- Enders, A., Hanley, K., Whitman, T., Joseph, S., & Lehmann, J. (2012). Characterization of biochars to evaluate recalcitrance and agronomic performance. *Bioresources Technology*, 114, 644-653.
- Evans, R. D. (2007). Soil nitrogen isotope composition. In: Lajtha K, Michener RH (eds) *Stable isotopes in ecology and environmental science*, 2nd edition. Blackwell, Oxford, pp 83-98.
- Fahmi, A. H., Samsuri, A. W., Hamdan, J., & Daljit Singh. (2018). Physical modification of biochar to expose the inner pores and their functional groups to enhance lead adsorption. *Royal Society of Chemistry Advances*, 8, 38270-38280.
- Feigin, A., & Halevy, J. (1989). Irrigation-fertilization-cropping management for maximum economic return and minimum pollution of ground water. Research report, *Institute Soil Water*, ARO, The Volcani Center, Bet Dagan.
- Foster, H. L., Zin, Z. Z., & Mohd, T. D. (1988). Evaluation of the efficiency of urea as a nitrogen fertilizer for oil palm in Malaysia. Proc. of the International Symposium on Urea Technology and Utilization (Pushparajah, E; A Husin and A T Bachik eds.). 16-19 March 1987. *Malaysian Soil Science Society*, Kuala Lumpur, pp 403-419.
- Foster, H. L., & Goh, H. S. (1977). Fertilizer requirements of oil palm in west Malaysia. In *International Developments in Oil Palm* (eds. D. A. Earp and W. Newall). *Incorporated Society of Planter*, Kuala Lumpur, pp 234-261.
- Gale, N. V., Sackett, T. E., & Thomas, S. C. (2016). Thermal treatment and leaching of biochar alleviate plant growth inhibition from mobile organic compounds. *PeerJ Journal*, 4, e2385.

- Gallais, A., Coque, M., Quill  r  , I., Prioul, J. L., & Hirel, B. (2006). Modelling postsilking nitrogen fluxes in maize (*Zea mays*) using 15N-labelling field experiments. *New Phytologies*, 172, 696–707.
- Gao, Y., Yue, Q., & Gao, B. (2013). Preparation of high surface area-activated carbon from lignin of papermaking black liquor by KOH activation for Ni (II) adsorption. *Chemical Engineering Journal*, 217, 345-353.
- Gaskin, J. W., Steiner, C., Harris, K., Das, K. C., & Bibens, B. (2008). Effects of low-temperature pyrolysis conditions on biochar for agriculture use. *Transactions of ASABE*, 51(6), 2061-2069.
- Gaunt, J. L., & Lehmann, J. (2008). Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. *Environmental Science and Technology*, 42, 4152-4158.
- Gerlach, H., & Schmidt, H.P. (2012). Biochar in poultry farming. *Ithaka Journal*, 2012, 262–264.
- Geoffrey, L. (2008). Ancient skills could reverse global warming. The Independent. Archived from the original on 13 September 2011. Retrieved 1 October 2011. <http://www.independent.co.uk/environment/climate-change/ancient-skills-could-reverse-global-warming-1055700.html>
- G  b, T., Palmowska, J., Zaleski, T., & Gondek, K. (2016). Effect of biochar application on soil hydrological properties and physical quality of sandy soil. *Geoderma*, 281, 11–20.
- Glaser, B., Haumaier, L., Guggenburger, G., & Zech, W. (2001). The “Terre Preta” phenomenon: A model for sustainable agricultural agriculture in the humid tropics. *Naturwissenschaften*, 88, 37-41.

- Glaser, B., Lehmann, J., & Zech, W. (2002). Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal- A review. *Biology and Fertility of Soils*, 35, 219-230.
- Goh, K. J. (1997). Interpretations of analytical data from soil survey reports for manuring recommendations: some pointers. Annual Journal/Report 1997, *Royal Johore Planters' Association*, 25-30.
- Goh, K. J., Teo, C. B., Chew, P. S., & Chiu, S. B. (1999). Fertiliser management in oil palm: Agronomic principles and field practices. In: *Fertiliser management for oil palm plantations, 20-21, September 1999*, ISP North-east Branch, Sandakan, Malaysia: 44 pp
- Goh, K. J., & Hardter, R. (2003). General oil palm nutrition. In “Oil Palm: Management for Large and Sustainable Yields” (T. Fairhurst and R. Hardter, Eds.), pp. 191–230. PPI/PPIC and IPI, Singapore.
- Goh, K. J., Hardter, R., & Fairhurst, T. (2003). Fertilizing for maximum return. In T. Fairhurst and R. Hardter (Eds.), *Oil palm management for large and sustainable yields: PPI, PPIC and IPI*.
- Goh, K. J. (2005). Fertilizer recommendation systems for oil palm: Estimating the fertiliser rates. Paper presented at the proceedings of MOSTA best practices workshops - Agronomy and Crop Management.
- Gomez, L. D., Steele-King, C. G., & McQueen-Mason, S. J. (2008). Sustainable liquid biofuels from biomass: The writing's on the walls. *New Phytologist*, 178(3), 473-485.

- Gundale, M. J., & DeLuca, T. H. (2006). Temperature and substrate influence the chemical properties of charcoal in the ponderosa pine/douglas-fir ecosystem. *Forest Ecology and Management*, 231, 86-93.
- Gunarathne, V., Vithanage, M., & Mayakaduwa, S. (2017). Biochar's influence as a soil amendment for essential plant nutrient uptake. *Essential Plant Nutrients*, pp 47-66.
- Graber, E. R., & Kookana, R. S. (2015). Biochar and retention/efficacy of pesticides, in J. Lehmann (Eds.). Biochar for environmental management: *Science and Technology*. London: Earthscan Books Ltd, pp. 655–678.
- Grenon, F., Bradley, R. L., & Titus, B. D. (2004). Temperature sensitivity and mineral n transformation rates, and eterotrophic nitrification: possible factors controlling the post-disturbance mineral n flush in forest floor. *Soil Biology and Biochemistry*, 36, 1465-1474.
- Hagner, M., Kemppainen, R., Jauhiainen, L., Tiilikkala, K., & Setälä, H. (2016). The effects of birch (*Betula* spp.) biochar and pyrolysis temperature on soil properties and plant growth. *Soil and Tillage Research*, 163, 224–234.
- Haider, G., Steffens, D., Müller, C., & Kammann, C.I. (2016). Standard extraction methods may underestimate nitrate stocks captured by field-aged biochar. *Journal of Environmental Quality*, 45, 1196–1204.
- Havlin, J. L., Tisdale, S. L., Nelson, W. L., & Beaton, J. D. (1999). *Soil fertility and fertilizers*. 6th Ed. Englewood Cliffs (NJ): Prentice Hall, pp 499.
- Hamilton, S. D., Chalk, P. M., Smith, C. J., & Hopmans, P. (1991). Effect of N fertilizer rate on the estimation of N₂ fixation by isotope dilution. *Soil Biology and Biochemistry*, 23(12), 1105-1110.

- Hanson, W. C. (1950). The photometric determination of phosphorous in fertilisers using the phosphovanadomolybdate complex. *Journal of the Science of Food and Agriculture* 1, 172-173.
- Harvey, O. M., Herbert, B. E., Kuo, L. J., & Louchouart, P. (2012). Generalized two-dimensional perturbation correlation infrared spectroscopy reveals mechanisms for the development of surface charge and recalcitrance in plant-derived biochars. *Environmental Science and Technology*, 46(19), 10641–10650.
- He, X., Yin, H., Han, L., Cui, R., Fang, C., & Huang, G. (2019). Effects of biochar size and type on gaseous emissions during pig manure/wheat straw aerobic composting: Insights into multivariate-microscale characterization and microbial mechanism. *Bioresource Technology*, 271, 375–382.
- Horie, T., Brodsky, D. E., Costa, A., Kaneko, T., Schiavo, F.L, Katsuhara, M., & Schroeder, J. I. (2011). K⁺ transport by the OsHKT2;4 transporter from rice with atypical Na⁺ transport properties and competition in permeation of K⁺ over Mg²⁺ and Ca²⁺ ions. *Plant Physiology*, 156, 1493–1507.
- Howell, J. (2005). Organic Matter: Key to Soil Management. Available at http://www.hort.uconn.edu/ipm/veg/croptalk/croptalk1_4/page8.html. [verified 1.19.11]
- Huang, J. W., Grunes, D. L., & Welch, R. M. (1990). Magnesium, nitrogen form, and root temperature effects on grass tetany potential of wheat forage. *Agronomy Journal*, 82, 581–587.
- Hunt, J., DuPont, M., Sato, D., & Kawabata, A. (2010). The basic of biochar: A natural soil amendment. Soil and crop management, University of Hawai'i at Mānoa, SCM-30, 1-6.

- IAEA. (1983). A guide to the Use of Nitrogen-15 and radioisotopes in studies of plant nutrition: calculations and interpretation of data: *International Atomic Energy Agency (IAEA)*, TECDEC-288, Vienna, Austria.
- Idris, J., Shirai, Y., & Andou, Y. (2015a). Self-sustained carbonization of oil palm biomass produced an acceptable heating value charcoal with low gaseous emission. *Journal of Cleaner Production*, 89, 257–261.
- Idris, J., Shirai, Y., & Andou, Y. (2015b). Improved yield and higher heating value of biochar from oil palm biomass at low retention time under self-sustained carbonization. *Journal of Cleaner Production*, 104, 475–479.
- Ippolito, J. A., Novak, J. M., Busscher, W. J., Ahmedna, M., Rehrich, D., & Watts, D. W. (2012). Switchgrass biochar affects two aridisols. *Journal of Environmental Quality*, 41, 1123-1130.
- Ippolito, J. A., Ducey, T. F., Cantrell, K. B., Novak, J. M., & Lentz, R. D. (2016). Designer, acidic biochar influences calcareous soil characteristics. *Chemosphere*, 142, 184-191.
- Islam, A., Chen, D., & White, R. E. (2007). Heterotrophic and autotrophic nitrification in two acid pasture soil. *Soil Biology and Biochemistry*, 39, 972-975.
- Iswaran, V., Jauhri, K. S., & Sen, A. (1980). Effect of charcoal, coal and peat on the yield of moong, soybean and pea. *Soil Biology and Biochemistry*, 12, 191-192.
- Jayawardhana, Y. (2016). Detection of benzene in landfill leachate from gohagoda dumpsite and its removal using municipal solid waste derived biochar. <http://dl.lib.mrt.ac.lk/handle/123/11579>

- Jeffery, S., Verheijen, F. G. A., van der Velde, M., & Bastos, A. C. (2011). A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agriculture, Ecosystems and Environment*, 144(1), 175–187.
- Jeffery, S., Meinders, M. B. J., Stoof, C. R., Bezemer, T. M., van de Voorde, T. F. J., Mommer, L., & van Groenigen, J. W. (2015). Biochar application does not improve the soil hydrological function of a sandy soil. *Geoderma*, 251-252, 47–54.
- Jiang, T. Y., Jiang, J., Xu, R. K., & Li, Z. (2012). Adsorption of Pb(II) on variable charge soils amended with rice-straw derived biochar. *Chemosphere*, 89(3), 249-256.
- Jin, S. C., Sung, H. P., Jung, S. C, Ryu, C. K., Jeon, & J. K. (2016). Production and utilization of biochar: A review. *Journal of Industrial and Engineering Chemistry*, 40, 1-15.
- Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M. A., & Sonoki, T. (2014). Physical and chemical characterization of biochars derived from different agricultural residues. *Biogeosciences*, 11, 6613–6621.
- John, M. K., Chuah, H. H., & Neufeld, J. H. (1975). Application of improved azomethine-H method to determine the boron in soils and plants. *Analytical Letters*, 8, 559-568.
- Jones, J. (2011). *Mechanism of pyrolysis*. Proceedings of the 2011 Regional Meeting of the Australia and New Zealand Biochar Research Network, Massey University, Melbourne, September 29-30.
- Johnston, A. E. (2005). Understanding potassium and its use in agriculture. Brussels: EFMA.
- Joseph, S. D., Camps-Arbestain M., Lin, Y., Munroe P., Chia, C. H., Hook, J., & van Zwieten, L. (2010). An investigation into the reactions of biochar in soil. *Soil Research*, 48, 501–515.

- Julie, M. (2010). Guidelines on Practical Aspects of Biochar Application to Field Soil in Various Soil Management Systems. *International Biochar Initiative, Version 1.0*, 9 November 2010, pp 1-23.
- Kammann, C. I., Schmidt, H. P., Messerschmidt, N., Linsel, S., Steffens, D., Muller, C., Koyro, H. W., Conte, P., & Stephen, J. (2015). Plant growth improvement mediated by nitrate capture in co-composted biochar. *Scientific Reports*, 5, 1-12.
- Kanokporn, S. (2015). Soil carbon and nitrogen ratio in different land use. International Conference on Advances in Environment Research Volume 87 of IPCBEE. DOI: 10.7763/IPCBEE. 2015. V87. 7
- Karhu, K, Mattila, T, Bergström, I, & Regina, K. (2011). Biochar addition to agricultural soil increased CH₄ uptake and water holding capacity - results from a short-term pilot field study. *Agricultural Ecosystems and Environment*, 140(1), 309-313.
- Kasozi, G. N., Zimmerman, A. R., Nkedi-Kizza, P., & Gao, M .B. (2010). Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars). *Environmental Science Technology*, 44, 6189–6195.
- Karer, J., Wimmer, B., Zehetner, F., Kloss, S., & Soja, G. (2013). Biochar application to temperate soils: Effects on nutrient uptake and crop yield under field conditions. *Agricultural and Food Science*, 22, 390-403.
- Kastner, J. R., Miller, J., & Das, K.C. (2009). Pyrolysis conditions and ozone oxidation effects on ammonia adsorption in biomass generated chars. *Journal of Hazardous Materials*, 164, 1420–1427.
- Keech, O., Carcaillet, C., & Nilsson, M. C. (2005). Adsorption of allelopathic compounds by wood-derived charcoal: The role of wood porosity. *Plant and Soil*, 272, 291-300.

- Keiluweit, M., Nico, P. S., Johnson, G., & Kleber, M. (2010). Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environmental Science and Technology*, 44(4), 1247-1253.
- Kim, J., Sparovek, G., Longo, R. M., De Melo, W. J., & Crowley, D. (2007). Bacterial diversity of terra preta and pristine forest soil from the Western Amazon. *Soil Biology and Biochemistry*, 39(2), 684-690.
- Kim, K., Kim, J., Cho, T., & Choi, J. (2012). Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (*Pinus rigada*). *Bioresource Technology*, 118, 158-162.
- Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., & Liedtke, V. (2012). Characterization of slow pyrolysis biochars: Effects of feedstocks and pyrolysis temperature on biochar properties. *Journal of Environmental Quality*, 41, 990-1000.
- Knoepp, J. D., DeBano, L. F., & Neary, D. G. (2005). Soil chemistry, Chapter 3. Ogden, UT: US Department of Agriculture, Forest Service, *Rocky Mountain Research Station*, 42(4), 53-71.
- Kong, S. H., Loh, S. K., Robert, T. B., Sahibin, A. R., & Jumat, S. (2014). Biochar from oil palm biomass: A review of its potential and challenges. *Renewable and Sustainable Energy Reviews*, 39, 729-739.
- Kookana, R. S., Sarmah, A. K., Van Zwieten, L., Krull, E., & Singh, B. (2011). Biochar application to soil: Agronomic and environmental benefits and unintended consequences. *Advance in Agronomy*, 112, 103–143.
- Kraska, P., Oleszczuk, P., Andruszczak, S., Kwiecińska-Poppe, E., Rożyło, K., Pałys, E., Gierasimiuk, P., & Michałojć, Z. (2016). Effect of various biochar rates on winter

- rye yield and the concentration of available nutrients in the soil. *Plant, Soil and Environment*, 62, 483–489.
- Krishnakumar, S., Kumar, S.R., Mariappan, N., & Surrender, K.K. (2013). Biochar-boon to soil health and crop production. *Agricultural Research*, 8, 4726-4739.
- Kwabiah, A. B., Palm, C. A., Stoskopf, N. C., & Voroney, R. P. (2003). Response of soil microbial biomass dynamics to quality of plant materials with emphasis on p availability. *Soil Biology and Biochemistry*, 35, 207–216.
- Laird, D., Fleming, P., Davis, D. D., Horton, R., Wang, B., & Karlen, D. L. (2010). Impact of biochar amendments on the quality of a typical midwestern agricultural soil. *Geoderma*, 158(3-4), 443-449.
- Laird, D., Fleming, P., Wang, B., Horton, R., & Karlen, D. (2010). Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma*, 158, 436–442.
- Laine, J., & Yunes, S. (1992). Effect of the preparation method on the pore size distribution of activated carbon from coconut shell. *Carbon*, 30, 601-604.
- Lewandowski, W., Radziemska, M., Ryms, E., & Ostrowski, P. (2010). Nowoczesne metody termochemiczne konwersji biomasyw paliwa gazowe, ciekłe i stałe. Proceedings of ECOpole 4(2) (in Polish)
- Lee, X. J., Lee, L. Y., Gan, S., Thangalazhy-Gopakumar, S. & Ng, H. K. (2017). Biochar potential evaluation of palm oil wastes through slow pyrolysis: thermochemical characterization and pyrolytic kinetic studies. *Bioresource Technology*, 236, 155-163.
- Le Leuch, L. M., & Bandosz, T. J. (2007). The role of water and surface acidity on the reactive adsorption of ammonia on modified activated carbons. *Carbon*, 45, 568–578.

- Lehmann, J., Silva, D., Steiner, Jr. J. P., Nehl, C. T., Zech, W., & Glaser, B. (2003). Nutrient availability and leaching in an archaeological anthrosol and a ferralsol of the central amazon basin: fertilizer, manure and charcoal amendments. *Plant and Soil*, 249, 343-357.
- Lehmann, J., Kern, D. C., German, L. A., McCann, J., Martins, G. C., & Moreira, A. (2003). Soil fertility and production potential. In: Lehmann, J., Kern, D.C., Glaser, B., & Woods, W. (eds.). *Amazonian dark earths: Origin, properties, management*. Dordrecht, The Netherlands: Kluwer Academic Publishers, pp 105–124.
- Lehmann, C. J., & Rondon, M. (2006). Bio-char soil management on highly-weathered soils in the tropics. In: N.T. Uphoff, (Ed.), *Biological approaches to sustainable soil systems*. CRC Press, Boca Raton, pp 517-530.
- Lehmann, J., Gaunt, J., & Rondon, M. (2006). Bio-char sequestration in terrestrial ecosystems – A review. *Mitigation Adaptation Strategies for Global Change*, Springer, 11(2), 395–419.
- Lehmann, J. (2007). Bio-energy in the black. *Frontiers in Ecology and the Environment*, 5, 381-387.
- Lehmann, J., Czimczik, C., Laird, D., & Sohi, S. (2009). Stability of biochar in soil. In: Lehmann J, Joseph S, editors. Biochar for environmental management. *Science and Technology*. London: Earthscan, pp 169-182.
- Lehmann, J., Rillig, M. C., Thies, J., Masiello, C. A., Hockaday, W. C., & Crowley, D. (2011). Biochar effects on soil biota – A review. *Soil Biology and Biochemistry*, 43, 1812-1836.
- Lehmann, J., Abiven, S., Kleber, M., Pan, G., Singh, B. P., Sohi, S., & Zimmerman, A. R. (2015). Persistence of biochar in soil. In *Biochar for Environmental Management*:

- Science, Technology and Implementation; Lehmann, J., Joseph, S., Eds.; Routledge: Oxford, UK.
- Leininger, S., Urich, T., Schlöter, M., Schwark, L., Qi, J., Nicol, G. W., Prosser, J. I., Schuster, S. C., & Schleper, C. (2006). Archaea predominate among ammonia-oxidizing prokaryotes in soils. *Nature*, *442*, 806–809.
- Lentz, R., & Ippolito, J. (2012). Biochar and manure affect calcareous soil and corn silage nutrient concentrations and uptake. *Journal of Environmental Quality*, *41*(4), 1033–1043.
- Li, L., Liu, Y., & Lu, Y.C. (2011). Review on environment effects and application of biochar. *Environment Chemistry*, *30*(8), 1412-1420.
- Li, S., & Shangguan, Z. (2018). Positive effects of apple branch biochar on wheat yield only appear at a low application rate, regardless of nitrogen and water conditions. *Journal of Soils and Sediments*, *18*, 3235–3243.
- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., & O'Neill, B., Skjemstad, J. O., Thies, J., Luizão, F.J., Peterson, J., & Neves, E.G. (2006). Black carbon increases cation exchange capacity in soils. *Soil Science Society of America Journal*, *70*(5), 1719-1730.
- Liang, B., Lehmann, J., Solomon, D., Sohi, S., Thies J. E., Skjemstad, J. O., Luizao, F. J., Engelhard, M. H., Neves E. G., & Wrick, S. (2008). Stability of biomass-derived black carbon in soils. *Geochimica et Cosmochimica Acta*, *72*, 6096-6078.
- Liu, Z., He, T., Cao, T., Yang, T. X., Meng, J., & Chen, W.F. (2017). Effect of biochar application on nitrogen leaching, ammonia volatilization and nitrogen use efficiency in two distinct soils. *Journal of Soil Science and Plant Nutrition*, *17*(2), 515-528.

- Lua, A. C., Yang, T., & Guo, J. (2004). Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. *Journal of Analytical and Applied Pyrolysis*, 72(2), 279–287.
- Mahmood, W. M. F. W., Ariffin, M.A., Harun, M. A., ISHAK, Z. A. I. M. D., Ghani, J.A., & Rahman, M. N. A. B. (2015). Characterization and potential use of biochar from gasified oil palm wastes. *Journal of Engineering Science and Technology*, pp 45-54.
- Maia, C., Madari, B. E., & Novotny, E. H. (2011). Advances in biochar research in Brazil. *Dynamic soil, Dynamic Plant*, 5, 53-58.
- Major, J., Steiner, C., Ditommaso, A., Falcao, N. P. S., & Lehmann, J. (2005). Weed composition and cover after three years of soil fertility management in the central Brazilian amazon; compost, fertilizer, manure and charcoal applications. *Weed Biology and Management*, 5, 69-76.
- Major, J., Rondon, M., Molina, D., Riha, S.J., & Lehmann, J. (2010). Maize yield and nutrition after 4 years of doing biochar application to a Colombian Savanna Oxisol. *Plant and Soil*, 333, 117-128.
- Major, J., Rondon, M., Molina, D., Riha, S. J., & Lehmann, J. (2012). Nutrient leaching in Colombian Savanna Oxisol amended with biochar. *Journal of Environmental Quality*, 41, 1076-1086.
- Malaysian Standard, MS 677, Part 1 to VIII. (1980). Recommended method for plant chemical analysis. Shah Alam: Standards and Industrial Research Institute of Malaysia (SIRIM).
- Malaysian Standard, MS 678, Part V1 to IX. (1980). Recommended method for soil chemical analysis. Shah Alam: Standards and Industrial Research Institute of Malaysia (SIRIM).

- Malaysian Standard, MS 679, Part 1 to V. (1980). Recommended method for soil chemical analysis. Shah Alam: Standards and Industrial Research Institute of Malaysia (SIRIM).
- Manyà, J. J. (2012). Pyrolysis for biochar purposes: A review to establish current knowledge gaps and research needs. *Environmental Science Technology*, 46, 7939-7954.
- Mara dos Santos Barbosa, J., Ré-Poppi N., & Santiago-Silva M. (2006). Polycyclic aromatic hydrocarbons from wood pyrolysis in charcoal production furnaces. *Environment Research*, 101, 304-311.
- Maschio, G., Koufopoulos, C., & Lucchesi, A. (1992). Pyrolysis, a promising route for biomass utilization. *Bioresource Technology*, 42, 219-231.
- Masto, R. E., Kumar, S., Rout, T. K., Sarkar, P., George, J., & Ram, L. C. (2013). Biochar from water Hyacinth (*Eichornia crassipes*) and its impact on soil biological activity. *Catena*, 111, 64–71.
- McClellan, T., Deenik, J., Uehara, G., & Antal, M., (2007). *Effects of flashed carbonized-Macadamia nutshell charcoal on plant growth and soil chemical properties*. November 6, 2007, ASA-CSSA-SSA International Annual Meetings, New Orleans, Louisiana. <http://a-c-s.confex.com/crops/2007am/techprogram/P35834.HTM>.
- McLaughlin, H., Anderson, P. S., Shields, F. E., & Reed, T. B. (2009). *All biochars are not created equal, and how to tell them apart*. Proceedings. North American Biochar Conference, Boulder, Colorado.
- McLaren, R. G., & Cameron, K. (1996). *Soil Science: Sustainable production and environmental protection* (2nd Edition), Oxford University Press. ISBN-13: 978-0195583458.

- Mehmet, S., Heike, T., & Andreas, G. (2015). Role of magnesium fertilizer in agriculture: Plant-soil continuum. *Crop and Pasture Science*, 66, 1219-1229.
- Mészáros, E., Jakab, E., Varhegyi, G., Bourke, J., Manly-Harris M., Nunoura, T., & Antal. M.J. (2007). Do all carbonized charcoals have the same chemical structure? Implications of thermogravimetry: Mass Spectrometry Measurements. *Industrial and Engineering Chemistry Research*, 46(18), 5943-5953.
- Mohamad, I., Zhang, G. S., Li, Z. G., Liu, Y., Chen, F., & Dai, K. (2015). Ecological restoration 612 of an acidic Cd contaminated soil using bamboo biochar application. *Ecological Engineering*, 84, 67-76.
- Malaysian Palm Oil Board (MPOB). (2019). Number and capacities of palm oil sectors in operation as in August 2019.
<http://bepi.mpob.gov.my/index.php/en/statistics/sectoral-status/370-sectoral-status-2019/917-number-a-capacities-of-palm-oil-sectors-2019.html>
- Morgan, T., Turn, S., & George, A. (2015). Fast pyrolysis behavior of banagrass as a function of temperature and volatiles residence time in a fluidized bed reactor. *PLoS ONE* 10(8), e0136511.
- Mukherjee, A., Zimmerman, A. R., & Harris, W. (2011). Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma*, 163, 247-255.
- Mukherjee, A., & Zimmerman, A. (2013). Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar-soil mixtures. *Geoderma*, 193, 122-130.
- National Innovation Agency of Malaysia. (2013). National Biomass Strategy 2020: *New Wealth Creation for Malaysia's Palm Oil Industry*, Version 2.0, 1-37.

- Nartey, D. O., & Zhao, B. (2014). Biochar preparation, characterization, and adsorption capacity and its effect on bioavailability of contaminants: An overview. *Advances in Materials Science and Engineering*. [online] Available at: <http://www.researchgate.net/publication/285463334>.
- Nasri, N. S., Hamza, U. D., Abdulkadir, A., Siti Noraishah, I., & Hamed, M. M. (2013). *Utilization of sustainable palm empty fruit bunch sorbents for carbon dioxide capture*. In the 6th International Conference on Process System Engineering (PSE ASIA), Kuala Lumpur, Malaysia: pp 582-587.
- Neary, D. G., Klopatek, C. C., DeBano, L. F., & Folliott, P. F. (1999). Fire effects on below ground sustainability. A review and synthesis. *Forest Ecology and Management*, 122, 51-71.
- Neary, D. G., Ryan, K. C., & DeBano, L. F. (2005). Wildland fire in ecosystems: Effects of fire on soil and water. Department of Agriculture, Forest Service, *Rocky Mountain Research Station*, 42(4), pp 250.
- Nelissen, V., Rütting, T., Huygens, D., Staelens, J., Ruyschaert, G., & Boeckx, P. (2012). Maize biochars accelerate short-term soil nitrogen dynamics in a loamy sand soil. *Soil Biology and Biochemistry*, 55, 20-27.
- Nelissen, V., Rütting, T., Huygens, D., Ruyschaert, G., & Boeckx, P. (2014). Temporal evolution of biochar's impact on soil nitrogen processes—A ¹⁵N tracing study. *Global Change Biology Bioenergy*, 7, 635-645.
- Nelson, D. W., & Sommers, L. E. (1982). Total carbon, organic carbon and organic matter: In: A.L. Page, R.H. Miller and D.R. Keeney) methods of soil analysis. Part 2 *Chemical and Microbiological Properties*, pp 539-579.

- Nigussie, A., Kissi, E., Misganaw, M., & Ambaw, G. (2012). Effect of biochar application on soil properties and nutrient uptake of lettuces (*Lactuca Sativa*) grown in chromium polluted soils. *American-Eurasian Journal of Agriculture and Environmental Science*, 12(3), 369-376.
- Niemeyer, T., Niemeyer, M., Mohamad, A., Fottner, S., & Härdtle, W. (2005). Impact of prescribed burning on the nutrient balance of health lands with particular reference to nitrogen and phosphorus. *Applied Vegetation Science*, 8, 183-192.
- Nguyen, B.T., & Lehmann, J. (2009). Black carbon decomposition under varying water regimes, *Organic Geochemistry*, 40(8), 846-853.
- Nguyen, T. T. N., Xu, C. Y., Tahmasbian, I., Che, R., Xu, Z., Zhou, X., Wallace, H. M., & Bai, S. H. (2017). Effects of biochar on soil available inorganic nitrogen: A review and meta-analysis. *Journal of Geoderma*, 288, 79-96.
- Noraliza, A. S., Che, F. I., & Rosenani, A. B. (2014). Characterization of oil palm empty fruit bunch and rice husk biochars and their potential to adsorb arsenic and cadmium. *American Journal of Agricultural and Biological Sciences*, 9(3), 450-456.
- Norman, P. A. H., & William, H. (2008). *Introduction to Plant Physiology*, 4th Edition. John Wiley & Sons, Inc. ISBN 978-0-470-24766-2, pp 528.
- Novak, J. M., Lima, L. M., Xing, B., Gaskin, J. W., Steiner, C., Das, K. C., Ahmedna, M., Rehrah, D., Watts, D. W., Busscher, W. J., & Schomberg, H. (2009). Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Annals of Environmental Science*, 3, 195–206.
- Novak, J. M., Busscher, W. J., Watts, D. W., Laird, D. A., Ahmedna, M. A. & Niandou, M. A. S. (2010). Short-Term CO₂ mineralization after additions of biochar and switchgrass to a typic Kandiudult. *Geoderma*, 154, 281–288.

- Novak, J. M., Busscher, W. J., Watts, D. W., Amonette, J. E., Ippolito, J. A., Lima, I. M., Gaskin, J., Das, K. C., Steiner, C., Ahmedna, M., Rehrh, D., & Schomberg, H. (2012). Biochar impact soil-moisture storage in an Udisol and two Aridisols. *Soil Science*, 177(5), 310-320.
- Nunes, L., Godina, R., Matias, J., & Catalão, J. (2018). Torrefaction of Portuguese woody biomasses and the evaluation of its properties. In Proceedings of the International Conference on Renewable Energies and Power Quality (ICREPQ'18), Salamanca, Spain, 21–23 March 2018; EA4EPQ—University of Vigo and University of Granada: Vigo, Spain.
- Oh, T. K., Choi, B., Shinogi, Y., & Chikushi, J. (2012). Characterization of biochar derived from three types of biomass. *Journal of the Faculty of Agriculture*, 57, 61-66.
- Owen, D. (1953). Determination of available nutrients in Malayan soils. *Journal of Rubber Research Institute of Malaya*, 14, 109-120.
- Özçimen, D., & Ersoy- eriçboyu, (2010). Characterization of biochar and bio-oil samples obtained from carbonization of arious biomass materials. *Renewable Energy*, 35(6), 1319-1324.
- Pardo, L. H., Templer, P. H., & Goodale, C. L. (2006). Regional assessment of n saturation using foliar and root $\delta^{15}\text{N}$. *Biogeochemistry*, 80,143-171.
- Park, J. H., Lamb, D., Paneerselvam, P., Choppala, G., Bolan, N., & Chung, J. (2011). Role of organic amendments on enhanced bioremediation of heavy metal (Loid) contaminated soils. *Journal of Hazardous Materials*, 185(2-3), 549-574.

- Peng, F., He, P. W., Luo, Y., Lu, X., Liang, Y., & Fu, J. (2012). Adsorption of phosphate by biomass char deriving from fast pyrolysis of biomass waste. *Clean – Soil, Air, Water*, 40, 493–498.
- Pennise, D. M., Smith, K. R., Kithinji, J. P., Rezende, M. E., Raad, T. J., Zhang, J., & Fan, C. (2001). Emissions of greenhouse gases and other airborne pollutants from charcoal making in Kenya and Brazil. *Journal of Geophysical Research*, 106, 24143-24155.
- Pietikäinen, J., Kiikkila, O., & Fritze, H. (2000). Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus. *OIKOS*, 89, 231-242.
- Pretty, K. M., & Stangel, P. J. (1985). Current and future use of world potassium. In: Munson RD, ed. Potassium in Agriculture. Madison, Wisconsin, USA: *American Society of Agronomy*, pp 99–128.
- Prins, M. J. (2005). Thermodynamic Analysis of Biomass Gasification and Torrefaction. Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands.
- Puga, A., Abreu, C., Melo, L., & Beesley, L. (2015). Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. *Journal of Environmental Management*, 159, 86–93.
- Putun, A. E., Ozbay, N., Onal, E. P., & Putun, E. (2005). Fixed-bed pyrolysis of cotton stalk for liquid and solid products. *Fuel Processing Technology*, 86, 1207-1219.
- Qi, D., Xiaoli, C., Guoyi, Z., Juxiu, L., Shizhong, L., Quanfa, Z., & Deqiang, Z. (2013). Seasonal responses of soil respiration to elevated CO₂ and N addition in young subtropical forest ecosystems in young subtropical forest ecosystems in Southern China. *Ecological Engineering*, 61, 65-73.

- Qi, Z., & Spalding, E. P. (2004). Protection of plasma membrane K⁺ transport by the salt overly sensitive Na⁺-H⁺ antiporter during salinity stress. *Plant Physiology*, 136, 2548–2555.
- Radin, R., Abu Bakar, R., Ishak, C. F., Ahmad, S. H., & Lim, C. T. (2017). Biochar-compost mixture as amendment for improvement of polybag-growing media and oil palm seedlings at main nursery stage. *International Journal of Recycling of Organic Waste in Agriculture*, 7, 11-23.
- Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmermann, A. R., & Lehmann, J. (2012). Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and Fertility of Soils*, 48, 271–284.
- Ramin, L., Assadi, M., Hussein, N., & Sahajwalla, V. (2014). High-density polyethylene degradation into two molecular weight gases at 1823K: An atomistic simulation. *Journal of Analytical and Applied Pyrolysis*, 110, 318–321.
- Rattan, L., & Steward, B. A. (2018). Soil nitrogen uses and environmental impacts. Boca Raton, CRC Press. *Advance in Soil Science*, pp 28.
- Rehrah, D., Reddy, M. R., Novak, J. M., Bansode, R. R., Schimmel, K. A., Yu, J., Watts, D. W., & Ahmedna, M. (2014). Production and characterization of biochars from agricultural by-products for use in soil quality enhancement. *Journal of Analytical and Applied Pyrolysis*, 108, 301-309.
- Ribeiro, J. M. C., Godina, R., Matias, J. C. D. O., & Nunes, L. J. R. (2018). Future Perspectives of Biomass Torrefaction: Review of the Current State-Of-The-Art and Research Development. *Sustainability*, 10(7), 2323.

- Robertson, S. J., Rutherford, M. P., López-Gutiérrez, J. C., & Massicotte, H. B. (2012). Biochar enhances seedling growth and alters root symbioses and properties of sub-boreal forest soils. *Canadian Journal of Soil Science*, 92, 329–340.
- Rondon, M. A., Lehmann, J., Ramirez, J., & Hurtado, M. (2007). Biological nitrogen fixation by common beans (*Phaseolus Vulgaris* L.) increases with biochar additions. *Biology and Fertility of Soils*, 43, 669–708.
- Rubab, S., Awais, S., Muhammad, A., Ammara, A., Azhar, H., & Shihe, X. (2017). Impact of integrated application of biochar and nitrogen fertilizers on maize growth and nitrogen recovery in alkaline calcareous soil. *Soil Science and Plant Nutrition*, 63, 488–498.
- Rus, A., Lee, B. H., Munoz-Mayor, A., Sharkhuu, A., Miura, K., Zhu, J. K., Bressan, R. A., & Hasegawa, P.M. (2004). AtHKT1 Facilitates Na⁺ homeostasis and K⁺ nutrition in planta. *Plant Physiology*, 136, 2500–2511.
- Rutigliano, F. A., Romano, M., Marzaioli, R., Baglivo, I., Baronti, S., Miglietta, F., & Castaldi, S. (2014). Effect of biochar addition on soil microbial community in a wheat crop. *European Journal of Soil Biology*, 60, 9–15.
- Rutherford, D. W., Wershaw, R. L., Rostad, C. E., & Kelly, C. N. (2012). Effect of formation conditions on biochars: Compositional and structural properties of cellulose, lignin, and pine biochars. *Biomass and Bioenergy*, 46, 693–701.
- Ruysschaert, G., Nelissen, V., Postma, R., Bruun, E., O'Toole, A., Hammond, J., Rödger, J. M., Hylander, L., Kihlberg, T., Zwart, K., Hauggaard-Nielsen, H., & Shackley, S. (2016). Field applications of pure biochar in the North Sea region and across Europe, in: Shackley, S., Ruysschaert, G., Zwart, K., Glaser, B. (Eds.), *Biochar in*

European soils and agriculture-science and practice. Routhledge, Oxon, UK and New York, USA.

- Sabri, M. A. (2009). Evolution of Fertilizer Use by Crops in Malaysia: *Recent Trends and Prospects IFA Crossroads Asia-Pacific 2009 Conference*. Kota Kinabalu, Malaysia.
- Schneour, E. A. (1996). Oxidation of graphite carbon in certain soils. *Science*, 151, 991–992.
- Scheuner, E. T., Makeschin, F., Well, E. D., & Cater, P.Q. (2004). Short-term impacts of harvesting and burning disturbances on physical and chemical characteristics of forest soils in western Newfoundland, Canada. *European Journal of Forest Research.*, 123(4), 321-330.
- Schulz, H., & Glaser, B. (2012). Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. *Journal of Plant Nutrition and Soil Science*, 175, 410- 653 422.
- Schulz, H., Dunst, G., & Glaser, B. (2013). Positive effects of composted biochar on plant growth and soil fertility. *Agronomy and Sustainable Development*, 33, 817–827.
- Seggewiss, B., & Jungk, A. (1988). Einfluss der kaliumdynamik im wurzelnahen boden auf die magnesiumaufnahme von pflanzen. *Zeitschrift für Pflanzenernährung und Bodenkunde*, 151, 91 –96.
- Shamshuddin, J., & Anda, M. (2012). Enhancing the productivity of ultisols and oxisols in Malaysia using basalt and/or compost. *Pedologist*, 55(3), 382–391.
- Shen, Q., Hedley, M., Camps Arbestain, M., & Kirschbaum, M. U. F. (2016). Can biochar increase the bioavailability of phosphorous? *Soil Science and Plant Nutrition*, 16(2), 268-286.

- Sheng, J., Ji, D., Yu, F., & Li, C. (2014). Influence of chemical treatment on rice straw pyrolysis by TG-FTIR. *Procedia*, 8, 30-34.
- Sika, M. P., & Hardie, A. G. (2014). Effect of pine wood biochar on ammonium nitrate leaching and availability in a South African sandy soil. *European Journal of Soil Science*, 65, 113–119.
- Singh, B., Singh, B. P., & Cowie, A. L. (2010). Characterisation and evaluation of biochars for their application as a soil amendment. *Australian Journal of Soil Research*, 48(7), 516-525.
- Sjostrom, E. (1993). *Wood Chemistry: Fundamental and applications*. 2nd edition. San Diego, CA: Academic Press, pp 293.
- Slavich, P. G., Sinclair, K., Morris, S. G., Kimber, S. W. L., Downie, A., & Van Zwieten, L. (2013). Contrasting effects of manure and green waste biochars on the properties of an acidic ferralsol and productivity of a subtropical pasture. *Plant and Soil*, 366, 213-227.
- Smider, B., & Singh, B. (2014). Agronomic performance of a high ash biochar in two contrasting soils. *Agriculture, Ecosystems and Environment*, 191, 99–107.
- Smith, J. L., Collins, H. P., & Bailey, V.L. (2010). The effect of young biochar on soil respiration. *Soil Biology and Biochemistry*, 42, 2345–2347.
- Sohi, S., Loez, C. E., Krull, E., & Bol, R. (2009). Biochar's roles in soil and climate change: A review of research needs. CSIRO Land and Water Science Report 05/09, pp 64.
- Sohi, S. P., Krull, E., Lopez-Capel, E., & Bol, R. (2010). A review of biochar and its use and function in soil. *Advances in Agronomy*, 105(1), 47-52.

- Sombroek, W., Ruivo, M. D. L., Fearnside, P. M., Glaser, B., & Lehmann, J. (2003). Amazonian dark earths as carbon stores and sinks. *Amazonian Dark Earths*, pp.125-129.
- Spalding, E. P., Hirsch, R. E., Lewis, D. R., Qi, Z., Sussman, M. R., & Lewis, B.D. (1999). Potassium uptake supporting plant growth in the absence of AKT1 Channel Activity: Inhibition by ammonium and stimulation by sodium. *Journal of General Physiology*, 113, 909–918.
- Sparks, D. L., & Huang, P. M. (1985). Physical Chemistry of Soil Potassium. In: Potassium in agricultural (Ed. Munson, R.D.). *American Society of Agronomy*, Madison, Wisconsin, USA, pp 201-276.
- Spokas, K. A., Bakar, J. M., & Reikoski, D. C. (2010). Ethylene: Potential key for biochar amendment impacts. *Plant and Soil*, 333, 443–452.
- Spokas, K. A., Novak, J. M., & Venterea, R. T. (2011). Biochar's role as an alternative N-fertilizer: ammonia capture. *Plant Soil*, 350, 35–42.
- Spokas, K. A., Cantrell, K. B., Novak, J. M., Archer, D. W., Ippolito, J. A., Collins, H. P., Boateng, A. A., Lima, I. M., Lamb, M. C., & McAloon, A.J. (2012). Biochar: A synthesis of its agronomic impact beyond carbon sequestration. *Journal of Environmental Quality*, 41(4), 973–989.
- Steiner, C. (2007). Slash and char as alternative to slash and burn - soil charcoal amendments maintain soil fertility and establish a carbon sink [thesis]. Bayreuth: University of Bayreuth.
- Steiner, C., Teixeira, W. G., Lehmann, J., Nehls, T., De Macedo, J. L. V., Blum, W. E. H., & Zech, W. (2007). Long term effects of manure, charcoal, and mineral

- fertilization on crop production and fertility on a highly weathered central Amazonian upland soil. *Plant and Soil*, 291, 275–290.
- Steiner, C., Glaser, B., Teixeira, W.G., Lehmann, J., Blum, W. E. H., & Zech, W. (2008). Nitrogen retention and plant uptake on a highly weathered central amazonian ferralsol amended with compost and charcoal. *Journal of Plant Nutrition and Soil Science*, 171, 893-899.
- Stevenson, F. J., & Cole, M. A. (1999). Cycles of soil: *Carbon, nitrogen, phosphorus, sulfur, micronutrients*, John Wiley and Sons, Inc., New York, pp 448.
- Stuart, B. (1996). *Modern infrared spectroscopy*. John Wiley and Sons Ltd, Chichester, United Kingdom, pp 200.
- Sudiyani, Y., Styarini, D., Triwahyuni, E., Sudiyarmanto, Sembiring K.C., Aristiawan Y., Abimanyu. H., & Han, M. H. (2013). Utilization of biomass waste empty fruit bunch fiber of palm oil for bioethanol production using pilot – scale unit. *Energy Procedia*, 32, 31-38.
- Sukreeyapongse, O., Panichsakpatana, S., & Thongmarg, J. (2001). Nitrogen leaching from soil treated with sludge. *Water Science and Technology*, 44(7), 145-150.
- Sun, H., Lu, H., Lei, C., Shao, H., & Shi, W. (2017). Biochar applied with appropriate rates can reduce N leaching, keep N retention and not increase NH₃ volatilization in coastal saline soil. *Science of the Total Environment*, 575, 820-825.
- Syers, J.K. (1998). *Soil and plant potassium in agriculture*. The Fertiliser Society, York, United Kingdom.
- Taghizadeh-Toosi, A., Clough, T., Sherlock, R. R., & Condon, L. M. (2012). Biochar adsorbed ammonia is bioavailable. *Plant and Soil*, 350(1), 57-69.

- Taghizadeh-Toosi, A., Clough, T. J., Sherlock, R. R., & Condron, L.M. (2012). A wood based low-temperature biochar captures NH₃-N generated from ruminant urine-N, retaining its bioavailability. *Plant and Soil*, 353(1-2), 73–84.
- Takahashi, M., & Ono, Y. (2003). Pulse-chase analysis of protein kinase C. *Methods in Molecular Biology*, 233, 163-170.
- Tammeorg, P., Simojoki, A., Mäkelä, P., Stoddard, F. L., Alakukku, L., & Helenius, J. (2013). Biochar application to a fertile sandy clay loam in boreal conditions: Effects on soil properties and yield formation of wheat, turnip rape and faba bean. *Plant and Soil*, 374(1/2), 89-107.
- Tan, Z., Lin, C. S. K., Ji, X., & Rainey T. J. (2017). Returning biochar to fields: A review. *Applied Soil Ecology*, 116, 1-11.
- Tejada, M., Garcia, C., Gonzalez, J. L., & Hernande, M. T. (2006). Use of organic amendment as a strategy for saline soil remediation: Influence on the physical, chemical and biological properties of soil. *Soil Biology and Biochemistry*, 38, 1413-1421.
- Thies, J. E., & Rillig, M. C. (2009). Characteristics of biochar: biological properties. In: Lehmann J, Joseph S, editors. Biochar for environmental management science and technology. London: Earthscan, pp 85-105.
- Thomsen, T., Hauggaard-Nielsen, H., Bruun, E.W., & Ahrenfeldt, J. (2011). The potential of pyrolysis technology in climate change mitigation influence of process design and parameters, simulated in SuprPro Designer Software. Roskilde: Technical University of Denmark.

- Tumuluru, J. S., Sokhansanj, S., Hess, J. R., Wright, C. T., & Boardman, R. D. (2011). REVIEW: A review on biomass torrefaction process and product properties for energy applications. *Industrial Biotechnology*, 7, 384–401.
- Tyron, E. H. (1948). Effect of charcoal on certain physical, chemical, and biological properties of forest soil. *Ecological Monographs*, 18, 82-115.
- United States Department of Agriculture, USDA. (2011). Carbon to Nitrogen Ratios in Cropping Systems. USDA Natural Resources Conservation Service (NRCS), East National Technology Support Centre, Greensboro, NC, in cooperation with North Dakota NRCS.
- Uzoma, K. C., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A., & Nishihara, E. (2011). Effect of cow manure biochar on maize productivity under sandy soil condition. *Soil Use and Management*, 27, 205-212.
- Van Zwieten, L., Kimber, S., Morris, S., Chan, K. Y., Downie, A., Rust, J., Joseph, S., & Cowie, A. (2010). Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil*, 327(1-2), 235-246.
- Vitousek, P. M., & Howarth, R. W. (1991). Nitrogen limitation on land and in the sea: How can it occur? *Biogeochemistry*, 13, 87–115.
- Verheijen, F. G. A., Jeffrey, S., Bastos, A. C., van der Vilde, M., & Dias, I. (2009). Biochar application to soils – A critical scientific review of effects on soil properties. Processes and Functions. *European Commission*, pp 149.
- Wang, Z., Li, Y., Wang, S., Ju, X., Guan, H., & Wang, Y. (2015). Preliminary study on nitrogen leaching characteristics in Aeolian sandy soil and control technology. *Journal of Soil and Water Conservation*, 29, 239-242.

- Wang, S., Xu, Y., Namkha, N., & Wang, Z. (2018). Remediation of biochar on heavy metal polluted soils. *IOP Conference Series Earth and Environmental Science*, 108(4), 1-7.
- Wardle, D. A., Zackrisson, O., & Nilsson, M. C. (1998). The charcoal effect in boreal forests: Mechanisms and Ecological Consequences. *Oecologia*, 115, 419-426.
- Warnock, D. D., Lehmann, J., Kuyper T. W., & Rillig, M. C. (2007). Mycorrhizal responses to biochar in soil – Concepts and Mechanisms. *Plant and Soil*, 30, 9–20.
- Wen, J. L., Sun, S. L., Yuan, T.Q., Xu, F., & Sun, R.C. (2014). Understanding the chemical and structural transformations of lignin macromolecule during terrofaction. *Applied Energy*, 121, 1-9.
- White, R. E. (2005). Principles and practice of soil science: *The Soil as a Natural Resource* (4th ed.). Wiley-Blackwell, United Kingdom, pp 363.
- Wilkinson, S. R., Welch, R. M., Mayland, H. F., & Grunes, D. L. (1990). Magnesium in plant uptake, distribution, function, and utilization by man and animals. *Metal Ions in Biological Systems*, 26, 33-56.
- Wijitkosum, S., & Kallayasiri, W. (2015). The use of biochar to increase productivity of indigenous upland rice (*Oryza sativa* L.) and improve soil properties. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 6, 1326-1336.
- Wu, W., Yang, M., Feng, Q., McGrouther, K., Wang, H., Lu, H., & Chen, Y. (2012). Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass Bioenergy*, 47, 268–276.
- Woolf, D., James, E., Amonette, F., Street-Perrott, A., Lehmann, J., & Stephen, J. (2010). Sustainable biochar to mitigate global climate change. *Nature Communications*, 1, 1-9.

- Xu, C., Lin, X., & Wu, Q. (2012). Impact of biochar on availability of heavy metals and nutrient content of contaminated soil under waterlogged conditions. *Journal of Soil and Water Conservation*, 26(6), 194-199.
- Xu, Z., Zhao, Y., Sima, J., Zhao, L., Masek, O., & Cao, Z. (2017). Indispensable role of biochar – inherent mineral constituents in its environmental applications: A review. *Bioresource Technology*, 241, 887-899.
- Yaman, S. (2004). Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Conversion Management*, 45, 651-671.
- Yanai, J., Linehan, D. J., Robinson, D., Young, I. M., Hackett, C. A., Kyuma, K., & Kosaki, T. (1996). Effects of inorganic nitrogen application on the dynamics of the soil solution composition in the root zone of maize. *Plant and Soil*, 180, 1–9.
- Yanai, Y., Toyota, K., & Okazaki, M. (2007). Effects of charcoal addition on N₂O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. *Soil Science and Plant Nutrition*, 53(2), 181–188.
- Yang, D., Yunguo, L., Shaobo, L., Zhongwu, L., Xiaofei T., Xixian, H., Guangming Z., Lu, Z., & Bohong, Z. (2016). Biochar to improve soil fertility. A review. *Agronomy for Sustainable Development*, 36(2), 1-18. <https://doi.org/10.1007/s13593-016-0372-z>
- Yang, X., Liu, J., & McGrouther, K. (2016). Effect of biochar on the extractability of heavy metals (Cd, Cu, Pb, and Zn) and enzyme activity in soil. *Environmental Science and Pollution Research International*, 23(2), 974–984.
- Yanti, R. N., Hambali, E., Pari, G., & Suryani, A. (2018). The characteristics of palm oil plantation solid biomass wastes as raw material for bio oil. IOP Conference Series: *Earth and Environmental Science*, 141, 1-7.

- Yao, Y., Gao, B., Zhang, M., Inyang, M., & Zimmerman, A.R. (2012). Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere*, 89, 1467–1471.
- Yao, Y., Gao, B., Chen, J. J., Zhang, M., Inyang, M., Li, Y. C., Alva, A., & Yang, L. Y. (2013). Engineered carbon (biochar) prepared by direct pyrolysis of Mg-accumulated tomato tissues: Characterization and phosphate removal potential. *Bioresource Technology*, 138, 8–13.
- Yooyen, J., Wijitkosum, S., & Sriburi, T. (2005). Increasing yield of soybean by adding biochar. *Journal of Environmental Research and Development*, 9(4), 1066-1074.
- Yuan, J. H., & Xu, R. K. (2011). The amelioration effects of low temperature biochargetenerated from nine crop residues on an acidic Ultisol. *Soil Use Management*, 27, 110–115.
- Zackrisson, O., Nilsson, M. C., & Wardle, D. A. (1996). Key ecological function of charcoal from wildfire in the boreal forest. *OIKOS*, 77, 10–19.
- Zaharah, A. R., Siti Nor, A. A., & Husni, H. (2012). Evaluation of nitrogen uptake efficiency of different oil palm genotypes using ¹⁵N isotope labelling method. *Pertanika Journal of Tropical Agricultural Science*, 35(4), 755-766.
- Zhang, J., Cai, Z., Cheng, Y., & Zhu, T. (2009). Denitrification and total nitrogen gas production from forest soils of Eastern China. *Soil Biology and Biochemistry*, 41(12), 2551–2557.
- Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., & Zhang, X. (2010). Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China. *Agricultural Ecosystems and Environment*, 139, 469–475.

- Zhang, J., Liu, J., & Liu, R. (2015). Effects of pyrolysis temperature and heating time on biochar obtained from the pyrolysis of straw and lignosulfonate. *Bioresource Technology*, 176, 288-291.
- Zhang, J., & Wang, Q. (2016). Sustainable mechanisms of biochar derived from Brewers' spend grain and sewage sludge for ammonia-nitrogen capture. *Journal of Cleaner Production*, 112, 3927-3934.
- Zhang, H. Z., Chen, C. R., Gray, E. M., Boyd, S. E., Yang, H., & Zhang, D. K. (2016a). Roles of biochar in improving phosphorus availability in soils: A phosphate adsorbent and a source of available phosphorus. *Geoderma*, 276, 1-6.
- Zhang, J. X., Zhang, Z. F., Shen, G. M., Wang, R., Gao, L., Kong, F. Y., & Zhang, J. G. (2016b). Growth performance, nutrient absorption of tobacco and soil fertility after straw biochar application. *International Journal of Agriculture and Biology*, 18, 983-989.
- Zhang, R. H., Li, Z. G., Liu, X. D., Wang, B. C., Zhou, G. L., Huang, X. X., Lin, C. F., Wang, A. H., & Brooks, M., (2017). Immobilization and bioavailability of heavy metals in greenhouse soils amended with rice straw-derived biochar. *Ecological Engineering*, 98, 183-188.
- Zheng, H., Wang, Z., Deng, X., Herbert, S., & Xing, B. (2013). Impacts of adding biochar on nitrogen retention and bioavailability in agricultural soil. *Geoderma*, 206, 32-39.
- Zhou, H., Wu, C., Meng, A., Zhang, Y., & Williams, P. T. (2014). Effect of intereactions of biomass constituents on polycyclic aromatic hydrocarbons (PAH) formation during fast pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 110, 264-269.

- Zhou, J., Chen, H., Huang, W., Arocena, J.M., & Ge, S. (2016). Sorption of Atrazine, 17 α -estradiol, and phenanthrene on wheat straw and peanut shell biochars. *Water Air and Soil Pollution*, 227, 7(1), 1-13. DOI: 10.1007/s11270-015-2699-5
- Zornoza, R., Moreno-Barriga, F., Acosta, J.A., Munoz, M.A., & Faz, A. (2016). Stability, nutrient availability and hydrophobicity of biochars derived from manure, crop residues, and municipal solid waste for their use as soil amendments. *Chemosphere*, 144, 122–130.
- Zvomuya, F., Rosen, C. J., Russelle, M. P., & Gupta, S. C. (2003). Nitrate leaching and nitrogen recovery following application of polyolefincoated urea to potato. *Journal of Environment Quality*, 32(2), 480-489.