

UTILIZATION OF BIOCHAR COUPLED WITH COAL
COMBUSTION PRODUCTS FOR DEGRADED SOIL
AMENDMENT

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การใช้ประโยชน์ด้านชีวภาพร่วมกับผลิตภัณฑ์จากการเผาไหม้ถ่านหินเพื่อการปรับปรุงดิน
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ในปัจจุบัน เกษษณกรและอภิปษณกรจกการจับสารซัลเฟอร์หรือเอพดีอภิปษณกรซึ่งป็นผลลคกษณกรที่ได้จกการเผาถ่านหินจกโรงไฟฟ้า สามารถนำมประยูกค้ใช้ในงานหลายประเภท เช่น การถมที่ ใช้ในลคคสาหรรมซิมเมนด์ และอื่่น ๆ นอกจากนี้สารลคคถ่านหินยังสามารถนำมาใช้ในการเกษตรเพื่อใช้ในการปรับปรุงลคคสภาพดินโดยปริมาตรการใช้ยังต่ำอยู่ นอกจากนี้ยังมีกรใช้ถ่านชีวภาพเพื่อใช้ในการเพิ่มลคคสมบรูณค้ของดินและปรับสภาพดินโดยการเพิ่มพื้นที่ในการลคคสารอาหาร ลคคความหนาแน่นของดินให้ดินมีพื้นที่เก็บน้ำเพิ่มขึ้นและอื่่น ๆ

ในประเทศไทยบางพื้นที่เช่นจังหวัดน่านจะมีปัญหาเรื่องกรเสื่อมสภาพของดิน จกการตัดไม้และการใช้ปุ๋ยเคมีมากเกินไป ดังนั้นงานวิจัยนี้จะทำการประเมินผลของถ่านหินและเอพดีอภิปษณกรร่วมกับถ่านชีวภาพเพื่อปรับปรุงลคคสภาพดินโดยศึกษาลคคสมบรูณค้ เช่น ลคคความเป็นกรด โครงสร้างเนื้อดิน ลคคความหนาแน่นของดิน ลคคความนำไฟฟ้าหรืออภิปษณกรที่ต่อกรปลูกพืช ในงานนี้ความเข้มข้นของถ่านชีวภาพจะอยู่ในช่วงร้อยละ 5 ถึง 30 โดยน้ำหนัก และลคคความเข้มข้นของถ่านหินและเอพดีอภิปษณกรจะอยู่ในช่วงร้อยละ 5 ถึง 25 โดยน้ำหนัก โดยวัดลคคค่าลคคสมบรูณค้ของดินลคคกษณกรถ่านหิน นอกจากนี้พืชที่ใช้ทดลองปลูกคือข้าวโพด ซึ่งจะปลูกในพื้นที่จังหวัดน่าน โดยลคคปลูกในพื้นที่จริงและในกระถางปลูกในช่วงเดือนกันยายนถึงเดือนพฤศจิกายน 2561 และเดือนมกราคมถึงเดือนเมษายน 2562 ตามลำดับ โดยจะทำการวัดลคคค่าลคคความสูงของข้าวโพด ลคคผลผลิต ลคคความชื้นสัมพัทธ์ ค่าอภิปษณกร อุณหภูมิของดินและปริมาตรลคคความของผลผลิตที่ได้ นอกจากนี้ยังทำการวัดปริมาตรโลหะหนัก ได้แก่ สารปรอท สารหนู ตะกั่ว แคดเมียม และโครเมียมในดินก่อนและหลังการปลูก โดยดินแม่ลคคข้าวโพด กาบ และซังข้าวโพดรวมถึงราก ลำต้น และใบข้าวโพด จะถูกวิเคราะห์ปริมาตรโลหะหนักเช่นกัน

ผลการศึกษาได้แสดงให้เห็นว่าลคคสภาพของดินจะดีขึ้นในแง่ที่ว่าลคคความเป็นกรดมีค่าลดลงทุกสัณค้ส่วนการผสม โครงสร้างของดินมีลคคความดีขึ้นโดยเปลี่ยนจกดินเหนียวเป็นดินร่วนและดินร่วนปนทราย ลคคความหนาแน่นของดินมีค่าลดลงทำให้มีที่ว่างให้น้ำและอากาศเพิ่มมากขึ้นซึ่งเป็นผลลคคต่อกรปลูกพืช นอกจากนี้ลคคความเข้มข้นของโลหะหนักในสารทุกค้มีค่าต่ำกว่าปริมาตรเข้มข้นค้ที่ระบุในมาตรฐานสากลโดยเฉพาะอย่างยิ่งหลังการปลูก โดยสารปรอทและแคดเมียมมีค่าน้อยกว่า 0.25 มิลลิกรัมต่อกิโลกรัม ลคคความเข้มข้นของโลหะหนักในผลลคคข้าวโพดมีค่าน้อยกว่า 0.25 มิลลิกรัมต่อกิโลกรัมเช่นกัน ในทางตรงกันข้ามลคคความเข้มข้นของโลหะหนัก เช่น ตะกั่ว สารหนู และแคดเมียมในราก ลำต้น และใบของข้าวโพดมีค่าน้อยกว่ามาตรฐานเล็กน้อย แต่ปรอทและแคดเมียมมีค่าต่ำกว่า 0.25 มิลลิกรัมต่อกิโลกรัม จกผลการศึกษาที่ได้ ลคคคทราบว่าถ่านชีวภาพร่วมกับถ่านหินและเอพดีอภิปษณกรจะสามารถประยุกต์ใช้ในการปรับปรุงลคคสภาพของดินเสื่อมสภาพและเพิ่มลคคความของผลผลิตที่ได้จกการเกษตรในอนาคต

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Thidphavanh Sengsingkham : UTILIZATION OF BIOCHAR COUPLED WITH COAL COMBUSTION PRODUCTS FOR DEGRADED SOIL AMENDMENT. Advisor: Asst. Prof. Kreangkrai Maneeintr, Ph.D. Co-advisor: Pimsiri Tiyyon, Ph.D.

Nowadays, bottom ash and flue gas desulfurization (FGD) gypsum are by-products of the coal combustion process from coal-fired power plant. Bottom ash has been applied in many applications such as landfill, cement industry etc., and FGD gypsum is applied in cement and wallboard industry. Also, they can be used in agricultural activities for soil amendment but the amount of bottom ash and FGD used in this function is still low. Furthermore, biochar has long been used to improve soil fertility. The positive impacts of biochar amendment on soils are that it can increase soil capacity to adsorb plant nutrients, decrease soil bulk density, increase plant available water retention and so on.

In Thailand, some areas like Nan province have a problem of soil degradation from deforestation and excess use of chemical fertilizer. Therefore, this study was to evaluate the effects bottom ash and FGD of coal combustion coupled with biochar as a soil amendment on the qualities of soil such as pH, soil texture, soil bulk density, electrical conductivity (EC) and on plant growing. In this study, the concentration of biochar was ranged from 5-30% by weight, and the concentration of bottom ash and FGD were ranged from 5-25% by weight. For the parameters used to measure the properties of soil are pH, soil texture, soil bulk density and electrical conductivity (EC). Also, corn is selected to grow at Nan province, Thailand, in the real field and in the container from September to November 2018 and January to April 2019, respectively. The parameters used to measure for corn grow including corn height, chlorophyll, relative humidity (RH), conductivity (EC_p), temperature of soil and corn yields. In addition, heavy metal such as mercury (Hg), arsenic (As), lead (Pb), cadmium (Cd) and chromium (Cr) is measured in the samples before corn growing, and after corn growing in 2 times. Soil, corn seed, combined shell and core of corn and combined root, stem and leaf of corn were sent to analyze heavy metal.

From the results show that the soil quality has been improved in that pH can increase in all ratios. The soil texture has changed in the better quality from clay to silty loam, loam and sandy loam. The bulk density of soil is reduced to have more space for air and water for all mixtures which are conducive to plant growth. Furthermore, biochar coupled with CCPs applied for soil amendment can help plant growth compared to the normal soil. It is better if used the biochar coupled with CCPs and fertilizer for growing a plant. Moreover, the concentrations of all metals in soil, bottom ash, FGD, biochar and fertilizer are below the minimum permissible limit of heavy metal for soil FAO/WHO. After corn growing from both cases, the concentrations of heavy metals in all soil samples are lower than the minimum permissible limit of heavy metal for soil (FAO/WHO), mercury (Hg) and cadmium (Cd) in soil are not detectable (<0.25 mg/kg). The concentration of heavy metals in seed of corn, heavy metals are not detectable (<0.25 mg/kg) as well. On the other hand, the concentration of heavy metals in combined of root + stem + leaf of corn and shell + core of corn, lead (Pb), arsenic (As) and chromium (Cr) are higher than the minimum permissible limit FAO/WHO standard for concentration of heavy metal in plant, but mercury (Hg) and cadmium (Cd) cannot detect (<0.25 mg/kg). From the results of this research, it is expected that biochar coupled with bottom ash and FGD can be applied to increase the quality of soil and products in agriculture for the future.

Field of Study:	Georesources and Petroleum Engineering	Student's Signature
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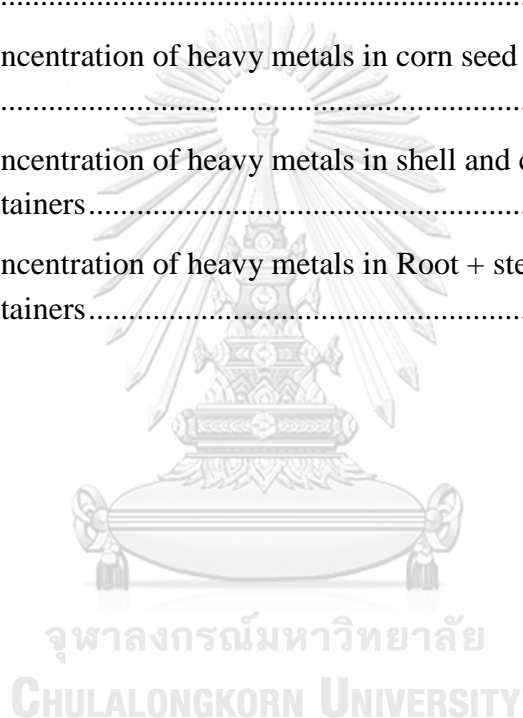
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CHAPTER 1

INTRODUCTION

1.1 Background

Coal remains the world's dominant source of power, with a share of 38.1% in 2017, almost as much as natural gas (23.2%) and hydroelectricity (15.9%) combined, which sit in second and third positions (BP, 2018). Renewables' share of power generation was 8.4% in 2017, having risen 6.1 percentage points since 2007. Over the same period, nuclear's share declined by 3.4 percentage points while coal lost 3.1 percentage points (BP, 2018) as shown in figure 1.1.

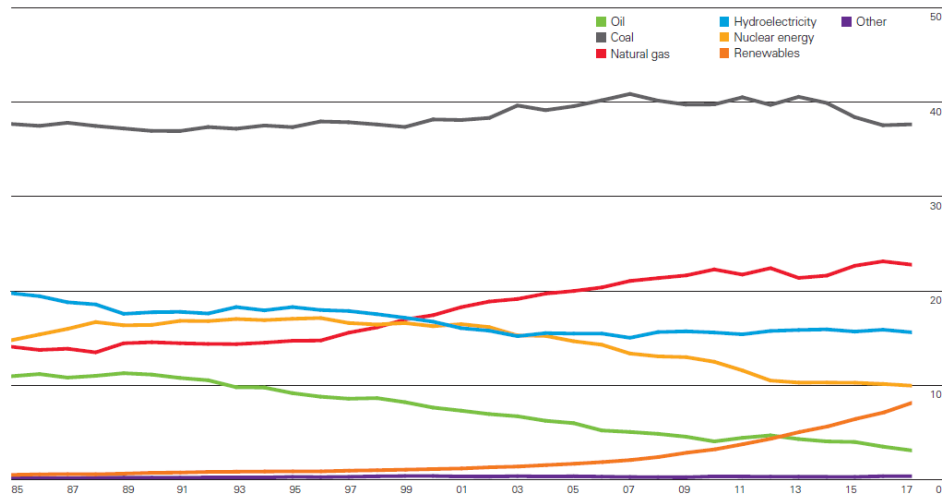


Figure 1.1 Global electricity by source (BP, 2018)

In every year, coal-fired power plant generates large amount of the coal combustion products (CCPs). Typically, the combustion of 15-18.75 tons of coal in coal-fired power plant generates 1 megawatt of electricity, and produces 4.3-11 tons of bottom ash and fly ash (Asokan et al., 2005). The generation and utilization of CCPs in different countries in 2010 are shown in table 1.1.

The residues that occur from coal-fired power generation are collectively called as coal combustion products (CCPs). Their nature and characteristics depend on the properties of the coal, the combustion technology utilized, and the flue gas treatment employed .

The history of CCPs utilization is an achievement story of technical innovation that enabled the development of environmentally sustainable options to nonrenewable resources. In addition, reducing the effect of fossil fuel energy generation, the use of CCPs instead for mined or manufactured materials within the building, construction, and civil engineering industries lowers costs, conserves resources, decreases energy consumption, and promotes sustainability (Robl et al., 2017).

Subject on the boiler technology and the measures used to limit environmental effect, a series of CCPs are produced while coal combustion. Firing the boiler with pulverized coal generates ecospheres, fly ash, and bottom ash. within the case of furnaces that function at very high temperatures, boiler slag, as opposed to bottom ash, is formed. Depending on the method used, flue-gas desulfurization (FGD) produces both dry or semidry absorption product (SDA) or wet FGD gypsum (Robl et al., 2017).

Table 1.1 Generation and utilization of coal ash in different countries.

(American Coal Ash Association, 2006)

Country/region	CCPs production (metric tons)	CCPs utilization (metric tons)	Utilization rate (%)
Australia	13.1	6.0	45.8
Canada	6.8	2.3	33.8
China	395.0	265.0	67.1
Europe (EU 15)	52.6	47.8	90.9
India	105.0	14.5	13.8
Japan	11.1	10.7	96.4
Middle East & Africa	32.2	3.4	10.6
United State of America	118.0	49.7	42.1
Others Asia	16.7	11.1	66.5
Russian Federation	26.6	5.0	18.8
Totals	777.1	415.5	53.5

1.2 Coal Combustion Products (CCPs)

1.2.1 Types of Coal Combustion Products

Coal combustion products (CCPs) include fly ash, bottom ash, boiler slag and flue gas desulfurization (FGD) are produced by the combustion of coal in coal-fired power plants.

Fly ash is collected from the flue gases by using electrostatic precipitators (ESP) or in filter fabric collectors, commonly referred to as baghouses. The physical and

chemical characteristics of fly ash vary among combustion methods, coal source, and particle shape (Ramme & Tharaniyil, 2013).

Bottom ash is formed when ash particles soften or melt and adhere to the furnace walls and boiler tubes. These larger particles agglomerate and fall to hoppers located at the base of the furnace where they are collected and normally ground to a predominantly sand size gradation (Ramme & Tharaniyil, 2013).

Flue gas desulfurization (FGD) is the solid material resulting from the removal of sulfur dioxide gas from the utility boiler stack gases in the FGD process. The material is produced in the flue gas scrubbers by reacting slurry limestone or lime with the gaseous sulfur dioxide to produce calcium sulfite (Ramme & Tharaniyil, 2013).

Boiler slag is molten bottom ash from slag tap and cyclone type furnaces that turns into pellets smooth glassy appearance after it is cooled with water.

Figure 1.2 shows the by-products distribution and their production situated on layout of the coal combustion process.

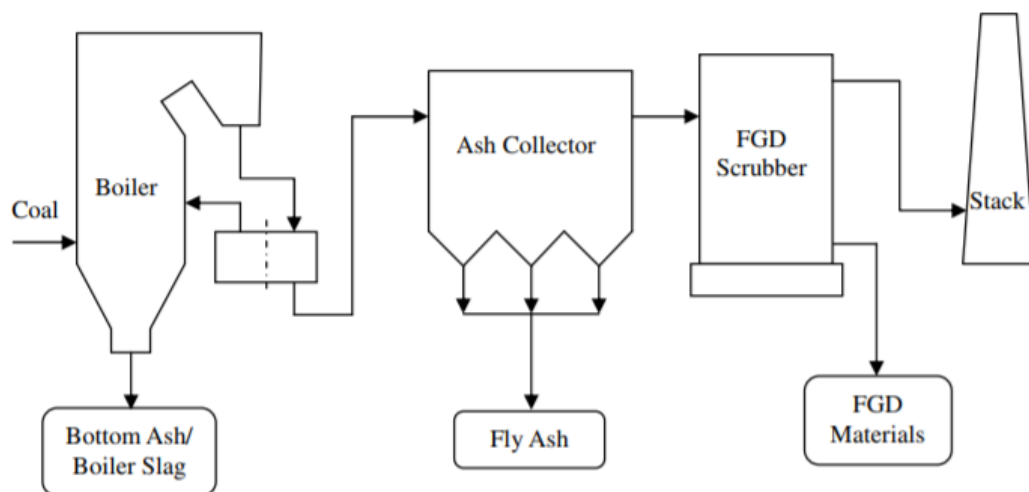


Figure 1.2 Diagram of the process of coal combustion products (Fu, 2010)

1.2.2 Coal combustion products utilization

Disposal in landfills and surface impoundments are the most commonly used CCPs. The America Coal Ash Association (ACAA) reported in 2009 that the overall CCPs production for 2008 is estimated at 136.1 million tons, while 60.6 million tons, which represents a 44.5% of total CCPs generation, are beneficially used. However, coal combustion products beneficial use continues to increase in every year. According

to Coal Ash Association in 2018, 71.8 million tons of coal combustion products are beneficially used in 2017 out of 111.3 million tons that are produced. The rate of ash utilization increased from 56 percent to 64.4 percent and the total volume of material utilized increased by 11.6 million tons. Coal ash production volume increased 4 percent from 2016 levels as shown in figure 1.3.

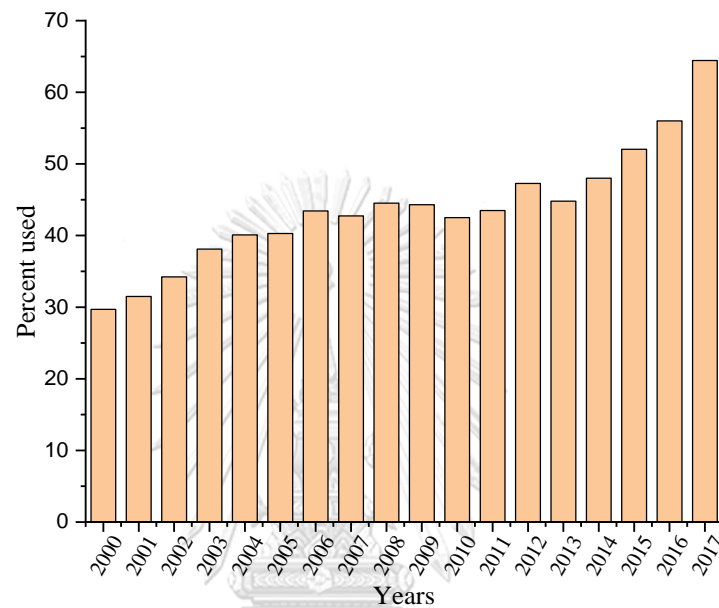


Figure 1.3 All CCPs use with percent

According to the properties of coal combustion products, there are many applications in the utilization of CCPs such as concrete products (37.13 %), structural fills/embankments (18.06%), blended cement (10.40%), cement raw material (8.29%) and agriculture (0.05%) and etc. (Jayaranjan et al., 2014) as shown in figure 1.4.

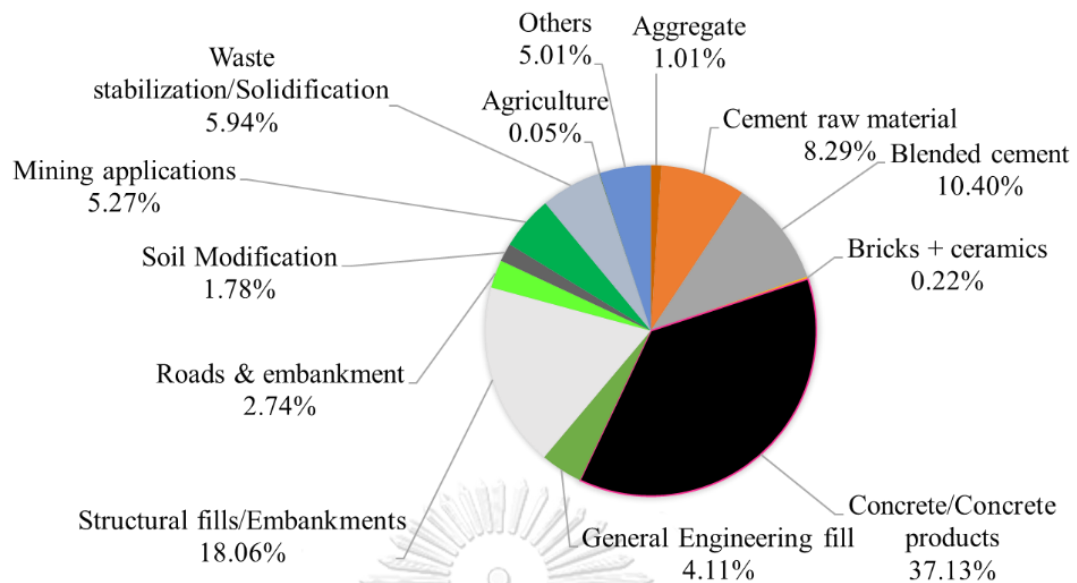


Figure 1.4 Coal combustion products utilization in various sector (ACAA, 2010; Dewangan et al., 2010; ECOBA, 2008).

Coal ash (fly ash and bottom ash) is used as a pozzolanic extender for the production blended cements, as a supplementary binder for concrete and grout, and also as a constituent of the feedstock for the manufacture of Portland cement clinker. The utility of FGD gypsum is meant to be a substitute for the natural gypsum within the manufacture of wallboard, as well as a fixed retarder for Portland cement and for soil amelioration. FBC ash is extensively utilized in mine reclamation, in which the inherent alkalinity of mitigates the effects of acid mine drainage (Robl et al., 2017).

1.3 Biochar

In Thailand, more than 134 million tons of crop residue are abandoned per year, including rice straws and husks, sugar cane residues, palm bunches and corn stalks in Thailand (Department of Alternative Energy Development and Efficiency, 2013). The way for managing these wastes are burned in the fields before the starting of the next agricultural season. Also, in northern part of Thailand, there is a variety of feedstock materials available, which can serve as the base for good biochar (Tiyayon et al., 2016). Biochar is the material rich in carbon produced from biomass that has undergone combustion under low to no oxygen conditions, and this process called pyrolysis. There are two methods to produce biochar fast pyrolysis and slow pyrolysis. The production

of biochar by using slow pyrolysis use the average temperature about 500 °C, the product of biochar is more than 50%, but take more than 1 hours that different from fast pyrolysis at the temperature 700 °C which take seconds minutes for combustion, the products are bio-oil 60%, syngas (H₂, CO and CH₄) 20% and biochar 20% (Winsley, 2007).

Biochar is different from charcoal that the utilization, charcoal is used for fuel in cooking, while biochar is charcoal used to sequester carbon in soil and improve soil qualities (Hagemann et al., 2018). Biochar is a porous material can help retain water and nutrients in the soil for the plants to take up as they grow.

In addition, biochar can provide many benefit at the same time including: 1) soil amendment 2) decrease greenhouse gas 3) alternative energy production 4) waste management such as biomass 5) poverty solutions such as reduce the cost of using chemical fertilizer and increase income from the agricultural productivity (Marris, 2006).

Table 1.2 Comparison types of char

	Charcoal	Biochar	Activated Carbon
Feedstock	Hardwood, sawdust	Forestry, organic material	Coconut shells, petroleum pitch
Common use	Fuel (cooking)	Soil amendment Remediation Filtration	Filtration Remediation
Relevant Qualities	Burn ability, low smoke	Adsorption	Adsorption
Carbon footprint	Carbon neutral	Carbon negative	Carbon positive

1.4 Soil degradation

Degradation of the soil is the serious decrease in soil quality. The word involves soil erosion, salinization, soil exhaustion (low fertility), soil acidity or alkalinity, etc. Globally, soil degradation is mainly caused by overgrazing (35%), industrial activities (28%), deforestation (30%), over-exploitation of soil to generate fuelwood (7%), and industrialization (1%) as shown in figure 1.5 (Folnovic, 2018).

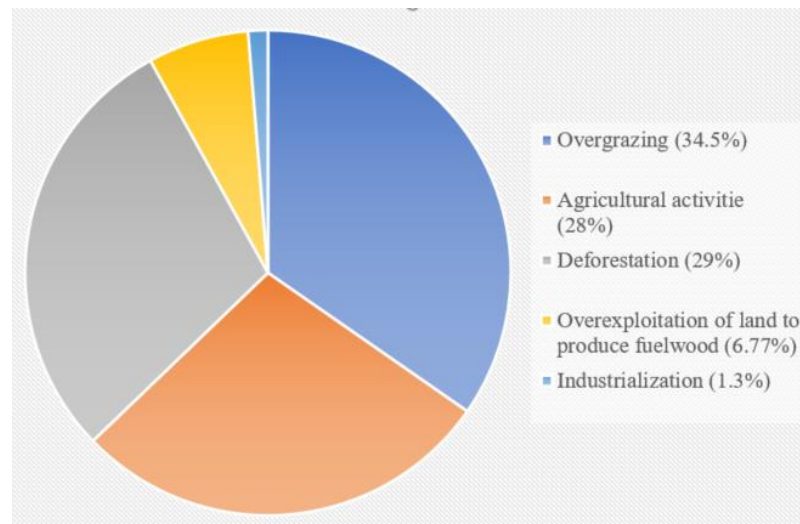


Figure 1.5 Cause of soil degradation in global (Folnovic, 2018)

Overgrazing removes vegetation cover and exposes the soil to wind and water erosion. Overgrazing can also remove nutrient matter from the cycle. The loss of decaying grass changes the amount of humus in the soil. Soil lacking in humus are nutrient poor and less able to hold moisture. Agricultural activities are one cause of soil degradation by overuse of pesticides may kill helpful organisms in soil. Bacteria, fungus and insects all assist in the decomposition and transfer of organic matter in soil. Poor ploughing practices may expose soil to erosion and result in moisture loss. Ploughing turns the soil over and loosens it. In addition, deforestation as a cause of soil erosion to removal of tree and other vegetation results in the soil being exposed to water and wind erosion, and remove nutrient from nutrient cycle, less nutrient available to the soil. Less decaying organic matter in the soil means less water retention by the soil (Folnovic, 2018).

1.5 Soil amendment

A soil amendment is any material added to a soil to improve its physical properties, such as water retention, permeability, water infiltration, drainage, aeration and structure. The goal is to provide a better environment for roots (Davis et al., 2000). The materials use for improving soil qualities as shown in table 1.3.

There are at least four factors to consider in selecting a soil amendment: how long the amendment will last in the soil, soil texture, soil salinity and plant sensitivities to salts, and salt content and pH of the amendment.

When amending sandy soils, the goal is to increase the soil's ability to hold moisture and store nutrients and for clay soil the goal is to improve soil aggregation, increase porosity and permeability, and improve aeration and drainage.

Table 1.3 Some materials use for improv soil qualities (Davis et al., 2000)

Materials	Function/purpose
Lime	Makes soil less acidic
Manure, peat, or compost	Increase fertilizers for plant nutrients
Clay, shredded bark, or vermiculite	Use for water retention
Gypsum	Releases nutrients and improves structure

1.6 Research objective, scope of research study and contribution

1.6.1 The objective of research

1. To evaluate the effects bottom ash and FGD of coal combustion coupled with biochar as a soil amendment on the qualities of soil such as pH, soil texture, water holding capacity, soil bulk density and electrical conductivity (EC) and on plant growing.

2. To investigate the optimum conditions for coal combustion products for plant growing.

1.6.2 Scope of research study

- The study used coal bottom ash and FGD form Mae - Moh thermal power plant, Lampang Province for testing. The soil and biochar collected in Nan province, Thailand. The sweet corn is selected for plant growing.

- This study is performed by laboratory experiments in Chulalongkorn University and real field experiment in Nan province.

1.6.3 Contribution

According to unique properties of coal combustion products and biochar, this study is expected that they can be used in agriculture to reduce costs of farming

associated with CCPs disposal, to reduce environmental impact from CPPs and to increase the revenue from CPPs and biochar.

This thesis consists of five chapters. Chapter 1 presents background, objective, scope of study, contribution of this study, and summary outline of the research. A literature reviews, theory of using coal combustion products as a soil amendment, theory of using biochar as soil amendment and previous researches relate to research of this study are shown in Chapter 2. The experimental work is shown in Chapter 3. Chapter 4 presents the results of experiment of this study and the effect of biochar coupled with CCPs on soil qualities and corn growing. Followed by the recommendation in using biochar coupled with CCPs in agriculture will be presented in Chapter 5.



CHAPTER 2

THEORIES AND LITERATURE REVIEW

2.1 Characteristics of bottom ash and FGD gypsum

2.1.1 Characteristics of bottom ash

2.1.1.1 Physical properties of bottom ash

Typically, bottom ash is a dark gray, black, or brown granular, porous, predominantly sand size material as shown in table 2.1. The characteristics of the bottom ash depend on the type of furnace used to burn the coal, the variety of coal, transportation system (wet or dry), whether the bottom ash is ground prior to transport and storage (Ramme & Tharaniyil, 2013).

Table 2.1 Typical the properties of bottom ash (Jayaranjan et al., 2014)

Parameters	Bottom ash	Unit
Color	Dark grey	
Specific gravity	2.3-3.0	-
Particle size distribution	0.1-10	mm
Moisture content	11.74-52.24	wt%
Bulk density	1.15-1.76	g/cm ³
Specific surface area	0.17-1.0	m ² /g

2.1.1.2 Chemical properties of bottom ash

The chemical composition of bottom ash may depend on the coal source, size, type of coal burner. Mostly, the chemical composition of bottom ash consists silicate, carbonate, aluminate, ferrous materials and several of heavy metals and metalloids (Jayaranjan et al., 2014). The chemical composition and trace elements of bottom ash are presented in table 2.2 and 2.3, respectively.

Table 2.2 Major chemical composition of bottom ash (Jayaranjan et al., 2014)

Composition as a percentage (%) otherwise stated				
Composition	Lignite	Sub-bituminous	Bituminous	Anthracite
SiO ₂	10.80-48.30	45.3	48.81-58.9	53.5
Al ₂ O ₃	2.50-24.90	24	10.12-36.0	27.6
Fe ₂ O ₃	0.50-8.20	18	2.4-6.10	6
MgO	0.40-4.60	0.58	0.2-5.61	2.1
CaO	8.60-45.10	1.4	1.3-11.81	3.4
Na ₂ O	0.15-1.15	0.45	0.04-0.92	1
K ₂ O	0.02-3.60	0.53	0.6-2.31	4.9
TiO ₂	0.18-1.32	1.5	0.39-0.60	1
P ₂ O ₅	-	2.2	0.02-0.79	0.5
MnO	0.03-0.21	0.05	0.02-0.08	-
SO ₃	5.10-20.20	2.2	<0.1-4.06	-
S	0.1	0.2-0.3f	0.01	0.54
LOI	4.6	9-17.8	9.75	-

Table 2.3 Trace elements concentrations in bottom ash (Jayaranjan et al., 2014)

Trace elements	Trace element composition of bottom ash (mg kg ⁻¹ dry basis)			
	Lignite	Sub-bituminous	Bituminous	Anthracite
As	-	25-30	1.8	<5
B	-	321-467	15.30	-
Ba	62-109	428-523	-	-
Cd	<5	0.5-0.6	0.3	<2
Co	3-7	10-13	17.5	-
Cr	47-194	65-99	47	21-30
Cu	18-21	33-49	32	42-80
Hg	04-1.8	-	-	<0.5
Li	4-30	93-147	28	-
Mn	97-328	295-402	991	-
Ni	30-293	34-53	30	-
Pb	5-33	16-29	2.6	62-80
Zn	33-226	59-99	47	1,250-2,000

2.1.2 Characteristics of FGD gypsum

2.1.2.1 Physical properties of FGD gypsum

The FGD gypsum is composed of tetrahedron crystals, ranging on average from 40-50 μm in particle size, appears light brown in color, with soil-like consistency, no odor, and low moisture content (Ramme & Tharaniyil, 2013). The physical properties of FGD gypsum are presented in table 2.4.

Table 2.4 Typical physical properties of FGD gypsum

(J. Li et al., 2018; Ramme & Tharaniyil, 2013)

Properties			
Color	Range size (μm)	Odor	Moisture (%)
Yellow, light brown	40 - 50	no	10 - 15

2.1.2.2 Chemical properties of flue gas desulfurization (FGD) gypsum

Chemical composition of flue gas desulfurization is mainly composed of CaO and SO₃. In addition, FGD gypsum containing low percentage of SiO₂, Al₂O₃, Fe₂O₃, K₂O, Na₂O, and MgO are shown in table 2.5.

Table 2.5 Chemical composition of FGD gypsum (J. Li et al., 2018)

Oxide	SO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	SO ₃	MgO
wt. %	0.8-7.2	0.3-3.7	0.1-0.9	25-50	0.1-0.3	0.3	24-53	0.1-1.8

Oxide	MnO	TiO ₂	LOI
wt. %	0.01	0.07	19.2-23.4

2.2 Application of bottom ash and FGD gypsum in agriculture

2.2.1 Application of bottom ash in agriculture

Wearing et al. (2004) were studied five different rates of bottom ash mixed with soil. The depth of mixing was about 15 cm, and the rates of application were 0, 25, 50, 100 and 150 tons per hectare. This study is found that bottom ash increase water holding capacity and increase yield of peanut.

Bottom ash is a material the size of sand or fine gravel, suitable for mixing with clay soils to improve the texture of soil (Sell et al., 1989), and bottom ash has been studied the properties to improve the heavy clay by We Energies (Ramme & Tharaniyil, 2013). It can help increase soil workability and porosity, improve crop yield as well as have no impact on environment. In addition, bottom ash is added into acid soil to improve pH of soil (Korcak, 1998).

The properties of bottom ash of We Energies have been studied by The Scott's Company of Maryville, Ohio. It is found that it is suitable as an ingredient in

manufactured soil products (Ramme & Tharaniyil, 2013). The bottom ash from Milwaukee County Power Plant, Port Washington Power Plant, and Valley Power Plant are used in their studies. The investigation determined that the addition of 10-15% (weight basis) of bottom ash provides desired soil porosities. In addition, the bottom ash blended soils exhibit excellent micronutrient composition (Ramme & Tharaniyil, 2013).

2.2.2 Application of flue gas desulfurization (FGD) gypsum in agriculture

The benefits of applying FGD gypsum and humic acid can improve the physical and chemical properties of soil, and FGD can increase the productivity of rapeseed yield (Nan et al., 2016).

FGD can be used to improve the physical and chemical properties of soil, prevent soil erosion, water quality, and enhance efficient soil capture of rainfall and crop production (Baligar et al., 2011)

Clark et al. (2001) observed that although limestone (CaCO_3 and/or $\text{CaMg}(\text{CO}_3)_2$) has been commonly used as an amendment to increase soil pH, FGD can be applied to increase pH of soil as well, because FGD is more soluble than limestone. Also, it can move to soil column easily. The aggregation of clay particles is promoted by the calcium ion, which can increase water filtration and storage in soil. Therefore, it can reduce runoff and erosion.

Kost et al. (2014) study the effects of gypsum applications in two field experiments, one on hay and the other on corn. In these tests, the effects of gypsum applications are mixed. Although corn yields are influenced by the amount of gypsum applied, there is no clear effect, and the yields are not significantly different from the control (no applied FGD gypsum). On the hay fields, high rates of application results in increases in Ca and S, but there are decreases in Mg when compared to the control.

The effectiveness of applications of FGD gypsum in the treatment of tidal lands undergoing reclamation is examined by X. Li et al. (2015). The results show that the significant doses of FGD gypsum can be used to accelerate the processes of desalination and vegetation of reclaimed land.

Chen et al. (2005) investigate that gypsum and FGD products use for the enhancement of crop growth. Gypsum and FGD products are applied at 0, 8, 16, and 24 kg sulfur (S) per hectare to five establish alfalfa stands in different Ohio regions. It

is found that alfalfa yield is significantly ($P \leq 0.05$) increased by approximately 5.0% in 2001 and 6.0% in 2002 with the sulfur (S) treatments of FGD products or gypsum compared with the untreated control. Alfalfa yields for FGD products and gypsum treatments are similar. In addition, FGD gypsum dose not increase the concentrations of potentially toxic metals such as mercury (Hg), lead (Pb) and arsenic (As) in the examined plant tissues.

2.3 Biochar properties

2.3.1 Surface area

Surface area is an important criterion in soil fertility because it impacts microbial activity, nutrients, the cycle of air and water (Downie et al., 2009). According to Troeh and Thompson (2005), a surface area of sands is ranging from 0.01 m²/g to 0.1 m²/g, and clays have surface area 5 m²/g to 750 m²/g. The high content of clay in the soil has a high ability for keeping water, but there is not enough air in the soil. On the other hand, high content sands in soil has low water capacity and high aeration. These 2 cases may be overcome when it is added the organic matter into soil (Troeh & Thompson, 2005). Biochar can help both clay and sandy soil. For example, biochar can increase water capacity in sand, and it can increase air, bulk density and porosity in clay.

Surface area of biochar from willow tree with 0.52 m²/g, and surface area from pine with 2.49 m²/g are reported by Ścisłowska et al. (2015). Usman et al. (2016) find that their biochar made from conocarpus wood has a surface area of 109.8 m²/g, and Han, Ren and Zhang (2016) find that biochar made from Chinese pine and locust has a surface area of 247 m²/g.

2.3.2 Porosity

The majority of the surface area of biochar comes from pores of less than 2 nm diameter, known as micropores (Downie et al., 2009). Micropores are important because of their adsorptive capacities for small molecules such as gases or solvents (Downie et al., 2009; Rouquerol et al., 2013). There is also a strong correlation between the highest treatment temperature (HTT) the biochar reached during pyrolysis, as well as the time it spends at that temperature also known as residence time. There is an HTT

at which deformation occurs and the walls in between micropores are destroyed reducing the surface area and increasing total pore volume (Downie et al., 2009).

Zhang and You (2013) find that the water holding capacity of soils fit a trend with the total pore space of biochar. Total pore space is positively correlated with water holding capacity, with a Pearson correlation coefficient of 0.986. Total pore space plays a more important role in this determination than the surface area of the biochar

Bacteria, fungal hyphae, root hairs, and nematodes are all under 5nm in diameter. So, macropores find in biochar may be of suitable dimensions for clusters of micro-organisms to inhabit (Downie et al., 2009).

2.4 Application of biochar in agriculture

2.4.1 Effect of biochar on soil qualities

An experiment done by Agegnehu et al. (2016) observes at the effects of biochar, compost and a combination thereof on maize yield and GHG emissions. The biochar is made from willow wood, and the compost is made of green waste, bagasse, chicken manure and compost. Soil with available phosphorus (P), CEC and exchangeable calcium are all shown to increase with a biochar amendment.

Han et al. (2016) investigate that the influence of biochar, compost and mixtures of the two on soil fertility, maize yield and greenhouse gas (GHG) emissions in a tropical Ferralsol. In this study, the five rates of biochar application are applied to multiple abandoned farms. The experiment is over a three-year time period, to examine the soil qualities before and after the three years of biochar application. It is found that biochar amendments result in significant improvements in soil organic carbon, nitrate nitrogen, and total soil nitrogen. The biochar does not have significant effect on soil ammonium nitrogen, and reduced soil phosphorus (P), indicating the need for phosphorus (P).

Albuquerque et al. (2014) tested biochar made from five feedstocks at five different application rates each. Sunflowers are grown in a greenhouse for two months and tested both soil and plant yield. Biochar is found to reduce the bulk density and increase field capacity of the soils. The biochar is not treated prior to mixing with soil, and biochar application is found to reduce available nitrogen (N) in the soil.

Vaughn et al. (2015) replicated golf course root zones to USGA standards and tested the effects of three types of biochar on creeping bent grass in the USGA root zones. A commercially available fast pyrolysis biochar in a gasifier from Paulownia and Frost grape

are used. The root zones are mimicked in long PVC tubes, with different biochar application amounts mixed into the sand part of the root zone. It is found that biochar enhanced the nutrient and water holding capacities of the substrates, generally more than treatments which using peat in place of biochar. In all cases, biochar increases nutrient retention, pH, and pore space, in most cases more than peat.

2.4.2 Effect of biochar on plant yield

According to Agegnehu et al. (2016), it is found that in a field study growing maize by treatment with biochar and compost, and the result shows that both biochar and compost treatment are greater than control. Biochar can increase by 29%, and compost can increase by 10 %. When compare with control.

Albuquerque et al. (2014) are found that the sunflower germination is significantly affected by both the biochar feedstock and the rate of application. The biochar also impacts the allocation of biomass within the plants, with biochar samples showing higher leaf allocation and decreases stem allocation. Root allocation is also lower than the control, but not statistically significant.

After the five-week period Vaughn et al. (2015) found that grass grown in biochar treatments has greater height and root length, whereas less than half has increased dry weight compared to a control. It can be concluded that some biochar appears to be very useful in sand-based root zones.

Ścisłowska et al. (2015) examined three biochar from three feedstocks, pine, willow and Miscanthus. Based on proximate, ultimate and porosimetric analysis of the three biochar, it is decided to use Miscanthus biochar for a field test based on its high carbon content and porosity. In their brief article, a statistical analysis is not conducted, but it is concluded that the physiochemical and porosimetric properties are highly dependent on feedstock, and that biochar amendments positively affect plant growth and can increase plant mass.

2.5 Soil degradation in Nan province, Thailand

According to land development department of Thailand, soil in Nan is a group of soil series No. 7. This group of soils is poorly drained or somewhat poorly drained. Fine textured (clay loam or silty clay loam to clay or silty clay) that commonly occur on flood plain and low-lying terrace or alluvial fans. They are moderate fertility with

reaction ranging from medium acid to neutral. The problem of this soil is massive structure, lack of water in dry season and water logging in rainy season (Land Development Department of Thailand).

Table 2.6 Properties of soil in Nam province, Thailand
(Land Development Department of Thailand)

Deep (cm)	Organic matter	Cation Exchange Capacity	Saturation	Useful Phosphorus	Useful Potassium	Soil fertility
0-25	Moderate	Moderate	Moderate	Low	Moderate	Moderate
25-50	Low	Moderate	Moderate	Low	Moderate	Moderate
50-100	Low	Moderate	Moderate	Low	Moderate	Moderate

Soil degradation is the soil deferent form the original soil and unfavorable for agricultural due to soil properties are not suitable for plant growth such as the chemical properties of soil are acidic, salty and physical properties are loss structure to make the soil is compression, lack soil porosity and lack soil fertility or nutrient of plants reduce (Food and Agriculture Organization of the United Nation).

Soil degradation is made the problem in agriculture in Nan Province, Thailand. The cause of soil degradation is mainly due to human activities such as the deforestation and clearing the land for agriculture, using the chemical fertilizer and insecticides., exploitation of marginal soils under inadequate soil management practices (Aumtong & Magid, 2006).

Soil erosion is the deterioration of soil by the physical movement of soil particles from a given site. The mainly topography in Northern of Thailand is mountain and high annual rainfall as well as agricultural activity of man leading to the soil erosion. Tingting et al. (2008) use application of IMAGE\LDM to conduct assessment of soil erosion risk in Northern of Thailand. The result of this study shows about 90 % of slope farmland has very high soil erosion grade.

2.6 The important of properties of soil for soil amendment

2.6.1 Soil texture

Soil texture refers to the size of the particles in the soil. Sandy soil feels grainy and has large particles. Loam has been compared to the texture of chocolate cake. It feels moist not wet and light and crumbly. Loam has particles of medium size. Silt feels soft and smooth and contains small particles. Clay soils have the smallest particles. Clay feels sticky, dense and hard. The size of each soils as shown in table 2.7.

Table 2.7 The size of sand, silt and clay

Texture	Particle size
Very coarse sand	2.00-1 mm
Coarse sand	1.00-0.50 mm
Medium sand	0.5 -0.25 mm
Fine sand	0.25-0.10 mm
Very fine sand	0.10-0.05
Silt	0.05 - 0.002 mm
Clay	< 0.002 mm

Soil texture determines the rate at which water drains through a saturated soil; water moves more freely through sandy soils than it does through clayey soils. When amending sandy soils, the goal is to increase the soil's ability to hold moisture and store nutrients. To achieve this, use organic amendments that are well decomposed, like composts, peat, or aged manures. With clay soils, the goal is to improve soil aggregation, increase porosity and permeability, and improve aeration and drainage. Fibrous amendments like peat, wood chips, tree bark or straw are most effective in this situation (Davis et al., 2000).

2.6.2 Soil pH

Soil pH affects the soil's physical, chemical, and biological properties and processes, as well as plant growth. The nutrition, growth, and yields of most crops decrease where pH is low and increase as pH rises to an optimum level as shown in table 2.8.

Table 2.8 Relative yield of selected crops grown in a corn, small grain, legumes or timothy rotation at different pH levels (Smith & Doran, 1996)

Crop	pH				
	4.7	5.0	5.7	6.8	7.5
	Relative Average Yield				
Corn	34	73	83	100	85
Wheat	68	78	89	100	99
Oats	77	93	99	98	100
Barley	0	23	80	95	100
Alfalfa	2	9	42	100	100
Soybean	65	79	80	100	93
Timothy	31	47	66	100	95

2.6.3 Soil Electrical Conductivity (EC)

Soil electrical conductivity (EC) is a measure of the amount of salts in soil (salinity of soil). It is a significant soil health indicator. It impacts crop yields, crop suitability, plant nutrient accessibility, and soil microorganisms activity that affect important soil procedures including greenhouse gas emissions such as nitrogen oxides, methane, and carbon dioxide. Excess salts impede plant growth by influencing the soil-water stability. Soils containing excess salts happen naturally in arid and semi-arid areas. Salt concentrations can increase as a result of crops, irrigation and land management. Although EC does not provide a direct measurement of particular ions or salt compounds, it has been related with concentrations of nitrates, potassium, sodium, chloride, sulfate, and ammonia. Determining EC can be a convenient and economical way to estimate the quantity of nitrogen (N) available for plant growth for certain non-saline soils. In general, crops tolerate salinity to a threshold level above which yields decrease roughly linearly as salt levels increase as shown in figure 2.1.

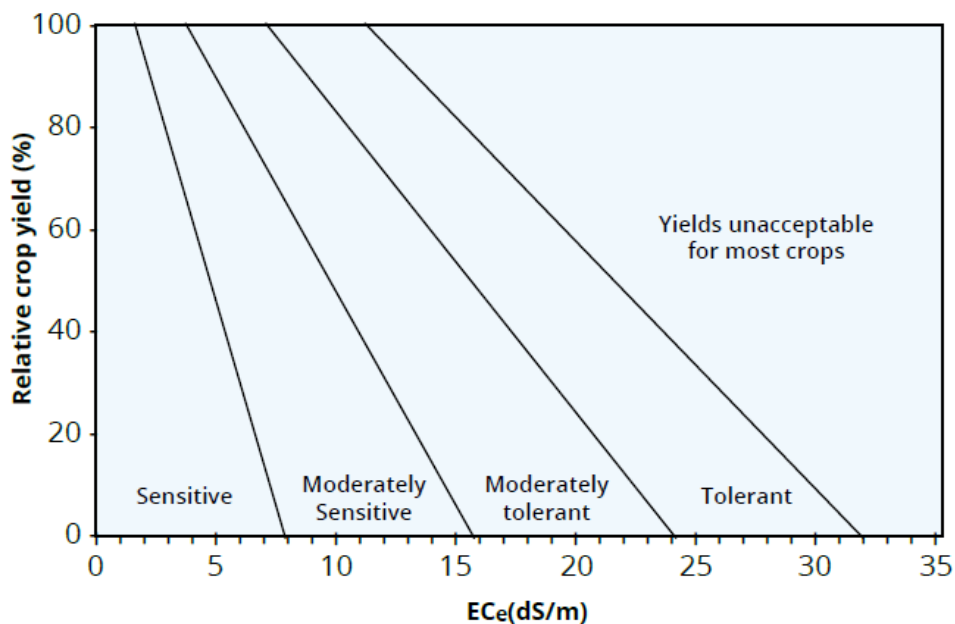


Figure 2.1 Division for classifying crop tolerance to salinity
(Maas & Hoffman, 1977)

The elements influencing the electrical conductivity of soils consist of the amount and kind of soluble salts in solution, porosity, soil texture (especially clay content and mineralogy), soil moisture, and soil temperature (Corwin & Lesch, 2005). Excessive levels of precipitation can flush soluble salts out of the soil and decrease EC. Conversely, in arid soils (with low levels of precipitation), soluble salts are more likely to accumulate in soil profiles ensuing in excessive EC. The electrical conductivity decreases sharply whilst the temperature of soil water is beneath the freezing factor (EC decreases approximately 2.2% per degree centigrade because of increased viscosity of water and decreased mobility of ions). In general, EC will increase as clay content increases. Soils with clay dominated by using excessive cation-exchange capacity (CEC) clay minerals (e.g., smectite) have higher EC than those with clay dominated through low CEC clay minerals (e.g., kaolinite). Arid soils with high content of soluble salt and exchangeable sodium commonly exhibit extremely high EC. In soils wherein, the water desk is excessive and saline, water will rise through capillarity and increase salt concentration and EC within the soil surface layer (USDA Natural Resources Conservation Service, 2011)

2.6.4 Bulk density of soil

Bulk density is a soil compaction measure. It is determined as the soil's dry weight divided by its density. This volume involves the number of soil particles and the volume of pores between soil particles. Typically, bulk density is expressed in g/cm^3 .

Bulk density represents the ability of the soil to function for structural help, water and solvent motion, and soil aeration. Bulk densities above thresholds indicate impaired function. Density is also used to convert soil weight and volume. It is used to convey physical, chemical and biological soil measurements on a volumetric basis for assessing soil quality and comparing management schemes.

This increases the validity of comparisons by removing errors associated with variations in soil density at the sampling moment.

Table 2.9 General relationship of soil bulk density to root growth based on soil texture (Hanks & Lewandowski, 2003)

Soil Texture	Ideal bulk densities for plant growth (grams/cm^3)	Bulk densities that affect root growth (grams/cm^3)	Bulk densities that restrict root growth (grams/cm^3)
Sands, loamy sands	<1.6	1.69	>1.8
Sandy loams, loams	<1.4	1.63	>1.8
Sandy clay loams	<1.4	1.6	>1.75
Silts	<1.4	1.6	>1.75
Silt loams, silty clay loams	<1.4	1.55	>1.65
Sandy clays, silty clays, clay loams	<1.1	1.49	>1.58
Clays (> 45% clay)	<1.1	1.39	>1.47

2.7 Heavy metals

Heavy metals are elements that have high density greater than 5 g/cm^3 in their elemental form (Tchounwou et al., 2012). Heavy metals are considered serious pollutants because of their toxicity, persistence and nonbiodegradable conditions in the environment, thereby constituting a threat to human beings and other forms of biological life (Adelekan & Abegunde, 2011).

Arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb) and mercury (Hg) etc., are heavy metals that effect on human health as the concentration is over safety standard.

Table 2.10 shows the maximum permissible limit (MPL) values of the trace heavy metals in agricultural soil and vegetable by different sources.

Table 2.10 Recommended the maximum permissible limits of heavy metals for soil and vegetable

Parameters	Unit	The MPL of heavy metal in soil			The MPL of heavy metal in plant
		Land Application of Biosolid of Home Vegetable Gardens (Gorospe, 2012)	Thailand standard (Department, 2004)	FAO/WHO (2001) (Heidrich et al., 2013)	FAO/WHO, (2001) (Heidrich et al., 2013)
Nickel (Ni)	mg/kg	420	1600	50	67
Chromium (Cr)	mg/kg	-	300	100	2.3
Cadmium (Cd)	mg/kg	39	37	3	0.2
Lead (Pb)	mg/kg	300	400	100	0.3
Arsenic (As)	mg/kg	41	3.9	20	0.43
Mercury (Hg)	mg/kg	17	23	1	0.03
Note:		MPL: maximum permissible limit			

Heavy metals such as arsenic (As), lead (Pb), cadmium (Cd) and chromium (Cr) can be found in the area of industry sites and they do have the potential of contaminating soils which can be transported to plants, animals, and humans causing their health effects: carcinogenicity, mutagenicity, disruption of DNA (Fite & Leta, 2015). There are several factors affect their toxicity such as the dose, route of exposure, as well as the gender, age, and nutritional status of exposed people (Tchounwou et al., 2012). The effects of arsenic on human health including: birth defects, carcinogen: lung, skin, liver, bladder, kidneys, Gastrointestinal damage, Severe vomiting, diarrhea, death (ATSRD, 2007a). Effects on human health Humans are exposed to cadmium by inhalation and ingestion although the main health impacts recorded in the literature are through dietary

exposure (kidney and bone damage) and inhalation from smoking tobacco and occupational exposure (lung damage) (Mahurpawar, 2015). Chromium (Cr) enter to human body by inhalation, ingestion and dermal contact, the effect of chromium on human health including respiratory tract, stomach and small intestine, male reproductive system and cause tumors to the stomach, intestinal tract, and lung (ATSRD). Ingestion of large amount of mercury can lead to disruption of the nervous system damage to brain functions, DNA damage and chromosomal damage, allergic reactions, tiredness and headaches, negative reproductive effects, such as sperm damage, birth defects and miscarriages (ASTDR, 1999). When human health Humans are exposed to lead (Pb) by ingestion although the main health impact such as anemia (less Hb), hypertension, kidney damage, miscarriages, disruption of nervous systems, brain damage, infertility, intellectual disorders (ATSRD, 2007b). Effects on human health Humans are exposed to cadmium by inhalation and ingestion although the main health impacts recorded in the literature are through dietary exposure (kidney and bone damage) and inhalation from smoking tobacco and occupational exposure (lung damage).

Normally, trace elements including B, Ba, Cd, Co, Cr, Cu, Hg, Li, Mn, Ni, Pb and Zn are contained in bottom ash (Jayaranjan et al., 2014). According to Wearing et al. (2004), bottom ash is applied for soil amendment to grow peanut, 5 rates of bottom ash are applied: 0 tones/acre, 10 tones/acre, 20 tones/acre, 40 tones/acre and 60 tones/acre. It is showed that the metal content for the elements tested either decreased with increasing bottom ash addition or there is no significant difference between the treated and untreated areas.

Sloan and Cawthon (2003) evaluate the effect of coal ash plus compost mixtures on soil chemistry and plant growth in acid mine soils. The coal ash + compost mixtures were blended with acid mine soil (pH 4.0) at rates of 15, 30, and 45% (v/v). As for the results of heavy metals, bottom ash has no significant effect on heavy metal uptake or leachate composition. The results demonstrate that combinations of animal manure compost with coal combustion ashes can effectively stimulate biomass production in acidic surface mine soils.

Knox et al. (2006) reported that there are 20 elements were measured in maize tissues, but only five elements (Cd, Cr, Cu, Pb and Sb) were not significant influenced by FGD gypsum.

Briggs et al. (2014) investigated Hg release to air from FGD gypsum-treated soils. In this study, three FGD gypsum sources were mixed with three soils (0-15 cm soil layer) at 4.5, 45, and 170 Mg ha⁻¹, representing approximately 1, 10, and 80 yr of application. Flue gas desulfurization gypsum was also surface applied at a rate of 4.9 Mg ha⁻¹, simulating no-till management. Mercury concentrations of the three FGD gypsum sources ranged from 79 to 391 mg kg⁻¹, compared with 1.0 and 2.0 mg kg⁻¹ in mined gypsum, used as a comparison treatment.

A study by Chen et al. (2014) investigated Hg as well as 14 other trace elements in soil and earthworms, used as bioindicators of element availability, when FGD gypsum was land applied. This study was conducted at four field sites across the United States (Wisconsin, Ohio, Indiana, and Alabama). Gypsum application rates ranged from 2.2 Mg ha⁻¹ in Indiana to 20 Mg ha⁻¹ in Ohio and Alabama. These rates are 2 to 10 times higher than typically recommended. The length of time from gypsum application to sampling was 4 mo in Wisconsin, 5 and 18 mo in Ohio, 6 mo in Indiana, and 11 mo in Alabama. Among the elements examined, Hg was slightly increased in soils and earthworms from FGD gypsum treatments compared with both the control and mined gypsum treatments. Differences were not statistically significant except for soil Hg concentrations at the Wisconsin site. Bioaccumulation factors for nondepleted earthworms, i.e., earthworms containing gut material, were statistically similar or lower for the FGD gypsum treatments compared with controls for all elements.

Lu et al. (2015) explore heavy metal residues in soil and accumulation in maize at long-term wastewater irrigation area in Tongliao, China. Cr, Pb, Ni, and Zn are analyzed heavy metals. In this study, the result show that the concentrations of metals in the maize increased as follows: Pb < Ni < Zn < Cr. In addition, Cr, Pb, and Ni mainly accumulated in the maize roots, and Zn mainly accumulated in the maize fruit.

Wang et al. (2017) review the accumulation of heavy metals such as Cd, Cr, As, Pb, Hg, Cu, and Zn-in soil-corn and soil-wheat systems. The findings show that the accumulation of heavy metals in wheat is more than corn, and the minimum bioconcentration factor (BCFs) of Cd, Cr, As, Pb, Hg, Cu, and Zn in corn grains are 0.054, 6.65×10^{-4} , 7.94×10^{-4} , 0.0044, 0.028, 0.13, and 0.19 mg/kg⁻¹, respectively.

CHAPTER 3

EXPERIMENT

3.1 Materials

For this study, the coal combustion products (bottom ash and FGD gypsum) are collected from Mae-Moh thermal power plant, Lampang province, Thailand, and degraded soil is collected from Wang tao sufficient agricultural learning center, school of Agricultural resources Chulalongkorn University (CUSAR) , Sanian sub-district, Mueang Nan District, Nan province. Biochar is produced from longan and lychee trees by a small kiln from local people in Nan province. In addition, this study also uses fertilizer, cow dust and sheep manure. With regard to the study, corn is selected to grow in the field. figure 3.1 and 3.2 show the materials which use to do the experiment in this study.

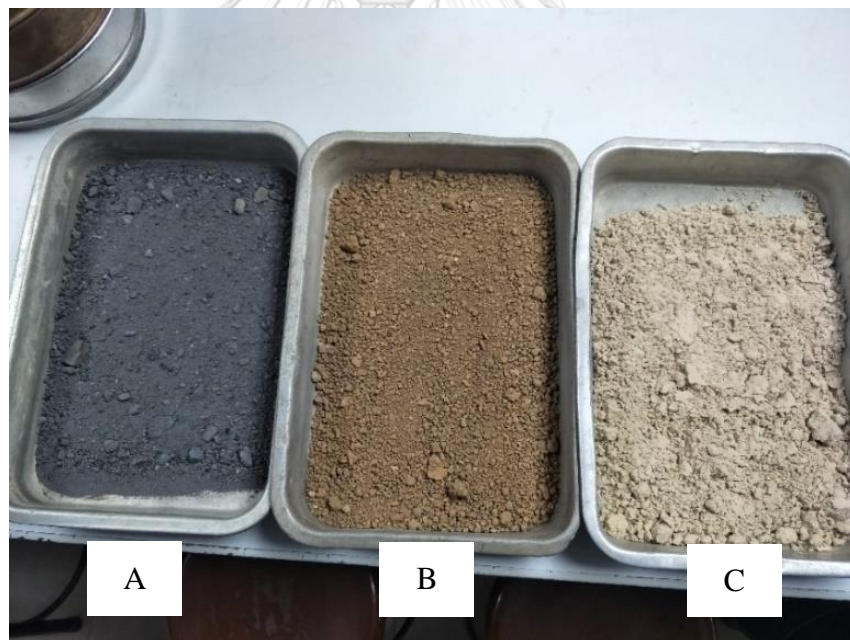


Figure 3.1 Bottom ash (A), Soil (B) and FGD gypsum (C)



Figure 3.2 Biochar

The main composition of soil, bottom ash, FGD gypsum and biochar are analyzed by the XRF equipment as shows in table 3.1 and 3.2.

Table 3.1 The composition of soil, bottom ash and FDG gypsum.

Parameters	Soil (%)	Bottom Ash (%)	FGD
SiO ₂	54.70	27.00	0.75
Al ₂ O ₃	21.99	11.80	0.35
Fe ₂ O ₃	10.10	12.00	0.11
K ₂ O	2.41	1.42	0.11
TiO ₂	0.98	0.29	-
Na ₂ O	0.08	1.21	0.4
MgO	0.52	2.48	0.37
CaO	0.17	23.90	35.10
MnO	0.04	-	-
P ₂ O ₅	0.12	0.28	0.03
BaO	0.03	0.15	-
SO ₂	-	3.67	-
SO ₃	0.05		45.70
ZrO ₂	0.03	0.01	-
SrO	0.05	-	-
ZnO	-	0.01	-
Rb ₂ O	0.01	-	-
Cr ₂ O ₅	0.02	0.01	-
SrO	-	0.01	0.02
Cl	0.01		0.02
CuO	-	0.01	-

Table 3.2 The composition of biochar

Concentration (% by wt.)								
Ca	K	P	Mg	Si	S	Fe	Cl	Al
0.98	0.91	0.20	0.20	0.07	0.03	0.02	0.02	0.02

According to table 3.1, the main compositions of bottom ash are SiO_2 and CaO . Furthermore, bottom ash contains different essential elements for plant growth, including both macronutrients P, K, Ca, Mg, S, and micronutrients Zn, Fe, Cu, Mn. For FGD, the main compositions are SO_3 and CaO , and Ca and S are essential elements for plant growth. Therefore, all of bottom ash and FGD gypsum can be used to improve the chemical property of soil.

With regard to the samples, the physical properties of soil, bottom, FGD and biochar are shown in table 3.3.

Table 3.3 Physical properties of bottom ash, FGD gypsum, biochar and soil.

Samples	Color	pH	EC		Bulk density (g/cm^3)
Bottom Ash	Dark grey	9.739	0.281	(S/m)	1.33
FGD	Light brown	7.871	0.306	(S/m)	1.14
Biochar	Black	10.175	0.224	(S/m)	0.25
soil	Brown	5.839	0.011059	(S/m)	1.27

As shown in table 3.3, soil in Nan province is acid with pH at 5.84. Biochar and bottom ash are alkalinity with pH at 10.17 and 9.74, but FGD gypsum is weak alkalinity with pH at 7.87.

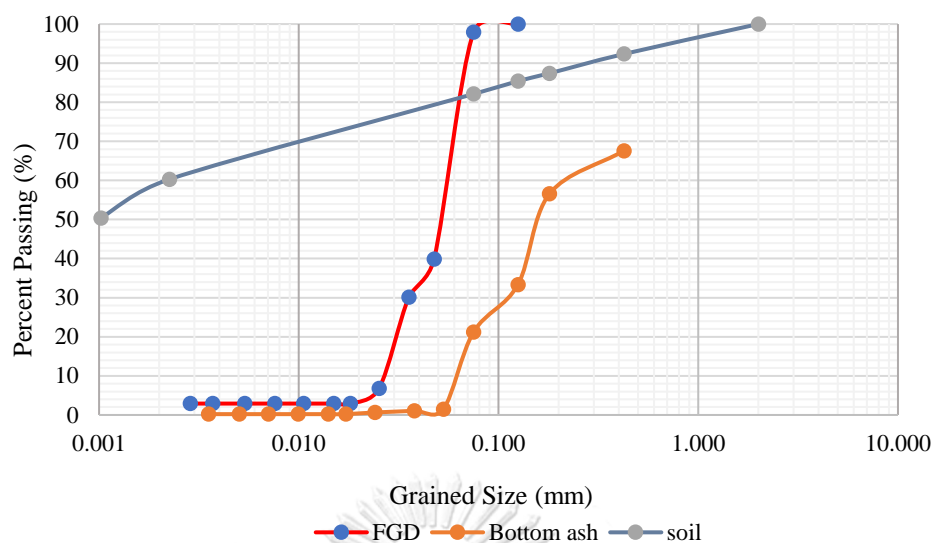


Figure 3.3 Particle size distribution of soil, bottom ash and FGD gypsum

According to figure 3.1, the texture soil is clay (20% of sand, 20% of silt and 60% of clay), bottom ash is sand (98.5% of sand and 1.5% of silt) and FGD gypsum is sandy loam (60% of sand, 40% of silt). For biochar, the particle size is range from 1 mm - 2.80 mm, so the particle size of biochar is sand particle. The particle size distribution of soil, bottom ash and FGD are shown in figure 3.3.

The major heavy metals (Cd, Hg, As, Pb and Cr), a primary concern with regard to CCPs use in agricultural fields, are also evaluated, and the results are presented in table 3.4. The concentrations of all the metals in soil, bottom ash, FGD, biochar and fertilizer are well below the minimum permissible limit of heavy metal for soil FOA/WHO, but the concentration of arsenic (As) in soil (6.72 mg/kg) and bottom ash (mg/kg) is above the minimum permissible limit of Thai Standard (3.9 mg/kg). In the other hand, cadmium (Cd) is not detected in all of the initial sample.

Table 3.4 The concentration of heavy metals in the samples

Parameters	Unit	Results					
		Soil	FGD	Biochar	Bottom ash	Cow manure	Sheep manure
Mercury (Hg)	mm/kg	0.16	0.23	0.09	0.04	0.15	0.14
Lead (Pb)	mm/kg	9.7	0.3	17.1	6.0	1	<0.25
Arsenic (As)	mm/kg	6.72	1.72	1.54	33.2	0.84	0.25
Cadmium (Cd)	mm/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Chromium (Cr)	mm/kg	25.4	20.1	0.7	61.7	4.1	0.8

3.2 Experiment

3.2.1 pH measurement

The materials used to measure pH value such as soil, bottom, FGD gypsum, and biochar, are measured for by a pH/ION/COND METER with model LAQUA F-74G which is produced from Horiba.Ltd, Japan as shown in figure 3.4.

**Figure 3.4** A pH/ION/COND METER



Figure 3.5 A balance

As figure 3.5 shows the balance used to weight the materials and produced from Ohaus Company. It has the maximum capacity of 200 g, and an accuracy of 0.0001 g.

To do this experiment, distilled water is used in this experiment.

❖ Procedure (Therajindakajorn, 2011)

The samples are dried and passed sieve No. 10 to remove coarse size of samples. Weigh 10 g of sample and put into the beaker. Add distilled water approximately 25 ml into the sample that is contained in beaker. After that stir the sample and distilled water for about 5 minutes then allow the soil to settle for 10 minutes.

Before measuring the pH value of sample, calibrate pH meter by using buffer pH 4 and buffer pH 7 as shown in figure 3.6, and then measure pH value for 3 times with using Benchtop pH/Water Quality Analyzer LAQUA F-74.



Figure 3.6 Calibrated pH meter by using buffer pH 4 (A) and buffer pH 7 (B)

3.2.2 Electrical conductivity ($EC_{1:5}$) measurement

❖ Materials and equipment

Soil, bottom, FGD gypsum, and biochar are the materials used to measure $EC_{1:5}$, and $EC_{1:5}$ is measured by a pH/ION/COND METER with model LAQUA F-74G which is produced from Horiba.Ltd, Japan as shown in figure 3.4.

A balance and water used in this experiment are the same equipment with the pH experiment.

❖ Procedure (Therajindakajorn, 2011)

Firstly, the samples are dried and passed sieve No. 10 to remove coarse size of samples and weighed 10 g of sample and put into the beaker (100 ml). Then add 50 ml distilled water into the sample that is contained in beaker. Stir the sample and distilled water for periodically 30 minutes, and then allow the soil to settle for 30 minutes.

Next, pour the solution in the top of beaker to another beaker. After taking the solution to measure the electrical conductivity ($EC_{1:5}$) for 3 times with using Benchtop pH/Water Quality Analyzer LAQUA F-74.

Before measuring the electrical conductivity, calibrate Benchtop pH/Water Quality Analyzer LAQUA F-74 by using std. 0.01 N KCl.

3.2.3 Soil texture measurement by using soil hydrometer

❖ Materials and equipment

ASTM 151H Soil Hydrometer is graduated to read specific gravity. It has a range of 0.995-1.038 in 0.001 divisions at 68 °F (20 °C) as shown in figure 3.7.

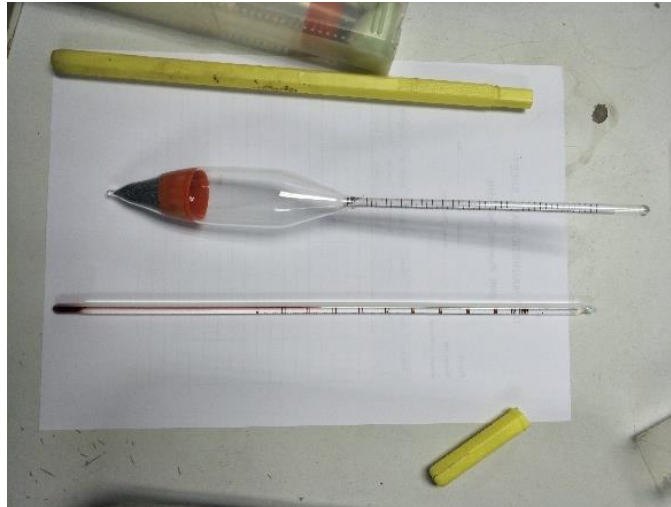


Figure 3.7 Soil hydrometer 151H and thermometer

A thermometer is used to measure the temperature of distilled water in the cylinder. It is readable up to 0.5 °C as shown in figure 3.7.



Figure 3.8 Cylinder (1000 ml)

The cylinder is used for the soil suspension, and it has a stable base and is made of heavy-wall clear glass scribed at the 1,000 ml as shown in figure 3.8.

Figure 3.9 is the set of sieves. For sieve No. 10 is used to remove coarse size of soil, and sieve No. 40, No. 80, No. 120, and No. 200 are used to do wet sieve.



Figure 3.9 Sieve No. 10, No. 40, No. 80, No. 120, and No. 200



Figure 3.10 A balance

Figure 3.10 is a balance model GB6001-S used in this experiment. It is produced from Mettler Toledo Company, and this balance has a maximum capacity at 6100 g, a minimum capacity at 0.5 g and an accuracy at 0.1 g.

Sodium hexametaphosphate 68% extra pure as shown in figure 3.11, it is produced from LOBA CHEMIE PVT Limited. It is selected as the dispersion agent in this experiment to prevent the fine particles in suspension from coalescing or flocculating.



Figure 3.11 Sodium hexametaphosphate



Figure 3.12 An oven

Figure 3.12 is the oven that uses to dry the wet samples. In this experiment, the oven is used to dry the samples approximately 110 ± 5 °C.

All of the water in this experiment, distilled water is used to do the experiment.

❖ Procedure

Firstly, Prepare the solution of sodium hexametaphosphate at the rate 40 g of sodium hexametaphosphate per 1000 ml of distilled water.

Next, weigh 100 g air-dried soil sample passing sieve No 10 (less than 2 mm). Place the sample in a 500 ml breaker. Then add 125 ml of sodium hexametaphosphate solution (40 g/l) and 125 ml distilled water into the beaker that contained the sample. Stir until the soil is thoroughly wetted. Allow soaking for at least 16 hours.



Figure 3.13 Cover the cylinder by parafilm

Transfer the sample from the beaker to the 1000 ml cylinder, and add the distilled water until the total volume is 1000 ml. Then use parafilm cover the mouth of cylinder as shown in figure 3.13. Then shake the cylinder about 1 minute as shown in figure 3.14.



Figure 3.14 shake the cylinder

After that take the hydrometer into the cylinder. Then read the hydrometer and measure the temperature at the time 0, 1, 2, 5, 10, 15, 30, 60, 120, 250, 420, and 1440 minutes.



Figure 3.15 Do wet sieve experiment

Next step continue with wet sieve experiment, after taking the final hydrometer reading, transfer the sample from the cylinder to a pan, and do a wet sieve by using

sieves as No. 40 (0.425-mm), No.80 (0.18-mm), No 120 (0.125-mm) and No. 200 (0.075 mm) as shown in figure 3.15.

After finished to do wet sieve, dry the samples that retained sieves No. 40, No. 80, No. 120 and No. 200 in the oven at the temperature of 110 ± 5 °C, and then weigh the dry samples.

This experiment results are shown in particle size distribution curve and plotted on soil texture triangle to determine the texture of soil as shown in figure 3.16.

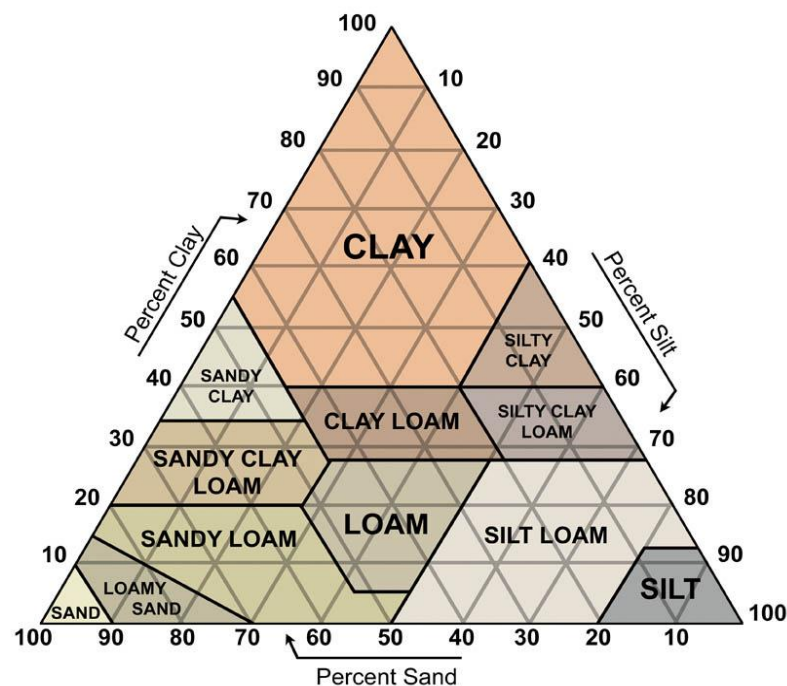


Figure 3.16 Soil texture triangle

3.2.4 Moisture contents

The result of the moisture experiment provides the data for the calculation process of the hydrometer experiment

❖ Materials and equipment

Figure 3.75. is a balance that use to weigh the samples and it is produced from Ohaus Company. It has the maximum capacity of 200 g, and an accuracy of 0.0001 g.

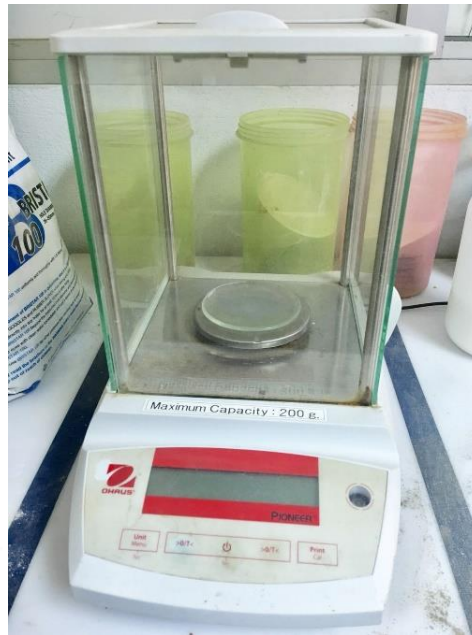


Figure 3.17 A balance

Figure 3.18 shows the containers used to determine moisture contents. The oven uses to dry the samples as shown in figure 3.12. In this experiment uses the temperature to dry the samples approximately 110 ± 5 °C.



Figure 3.18 The containers used to determine moisture contents

❖ Procedure

Firstly, weigh the clean and dry container by using balance and then record (M_c). Next step put the sample into the container, and then weigh the container with wet sample (M_{cms}). Then take the container with the wet sample to the oven to dry the

sample at the temperature 110 ± 5 °C. In this moisture contents experiment, drying a test samples overnight (about 12 to 16 hours) is sufficient. After drying the samples, weigh the container with dry sample ($M_{c ds}$). Then calculate the moisture contents with the formula below:

$$W = [(M_{cms} - M_{c ds}) / (M_{c ds} - M_c)] \times 100 = (M_w / M_s) \times 100 \quad \text{Equation 3.1}$$

Where:

W is water content (%)

M_{cms} is weight of container and wet sample (g)

$M_{c ds}$ is weight of container and oven dry sample (g)

M_c is weight of container (g)

M_w is weight of water ($M_w = M_{cms} - M_{c ds}$) (g)

M_s is weight of oven dry sample ($M_s = M_{c ds} - M_c$) (g)

3.2.5 Specific gravity

The result of specific gravity provides the data for the calculation process of the hydrometer experiment, and specific gravity was determined by water replacement.

❖ Materials and equipment

In this experiment, graduated cylinders have capacity at 100 ml as shown in figure 3.19.

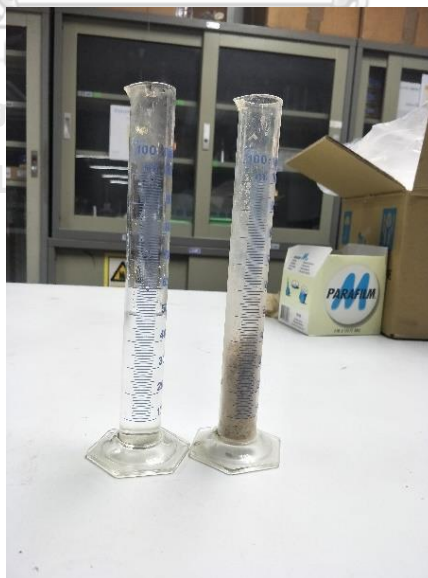


Figure 3.19 Graduated cylinder of 100 ml

❖ Procedure

Firstly, clean and dry the graduated cylinder by water. Then weigh the minerals sample (W_0) (approximate 20 g)

Next step adds 50 ml of distilled water in the graduated cylinder, and then put the sample in the graduated cylinder.

Observing the water volume changed as shown in figure 3.20. After that record and calculate the specific gravity (S_0)

$$\text{Specific gravity } (S_0) = \frac{\text{Weight of sample } (W_0)}{\text{water volume changed } (V_0)} \quad \text{Equation 3.2}$$

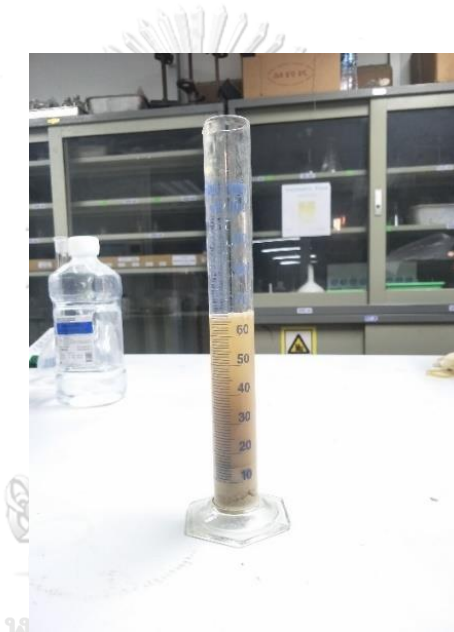


Figure 3.20 The sample with distilled water in cylinder

3.2.6 Bulk density measurement (Tan, 2005)

❖ Materials and equipment

A cylinder has a volume of about 172 cm³ as shown in figure 3.21. that uses to measure bulk density of soil.

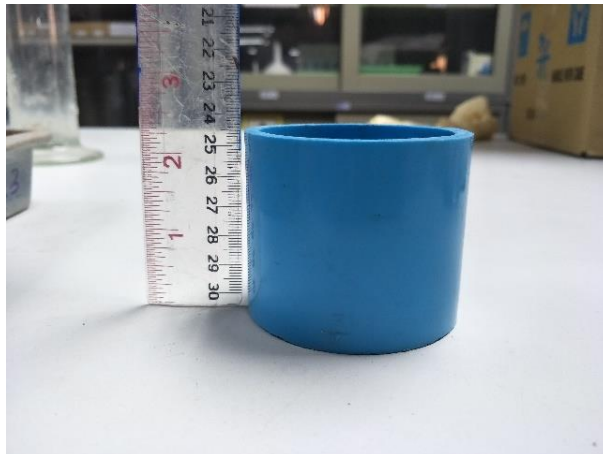


Figure 3.21 A cylinder for core sample

Figure 3.10 is a balance model GB6001-S that used in this experiment. It is produced from Mettler Toledo Company, and this balance has a maximum capacity at 6100 g, a minimum capacity at 0.5 g and an accuracy at 0.1 g.

The oven uses to dry the samples as shown in figure 3.12. In this experiment uses the temperature to dry the samples approximately 110 ± 5 °C.

❖ Procedure

The cylinder is weighed by using a balance and recorded. In the next step, cylinder is filled that had passed a 2 mm sieve.

Compact the first addition of soil by tapping the bottom of the cylinder 10 times with palm of hand as shown in figure 3.22. Keep adding soil and tapping the cylinder until the cylinder is full as in figure 3.23. Weigh the cylinder containing the soil and record.



Figure 3.22 Compact the soil by tapping

After that dry the soil for 12 hours in a conventional oven at 105 °C. Bulk density is calculated by using formula below:

$$\text{Bulk density } \left(\frac{\text{g}}{\text{cm}^3}\right) = \frac{\text{oven dry weight of soil in cylinder (g)}}{\text{Volume of cylinder (cm}^3\text{)}} \quad \text{Equation 3.3}$$

$$\text{Soil porosity (\%)} = 1 - (\text{bulk density/sample's particle density}) \quad \text{Equation 3.4}$$



Figure 3.23 Bulk density ring with intact soil core inside

3.2.7 Size reduction of biochar

❖ Materials and equipment



Figure 3.24 Biochar

Figure 3.24 is the biochar used to reduce the size by using jaw crusher and roller crusher as shown in figure 3.25 and 3.26, respectively.



Figure 3.25 Jaw crusher



Figure 3.26 Roller crusher



Figure 3.27 Aggregate sieve machine

Aggregate sieve machine uses to separate size of biochar as shown in figure 3.27.

❖ Procedure

First step, feed biochar to the jaw crusher is the primary crusher. Then biochar is ground from jaw crusher, feed to the roller crusher.

In the next step, take the biochar that already grinded from roller crusher to separate the sizes with using aggregate sieve. Collect the biochar passed sieve No. 4 and retained sieve No. 7. The sample has passed sieve No. 7 and retained sieve No. 18 and collected the sample has passed sieve No. 18 and retained on the pan.

For the biochar retained sieve No. 4 and No. 7, return to feed the roller again, and then repeat to separate by using aggregate sieve machine again.

3.3 Plant growing

Growing plant is the second part of this study. Degraded soil is mixed with coal combustion products (bottom ash and FGD) and biochar. Some treatments mix with coal combustion products, biochar and fertilizer. Sweet corn is grown in the real field at Wang tao sufficient agricultural learning center, school of Agricultural resources Chulalongkorn University (CUSAR), Sanian sub-district, Mueang Nan District, Nan province and sweet corn grows in the container at school of Agricultural resources Chulalongkorn University (CUSAR), Sanian sub-district, Mueang Nan District, Nan province from September to November 2018 and January to April 2019 as shown in figure 3.28 and 3.29, respectively. The parameters used to measure for corn growing are corn height, chlorophyll, relative humidity (RH), conductivity (EC_p) and temperature of soil and corn yields.



Figure 3.28 Growing corn in real field



Figure 3.29 Growing corn in containers

3.3.1 Plant height measurement

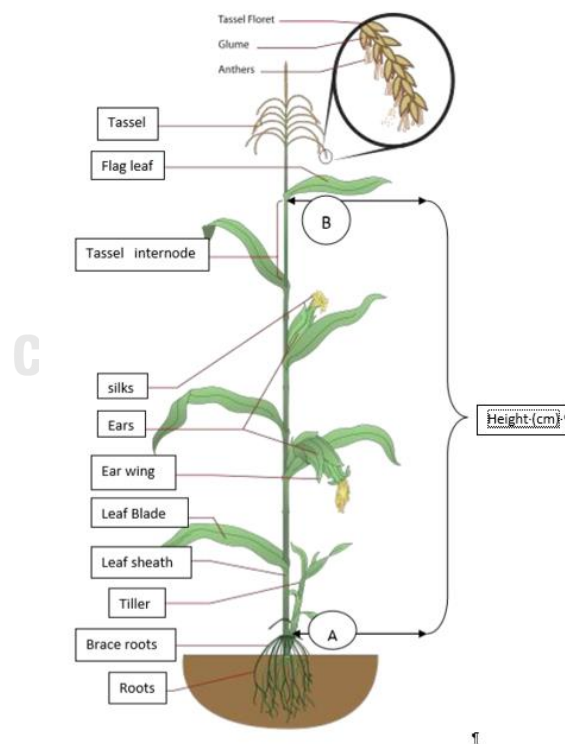


Figure 3.30 Determination of the height of corn

Corn height is measured from the soil surface to the flag leaf of corn. The meter stick is used to measure height of corn as shows in figure 3.30. For the corn height measurement, it was measured the height of corn once a week.

3.3.2 Chlorophyll measurement

Chlorophyll is the green pigment that allows plants to photosynthesize. This process uses sunlight to convert carbon dioxide and water into the building blocks of plants. Because nitrogen is a part of chlorophyll, by measuring chlorophyll, one can indirectly measure the amount of nitrogen in the plant. This allows for more efficient scheduling of fertilizer applications.

Chlorophyll in corn is measured with the chlorophyll meter SPAD-502 Plus as shown in figure 3.31.



Figure 3.31 Chlorophyll meter SPAD-502

The procedure of measurement of chlorophyll was done by the step below:

At first turn power switch ON. Next, calibrate the chlorophyll meter by the press on the finger to close the measuring head. Then insert the corn leaf into the receptor window as shown in figure 3.31. Finally, record the chlorophyll value from the display.

3.3.3 Relative humidity (RH), conductivity (EC_p) and temperature measurement

Relative humidity (RH), conductivity (EC_p) and temperature are measured with the moisture meter HH2+WET Sensor as shown in figure 3.32, and the procedure measurement is done by the step below:



Figure 3.32 Moisture Meter HH2+WET Sensor

First step, connect the soil moisture probe to the connector on the moisture meter. Then press the Esc button on the command board to turn on the moisture meter.

In the next step, Press the soil moisture probe in the position near the root of plants to measure soil moisture. Then press the Read button to read the soil moisture content (relative humidity (RH)) at the display.

Finally, press the up or down button to read the electrical conductivity (EC_p) and temperature values.

3.3.4 Corn yields

3.3.4.1 Length and diameter of ear corn



Figure 3.33 Measured the length of ear corn

A ruler is used to measure the length and diameter of ear corn. The length of ear corn is measured from the total of ear corn as shown in figure 3.33.

3.3.4.2 Weight of ear corn

An ear corn and a corn shell are measured with a balance as shown in figure 3.34 and 3.35, respectively.



Figure 3.34 Weight of ear corn



Figure 3.35 Weight of corn shell

3.3.4.3 Corn seeds measurement

Corn seeds are measured by count amount of corn seeds in row and vertical as shown in figure 3.36.

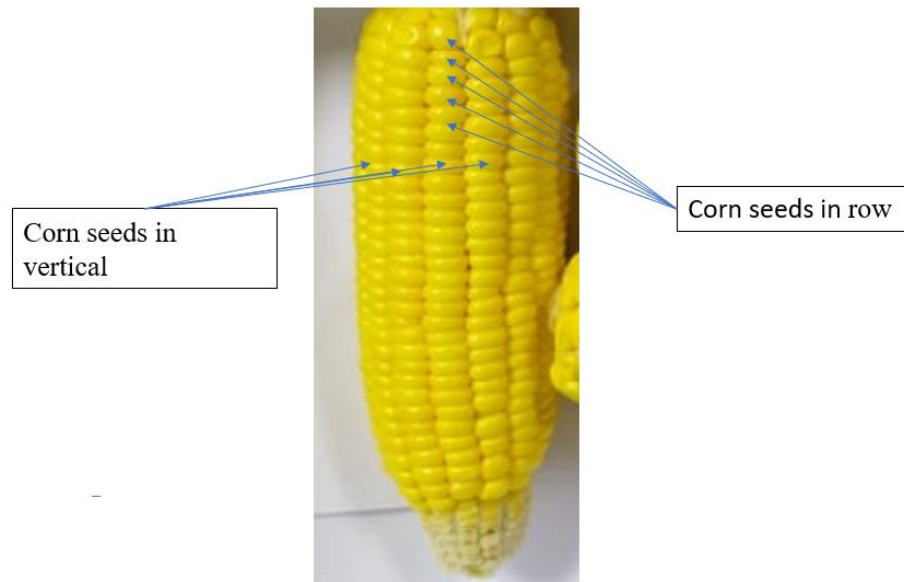


Figure 3.36 Count corn seeds

3.3.4.4 Length of corn root

Length of corn root is measured by using the meter stick as shown in figure 3.37.



Figure 3.37 Measure the length of root

3.4 Heavy metals analysis

Heavy metals are analyzed with Inductively coupled plasma (IPC) instrument, and the samples are sent to Environmental Research Institute Chulalongkorn University (ERIC) for heavy metal analysis including cadmium (Cd), Arsenic (As), chromium (Cr), lead (Pb), and mercury (Hg). For the method uses to analyze heavy metals follow the standard method for the examination of water and wastewater 22nd edition (2012).

The samples send to analyze heavy are considered from the best products of corn, and the parts of corn that send to analyze heavy metals such as soil (the post soil after grow corn), seed of corn, leaf + stem + root of corn (combined leaf, stem, and root), and core + shell of corn (combined core and shell of corn). In additional, the original soil, bottom ash, FGD gypsum, biochar, and fertilizer are also analyzed heavy metals.



Figure 3.38 corn seed



Figure 3.39 Soil which send to analyze heavy metal



Figure 3.40 Leaf, stem and root



Figure 3.41 Shell of corn

3.5 Operating conditions

3.5.1 The operating conditions before corn growing

The operating conditions are condition by weight of biochar mixed with soil, biochar and bottom ash mixed with soil (Soil + biochar + bottom ash), and biochar and FGD mixed with soil (Soil + biochar + FGD) as shown in table 3.5.

Table 3.5 The operating conditions before corn growing

No	Mixer	Ratio (%)
1	Normal soil	100
2	Soil + biochar	(95:5)
3	Soil + biochar	(90:10)
4	Soil + biochar	(80:20)
5	Soil + biochar	(70:30)
6	Soil + biochar + bottom ash	(90:5:5)
7	Soil + biochar + bottom ash	(80:5:15)
8	Soil + biochar + bottom ash	(70:5:25)
9	Soil + biochar + bottom ash	(80:10:10)
10	Soil + biochar + bottom ash	(70:10:20)
11	Soil + biochar + FGD	(90:5:5)
12	Soil + biochar + FGD	(80:5:15)
13	Soil + biochar + FGD	(70:5:25)
14	Soil + biochar + FGD	(80:10:10)
15	Soil + biochar + FGD	(70:10:20)

3.5.2 The operating conditions before corn growing

Base on the results of pH, EC, soil texture and bulk density before corn growing, the corns are grown at the optimum conditions as shown on table 3.6.

Table 3.6 The operating conditions for corn growing

No	Mixer	Ratio (%)
1	Normal soil	100
2	Normal soil	100 + fertilizer
3	Soil + biochar	90:10
4	Soil + biochar	90:10 +fertilizer
5	Soil + biochar	80:20
6	Soil + biochar	80:20 + fertilizer
7	Soil + biochar + bottom ash	70:5:25
8	Soil + biochar + bottom ash	70:5:25 + fertilizer
9	Soil + biochar + bottom ash	70:10:20
10	Soil + biochar + bottom ash	70:10:20 + fertilizer
11	Soil + biochar + FGD	70:10:20
12	Soil + biochar + FGD	70:10:20 + fertilizer

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of bottom ash, FDG gypsum and biochar on soil quality

4.1.1 Effect of bottom ash, FDG gypsum and biochar on soil pH

Soil pH affects the soil physical, chemical, and biological properties and processes, as well as plant growth. The nutrition, growth, and yields of most crops decrease where soil pH is low and increases as pH rises to an optimum level.

The results of pH of samples before corn growing are shown in figure 4.1. Figure 4.2 and 4.3 present the pH of samples after corn growing in the real field and corn growing in the containers compare with pH of samples before corn growing, respectively.

The result of pH is shown that biochar, FGD gypsum and bottom ash can increase pH of soil. First, soil in Nan province is acid with pH at 5.66. Biochar is alkalinity with pH at 10.17 and FGD gypsum is weak alkalinity with pH at 7.87 as shown in figure 4.1.

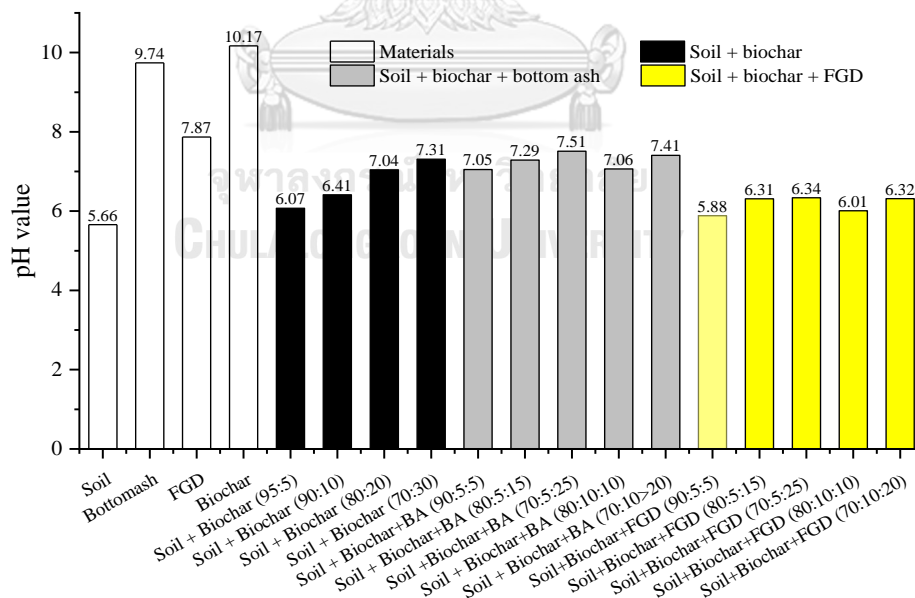


Figure 4.1 Results of pH of soil before corn growing

The result is shown in figure 4.1 that pH increases when biochar, bottom ash and FGD gypsum are mixed with soil. The application of biochar at 5% to 20% is

considered the suitable ratios for improvement of soil pH, and it can increase pH of soil from 5.66 to 7.04, but at the ratio 30% biochar, pH of soil becomes weak alkalinity. The application of biochar coupled with FGD gypsum, at the ratio soil + biochar + FGD (80:5:15), soil + biochar + FGD (70:10:20) and soil + biochar + FGD (70:5:25) are the good conditions for soil pH improvement, and pH of soil increase at 6.31, 6.32 and 6.34, respectively. For the application of biochar coupled with bottom ash before corn growing, pH of soil can increase all of ratio as shown in figure 4.1. The pH value of treatment before and after corn growing two time is summarized in table 4.1.

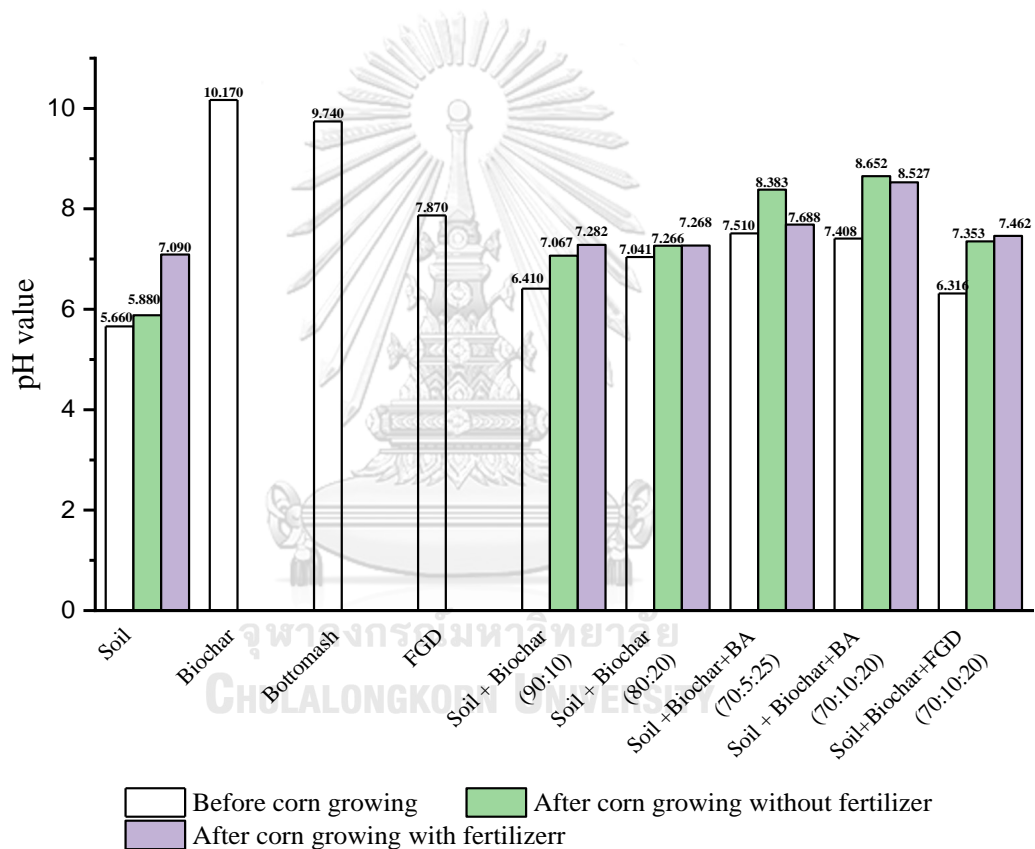


Figure 4.2 Results of pH of soil after corn growing in the real field

Table 4.1 pH value of treatment before and after corn growing in real field and the containers

Treatment	Before corn growing	After corn growing in real field		After corn growing in containers	
		Without fertilizer	Fertilizer	Without fertilizer	Fertilizer
Soil	5.664	5.887	7.090	6.203	7.512
Biochar	10.170	-	-	-	-
Bottom ash	9.740	-	-	-	-
FGD	7.870	-	-	-	-
Soil + Biochar (90:10)	6.410	7.067	7.282	7.045	7.368
Soil + Biochar (80:20)	7.041	7.266	7.268	7.380	7.463
Soil + Biochar +BA (70:5:25)	7.510	8.383	7.688	7.824	7.824
Soil + Biochar + BA (70:10:20)	7.408	8.652	8.527	7.767	7.656
Soil+ Biochar +FGD (70:10:20)	6.316	7.353	7.462	7.593	7.457

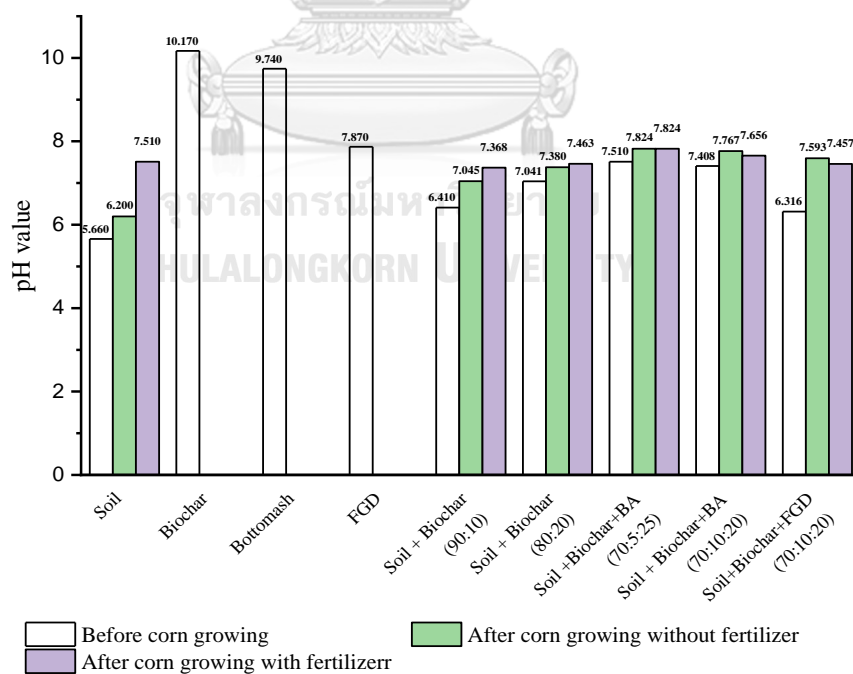


Figure 4.3 Results of pH of soil after corn growing in the containers

4.1.2 Effect of bottom ash, FDG gypsum and biochar on soil electrical conductivity

Soil electrical conductivity (EC) is a measure of the amount of salts in soil (salinity of soil). It is an important indicator of soil health. It affects crop yields, crop suitability, plant nutrient availability. In this research, an EC_{se} value of FGD and bottom ash are very high at 37.82 dS/m and 34.20 dS/m, respectively.

Figure 4.4 shows the application of biochar coupled with coal combustion products increase EC_{se} value of soil at all of combination ratios. However, when biochar, bottom ash and FGD gypsum are added into soil, EC_{se} is still suitable for plant growth.

EC_{se} of the samples after harvesting is shown in figure 4.5 and 4.6. The EC_{se} of samples decreases after corn growing all of two times. Except the treatment of soil with fertilizer increase to slightly saline, treatment 10% of biochar and 10% of biochar with fertilizer increases to moderately saline for after corn growing in the real field as shown in figure 4.5. After corn growing in the containers, the treatment of soil with fertilizer increase to slightly saline and treatment 10% of biochar increases to moderately saline, but 10% of biochar with fertilizer increases to slightly saline as shown in figure 4.6. Table 4.2 summarizes the result of EC_{se} in all of corn growing in the real field and the containers after corn growing.

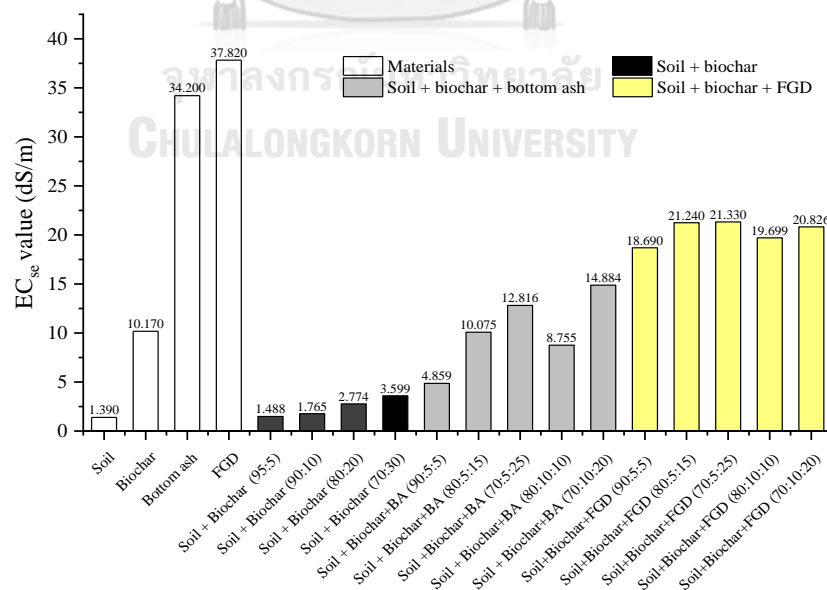


Figure 4.4 Results of EC_{se} value of soil before growing corn

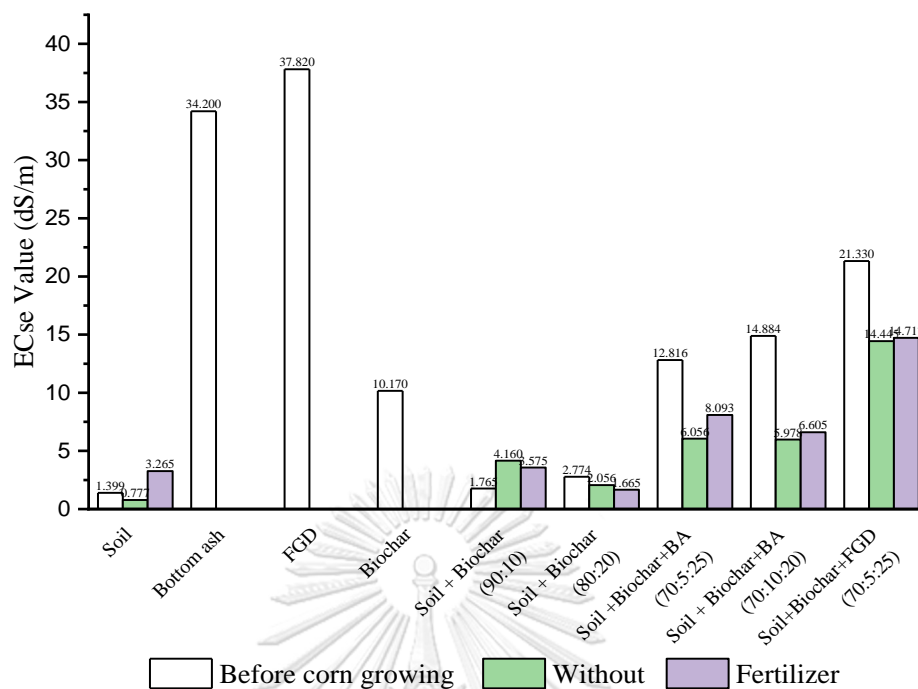


Figure 4.5 Results of EC_{se} value of soil after corn growing in the real field

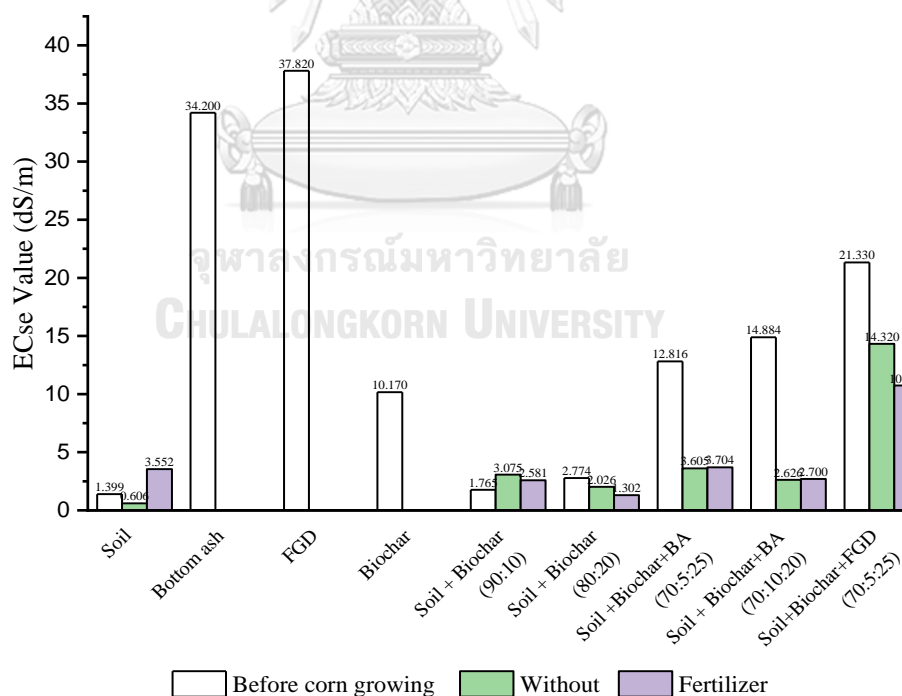


Figure 4.6 Results of EC_{se} value of soil after corn growing in the containers

Table 4.2 Summarized the value of EC_{se} (dS/m)

Treatment	Before corn growing	After corn growing at the first time		After corn growing at the second time	
		Without fertilizer	Fertilizer	Without fertilizer	Fertilizer
Soil	1.399	0.777	3.265	0.606	3.552
Bottom ash	34.2	-	-	-	-
FGD	37.82	-	-	-	-
Biochar	10.17	-	-	-	-
Soil + Biochar (90:10)	1.765	4.16	3.574	3.074	2.581
Soil + Biochar (80:20)	2.773	2.055	1.665	2.026	1.302
Soil + Biochar + BA (70:5:25)	12.816	6.056	8.092	3.604	3.704
Soil + Biochar + BA (70:10:20)	14.884	5.977	6.605	2.625	2.7
Soil + Biochar + FGD (70:5:25)	21.33	14.445	14.717	14.32	10.744

4.1.3 Effect of biochar coupled with CPPs on texture of soil

Figure 4.7 shows the particle size distribution curve of soil and soil mixed with biochar. Firstly, the soil is clay (20% of sand, 20% of silt and 60% of clay), but biochar is ground in sand size, it is ranged from 1mm to 2.8 mm. From the result of hydrometer, when biochar added into soil, the percentage of clay is decreased. On the other hand, the percent of sand and silt increase with the percent of biochar is added into soil by weight as shown in figure 4.7.

The particle size distribution of soil mixed with biochar after corn growing compared the initial samples and shown in figure 4.8 and 4.9. It is presented that after corn growing, the percent of clay and sand particle in soil and soil with fertilizer reduce when compare to soil before corn growing, but the treatments 10% and 20% of biochar increase percent of clay and silt after corn growing in the real field and the containers.

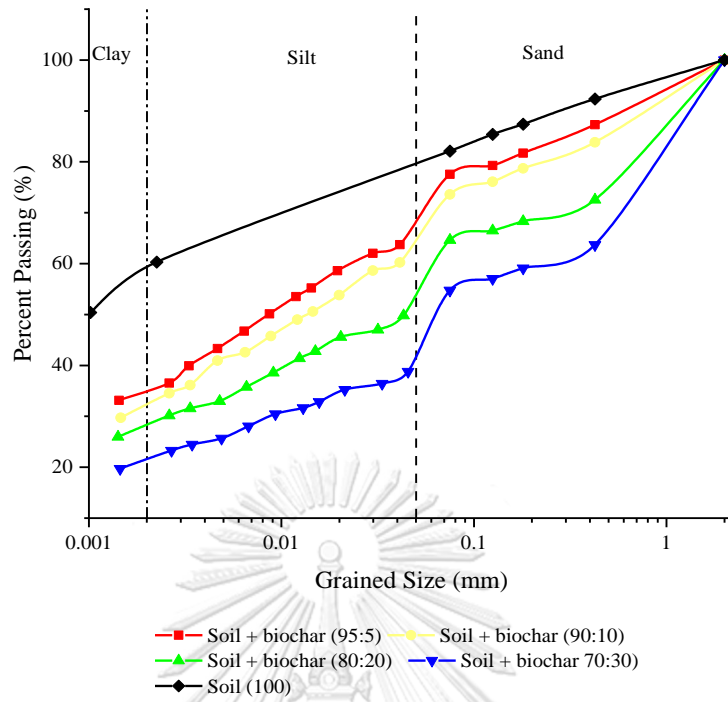


Figure 4.7 Particle size distribution of soil mixed with biochar before corn growing

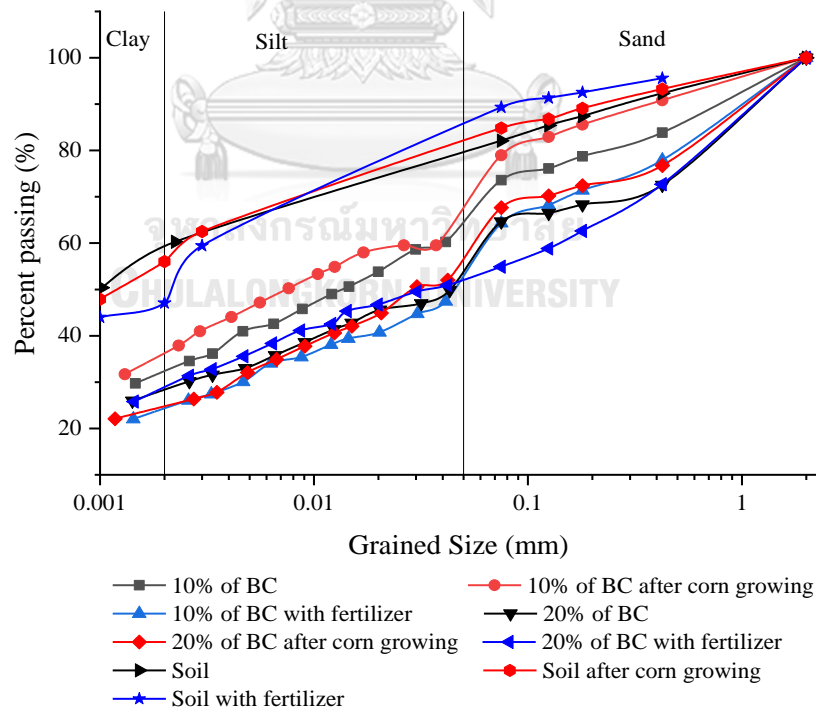


Figure 4.8 Particle size distribution of soil mixed with biochar after corn growing in the real field compared before corn growing

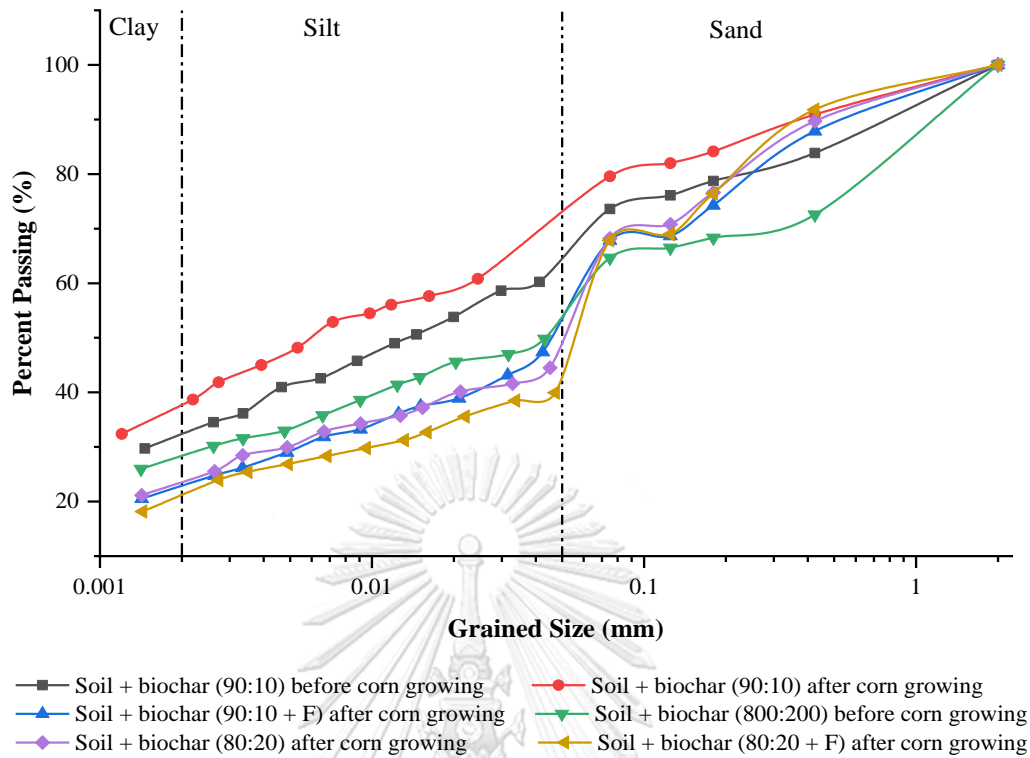


Figure 4.9 Particle size distribution of soil mixed with biochar after corn growing in the containers compared before corn growing

Figure 4.10 shows the particle size distribution of soil mixed with biochar and bottom ash before corn growing. It is clear that the percentage of particle sand increase with an increase bottom ash and biochar, and the application of biochar coupled with bottom ash can change the texture of normal soil from clay to clay loam, except the treatment Soil + biochar + bottom ash (70:5:25) is medium loam. In addition, the particle size distribution of soil mixed with biochar and bottom ash after corn growing at the first and second time compared before corn growing as shown figure 4.11 and 4.12. It is shown that after corn growing, percent of clay is dropped when compared with the initial sample.

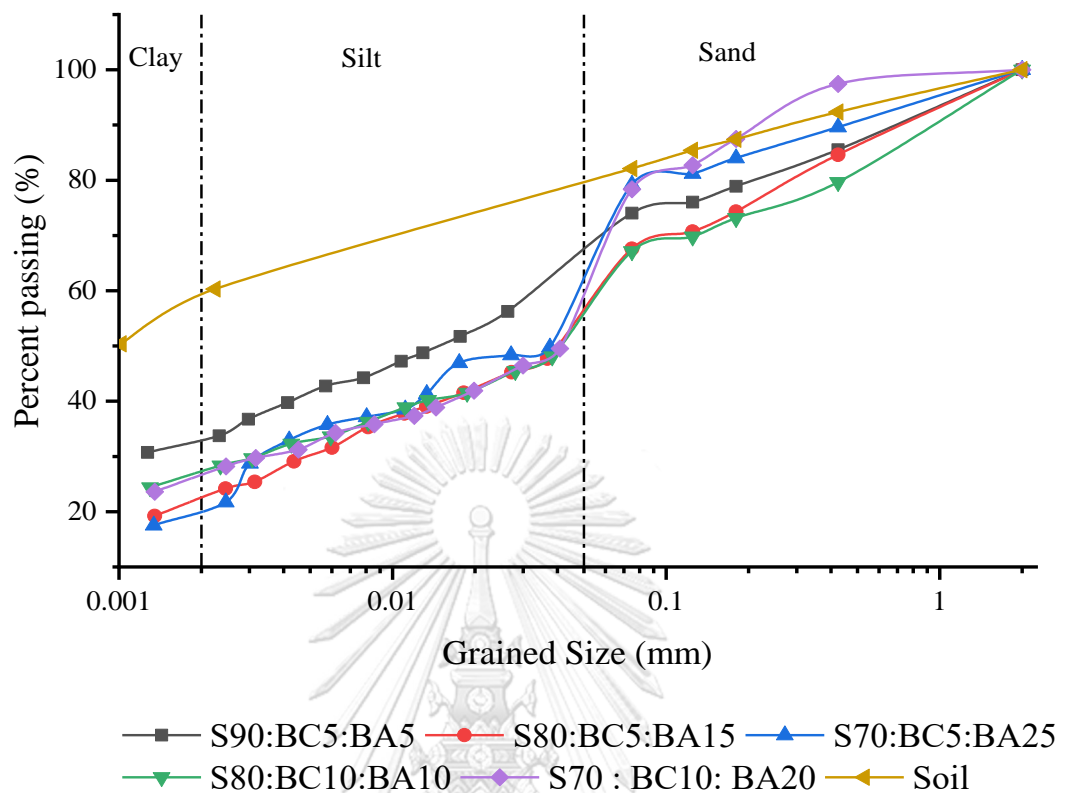


Figure 4.10 Particle size distribution of soil mixed with biochar and bottom ash before corn growing

The particle size distribution of soil mixed with biochar and FGD before corn growing as shown in figure 4.13. At the first, FGD contains 40% of silt and 60% of sand. The application of biochar coupled FGD gypsum, it can increase the percent of silt, and all of treatments used biochar coupled with FGD change the texture of soil from clay to silty loam. As for the particle size distribution of soil mixed with biochar and FGD after corn growing is shown in figure 4.14 and 4.15. It is found that in the comparison of the texture of soil before and after corn growing, it is not different from the initial sample, and it is still silty loam.

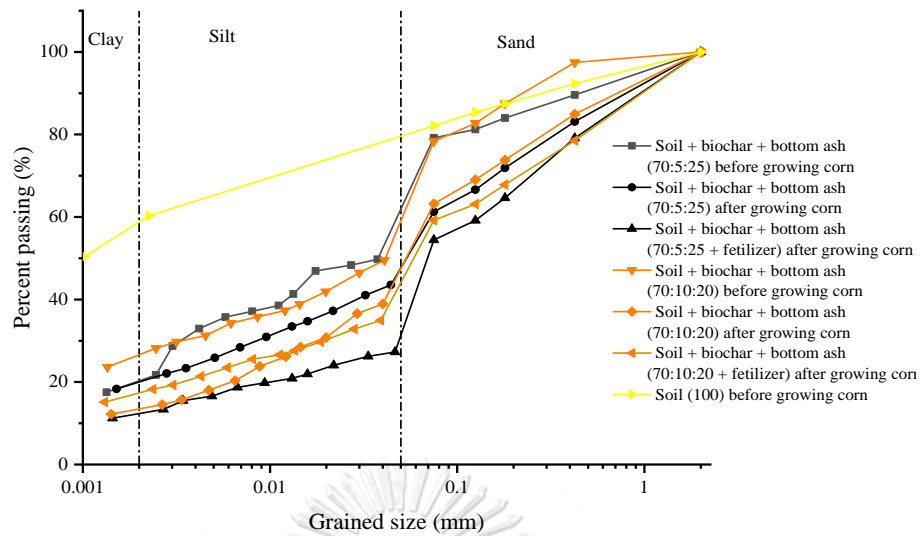


Figure 4.11 Particle size distribution of soil mixed with biochar and bottom ash after corn growing in the real field compared with before corn growing

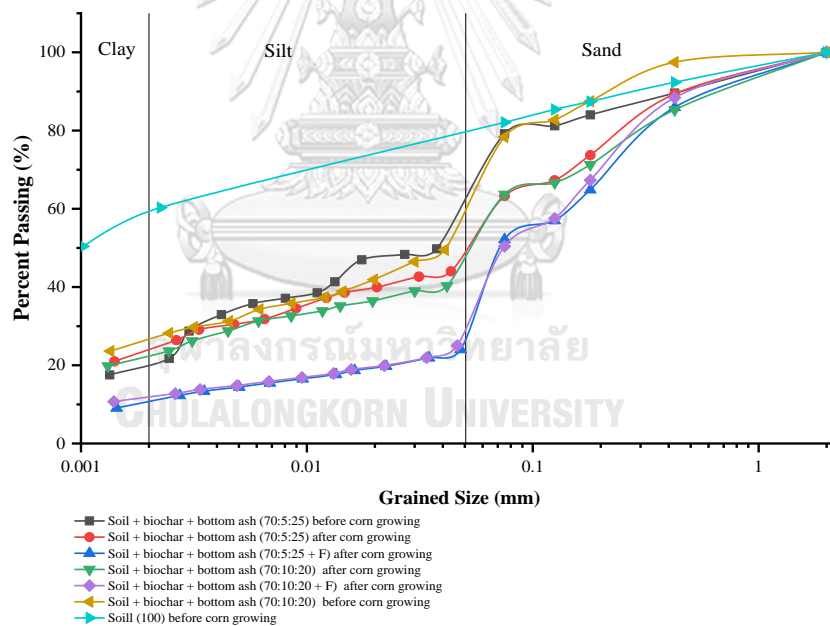


Figure 4.12 Particle size distribution of soil mixed with biochar and bottom ash after corn growing in containers time compared before corn growing

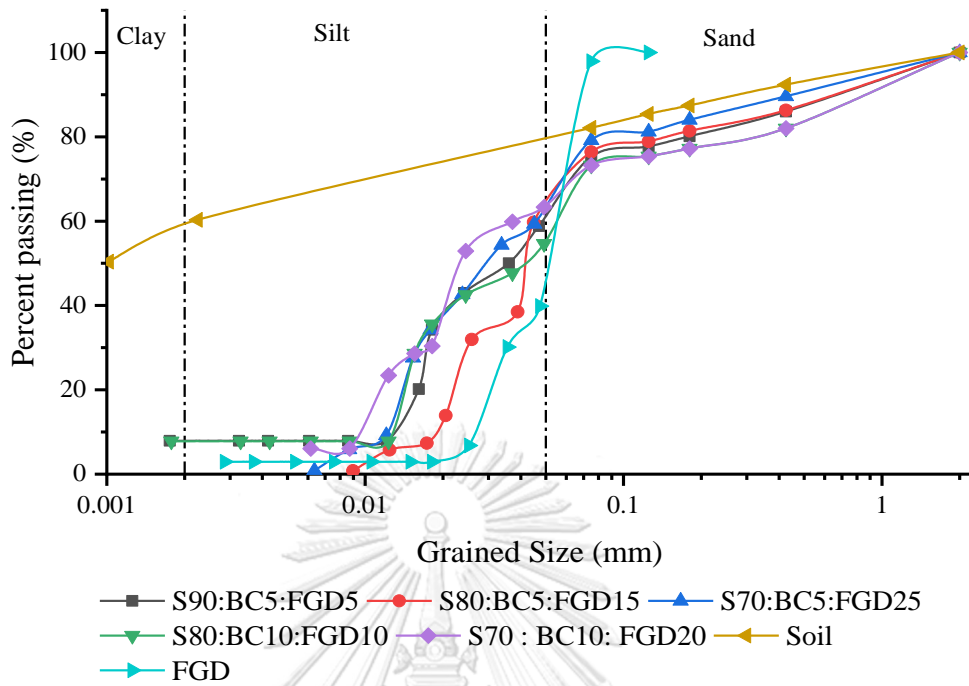


Figure 4.13 Particle size distribution of soil mixed with biochar and FGD before corn growing

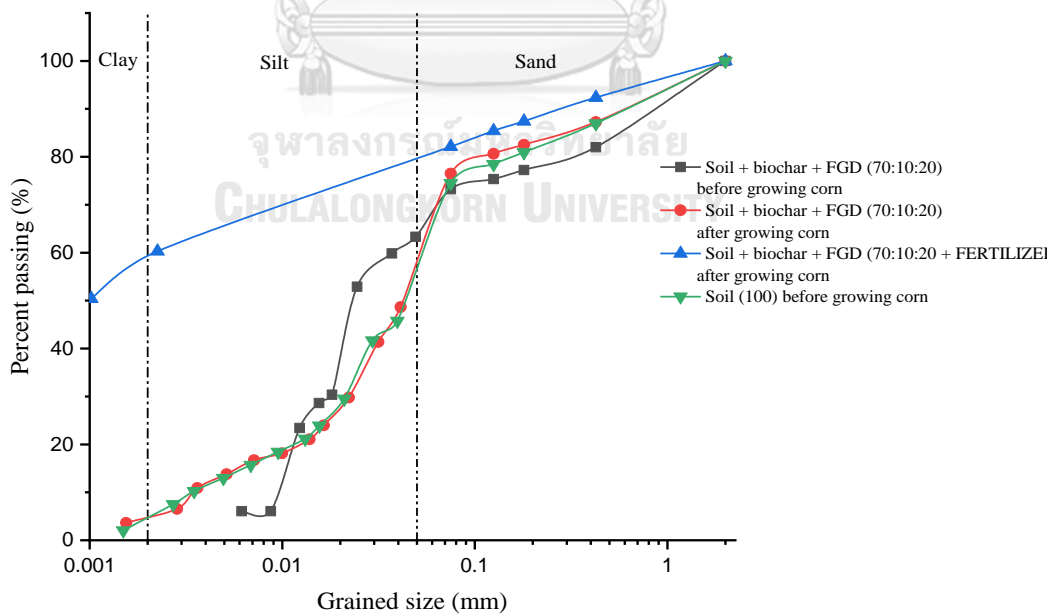


Figure 4.14 Particle size distribution of soil mixed with biochar and FGD after corn growing real compared with before corn growing

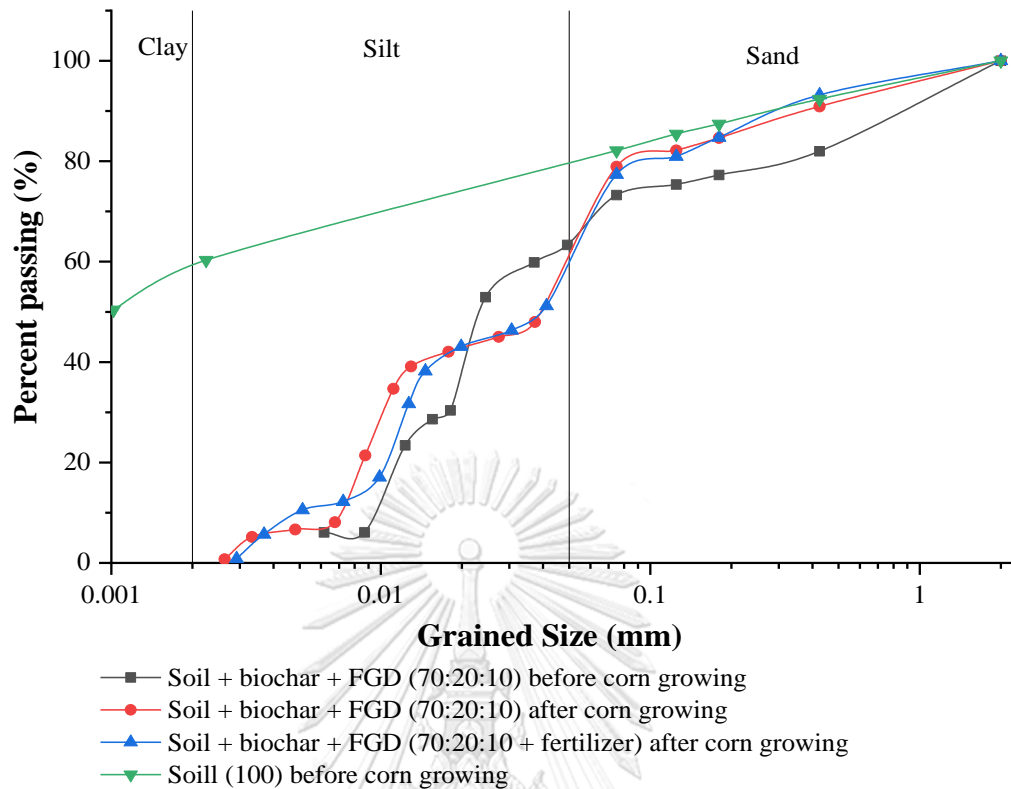


Figure 4.15 Particle size distribution of soil mixed with biochar and FGD after corn growing in the containers time compared with before corn growing

From the result as shown in table 4.3, the biochar mixed with soil before corn growing ranging at 5-20% can change the texture of normal soil from clay to clay loam, and at 30% of biochar changes the texture of soil to loam as shown figure 4.16. In addition, the biochar coupled with bottom ash before corn growing changes the texture of soil from clay to clay loam and loam as shown in figure 4.17. From the figure 4.18, it is shown that the biochar coupled with FGD before corn growing changes the texture of normal soil from clay to silty loam.

Table 4.3 Soil texture classification

No	Samples	Ratio	Before corn growing	After corn growing in the real field		After corn growing in the containers	
				Without fertilizer	Fertilizer	Without fertilizer	Fertilizer
1	Normal soil	100	Clay	Clay	Clay	Clay	Clay loam
2	Bottom ash		Sand	-	-	-	
3	FGD		Sandy loam	-	-	-	-
4	Biochar		Sand	-	-	-	-
5	Soil + biochar	(95:5)	Clay loam	-	-	-	-
6	Soil + biochar	(90:10)	Clay loam	Clay loam	Clay loam	Clay loam	Loam
7	Soil + biochar	(80:20)	Clay loam	Loam	Sandy clay loam	Sandy clay loam	Sandy clay loam
8	Soil + biochar	(70:30)	loam	-	-	-	-
9	Soil + biochar + bottom ash	(90:5:5)	Clay loam	-	-	-	-
10	Soil + biochar + bottom ash	(80:5:15)	Loam	-	-	-	-
11	Soil + biochar + bottom ash	(70:5:25)	Loam	Sandy loam	Sandy loam	Sandy clay loam	Sandy loam
12	Soil + biochar + bottom ash	(80:10:10)	Loam	-	-	-	-
13	Soil + biochar + bottom ash	(70:10:20)	Loam	Sandy loam	Sandy loam	Sandy clay loam	Sandy loam
14	Soil + biochar + FGD	(90:5:5)	Silty loam	-	-	-	-
15	Soil + biochar + FGD	(80:5:15)	Silty loam	-	-	-	-
16	Soil + biochar + FGD	(70:5:25)	Silty loam	-	-	-	-
17	Soil + biochar + FGD	(80:10:10)	Loam	-	-	-	-
18	Soil + biochar + FGD	(70:10:20)	Silty loam	Silty loam	Silty loam	Silty loam	Silty loam

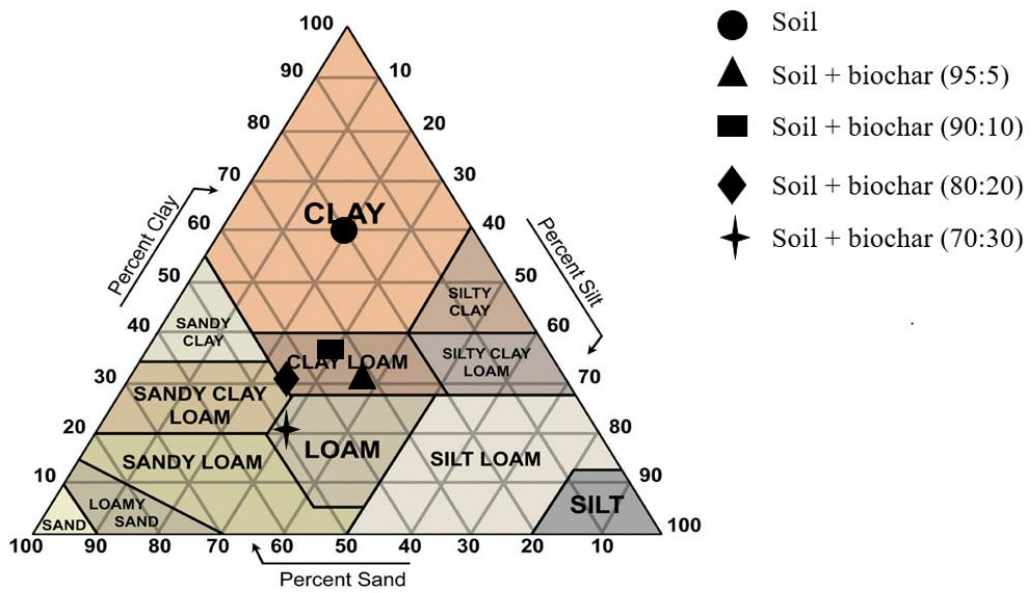


Figure 4.16 Texture of samples when applied biochar before corn growing

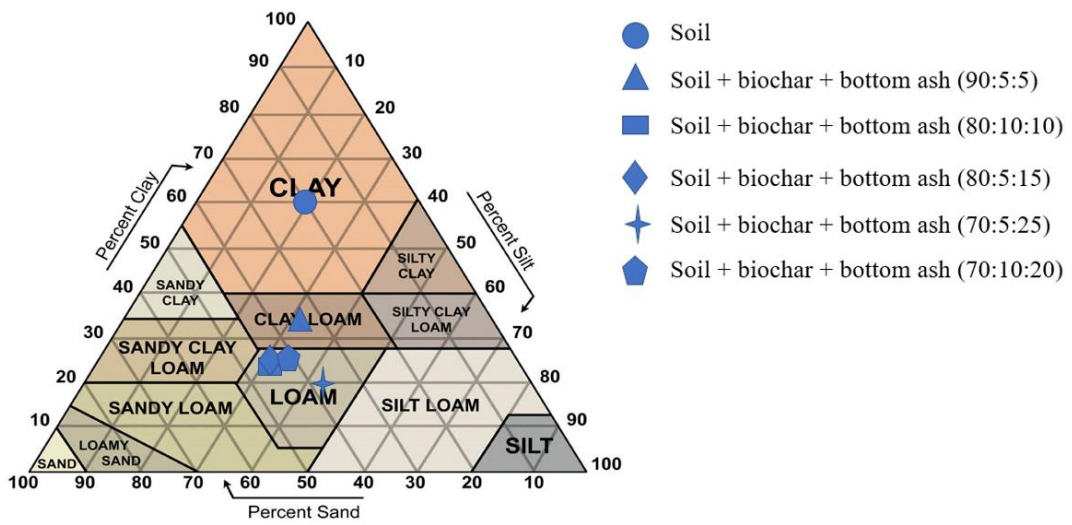


Figure 4.17 Texture of samples when applied biochar coupled with bottom ash before corn growing

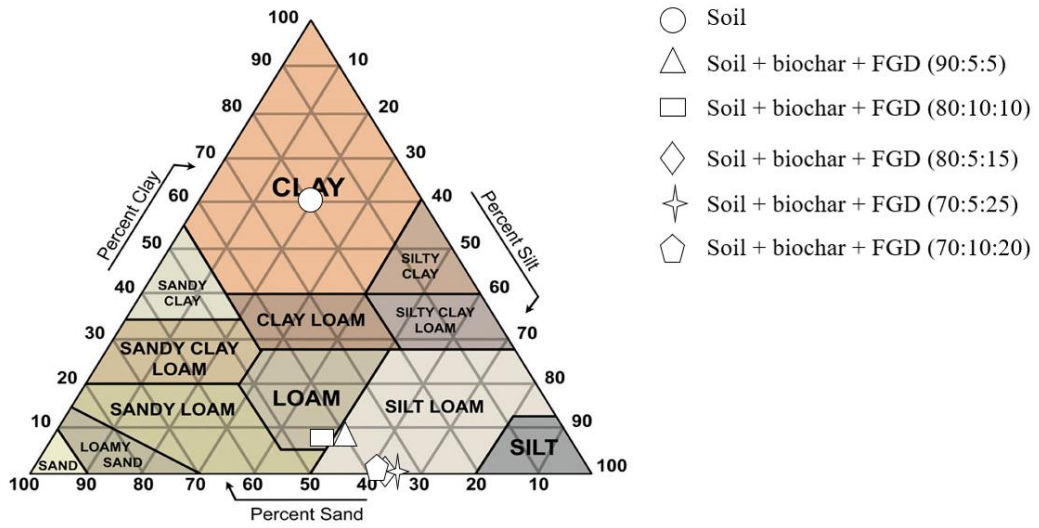


Figure 4.18 Texture of samples when applied biochar coupled with FGD before corn growing

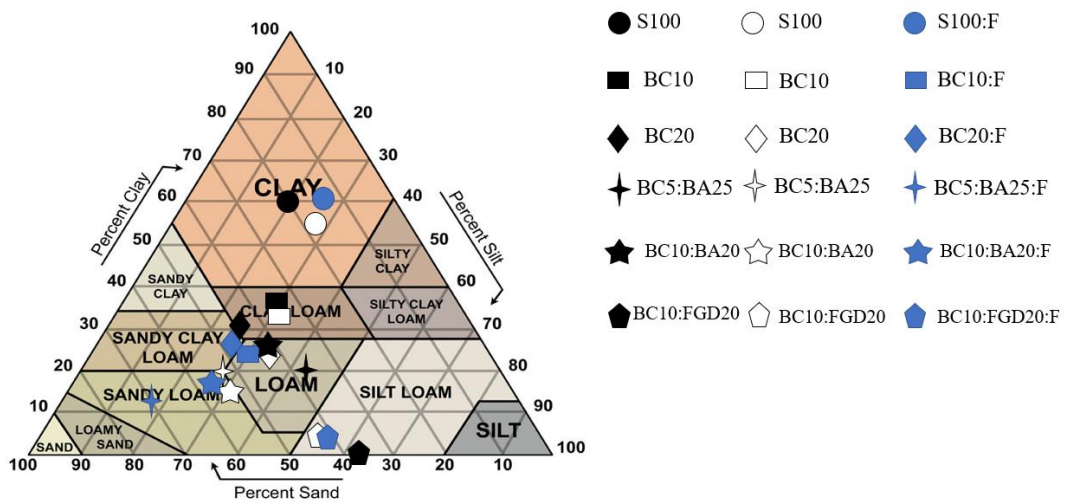


Figure 4.19 Texture of samples when applied biochar coupled with CCPs after corn growing in the real field

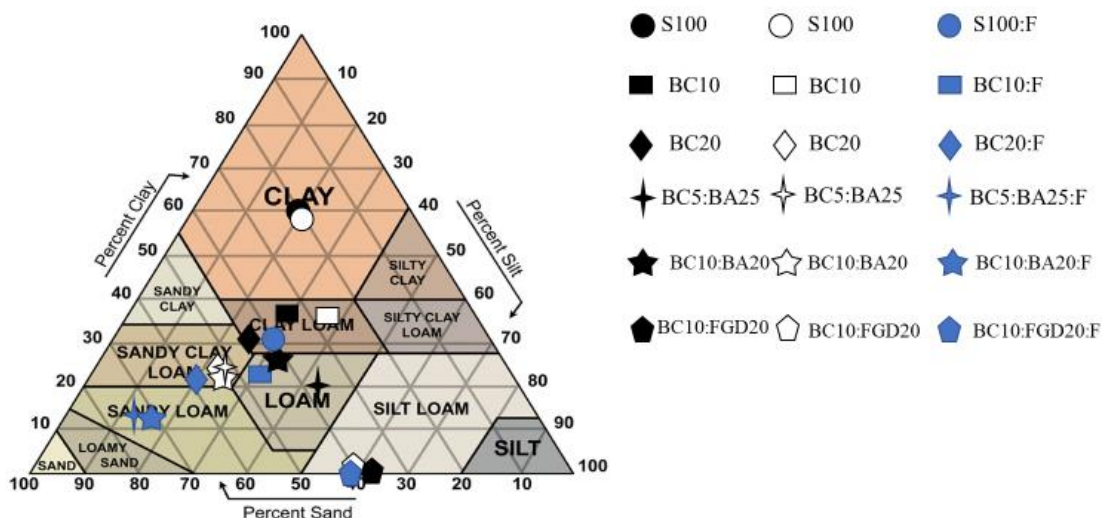


Figure 4.20 Texture of samples when applied biochar coupled with CCPs after corn growing in the containers

The texture of soil after the harvesting corn in the real field and the containers as shown in figure 4.19 and 4.20, respectively. It is shown that the texture of soil after corn growing is changed from the initial samples, especially, the percent of sand increases with the treatments used fertilizer, but the treatment of biochar coupled with FGD does not change the texture. It is still silty loam.

4.1.4 Effect of bottom ash, FDG gypsum and biochar on soil bulk density

Bulk density is an important physical property of soil. It is presented soil compaction and soil health. Bulk density affects with root growth, infiltration, available capacity, plant nutrient availability and soil microorganism activity. High bulk density of soil is an indicator of low soil porosity and soil compaction. It can restrict to root growth, and poor movement of air and water through soil. Each soil will have different ideal bulk density for plant growth and threshold of bulk density value that restricts root growth depending on the texture of soil.

The result of experiment of bulk density before corn growing is shown in figure 4.21. Following the results experiment, the application of biochar coupled with CCPs can reduce bulk density of normal soil from 1.27 g/cm³ to 0.74 g/cm³.

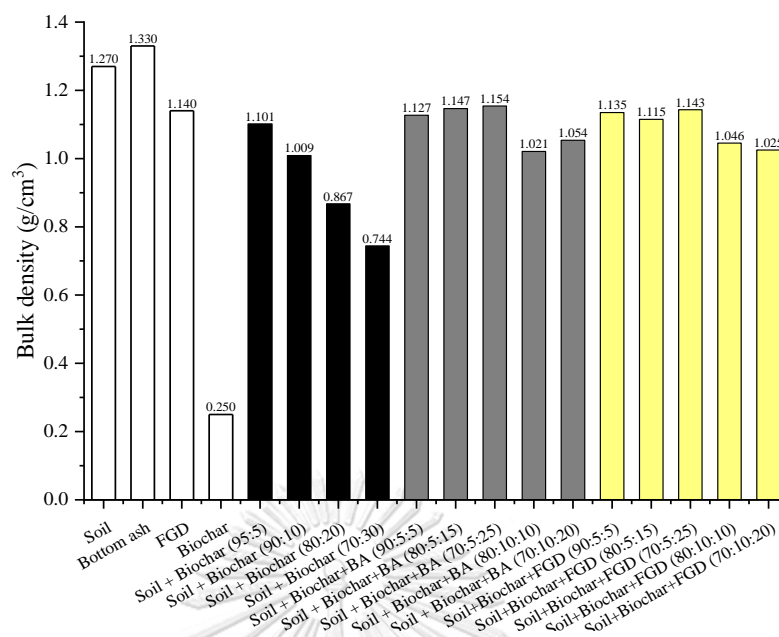


Figure 4.21 Results of bulk density of soil before growing corn

Figure 4.22 and 4.23 present the result of bulk density of soil after corn growing in the real field and the containers, respectively, compared with the samples before corn growing. It is found that the bulk density of samples tends to increase after harvesting, but the bulk density of samples which used fertilizer decreases. It can be summarized in table 4.4.

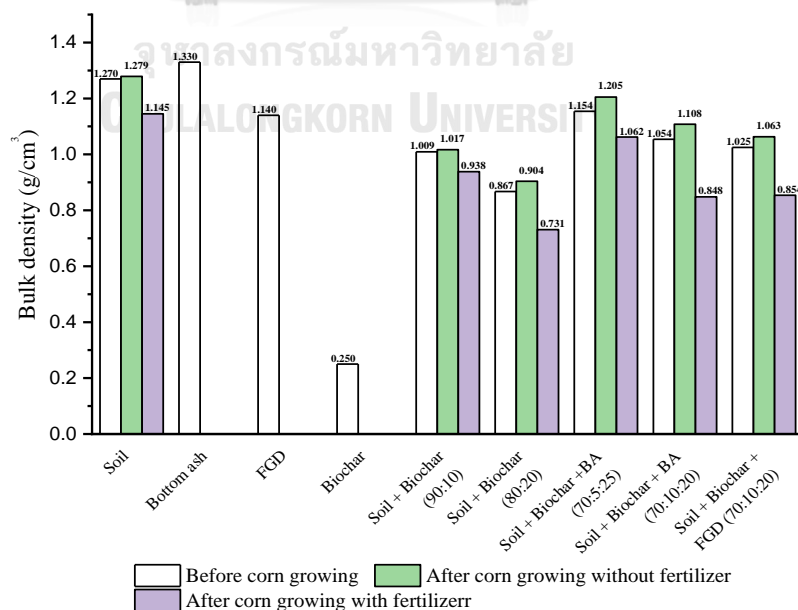


Figure 4.22 Results of bulk density of soil after corn growing in the real field

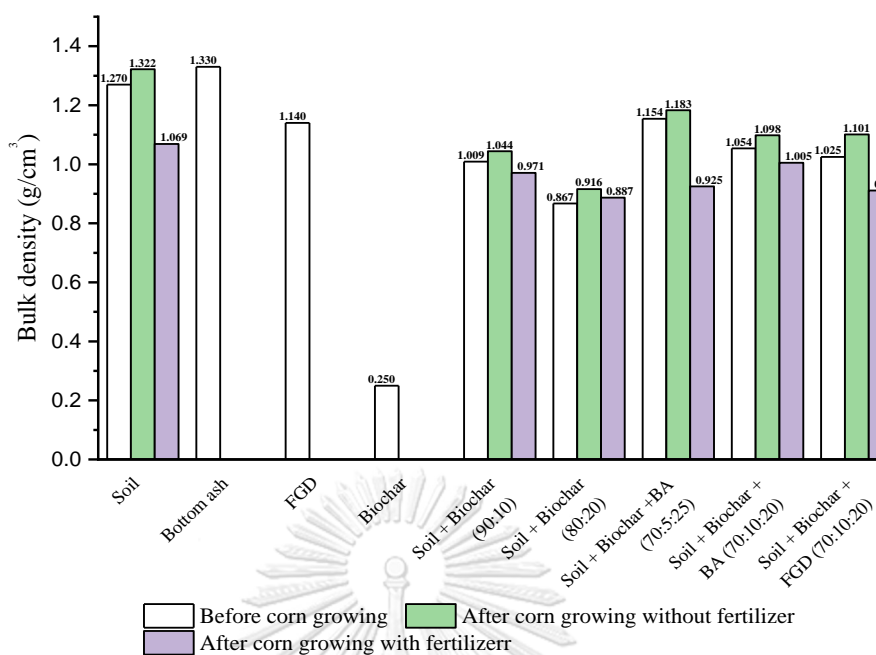


Figure 4.23 Results of bulk density of soil after corn growing in the containers

Table 4.4 Summarized the results of bulk density (g/cm³)

Treatment	Before corn growing	After corn growing in the real field		After corn growing in the containers	
		Without fertilizer	Fertilizer	Without fertilizer	Fertilizer
Soil	1.270	1.279	1.145	1.322	1.069
Bottom ash	1.330	-	-	-	-
FGD	1.140	-	-	-	-
Biochar	0.250	-	-	-	-
Soil + Biochar (90:10)	1.009	1.017	0.938	1.044	0.971
Soil + Biochar (80:20)	0.867	0.904	0.731	0.916	0.887
Soil + Biochar +BA (70:5:25)	1.154	1.205	1.062	1.183	0.925
Soil + Biochar + BA (70:10:20)	1.054	1.108	0.848	1.098	1.005
Soil + Biochar + FGD (70:10:20)	1.025	1.063	0.854	1.101	0.911

4.2 Effect of biochar coupled with CCPs on plant growth

4.2.1 Effect of biochar coupled with CCPs on corn height

Figure 4.24 - 4.26 show the height of corn when applying biochar coupled with CCPs compared normal soil for corn growing in the real field. Figure 4.27 - 4.29 shows the height of corn when applying biochar coupled with CCPs compared to normal soil for corn growing in the containers. Firstly, corn is grown in the real field and it makes the results unclear, because the whole area is not the same soil properties. From results of corn height for corn growing in the real field, it is shown that the height of corn at normal soil is higher than treatment used biochar coupled with CCPs as shown in figure 4.24 - 4.26.

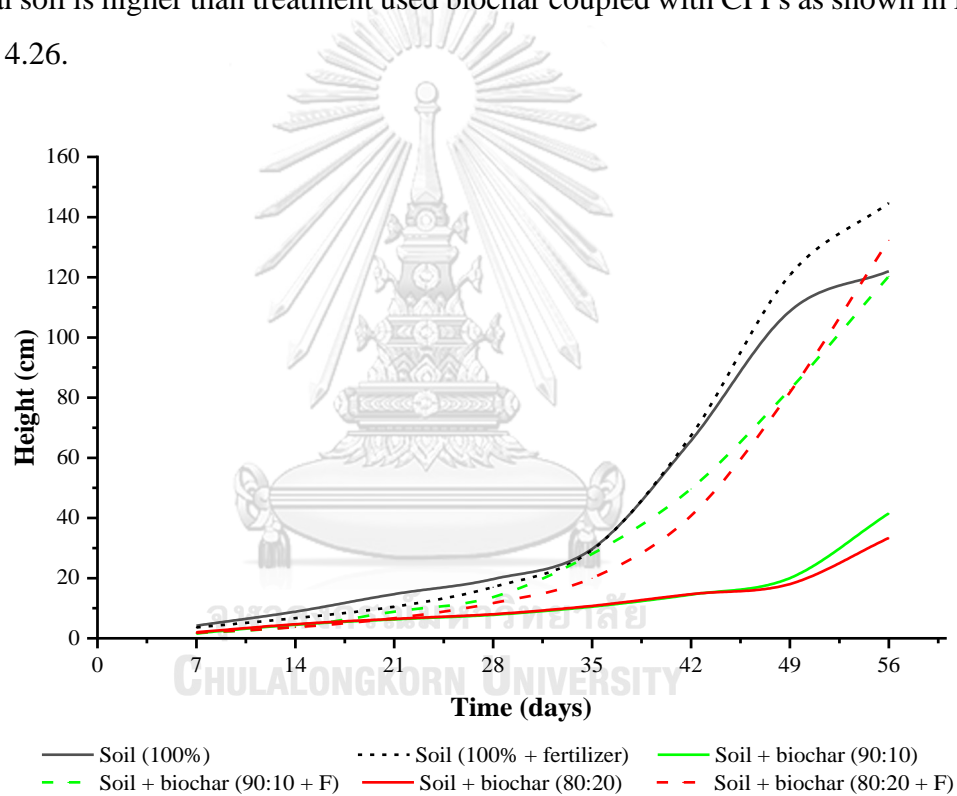


Figure 4.24 The height growth of corn when applying biochar compared normal soil for corn growing in the real field

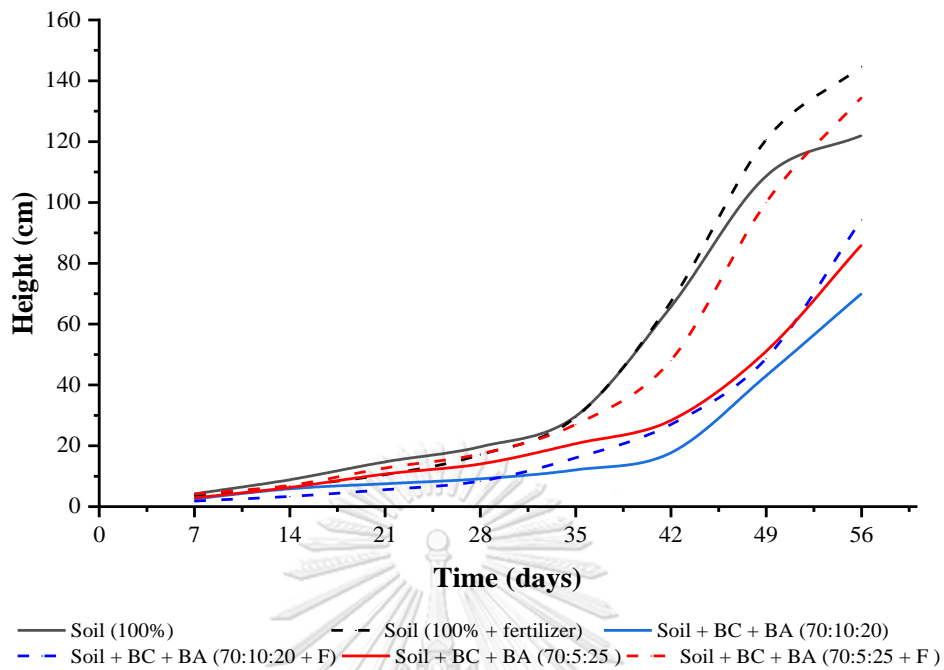


Figure 4.25 The height growth of corn when applying biochar coupled with bottom ash compared with normal soil for corn growing in the real field

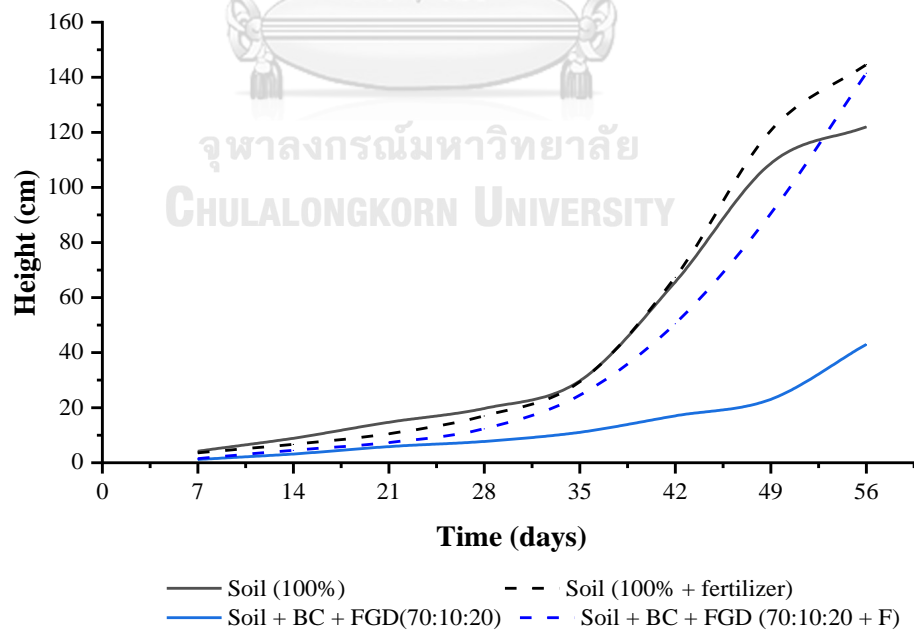


Figure 4.26 The height growth of corn when applying biochar coupled with FGD compared with normal soil for corn growing in the real field

At the corn growing in the containers, corn is grown in the containers. the height of corn is shown in figure 4.27-4.29. The result shows that biochar applied for soil amendment can increase the height of corn compared to the normal soil. It can be clearly seen in the different corn height between using biochar and normal soil at 6th week after planting. And the highest corn is at 10% of biochar coupled with fertilizer as shown in figure 4.27.

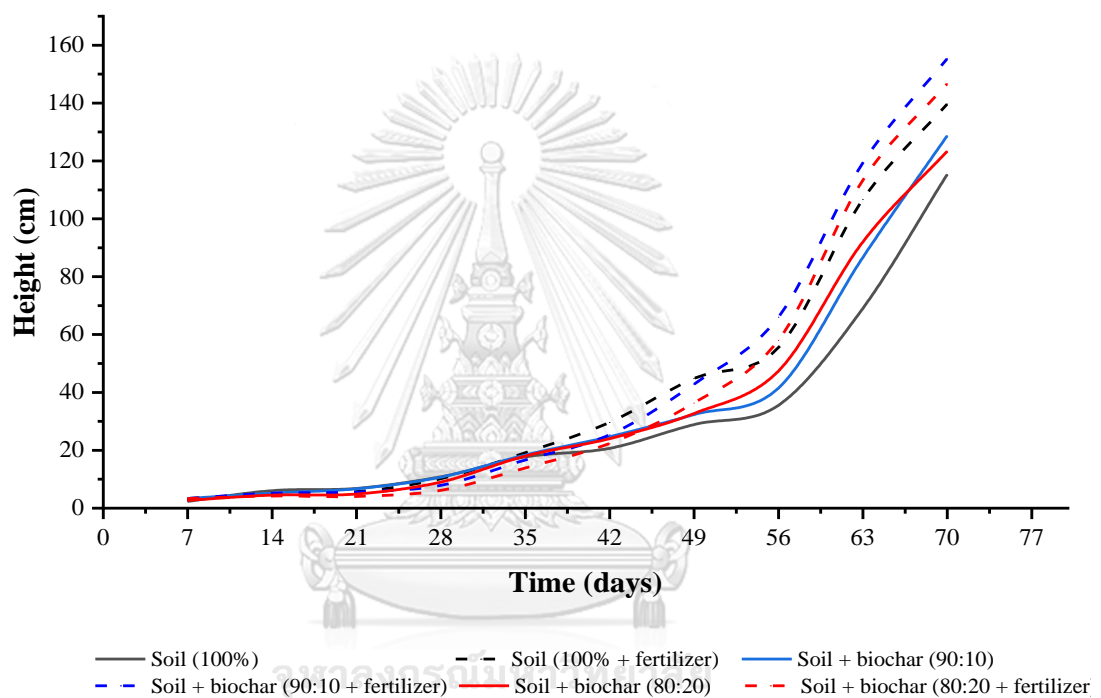


Figure 4.27 The height growth of corn when applying biochar compared to normal soil for corn growing in the containers

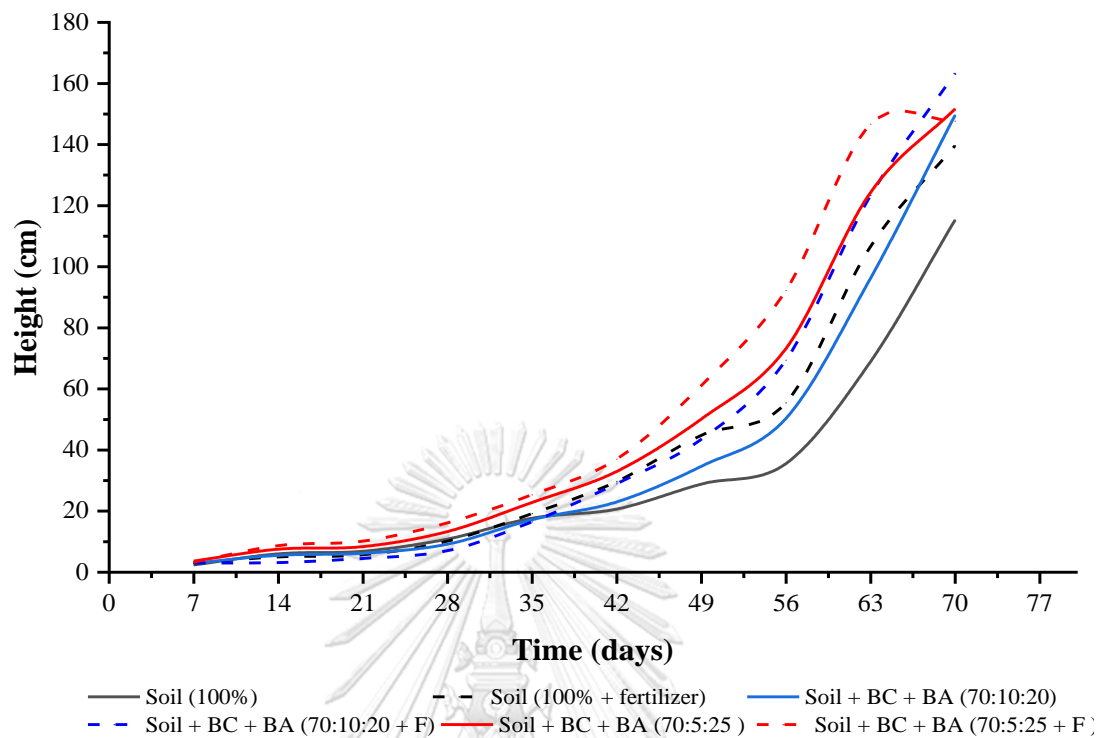


Figure 4.28 The height growth of corn when applying biochar coupled with bottom ash compared with normal soil for corn growing in the containers

Figure 4.28 shows the height growth of corn when applying biochar coupled with bottom ash compared to normal soil for corn growing in the containers. It is found that biochar coupled with bottom ash can increase the height of corn compared to the normal soil. It can clearly see in the different corn height between using biochar and normal soil at 6th week after planting, and the highest of corn is at soil + biochar + bottom ash (70:5:25 + F).

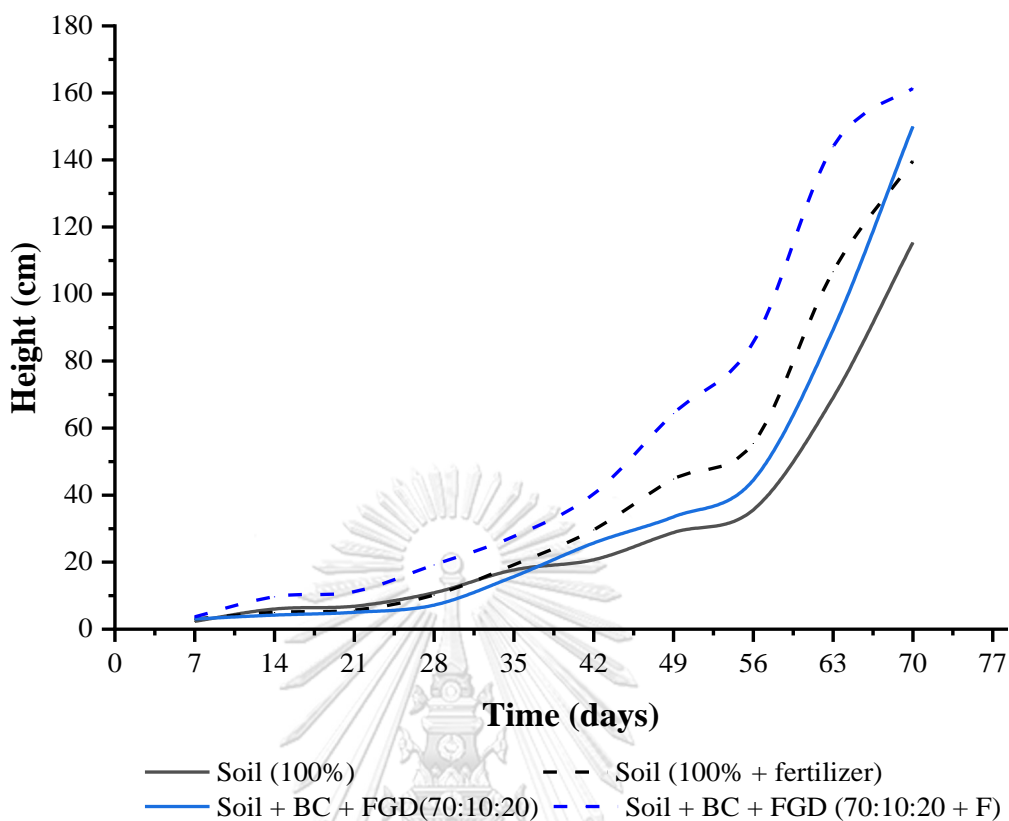


Figure 4.29 The height growth of corn when applying biochar coupled with bottom ash compared with normal soil for corn growing in the containers

As in figure 4.29, it is shown that biochar coupled with FGD can increase the height of corn compared to normal soil. The treatment of soil + biochar + FGD (70:10:20 + F) is the best for corn height.

4.2.2 Effect of biochar coupled with CCPs on chlorophyll in corn leaf

Leaf chlorophyll is quantified by the SPAD 502 chlorophyll meter for corn growing in the real field and in the containers as in figure 4.30 - 4.35, respectively. It is found that the chlorophyll value in the treatment with fertilizer is higher than the treatment without fertilizer.

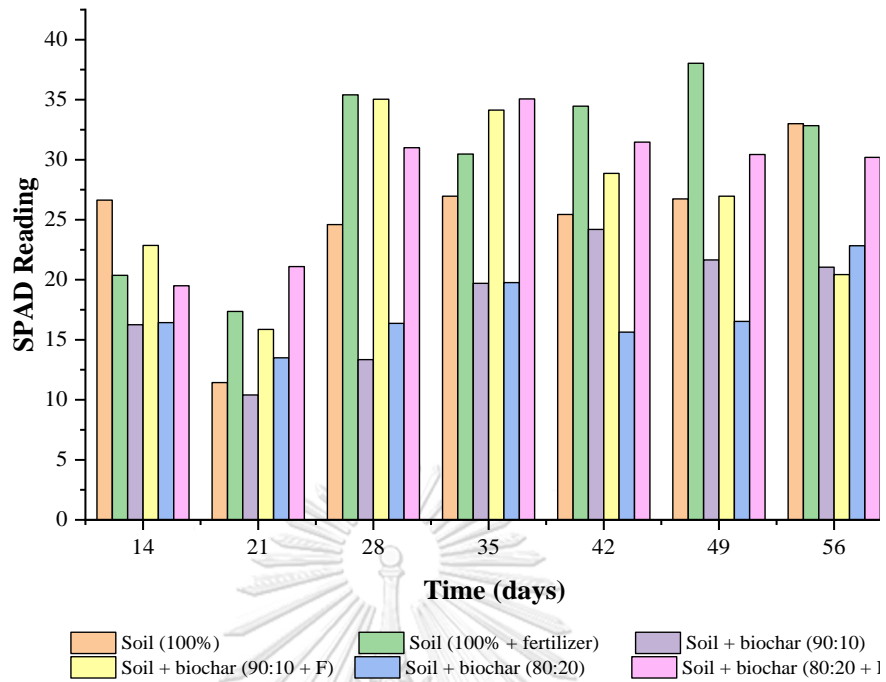


Figure 4.30 Chlorophyll contents of corn leaf when applying biochar for corn growing in the real field

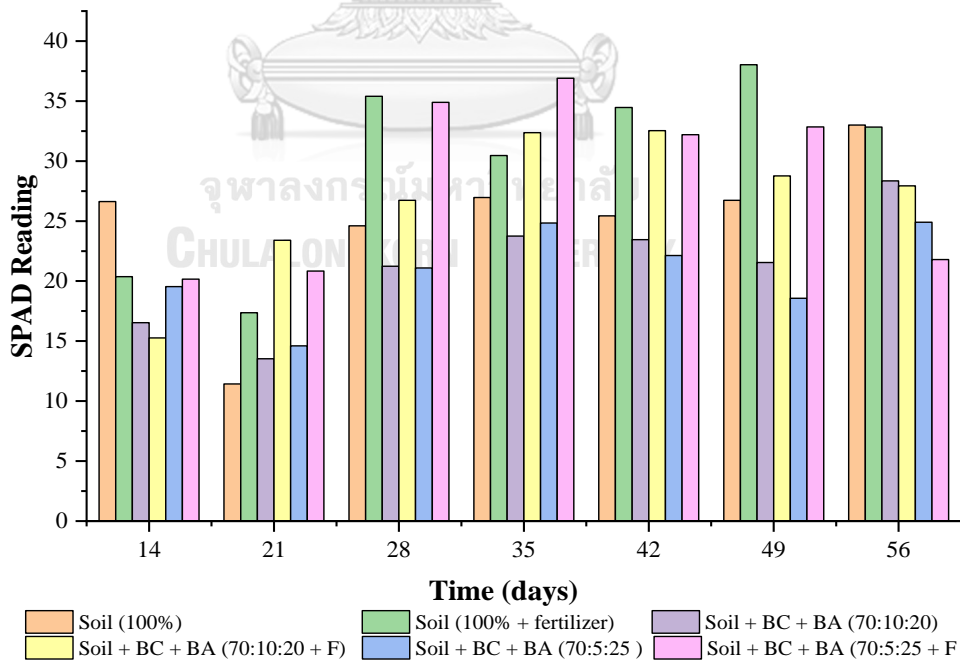


Figure 4.31 Chlorophyll contents of corn leaf when applying biochar coupled with bottom ash for corn growing in the real field

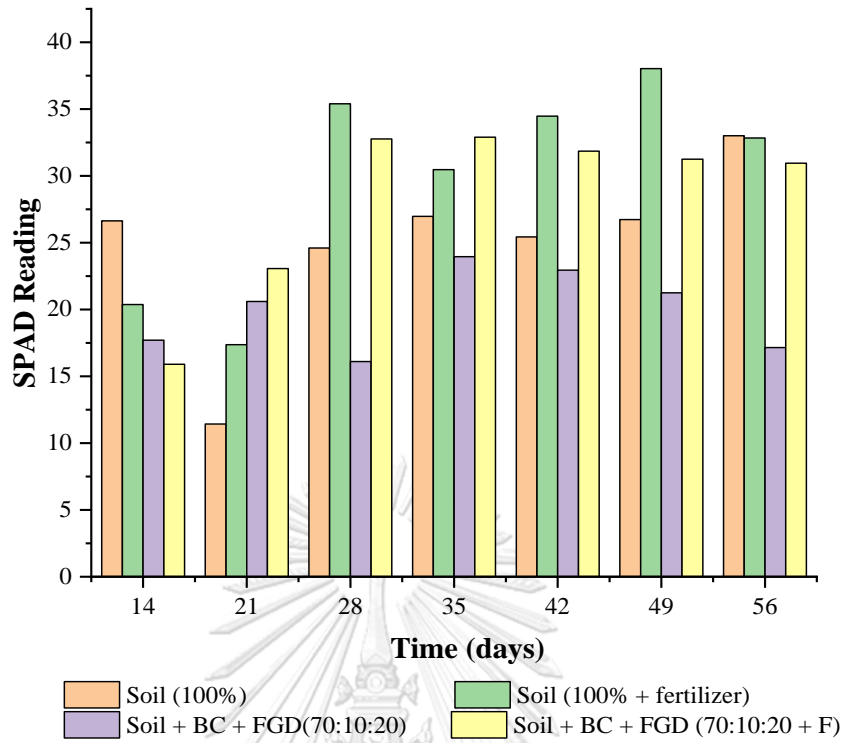


Figure 4.32 Chlorophyll contents of corn leaf when applying biochar coupled with FGD for corn growing in the real field

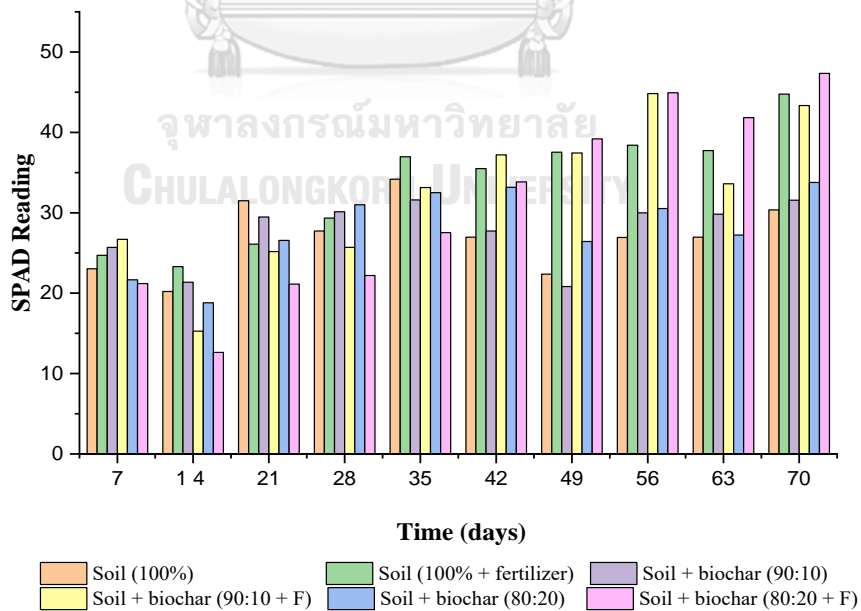


Figure 4.33 Chlorophyll contents of corn leaf when applying biochar for corn growing in the containers

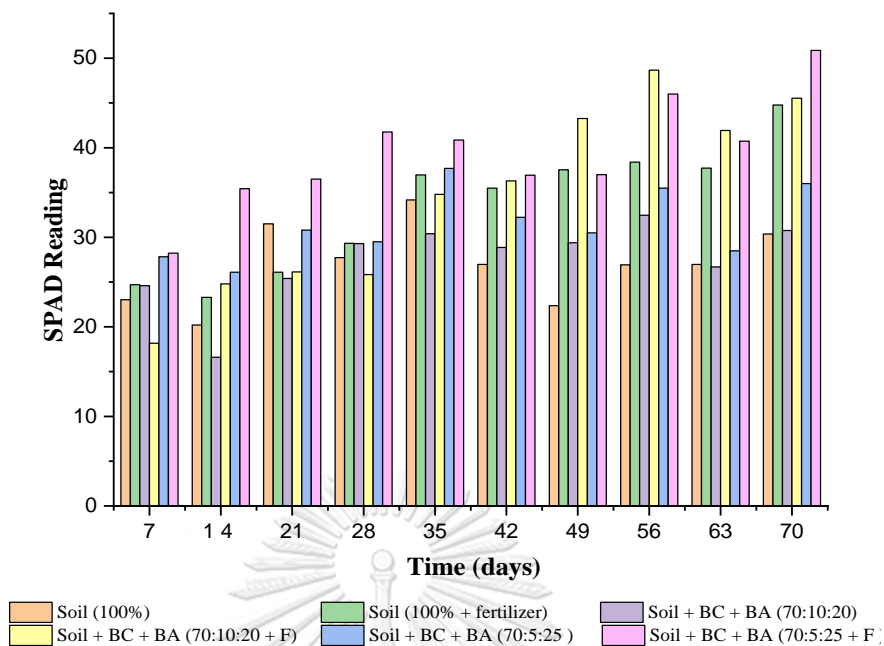


Figure 4.34 Chlorophyll contents of corn leaf when applying biochar coupled with bottom ash for corn growing in the containers

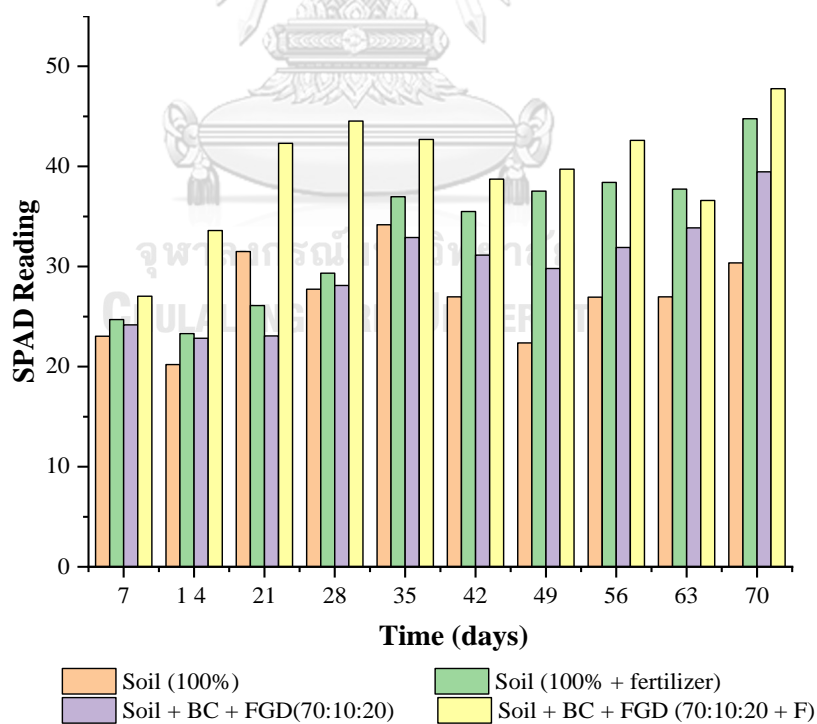


Figure 4.35 Chlorophyll contents of corn leaf when applying biochar coupled with FGD for corn growing in the containers

4.2.3 Effect of biochar coupled with CPPs on relative humidity (RH), conductivity (EC_p) and temperature in soil

The soil moisture content of soil is the quantity of water containing in the soil. The relative humidities (RH) of soil when applying biochar couple with CCPs for corn growing for corn growing in the real field and in the containers are shown in figure 4.36 - 4.41, respectively. From the results of two cases for corn growing, it is found that the treatments increase the relative humidity when applying biochar and biochar coupled with CCPs and fertilizer. From he studied period, shoot length increases considerably by raising the RH and the number of leaves are increased by RH (Mortensen, 1986).

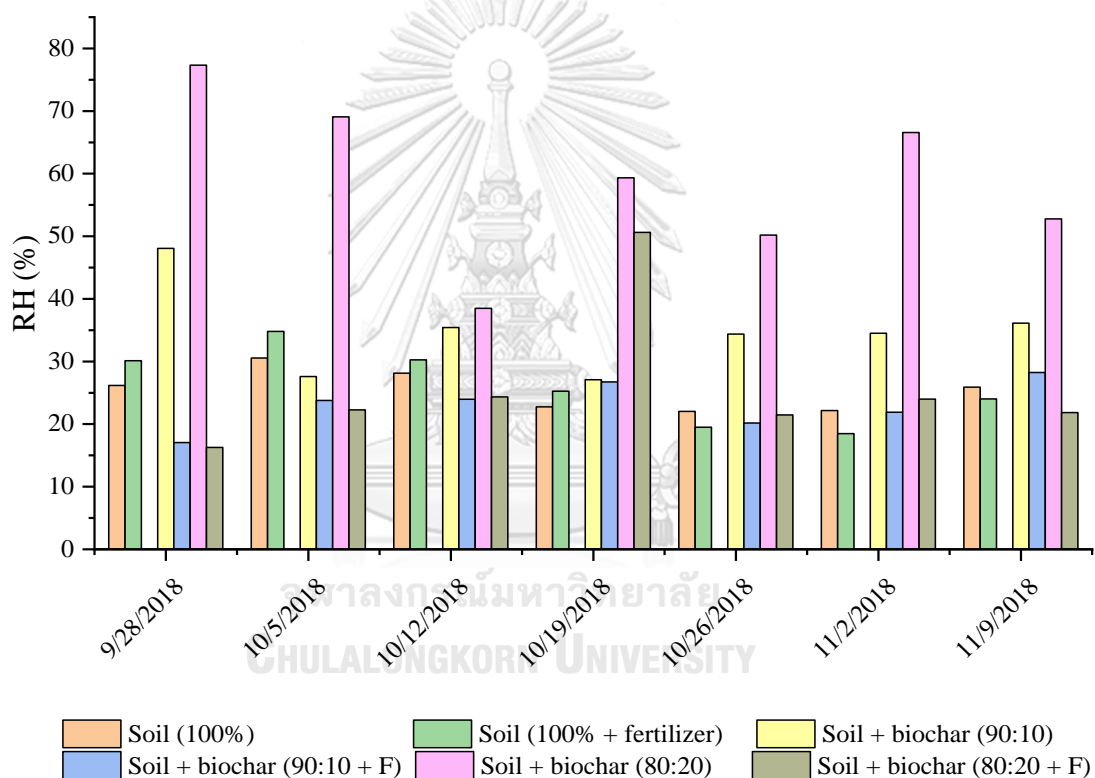


Figure 4.36 The relative humidity (RH) of soil when applying biochar for corn growing in the real field

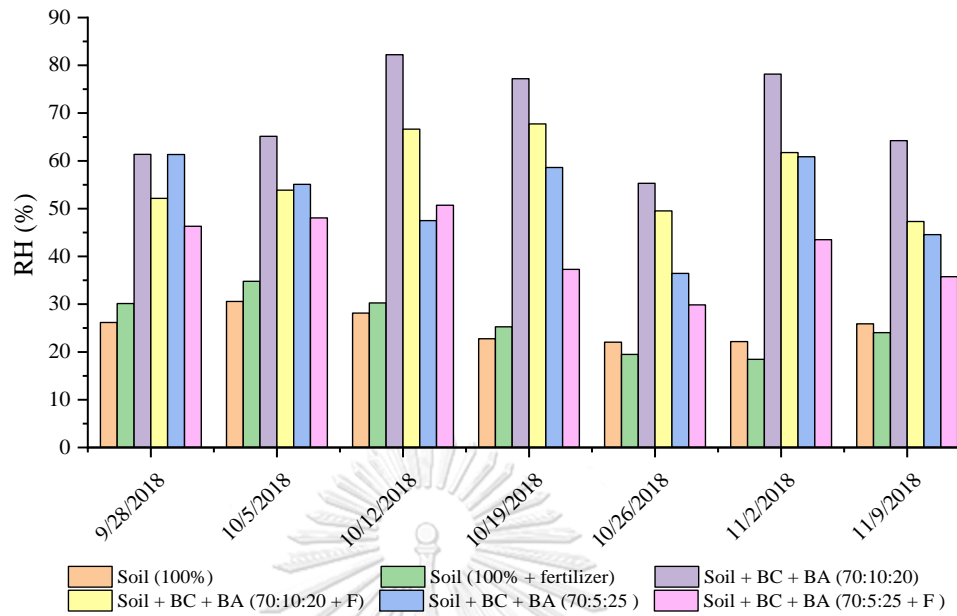


Figure 4.37 The relative humidity (RH) contents of soil when applying biochar couple with bottom ash for corn growing in the real field

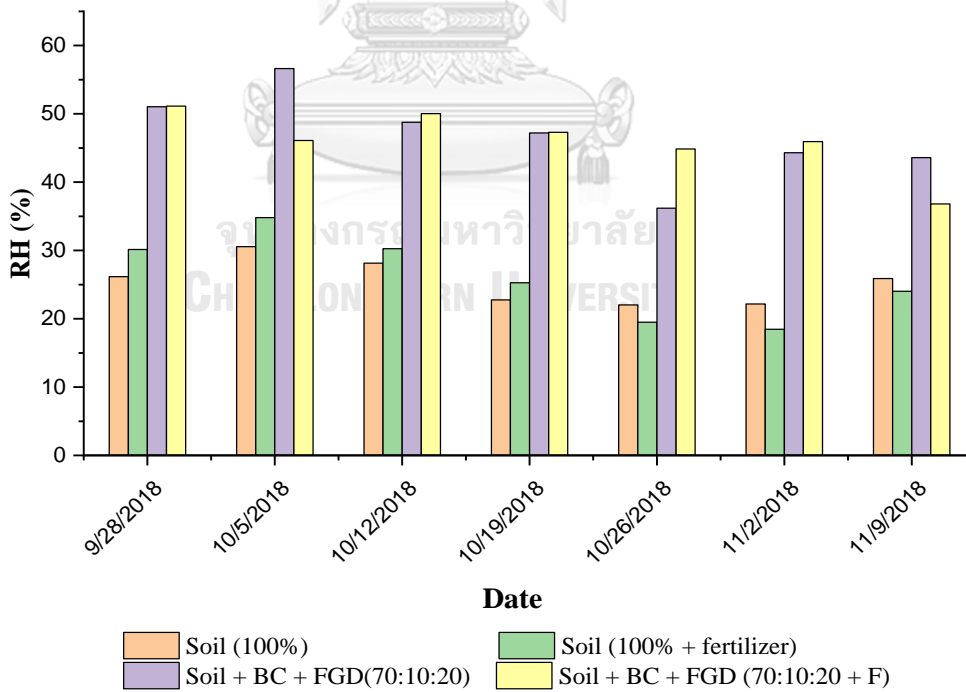


Figure 4.38 The relative humidity (RH) contents of soil when applying biochar couple with FGD for corn growing for corn growing in the real field

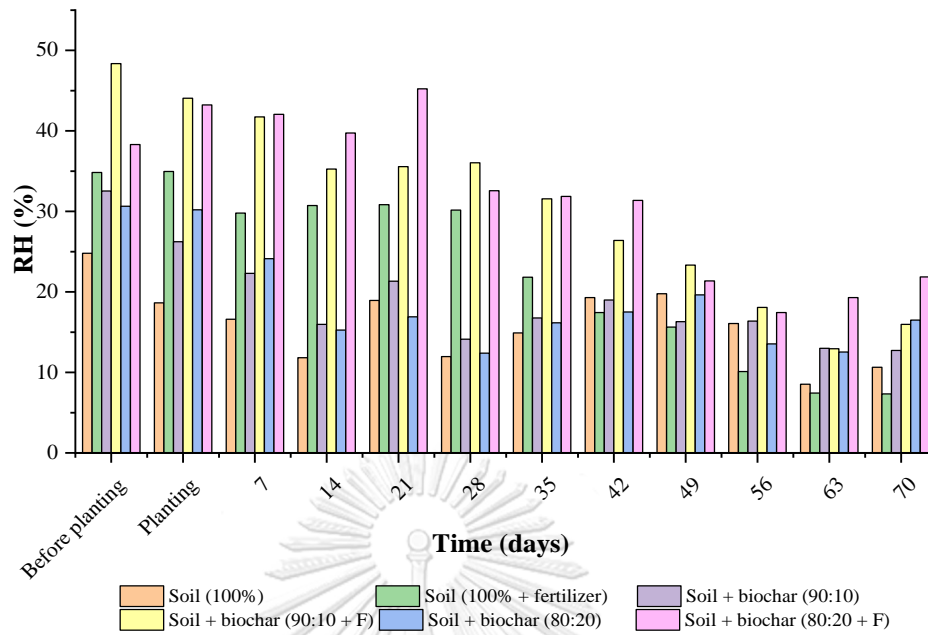


Figure 4.39 The relative humidity (RH) contents of soil when applying biochar for corn growing in the containers

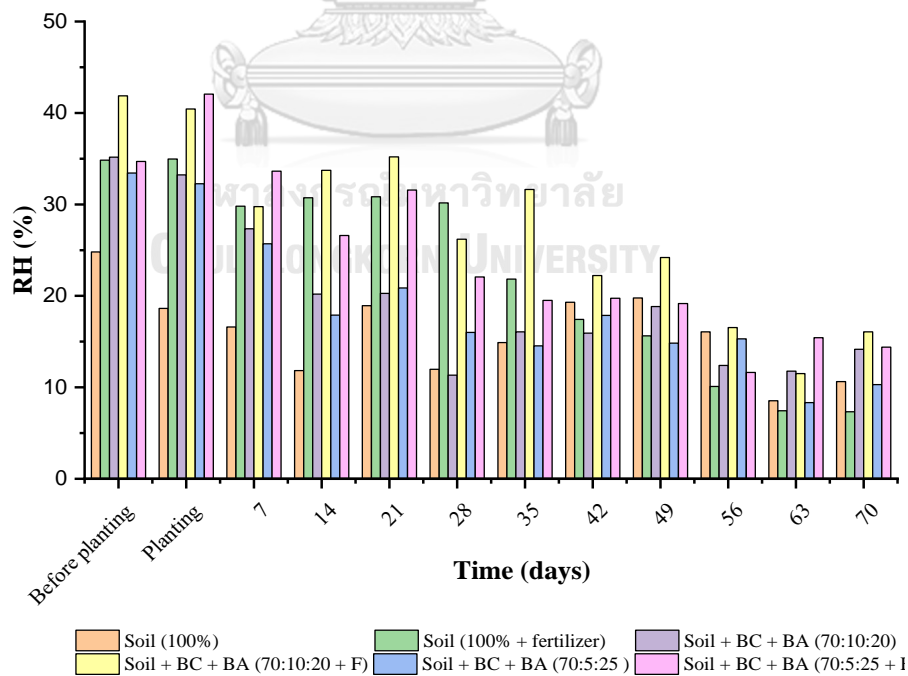


Figure 4.40 The relative humidity (RH) contents of soil when applying biochar coupled with bottom ash for corn growing in the containers

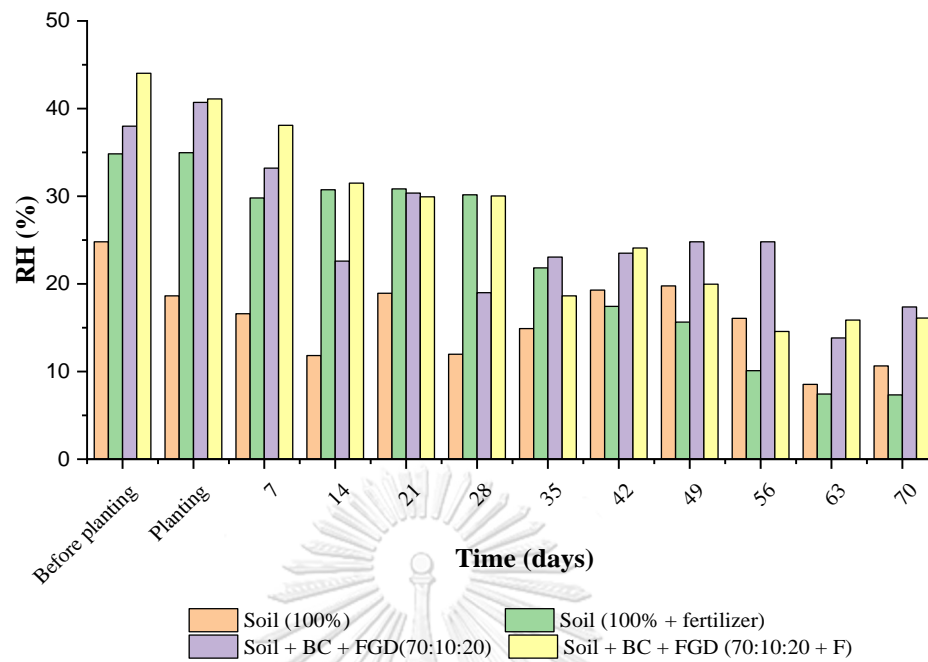


Figure 4.41 The relative humidity (RH) contents of soil when applying biochar coupled FGD corn growing in the containers

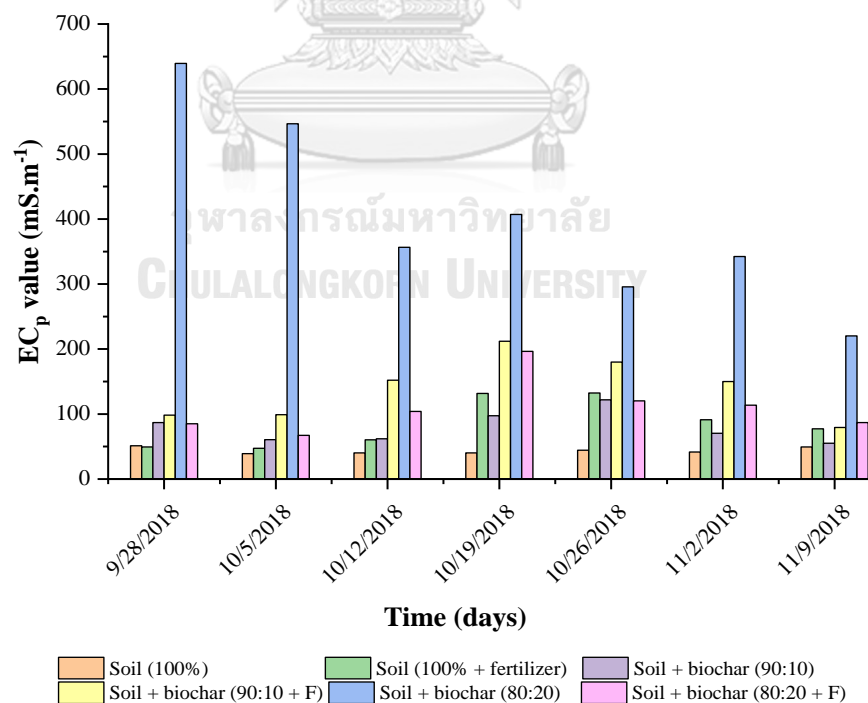


Figure 4.42 The EC_p value of soil when applying biochar for corn growing in the real field

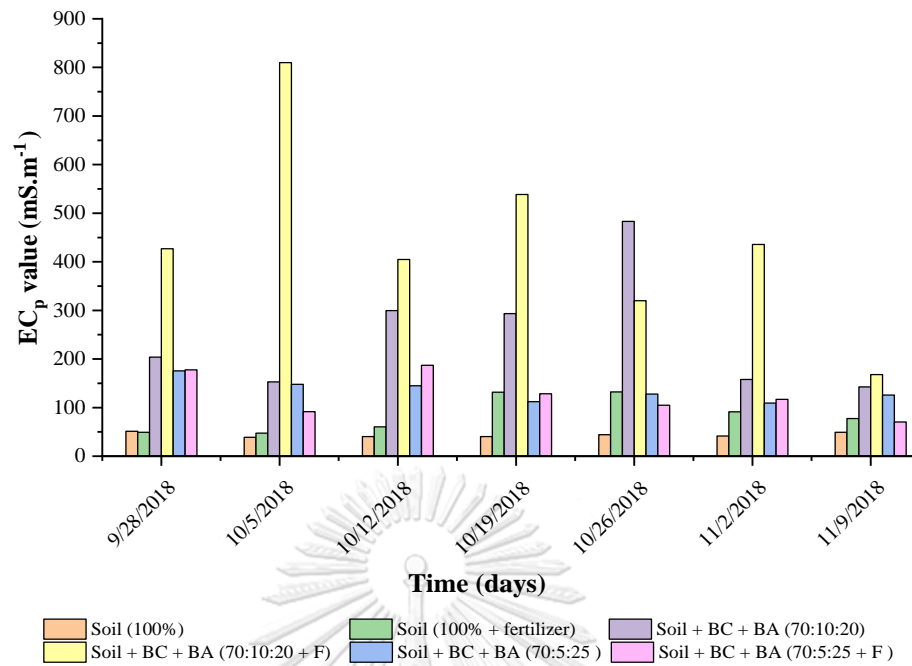


Figure 4.43 The EC_p value of soil when applying biochar coupled with bottom ash for corn growing in the real field

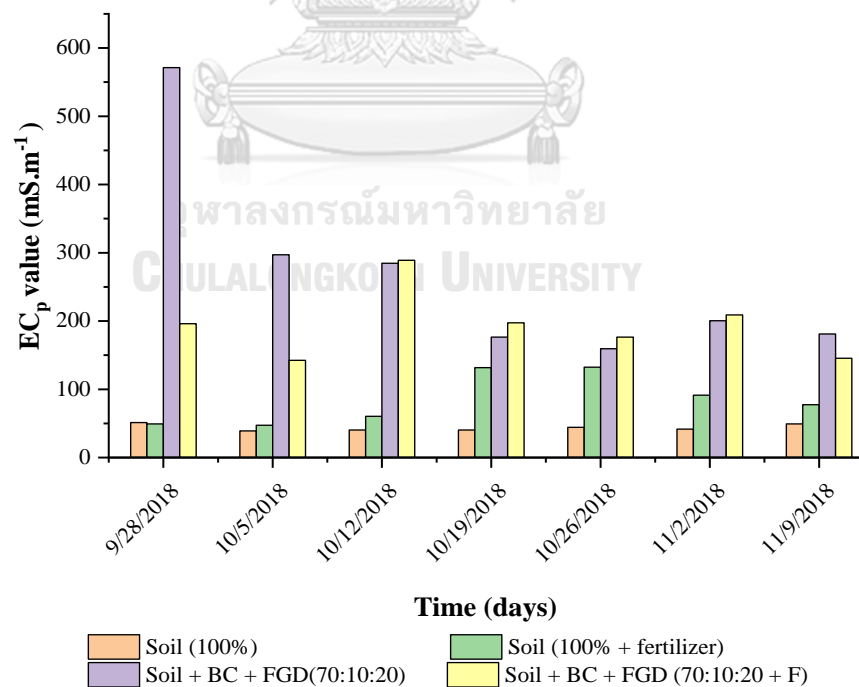


Figure 4.44 The EC_p value of soil when applying biochar coupled with FGD for corn growing in the real field

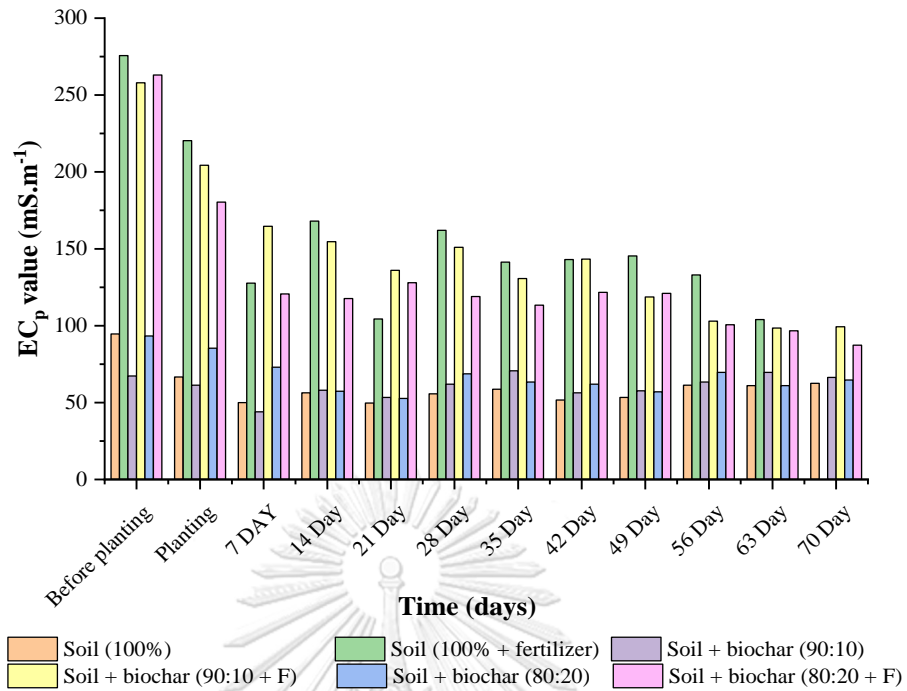


Figure 4.45 The EC_p value of soil when applying biochar for corn growing in the containers

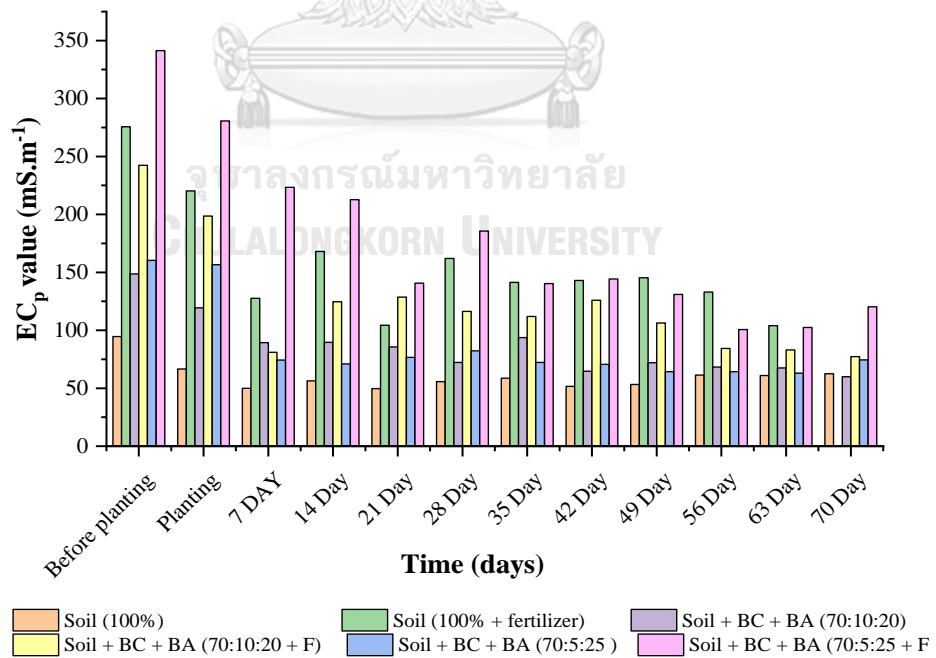


Figure 4.46 The EC_p value of soil when applying biochar coupled with bottom ash for corn growing in the containers

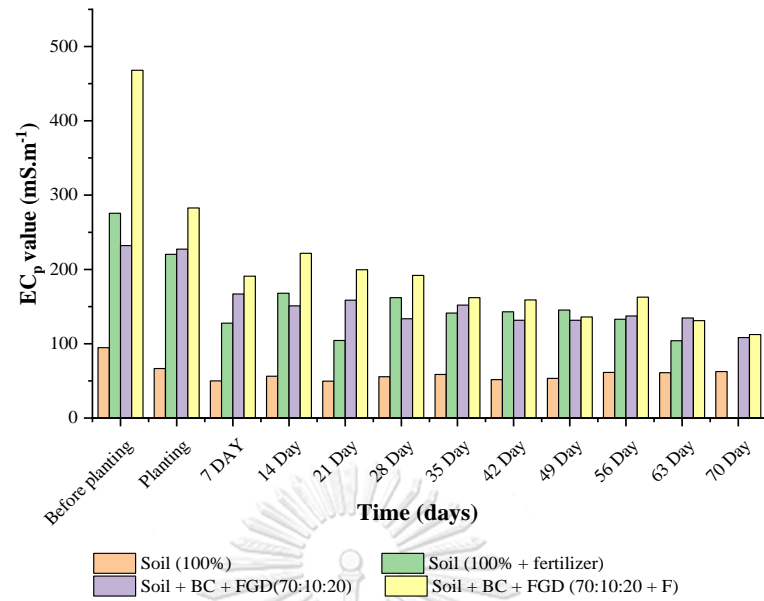


Figure 4.47 The EC_p value of soil when applying biochar coupled with FGD for corn growing in the containers

The WET Sensor is able to calculate pore water conductivity (EC_p) which is the EC of the water available to plant roots. The result of EC_p value is shown in figure 4.42 - 4.47.

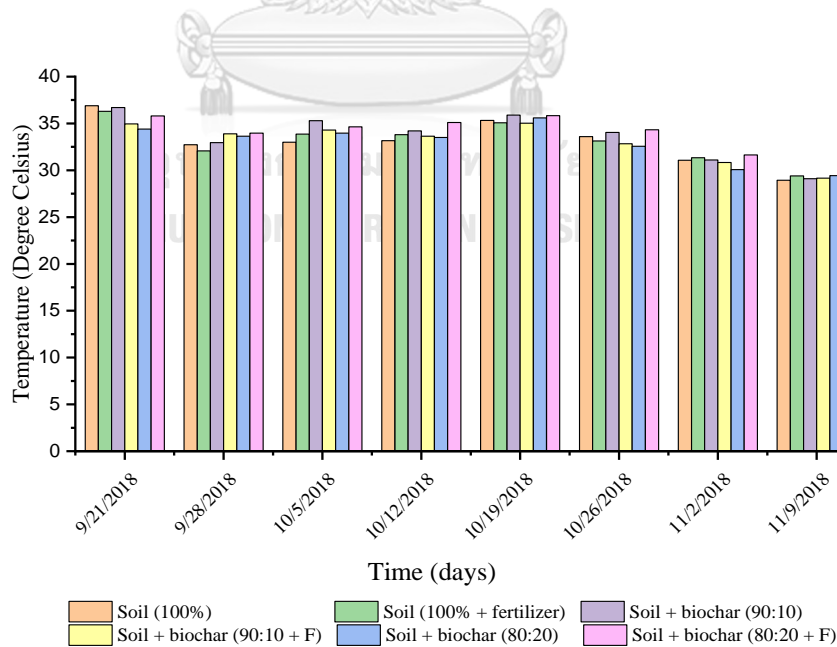


Figure 4.48 The temperature of soil when applying biochar for corn growing in the real field

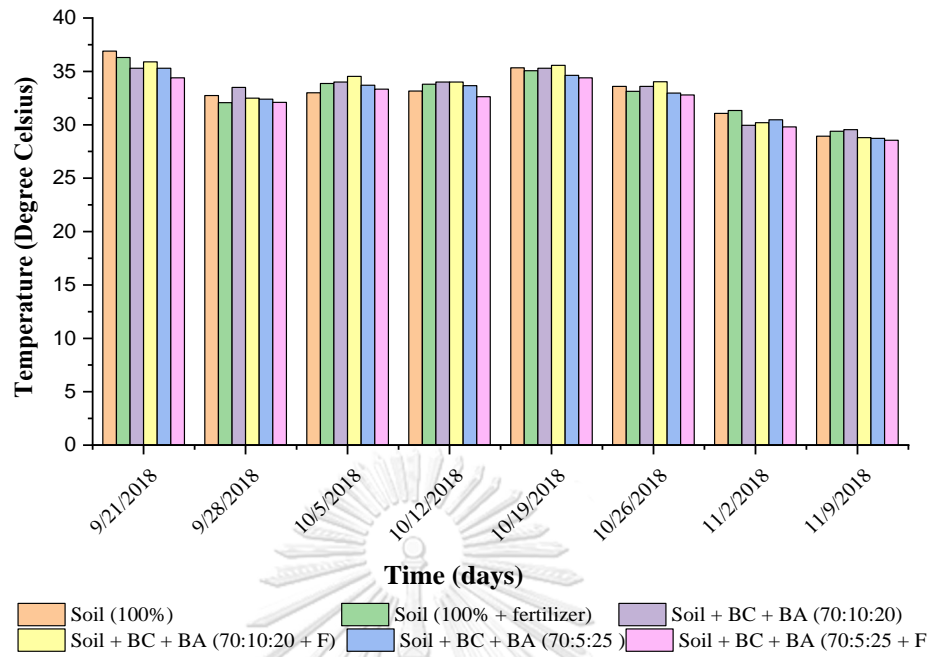


Figure 4.49 The temperature of soil when applying biochar coupled with bottom ash for corn growing in the real field

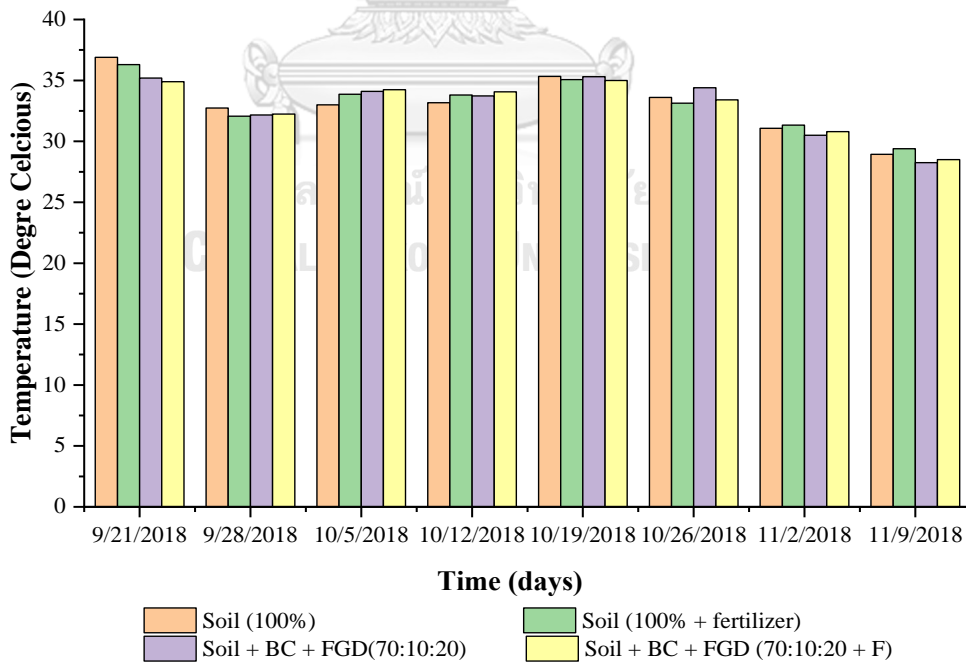


Figure 4.50 The temperature of soil when applying biochar coupled with FGD for corn growing in the real field

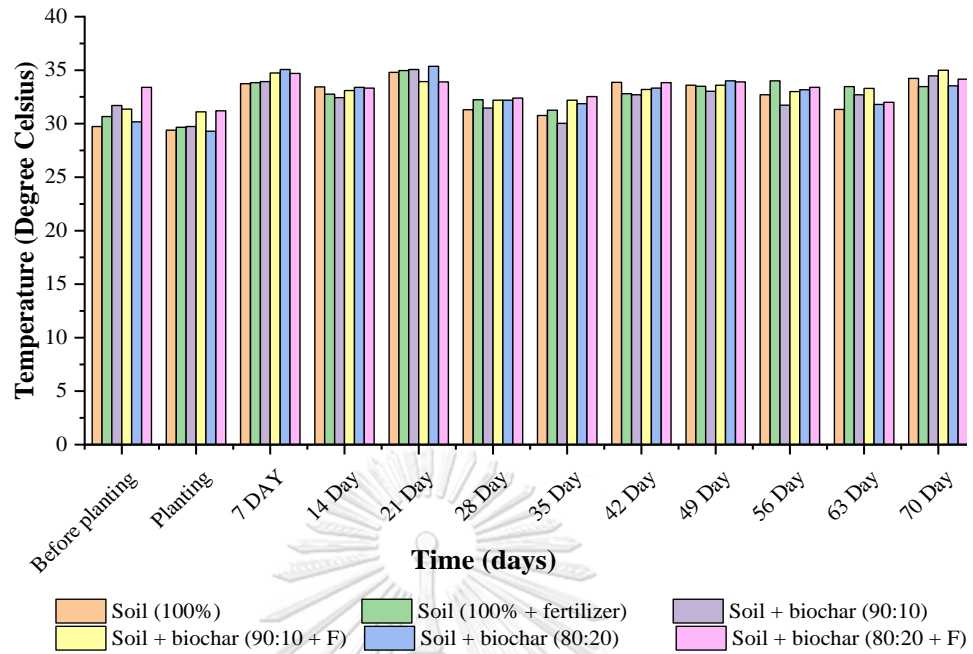


Figure 4.51 The temperature of soil when applying biochar for corn growing in the containers

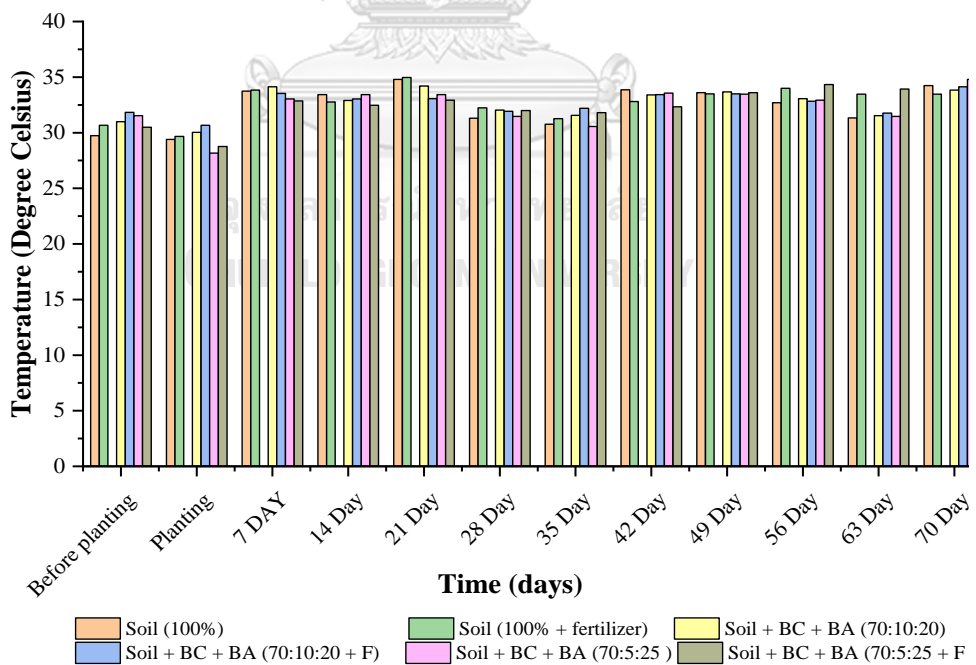


Figure 4.52 The temperature of soil when applying biochar coupled with bottom ash for corn growing in the containers

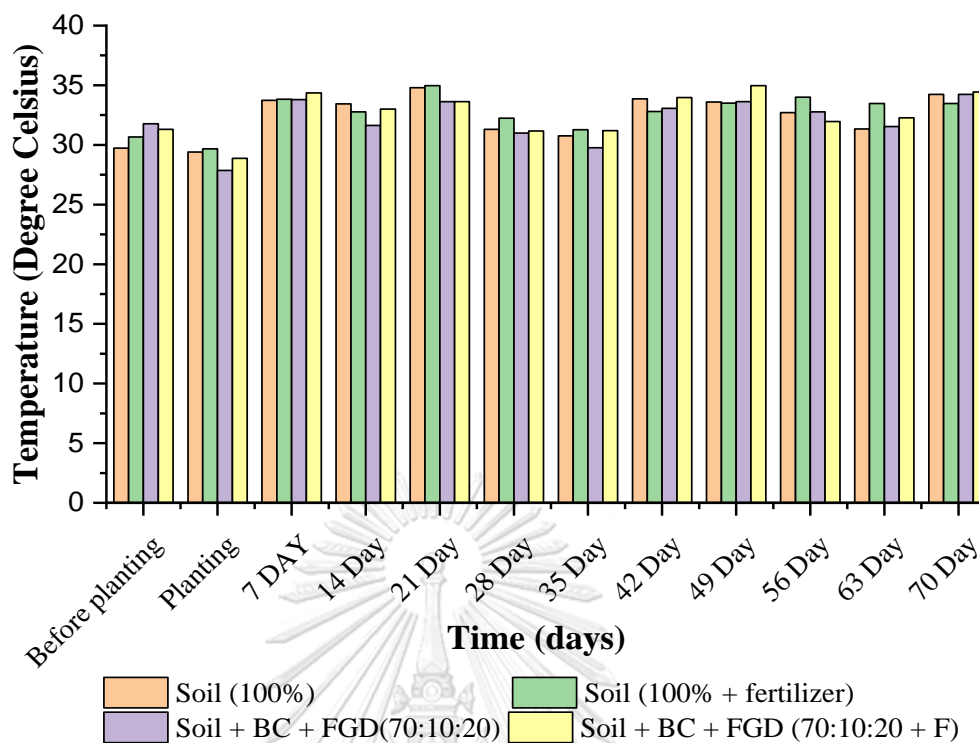


Figure 4.53 The temperature of soil when applying biochar coupled with FGD for corn growing in the containers

Soil temperature affects plant growth indirectly by affecting water and nutrient uptake as well as root growth. At a constant moisture content, a decrease in temperature results in a decrease in water and nutrient uptake. At low temperatures, the transportation from the root to the shoot and vice versa is reduced. The results of soil temperature for corn growing in both cases are presented in figure 4.48 - 4.53. Effect of biochar coupled with CCPs on corn yield.

4.2.4 Effect of biochar coupled with CPPs on corn products qualities

The results of corn products are shown in According to Thai Agriculture Standard (TAS 1512-2011), based on the qualities of sweet corn, it can be classified into three groups Extra class, Class I and Class II, and based on size, it is also classified into three groups large, medium and small (National Bureau of Agricultural Commodity and Food Standards Ministry of Agriculture and Cooperatives, 2012). The qualities of corn products for corn growing in the containers are shown in table 4.5, and Table 4.6 presents the classification of corn products follow Thai Agriculture Standard (TAS 1512-2011). The results show that the products with Soil + biochar (90:10 + F), Soil +

biochar + bottom ash (70:10:20 + F), Soil + biochar + FGD (70:10:20) and Soil + biochar + FGD (70:10:20 + F) are classified in Extra class, but at normal soil and Soil + biochar + bottom ash (70:10:20) are classified in Class II as shown in table 4.6. From the results, the weight and length of corn are not significantly affected by biochar and CCPs, but weight and length of corns which added biochar and CCPs increased when compare with the treatment of normal. Although the arrangement of kernels of corn which added biochar and CCPs coupled with fertilizer is better than the treatments that not use fertilizer. The treatments used biochar and CPPs without fertilizer, they are better than the treatment of normal soil as shown in figure 4.54 - 4.56.

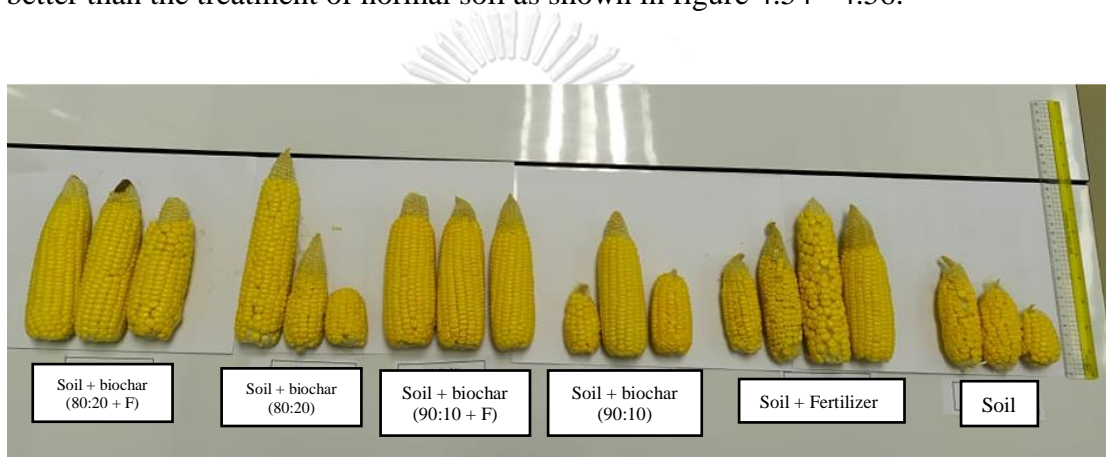


Figure 4.54 The effect of biochar on corn yield

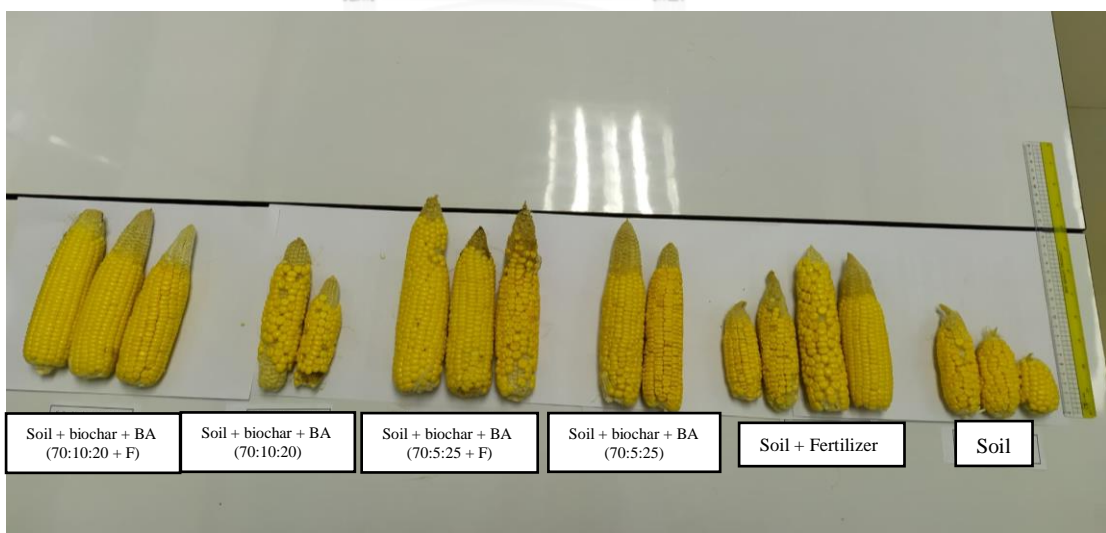


Figure 4.55 The effect of biochar coupled with bottom ash on corn yield

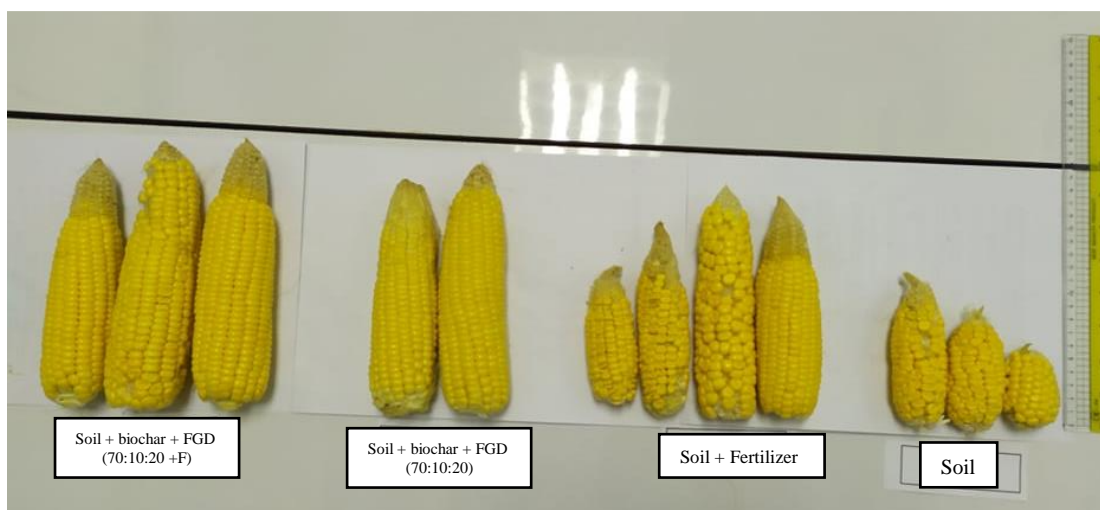


Figure 4.56 The effect of biochar coupled with FGD on corn yield

According to Thai Agriculture Standard (TAS 1512-2011), based on the qualities of sweet corn, it can be classified into three groups Extra class, Class I and Class II, and based on size, it is also classified into three groups large, medium and small. The qualities of corn products for corn growing in the containers are shown in table 4.5, and table 4.6 presents the classification of corn products follow Thai Agriculture Standard (TAS 1512-2011). The results show that the products with Soil + biochar (90:10 + F), Soil + biochar + bottom ash (70:10:20 + F), Soil + biochar + FGD (70:10:20) and Soil + biochar + FGD (70:10:20 + F) are classified in Extra class, but at normal soil and Soil + biochar + bottom ash (70:10:20) are classified in Class II as shown in table 4.6.

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Table 4.5 The qualities of corn products

Treatments	Total weight (g)	Corn shell weight (g)	Corn ear weight (g)	Ear length	Ear diameter	Root length	No.row	No.seed vertical	oBrix	
Normal soil	100	61.77	8.90	52.23	84.28	38.10	26.33	10.00	13.33	12.27
Normal soil	(100 + F)	208.10	9.03	99.10	108.40	38.93	67.67	13.33	19.00	16.40
Soil + biochar	(90:10)	126.43	25.27	99.00	100.93	42.88	55.50	13.33	17.33	15.40
Soil + biochar	(90:10 + F)	238.20	38.73	196.10	174.33	50.29	47.67	14.67	29.67	16.01
Soil + biochar	(80:20)	147.80	33.43	111.03	129.68	43.83	63.33	14.33	18.00	14.77
Soil + biochar	(80:20 + F)	259.50	74.80	176.33	166.67	49.05	44.50	14.00	24.67	15.49
Soil + biochar + bottom ash	(70:5:25)	158.93	37.63	118.57	164.38	37.97	63.00	10.00	20.00	16.05
Soil + biochar + bottom ash	(70:5:25 + F)	305.90	62.33	235.97	206.67	51.84	52.00	14.67	31.00	16.14
Soil + biochar + bottom ash	(70:10:20)	122.40	27.70	96.60	139.27	39.67	68.00	13.50	15.50	14.34
Soil + biochar + bottom ash	(70:10:20 + F)	260.97	59.47	195.70	192.33	48.22	52.00	15.33	27.67	17.34
Soil + biochar + FGD	(70:10:20)	224.17	65.23	152.57	157.20	41.04	65.67	14.00	31.50	15.47
Soil + biochar + FGD	(70:10:20 + F)	305.97	64.80	233.30	206.67	51.01	83.00	16.33	26.33	16.53

Table 4.6 The classification of corn

Treatments		Qualities Classification	Size classification	
			Length	Diameter
Normal soil	100	Class II	Small	Medium
Normal soil	(100 + F)	Class I	Small	Medium
Soil + biochar	(90:10)	Class I	Small	Large
Soil + biochar	(90:10 + F)	Extra Class	Medium	Large
Soil + biochar	(80:20)	Class I	Small	Large
Soil + biochar	(80:20 + F)	Class I	Medium	Large
Soil + biochar + bottom ash	(70:5:25)	Class I	Medium	Medium
Soil + biochar + bottom ash	(70:5:25 + F)	Class I	Large	Large
Soil + biochar + bottom ash	(70:10:20)	Class II	Small	Medium
Soil + biochar + bottom ash	(70:10:20 + F)	Extra Class	Medium	Large
Soil + biochar + FGD	(70:10:20)	Extra Class	Medium	Large
Soil + biochar + FGD	(70:10:20 + F)	Extra Class	Large	Large

4.2.5 Effect of biochar coupled with CPPs on corn root

Figure 4.60 depicts an increase in root length of corn when applied biochar and biochar coupled with CCPs. From all treatments, there is no significant difference in root lengths when increase biochar, bottom ash and FGD. The root length of biochar coupled with CCPs treatments are shorter than biochar coupled with CCPs with fertilizer as shown in figure 4.57 - 4.59.

As shown in figure 4.57, it is the root of corn when added biochar and biochar with fertilizer. The fibrous root of corn can be shown that treatment with fertilizer is higher than treatment without fertilizer. Also, figure 4.58 and 4.59 show the root of corn when added biochar coupled with bottom ash and FGD gypsum, respectively. They are also found that the fibrous root in treatment with fertilizer is longer than treatment without fertilizer, but the fibrous root in the treatment of biochar coupled with CPPs without fertilizer is longer than the treatment of normal soil.



Figure 4.57 Effect of biochar on corn root



Figure 4.58 Effect of biochar coupled with bottom ash on corn root



Figure 4.59 Effect of biochar coupled with FGD on corn root

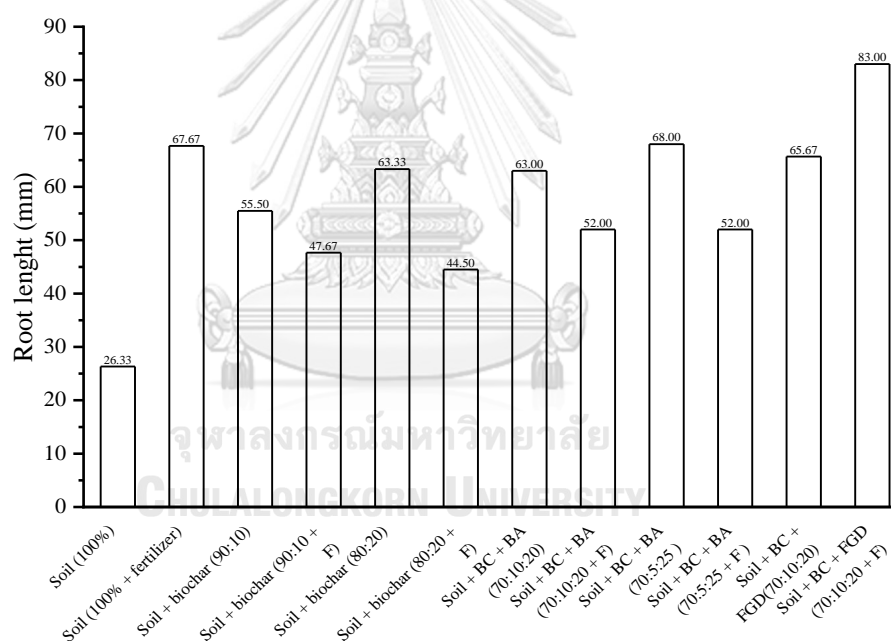


Figure 4.60 Effect of biochar coupled with CPPs on roots length of corn

4.3 Effect of biochar coupled with CCPs on heavy metals uptake by corn

The major heavy metals (Cd, Hg, As, Pb and Cr) in the primary concern with regard to CCPs use in agricultural fields. They are divided and evaluated, and the results are presented in table 4.7. The concentrations of all metals in soil, bottom ash, FGD, biochar and fertilizer are below the minimum permissible limit of heavy metal for soil FAO/WHO, but the concentration of arsenic (As) in soil (6.72 mg/kg) and bottom ash

(33.2 mg/kg) is higher than the minimum permissible limit of Thai Standard (3.9 mg/kg). On the other hand, cadmium (Cd) is not detected in all of the initial samples.

Table 4.7 The concentration of heavy metals in the samples

Parameters	Unit	Results					
		Soil	FGD	Biochar	Bottom ash	Cow manure	Sheep manure
Mercury (Hg)	mm/kg	0.16	0.23	0.09	0.04	0.15	0.14
Lead (Pb)	mm/kg	9.7	0.3	17.1	6.0	1	<0.25
Arsenic (As)	mm/kg	6.72	1.72	1.54	33.2	0.84	0.25
Cadmium (Cd)	mm/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Chromium (Cr)	mm/kg	25.4	20.1	0.7	61.7	4.1	0.8

From the harvested corn in both cases soil (after corn growing), seed of corn, leaf + stem + root of corn (combined leaf, stem, and root), and core + shell of corn (combined core and shell of corn) are studied. Table 4.8 shows the results of heavy metals in soil and corn seed for corn growing in the real field. It is found that the concentrations of heavy metals in soil with the treatments of S100: F and S90: BC10: F are less than the minimum permissible limit of heavy metal for soil (FAO/WHO). It is found that the concentration of arsenic (As) in soil (S100: F and S90: BC: F) is higher than the minimum permissible limit of Thailand Standard (3.9 mg/kg). The concentration of heavy metals in seed of corn for corn growing in the real field as shown in table 4.8. It is found that Hg, Cd, Pb and Cr are not detectable (lower than 0.25 mg/kg), but arsenic (As) in treatment of soil with fertilizer (0.56 mg/kg) is higher than the minimum permissible limit FAO/WHO standard for concentration of heavy metal in plant (0.43 mg/kg). On the other hand, arsenic (As) in 10% biochar and fertilizer is lower than the minimum permissible limit F/WHO standard for concentration of heavy metal in plant (0.43 mg/kg). In the combined root, stem and leaf, mercury (Hg) and cadmium (Cd) cannot detectable in treatment of soil with fertilizer and 10% of biochar with fertilizer, but lead (Pb), arsenic (As) and chromium (Cr) are higher than the minimum permissible limit FAO/WHO standard for concentration of heavy metal in plant as shown in table 4.9.

Table 4.8 The concentration of heavy metals in soil and corn seed for corn growing in the real field

Parameters	Unit	Soil		Seed of corn	
		S100: F	S90:BC10: F	S100: F	S90:BC10: F
Mercury (Hg)	mg/kg	<0.25	<0.25	<0.25	<0.25
Lead (Pb)	mg/kg	9.91	8.97	<0.25	<0.25
Arsenic (As)	mg/kg	9.29	7.08	0.56	0.38
Cadmium (Cd)	mg/kg	<0.25	<0.25	<0.25	<0.25
Chromium (Cr)	mg/kg	32.0	26.3	<0.25	<0.25

Table 4.9 The concentration of heavy metals in root + stem + leaf and Shell + Core of corn for corn growing in the real field

Parameters	Unit	Root + stem +leaf of corn		Shell + Core of corn	
		S100: F	S90:BC10: F	S100: F	S90:BC10: F
Mercury (Hg)	mg/kg	<0.25	<0.25	2.02	<0.25
Lead (Pb)	mg/kg	0.37	1.22	1.02	0.26
Arsenic (As)	mg/kg	4.21	1.66	0.57	0.60
Cadmium (Cd)	mg/kg	<0.25	<0.25	0.21	<0.25
Chromium (Cr)	mg/kg	43	26.2	14.2	21.7

Table 4.10 The concentration of heavy metals in soil after corn growing in the containers

Parameters	Unit	Soil					
		S100	S100: F	S90:BC10: F	S70:BA25:BC5: F	S70:BA20:BC10: F	S70:FGD20:BC10: F
Mercury (Hg)	mg/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Lead (Pb)	mm/kg	9.386	3.581	5.358	2.433	2.316	2.379
Arsenic (As)	mm/kg	6.830	4.286	4.206	11.51	8.769	4.453
Cadmium (Cd)	mm/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Chromium (Cr)	mm/kg	23.58	43.78	43.55	31.40	54.90	40.990

After harvested the corn for corn growing in the containers, the treatments S100, S100: F, S90: BC10: F, S70: BA25: BC5: F , S70: BA20: BC10: F and S70: FGD20: BC10: F are collected to analyze the heavy metal. The results of heavy metals of corn

Table 4.12 The concentration of heavy metals in shell and core of corn for corn growing in the containers

Parameters	Unit	Shell + core					
		S100	S100: F	S90:BC10: F	S70:BA25: BC5: F	S70:BA20: BC10: F	S70:FGD20 : BC10: F
Mercury (Hg)	mg/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Lead (Pb)	mg/kg	<0.25	0.482	<0.25	<0.25	0.582	<0.25
Arsenic (As)	mg/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Cadmium (Cd)	mg/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Chromium (Cr)	mg/kg	4.604	20.82	10.55	7.180	15.54	5.395

Table 4.13 The concentration of heavy metals in Root + stem + leaf of corn a for corn growing in the containers

Parameters	Unit	Root + stem + leaf					
		S100	S100: F	S90:BC10: F	S70:BA25: BC5: F	S70:BA20: BC10: F	S70:FGD20 : BC10: F
Mercury (Hg)	mg/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Lead (Pb)	mg/kg	0.584	0.876	2.041	0.566	0.453	0.499
Arsenic (As)	mg/kg	0.669	2.343	2.737	1.952	1.019	1.420
Cadmium (Cd)	mg/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Chromium (Cr)	mg/kg	19.72	52.3	47.30	38.50	31.45	34.17

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Coal combustion products (CCPs) is generated by coal combustion process from coal fired power plant, they have been increased over the years. Bottom ash (BA) has been applied in many applications such as landfill and concrete. Mostly, FGD gypsum is applied in cement and wallboard industry. Also, BA and FGD can be used in agricultural activities for soil amendment but the amount of them used in this function is still low. Furthermore, biochar has long been used to improve soil fertility. The positive impacts of biochar amendment on soils are that it can increase soil capacity to adsorb plant nutrients, decrease soil bulk density, increase plant available water retention and so on. In Thailand, some areas like Nan province has a problem of soil degradation from deforestation and excess use of chemical fertilizer. This research is aimed to apply BA and FGD coupled with biochar to improve soil quality from degraded soil in Nan Province. From the results of the study, it can be concluded:

1. Soil in Nan province is acid with pH at 5.84. Biochar and BA are alkalinity with pH at 10.17 and 9.74, respectively, and FGD gypsum is weak alkalinity with pH at 7.87. The application of biochar at 5% to 20% is considered the best ratio for improvement of soil pH, and it can increase pH of soil from 5.84 to 7.04, but at the ratio 30% biochar, pH of soil becomes weak alkalinity. The application of biochar coupled with FGD gypsum, at the ratio soil + biochar + FGD (80:5:15), soil + biochar + FGD (70:10:20) and soil + biochar + FGD (70:5:25) are the good conditions for soil pH improvement. For the application of biochar coupled with bottom ash before corn growing, pH of soil can increase all ratios.
2. The application of biochar coupled with coal combustion products increase EC_{SE} value of soil at all of combination ratios. However, when biochar, BA and FGD gypsum are added into soil, EC_{SE} is still suitable for plant growth.
3. From the texture of soil, the biochar mixed with soil before corn growing ranging at 5-20% can change the texture of normal soil from clay to clay

loam, and at 30% of biochar changes the texture of soil to loam. In addition, the biochar coupled with bottom ash before corn growing changes the texture of soil from clay to clay loam and loam. The application biochar coupled with FGD before corn growing changes the texture of normal soil from clay to silty loam.

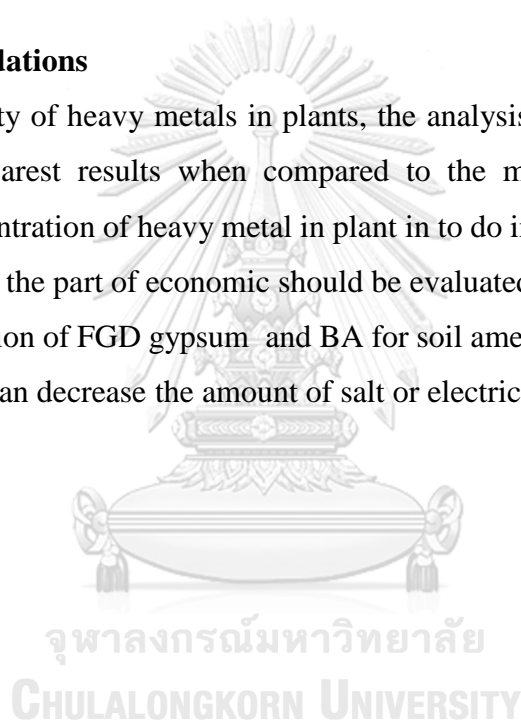
4. Biochar coupled with CCPs can decrease bulk density of soil at all of ratio from 1.27 g/cm^3 to 0.74 g/cm^3 .
5. After corn growing, soil pH and bulk density are increased when compared with the initial samples, but EC_{se} value is decreased when compared with the initial samples. The texture of soil after corn growing is changed from the initial samples, especially, the percent of sand increases with the treatments used fertilizer, but the treatment of biochar coupled with FGD does not change the texture. It is still silty loam.
6. The biochar coupled with CCPs applied for soil amendment can help plant growth compared to the normal soil. It is better if the biochar coupled with CCPs and fertilizer for growing a plant is used.
7. According to Thai Agriculture Standard (TAS 1512-2011), Soil + biochar (90:10 + F), Soil + biochar + BA (70:10:20 + F), Soil + biochar + FGD (70:10:20) and Soil + biochar + FGD (70:10:20 + F) are classified in Extra class but at normal soil are classified in Class II. It can be concluded that biochar coupled with CCPs and fertilizer can increase corn product quality when compared to the treatment of normal soil. Also, the biochar coupled with CCPs can increase root length and fibrous root when compared with normal soil.
8. Finally, the concentrations of all metals in soil, BA, FGD, biochar and fertilizer are below the minimum permissible limit of heavy metal for soil FOA/WHO, but the concentration of arsenic (As) in soil (6.72 mg/kg) and BA (33.2 mg/kg) is above the minimum permissible limit of Thai Standard (3.9 mg/kg). On the other hand, cadmium (Cd) is not detected in all initial samples. After corn growing in both cases, the concentration of heavy metal in all of soil sent to analyze heavy metal is lower than the minimum permissible limit of heavy metal for soil (FAO/WHO), mercury (Hg) and

cadmium (Cd) in soil are not detectable (<0.25 mg/kg). the concentrations of heavy metals in seed of corn, mercury (Hg), lead (Pb), arsenic (As), cadmium (Cd) and chromium (Cr) are not detectable (<0.25 mg/kg). On the other hand, the concentration of heavy metals in combined of root + stem +leaf of corn and shell + Core of corn, lead (Pb), arsenic (As) and chromium (Cr) are higher than the minimum permissible limit FAO/WHO standard for concentration of heavy metal in plant, but mercury (Hg) and cadmium (Cd) cannot detect (<0.25 mg/kg).

5.2 Recommendations

For the clarity of heavy metals in plants, the analysis of heavy metals in plants should be the clearest results when compared to the minimum permissible limit standard for concentration of heavy metal in plant in to do in the future study. The pre-feasibility study in the part of economic should be evaluated.

The application of FGD gypsum and BA for soil amendment is taken at a longer period because it can decrease the amount of salt or electrical conductivity (EC) value.



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APPENDIX

A.1 Hydrometer experiment calculations

A.1.1 Calculation of particle diameter in suspension

Diameter of particle in suspension is calculated based on hydrometer reading value during the hydrometer experiment. Eq.A.1 is used to calculate particle diameter.

$$D_m = 10 \sqrt{\frac{18\mu L_m}{\rho_w(G_s-1)t_m}} \quad \text{Eq.A.1}$$

Where:

D_m = particle diameter, two significant digits, mm

μ = viscosity of water at reading temperature (Table A.1)

ρ_w = mass density of water at reading temperature, g/cm² (Table A.2)

G_s = specific gravity of soil, three significant digits (dimensionless)

t_m = elapsed (fall) time, two significant digits, s

L_m = particle fall distance, two significant digits, cm (Table A.3)

m = subscript indicating the reading number during the sedimentation test.

Table A.1 Viscosity of water (μ) versus temperature (TCVN4198, 2014)

Temperature (0°C)	μ	Temperature (°C)	μ
10	0,01308	26	0,00874
11	0,01272	27	0,00854
12	0,01236	28	0,00836
13	0,01208	29	0,00818
14	0,01171	30	0,00801
15	0,01140	31	0,00784
16	0,01111	32	0,00768
17	0,01086	33	0,00752
18	0,01056	34	0,00737
19	0,01050	35	0,00722
20	0,01005	36	0,00718
21	0,00981	37	0,00695
22	0,00958	38	0,00681
23	0,00936	39	0,00668
24	0,00914	40	0,00656
25	0,00894		

Table A.2 Density of water (ρ_w) versus temperature (ASTM-D7928-16, 2016)

T (°C)	ρ_w (g/mL)	T (°C)	ρ_w (g/mL)	T (°C)	ρ_w (g/mL)	T (°C)	ρ_w (g/mL)
15.0	0.9991	16.0	0.99895	17.0	0.99878	18.0	0.9986
15.1	0.99909	16.1	0.99893	17.1	0.99876	18.1	0.99858
15.2	0.99907	16.2	0.99891	17.2	0.99874	18.2	0.99856
15.3	0.99906	16.3	0.9989	17.3	0.99872	18.3	0.99854
15.4	0.99904	16.4	0.99888	17.4	0.99871	18.4	0.99852
15.5	0.99902	16.5	0.99886	17.5	0.99869	18.5	0.9985
15.6	0.99901	16.6	0.99885	17.6	0.99867	18.6	0.99848
15.7	0.99899	16.7	0.99883	17.7	0.99865	18.7	0.99847
15.8	0.99898	16.8	0.99881	17.8	0.99863	18.8	0.99845
15.9	0.99896	16.9	0.99879	17.9	0.99862	18.9	0.99843
19.0	0.99841	20.0	0.99821	21.0	0.99799	22.0	0.99777
19.1	0.99839	20.1	0.99819	21.1	0.99797	22.1	0.99775
19.2	0.99837	20.2	0.99816	21.2	0.99795	22.2	0.99773
19.3	0.99835	20.3	0.99814	21.3	0.99793	22.3	0.9977
19.4	0.99833	20.4	0.99812	21.4	0.99791	22.4	0.99768
19.5	0.99831	20.5	0.9981	21.5	0.99789	22.5	0.99766
19.6	0.99829	20.6	0.99808	21.6	0.99786	22.6	0.99764
19.7	0.99827	20.7	0.99806	21.7	0.99784	22.7	0.99761
19.8	0.99825	20.8	0.99804	21.8	0.99782	22.8	0.99759
19.9	0.99823	20.9	0.99802	21.9	0.9978	22.9	0.99756
23.0	0.99754	24.0	0.9973	25.0	0.99705	26.0	0.99679
23.1	0.99752	24.1	0.99727	25.1	0.99702	26.1	0.99676
23.2	0.99749	24.2	0.99725	25.2	0.997	26.2	0.99673
23.3	0.99747	24.3	0.99723	25.3	0.99697	26.3	0.99671
23.4	0.99745	24.4	0.9972	25.4	0.99694	26.4	0.99668
23.5	0.99742	24.5	0.99717	25.5	0.99692	26.5	0.99665
23.6	0.9974	24.6	0.99715	25.6	0.99689	26.6	0.99663
23.7	0.99737	24.7	0.99712	25.7	0.99687	26.7	0.9966
23.8	0.99735	24.8	0.9971	25.8	0.99684	26.8	0.99657
23.9	0.99732	24.9	0.99707	25.9	0.99681	26.9	0.99654
27.0	0.99652	28.0	0.99624	29.0	0.99595	30.0	0.99565
27.1	0.99649	28.1	0.99621	29.1	0.99592	30.1	0.99562
27.2	0.99646	28.2	0.99618	29.2	0.99589	30.2	0.99559
27.3	0.99643	28.3	0.99615	29.3	0.99586	30.3	0.99556
27.4	0.99641	28.4	0.99612	29.4	0.99583	30.4	0.99553
27.5	0.99638	28.5	0.99609	29.5	0.9958	30.5	0.9955
27.6	0.99635	28.6	0.99607	29.6	0.99577	30.6	0.99547
27.7	0.99632	28.7	0.99604	29.7	0.99574	30.7	0.99544
27.8	0.99629	28.8	0.99601	29.8	0.99571	30.8	0.99541
27.9	0.99627	28.9	0.99598	29.9	0.99568	30.9	0.99538

Table A.3 Values of Effective Depth Based on Hydrometer and Sedimentation
Cylinder of Specified Sizes (ASTM-D422-63, 1998)

Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.000	16.3	1.020	11.0
1.001	16.0	1.021	10.7
1.002	15.8	1.022	10.5
1.003	15.5	1.023	10.2
1.004	15.2	1.024	10.0
1.005	15.0	1.025	9.7
1.006	14.7	1.026	9.4
1.007	14.4	1.027	9.2
1.008	14.2	1.028	8.9
1.009	13.9	1.029	8.6
1.010	13.7	1.030	8.4
1.011	13.4	1.031	8.1
1.012	13.1	1.032	7.8
1.013	12.9	1.033	7.6
1.014	12.6	1.034	7.3
1.015	12.3	1.035	7.0
1.016	12.1	1.036	6.8
1.017	11.8	1.037	6.5
1.018	11.5	1.038	6.2
1.019	11.3		

A.1.2 Cumulative percent passing

Cumulative percent passing of particle in suspension is calculated by using Eq.A2 and Eq.A3.

$$\%F = \frac{100G_s R_c}{(G_s - 1)W_s} \quad \text{Eq.A.2}$$

Where:

G_s = Specific density of sample

R_c = Hydrometer reading after calibration

W_s = Dry soil weigh used to do hydrometer experiment, g

$$\%F' = \%FF_{200} \quad \text{Eq.A.3}$$

Where:

$\%F$ = Cumulative Percent passing when using hydrometer, %

$\%F_{200}$ = Percent Passing the No. 200 (75- μm), %

A.2 Sweet corn classification and grading

A.2.1 Appearance classification (TAS-1512, 2011)

Based on corn general appearance, quality and condition, it is classified into three main class:

Extra class: In this class, corn shall be of superior quality and meet conditions bellow:

Free of abnormality in cob shape and kernel colour

Regular arrangement of kernels and kernels are fully formed around the cob;

Free of defect with the exception of very slight superficial defects.

Class I: Sweet corn in this class shall be of good quality. The following slight defects or abnormality may be allowed:

Slight abnormality in cob shape and kernel colour;

Irregular arrangement of kernels;

Slight defects on the kernel skin due to scratches, abrasion or other mechanical damage not exceeding 5% of the total surface area of the sweet corn.

Class II: The following defects or abnormality may be allowed:

Abnormality in cob shape and kernel color.

Irregular arrangement of kernels;

Defects on the kernel skin due to scratches, abrasion or other mechanical damage not exceeding 10% of the total surface area of the sweet corn.

A.2.2 Size classification (PNS/BAFPS-98, 2011)

Based on ear corn length and diameter, corn ear is classified into three main classes as shown in table A.4.

Table A.4. Corn ear size classification

Classification	Ear length (cm)	Ear diameter (cm)
Large	>20.0	>4.0
Medium	15.0 - 20.0	3.0 - 4.0
Small	<15.0	<3.0



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