

# **THERMO-CHEMICAL DECOMPOSITION OF WHEAT CROP RESIDUE IN PRESENCE OF FLY-ASH AND ITS APPLICATION FOR SOIL AMELIORATION**

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For the Award of

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In

**Environmental Science and Technology**

BY

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**June, 2013**

## CERTIFICATE

I declare that the dissertation entitled **“THERMO-CHEMICAL DECOMPOSITION OF WHEAT CROP RESIDUE IN PRESENCE OF FLY-ASH AND ITS APPLICATION FOR SOIL AMELIORATION”** has been prepared by me under the guidance of Administrative Guide, Prof. A. K. Jain, Dean, Centre for Environmental Science and Technology and Dr. J. N. Babu, Assistant Professor, Centre for Environmental Science and Technology, School of Environment and Earth Sciences, Central University of Punjab. No part of this dissertation has formed the basis for the award of any degree or fellowship previously.

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## **ABSTRACT**

### **THERMO-CHEMICAL DECOMPOSITION OF WHEAT CROP RESIDUE IN PRESENCE OF FLY-ASH AND ITS APPLICATION FOR SOIL AMELIORATION**

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Key words: Wheat crop residue, fly-ash, slow pyrolysis, biochar, biochar/fly-ash composite and soil amelioration

In the present work, pyrolysis of wheat crop residue is studied in the presence and absence of fly-ash at three different pyrolysis temperatures (viz., 250<sup>0</sup>C, 350<sup>0</sup>C and 450<sup>0</sup>C) with a temperature hold time of 1 to 4 hours. Biochar yield, in absence of fly-ash, was found to decrease with increase in pyrolysis temperature and hold time. Biochar yield was found to increase significantly with increase in fly-ash content at 250<sup>0</sup>C, whereas, a significant decrease in biochar yield was observed with increase in fly-ash content at 450<sup>0</sup>C. The biochar/fly-ash composite samples were characterized by FTIR, SEM, CHNS analysis and other physico-chemical parameters like pH, EC, alkalinity, total P, K, Na and extractable micronutrient content. pH, EC, alkalinity, total P, K and Na contents were found to be modulated by increase in fly-ash content and pyrolysis temperature. Further, effect of the biochar/fly-ash composites on the soil amelioration were studied and found to have a significant effect on soil physico-chemical properties like, water holding capacity (WHC), pH, EC, CEC, exchangeable cations, organic carbon, available P and micronutrients content.

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**(Dr. J. N. Babu)**

**(Prof. A. K. Jain)**

## **DEDICATION**

This dissertation is dedicated to all the people who never stop believing in me and who along with God, have been my 'footprints in the sand'

**My Grand father**

**My Family**

To my Teacher, who taught me to get up after a fall and start again

Finally, this dissertation is dedicated to all those who believe in the richness of learning

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**(Rishikesh Singh)**

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## LIST OF ABBREVIATIONS

Sr.No.	Full Form	Abbreviation
1	Black Carbon	BC
2	Bureau of Indian Standard	BIS
3	Centimoles per kilogram	Cmoles/kg
4	Crop Residue Burning	CRB
5	Crop Residue Management	CRM
6	Diethylenetriaminepentaacetic acid	DTPA
7	Fourier Transform-Infrared Spectroscopy	FTIR
8	Gram	g
9	Highest Treatment Temperature	HTT
10	Kilo gram	kg
11	Million Ton	MT
12	Ministry of Environment and Forest	MoEF
13	Nitrogen/Carbon	N/C
14	Non-methane Hydrocarbon Compounds	NMHCs
15	Organic Matter	OM
16	Particulate Matter	PM
17	Polycyclic Aromatic Hydrocarbons	PAHs
18	Pyrolysis Temperature	PT
19	Surface Area	SA
20	Thermo-gravimetric Analysis	TGA
21	Temperature Hold Time	THT
22	Water Holding Capacity	WHC
23	X-ray Diffraction	XRD

# CHAPTER – I

## INTRODUCTION

## CHAPTER I

### INTRODUCTION

In this era of Green Revolution, the staple crop production has increased several folds, leading to key environmental issues to address like soil quality deterioration, fertilizers and pesticides management and crop residue management (FAO, 2010; Fujita, 2010). These issues lead to un-sustainability in agriculture. Increased crop residue generation as a by-product of grain production is of utmost relevance because of its impact on soil quality and local as well as regional environmental issues. The main contributors to the global crop residue generation are wheat, rice, maize, barley, millet and sorghum (Singh, 2011). Of these, rice and wheat are the main crops grown in Asian countries. Approximately 529 MT and more than 700 MT wheat and rice crop residue, respectively, are generated per year all over the world, of which ~43% (228 MT) and ~90% (623 MT) of wheat and rice crop residue, respectively, are generated from Asian countries (Kim and Dale, 2004; FAO, 2006; Buranov and Mazza, 2008). Most of the wheat crop residue is used as feed for livestock, with only 7-25% reported to be burnt in the fields, whereas most of the rice straw residue is burnt openly in the field because of its higher waste volume, higher silica content, reduction in milk yield of cattle, and for early seed-bed formation for next crop (Sidhu et al., 1998). Thus, open crop residue burning (CRB) is a very common practice and it leads to release of various air pollutants including non-methane hydrocarbon compounds (NMHCs), particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>) primarily originating from ash, polycyclic aromatic hydrocarbons (PAHs), and soot (organic carbon and black carbon) in the atmosphere (Jain et al., 2006). Apart from this, the agricultural land undergoes various changes like loss of soil fertility due to enhanced soil temperature, changes in soil C/N ratio, nutrient loss and killing of friendly pests and bacteria due to CRB (SoE: Punjab, 2007).

CRB is regarded as a major contributor (50-90%) to Atmospheric Brown Clouds (ABCs) formation (Stone et al., 2007; Ramanathan and Carmichael, 2008; Gustafsson et al., 2009). Usually open rice straw burning occurred during the months of October and November each year, in the absence of surplus crop residue management, leading to a significant impact on greenhouse gas emissions and aerosol loading (Mittal et al., 2009) and is reported for the state of

Punjab (Sharma et al., 2010). Particulate matter i.e., black carbon (BC) and organic carbon (OC) released from the CRB is regarded as a major cause for ABCs that leads to various public and environmental issues. Also, OC and BC are reported to weakening the radiative-convective coupling of the Geosphere-Atmosphere and decrease in global mean evaporation and rainfall (Ramanathan and Carmichael, 2008).

Thus, for achieving sustainability in agriculture and avoiding various environmental issues related to CRB, a proper crop residue management (CRM) strategy is necessary. However, CRM has received less attention but its probable contribution to soil fertility, soil organic matter, soil structure, soil nutrient status and soil health will lead towards sustainability in agriculture with substantial carbon sequestration (Erenstein, 2011). Various CRM practices can be grouped into physical, biochemical and thermo-chemical conversion processes. Physical or mechanical processes involve removal of crop residue manually or mechanically from field for feeding to livestock, incorporation of crop residue back to soil mechanically, no-till or zero-tillage, seeding inside the crop residue blanketed soil through modified seeders, partial removal of residue and burning at a common place (Thakur and Kumar, 2005; Singh, 2011). The second CRM practice is biochemical conversion of crop residue to bio-ethanol. There is a scope for this technology but the major constrain is that bio-ethanol does not find its place to be used as a primary fuel; however it is used as an additive (Demirbas, 2006; Rass-Hansen, 2007, Lal, 2008a). The third CRM practice is thermo-chemical conversion of crop residue biomass to liquid, gas and solid products in absence or less amount of oxygen. There are various technologies for thermo-chemical conversion such as combustion, pyrolysis (in absence/less of O<sub>2</sub> environment), torrefaction, and gasification (at high temperature and absence of O<sub>2</sub>). Massive crop residue biomass, which was earlier considered as a waste, is a good feedstock for the thermo-chemical conversion technologies (Buranov and Mazza, 2008).

Bio-oil formation from crop residue is presently being recognized because of rising prices of fossil fuels and related pollution issues. Bio-oil, which is mixture of aliphatic compounds, produced from crop residue biomass, has the potential to be used as a primary fuel in present vehicle engine. Bio-oil is produced from pyrolysis of ligno-cellulosic crop residue biomass at a temperature of 500-700°C in an O<sub>2</sub>

deficient environment (Mullen et al., 2010; Demiral and Ayan, 2011). The solid residue generated from pyrolysis and gasification is a carbon-rich, charcoal like product which is called biochar when used for soil amendment (Lal, 2008b; Lehmann, 2009).

Biochar is the solid by-product obtained from the pyrolysis of biomass in limited oxygen environment (Schmidt and Noack, 2000; Shackley et al., 2011). Because of its higher surface area and high pore volume, it has the tendency to adsorb materials like heavy metals and pesticides (Jones et al., 2011). Also, due to pyrolysis, various mineral matter present in the plant material get concentrated into biochar, thus, it has a greater potential to improve soil mineral matter content (Bruun et al., 2011). At present, research on the utilization of biochar derived from various crop residue biomass as a soil ameliorating agent, proved biochar as a good soil nourishment agent by improving various soil properties like pH, cation exchange capacity (CEC), water holding capacity (WHC), soil bulk density, porosity, moisture content, nutrient content, soil organic matter, etc. (Lehmann and Rondon, 2006). Thus, biochar formation from crop residue biomass either directly or as a by-product of bio-oil or gasification technology can be a CRM practice. Recently, increase in the yield and quality of bio-oil has been reported by utilizing certain catalysts like activated alumina (Sanna et al., 2011),  $\text{ZnCl}_2$  (Lu et al., 2011),  $\text{CaO}$  (Han et al., 2010),  $\text{TiO}_2$  (Jun et al., 2006) and zeolites like ZSM-5 (Carlson et al., 2008), HZSM-5 (Jun et al., 2006; Pan et al., 2010; Parego and Bosetti, 2011), MCM-41 (Helwani et al., 2009), Ni-ZSM-5 (French and Czernik, 2010), etc. Studies suggest that fly-ash generated from combustion of coal in thermal power plants has a natural zeolitic characteristics (Landmann, 2003; Vereshchagin et al., 2003), thus it can be used as a catalyst for producing bio-oil from crop residue.

Alike crop residue management, fly-ash management has been drawing attention of the policy makers for a long time because of its surplus production from combustion of coal in thermal power plants (TPP) for electricity generation. Combustion of coal produces a sufficient amount of energy along with various coal combustion by-products (CCPs) or coal combustion residues (CCRs) like fly-ash, bottom ash and boiler slag, fluidized bed combustion ash and other solid fine particles (Davis, 2002; Ashokan et al., 2005). Potential fly-ash generating



countries are U.S., Russia, China, and India with a fly-ash generation potential of about 750 MT/Yr (ACAA, 2009). Usually fly-ash is utilized in cement and concrete industries (Siddique, 2003; Dhadse et al., 2008; Esteves et al., 2012), brick formation, road making, landfill, and as value added materials like adhesives, adsorbent (Dermatas and Meng, 2003; Al-Zboon et al., 2011, Singh et al., 2012a), wood substitutes, zeolites (Ojha et al., 2004; Querol et al., 2007; Neupane and Donahoe, 2009), etc. (Ashokan et al., 2005; Dhadse et al., 2008; CEA, 2011; Gupta et al., 2012). It is further being investigated for agricultural field applications (Pathan et al., 2003; Dermatas and Meng, 2003; Blissett and Rowson, 2012). Fly-ash utilization potential is greater in developed countries as compared to developing one. U.S., Europe, and Japan have fly-ash utilization potential of 39%, 47%, and 82%, respectively, whereas rest of these countries fly-ash utilization potential averaged around 25% (Blissett and Rowson, 2012).

As estimated by MoEF (2007), fly-ash production in India has been 112 MT in year 2005-06 and is expected to increase upto 273 MT/Yr till the end of 2020. However, according to a CEA report on fly-ash generation, 131 MT/Yr fly-ash is generated during 2010-11 of which 56% has been utilized in various processes (CEA, 2011). Thus, fly-ash management of remaining 44% through its utilization for ameliorating cultivable as well as non-cultivable soil has been studied, because of the potential of fly-ash to provide the major soil macro- and micronutrients to the plants and related microbial communities. Fly-ash has a capacity to decrease soil aggregation, increase water holding capacity, moisture content, porosity, electrical conductivity, etc. (Blissett and Rowson, 2012; Yunusha et al., 2012). India has around 175 MHa non-cultivable land area because of water logging, high sand proportion, salinity, acidic nature and alkalinity, which has a great scope for utilization of fly-ash for soil amelioration (Ashokan et al., 2005; Jala and Goyal, 2006; Blissett and Rowson, 2012). However, high toxic metal content of the fly-ash is one of the major constrain as a soil amelioration agent, but toxicity varies with soil types (Ashokan et al., 2005; Jala and Goyal, 2006; Blissett and Rowson, 2012; Yunusha et al., 2012). However, there are issues related to the use of fly-ash as soil ameliorant like the leaching of various toxic inorganic elements, significant lowering of microbial activities and the presence of low concentration of

macronutrients and significantly high content of micronutrients in fly-ash (Tripathi et al., 2010; Masto et al., 2011).

Thus, biochar and fly-ash both are used as a soil amendment for a long time. Presently, few reports have been published revealing a combined approach for biochar/fly-ash composite utilization for soil amelioration (Palumbo et al., 2009). However, biochar formation in presence of fly-ash and utilization of the composite material lacks proper characterization as soil ameliorating agent. However, biochar is reported to decrease the leaching properties of various metals in soil (Sohi et al., 2010), thus it would be beneficial to use this combination which might give a synergistic effect on soil.

Thus, in an attempt to resolve few of the issues related to these materials, we were interested in the study for the preparation of the composite material and its effect on various physicochemical properties of soil. This study would achieve a preliminary advance into the understanding of the catalytic slow pyrolysis behaviour of fly-ash for biomass substrate and the relation between the properties of biochar/fly-ash composite, thus synthesized and its relation to the biochar and fly-ash sample. Further, this composite has been analyzed for affecting various physico-chemical properties of soil.

Thus, the objectives of the present study are:

- To study the slow pyrolysis behaviour of wheat crop residue in presence of fly-ash at different temperatures
- To study the physico-chemical properties of biochar/fly-ash composite material
- To study the effect of amending biochar/fly-ash composite on the physico-chemical properties of soil

# CHAPTER II

## REVIEW OF LITERATURE

## **CHAPTER II**

### **REVIEW OF LITERATURE**

In the present scenario, waste generation from various agricultural and industrial processes is posing a problem to the policy makers for their management. Agricultural wastes include surplus crop residue generated and processed wastes like rice husk and related issues. Industrial wastes includes plastic wastes (Brebu et al., 2010), coal combustion residues mainly fly-ash and bottom-ash (Ashokan et al., 2005), sewage sludge (Sorum et al., 2004), etc. Recycling and management of these wastes is difficult, however, various management practices are being used but the complete utilization has not achieved. These wastes are a rich source of various macro- (C, N, P, S, Ca, Mg, Na, K, etc.) and micro-nutrients (Fe, Co, Zn, Cu, Mn, B, Mo, etc.) (Tripathi et al., 2010; Masto et al., 2011). Application of fly-ash, sewage sludge, and crop residue to soil has been practiced for a long time for improving soil physico-chemical properties and nutrient status. Bio-fuel generation by pyrolysis and gasification of crop residue is one of the management practice adopted now-a-days which is considered as sustainably sound practice for crop residue management. Biochar is a by-product of bio-fuels technology which has a greater potential to improve soil properties.

Thus, the present review covers the lignocellulosic crop residue status at world level and in Punjab, the biochar formation from crop residue, and biochar formation in presence of various solid catalysts like zeolites, activated alumina under different pyrolysis conditions. Effect of various pyrolysis conditions on properties of biochar has been reviewed. Application of biochar, fly-ash and various organic-inorganic composites for soil amelioration has been reviewed.

#### **2.1 Status of crop residue**

According to an estimation of Lal (2008a), about 4000 MT/Yr crop residue is produced worldwide from 27 food crops, with a 3000 MT/Yr lignocellulosic residue is alone produced by cereal crops, which can be used for biofuels production. The agrarian economy of India is rendered unsustainable with the issue of more than 500 MT of crop residue generated every year (MNRE, 2009). This residue generation is highest in the states covered under Indo-Gangetic Plains (IGP)

particularly, Uttar Pradesh and Punjab (51 MT of which 25 MT is contributed by Punjab). About 2 MT of total over 10 MT of rice crop residue generation in Punjab has been utilized in various processes like cattle feed, making form structures, paper and card boards, a few industrial goods, whereas remaining about 8 MT is burnt openly in the fields (Thakur and Kumar, 2005). Thakur and Kumar (2005) suggest that recycling of the entire crop residue to the field may pose problems. However, crop residue is considered as an important source of soil organic matter and improve soil physical properties, thus its complete removal has not been suggested as a sustainable practice (Blanco-Cancui and Lal, 2009a). Blanco-Cancui and Lal (2009a) reviewed the effect of crop residue removal from field and concluded that with the removal of crop residue, soil physico-chemical and biological properties are affected differently for soil to soil. Graham et al. (2007) has suggested that 30-50% removal of stover crop residue from U.S. has no significant adverse effect on soil. Blanco-Cancui and Lal (2009b) has reported slight increase in pH and EC whereas a decrease in CEC of soil with the removal of stover crop residue from field.

## **2.2 Thermo-chemical treatment of Crop Residue**

Thermo-chemical treatment of biomass in an inert atmosphere, with the temperature ranging from 450-600<sup>0</sup>C, leads to liquid condensate known as bio-oil. Apart from this, there is the formation of char and gases particularly, CO<sub>2</sub>, H<sub>2</sub> and CO in relatively lower amount during this process. The thermo-chemical process is also known as pyrolysis. There are various types of pyrolysis being carried out which could be classified under either as slow, intermediate, fast or ablative pyrolysis (Mohan et al., 2006). It has been quite significantly established that the bio-oil yield increases upon fast and ablative pyrolysis whereas the slow pyrolysis leads to the formation of char (Crocker, 2010). Different type of pyrolysis technologies has been applied for pyrolysis of biomass as given in **Table-2.1**

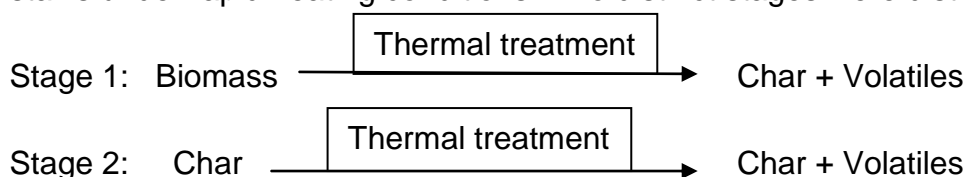
Shuangning et al. (2006) studied flash pyrolysis behaviour of crop residue biomass and reported that yield of volatiles depends upon the final pyrolysis temperature and residence time.

**Table-2.1:** Typical products yields (dry basis) for different modes of pyrolysis  
(Source: Bridgewater, 2007; Lehmann, 2009)

Mode	Conditions	Liquid (%)	Char (%)	Gas (%)
Fast	Moderate temperature $\sim 500^{\circ}\text{C}$ Short vapour residence time $\sim 1$ sec	75	12	13
Moderate	Moderate temperature $\sim 500^{\circ}\text{C}$ Moderate vapour residence time $\sim 10\text{-}20$ sec	50	20	30
Slow	Moderate temperature $\sim 500^{\circ}\text{C}$ Very long vapour residence time $\sim 5\text{-}30$ min	30	35	35
Gasification	High temperature $> 750^{\circ}\text{C}$ Moderate vapour residence time $\sim 10\text{-}20$ sec	5	10	85

Demirbas (2006) studied the slow pyrolysis behaviour of nutshells at 500-1200 K pyrolysis temperatures and varying residence time and found a decrease in char yield with the increase in pyrolysis temperature and residence time. Bruun et al. (2011) studied fast pyrolysis of wheat straw and found a significant bio-oil formation, whereas, the carbon present in the biochar produced from fast pyrolysis was found to be less stable. Lee et al. (2013) studied pyrolysis behaviour of giant Miscanthus by slow pyrolysis and found that, with the increase in pyrolysis temperature biochar yield decreases significantly. Crop residue biomass is mainly composed of celluloses, hemicelluloses, lignin and a small portion of inorganic salts. A typical proportion of wheat straw is given in **Table-2.2**.

Lanzetta and Blasi (1998) performed two stage pyrolysis of wheat straw and corn stalks under rapid heating conditions. Two distinct stages were distinguished:



**Table-2.2:** Typical composition of wheat crop residue (Source: Thakur and Kumar, 2005)

Component name	% Contribution
Salts	6
Various organic compounds	8
Hemicellulose	25
Lignin	18
Cellulose	30
Insoluble ash (silica)	7

Two possible steps in any pyrolysis process comprising of devolatilization of the material where different zones can appear corresponding to (a) the thermal decomposition of the main constituents leading to dehydration, dehydrogenation, decarboxylation and decarbonylation reaction; and (b) secondary pyrolysis, which covers the secondary decomposition reactions in solid matrix, as well as secondary reactions between the volatiles release or between the volatiles and the carbonaceous residue. This leads to the process known as cracking, where heavy compounds further break into gases, or char is also converted into gaseous as well as partially oxidized products (Lanzetta and Blasi, 1998).

Thermo-gravimetric analysis (TGA) of crop residue supports the two stage decomposition of biomass during pyrolysis (Xiao et al., 2001; Kim et al., 2012; Cao et al., 2013; Lee et al., 2013). Loss in weight of biomass is observed initially at 100<sup>0</sup>C which is due to release of moisture from crop residue. Second significant mass loss stage was observed near 200<sup>0</sup>C-300<sup>0</sup>C and 300<sup>0</sup>C-400<sup>0</sup>C which is due to degradation and decomposition of hemicellulosic and cellulosic components of biomass, respectively (Kim et al., 2012). However, the char obtained at this stage is significantly rich in lignocellulosic components which get further decomposed upon raising the temperature to 400<sup>0</sup>C and above, resulting in the release of volatiles with lower char yield (Cao et al., 2013).

### 2.3 Biochar from Crop Residues

Biochar is the solid by-product obtained from the pyrolysis of biomass in limited oxygen environment (Schmidt and Noack, 2000; Shackley et al., 2011). Lehmann

and Joseph (2009) defined biochar as a carbon-rich crystalline graphene structured product obtained by thermally decomposing the biomass such as wood, manure, leaves or crop residue in a closed pyrolysis chamber at a temperature  $<700^{\circ}\text{C}$  in  $\text{O}_2$  deficient environment. The exact chemical nature of a biochar produced depends upon the type of biomass used and pyrolysis condition (Demirbas, 2006; Lehmann, 2009; Kim et al. 2012). Studies in the biochar formation from different crop residues like from *Miscanthus* (Lee et al., 2013), olive kernels (Zabaniotou et al., 2008); straws of canola, corn, soybean and peanut (Yuan et al., 2011); rice straw and rice husk (Haefele et al., 2011), wheat straw (Jung et al., 2011; Wild et al., 2012; Bruun et al., 2012), rape and sunflowers residues (Sanchez et al., 2009); and also from residues of sugarcane, sorghum, millet, coconut, oil palm, coffee, cocoa, maize, etc. (Duku et al., 2011) have been reported. Also, earlier reports suggested the formation of biochar from poultry litter (Gaskin et al., 2008), wood, municipal biowastes (Yanai et al., 2007), yard wastes, etc. which are in practice for a long time for soil amendment (Lehmann, 2009). Herbaceous crop residue biomass is a worth source for biochar formation (Buranov and Mazza, 2008) as studies have reported double yield of biochar produced from crop residue than wood biomass (Ioannidou and Zabaniotou, 2007).

### **2.3.1 Physiochemical Characteristics of Crop Residue Biochar**

Various physicochemical properties of biochar produced from various crop residue sources are summarized in **Table-2.3**. The biochar characteristics are very much variable and they depend upon the biomass source and operating pyrolysis conditions like highest treatment temperature (HTT), pressure, reaction residence time, vapour residence time, moisture content of biomass source, reaction vessel, pre-treatment, flow rate of gas/air and post treatment. Biochar has large surface area, high pore space (micropores, mesopores and macropores), permeability, lower bulk density and high water holding capacity (WHC) (Lehmann and Rondon, 2006). Temperature has a very important role in determining the characteristics and application of biochar (**Table-2.3**), as biochar prepared at low temperature can be used for controlling the release of nutrients from fertilizers (Day et al., 2005) and high temperature leads to the formation of activated carbon like material

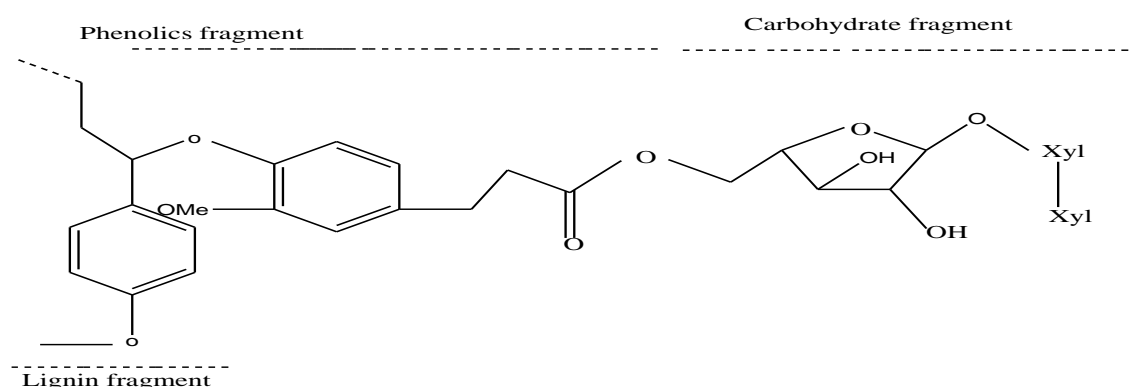


(Ogawa et al., 2006). With the increase in pyrolysis temperature, pH, surface area, ash content, fixed carbon content of the biochar produce increases. However, with the increase in pyrolysis temperature, a decrease in nitrogen and oxygen content and an increase in carbon and phosphorus content are reported (Yuan et al., 2011; Spokas et al., 2011). Proximate and ultimate analyses of crop residue derived biochar samples revealed that biochar has higher fixed carbon, ash, %N than parent biomass, low volatile matter, %H, and %O content than parent biomass material, thus has lower H/C ratio, lower O/C ratio and lower N/C ratio (Shuangning et al., 2006; Bruun et al., 2011; Sanna et al., 2011; Kim et al., 2012). Biochar is a highly porous material with high surface area. This is responsible for the lower bulk density and high water holding capacity of the biochar materials. Porosity of the biochar increases with increase in pyrolysis temperature because of the loss of volatile matter, thus, in turn leading to decrease in bulk density. Porous structure of biochar is further supported by various SEM studies which revealed that with the increase in pyrolysis temperature, volatilization from the crop residue increases leaving behind the unordered pore spaces which is responsible for the characteristic biochar properties (Chia et al., 2012; Kim et al., 2012; Oh et al., 2012; Muradov et al., 2012)

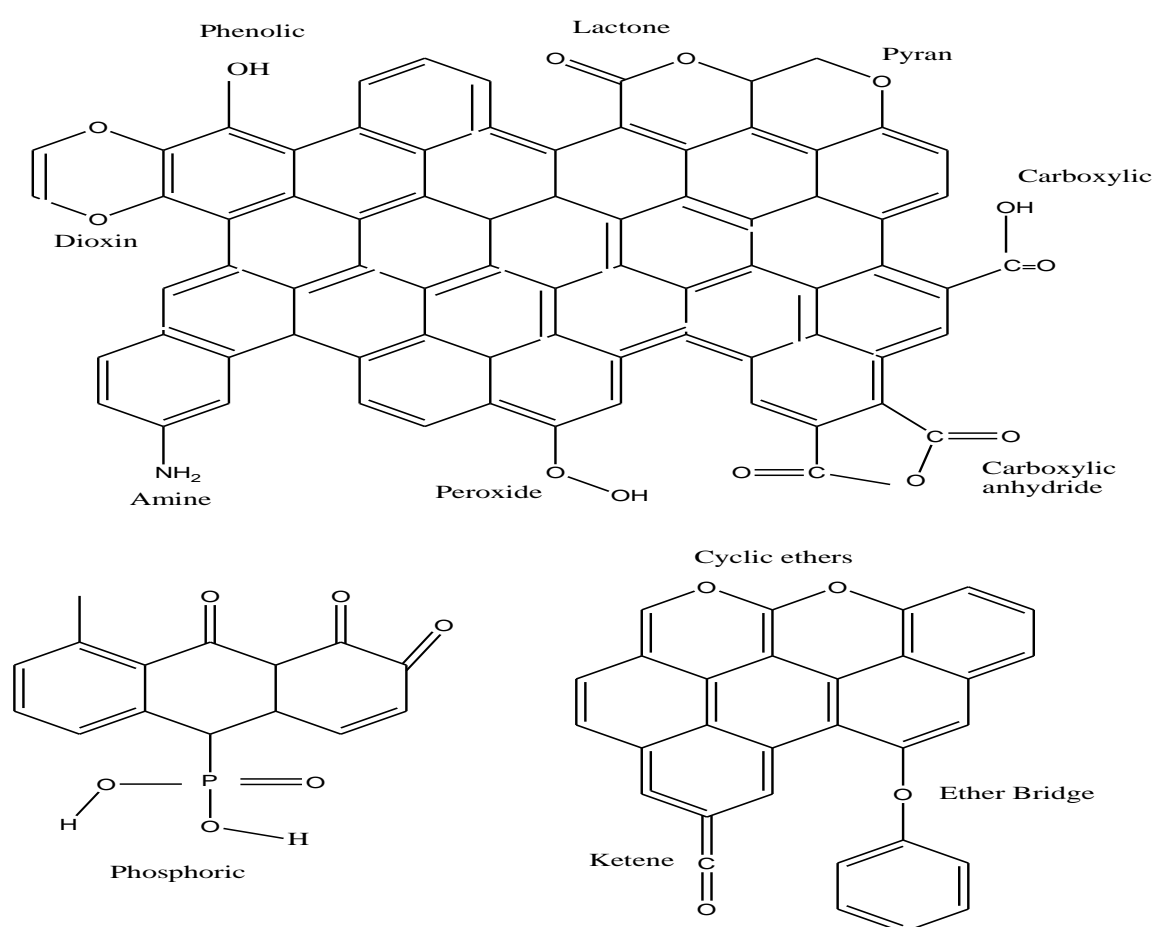
### **2.3.2 Chemical properties of biochar**

Chemically, biochar is a highly aromatic compound that contains random stacks of graphitic layers (Schmidt and Noack, 2000) i.e., has high carbon content followed by oxygen, hydrogen and nitrogen and has lower N/C, H/C, O/C ratios and lesser volatile matter content than the parent material (Spokas, 2010). Biochar is highly stable, resistant to various erosion, having high cation exchange capacity (CEC) and a variable range of pH (depending upon biomass source and heating temperature) (Lehmann and Joseph, 2009; Yuan and Xu, 2011). High cation exchange capacity (CEC) of biochar is due to the presence of various functional groups like pyranone, phenolic, carboxylic, lactone and amine (Brennan et al., 2001) derived from the volatilization of lignocellulosic biomass as given in **Figure-2.1** and **2.2**. The presence of these functional groups has been supported by FTIR studies, which revealed the variation in functional groups of biochar produce with the variation in temperatures (Keilweit et al., 2010; Contrell et al., 2012; Kim et al., 2012; Cao et al., 2013). Several workers regard biochar as a rich source of

nitrogen along-with carbon, which can be used to further improve soil nutrient status (Woods et al., 2009). Because of its higher adsorption capacity in comparison to soil, biochar is regarded as a better soil phosphorus retaining material (Schmidt and Noack, 2000).



**Figure-2.1:** Lignocellulosic component of wheat crop residue biomass (Sun et al., 1997; Buranov and Mazza, 2008)



**Figure-2.2:** Structure of biochar with different functional groups present on its surface (Brennan et al., 2001; Lehmann et al., 2009)

**Table 2.3:** A comparative study of various physico-chemical characteristics of various biochar prepared at different pyrolysis temperature

Source	PT (°C)	pH	SA (m <sup>2</sup> /gm)	% dry weight basis								References
				C	N	O	H	P	N/C	H <sub>2</sub> O	Ash	
Corn stover	500	8.9	4.20	25.00	0.60	5.00	1.10	n/a	0.024	9.1	69.00	Spokas et al., 2011
	515	9.5	4.40	45.00	0.50	1.00	1.70	n/a	0.011	11.5	55.00	Spokas et al., 2011
Coconut shell	550	8.9	15.10	80.10	0.50	2.50	n/a	n/a	0.006	12.4	n/a	Spokas et al., 2011
Peanut hulls	481	8.0	1.00	59.00	2.70	12.00	2.30	n/a	0.046	7.2	18.00	Spokas et al., 2011
Corn cob	400	9.0	< 0.1	80.10	0.60	8.80	3.70	n/a	0.007	3.1	3.70	Spokas et al., 2011
Sugarcane bagasse	350	5.0	n/a	75.20	0.66	15.80	4.60	n/a	0.009	3.42	3.60	Spokas et al., 2011
Poultry litter	400	10.3	n/a	42.30	4.20	n/a	n/a	n/a	0.099	n/a	n/a	Spokas et al., 2011
Cottonseed hull	500	8.5	<0.1	78.70	2.50	6.90	2.50	n/a	0.032	6.5	7.90	Spokas et al., 2011
	800	7.7	322.00	84.30	0.60	6.60	0.60	n/a	0.007	5.9	9.20	Spokas et al., 2011
Rape residue	550	n/a	n/a	72.20	1.30	25.60	0.90	n/a	0.018	3.2	21.80	Sanchez et al., 2009
Sunflower residue	550	n/a	n/a	63.40	1.60	34.30	0.70	n/a	0.025	4.73	28.90	Sanchez et al., 2009
Wheat straw	n/a	n/a	n/a	43.20	0.61	39.40	5.00	n/a	0.014	n/a	n/a	Spokas 2010
Rice hulls	n/a	n/a	n/a	38.30	0.83	35.45	4.36	n/a	0.022	n/a	n/a	Spokas 2010
Olive kernel	800	n/a	n/a	75.68	1.35	12.18	0.79	n/a	0.018	n/a	n/a	Zabaniotou et al., 2008
Canola straw	500	9.4	n/a	63.40	0.04	n/a	n/a	0.30	0.001	n/a	18.40	Zabaniotou et al., 2008
	700	10.8	n/a	54.90	0.04	n/a	n/a	0.50	0.001	n/a	28.55	Zabaniotou et al., 2008
Soyabean straw	500	10.9	n/a	62.60	0.40	n/a	n/a	0.40	0.006	n/a	17.85	Yuan et al., 2011
	700	11.1	n/a	57.90	0.10	n/a	n/a	0.60	0.002	n/a	23.70	Yuan et al., 2011
Corn straw	500	10.8	n/a	41.90	0.90	n/a	n/a	0.40	0.021	n/a	50.70	Yuan et al., 2011
	700	11.3	n/a	24.50	0.80	n/a	n/a	0.70	0.033	n/a	73.30	Yuan et al., 2011
Peanut straw	500	10.7	n/a	48.50	1.50	n/a	n/a	0.10	0.031	n/a	32.50	Yuan et al., 2011
	700	11.2	n/a	47.00	1.50	n/a	n/a	0.12	0.032	n/a	38.50	Yuan et al., 2011

(Here, PT= pyrolysis temperature; SA= surface area; H<sub>2</sub>O= moisture content; and n/a= data not available)

### **2.3.3 Life cycle analysis of biochar**

Biochar has been a very stable and resistive element in soil and so it has long-life (thousand to millions of years) in soil, because the recalcitrance of biochar depends upon biomass source, pyrolysis condition, soil properties and climate (Lehmann, 2007). Terra Preta soil or Amazonian Dark Earths (ADE), regarded as a type of biochar, is considered as an example for describing the longevity of biochar in soil (Hunt et al., 2010). Various lab-scale studies have predicted that biochar has a mean residence time of 1300-4000 years in soil (Cheng et al., 2008). Its degradation and mineralization is very slow and because of this property, it is considered as a good method for mitigating Climate change by locking a huge amount of atmospheric CO<sub>2</sub> (Lal, 2008b). Also, various studies suggested that a fraction of C (present as mineral carbonates and organic molecules) from biochar, called labile carbon content, is mineralized abiotically and biotically to CO<sub>2</sub> within a short period of time (Lehmann and Joseph, 2009; Singh et al., 2012b). Singh et al. (2012b) have performed five year study on stability of biochar carbon in clayey soil, and they found that biochar prepared at low pyrolysis temperature has more labile carbon which get mineralized faster than the high temperature biochar. Bruun et al. (2011) studied the stability of labile fraction and short term C loss from loamy soil amended with wheat straw biochar produced by fast pyrolysis and found that about 90% of biochar C has lost within few weeks after amelioration. Bruun et al. (2012) further studied on C and N turnover dynamics of fast and slow pyrolysis wheat crop residue biochar ameliorated soil. They found that biochar produced from fast pyrolysis has higher labile C content which was due to incomplete decomposition of lignocellulosic biomass material at fast pyrolysis, thus this carbon was more prone to microbial degradation whereas slow pyrolysis biochar C was found to be comparatively stable in soil.

Thus, the stability of biochar C depends upon the pyrolysis conditions. Biochar prepared at higher temperatures and slow pyrolysis would have more recalcitrant C and thus, more stable and could be used for sequestering atmospheric CO<sub>2</sub> to soil for long time. On the other hand, biochar prepared at lower temperature or fast pyrolysis could be used for improving soil organic carbon pool.

### **2.3.4 Biochar for Soil Amendment: An Approach to Agricultural Sustainability**

Enhanced mineralization of soil organic matter and depletion of soil nutrients are currently considered as the two important limitations for sustainable agriculture. Biochar having high adsorption capacity and nutrient retention capacity is considered as an effective soil amendment than compost and organic manure (Chan et al., 2008). The amount of biochar incorporation in soil requires the understanding of soil characteristics and climatic conditions. Although, after performing various experiments of biochar application to soil, especially for crop production, Lehmann (2007) concludes that: “crops respond positively to biochar addition up to 50 MgC/ha and may show growth reduction only at very high applications”. The use of crop residue biochar as soil ameliorating agent for sustainable agriculture, are identified as direct use benefits and indirect use benefits.

#### **2.3.4.1 Direct use benefits of biochar**

As biochar is a highly porous structure, thus after its addition to soil it leads to increase in the soil aeration, soil water holding capacity and decrease in soil aggregation, soil strength and bulk density, increase soil organic carbon, nitrogen, available P, K and soluble salts and ultimately increased crop yield (Li et al., 2012; Zhang et al., 2012). The pH of biochar varies from slightly acidic to alkaline range (mostly in alkaline range from pH = 8.0-10.0), thus, alkaline pH leads to better functioning of soil microbial communities and resurrecting buffering capacity to soil after its application (Yuan et al., 2011; Yuan and Xu, 2011). Also, biochar application can be beneficial in acidic soil reclamation and the soil that has been degraded by long term continuous cultivation (Kimetu et al., 2008). Various anionic functional groups of biochar (Brennan et al., 2001) on its surface behaves as a cation exchange resin leading to the retention of essential cations for exchange, thus increase the soil CEC, leading to increased crop productivity (Chan et al., 2008; Asai et al., 2009). Biochar application to soil increases the soil organic carbon pool and soil-N. During the initial periods of its application, biochar has less resistance and is more prone to degradation because a small fraction of carbon is present in the labile form (Krull et al., 2006), so the microbial activity is enhanced during this time period. Excellent

nutrient retention property of biochar leads to longer retention of nutrients in topsoil after fertilizer application. High porosity and larger surface area of soil after biochar amendment would lead to the growth of micro-organism, thus, leading to better symbiosis of the crop with bacteria and fungi, which results in the dissolution of nutrients and bioavailability of nutrients for the crop (Warnock et al., 2007). Borchard et al. (2012) studied the effect of biochar application to soil nutrient conditions in a greenhouse experiment and found that biochar has a significant effect over soil nutrient retention and fertility as biochar surface have been found to undergo very slow changes in its surface structures.

#### ***2.3.4.2 Indirect use benefits of biochar***

The nutrient retention capacity of biochar leads to the reduction of fertilizer use, so it indirectly results in reduction in production, energy and environmental cost of fertilizer manufacturing. Also, biochar application to soil leads to subdued release of  $N_2O$  and  $CH_4$  like potent greenhouse gases (Yanai et al., 2007; Dalal et al., 2008). According to an estimation of Woolf (2008), all the crop residues of the world if converted into biochar, would sequester about 1 gigatonne of carbon to soil and is assumed to be a better carbon capture and storage (CCS) alternative for mitigating Climate Change. Biochar has a carbon negative effect on the atmosphere (Lal, 2008b; Lehmann, 2007). By-products of biochar production (syn-gas and bio-oil) from crop residue are cleaner fuels with high calorific value, thus can be used as an alternative source of energy (Sanchez et al., 2009; Haefele et al., 2011; Wild et al., 2012).

#### **2.3.5 Crop residue biochar as an adsorbent material**

Xu et al. (2011) reported significant adsorption of methyl violet from aqueous solutions by various crop residue derived biochars, due to specific electrostatic interaction between dye and negative charge on biochar surface. A comparative adsorption study, of rice-straw biochar and fly-ash by Lou et al. (2012), advocated biochar as a significant sorption material for pentachlorophenol (PCP). Rice-straw biochar amended in soil sediments has a significant sorption capacity for

pentachlorophenol (PCP), than aged fly-ash. However, fresh fly-ash has greater sorption capacity for FCP.

### **2.3.6 Limitations and Risks Associated with Biochar for Soil Amendment**

The following are the major limitations and risks associated with biochar application to soil, which limit its use as soil ameliorant (Sparkes and Stoutjesdijk, 2011):

- A standardized application rate is still needed.
- Effect on agrochemicals: application of biochar increases the binding of various agrochemicals on its surface, thus reduces killing of pests and enhances the longevity of chemical in soil by avoiding them from microbial decay.
- PAH production: during slow pyrolysis of biochar remain attached with the anionic surfaces of biochar and might cause negative impact to soil and microbial diversity.
- Biochar decreases soil albedo by providing black surface to soil and increases absorption of sunlight, thus, indirectly leading Global warming phenomenon.
- Soil residence time of biochar is estimated as centennial to millennial with an average residence time of 600 years.
- Soil Organic Matter/Carbon (SOM/C): no conclusive evidence is available which signify that biochar either increases or decreases the SOM content.
- Heterogeneous nature of biomass as well as pyrolysis conditions lead to variation in the properties of biochar.
- Higher cost of production.

### **2.4 Fly-ash from Coal Combustion**

Fly-ash is an inorganic finely divided heterogeneous mixture of amorphous and crystalline phases dominated by ferroaluminosilicate materials collected from electrostatic precipitators produced from pulverised coal combustion process (Vereshchagin et al., 2003; Lokeshappa and Dikshit, 2011). Fly-ash is a waste material coming in light after 1920s and 1930s, as the use of finer pulverised coal has been practiced for efficient energy generation. Thus, production of fly-ash increases as the size of parent coal material decreases. However, this waste generated is

named “Fly-ash” because of its very light weight, due to the inherent behaviour of existence as suspension in air, collected from exiting flue gases from electrostatic precipitators and cyclones (Joshi, 2010). Fly-ash is one of the by-products of coal combustion residues (CCRs) viz., boiler slag, fly-ash, bottom ash, fluidized bed combustion ash, etc., produced from thermal power plants, municipal solid waste incinerators and biomass combustion industries. Thermal power plants are the major contributors to the fly-ash generation worldwide as coal is used for generation of electricity in thermal power plants. India is one of the leading countries in fly-ash generation potential worldwide, along with U.S., Russia, and China with the share of about 1/6<sup>th</sup> of the global fly-ash production of 750 MT/Yr (ACAA, 2009). Electricity demand is increasing progressively, thus, fly-ash generation is also expected to increase.

According to annual report of CEA (Central Electricity Authority, April 2012), total coal/lignite consumption in India is more than 407.61 MT in 90 coal/lignite based thermal power plants with a total installed capacity of 83,797 MW. This has led to generation of 66.49 MT fly-ashes in the earlier half of 2011-12, of which 54.53% has been utilized in various processes like cement manufacturing, brick formation, reclamation, land filling, agriculture, etc. (CEA, 2012).

#### **2.4.1 Morphological and mineralogical structure of fly-ash**

Morphological and mineralogical studies of fly-ash have been carried out using scanning electron microscope and energy dispersive spectrophotometer (SEM-EDS), X-ray photoelectron spectrophotometer (XPS) and X-ray diffraction (XRD) studies. The SEM-EDS studies revealed that fly-ash has a regular shape and size consisting of 2% spherical, hollow and solid structures collectively known as microspheres having very high thermal and magnetic properties, spherical design and chemical inertness (Davis, 2002; Landman, 2003; Vereshchagin et al., 2003). XRD studies of fly-ash revealed that it is composed of various phases like glass, mullite, cristobalite, hematite, anhydrite, quartz, feldspar, plagioclase, kaolinite, mica, illite, etc. depending upon the parent coal material used for combustion process (Vereshchagin



et al., 2003, Sarkar et al., 2006). Mullite and quartz are essentially present in non-magnetic components of fly-ash. The bulky microspheres are mainly present as:

- (i) crystalline monolith,
- (ii) porous,
- (iii) Cenospheres: spheres formed by alluminosilicate in which the particle diameter to wall thickness ratio can reach more than 50,
- (iv) Plerospheres: a hollow large sphere is filled with various small spherical particles (Vereshchagin et al., 2003; Ashokan et al., 2005), and
- (v) Ferrospheres: flower like structures formed by aluminosilicate glass particles of fly-ash (Sarkar et al., 2006)

#### **2.4.2 Physical properties of fly-ash**

Fly-ash is mainly composed of kaolinite phase minerals which are analogous to clay particles. Fly-ash dominated by hollow plerospheres and cenospheres have lower bulk density and high porosity than soils, high surface area, higher water retention capacity than soil due to presence of these hollow spheres which requires more water to fill the pores, better aggregation capacity, lower hydraulic conductivity, etc. However, iron oxide is heavy in weight and usually present in the centre of the hollow structures and iron oxide dominated fly-ash samples were reported to have high density. Particle diameter of fly-ash usually ranges between 1-150  $\mu\text{m}$ , however 60% of fly-ash is constituted by particles having diameter  $< 3 \mu\text{m}$  (comprise only 10 wt% of fly-ash) (Vereshchagin et al., 2003). Color of fly-ash depends upon the source material; however it is usually from grayish to black in color (Vereshchagin et al., 2003; Ashokan et al., 2005).

#### **2.4.3 Chemical Composition of Fly-ash**

Aluminosilicates are the major constituents of fly-ash comprising of about 70-90% followed by oxides of iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), sulphur (S), phosphorus (P), along with various trace metals oxides like lead (Pb), cadmium (Cd), nickel (Ni), zinc (Zn), boron (B), molybdenum (Mo), vanadium (V), copper (Cu), manganese (Mn), arsenic (As), mercury (Hg), titanium

(Ti) and certain radioactive oxides of uranium (U) depending upon the parent coal materials. General chemical composition of fly-ash is  $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{CaO} > \text{MgO} > \text{K}_2\text{O} > \text{Na}_2\text{O} > \text{TiO}_2$  (Blissett and Rowson, 2012). pH of fly-ash varies from 4.0 to 12.0 depending upon parent coal material, combustion condition, and point of collection. Electrical conductivity of fly-ash is usually higher than soil, depending upon the ionic composition of fly-ash. The presence of alkali and alkaline earth metals in the fly-ash sample are exchangeable and lead to the higher pH and electrical conductivity. Fly-ash has higher cation exchange capacity than soil, though their Si/Al ratio are similar but the Si-Al network differ in the fact that the Si-Al are uniformly distributed and Al-O is responsible for the extent of acidic nature of fly-ash. Fly-ash is a rich source of exchangeable Ca, Mg, K and Na; however release of Na was reported lower than the other exchangeable cations. The coal phosphorus ends up in fly-ash as phosphate; the phosphate is immobilized by various alkaline and heavy metals, but is bioavailable as alkali metal phosphate. Thus, fly-ash phosphorus is more available than the soil itself, leading to potential cost saving upon reduced phosphorus fertilizer usage. Combustible matter content of fly-ash depends upon combustion conditions, however, a significant amount of organic matter is found in fly-ash which further increases with decrease in combustion temperature and increase in particle size of fly-ash (Sarkar et al., 2006).

Further, Sarkar et al. (2006) characterized fly-ash collected from Bokaro TPP for weight percentage distribution, particle density, particle size, loss on ignition (LOI), chemical composition using X-ray fluorescence (XRF), morphological analysis using SEM-EDX and functional group analysis using FTIR spectroscopic analysis. They have observed two components in fly-ash viz., magnetic and non magnetic component. Quartz and mullite mineral phases were essentially present in non-magnetic components, however ferrospheres bear crystallite phases. Proximate analysis of fly-ash revealed that fly-ash has significantly high fixed carbon (41.7%) and volatile matter (15.7%), with low ash content (41.8%). SEM images revealed that activated carbon particles are present as embedded on fly-ash surfaces. SEM images of fly-ash revealed the presence of perfectly spheroidal structures with well known crystallites on the surfaces which belongs to ferrospheres. Perfect spheroidal

structures in SEM images are also exhibited by cenospheric and pleurospheric components of fly-ash. Fourier transformed Infra-red Spectroscopy of fly-ash suggests that several aliphatic groups like  $-CH_2$ ,  $-CH_3$ ,  $Si-O-Si$ ; and aromatic groups like benzene, are characterized by the absorption band characteristic of  $-CH$  bending, H-bond,  $-OH$ , FeS pyritic etc., are present in fly-ash material which varies with source of parent coal material used and combustion processes involved.

#### 2.4.4 Classification of fly-ash

On the basis of amount of combustible organic matter, %CaO, %SiO<sub>2</sub>, %Al<sub>2</sub>O<sub>3</sub> and %Fe oxides, ASTM C618-93 procedure categorized fly-ash into three classes, viz., Class N, Class C and Class F (**Table-2.4**). However, mainly two classes i.e., Class C and Class F are described further depending upon the CaO, Fe<sub>2</sub>O<sub>3</sub>, and aluminosilicate proportions (Joshi and Lohtia, 1997).

**Table-2.4:** A comparative study of general characteristics of Class C and Class F fly-ash (Source: Yunusha et al., 2012)

Characteristics	Class C	Class F
Source Coal	Lignite and Sub-bituminous	Bituminous and Anthracite
Major Producers	U.S., South African countries	Australia, Canada, China, India, South Africa, U.S.
Basic Nature	Pozzolanic and Cementious	Pozzolonic
<b>Typical Composition (%)</b>		
SiO <sub>2</sub>	40	55
Al <sub>2</sub> O <sub>3</sub>	17	26
Fe <sub>2</sub> O <sub>3</sub>	6	7
CaO	33	9
SO <sub>3</sub>	3.3	0.6
Available alkalies(Na <sub>2</sub> O)	0.7	0.5
Fineness (retained on 325 mess)	8	14

- **Class C:** combustion of lignite and sub-bituminous coal leads to the formation of Class C fly-ash which has a high content of CaO (33%), Na<sub>2</sub>O (0.7%) and comparatively lower contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe oxides (**Table-2.4**). Higher content of CaO provides self cementing property to Class C fly-ash. Class C fly-ash contains less than 1% un-burned carbon (Joshi, 2010).
- **Class F:** combustion of harder and older bituminous and anthracite coal leads to the production of Class F fly-ash which is more finer than the Class C fly-ash because of the presence of higher contents of SiO<sub>2</sub> (53%), Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>, a lesser CaO (9%) content (**Table-2.4**), thus requires an activator e.g. lime for liming property (Rai et al., 2010; Yunusha et al., 2012). Class F fly-ash contains about 2% un-burned carbon (Joshi, 2010).

#### 2.4.5 Utilization of fly-ash

Fly-ash is surplus worldwide as it is produced at the rate of 750 MT/Yr and this has further increased with increase in electricity demand (ACAA, 2009). Fly-ash utilization potential is greater in developed countries as compared to developing countries. U.S., Europe, and Japan have fly-ash utilization potential of 39%, 47%, and 82%, respectively, whereas for rest of the countries, fly-ash utilization potential averaged around 25% (Blissett and Rondon, 2012). A few countries like Netherland and Germany has been reported to utilize 100% of total generated fly-ash, however, fly-ash generation potential is also very low in these countries (Aswar, 2000). Concrete, cement and structural fill have been potentially utilizing 10-30% of fly-ash worldwide (Joshi 2010). In India ~55% of total fly-ash generated is potentially used as raw material as well as additive for various value added products such as in cement and concrete industries (Siddique, 2003; Dhadse et al., 2008; CEA, 2011; Esteves et al., 2012); construction and geotechnical applications like brick kilns, road formation, embankments, additive to clayey soil, etc. (Sharma et al., 2012); paper manufacturing (Sinha et al., 2010); mine fillers, electronics (Sreenivas et al., 2011); geopolymers (Al-Zboon et al., 2011; Chindaprasirt and Rattanasak, 2010); adsorbent (Al-Zboon et al., 2011; Singh et al., 2012a); extraction of metals (Sarkar et al., 2006; Blissett and Rowson, 2012); and zeolites (Querol et al., 2007; Ojha et al., 2004; Neupane and

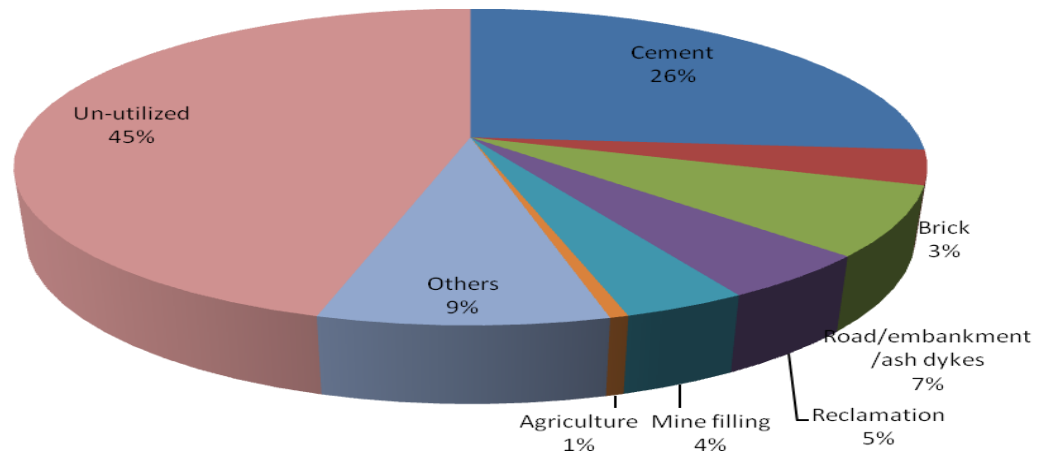
Donahoe, 2009), which is further used for removal of heavy metals from wastewaters, adhesives, wall board, paint, wood substitute, and as a potential soil amendment agent (Basu et al., 2009; Blissett and Rowson, 2012).

Use of fly-ash in cement and soil amelioration also helps in carbon sequestration (Ashokan et al., 2005). According to a study by Montes-Hernandez et al. (2009), one tonne fly-ash can sequester 26 kg of CO<sub>2</sub>, i.e. 38.18 tonne fly-ash will sequester one tonne of CO<sub>2</sub>, thus making the way for the utilization of alkaline fly-ash residue for CO<sub>2</sub> mitigation. Studies have reported that about 1 tonne CO<sub>2</sub> is produced for producing 1 tonne of cement in normal production process whereas a significant amount of CO<sub>2</sub> emission can be reduced by applying fly-ash as an additive (Joshi, 2010). Kumar et al. (2011) studied CO<sub>2</sub> adsorption by alumino-silicates extracted from fly-ash along with certain additives like APTES ((3-aminopropyl) triethoxysilane), TRIS buffer (tris (hydroxymethyl) aminomethane), and AMP (3-amino-2-methyl-1-propanol) for providing basicity and found four fold increase in CO<sub>2</sub> adsorption from 6.62 mg/g to 26.5 mg/g at 55<sup>0</sup>C in AMP-functionalized FAS (fly-ash based alumino-silicate) than FAS only, respectively. Vitekari et al. (2012) studied fly-ash as a carrier for bio-pesticides and bio-fertilizer formulations.

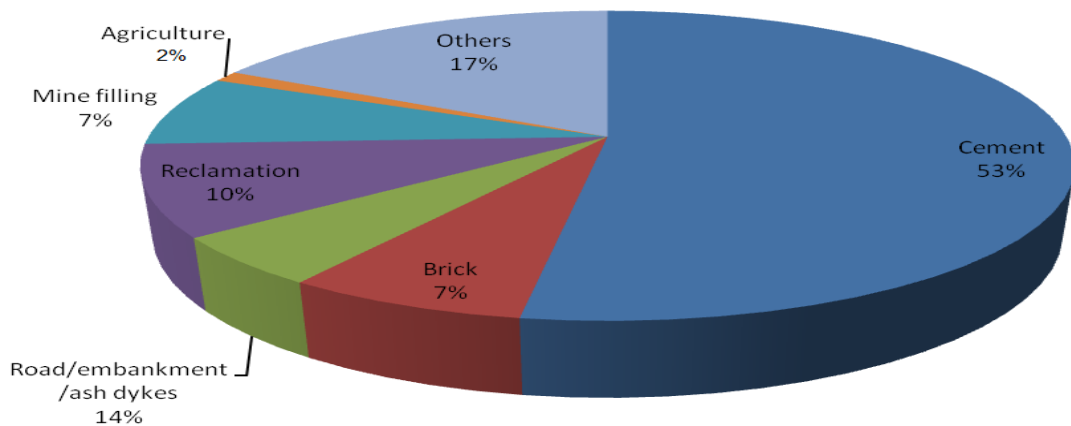
#### **2.4.5.1 Indian Government initiative for fly-ash utilization**

Fly-ash Utilization Programme (FAUP) has been started by Technology Information Forecasting and Assessment Council (TIFAC) in 1994 for the proper management and utilization of fly-ash as useful by-products for reducing environmental pollution and load on land for disposal (Dhadse et al., 2008). For motivating utilization of fly-ash various Governmental agencies and Institutes have taken initiation and have started research on characterization of fly-ash. IS 10153:1982 standard has been released by Bureau of Indian Standard (BIS) which designate the application of various coal combustion residues (Joshi, 2010; Sharma et al., 2012). MoEF has issued a regulation in 1999 for the 100% utilization of fly-ash generated from a power plant within the range of 50 Km<sup>2</sup> in a time period of 10-15 years (Bhattacharjee and Kandpal, 2002; Dhadse et al., 2008).

In India, about 55% fly-ash generated has been utilized in various processes like cement industries which shares major part of fly-ash utilization (26%), followed by roads/embankment/ash dykes (7%), reclamation of degraded land (5%), for mine filling (4%), in agriculture (1%), and various other processes sharing about 9% of total fly-ash utilization in India. However, fly-ash utilization in agricultural field is only 1%, whereas about 45% fly-ash remains un-utilized (CEA, 2011).



(A)



(B)

**Figure 2.3:** (A) Total fly-ash generation and its utilization in various processes; (B) Relative fly-ash utilization in various processes (CEA, 2012)

#### **2.4.6 Fly-ash as a Soil Ameliorant**

Use of fly-ash for soil amelioration has been advocated for decades as it is a rich source of soil macro- (P, K, Ca, Mg, and S) and micro- (Cu, Zn, Fe, Mn, etc.) nutrients required for plant growth (Yunusha et al., 2006), however nitrogen and carbon are limited nutrients in fly-ash, as it is generated from combustion of coal at a temperature of  $>1400^{\circ}\text{C}$  which results in volatilization of oxides of nitrogen and carbon. Class C fly-ash is used for neutralizing the acidic soils. Calcium carbonate equivalent (CCE) of fly-ash is mainly responsible for the neutralization of soil acidity (Yunusha et al., 2012). Thus, fly-ash amendment result into improvement of soil acidity, soil sodicity, nutrient supply, concentration and loss, and adverse soil physical properties (Yunusha et al., 2012).

Extensive research have been done for utilizing fly-ash for soil improvement and fly-ash management (Malik and Thapaliyal, 2009; Kruger and Surridge, 2009; Singh et al., 2010; Singh et al., 2011; Yunusha et al., 2012; Jayasinghe and Tokashiki, 2012). Low rate of fly-ash application to soil is reported to increase the VAM (vesicular arbuscular mycorrhiza) colonization (*Glomus aggregatum*) in plant roots (*Cajanus cajan*) and at high rate of application, growth is totally suppressed (Garampalli et al., 2005).

Bilski et al. (2011) studied growth of plants in fly-ash amended medium at lab scale and found that upto 10-30% fly-ash incorporation to the growth medium, a significant growth was observed for various plants as compared to pure fly-ash as growth medium. However, barley seedlings were capable to grow on the pure fly-ash concentration.

Pathan et al. (2003) studied the fly-ash application to Australian soil at the rate of 10% (w/w) and found a significant increase in water holding capacity, exchangeable P, CEC, varying degree of pH and a decrease in hydraulic conductivities. However, trace elements were found to be present in very low concentration.

Singh et al. (2011) studied the application of fly-ash at the rate of 10-50% (w/w) to soil and at the rate of 60-240 t/ha in a legume growing crop field and found a significant increase in crop yield and improvement in soil physical properties at 20-40% fly-ash application to soil and 120 and 180 t/ha fly-ash applications to soil. However, above

40% and 180 t/ha and below 10% and 120 t/ha reduction in growth was observed. This further signifies that fly-ash application to soil varies from soil to soil and crop to crop. Jayasinghe and Tokashiki (2012) studied the application of fly-ash to Brassica grown soil and found an increase in crop yield and improvement in the degraded grey soil in Japan. They propose fly-ash as a potential soil ameliorant for such type of degraded soil.

#### **2.4.7 Negative effects of fly-ash**

The following are some major negative effects of fly-ash (Kishore et al., 2010; Pandey et al., 2010):

- Variable pH (from 4-12) resulting into reduction in bioavailability of a few nutrients. Fly-ash having alkaline pH is more useful as it induces significant liming capacity to soil. At alkaline pH, leaching of heavy metals was observed to be less (Tripathi et al., 2010).
- High salinity
- High content of phytotoxic elements e.g., B, As, Mo, Se, etc. in the fly-ash sample (Sushil and Batra, 2006; Mittal et al., 2009). According to a study by Love et al. (2009) on *Cassia occidentalis* plant growing on weathered fly-ash suggests that fly-ash prompts genotoxicity in plant.
- Leaching from fly-ash: Fly-ash is mainly aluminosilicate along with oxides of various metals and trace metals. Most of the salts present in fly-ash are easily dissolved in water and have tendency to leach into groundwater (Neupane and Donahoe, 2009). However, Indian fly-ash has low trace metals content as compared to the fly-ash from other countries. However, Sushil and Batra (2006) studied on the heavy metal leaching from fly-ash and bottom-ash disposal sites in India and found a significant amount of Zn, Cr, Pb, Ni, Cu, Mn, Co, etc. trace metals which are at lower concentration and behave as a micronutrients required for plant growth and nutrition.
- Neupane and Donahoe (2009) studied on reduction of trace metal from leachate collected from sequential leaching of fly-ash with distilled and deionized water by SMZ zeolites (viz., HDTMA-Br modified clinoptilolite) which indicated an effective



reduction in concentration of trace metals viz., upto 30% of As, Mo and V; 80% of Cr; and 20% of Se and Sr associated with coal fly-ash.

- Radioactive radiation emission from fly-ash: various studies have reported radiation hazard from fly-ash containing concrete materials. Kovler (2012) reported higher level of radon emission from fly-ash containing concrete; however slight decrease in radon emanation coefficient was observed.

## **2.5 Organic and Inorganic Ash: An Integrated Approach**

### **2.5.1 Application of fly-ash and organic/inorganic supplement for soil amelioration (Externally added)**

Leaching of heavy metals from fly-ash is the major constrain for its use as soil ameliorant. However, various studies have reported use of fly-ash along-with organic/inorganic supplement leads to increase in crop yield by reduction in leaching of heavy metals and supplemented for nutrient like C, N, P which are deficient in fly-ash (Malik and Thapaliyal, 2009; Singh et al., 2010; Tripathi et al., 2010).

Wong and Selvam (2009) performed co-composting of fly-ash with sludge and reported that the heavy metal content of fly-ash decreased with the increase in compost ash content, however, Boron (B) content was increased with the increase in ash content.

In present scenario of growth and development, sewage sludge and fly-ash both are the potential wastes generated worldwide and posing problem to the environment. Masto et al. (2011) studied on the co-application of sewage sludge along with fly-ash to an acidic soil and found that fly-ash stabilizes the metal leaching from sewage sludge and improve soil physico-chemical properties by improving pH, EC, CEC, OC, BD, WHC and reducing the bioavailability of certain micronutrients like Zn, Cu, Co. They found that fly-ash application to 10-30% along with sewage sludge have significant positive effect over soil biological activities like increased enzyme activities. pH of fly-ash was found to be the controlling factor for the stabilization of sewage sludge as variation in pH lead to the release of heavy metals back to soil.

Hanani et al. (2010) studied on the application of coal fly-ash along with sewage sludge to a Maize growing crop field and observed a significant increase in pH to

alkaline range which is responsible for reduction in leaching of heavy metals from the integrated material. However, exchangeable  $Mg^{2+}$  ion content was found to decrease in Maize at higher rate of fly-ash application due to imbalances in  $Ca^{2+}$  content of the soil systems. High B content of fly-ash was considered as a major limiting factor for the application of fly-ash to soil, as B is required in a minimum amount of 0.5-1.0 mg/L.

Zhang et al. (2012) studied the leaching behavior of fly-ash and sewage sludge system in integration as an artificial soil and found that the pH of the integrated material remain constant and except for Cd, other heavy metals like As, Ni, Cu, etc from the leachate get stabilized. He further investigated the growth of plant on this artificial soil material and found different behavior of leachates from different plant species.

Kharuba et al. (2012) studied on the metal leaching behavior for an integrated fly-ash/sewage sludge mixture and found a significant reduction in leaching of Pb (95%), Cd (36%), Ni (78%), and Cu (35%) for different ratios and washing conditions.

Elyaeva and Haynes (2012) studied the effect of fly-ash along with organic additives like biosolids, poultry manure, green waste compost and poultry manure-derived biochar on soil properties and found that organic additives integrated fly-ash has resulted into significant increase in porosity, WHC, extractable Mg, K, Na, P and CEC. However, these additives have less effect over soil biological activities.

Thind et al. (2012) studied on integrated incorporation of fly-ash with rice husk ash (RHA) and bagasse ash to rice-wheat cropping systems for a three years field study and found a significant increase in grain yield from wheat and rice after incorporation. Further, they observed a positive effect over P content of wheat-rice cropping system and no heavy metal content in grains.

### **2.5.2 Application of fly-ash and organic material (crop residue) in pyrolysis**

From the above literature, it is clear that both fly-ash and biochar are potential soil ameliorating agents and their use has been studied separately for a long time on soil amelioration. However, the integrative approach for the application of both the biochar and fly-ash has not been studied in detail. Particularly, there exists only one report by

Palumbo et al. (2009) whereby a combined study was performed on the leaching properties of fly-ash along with biochar which were mixed externally in various proportions. The study revealed the higher release of carbon from biochar formed at low temperature, minimal leaching of heavy metals, and no toxicity exposition by the fly-ash and biochar leachates. This study also revealed that the carbon leaching was higher @10% biochar application to soil but reduced by the addition of fly-ash @10% and biochar @10% in soil. This study also advocates that the biochar prepared at higher temperature has more recalcitrant carbon and lower temperature biochar has more bioavailable carbon. In a similar study on organo-inorganic materials from crop residue and fly-ash, Gaind and Gaur (2004) revealed improved chemical and microbiological properties of compost and fly-ash prepared by composting with wheat straw and 2 % rock phosphate for 90 days without any detrimental effect on C/N ratio as well as microbial population.

It is observed that the external incorporation of biochar with fly-ash, will only lead to enhancing the physical properties in the soil amendment, whereas the materials chemical properties and its life cycle would not be affected significantly. Thus, it would be interesting to have an organo-inorganic fusion in the pyrolysis stage, whereby the bioavailable carbon and porosity of the material is significantly increased leading to significant impact upon the soil. Few investigation have indicated similar preparation of the materials, however the characterization of such materials and implementation in soil amelioration have not been studied.

Pan et al. (2010) studied the pyrolysis of *Nannochloropsis* sp., (a kind of green microalga) in presence of HZSM-5 catalyst in a fixed bed reactor in nitrogen flow at different temperatures and reported that the bio-oils in presence of catalyst had lower oxygen content (19.5 wt.%) and higher heating value (32.7 MJ/Kg) than the bio-oils directly prepared having higher oxygen content (31.1 wt.%) and lower heating value (24.6 MJ/Kg).

Yorgun et al. (2008) studied the pyrolysis of *Miscanthus giganteus* using activated alumina catalyst under nitrogen condition and reported an increase in bio-oil and syn-gas yield and a significant decrease in biochar yield from 40.2% to 23% with the increase in catalyst loading rate from 10 to 100%, respectively. Also, the bio-oil

produced by this process was highly oxygenated along with higher aliphatic and aromatic hydrocarbons which can be useful for production of transport fuels.

Sanna et al. (2011) studied on bio-oil production by pyrolysis of wheat and barley spent grains at temperatures between 460-540<sup>0</sup>C using an activated alumina bed and by measuring viscosity profile reported that activated alumina could promote liquefaction and inhibits charring. Thus, the increase in yield of bio-oil and reduction in biochar yield was reported. However, the biochar formed by this method retained a major share of original carbon and nitrogen content, thus suitable for use in soil amelioration.

A study on Fe and Ni metal impregnation in biomass pyrolysis by Collard et al. (2012) revealed a significant reduction in tar yield and increase in char yield. Fe metal was reported to increase char yield by rearrangement reactions of the cellulosic and lignin compound whereas Ni was reported to increase char yield by depolymerization reaction of xylan compounds of biomass. The aromaticity of the tar and char produce was also reported to decrease by the metal impregnation.

Gasco et al. (2012) studied on application of sewage sludge as well as sewage sludge derived biochar prepared at 500<sup>0</sup>C pyrolysis temperature on soil physico-chemical properties and found that pyrolyzed sewage sludge biochar was more stable than sludge, however, the organic matter content of sewage sludge ameliorated soil was higher than the biochar ameliorated soil.

Lu et al. (2011) studied on fast pyrolysis behavior of corncob in presence of 15% (w/w) ZnCl<sub>2</sub> at 340<sup>0</sup>C pyrolysis temperature and observed a significant increase in bio-oil yield specially furfural (FF) and acetic acid (AA) in presence of ZnCl<sub>2</sub> impregnated material and the solid byproduct obtained was further pyrolyzed to 500<sup>0</sup>C for 2 hours and washed with 0.5N HCl and was found to rich in activated carbon which need to further characterization. However, char yield was found to decrease with increase in pyrolysis temperature and concentration of ZnCl<sub>2</sub>.

Jun et al. (2006) studied on pyrolysis of fir wood, cotton stalk and pine wood in presence of six inorganic materials viz., Na<sub>2</sub>CO<sub>3</sub>, NaOH, NaCl, Na<sub>2</sub>SiO<sub>3</sub>, TiO<sub>2</sub> and HZSM-5. They found that Na<sub>2</sub>CO<sub>3</sub>, NaOH, NaCl, Na<sub>2</sub>SiO<sub>3</sub> have significant devolatilization effect at lower temperatures resulting into high char yield as compared

to the biomass sample derived biochar yield, whereas  $\text{TiO}_2$  and HZSM-5 integrated biomass samples show significant decrease in char yield.

Han et al. (2010) studied on pyrolysis of wheat straw in presence of CaO catalyst and found increased hydrogenation and volatilization than the wheat straw pyrolysis alone. However, mass loss was found to decrease with the increase in CaO content due to adsorption of volatiles on CaO.

Thus, from the present review it could be inferred that fly-ash and biochar both have been used as soil ameliorating agents, however, associated with certain risks are there with them. However, present review revealed that fly-ash has been used alongwith various organic and inorganic additives as well as biochar which improve further the leaching behavior from the composite. It was also observed that the thermal treatment further stabilizes the material towards recalcitrant nature and make them available for long time to the soil systems. However, there was a gap observed in between the biochar production from catalytic pyrolysis, its characterization and further utilization for soil amelioration. However, no study has been done for the fly-ash utilization in the pyrolysis of crop residue biomass. Thus, leading to the objectives of the present study as given below:

- Study of pyrolysis behavior of wheat crop residue in presence of varying proportions of fly-ash
- Characterization of pyrolysis solid products
- Soil amelioration studies of the obtained solid products at lab scale study

# CHAPTER III

## MATERIALS AND METHODS

## CHAPTER III

### MATERIAL AND METHODS

#### 3.1 Specifications of instruments used in the present study

In the present study, pyrolysis process was performed in a KI-180 muffle furnace (Khera) working on 220 V A/C. All chemicals, crop residue, fly-ash and their mixtures were weighed on weighing balances (Mettler Toledo JB 1603-C/FACT, with a range of 1 mg to 120 g $\pm$ 0.1 mg; and Citizen balance for weighing >120 g). UV-Vis absorption was measured on PC based Double Beam UV-Vis Spectrophotometer 2202 (Systronics) in a 1 cm quartz cuvette. pH measurement was performed on Mettler Toledo AG pH meter (FE 20/FG2 with a precision of  $\pm$ 0.01) with a calibration of pH=4.0, 7.0, and 9.2. Electrical conductivity was measured by Mettler-Toledo conductivity meter (FE 30/FG3 with a precision of  $\pm$ 0.01) with pre-calibrated electrodes at 1413  $\mu$ S/cm and 12.88 mS/cm. Centrifugation was performed in a REMI CompuFuge (CPR-24). KI 140 (b) Flame photometer 128 with FPM Compressor-126 (Systronics) working at 220 V A/C was used for determination of alkali metals (Na, K). Micronutrients (Fe, Cu, and Mn) were determined by using Atomic Absorption Spectrophotometer AA-7000 (Shimadzu). KI 215 (b) Incubator shaker was used for incubation purpose. All metal acid digestion was carried out inside the fume hood. Characterization of all biochar, fly-ash and biochar/fly-ash composite samples was performed on Bruker Tensor-27 Fourier Transform-Infrared Spectrophotometer (FTIR) in a range of 600-4000  $\text{cm}^{-1}$  (wave number) using solid KBr pellet. Data was analyzed using OPUS 7.0 software. SEM analysis was done by JEOL JSM-6610LV with 3 nm resolution in high vacuum mode, with 300000 magnification, with an accelerating voltage of 0.3-30 KV working in range of 10-270 Pa pressure, at the Cebtral Instrumentation Facility, IIT-Ropar. Platinum/gold coating by Gold coating unit- JEOL JFC-1600 was used for making samples conductive. Whatman filter paper (A grade) was obtained from Fisher Scientific UK Ltd (Bishop Meadow Road, Loughborough). Distilled water and Milli Q ultra pure water from Basic 360 Series, respectively, and Ultra 370 Series were used in this study.

### 3.2 Chemicals used in the present study:

In the present study, AR grade chemicals and reagents manufactured by SDFCL, Loba Chemie and Merck were used for various chemical analyses.

### 3.3 Preparation of solutions:

- 3.3.1 Ammonium molybdate: 25.0 g anhydrous ammonium molybdate was dissolved in 200 ml distilled water and mixed with a solution of sulphuric acid (280 ml of conc.  $\text{H}_2\text{SO}_4$  in 400 ml) and volume maintained upto 1L solution.
- 3.3.2 Stannous chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ): 2.5 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 100 ml glycerol by heating on a boiling water bath.
- 3.3.3 Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ). 1N solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  was prepared for determining organic carbon by dissolving 49 g in distilled water and diluted to 1L solution.
- 3.3.4 Ferrous ammonium sulphate ( $\text{FeSO}_4 \cdot \text{NH}_4(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ): 0.5N solution of ferrous ammonium sulphate was prepared for organic carbon determination by dissolving 192.0 g in distilled water and 15 ml concentrated  $\text{H}_2\text{SO}_4$  was added to dissolve and maintained upto 1L solution.
- 3.3.5 Sodium acetate:
- 3.3.5.1 Sodium acetate 1N (pH= 5.0): 82.0 g of salt was dissolved in distilled water. pH was maintained to 5.0 by adding 28 ml acetic acid and volume maintained upto 1L solution.
- 3.3.5.2 Sodium acetate 1N (pH= 7.0): 82.0 g of salt was dissolved in distilled water. pH was maintained to 7.0 by adding acetic acid and NaOH and volume was maintained to 1L solution.
- 3.3.6 Calcium chloride ( $\text{CaCl}_2$ ): 1N solution of calcium chloride was prepared by dissolving 73.0 g of anhydrous  $\text{CaCl}_2$  in distilled water and volume was maintained to 1L solution.
- 3.3.7 Calcium carbonate ( $\text{CaCO}_3$ ): 0.01N of standard  $\text{CaCO}_3$  for determination of CEC and exchangeable Ca+Mg ions was prepared by dissolving 0.5005 g of pure dried  $\text{CaCO}_3$  in 0.2N HCl (or 10 ml of 3N HCl). The solution was boiled to expel  $\text{CO}_2$  and diluted to 1L solution.



- 3.3.8 Ammonium chloride-ammonium hydroxide buffer solution (pH=10.0): 67.5 g  $\text{NH}_4\text{Cl}$  was dissolved in 570 ml of  $\text{NH}_4\text{OH}$  and diluted to 1L solution.
- 3.3.9 Eriochrome Black T indicator: 0.5 g of indicator and 4.5 g of hydroxylamine hydrochloride was dissolved in 100 ml of Triethanolamine.
- 3.3.10 Versene (Disodium salt of EDTA): Disodium dihydrogen ethylenediamine tetraacetic acid (versene) was used for determination of CEC and exchangeable Ca+Mg content. 2.0 g of versenate and 50.0 mg of  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$  were dissolved in 900 ml of water and final volume was maintained upto 1L solution. The normality of versene is then determined by titration of 25 ml of standard Ca solution.
- 3.3.11 Ammonium acetate extractant (pH=7.0): 1N ammonium acetate solution was prepared by dissolving 77.0 g of ammonium acetate in distilled water and diluted to 1L solution by maintaining pH to 7.0. This solution was used for extraction of Ca+Mg from soil samples.
- 3.3.12 For preparing DTPA (0.005M), 0.01M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and 0.1M TEA extractant: 1.967 g Disodium salt of DTPA and 13.3 ml of triethanolamine (TEA) were added in 400 ml double distilled water in a 500 ml flask. 1.47 g of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 500 ml double distilled water separately by shaking in 1L flask. DTPA+TEA mixture was added to  $\text{CaCl}_2$  solution and final volume of the solution was made up to 1L after adjusting the pH to 7.3 by using 1M HCl.
- 3.3.13 Sodium bicarbonate extractant: 42.0 g of  $\text{NaHCO}_3$  was dissolved in 600 ml distilled water and the volume was maintained to 1L by adjusting the pH of the solution to 8.5. This was used for the extraction of available phosphorus of soil.

#### **3.4 Collection and characterization of wheat crop residue (straw)**

Wheat crop residue (straw) was collected from a local field from a wheat-cotton cropping system near Talwandi Sabo area. The straw sample was 1.18 mm sized sieve. Bulk density of grinded straw sample was determined for observing the variation in density after grinding. Proximate analysis and ultimate analysis of crop residue were done by using hot air oven and muffle furnace according to ASTM standard methods (ASTM D5142) for the determination of %MC (moisture content),

%VOC (volatile organic compounds), %Ash content and %FC (fixed carbon). Ultimate analysis of crop residue sample was performed on a Elementar Vario-Cube CHNS analyser using 10-100 mg of sample and the loading of two samples per run in duplicate.

#### 3.4.1 Determination of bulk density of wheat crop residue: (Pathak et al., 1986)

The wheat straw sample (1.0 cm) or grinded straw (sieved through 1.18 mm sieve) were filled separately in 250 ml measuring cylinders. Tapped 10 times with hand and weighed the sample. Bulk density was calculated by using following formula:

$$\text{Bulk Density} = \frac{\text{Weight of sample}}{\text{volume of the cylinder}} \times 1000 \text{ kg/m}^3$$

#### 3.4.2 Proximate analysis of crop residue sample: (ASTM D5142)

5.0 g of chopped wheat straw was weighted in a pre-weighted petridish, and put in a hot air circulated oven at 105°C for 24 hours. After 24 hours, weight of the dried sample was taken. The moisture content was determined by the following formula:

$$\begin{aligned} \text{\% Moisture Content} \\ = \frac{\text{wet weight of crop residue} - \text{dry weight of crop residue}}{\text{dry weight of crop residue}} \times 100 \% \end{aligned}$$

The straw sample was grinded to pass through 1.18 mm sized sieve. The moisture content was determined by the above method.

1.0 g sample was taken in a silica crucible which was fitted with a lid. 4-5 drops of toluene was added for homogenised combustion and heated at 950°C temperature for 7 minutes. After 7 minutes, crucible was removed and cooled to room temperature in a desiccator. After cooling, weight loss was determined by weighing. Loss in weight is reported as volatile matter content.

1.0 g oven dried sample was placed in open quartz crucible in a muffle furnace at 750°C for 4 hours. Weight of residue was taken as ash content of sample. Fixed carbon content was determined by subtracting % moisture, % volatile matter and % ash content from 100.

Fixed carbon content was determined by using following formula:

$$\text{Fixed carbon} = \{100 - (\% \text{ VM (weight loss)} + \% \text{ Ash content})\}$$

#### 3.4.3 pH and Electrical conductivity determination of crop residue: (Luo et al., 2011)

A suspension of 1.0 g crop residue sample in 15 ml of double distilled water was stirred for 1 hour using a magnetic stirrer. The suspension was allowed to settle for 10 minutes. pH of the solution was determined using a calibrated pH meter. EC of the solution was determined by using a calibrated EC meter.

#### 3.4.4 Alkalinity determination of crop residue: (Yuan et al., 2011)

0.2 g crop residue sample was suspended in 40 ml of 0.03M HCl in a 150 ml stoppered conical flask and shaken for 2 hours on a mechanical shaker at  $25 \pm 1^\circ\text{C}$  temperature. The samples were removed and kept standing for 2 hours. Residual HCl was determined by titrating to pH 7.0 with 0.1M NaOH. The alkalinity is directly determined by the amount of HCl consumed by the sample by using following formula:

$$\text{Alkalinity (Centimoles/kg)} = \text{Meq of NaOH (Volume used} \times \text{Normality)} / \text{Weight of sample taken (g)}$$

#### 3.4.5 Determination of total Na and K content of crop residue (Jackson, 1958):

1.0 g crop residue was digested in a mixture of  $\text{HNO}_3$  and  $\text{HClO}_4$  (2:1, v/v). Na and K content were determined on a flame photometer.

#### 3.4.6 Determination of total P of crop residue by Molybdenum blue method: (Jackson, 1973)

0.5 g sample was digested in  $\text{HNO}_3$  and  $\text{HClO}_4$  (2:1, v/v). The digested sample was filtered and diluted to 100 ml by double distilled water. 5 ml of this solution was taken alongwith 5 ml of acidic ammonium molybdate and 4-5 drops of  $\text{SnCl}_2$  prepared in glycerol. Volume of the solution was maintained to 100 ml. Absorbance was taken at 700 nm by UV-Vis spectrophotometer after 10 but before 15 min. Concentration of

total phosphorus was determined by multiplying 1250 in absorbance obtained and the result was reported as mg/Kg P.

### 3.5 Collection and characterization of fly-ash sample

Fly-ash sample was collected from ash pond of the National Fertilizers Limited (NFL), Bathinda. Various physical and chemical properties of fly-ash sample were determined by following standard methods which are as followed:

#### 3.5.1 Determination of bulk density of fly-ash (Brady and Weil, 2002)

Fly-ash sample was filled separately in 100 ml measuring cylinders. Weight of the sample was taken after drying in a hot air circulated oven at 105<sup>0</sup>C for 24 hours. Bulk density was calculated by using following formula:

$$\text{Bulk Density} = \frac{\text{Dry weight of sample}}{\text{volume of the cylinder}} \times 1000 \text{ kg/m}^3$$

#### 3.5.2 Proximate analysis of fly-ash sample: (ASTM D5142)

1.0 g fly-ash was put in an oven at 105±5<sup>0</sup>C for 24 hours. Loss in weight was divided by total dry weight of crop residue for determining moisture content.

$$\% \text{ Moisture Content} = \frac{(\text{moist weight of fly ash}) - (\text{dry weight of flyash})}{\text{dry weight of crop residue}} \times 100 \%$$

1.0 g sample was taken in a silica crucible which was fitted with a lid. 4-5 drops of toluene was added for homogenised combustion and heated at 950<sup>0</sup>C temperature for 7 minutes. After 7 minutes, crucible was removed and cooled to room temperature in a desiccator. After cooling, weight loss was determined by weighing. Loss in weight is reported as volatile matter content

1.0 g oven dried sample was placed in open quartz crucible in a muffle furnace at 750<sup>0</sup>C for 4 hours. Weight of residue was taken as ash content of sample. Fixed carbon content was determined by subtracting % moisture, % volatile matter and % ash content from 100.

Fixed carbon content was determined by using following formula:

$$\text{Fixed carbon} = (100 - (\% \text{ VM (weight loss)} + \% \text{ Ash content}))$$

### 3.5.3 Determination of water holding capacity (WHC) of fly-ash (Modified Piper et al., 1944):

Whatman filter paper No. 42 with a dimension of 5 cm × 5 cm was weighed (A), it was saturated with water and weighed again (D). 10.0 g of soil/fly-ash sample was taken in the filter paper; it was saturated completely with water for half an hour. Excess water was removed and the filter paper with sample was weighed (B). The filter paper containing saturated soil sample was put in an oven at 105°C for 24 hours (until weight become constant). After 24 hours, weight of oven dried filter paper containing soil/ fly-ash was taken (C). % WHC was calculated by following formula:

$$\%WHC = \frac{B-C-D}{C-A} \times 100$$

### 3.5.4 Determination of pH and electrical conductivity of fly-ash sample (IS:2720 (Part 26)-1987 and IS: 14767-2000):

A suspension of 30.0 gm of air dried sample in 75 ml of double distilled water was taken in a 100 ml beaker covered by glass watch and stirred for 1 hour on a magnetic stirrer. The suspension was allowed to settle for 10 minutes and pH of the suspension was taken by using a calibrated pH meter. EC of the suspension was determined by using a calibrated EC meter.

### 3.5.5 Determination of alkalinity of fly-ash (Yuan et al., 2011):

0.2 gram sample was taken in 40 ml of 0.03M HCl in a 150 ml conical flask with lid and shaken for 2 hours on a mechanical shaker at 200 RPM at 25±1°C. It was kept standing for 2 hours. Residual HCl was determined by titrating to pH 7.0 with 0.1M NaOH. Alkalinity is determined by the amount of HCl consumed by the sample by using following formula:

$$\text{Alkalinity (Centimoles/kg)} = \{\text{Meq of NaOH (Volume} \times \text{Normality)} / \text{weight of sample taken (g)}\}$$

### 3.5.6 Determination of organic carbon and organic matter content of fly-ash (Modified Walkley, 1947):

For the estimation of organic carbon and organic matter, Walkey-Black rapid titration method (Walkley, A., 1947) was used. 10 ml  $K_2Cr_2O_7$  and 20 ml conc.  $H_2SO_4$  were added to a dried sample (1.0 g) by shaking. The solution was allowed to stand for 1 hour. 200 ml of DDW was added, followed by few drops of O-Phenanthroline–ferrous complex indicator. The solution was titrated against 0.1N ferrous ammonium sulphate solution. At the end point, the green coloured solution was sharply changed from blue to red or maroon tinge. The reading was noted down.

$$\% \text{ Organic carbon} = \frac{(\text{meq. } K_2Cr_2O_7 - \text{meq. } FeSO_4) \times 0.003 \times 100 \times \text{correction factor}}{\text{weight of sample}}$$

where, meq. (milli-equivalent) = volume  $\times$  normality.

Correction factor: 1.33 for 0.5 g of sample, 2.66 for 1.0 g of sample.

% Organic matter = % Organic carbon  $\times$  1.724

### 3.5.7 Determination of available phosphorus content of fly-ash sample: (Modified Olsen et al., 1954)

To the fly-ash sample (2.5 g), 1.0 g activated charcoal and 50 ml  $NaHCO_3$  extractant solution were added and the whole content was shaken on mechanical shaker for 30 minutes. Solution was filtered and 5 ml of filtered suspension was taken alongwith 5 ml ammonium molybdate in a 50 ml volumetric flask. About 1.0 ml of distilled water was added to avoid direct contact of ammonium molybdate before adding 4-5 drops of  $SnCl_2$ . The whole solution was left as such by maintaining 50 ml for 15-20 minutes until an intense blue colour was developed. Absorbance of the solution was taken at 660 nm.

Available P content was calculated by using following formula:

$$\text{Available P } \left( \frac{\text{mg}}{\text{Kg}} \right) = A \times \frac{\text{Total volume of extract (50.0 ml)}}{\text{Volume of extract taken for estimation (5.0 ml)} \times \text{weight of soil sample (2.5 g)}}$$

Where,

A= amount of phosphorus as observed from standard curve (mg),

### **3.6 Preparation and characterization of biochar from wheat crop residue in presence of various proportions of fly-ash at different pyrolysis temperature and hold time**

Air dried wheat straw sample was grinded to pass through a 1.18mm size sieve. Crop residue and fly-ash were mixed together in the ratio of 3:1, 1:1 and 1:3, respectively, to a total weight of mixture being kept constant at 10.0 g. Different samples were named as BCxy10 (10.0 g crop residue), BCxy31 (crop residue 7.5 g and fly-ash 2.5 g), BCxy11 (crop residue 5.0 g and fly-ash 5.0 g), BCxy13 (crop residue 2.5 g and fly-ash 7.5 g), and BCxy01 (fly-ash 10.0 g) as the proportions of crop residue and fly-ash were taken. The samples were taken in a ceramic crucible and pyrolyzed in a Muffle Furnace at 250<sup>0</sup>C, 350<sup>0</sup>C and 450<sup>0</sup>C pyrolysis temperature for 1, 2, 3 and 4 hours hold time with a heating rate of 18-20<sup>0</sup>C/min. After prescribed temperature hold time, the samples were taken and immediately transferred to a dessicator. The residual yield was calculated by difference in weight.

Model Code: BCxyoo'

Here, BC stands for biochar

x stands for pyrolysis temperature (2 for 250<sup>0</sup>C; 3 for 350<sup>0</sup>C and 4 for 450<sup>0</sup>C)

y stands for temperature hold time (1,2,3 and 4 for 1, 2, 3 and 4 hours, respectively)

o stands for proportion of crop residue (1,2 and 3 for 25, 50 and 75%, respectively)

o' stands for proportion of fly-ash (1,2 and 3 for 25, 50 and 75%, respectively)

Residual yield = (initial weight of sample-weight of sample after pyrolysis)

$$\% \text{Yield} = \frac{(\text{initial weight of sample (10)} - \text{weight of sample after pyrolysis})}{\text{initial weight of sample (10)}} * 100$$

Weight of fly-ash was also taken at various pyrolysis temperatures and temperature residence time. For calculating the actual biochar yield from crop residue portion in various combinations of biochar/fly-ash composite, weight of fly-ash part was subtracted from the total yield and yield of actual biochar was calculated by using following formula:

Actual Yield of biochar from crop residue = (total yield- yield of fly-ash part)

$$\text{Normalized Yield} = \frac{(\text{Yield obtained}-\text{Fly-ash yield}) \times (\text{Weight of composite biomass})}{\text{Weight of biomass in composite}}$$

**Table-3.1:** Code name for various biochar and biochar/fly-ash composite samples

S.N.	Crop residue/Fly-ash composition		Pyrolysis Temperature (°C)	Hold time (hour)	Code name
	% Crop residue	% Fly-ash			
1	100	0	250	1	BC2110
2	100	0	250	2	BC2210
3	100	0	250	3	BC2310
4	100	0	250	4	BC2410
5	100	0	350	4	BC3410
6	100	0	450	1	BC4110
7	100	0	450	2	BC4210
8	100	0	450	3	BC4310
9	100	0	450	4	BC4410
10	0	100	250	1	BC2101
11	0	100	250	2	BS2201
12	0	100	250	3	BC2301
13	0	100	250	4	BC2401
14	0	100	350	4	BC3401
15	0	100	450	1	BC4101
16	0	100	450	2	BC4201
17	0	100	450	3	BC4301



18	0	100	450	4	BC4401
19	25	75	250	1	BC2113
20	25	75	250	2	BC2213
21	25	75	250	3	BC2313
22	25	75	250	4	BC2413
23	25	75	350	4	BC3413
24	25	75	450	1	BC4113
25	25	75	450	2	BC4213
26	25	75	450	3	BC4313
27	25	75	450	4	BC4413
28	50	50	250	1	BC2111
29	50	50	250	2	BC2211
30	50	50	250	3	BC2311
31	50	50	250	4	BC2411
32	50	50	350	4	BC3411
33	50	50	450	1	BC4111
34	50	50	450	2	BC4211
35	50	50	450	3	BC4311
36	50	50	450	4	BC4411
37	75	25	250	1	BC2131
38	75	25	250	2	BC2231
39	75	25	250	3	BC2331
40	75	25	250	4	BC2431
41	75	25	350	4	BC3431
42	75	25	450	1	BC4131
43	75	25	450	2	BC4231
44	75	25	450	3	BC4331
45	75	25	450	4	BC4431

Percentage increase or decrease in yield of biochar from crop residue in various proportions of fly-ash was calculated by following formula:

$$\% \text{ increase or decrease in yield} = \frac{(\text{proposed yield of biochar} - \text{actual yield of biochar})}{\text{actual yield of biochar}} * 100$$

3.6.1 Proximate analysis of biochar and biochar/fly-ash composite samples (ASTM D5142):

1.0 g biochar or biochar/fly-ash composite sample was put in pre-weighted petri dish in hot air circulated oven at 105<sup>0</sup>C for 24 hours. Dry weight was taken after 24 hours and % moisture content was determined by following formula:

$$\% \text{ Moisture Content} = \frac{\text{wet weight of sample} - \text{dry weight of sample}}{\text{dry weight of sample}} \times 100 \%$$

1.0 g sample was taken in a silica crucible which was fitted with a lid. 4-5 drops of toluene was added for homogenised combustion and heated at 950<sup>0</sup>C temperature for 7 minutes. After 7 minutes, crucible was removed and cooled to room temperature in a desiccator. After cooling, weight loss was determined by weighing. Loss in weight is reported as volatile matter content

1.0 g oven dried sample was placed in open quartz crucible in a Muffle Furnace at 750<sup>0</sup>C for 4 hours. Weight of residue was taken as ash content of sample. Fixed carbon content was determined by subtracting % moisture, % volatile matter and % ash content from 100.

$$\text{Fixed carbon} = \{100 - (\% \text{Moisture} + \% \text{Volatile matter} + \% \text{Ash}) \text{ contents}\}$$

3.6.2 Ultimate analysis of biochar and biochar/fly-ash composite samples

Ultimate analysis of biochar and biochar/fly-ash composite samples was performed on a Elementar Vario-Cube CHNS analyzer using 10-100 mg of sample and the loading of two samples per run in duplicate.

3.6.3 Determination of pH and EC of biochar and biochar/fly-ash composite materials (Luo et al., 2011):

A suspension of biochar or biochar/fly-ash composite (1.0 g) in 15 ml double distilled water was taken in 100 ml beaker which was covered with watch glass and stirred for about 1 hour on a magnetic stirrer. The suspension was allowed to settle for 10

minutes and pH of the suspension was taken by using a calibrated pH meter. EC of the suspension was determined by using a calibrated EC meter.

#### 3.6.4 Alkalinity determination of biochar and biochar/fly-ash composite (Yuan et al., 2011):

To a biochar or biochar/fly-ash composite (0.2 g sample was added) 40 ml of 0.03M HCl in a 150 ml stoppered conical flask and shaken for 2 hours at 200 RPM and  $25\pm 1^{\circ}\text{C}$  and kept standing for 2 hours. Residual HCl was determined by titrating to pH 7.0 with 0.1M NaOH. Alkalinity is determined by the amount of HCl consumed by the sample using following formula:

Alkalinity (Centimoles/kg) = Meq of NaOH (Volume  $\times$  Normality)/Weight of sample (g)

#### 3.6.5 Determination of total Na and K content of crop residue (Jackson, 1958):

1.0 g sample was digested in a mixture of  $\text{HNO}_3$  and  $\text{HClO}_4$  (2:1 v/v). Na and K content were determined on a flame photometer.

#### 3.6.6 Determination of total P of biochar and biochar/fly-ash composite samples by using Molybdenum blue method: (Jackson, 1973)

0.5 g sample was digested in 10 ml 2:1 (v/v) mixtures of  $\text{HNO}_3$  and  $\text{HClO}_4$ . The digested sample was filtered and diluted to 100 ml by double distilled water. 5 ml of this solution was taken alongwith 5 ml of acidic ammonium molybdate and 4-5 drops of  $\text{SnCl}_2$  solution prepared in glycerol. Volume of the solution was maintained to 100 ml. Absorbance was measured at a wavelength of 700 nm by UV-Vis spectrophotometer after 10 but before 15 min. Concentration of total phosphorus was determined by multiplying 1250 in absorbance obtained and the result was reported as mg/kg P.

#### 3.6.7 Scanning electron microscopy (SEM) analysis of fly-ash, biochar, and biochar/fly-ash composite material

SEM analysis of the biochar and biochar/fly-ash composite samples, prepared at 250<sup>0</sup>C and 450<sup>0</sup>C at 4 hours hold time, was done using JEOL JSM-6610LV Model instrument. A platinum coating was applied for providing conductivity to the samples.

#### 3.6.8 Fourier Transformed Infra-red (FTIR) analysis of crop residue, biochar, fly-ash, and biochar/fly-ash composite material

FTIR analysis of wheat crop residue, fly-ash, biochar, and biochar/fly-ash composite samples was performed with BRUKER Tensor-27 instrument with OPUS 7.0 as the data processing software, data acquisition, manipulation, and evaluation. To the sample, KBr was added in the ratio 1:20 and mixed well and KBr pellet was prepared using hydraulic press. The pellet was mounted on the FTIR spectra and spectrum was recorded at 600-4000 cm<sup>-1</sup>.

### 3.7 Collection and characterization of soil sample

Soil sample was collected in polythene bag from a cotton-wheat cropping system field nearby the University campus (30.1754N and 74.9371E) with the help of spade and soil corer from a depth of 5-15 cm. Soil sample was collected from five different places randomly inside same crop field of 100 × 100 m<sup>2</sup> area and mixed together for homogenization. Also, soil sample was collected from a soil corer from each place in separate polythene bag for determining soil bulk density. Various physical and chemical properties were determined for air dried soil by standard methods as described below.

#### 3.7.1 Determination of bulk density of soil sample: (Brady ad Weil, 2002)

Soil samples were collected from different quadrants by a soil corer designed in the lab. The samples were transferred and sealed in polybags for analysis in laboratory. The soil samples were put in oven at 105<sup>0</sup>C for 24 hours. Bulk density was determined by dividing oven dried weight of soil by volume of the soil corer. Bulk density was represented in g/cm<sup>3</sup>.

$$\text{Bulk Density} = \frac{\text{Oven dry weight of soil}}{\text{Volume of soil corer}} \text{ g/cm}^3$$

### 3.7.2 Determination of moisture content of soil sample (IS: 2720 (Part II)-1973):

A known weight of soil sample was put in oven at 105<sup>0</sup>C for 24 hours (until weight become constant). %Moisture content was determined by dividing change in weight of soil after oven drying to the initial weight of the soil and multiplied by 100.

## 3.8 Amendment of biochar and biochar/fly-ash composite (CFB) in soil

Biochar and biochar/fly-ash composite were amended to air dried soil at the rate of 10 Mg/ha. Amended soil samples were stored in polythene bags for various physico-chemical analyses.

Following parameters were studied for soil (2.25 mm sieved sample) and biochar (and biochar/fly-ash composite prepared at 250<sup>0</sup>C and 450<sup>0</sup>C pyrolysis temperature) amended soil samples.

**Note:** Following properties have been also determined for unamended soil sample as control soil.

### 3.8.1 Determination of bulk density of amended soil samples (Brady and Weil, 2002):

2.25 mm sieved sample was filled in 10 ml measuring cylinder and put in oven at 105<sup>0</sup>C for 24 hours. Bulk density was determined by using following formula:

$$\text{Bulk Density} = \frac{\text{dry weight of soil (gm)}}{\text{volume of the cylinder (cm}^3\text{)}} \text{ g/cm}^3$$

### 3.8.2 Determination of % Porosity (Brady and Weil, 2002):

It was calculated by the following formula:

$$\% \text{ Porosity} = 100 - \{100 - (D_p/D_b)\} \times 100$$

Where,  $D_p$  = particle density of soil (usually 2.65 g/cm<sup>3</sup>)

$D_b$  = bulk density of soil sample (g/cm<sup>3</sup>)

### 3.8.3 Determination of Water Holding Capacity (%WHC) of soil and amended soil samples (Piper, 1944):

Whatman filter paper No. 42 with a dimension of 5 cm × 5 cm was weighed (A), it was saturated with water and weighed again (D). 10 gm of soil/ fly-ash sample was taken in the filter paper; it was saturated completely with water for half an hour. Excess water was removed and the filter paper with sample was weighed (B). The filter paper containing saturated soil sample was put in an oven at 105<sup>0</sup>C for 24 hours (until weight become constant). After 24 hours, weight of oven dried filter paper containing soil/ fly-ash was taken (C). % WHC was calculated by following formula:

$$\%WHC = \frac{B-C-D}{C-A} \times 100$$

3.8.4 Determination of pH and EC of soil and amended soil samples (IS:2720 (Part 26)-1987 and IS: 14767-2000):

A suspension of 30.0 g of air dried sample in 75 ml of double distilled water was taken in a 100 ml beaker covered by watch glass and stirred for 1 hour on a magnetic stirrer. The suspension was allowed to settle for 10 minutes and pH of the suspension was taken by using a calibrated pH meter. EC of the suspension was determined by using a calibrated EC meter.

3.8.5 Determination of Cation Exchange Capacity (CEC) (IS: 2720 (Part XXIV)-1976):

To 5.0 g of soil sample taken in 100 ml centrifuge tube 50 ml of 1N sodium acetate (pH=5.0) was added and stirred with policeman-tipped rod. The suspension was digested in a near boiling water bath for 30 minutes with stirring. The suspension was centrifuged (10000 rpm for 5 minutes) and decanted to remove supernatant liquid containing the soluble salts. The residue was washed with 1N sodium acetate (pH=5.0) with 30 minutes digestion, in a boiling water bath, followed by 1N CaCl<sub>2</sub> washing. Excess salts were removed by washing with 80% acetone, until excess CaCl<sub>2</sub> was removed (indicated by negative AgNO<sub>3</sub> test for chloride). The washings were separated by centrifugation after the treatment. Calcium exchanged for all other cations in soil was removed by washing with 1N sodium acetate (pH=7.0) solution (5 × 50 ml) and centrifuged and supernatant collected in 500 ml conical flask. 10 ml of

ammonia buffer was added to maintain pH at 10.0. EBT indicator (2 drops) was added and the solution was titrated against standard versene solution (~ 0.1N) till a deep ocean blue colour was developed.

Calculation: the milli-equivalent cation exchange capacity per 100 g of soil was calculated as followed:

$$\text{meq exchange capacity per 100 g} = \text{ml of versene solution} \times N \times \frac{100}{\text{mass of soil sample}}$$

where, N is the normality of the versene solution.

3.8.6 Determination of exchangeable calcium (Ca) and magnesium (Mg) contents of soil and amended soil samples (Cheng and Bray, 1951):

Ca<sup>2+</sup> determination: To a dried soil sample (5.0 g) in 150 ml conical flask, 25 ml of neutral ammonium acetate (1N) extractant was added. The solution was shaken for 5 minutes on a mechanical shaker at 200 rpm/min and filtered through Whatman No.1 filter paper. 5 ml of filtered solution was taken in a 100 ml conical flask along with 5 ml NaOH (4N). 40-50 mg of the murexide indicator powder was added. This solution was titrated with 0.01N EDTA solution until the colour changes gradually from orange-red to purple. A reagent blank was studied for any metal impurity. The volume of EDTA used for titration was noted down.

When expressed on soil weight basis:

$$\text{Ca}^{++} \text{ meq/100 g} = \frac{\text{extract volume (25 ml)} \times 100}{\text{wt of soil} \times 1000} \times \text{Ca conc. in me/L}$$

Ca<sup>2+</sup> + Mg<sup>2+</sup> determination: To a dried soil sample (5.0 g) in 150 ml conical flask, 25 ml of neutral ammonium acetate (1N) extractant was added. The solution was shaken for 5 minutes on a mechanical shaker at 200 rpm/min and filtered through Whatman No.1 filter paper. 5 ml of filtered solution was taken in a 100 ml conical flask along with 5 ml NH<sub>4</sub>OH+NH<sub>4</sub>Cl buffer to maintain pH at 10.0 and 1-2 drops of EBT indicator. This solution was titrated with 0.01N EDTA solution until the colour changes gradually

from wine-red to a deep ocean blue. A blank was taken parallel. The volume of EDTA used for titration was noted down.

Total  $\text{Ca}^{2+} + \text{Mg}^{2+}$  was calculated by using following formula:

$$\text{Ca}^{2+} + \text{Mg}^{2+} \text{ meq/100 gm} = \frac{\text{extract volume (25 ml)} \times 100}{\text{wt of soil} \times 1000} \times \text{Ca + Mg conc.in me/L}$$

3.8.7 Determination of Soil Organic Carbon and Organic matter content (Walkley, 1947):

For the estimation of organic carbon and organic matter, Walkey-Black rapid titration method (Walkley, A. 1947) was used. 10 ml  $\text{K}_2\text{Cr}_2\text{O}_7$  (0.05N) and 20 ml conc.  $\text{H}_2\text{SO}_4$  were added to a dried sample (1 g) by shaking. The solution was allowed to stand for 1 hour. 200 ml of double distilled water was added followed by few drops of o-Phenanthroline–ferrous complex indicator. The solution was titrated against 0.1N ferrous ammonium sulphate solution. At the end point, the green coloured solution was sharply changed from blue to red or maroon tinge. The reading was noted down.

$$\% \text{ Organic carbon} = \frac{(\text{meq. K}_2\text{Cr}_2\text{O}_7 - \text{meq. FeSO}_4) \times 0.003 \times 100 \times \text{correction factor}}{\text{weight of soil}}$$

where, meq. (milli-equivalent) = volume  $\times$  normality.

Correction factor: 1.33 for 0.5 g of sample, 2.66 for 1.0 g of sample.

% Organic matter = % Organic carbon  $\times$  1.724

3.8.8 Determination of total potassium (K) and total sodium (Na) contents of soil and amended soil samples by Flame photometer (Jackson, 1958):

To a soil sample (1 g) was added a mixture of nitric acid and perchloric acid (2:1, v/v). The digested sample was cooled and diluted to 100 ml and filtered through Whatman No. 1 filter paper. The solution thus obtained was analyzed on Flame photometer for Na and K.

3.8.9 *Determination of total P of soil and amended soil samples by using Allen's method* (Jackson, 1973):



To a 0.5 g of soil sample was added in 10 ml of 1:2 (v/v) mixtures of nitric acid and perchloric acid and digested till appearance of white fumes. The solution was cooled by adding 25 ml double distilled water and filtered through Whatman filter paper No. 1 and the residue was washed repeatedly with double distilled water. The filtrate recovered was diluted to 100 ml by addition of double distilled water. 5 ml of this solution was taken along with 5 ml of ammonium molybdate in a 100 ml volumetric flask and 1.0 ml of distilled water added. 4-5 drops of stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) in glycerol was added in each flask and final volume was maintained to 100 ml. The absorbance of the solutions was recorded after 10-15 minutes of stay, at wavelength maxima of 700 nm. It was put for 10-15 minutes for developing an intense blue colour. Total P content was calculated by using following formula:

$$\text{Total P (mg/kg)} = \text{OD at 700 nm} \times 1250$$

**Caution:** The sample should not be dried completely, as it would lead to explosion.

3.8.10 Determination of Available P content of soil and different biochar amended soil samples (Olsen et al., 1954):

To the soil sample (2.5 g), 1.0 g activated charcoal and 50 ml  $\text{NaHCO}_3$  extractant solution were added and the whole content was shaken on mechanical shaker at 200 rpm for 30 minutes. Solution was filtered and 5 ml of filtered suspension alongwith 5 ml ammonium molybdate in a 50 ml volumetric flask. About 1.0 ml of distilled water was added to avoid direct contact of ammonium molybdate before adding 4-5 drops of  $\text{SnCl}_2$  solution (prepared in glycerol). The whole solution was left as such by maintaining 50 ml for 15-20 minutes until an intense blue colour was developed. Absorbance of the solution was taken at 660 nm.

Available P content was calculated by using following formula:

$$\text{Available P } \left( \frac{\text{mg}}{\text{Kg}} \right) = A \times \frac{\text{Total volume of extract (50.0 ml)}}{\text{Volume of extract taken for estimation (5.0 ml)} \times \text{weight of soil sample (2.5 g)}}$$

Where,

A= amount of P observed from standard curve (mg),

3.8.11 Determination of micronutrients (Cu, Fe and Mn) of soil and amended soil samples by using Atomic Absorption Spectrophotometer (AAS) (Lindsay and Norvell, 2008):

To a soil sample (10.0 g) taken in a 100 ml stoppered polypropylene bottle, 20 ml of DTPA extractant solution was added and shaken at 150 rpm/min at 25<sup>0</sup>C for 2 hours. The solution was filtered in polypropylene bottle through Whatman No. 1 filter paper and stored in polypropylene bottles for further analysis. A blank was prepared parallel. The extract so obtained is used for estimation of different micronutrients by AAS.

Calculation:

Content of micronutrient in the sample (mg/Kg) = C µg/ml × 2 (dilution factor)

Where:

Dilution factor = 2.0 (soil sample taken = 10.0 gram and DTPA used = 20 ml)

Absorbance reading on AAS of the soil extract being estimated for a particular element = X

Concentration of micronutrient as read from the standard curve for the given absorbance (X) = C µg/ml.

# CHAPTER IV

## RESULTS

## CHAPTER-IV

### RESULTS

The result of the present study can be divided into following sections:

4.1 Physico-chemical characteristics of wheat crop residue used for the present study

4.2 Physico-chemical characteristics of fly-ash used for present study

4.3 Preparation of biochar and biochar/fly-ash composite at different pyrolysis temperatures

4.4 Physico-chemical characteristics of biochar and biochar/fly-ash composite

4.5 Physico-chemical characteristics of soil used for present study

4.6 Physico-chemical characteristics of amended soil samples used for present study

#### **4.1 Physico-chemical characteristics of wheat crop residue used for present study**

Wheat crop residue was obtained from the nearby fields in Bathinda and was characterized by various proximate and ultimate analyses. The results of the analysis are given in **Table-4.1**. The wheat straw was grinded to pass through 1.18 mm sieve. However, upon grinding, the bulk density increased four folds from 37.6 kg/m<sup>3</sup> to 142.9 kg/m<sup>3</sup>. Similarly, moisture content of wheat straw was found to decrease from 15.5% in as such wheat straw to 6.8% in grinded sample. Proximate analysis of grinded wheat straw is given in **Table-4.1**. Proximate analysis results of wheat straw show a volatile matter content of 79.97%, fixed carbon of 7.26% and ash content of 5.96% (**Table-4.1**). Empirical formula of the wheat crop residue is found to be C<sub>1.23</sub>H<sub>2.03</sub>O as calculated from the ultimate analysis. Total potassium content was significantly high and ranged from 109.6-115.7 mg/kg. Total phosphorus content was determined by molybdenum blue method after digesting the sample in mixed acid (HNO<sub>3</sub> and HClO<sub>4</sub> in 2:1 v/v) and was found to be 70.7 mg/kg. Alkalinity of the straw sample was found to 10.0 centimoles/kg and accounted to the basic cations present in biomass sample.

Micronutrients (Fe, Cu and Mn) were analyzed for crop residue sample. The sample does not show the presence of these micronutrients.

**Table-4.1:** Physico-chemical characterization of wheat crop residue

Parameter Name	Unit	Mean±SD	Reference
<b>Physical properties</b>			
Bulk density (wheat straw)	kg/m <sup>3</sup>	37.60±0.89	Pathak et al., 1986
Bulk density (grinded straw)	kg/m <sup>3</sup>	142.89±1.53	Pathak et al., 1986
Moisture	%	15.46±0.96	ASTM D5142
<b>Proximate analysis:</b>			
Moisture (grinded straw)	%	6.82	
Volatile matter	%	79.97	
Ash	%	5.96	
Fixed carbon	%	7.26	
<b>Ultimate analysis:</b>			
C	%	41.85	
H	%	5.78	
N	%	0.45	
S	%	0.40	
H/C		0.138	
N/C		0.011	
<b>Physico-chemical properties</b>			
pH		7.2	Luo et al., 2011
EC	mS/cm	73.1	Luo et al., 2011
Alkalinity	Centimoles/kg	10.0±0.00	Yuan et al., 2011
Total Na	mg/kg	9.27±0.10	Jackson, 1958
Total K	mg/kg	110.73±4.51	Jackson, 1958
Total P	mg/kg	70.63±4.42	Jackson, 1973
			Lindsay and Norvell, 2008
<b>Micronutrients:</b>			
Cu	mg/kg	nd	
Mn	mg/kg	nd	
Fe	mg/kg	nd	

## 4.2 Physico-chemical properties of fly-ash

Fly-ash is one of the major wastes generated at global level. Fly-ash generated in India during 2010-11 was 131.09 MT (CEA, 2011). Fly-ash is one of the local issues of Bathinda particularly with the thermal power plant and NFL in the background of the district, with an average annual fly-ash generation of more than 1.94 MT (CEA, 2012). The fly-ash generation in the district would increase with new thermal power plants establishment proposed for the coming years at Goindwal Sahib and Talwandi Sabo, with a projected power generation being ~6460 MW/Yr (TSPL, 2013; PSPCL, 2013; <http://www.mapsofindia.com/energy/punjab-thermal-power-plants-map.html>). For the present study, fly-ash sample was brought from National Fertilizers Limited (NFL), Bathinda. According to annual environment statement (2008-09) of this organization, fly-ash generated from this organization was 0.2 MT/Yr tonnes of which about 96% is disposed off as land fill. Thus, fly-ash has a good scope for its utilization as soil ameliorant.

**Table-4.2:** Composition of fly-ash used for this study (Source: Annual environment statement of NFL, Bathinda, 2008-09)

Parameter Name	Value (%)
Combustible matter	7.0-8.0
On Combustible free basis	
SiO <sub>2</sub>	58.34
Al <sub>2</sub> O <sub>3</sub>	32.11
Fe <sub>2</sub> O <sub>3</sub>	6.85
CaO	0.84
MgO	0.62
Na <sub>2</sub> O	0.51
K <sub>2</sub> O	0.44
SO <sub>3</sub>	0.17
P <sub>2</sub> O <sub>5</sub>	0.11

Fly-ash mineral composition is reproduced in **Table-4.2** (as per NFL Annual environment statement, 2008-09). The aluminosilicate content was 90%, whereas iron oxide ( $\text{Fe}_3\text{O}_4$ ) content was found to be 6.85% (on combustible free basis). Low content of calcium oxide ( $\text{CaO}$ , 0.84%) indicates that the fly-ash is of class F as per the ASTM classification system (ASTM C618-93).

The fly-ash sample was studied for various physico-chemical parameters in correlation to crop residue and soil amelioration. Results for various physico-chemical properties of fly-ash are given in **Table-4.3**. Bulk density of fly-ash sample ranged from 63.0-66.0  $\text{kg/m}^3$ . Moisture content was very low i.e., 0.02-0.08%, as it is collected from the electrostatic precipitator. Water holding capacity of fly-ash used in the present study ranged from 52.89-53.43% which was much higher than a typical soil. Proximate analysis of the fly-ash used in this study is represented in **Table-4.3**. Ash (non-combustible) is a major constituent at 87.26%, whereas volatile matter and fixed carbon contents were 5.75% and 6.63%, respectively.

Fly-ash was found to be acidic with pH of 5.6, using a 1:2.5 (w/v) water suspension (IS: 2720 (Part 26)-1987). However, the electrical conductivity of fly-ash sample was 1324  $\mu\text{S/cm}$ , which is indicative of less soluble inorganic matter present in the fly-ash. Alkalinity of fly-ash was determined using a modified back titration method, used for the study of biochar samples (Yuan et al., 2011). Alkalinity of fly-ash was 25.0 Centimoles/kg, as fly-ash sample was acidic, bicarbonate and other weak bases contribute to the alkalinity of fly-ash. Cation exchange capacity of the fly-ash sample was found to be 12.28 Centimoles/100g. Organic carbon and organic matter content were calculated by Walkley-Black titration method and were found as 2.10% and 3.62%, respectively, which is accounted to the higher volatile matter content of fly-ash (ASTM D5142). Total phosphorus content of fly-ash was 0.11% (NFL Annual Environment Statement, 2008-09) and the available phosphorus content was found to be 0.03% (Olsen et al., 1954). These results indicate that 31% of the total phosphorus is in the available phosphorus form, which is available to the plants. Fly-ash is considered as a good source of plant micronutrient, viz., Fe, Mn and Cu, and was analyzed as diethylene triaminepentaacetic acid (DTPA) extractable micronutrients.

The DTPA extractable iron, manganese and copper were 18.7, 1.6 and 0.9 mg/kg, respectively.

**Table-4.3:** Physico-chemical characterization of coal fly-ash

Parameter Name	Unit	Mean±SD	Reference
<b>Physical properties</b>			
Bulk density	kg/m <sup>3</sup>	65.0 ±1.1	Brady and Weil, 2002
Moisture content	%	0.05±0.03	(IS:2720 (Part II)-1973)
Water holding capacity (WHC)	%	53.2±0.27	Piper, 1947
<b><u>Proximate analysis:</u></b>			ASTM D5142
Moisture	%	0.36	
Volatile matter	%	5.75	
Ash	%	87.26	
Fixed carbon	%	6.63	
<b>Physico-chemical properties</b>			
pH		5.6±0.01	IS: 2720(Part-26)
Electrical conductivity	µS/cm	1324±35	IS: 14767-2000
Alkalinity	Centimoles/kg	25.0±7.1	Yuan et al., 2011
Cation exchange capacity (CEC)	Centimoles/100gm	12.28±0.28	IS: 2720(Part-XXIV)
Organic carbon	%	2.1±0.05	Walkley, 1947
Organic matter	%	3.6±0.08	Walkley, 1947
Available phosphorus (P)	mg/kg	36.1±0.61	Olsen et al., 1954
<b><u>Micronutrients</u></b>			Lindsay and Norvell, 2008
Cu	mg/kg	0.92±0.01	
Mn	mg/kg	1.62±0.00	
Fe	mg/kg	18.72±0.26	



### 4.3 Preparation of biochar and biochar/fly-ash composite (CFB)

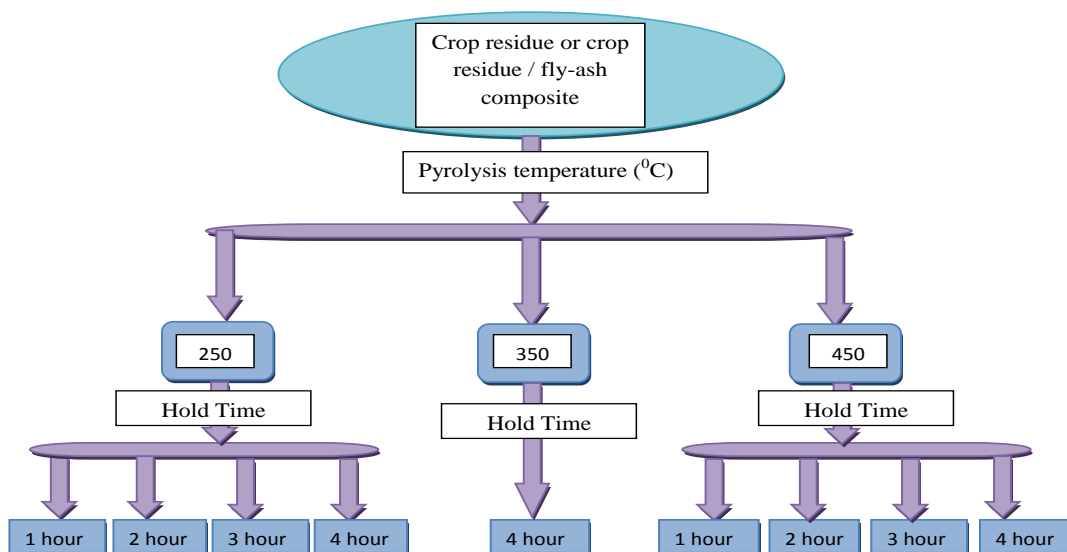
Fly-ash has suggestively been used in the formation of various zeolites like zeolite A, Faujasite, zeolite P1 after alkali treatment and have been studied for various catalytic processes. Microporous and mesoporous materials like zeolites have been utilized in various biorefinery concepts, particularly, the catalytic pyrolysis of biomass for its efficient management (Zhou et al., 2011). Thus, use of fly-ash directly instead of the zeolites would lead to an efficient and greener method for catalytic pyrolysis. However, there have been no reports on the study of the effect of fly-ash on the pyrolytic degradation of biomass. Thus, a preliminary study on the biochar prepared from the fly-ash catalyzed slow pyrolysis was carried out. The slow pyrolysis of wheat straw is carried out in presence of fly-ash at various composition, temperature and hold time.

Thus, in the present study, we have prepared and characterized the biochar and biochar/fly-ash composite (CFB) material for various physico-chemical properties. The study investigates the effect of fly-ash on the biochar formation by performing experiments at various temperatures, in a limited supply of air.

#### 4.3.1 Preparation of biochar

Pyrolysis of biomass in limited or no supply of oxygen is one of the methods for thermo-chemical conversion of biomass. Pyrolysis of crop residue biomass results in the production of bio-oil, syn-gas and solid residue called biochar. Pyrolysis temperature, heating rate and temperature hold time are the essential parameters which affect the yield and properties of obtained products i.e., biochar, bio-oil and syn-gas (Demirbas, 2006; Demiral and Ayan, 2011). The physico-chemical nature of the biochar produced depends upon the pyrolysis conditions. In this study, two pyrolysis parameters viz., pyrolysis temperature and hold time are taken into consideration as shown in **Scheme-4.1**. As the material was a composite mixture, the third dimension studied was that of the impact of fly-ash on the pyrolysis of crop residue biomass by varying the fly-ash addition to biomass composition in the ratio of 3:1, 1:1 and 1:3 (w/w).

The biochar/fly-ash composite materials were prepared by heating various ratio of biomass and fly-ash viz., 3:1, 1:1 and 1:3 (w/w) in limited oxygen environment. The pyrolysis of composite mixture was carried at 250°C, 350°C and 450°C. The heating rate of the substrate was constantly maintained between 18-20°C/min for all treatments. This heating rate signifies a slow pyrolysis process. Hold time was varied from 1 h to 4 h for different treatment temperatures (250, 350 and 450°C). It was observed that onset of charring of the biomass cellulose and hemicelluloses occur at 250°C, thus leading to different properties being imparted on the biochar composites (Sanchez-Silva et al., 2013). Upon slow pyrolysis at 350°C, cellulose and hemicelluloses degrade with partial degradation of lignin (Sanchez-Silva et al., 2012). However, under slow pyrolysis conditions at 450°C, optimum decomposition of cellulosic and hemicelluloses components of biomass occurs and whereas lignin shows a significant degradation (Lee et al., 2013; Sanchez-Silva et al., 2013).



**Scheme 4.1:** Various crop residue and crop residue/fly-ash composite pyrolysis experiments

Further for comparison, independent pyrolysis of crop residue and fly-ash was also performed and compared at the above said conditions. The results of the study are as given in **Table-4.4**. In general, with the increase in hold time from 1 hour to 4 hour for pyrolysis temperatures of 250°C and 450°C, the residue yield decreases in case of biochar, fly-ash and biochar/fly-ash composite.

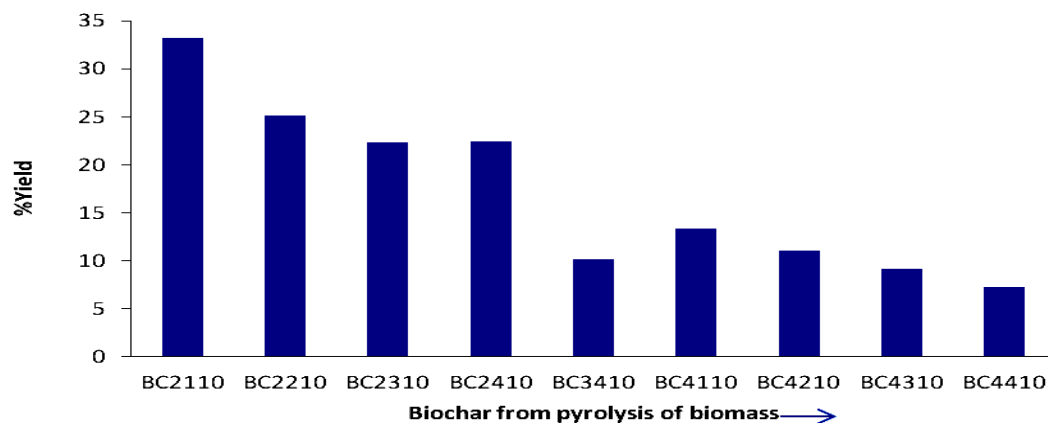
The fly-ash underwent a small change in residual mass of an insignificant 0.27% and 0.44% at pyrolysis temperatures of 250<sup>0</sup>C and 350<sup>0</sup>C, respectively. However, when the pyrolysis temperature is increased to 450<sup>0</sup>C, fly-ash underwent a significant loss of 4.19% in mass residue. Thus, there is an increase in the volatile matter loss from the fly-ash upon increasing the sample hold time at slow pyrolysis conditions. The yield of biochar prepared from wheat crop residue at different temperatures and hold time is summarized as given in the **Table-4.4** and **Figure-4.1**.

Thermal treatment of crop residue at various temperatures (250<sup>0</sup>C, 350<sup>0</sup>C and 450<sup>0</sup>C) showed a significant drop in yield of the residue (**Figure-4.1** and **4.2**). An interesting trend was observed upon increasing the pyrolysis temperature with same hold time. The biochar yield decreased significantly upon change of the pyrolysis temperature from 250<sup>0</sup>C to 350<sup>0</sup>C at 4 hours hold time. However, the decrease was not significant upon increasing the pyrolysis temperature from 350<sup>0</sup>C to 450<sup>0</sup>C. This phenomenon could be accounted to the complete decomposition and/or volatilization of the cellulose and hemicellulose component upto 350<sup>0</sup>C whereas the lignin decomposition is not so significant at this temperature and insignificant loss is seen upon change in pyrolysis temperature from 350<sup>0</sup>C to 450<sup>0</sup>C.

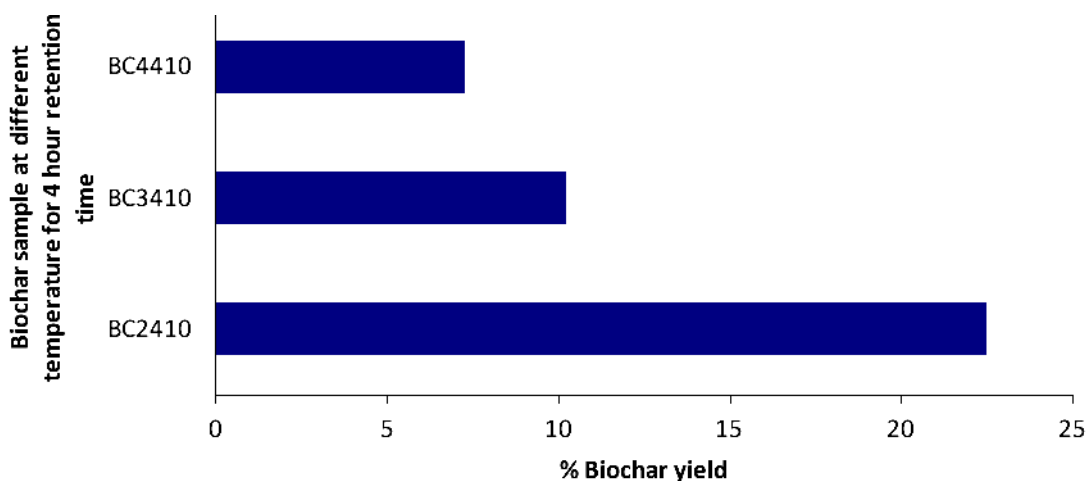
Maximum yield (33.20% w/w) of biochar was observed at 250<sup>0</sup>C for 1 hour hold time and minimum yield (7.27% w/w) was observed at 450<sup>0</sup>C for 4 hour hold time. As stated earlier, the significant decrease in residual mass was higher for 250<sup>0</sup>C to 350<sup>0</sup>C due to decomposition and volatilization of cellulose and hemicellulose to various volatile derivatives than that of 350<sup>0</sup>C to 450<sup>0</sup>C where cellulose and hemicellulose got their optimal decomposition and lignin decomposition was reported to start. Decrease in the yield of the biochar with temperature hold time was due to significant conversion of lignocellulosic material with higher hold time (**Figure-4.1** and **4.3**).

The biomass/fly-ash mixtures when subjected to pyrolysis underwent a loss of volatile matter, leaving behind the biochar/fly-ash composite. The yield of these materials and the effect of fly-ash on the formation of biochar are as reported in **Table-4.4** and **Table-4.5**. The composite formed at 250<sup>0</sup>C and 450<sup>0</sup>C showed an increase in the

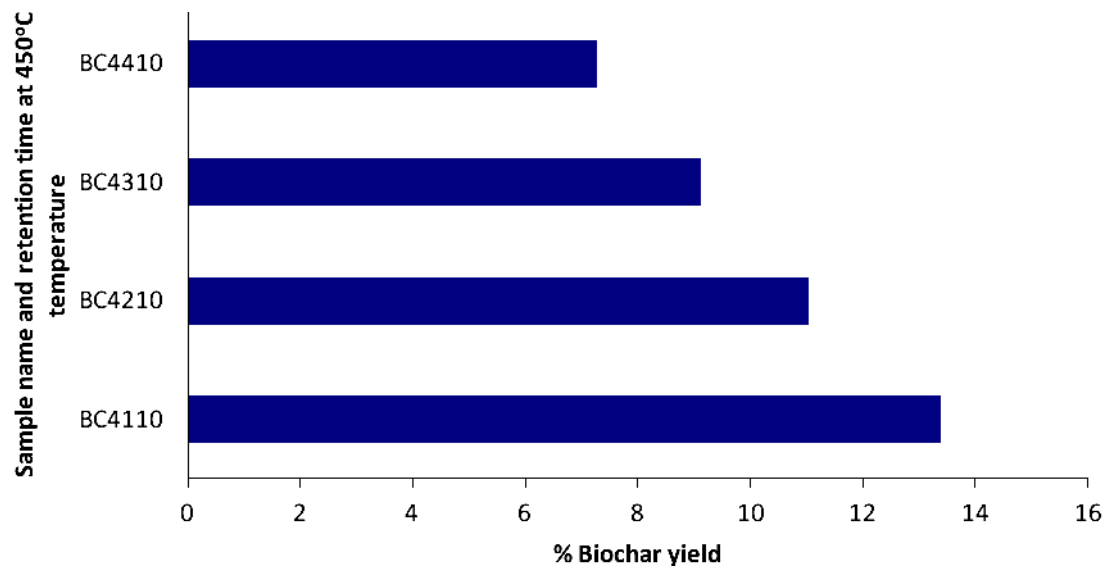
residual yield with increasing addition of fly-ash. This increase could be accounted to the significant loss in organic components of biomass and partly due to the insignificant loss by volatilization of fly-ash, during the pyrolysis process. Further, as observed in case of the preparation of pure biochar samples, the yield of the composite material decreased with increase in pyrolysis temperature and hold time (**Figure-4.2**).



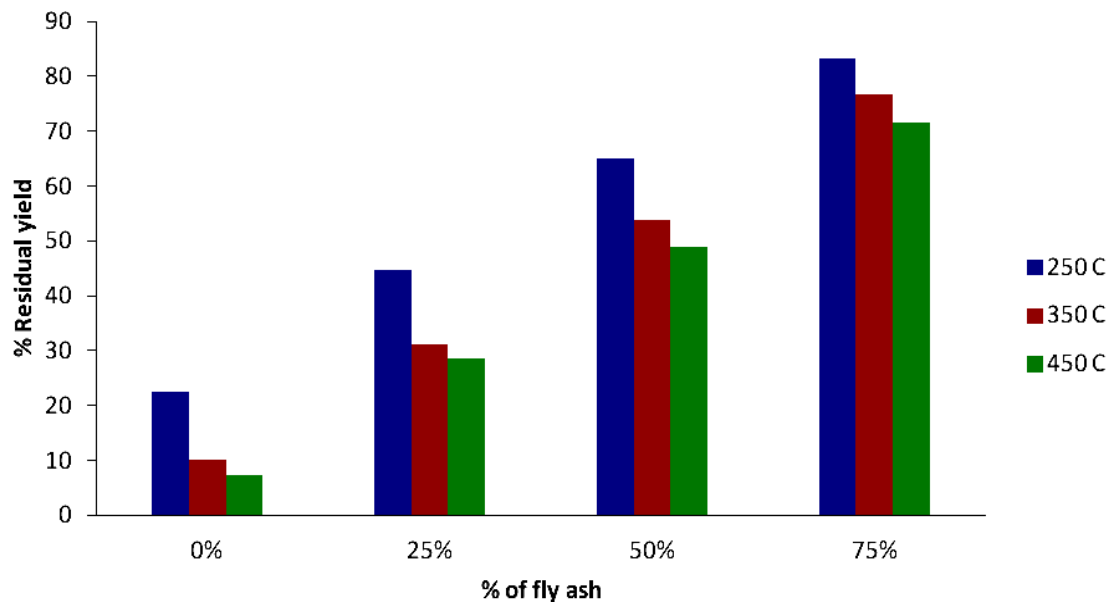
**Figure-4.1:** Comparison of the biochar yield (%), with the variation in the pyrolysis temperature and temperature hold time



**Figure-4.2:** Comparison of the biochar yield (%), for pyrolysis of crop residue with variation in pyrolysis temperature



**Figure-4.3:** Comparison of the biochar yield (%), for pyrolysis of crop residue with variation in temperature hold time at 450°C



**Figure-4.4:** Biochar and biochar/fly-ash composite yield (%), in presence of different proportion of biomass and fly-ash at 250°C, 350°C, and 450°C for 4 hours temperature hold time

**Table-4.4:** Comparative table for biochar, fly-ash and biochar/fly-ash composite yield per 10.0g and yield (%) at three pyrolysis temperatures (250°C, 350°C and 450°C) for 1 to 4 hours temperature hold time

Biochar/fly-ash composites yield										
% Fly-ash	0		25		50		75		100	
	Yield/10	%	Yield/10	%	Yield/10	%	Yield/10	%	Yield/10	%
PT/THT	g	Yield	g	Yield	g	Yield	g	Yield	g	Yield
BC/250/1h	3.32	33.20	5.47	54.74	7.25	72.49	9.44	94.44	9.97	99.71
BC/250/2h	2.51	25.09	4.64	46.38	6.62	66.20	8.37	83.71	9.97	99.67
BC/250/3h	2.24	22.35	4.61	46.06	6.53	65.35	8.37	83.71	9.97	99.69
BC/250/4h	2.25	22.47	4.47	44.68	6.51	65.14	8.34	83.37	9.97	99.73
BC/350/4h	1.02	10.21	3.12	31.21	5.39	53.88	7.68	76.82	9.96	99.56
BC/450/1h	1.34	13.38	3.22	32.18	5.44	54.40	7.68	76.76	9.94	99.37
BC450/2h	1.1	11.03	3.04	30.37	5.28	52.84	7.59	75.87	9.89	98.94
BC/450/3h	0.91	9.13	2.96	29.56	5.09	50.92	7.44	74.40	9.79	97.86
BC/450/4h	0.73	7.27	2.86	28.63	4.89	48.91	7.15	71.50	9.52	95.19

Where, PT = pyrolysis temperature,

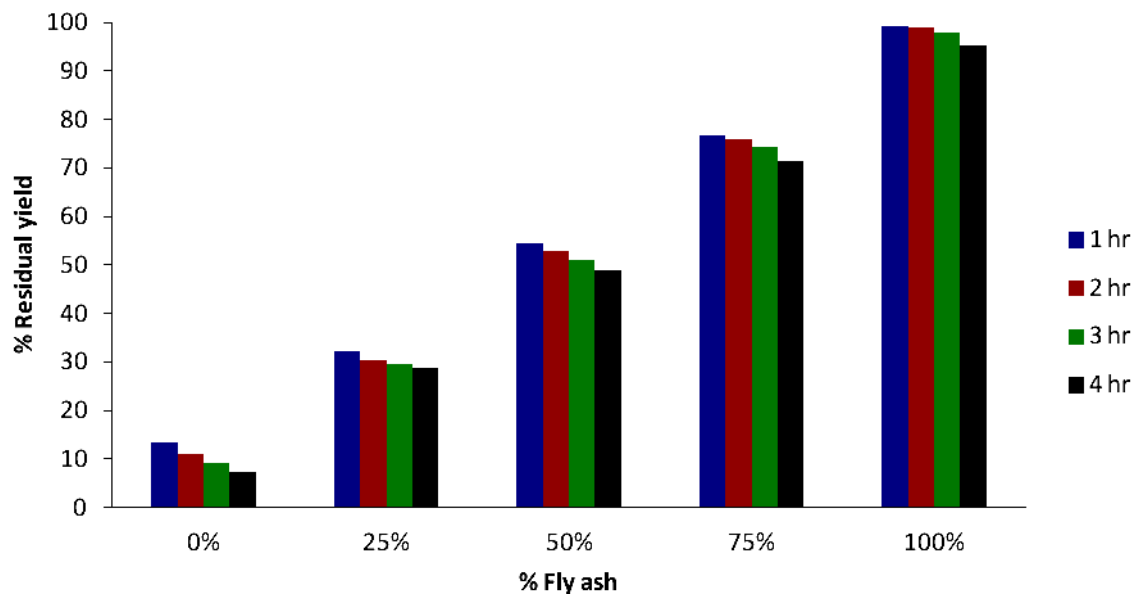
THT = temperature hold time, and

BC = biochar,

**Table-4.5:** Comparison of the yield of biochar in biochar/fly-ash composite normalized for 10g of biomass

%FA	25			50			75		
PT/TRT	Proposed Yield	Normalized yield	%Change	Proposed Yield	Normalized yield	%Change	Proposed Yield	Normalized yield	%Change
BC/250/1h	3.32	3.97	19.71	3.32	4.53	36.32	3.32	7.87	136.93
BC/250/2h	2.52	2.86	13.54	2.52	3.27	29.87	2.52	3.58	42.12
BC/250/3h	2.24	2.82	26.09	2.24	3.10	38.74	2.24	3.58	60.04
BC/250/4h	2.25	2.63	16.57	2.24	3.06	36.61	2.24	3.44	53.57
BC/350/4h	1.03	0.84	-18.18	1.02	0.82	-19.61	1.04	0.84	-19.23
BC/450/1h	1.33	01.03	-23.00	1.34	1.00	-25.37	1.32	0.88	-33.33
BC450/2h	1.11	0.77	-30.12	1.10	0.72	-34.55	1.12	0.68	-39.29
BC/450/3h	0.89	0.68	-23.88	0.92	0.46	-50.00	0.92	0.36	-60.87
BC/450/4h	0.73	0.65	-10.91	0.72	0.26	-63.89	0.72	0.01	-97.22

Where, % change means % increase or decrease in yield in presence of fly-ash

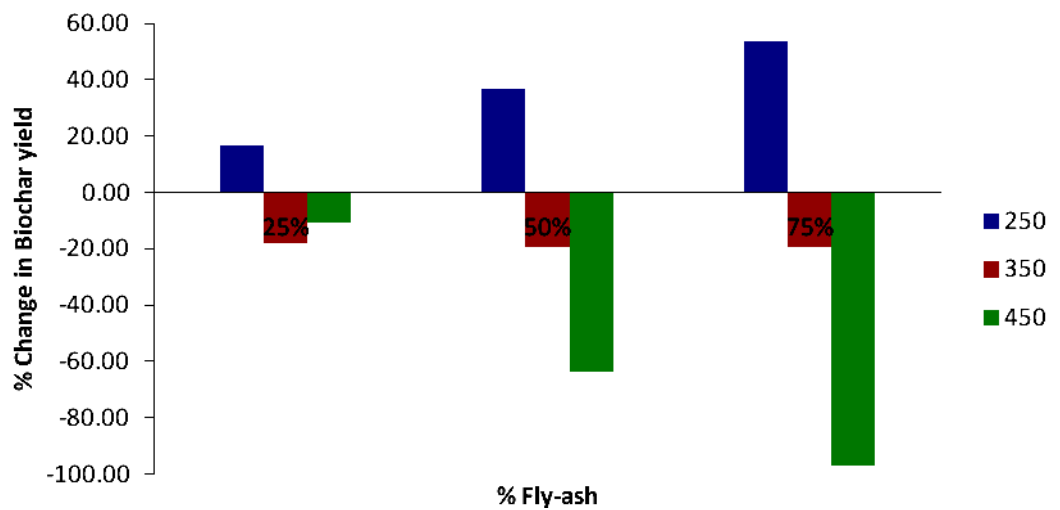


**Figure-4.5:** Biochar and biochar/fly-ash composite yield %, in presence of different proportions of fly-ash at 450°C for 1, 2, 3, and 4 hours temperature hold time

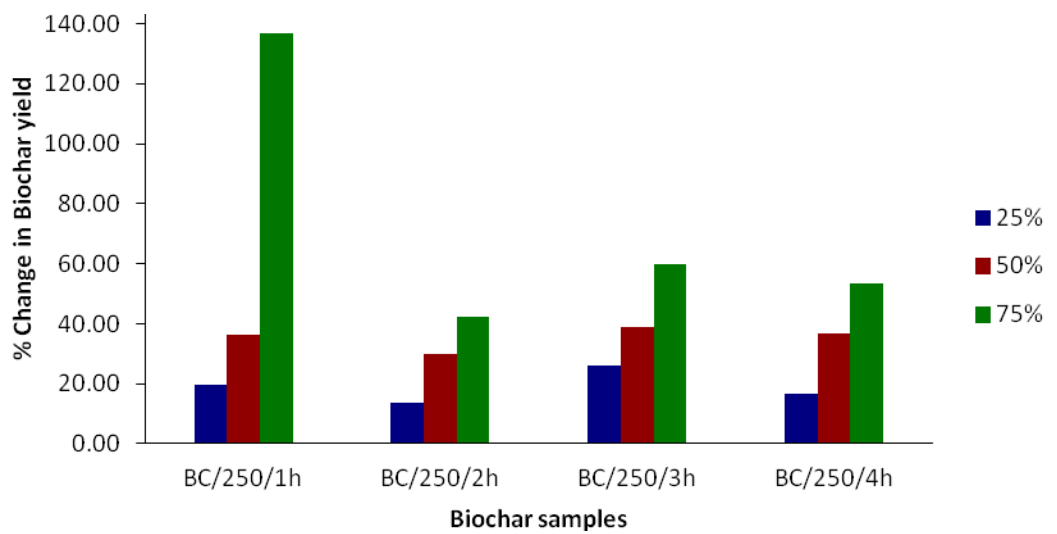
The studies carried out on slow pyrolysis of biomass in presence of fly-ash were significant. A significant variation in the biochar yield from crop residue was observed in presence of different concentration of fly-ash (**Table 4.5**) for different pyrolysis temperature (**Figure-4.4**) and temperature hold time (**Figure-4.5**). As it was reported earlier, fly-ash underwent a small change in residual mass at 250°C, and a significant increase in the yield of biochar 19.7% to 136.9% and 16.6% to 53.6% at 1 hour and 4 hour hold time, respectively, in comparison to pure biochar. This might be due to increased adsorption of volatiles on fly-ash material at lower temperature, further supported by the volatilization upon increasing the hold time. On contrary, a decrease in biochar yield from crop residue part was observed at 350°C and 450°C. However, a constant decrease of 18-19% biochar yield was observed at 350°C than 250°C in presence of different proportion of fly-ash (**Figure 4.4**). Exceptionally decrease of 63.89% and 97.22% in biochar yield was observed for 1:1 and 1:3 biomass to fly-ash containing samples, respectively, at 450°C for 4 hours temperature hold time. The % decrease in biochar yield was comparatively lower at 450°C for 1 hour hold time. Thus, it can be inferred from this observation that loss of residual biochar increased



due to volatilization with increase in temperature and hold time, in particular, in presence of fly-ash.

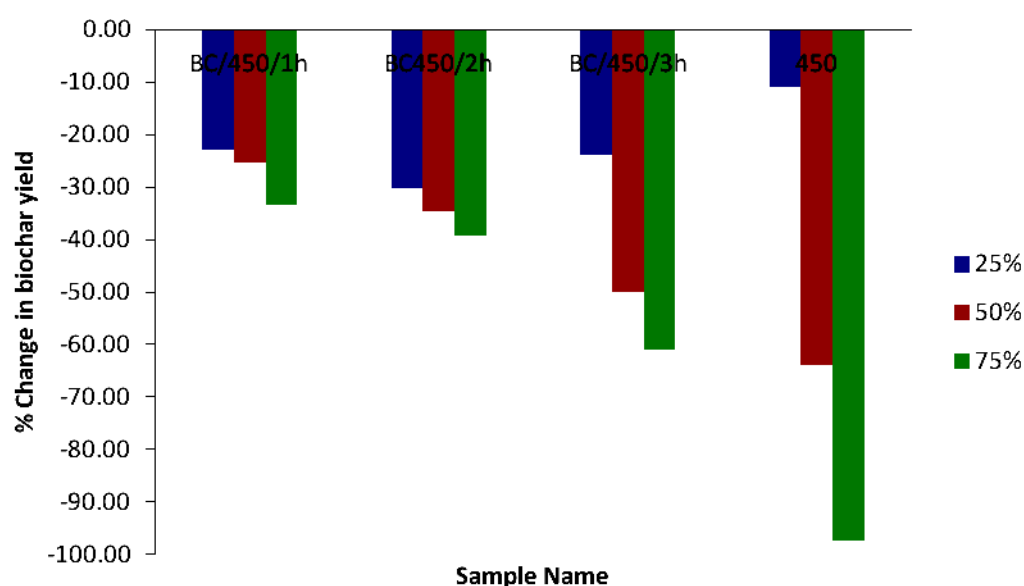


**Figure-4.6:** Deviation in biochar yield %, in presence of different fly-ash weight %, at 250°C, 350°C, and 450°C for 4 hours hold time



**Figure-4.7:** Deviation in biochar yield%, in presence of different fly-ash weight %, at 250°C for 1, 2, 3, and 4 hours hold time

This further supports that a significant volatilization of crop residue occurred in presence of high concentration of fly-ash at higher temperatures. Also, a significant decrease in biochar yield was observed with the increase in fly-ash content and temperature hold time (**Figure-4.6 to 4.8**). In conclusion, a significant decrease in biochar yield was observed in presence of higher proportion of fly-ash (75%) i.e., 1:3 biomass to fly-ash mixtures, due to increase in volatilization either by high temperature catalysis in presence of fly-ash or by better heat transfer by fly-ash to the biomass during pyrolysis.



**Figure-4.8:** Deviation in biochar yield in presence of different fly-ash weight %, at 450°C for 1, 2, 3, and 4 hours hold time

#### 4.4 Physico-chemical characteristics of biochar and biochar/fly-ash composite (CFB) material derived from wheat crop residue and fly-ash at different pyrolysis temperature and hold time

Recently various studies have been carried out on catalytic pyrolysis using various inorganic materials like alumina (Yorgan and Simsek, 2008; Sanna et. al., 2011), zeolites (Pan et. al., 2010), CaO (Han et. al., 2010), ZnCl<sub>2</sub> (Lu et al., 2011), etc. as catalyst for enhancing bio-oil and syn-gas yield in pyrolysis. However, the solid residue left after catalytic pyrolysis has not been characterized in these studies. Thus,

in the present study, biochar/fly-ash composite samples were prepared by slow pyrolysis at various temperatures (250<sup>0</sup>C, 350<sup>0</sup>C and 450<sup>0</sup>C) and at different hold time (from 1 hour to 4 hour) using fly-ash as catalyst. Physico-chemical characterization of residual solids obtained under different pyrolytic condition was performed. pH, electrical conductivity (EC), alkalinity, K and Na, total P and proximate and ultimate analyses of different biochar and biochar/fly-ash composite samples were performed. The results of the analysis are given in following tables (**Table-4.6 to Table-4.11**).

#### **4.4.1 Physico-chemical properties of fly-ash**

Proximate analysis result of thermally treated fly-ash sample is given in **Table-4.6**. % Moisture, %VM and %Fixed carbon content were found to be minimum and %Ash content was maximum for fly-ash sample as compared to biochar and biochar/fly-ash composite samples.

A little variation in fly-ash pH was observed with change in pyrolysis temperature and hold time. However, it was found to be slightly acidic at pH 6.5 at 250<sup>0</sup>C to pH 7.7 at 450<sup>0</sup>C. EC of thermally treated fly-ash sample was found to be significantly higher than untreated fly-ash sample. However, a little variation in EC of fly-ash sample was observed with variation in temperature and hold time and it was found to be in the range of 3.4 to 4.6 (mS/cm). However, alkalinity of fly-ash sample was not significantly affected by thermal treatment.

#### **4.4.2 Physico-chemical properties of pure biochar**

Proximate analysis and ultimate analysis of biochar sample is given in following **Table-4.6** and **Table-4.7**, respectively. Moisture, VM, Ash and Fixed carbon contents were significantly high for pure biochar samples and were maximum for 250<sup>0</sup>C followed by 450<sup>0</sup>C and minimum for 350<sup>0</sup>C, except %Fixed carbon which was found maximum for 450<sup>0</sup>C followed by 250<sup>0</sup>C and 350<sup>0</sup>C. Ultimate analysis of biochar sample was performed and a significant variation in CHN and S were observed for biochar samples from that of crop residue and with the increase in pyrolysis temperature. As reported earlier, at 250<sup>0</sup>C a little volatilization occurs, thus, CHN contents were very high for 250<sup>0</sup>C biochar sample than that of 450<sup>0</sup>C. However, an

increase in C as compared to crop residue was observed for 250<sup>0</sup>C biochar sample due to enrichment of biochar as a result of volatilization of oxygenated components; and a significant decrease in %C for 450<sup>0</sup>C biochar sample than crop residue was observed. This is accounted to significant decomposition and volatilization of crop residue biomass at 450<sup>0</sup>C. However, %S content was found significantly high for 450<sup>0</sup>C biochar sample than 250<sup>0</sup>C sample.

pH and electrical conductivity (EC) of any material depends upon its mineral constituents and free ions. Any material having higher concentration of free ions has high pH and EC. Biomass is mainly composed of cellulose, hemicelluloses and lignin materials which get decomposed into various organic and inorganic compounds like aldehydes, ketones, carboxylic acid functional groups as well as carbonates and bi-carbonates after thermal treatment. These chemical compounds lead to variation in the physico-chemical properties of biochar produced at various temperatures. Studies suggest that the decomposition of native cellulosic and hemi-cellulosic material increases with increase in temperature. In the present study, pH of biochar product was found to increase significantly from 6.4 to 11.7 with increase in pyrolysis temperature from 250<sup>0</sup>C to 450<sup>0</sup>C, respectively (**Table-4.8**).

Electrical conductivity of biochar samples prepared at various temperatures show an increase in the conductivity by upto 3.5 times (**Table-4.9**). The electrical conductivity of biochar sample was found to be 186.7 mS/cm at 250<sup>0</sup>C, which increases gradually to 297.0 mS/cm and 775.2 mS/cm at 350<sup>0</sup>C and 450<sup>0</sup>C, respectively. This increase can be attributed to the decrease in the biochar yield by four times upon increasing the temperature from 250<sup>0</sup>C to 450<sup>0</sup>C at 4 hours hold time. This is further supported by the conductivity measured for the biochar/fly-ash composite samples prepared at different hold time from 1 hour to 4 hours at 450<sup>0</sup>C.

**Table 4.6:** Proximate analysis of biochar/fly-ash composite samples prepared at 250<sup>0</sup>C, 350<sup>0</sup>C and 450<sup>0</sup>C at 4 hours hold time

Sample Name	% Moisture			% Volatile matter			% Ash			% Fixed Carbon		
PT ( <sup>0</sup> C)	250	350	450	250	350	450	250	350	450	250	350	450
BC10	5.5	1.73	3.27	38.72	19.58	32.06	23.8	72.89	20.92	31.99	5.81	43.75
BC31	3.39	0.59	0.42	21.89	12.76	7.48	60.64	83.92	93.66	14.09	2.73	ns
BC11	1.77	0.49	0.63	15.31	13.73	6.11	71.59	79.83	93.24	11.32	5.94	0.01
BC13	0.97	0.25	0.34	10.33	8.88	5.76	79.97	86.8	91.48	8.74	4.06	2.42
BC01	0.35	0.40	0.43	7.54	7.75	8.02	87.17	87.19	90.38	4.94	4.66	1.17

Where, ns = not significant

**Table 4.7:** Ultimate analysis of biochar/fly-ash composite samples prepared at 250<sup>0</sup>C and 450<sup>0</sup>C at 4 hours hold time

Sample Name	%C		%H		%N		%S		H/C		N/C	
PT ( <sup>0</sup> C)	250 <sup>0</sup> C	450 <sup>0</sup> C	250 <sup>0</sup> C	450 <sup>0</sup> C	250 <sup>0</sup> C	450 <sup>0</sup> C	250 <sup>0</sup> C	450 <sup>0</sup> C	250 <sup>0</sup> C	450 <sup>0</sup> C	250 <sup>0</sup> C	450 <sup>0</sup> C
BC10	47.29	6.62	2.56	0.70	0.87	0.16	0.27	0.87	0.054	0.106	0.018	0.025
BC31	28.82	3.63	1.48	0.19	0.56	0.11	0.22	0.00	0.051	0.051	0.020	0.032
BC11	21.79	5.28	0.66	0.07	0.41	0.13	0.00	0.00	0.030	0.013	0.019	0.025
BC13	16.18	6.94	0.31	0.00	0.29	0.18	0.00	0.00	0.019	0.000	0.018	0.026

**Table 4.8:** pH of biochar and biochar/fly-ash composite samples prepared at various temperatures at different temperature hold time

Sample Name		pH				
PT ( <sup>0</sup> C)/THT (h)	250/4	350/4	450/1	450/2	450/3	450/4
BC10	6.41	10.34	9.03	10.37	11.70	11.05
BC31	6.55	10.59	10.28	10.70	10.87	10.67
BC11	6.66	9.27	9.92	10.91	10.71	9.73
BC13	6.11	9.74	9.02	9.34	8.21	9.01
BC01	6.53	6.91	7.52	7.70	6.66	7.05

**Table 4.9:** Electrical conductivity (EC) of biochar and biochar/fly-ash composite samples prepared at various temperatures and temperature hold time (represented in mS/cm)

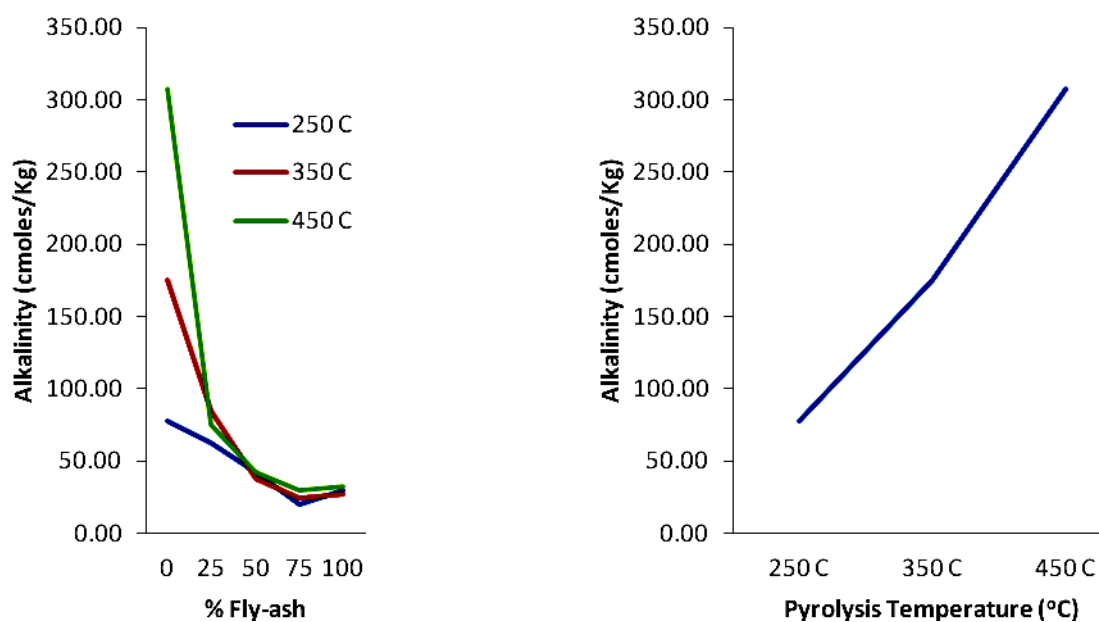
Sample Name		Electrical Conductivity (mS/cm)				
PT ( <sup>0</sup> C)/THT (h)	250/4	350/4	450/1	450/2	450/3	450/4
BC10	186.7	297.0	426.4	565.2	649.2	775.2
BC31	82.2	146.4	138.1	144.9	125.1	133.4
BC11	35.4	46.0	54.2	56.5	55.2	38.9
BC13	16.9	26.6	22.0	22.9	21.7	21.9
BC01	4.4	4.6	3.7	3.9	3.4	4.3

Alkalinity of material depends on the presence of carbonate, bi-carbonate and hydroxide ions concentrations. Crop residue is composed of ligno-cellulosic materials which may get decomposed upon thermal treatment into carbonates, bi-carbonates and the oxide/hydroxide components, being attributed to the presence of alkali/alkaline metal oxides. Fly-ash is dominated by aluminosilicate and oxides of various other metals which are thermally stable, thus, it has a little alkalinity than crop residue samples. A significant increase in alkalinity was observed in biochar samples with the increase in temperature from 250<sup>0</sup>C to 450<sup>0</sup>C. This further signifies the increase in decomposition of ligno-cellulosic plant biomass to their carbonate and bicarbonate compounds. Alkalinity of biochar sample prepared at 450<sup>0</sup>C was

significantly very high as compared to other biochar samples prepared at 350<sup>0</sup>C and 250<sup>0</sup>C (**Figure-4.9** and **Table-4.10**).

**Table 4.10:** Alkalinity (Centimoles/kg) of biochar and biochar/fly-ash composite materials prepared at 250<sup>0</sup>C, 350<sup>0</sup>C and 450<sup>0</sup>C pyrolysis temperatures for 4 hours hold time

Sample Name	Alkalinity and PT ( <sup>0</sup> C)		
	250	350	450
BC10	77.50	175.00	307.50
BC31	62.50	85.00	75.00
BC11	42.50	37.50	42.50
BC13	20.00	25.00	30.00
BC01	30.00	27.50	32.50



**Figure-4.9:** Alkalinity (Centimoles/kg) of biochar and biochar/fly-ash composite samples prepared at different pyrolysis temperatures

In the present study total phosphorus (P), total sodium (Na) and total potassium (K) content of a few biochar and biochar/fly-ash composite products were determined using standard methods and the results are given in **Table-4.11**.

Total P, K and Na content of crop residue sample is given in **Table-4.1**. Total P, Na, and K content get concentrated in biochar samples with pyrolysis of biomass and with increase in pyrolysis temperature as it was observed in this study at three temperatures viz., 250<sup>0</sup>C, 350<sup>0</sup>C and 450<sup>0</sup>C. P, K and Na content were found to increase with increase in temperature from 250<sup>0</sup>C to 350<sup>0</sup>C, however, a significant decrease in concentration of these elements was observed at 450<sup>0</sup>C. The observed decrease in total P, K and Na concentrations at 450<sup>0</sup>C can be accounted to the incomplete digestion of biochar sample in 2:1 (v/v) mixture of HNO<sub>3</sub> and HClO<sub>4</sub>.

**Table-4.11:** Total P (mg/kg), K (mg/kg) and Na (mg/kg) contents of various biochar/fly-ash composite samples prepared at 250<sup>0</sup>C, 350<sup>0</sup>C and 450<sup>0</sup>C pyrolysis temperatures

Sample Name	Total P (mg/kg)	Total K (mg/kg)	Total Na (mg/kg)
BC2410	160.83	244.57	19.32
BC2431	197.92	154.02	17.53
BC2411	195.42	82.21	13.06
BC2413	192.50	28.93	17.53
BC3410	242.50	152.84	29.22
BC4410*	46.25	81.26	13.15
BC4431	328.75	197.10	24.77
BC4411	254.17	45.32	11.31
BC4413	242.08	32.43	14.96

\* Data is not significant due to incomplete digestion of biochar sample



#### 4.4.3 Physico-chemical properties of biochar/fly-ash composite samples

Proximate analysis and ultimate analysis of biochar/fly-ash composite samples are given in **Table-4.6** and **Table-4.7**. Moisture, VM, Ash and Fixed carbon contents were significantly high for pure biochar samples than biochar/fly-ash composites and were maximum for 250<sup>0</sup>C followed by 450<sup>0</sup>C and minimum for 350<sup>0</sup>C, except Fixed carbon, which was found maximum for 450<sup>0</sup>C followed by 250<sup>0</sup>C and 350<sup>0</sup>C. A significant decrease was observed in Moisture, VM and Fixed carbon content, with the increase in fly-ash concentration, whereas Ash content was found to increase with increase in fly-ash concentration. This might be due to low volatility of fly-ash.

Ultimate analysis of biochar/fly-ash composite samples were performed and a significant variation in CHN and S content was observed for these samples from that of crop residue and with the increase in pyrolysis temperature. As reported earlier, at 250<sup>0</sup>C, volatilization occurs to a lesser extent, thus, CHN contents were found to be higher for 250<sup>0</sup>C composite samples than the 450<sup>0</sup>C composite samples.

The ultimate analysis of composite samples was a little too complicated to account for. With the increase in fly-ash concentration, a significant decrease in CHN and S content was observed for samples prepared at 250<sup>0</sup>C. On the other hand, for 450<sup>0</sup>C samples, a little increase was observed for %C and %N content, whereas, a significant decrease in %H and %S content with increase in fly-ash concentration which revealed that fly-ash has a significant effect over volatilization of crop residue carbon, hydrogen and sulphur components. H/C ratio is a measure of degree of aromatization of any material during thermo-chemical treatment. In this study, a significant decrease in H/C ratio was observed with increase in fly-ash concentration for 250<sup>0</sup>C and 450<sup>0</sup>C biochar and biochar/fly-ash composite samples, however, the decrease in H/C ratio was very high for 450<sup>0</sup>C samples, which revealed that degree of volatilization and aromatization was higher at 450<sup>0</sup>C than at 250<sup>0</sup>C. Comparatively, H/C ratio was high for 450<sup>0</sup>C pure biochar sample than 250<sup>0</sup>C pure biochar sample, which might be due to high rate of decomposition and volatilization in the form of CO, CO<sub>2</sub>, etc. at 450<sup>0</sup>C, however, a significant decrease in H/C ratio at 450<sup>0</sup>C than 250<sup>0</sup>C with increase in fly ash concentration reveal that aromatization and volatilization

increases significantly at 450<sup>0</sup>C with increase in fly ash proportion. The pH of biochar/fly-ash composite material was found very less affected by fly-ash as with increase in its concentration very little variation in pH was observed. The pH of biochar/fly-ash composite prepared at 250<sup>0</sup>C was not affected with increase in fly-ash proportion. However, the pH of biochar samples prepared at 450<sup>0</sup>C and 350<sup>0</sup>C were found to be in range of moderately alkaline to highly alkaline with the increase in fly-ash proportion.

The biochar/fly-ash composite prepared at 1 hour hold time showing an electrical conductivity of 426.4 mS/cm which is well above the conductivity of the sample prepared at 250<sup>0</sup>C or 350<sup>0</sup>C with 4 hours hold time. This again could be accorded to the yield of biochar obtained.

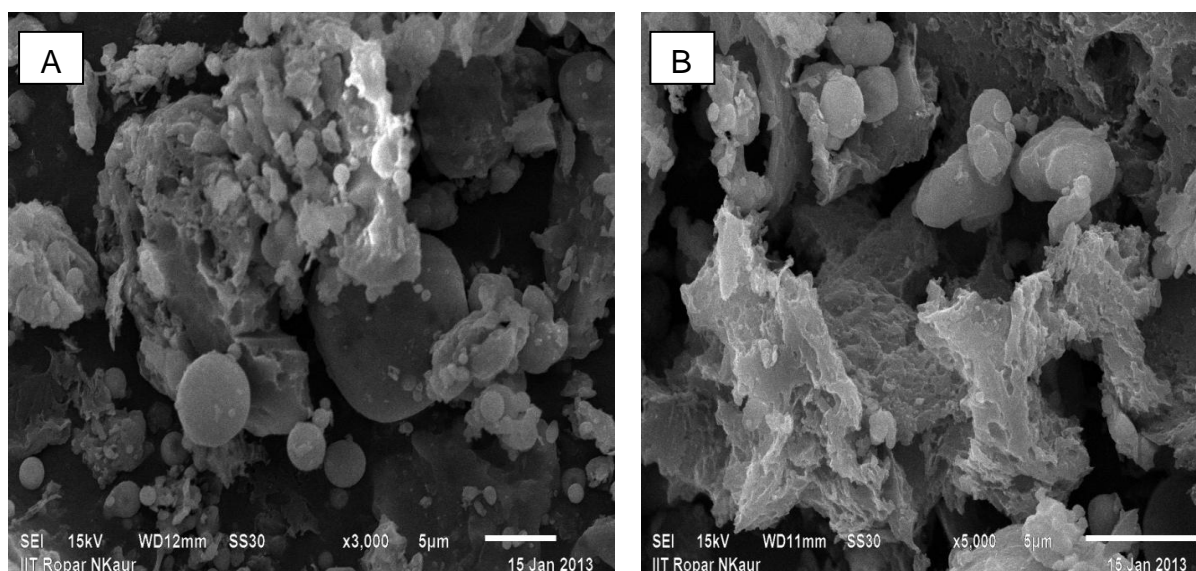
Alkalinity of biochar/fly-ash composite samples was found to decrease rapidly with increase in fly-ash concentration. Alkalinity was found to be significantly affected at higher concentration of fly-ash in biochar/fly-ash (1:3) composite samples, a significant decrease in alkalinity was observed in comparison to other samples (**Table-4.10**).

As given in the **Table-4.2**, fly-ash used in the present study, the constituents P, K, Na contents reported are 0.11% P<sub>2</sub>O<sub>5</sub>, 0.44% K<sub>2</sub>O and 0.51% Na<sub>2</sub>O. For fly-ash containing biochar samples total P, K and Na contents were high than the pure biochar samples at 250<sup>0</sup>C and 450<sup>0</sup>C, and a significant increase in concentration of these elements was found with increase in pyrolysis temperature from 250<sup>0</sup>C to 450<sup>0</sup>C. Biochar/fly-ash composite samples prepared at 250<sup>0</sup>C did not show significant variation in total P with increase in fly-ash concentration, however, a significant decrease in total P was observed in biochar/fly-ash composite samples prepared at 450<sup>0</sup>C with the increase in fly-ash concentration. Total K content of biochar/fly-ash composite was found to decrease with increase in fly-ash concentration at 250<sup>0</sup>C and 450<sup>0</sup>C. However, a significant increase in total K was observed in biochar/fly-ash (3:1) composite prepared at 450<sup>0</sup>C, i.e., K is found to concentrate with increase in temperature at low proportion of fly ash. Total Na content of biochar/fly-ash composite

was not varied significantly with increase in pyrolysis temperature and fly-ash concentration (**Table-4.11**).

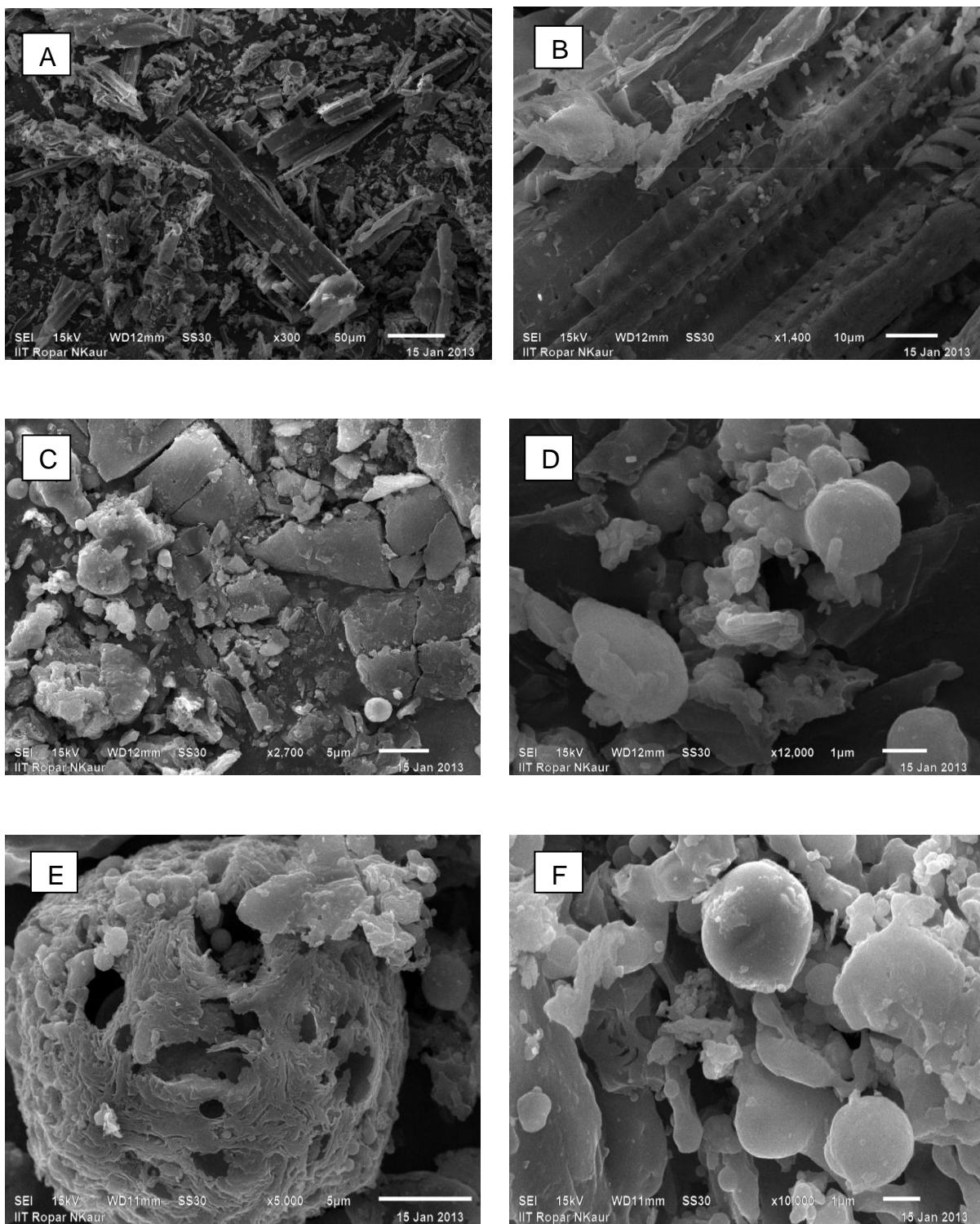
### **SEM analysis of biochar/fly-ash composite samples**

Structural analysis of different fly-ash, biochar and biochar/fly-ash composite samples prepared at 250<sup>0</sup>C and 450<sup>0</sup>C for 4 hours hold time was done using JSM JEOL SEM instrument after platinum coating of the samples (**Figure-4.10** to **4.12**).

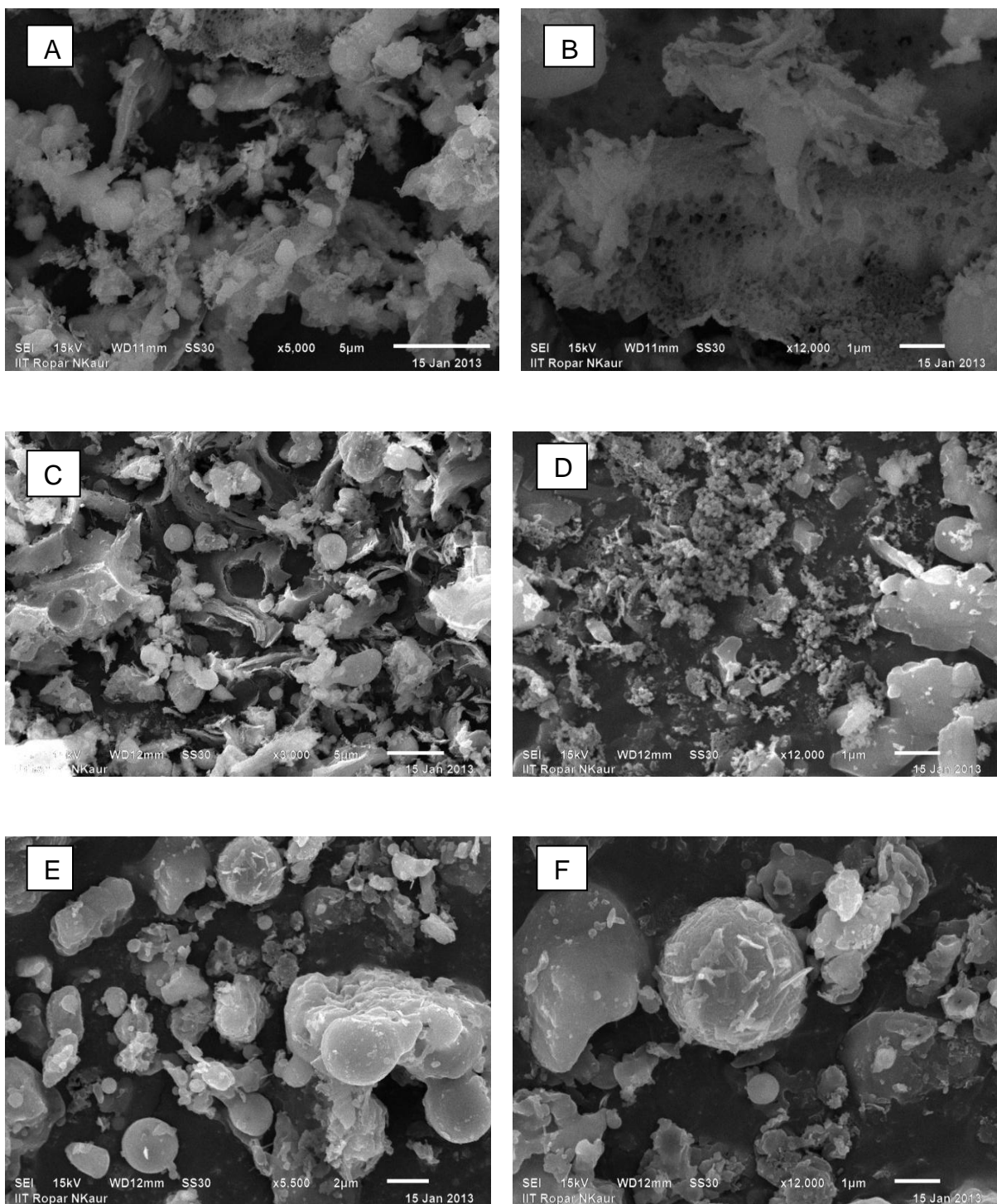


**Figure-4.10:** SEM images of fly-ash sample at (A) a magnification of 3000, and (B) a magnification of 5000

**Figure-4.10 (A) and (B)** depicts the SEM images of fly-ash sample, where spherical ball like structures are visible, which are representative of fly-ash structures of cenospheres and pleuroospheres. Fly-ash sample was found to be rich in carbonaceous material which is further supported by clearly visible SEM images of unorganized and asymmetrical weathered carbonaceous structures.



**Figure-4.11:** SEM images of biochar (A-B), biomass:fly-ash (3:1) (C-D), and biomass:fly-ash (1:3) (E-F) samples prepared at 250°C pyrolysis temperature at 4 hours hold time



**Figure 4.12:** SEM images of biochar (A-B), biomass:fly-ash (3:1) (C-D), and biomass:fly-ash (1:3) (E-F) samples prepared at 450<sup>0</sup>C pyrolysis temperature at 4 hours hold time

The SEM images of pure biochar material prepared at 250<sup>0</sup>C pyrolysis temperature at 50 µm and 10 µm scale, respectively, revealed the uncharred and undisturbed carbonaceous materials in which the crystallinity of parent crop residue material was less affected by pyrolysis temperature. Ordered submicron size pores with constant inter-pore spaces created due to the volatilization of hemicellulosic and cellulosic material at 250<sup>0</sup>C was observed (**Figure-4.11 A-B**). The SEM images of biochar/fly-ash (3:1) composite material prepared at 250<sup>0</sup>C pyrolysis temperature at 5 µm and 1 µm, respectively, showed the presence of spherical balls of mesospheric particles from fly-ash and found to interact with carbonaceous crop residue part to a lower extent (**Figure-4.11 C-D**). The SEM images of biochar/fly-ash (1:3) composite material prepared at 250<sup>0</sup>C pyrolysis temperature at 5 µm and 1 µm scale, respectively, show degradation of parent crop residue material in presence of fly-ash has occurred as crystallinity of the parent material has been significantly disturbed (**Figure-4.11 E-F**). Similar to the biochar/fly-ash composites (3:1), the marking of the charred crop residue by fly-ash was observed. This might lead to adsorption of volatiles on cenospheres of fly-ash.

The SEM images of pure biochar material prepared at 450<sup>0</sup>C pyrolysis temperature at 5 µm and 1 µm scale, respectively, reveal perfect charring of parent crop residue material at 450<sup>0</sup>C due to vigorous volatilization resulting into significant distortion in crystallinity of parent material. Unordered massive pores with irregular shape and size has been observed in **Figure-4.12 (B)** representing biochar prepared at 450<sup>0</sup>C as compared to 250<sup>0</sup>C biochar sample where found to have ordered pores with constant pore spaces observed. The SEM images of biochar/fly-ash (3:1) composite material prepared at 450<sup>0</sup>C pyrolysis temperature at 5 µm and 1 µm scale, respectively, showed a degradation of biochar structure in presence of fly-ash at 450<sup>0</sup>C as compared to 250<sup>0</sup>C and pure biochar sample (**Figure-4.12 C-D**). Fly-ash has been seen to impose further volatilization of crop residue by enhanced conduction of heat as it can be observed in **Figure-4.12 (C)** where a depression is observed where cenospheric particles of fly-ash are present and this further lead to increase in porosity of the material. Significantly, a higher extent of interaction can be seen at 450<sup>0</sup>C where cenospheric particles interact with carbonaceous structures of

crop residue than 250<sup>0</sup>C where a little interaction was observed. The SEM images of biochar/fly-ash (1:3) composite material prepared at 450<sup>0</sup>C pyrolysis temperature at 2  $\mu$ m and 1  $\mu$ m scale, respectively, showed a significant degradation of crop residue is observed as cenospheric particles from fly-ash are the major structures present in these images along with completely degraded carbonaceous material of crop residue and partial degradation of fly-ash carbonaceous structures (**Figure-4.12 E-F**). Interaction of fly-ash and crop residue is significant at 450<sup>0</sup>C in higher proportion of fly-ash as it was seen in 250<sup>0</sup>C biochar/fly-ash (1:3) composite sample as well. Flower like ferrosphere has been observed in **Figure-4.12 (F)** where carbonaceous structures of crop residue have been found on the surface of spherical structures.

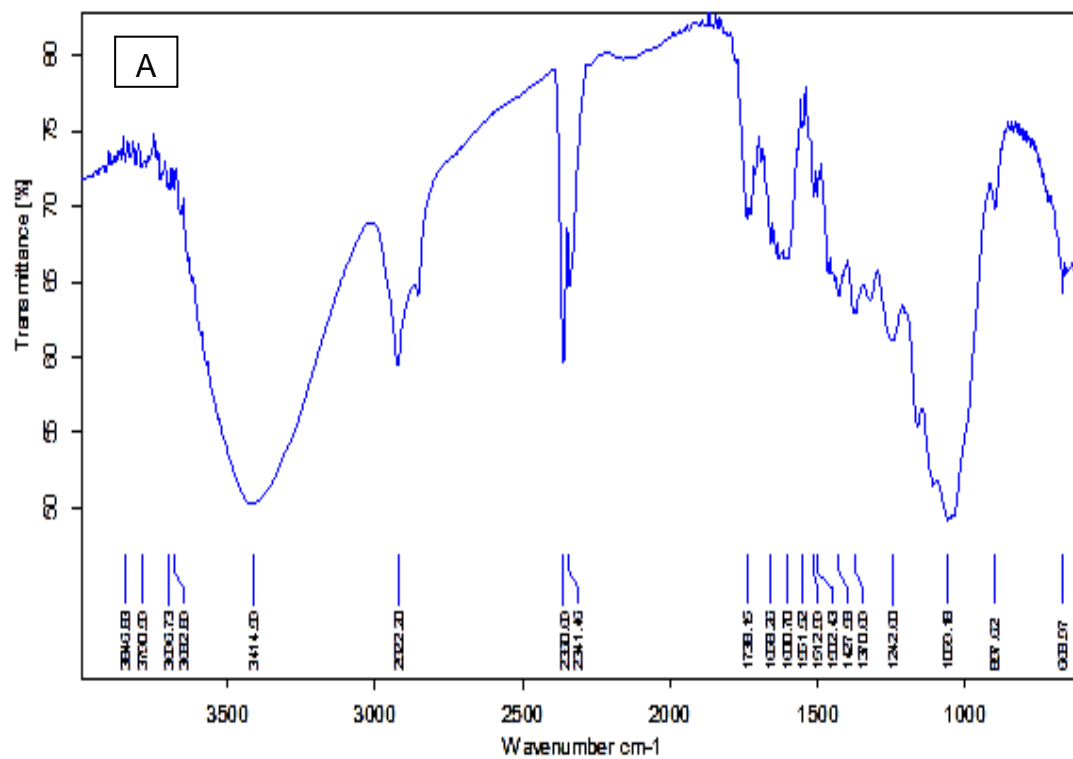
**FTIR analysis of the biochar, fly-ash and biochar/fly-ash composite samples prepared at 250<sup>0</sup>C and 450<sup>0</sup>C pyrolysis temperature for 4 hours hold time:**

The FTIR studies of the crop residue, fly-ash, biochar and biochar/fly-ash composite samples were performed using solid KBr pellet method of analysis of solid samples. The wheat crop residue showed strong IR absorption bands at 3415, 2922, 2360, 1738, 1659, 1601, 1551, 1512, 1370, 1243, 1059, 898, 790 and 669 cm<sup>-1</sup>. The broad band at 3415 cm<sup>-1</sup> corresponds to the hydrogen bonded hydroxyl moiety. Absorption band corresponding to aliphatic groups are observed at 2922 and 618 cm<sup>-1</sup>. The absorption band at 1738 cm<sup>-1</sup> corresponds to the carbonyl moiety and the band at 1659, 1601, 1551 and 1512 cm<sup>-1</sup> corresponds to the aromatic moiety, particularly characteristic of the phenolic and the benzene of lignin. The peak at 1370 cm<sup>-1</sup>, corresponds to the presence of functional group indicative of hemicelluloses. The peak at 1243, 1059, 898 and 790 cm<sup>-1</sup>, corresponds to the presence of characteristic inorganic metal oxides. Similarly, the fly-ash samples showed a characteristic peak at 3440, 2900, 2370, 1700, 1560, 1110, 1085, 900, 797 and 693 cm<sup>-1</sup>. The adsorption band at 3440, 1110, 1085, 900, 797 and 693 cm<sup>-1</sup> are characteristic of the fly-ash Si-O, Si-O-Si and T-O-Si bonds (Lee et al., 2002). The absorption band at 2900, 2370 and 1560 cm<sup>-1</sup> is indicative of the presence of organic aromatic and carboxylate moiety in the sample of fly-ash which might be a factor responsible for the loss on ignition of the sample.

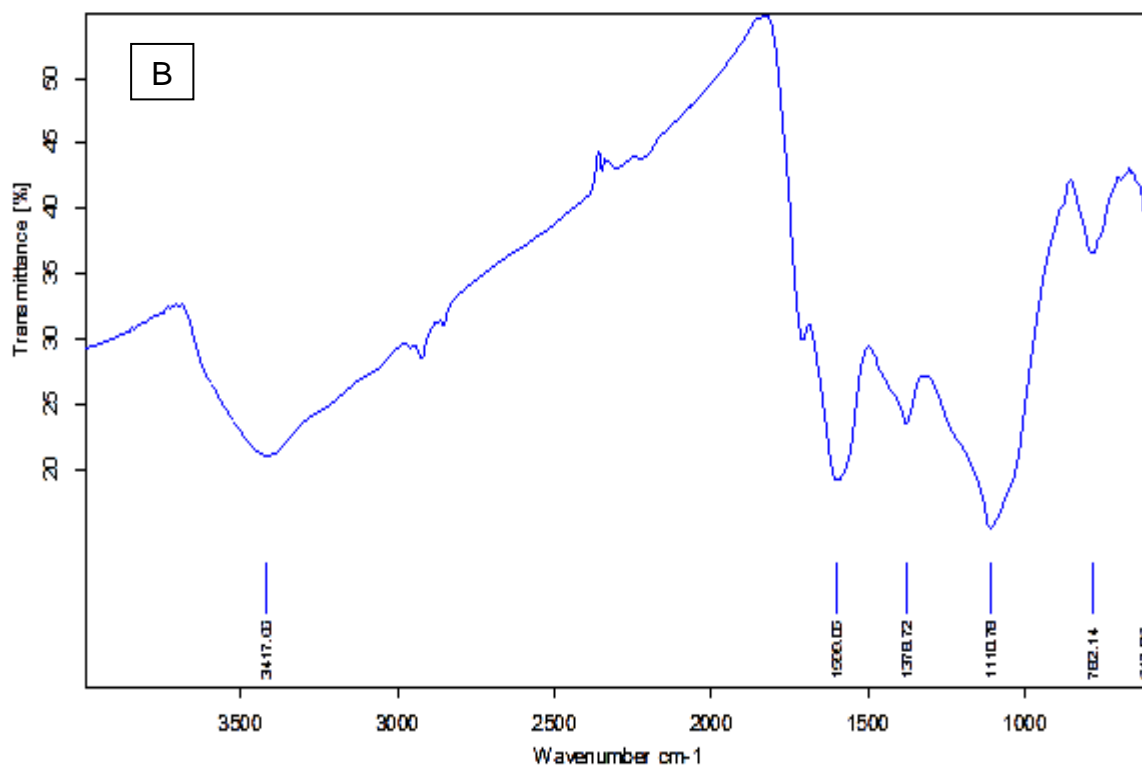
The band at  $3400\text{ cm}^{-1}$  corresponding to the hydroxyl moiety was found, in case of the biochar and biochar/fly-ash composite samples prepared at  $250^{\circ}\text{C}$  and  $350^{\circ}\text{C}$ , whereas the biochar and biochar/fly-ash composite samples prepared at  $450^{\circ}\text{C}$  showed a complete disappearance of the hydroxyl moiety in the sample. This is indicative of the fact that the cellulose and the hemicellulose of the material have undergone complete decomposition and volatilization at  $450^{\circ}\text{C}$ . The band at  $2900\text{ cm}^{-1}$  corresponding to the C-H stretching of aliphatic group decreases in intensity upon increase in the temperature of pyrolysis. This affirms the removal of the aliphatic scaffolds of cellulose and hemicelluloses at  $450^{\circ}\text{C}$ . Further, wheat crop residue has carbonyl compounds as indicated by the presence of the absorption band at  $1738\text{ cm}^{-1}$ . Similarly a small peak due to carbonyl appears to be formed around  $1700\text{ cm}^{-1}$  in the biochar sample prepared at  $250^{\circ}\text{C}$  and  $350^{\circ}\text{C}$ , however, the same is not existent in  $450^{\circ}\text{C}$ . The peaks in the range of the  $1500\text{-}1400\text{ cm}^{-1}$  corresponding to aromatic moieties are clearly visible in biochar samples prepared at  $350^{\circ}\text{C}$  and  $450^{\circ}\text{C}$ , which indicates the aromatization in the biochar residues upon the thermo-chemical treatment. Absorption bands at around  $690$  and  $610\text{ cm}^{-1}$ , which are indicative of the Si-O-Si bonds is a characteristic of flyash samples. These bands tend to increase in intensity in the biochar and biochar/fly-ash composite samples prepared with increase in the pyrolysis temperature upto  $450^{\circ}\text{C}$ . Thus, showing a more fly-ash like properties in the biochar prepared at  $450^{\circ}\text{C}$ .

FTIR spectra of crop residue (**Figure-4.13 A**),  $250^{\circ}\text{C}$  Biochar (**Figure-4.13 B**),  $350^{\circ}\text{C}$  biochar (**Figure-4.13 C**),  $450^{\circ}\text{C}$  biochar (**Figure-4.13 D**) and  $450^{\circ}\text{C}$  thermally treated fly-ash (**Figure-4.13 A**) are given in following **Figure-4.13**.

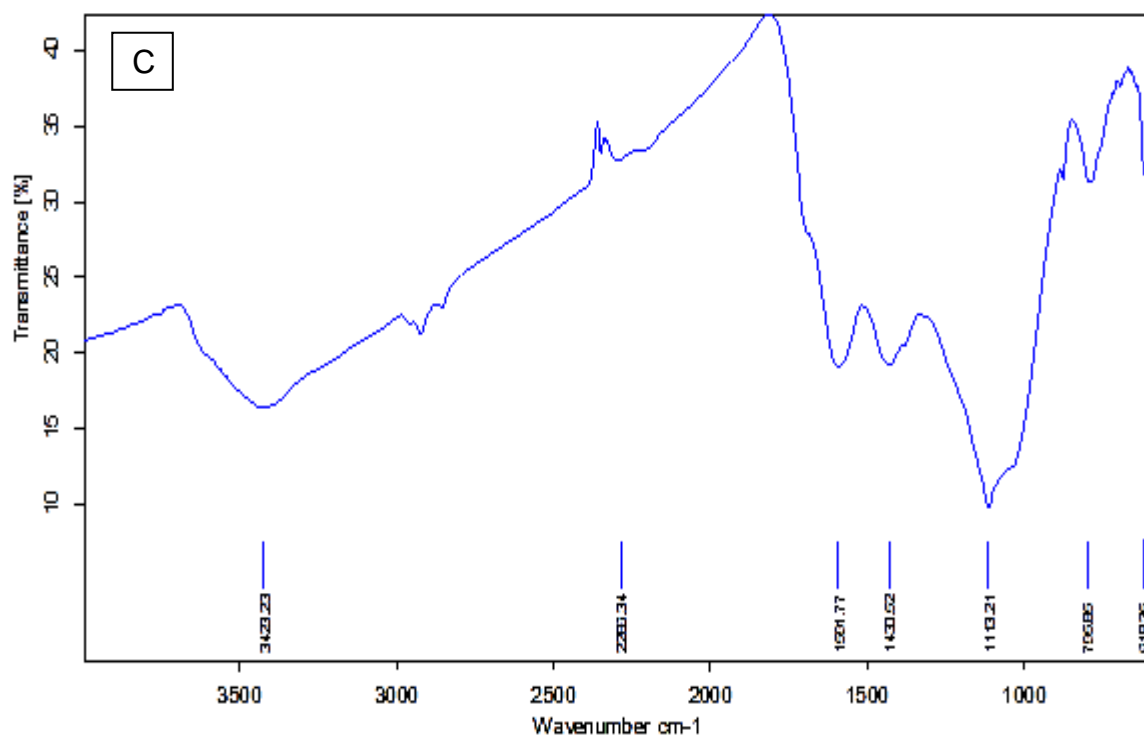




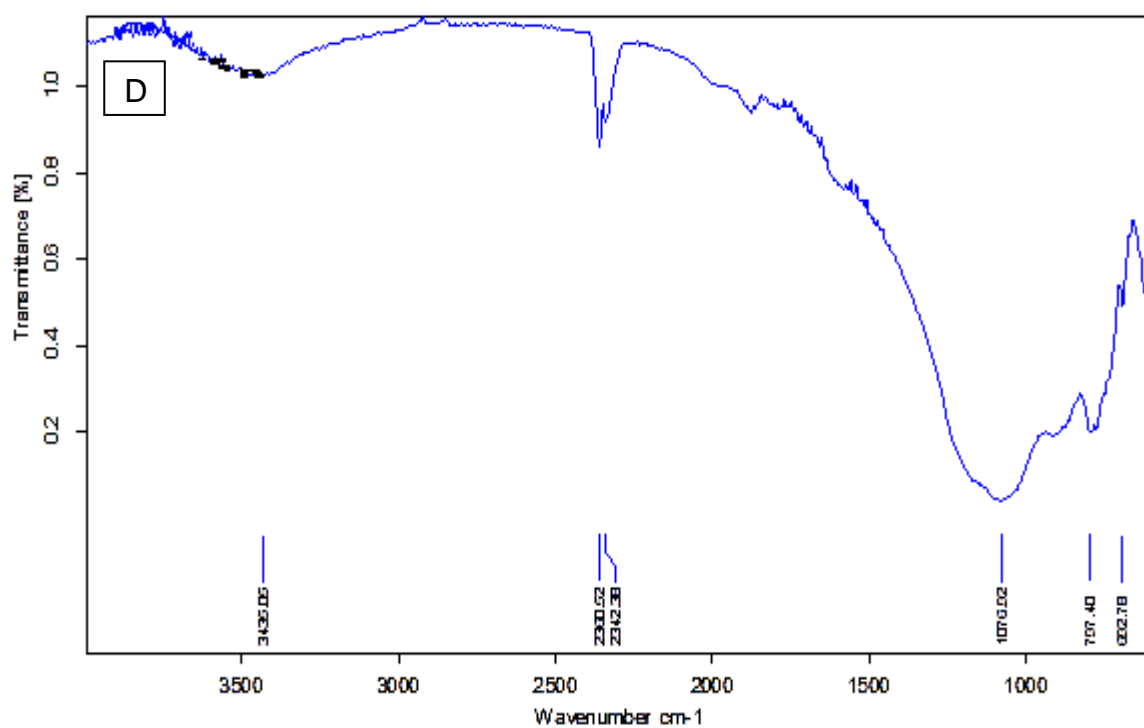
Crop residue sample



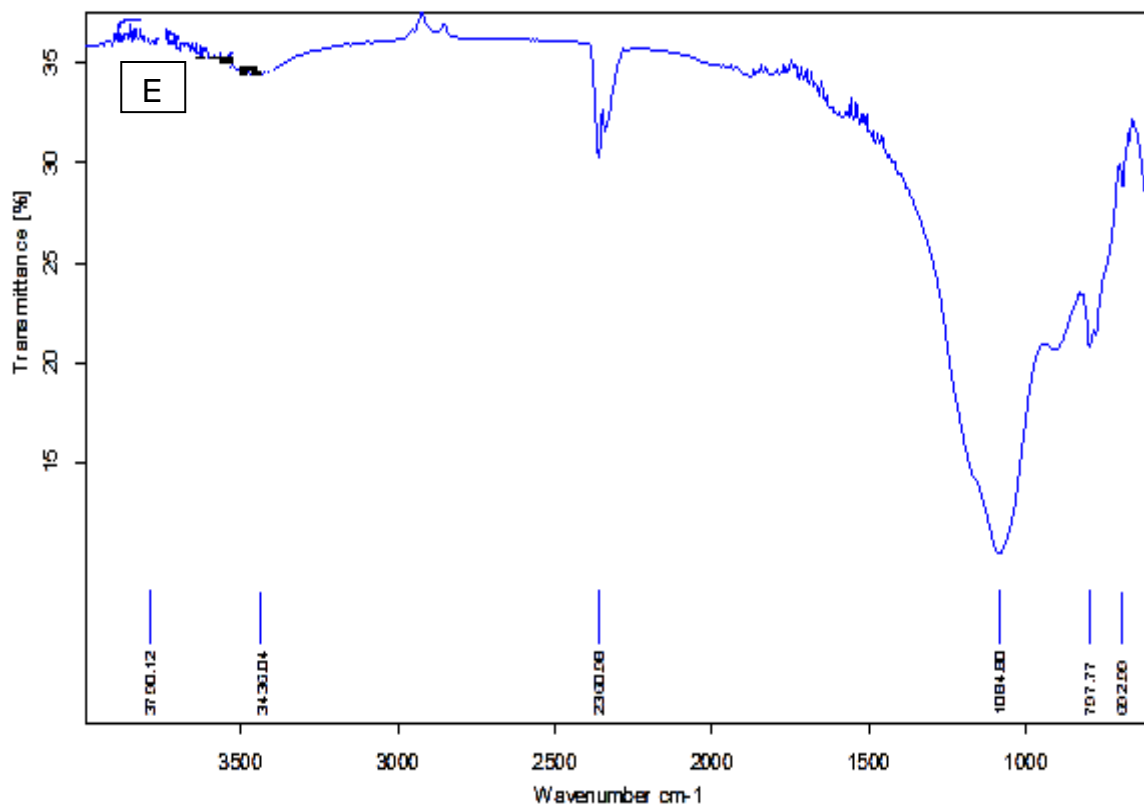
BC2410



BC3410



BC4410



BC4401

**Figure-4.13:** FTIR images of (A) crop residue; (B) BC2410; (C) BC3410; (D) BC4410 and (E) BC4401 samples

#### 4.5 Physico-chemical properties of soil

Soil sample was collected from the cotton-wheat cropping system field situated near the University campus, Bathinda. Bathinda region belongs to South-Western Punjab where calcareous soil developed under hot and arid to semi-arid conditions, having sandy loam to silt texture, grey to red desert soil is present. Bathinda region soil is further classified to sierozem soil. Alkalinity and salinity are reported to be the major problem for soil of this area. Various physico-chemical parameters of the soil were determined by the standard methods and listed in **Table-4.12**.

**Table-4.12:** Physico-chemical characterization of soil

Parameters Name	Unit	Mean±SD	References
<b>Physical properties</b>			
Bulk density	gm/cm <sup>3</sup>	1.40±0.04	Brady and Weil, 2002
Porosity	%	47.11±1.55	Brady and Weil, 2002
Soil Moisture	%	9.70±2.36	IS: 2720 (Part-II)
Water holding capacity (WHC)	%	17.99±1.63	Piper, 1947
<b>Physico-chemical properties</b>			
pH		8.6±0.04	IS: 2720 (Part 26)
Electrical conductivity	µS/cm	918.0±33.0	IS: 14767-2000
Cation exchange capacity (CEC)	Centimoles/100gm	9.56±0.05	IS: 2720 (Part XXIV)
Exchangeable Calcium	meq/100gm	7.85±0.07	Cheng and Bray, 1951
Exchangeable magnesium	meq/100gm	2.5±0.14	Cheng and Bray, 1951
Organic Carbon	%	1.04±0.11	Walkley, 1947
Organic matter	%	1.81±0.20	Walkley, 1947
Total sodium (Na)	mg/kg	38.37±2.72	Jackson, 1958
Total potassium (K)	mg/kg	9.44±0.30	Jackson, 1958
Total phosphorus (P)	mg/kg	201.25±3.54	Jackson, 1973
Available phosphorus (P)	mg/kg	54.035±8.95	Olsen et al., 1954

Soil sample was collected from a cotton growing field which was irrigated a few days earlier, thus the soil moisture content was found to be significantly high (9.70%); bulk density and soil porosity of soil were found to be 1.40 gm/cm<sup>3</sup> and 47.1%, respectively. Water holding capacity of these soils is reported very low and it was found to be 17.99%. Soil of this region is alkaline and the pH of the soil sample was found to be 8.6. Soil electrical conductivity was found to be low (918 µS/cm), due to

leaching of soluble ions of soil by irrigation water as irrigation was done a few days before sampling. Cation exchange capacity was found to be 9.56 Centimoles/100 g soil sample. Organic carbon and organic matter content for the soil sample were found to be 1.04% and 1.81%, respectively. Total Na and K content of the soil sample were found to be 9.44 mg/kg and 38.4 mg/kg respectively. Total P content of soil sample was found to be 201.3 mg/kg of which about 27% (54.0 mg/kg) was available P to plant.

#### **4.5 Physico-chemical properties of amended soil samples**

Fly-ash as well as biochar both has been reported to improve soil properties by increasing EC, CEC, improving pH, increasing porosity and permeability, decreasing soil bulk density, increasing surface area, water holding capacity (Ashokan et al., 2005; Jala and Goyal, 2006; Lehmann and Rondon, 2006; Blissett and Rowson, 2012; Yunusha et al., 2012), and also increasing microbial activities by providing them a source soil-C, soil-N and soil-P (Earthworm, Mycorrhizal and bacterial activities) after its incorporation into the soil (Warnock et al., 2007; Li et al., 2011). Having studied the effect of fly-ash on the biochar formation and the physico-chemical properties of the composite, a preliminary study was performed for observing the effect of the biochar, fly-ash and biochar/fly-ash composite produced in the present study for their further characterization and improving pyrolysis conditions. Various biochar, fly-ash and biochar/fly-ash composite samples prepared at 250<sup>0</sup>C and 450<sup>0</sup>C at 4 hours hold time were investigated for soil amelioration. The soil sample was mixed with various biochar, fly-ash and the biochar/fly-ash composite materials at the rate of 10 Mg/ha or 0.70 gm/100 gm soil (w/w) as reported in elsewhere.

Physical and chemical properties were determined by standard methods as mentioned in **Section-3.8**. The physical and chemical properties of the soil amended with the fly-ash, biochar and biochar/fly-ash composites were compared with the results obtained with unamended soil (control). A 13-19% increase in bulk density and 3-6% decrease in porosity was observed in biochar, fly-ash and biochar/fly-ash amended soil samples. The variation in bulk density and soil porosity with increase in fly-ash content was not significant. However, bulk density was comparatively lower in

450<sup>0</sup>C pure biochar and fly-ash amended soil than for the 250<sup>0</sup>C samples. A significant increase in water holding capacity was observed for amended soil samples. Water holding capacity increases with the increase in fly-ash concentration in composite samples for both 250<sup>0</sup>C and 450<sup>0</sup>C composite amended samples. However, no significant difference was observed in water holding capacity for 250<sup>0</sup>C and 450<sup>0</sup>C biochar/fly-ash composites amended soil samples (**Table-4.13**).

Biochar as well as fly-ash have been reported to have significant effect over soil physico-chemical properties. In the present study, pH, EC, CEC, exchangeable Ca and Mg, total Na, K and P as well as available P contents were estimated for amended soil samples. A significant variation in pH was observed in amended soil samples. As pH of 250<sup>0</sup>C biochar and composite samples were slightly acidic, a decrease in soil pH was observed for 250<sup>0</sup>C biochar amended soil sample. An increase in soil pH was observed with the increase in fly-ash concentration for 250<sup>0</sup>C composite amended soil samples. However, soil pH was not significantly affected after fly-ash amendment. A significant increase in pH was observed with 450<sup>0</sup>C biochar amended soil sample, however, soil pH was found to decrease as the concentration of fly-ash increases and approaches towards the pH that of the unamended soil samples (**Table-4.14**).

Electrical conductivity (EC) of soil is a measure of potential of free metals ions present in soil which are soluble in water solution. Fly-ash and biochar both the materials have high content of free metal ions, resulting in increased electrical conductivity. A significant increase in EC was observed for biochar, fly-ash and biochar/fly-ash composite amended soil samples. However, the increase in EC was less for 250<sup>0</sup>C biochar amended soil samples than 450<sup>0</sup>C samples. Two fold and four folds increase in EC was observed for the soil samples containing biochar prepared at 250<sup>0</sup>C and 450<sup>0</sup>C, respectively. A decrease in EC of the soil amended with biochar/fly-ash composite was observed with the increase in fly-ash concentration in composite samples.

**Table-4.13.** Table for various physical parameters of biochar/fly-ash composite amended to soil samples

Sample Name and data for various physical parameters for amended soil samples							
Soil Parameters	PT (°C)	Soil	SBC10	SBC31	SBC11	SBC13	SBC01
<b>Bulk Density</b> <b>(mg/cm<sup>3</sup>)</b>		1.02	1.14	1.17	1.16	1.15	1.17
	250	±0.04	±0.03	±0.02	±0.01	±0.06	±0.01
		1.02	1.13	1.19	1.17	1.18	1.11
	450	±0.04	±0.03	±0.02	±0.02	±0.02	±0.05
<b>Porosity (%)</b>		61.51	56.96	55.77	56.06	56.68	55.85
	250	±1.55	±1.00	±0.61	±0.27	±2.15	±0.53
		61.51	57.37	55.77	55.82	55.44	58.03
	450	±1.55	±1.27	±0.90	±0.80	±0.84	±2.03
<b>Water Holding</b> <b>Capacity (%)</b>		17.99	24.18	27.75	26.50	23.36	32.57
	250	±1.63	±0.12	±3.69	±0.90	±2.95	±0.95
		17.99	24.27	21.34	26.37	32.23	28.85
	450	±1.63	±0.08	±0.69	±5.12	±1.52	±0.15

**Table-4.14:** Physico-chemical and chemical properties of biochar/fly-ash composite amended to soil samples

Soil Parameter	PT (°C)	Sample Name and data for various physico-chemical and chemical parameters for amended soil samples					
		Soil	SBC10	SBC31	SBC11	SBC13	SBC01
pH	250	8.58	7.94	8.14	8.20	8.26	8.65
		±0.04	±0.06	±0.03	±0.02	±0.18	±0.07
	450	8.58	9.16	8.54	8.28	8.70	8.65
		±0.04	±0.03	±0.02	±0.02	±0.06	±0.06
EC (µS/cm)	250	918.0	2011.3	1492.3	1191.0	1306.3	1051.3
		±33.0	±123.8	±38.4	±51.9	±190.4	±25.8
	450	918.0	3633.3	1630.0	1240.7	1274.6	1177.0
		±33.0	±77.7	±88.9	±72.1	±78.2	±38.0
CEC (Centimoles/100 g soil)	250	9.56	10.52	8.96	10.88	11.04	10.76
		±0.06	±0.06	±0.23	±0.11	±0.57	±0.28
	450	9.56	9.76	11.52	10.20	10.36	11.12
		±0.058	±0.11	±0.11	±0.28	±0.06	±0.11
Exchangeable Ca (meq/100 g soil)	250	7.85	8.05	7.35	7.65	7.75	7.80
		±0.07	±0.07	±0.07	±0.21	±0.07	±0.28
	450	7.85	6.85	7.30	7.30	7.15	7.55
		±0.07	±0.35	±0.14	±0.00	±0.07	±0.07
Exchancheable Mg (meq/100 g soil)	250	2.50	3.10	2.90	2.70	2.90	2.35
		±0.14	±0.28	±0.00	±0.00	±0.00	±0.07
	450	2.50	3.60	3.30	2.75	2.55	1.60
		±0.14	±0.57	±0.14	±0.07	±0.07	±0.00
Organic carbon (%)	250	1.04±0.11	1.60±0.00	1.32±0.06	1.00±0.06	1.12±0.23	1.12±0.11
	450	1.04±0.11	1.12±0.00	0.96±0.00	0.84±0.06	1.00±0.06	0.96±0.00
Organic matter (%)	250	1.81±0.20	2.78±0.00	2.29±0.10	1.74±0.10	1.95±0.39	1.95±0.20
	450	1.81±0.20	1.95±0.00	1.67±0.00	1.46±0.10	1.74±0.10	1.67±0.00

Continued...



Soil Parameter	PT (°C)	Sample Name and data for various physico-chemical and chemical parameters for amended soil samples					
		Soil	SBC10	SBC31	SBC11	SBC13	SBC01
Total K content (mg/kg)	250	76.73	80.88	78.42	74.11	75.50	71.59
		±5.43	±2.84	±1.50	±2.36	±1.26	±1.21
		76.73	101.58	83.50	89.24	72.17	85.27
Total Na content (mg/kg)	450	±5.43	±2.93	±1.17	±3.97	±3.93	±2.38
		18.89	21.66	19.01	21.53	21.53	14.86
		±0.61	±2.75	±0.99	±1.76	±1.756	±0.34
Total P content (mg/kg)	250	18.89	17.60	16.80	22.21	18.87	18.81
		±0.61	±0.96	±1.36	±1.46	±1.06	±1.00
		199.58	182.50	174.17	165.83	170.83	179.17
Available P content (mg/kg)	450	±2.60	±2.50	±2.60	±2.60	±2.60	±9.38
		199.58	197.92	212.92	195.42	188.75	186.25
		±2.60	±2.60	±6.17	±1.44	±6.61	±2.500
<u>Micronutrients (mg/kg)</u>	250	13.51	17.37	24.82	19.74	34.74	48.86
		±2.24	±3.29	±3.33	±1.99	±3.23	±14.93
		13.51	27.37	11.40	11.14	10.88	19.30
Cu	450	±2.24	±2.97	±1.61	±1.45	±2.13	±6.17
		ns	0.02±0.01	ns	ns	ns	ns
		ns	0.12±0.00	0.02±0.01	0.06±0.00	ns	ns
Mn	250	ns	6.26±0.10	5.68±0.09	3.38±0.01	5.16±0.024	1.28±0.02
		ns	4.70±0.05	4.30±0.00	4.84±0.04	1.48±0.01	1.86±0.02
Fe	250	ns	2.88±0.05	2.58±0.02	3.06±0.05	2.98±0.03	1.74±0.01
		ns	3.96±0.02	2.82±0.02	2.86±0.02	1.96±0.01	1.80±0.04

Thus, it can be inferred that biochar incorporation to soil will lead to increase in EC which can be significantly controlled by addition of fly-ash, however, in all these cases the electrical conductivity of soil after amendment will remain higher than that of unamended (control) soil (**Table-4.14**). Cation exchange capacity (CEC) is an important parameter for defining soil condition. CEC is mainly because of the presence of various negative exchange sites which have capacity to bind with cations and to exchange them with root of plants for proper growth and nourishment. Fly-ash and biochar both have been reported to have high CEC and increase the CEC of the subsequently amended soils (Yuan et al., 2011). In the present study, biochar, fly-ash and biochar/fly-ash composites were found to increase soil CEC after amendment. 250<sup>0</sup>C pure biochar amended soil, CEC was higher than soil sample amended with biochar prepared at 450<sup>0</sup>C. CEC was found to increase with the increase in fly-ash concentration except 1:3 biochar/fly-ash composites. CEC was maximum for 450<sup>0</sup>C 3:1 biochar/fly-ash composite and minimum for 1:3 biochar/fly-ash composite amended soils. CEC was significantly high for 450<sup>0</sup>C treated fly-ash amended soil sample than 250<sup>0</sup>C fly-ash sample (**Table-4.14**).

For proper plant growth, some of the macro nutrients like C, N, P, Ca, Mg, Na, and K are very necessary because their deficiency limits the optimum growth of plants. These elements are integrated component of soil minerals but because of extensive agriculture their concentration has become limited for most of the soil. For this, various inorganic/organic supplements like fertilizers, composts, fly-ash and biochar have been added to soil. Biochar is a rich source of carbon material, however, is it available to plant or not, require further investigations. Likewise, fly-ash is also a source of carbon which may have positive effect over soil carbon pool. Organic matter has significant effect over other soil properties like nitrogen availability and results in increase in WHC and moisture content of soil. Organic carbon and organic matter contents of soil have been estimated by Walkley-Black rapid titration method in which organic matter is determined by multiplying 1.742 factor in organic carbon (OC) content. In the present study, fly-ash and crop residue biochar as such and the composites prepared during slow pyrolysis have been added to soil and the organic content estimated for these amended samples. A significant increase in %OC and

%OM contents was observed in pure biochar amended soil samples and the increase in %OC and %OM was very high for 250<sup>0</sup>C biochar amended soil sample than 450<sup>0</sup>C biochar amended soil sample. An initial decrease in %OC and %OM was observed with increase in fly-ash concentration up to 50% at 250<sup>0</sup>C as well as 450<sup>0</sup>C biochar/fly-ash composite amended soil samples, however, with further increase in fly-ash concentration, no significant variation in %OC and %OM of soil was observed. As carbon at 450<sup>0</sup>C might have become volatilized or recalcitrant, thus the variation in %OC and %OM for 450<sup>0</sup>C biochar, fly-ash as well as biochar/fly-ash composite samples was lesser than 250<sup>0</sup>C amended soil samples (**Table-4.14**).

Fly-ash and biochar both have been reported to increase Ca, Mg, Na and K contents of soil after their amendment. Exchangeable Ca<sup>++</sup> content was not significantly affected after amendment. Exchangeable Mg<sup>++</sup> content was higher for the biochar and biochar/fly-ash composite amended soil samples and a decrease was observed with the increase in fly-ash concentration in composite. Exchangeable Mg<sup>++</sup> content of fly-ash amended soil samples was significantly lower than the unamended soil. Soil samples amended with biochar and biochar/fly-ash composite prepared at 450<sup>0</sup>C amended soil samples had high exchangeable Mg<sup>++</sup> than that of biochar and biochar/fly-ash composites prepared at 250<sup>0</sup>C amended soil samples. Total K content was higher for soil samples containing pure biochar. With increase in fly-ash content, total K content was found to decrease. Increase in K content was significantly high for 450<sup>0</sup>C biochar amended soil than 250<sup>0</sup>C biochar amended soil. Total K content was lower for fly-ash amended soil than biochar amended soil. A decrease in total K content was observed for 250<sup>0</sup>C biochar/fly-ash composite (1:1 and 3:1) samples and fly-ash only amended soil samples than unamended soil. Total Na content did not vary with biochar, fly-ash or biochar/fly-ash composite application, however, a slight increase was observed for biochar and biochar/fly-ash composite prepared at 250<sup>0</sup>C amended soil samples. A decrease in total Na content was observed for pure 450<sup>0</sup>C biochar amended soil and further it was constant for other amendments of 450<sup>0</sup>C (**Table-4.14**).

Both total and available P contents for biochar, fly-ash and biochar/fly-ash composite amended soil samples were analysed and a decrease in total P content was observed for 250<sup>0</sup>C amended soil sample from the unamended soil sample. An increase in total P content was observed for 450<sup>0</sup>C biochar and 1:3 biochar/fly-ash composite amended soil samples. A decrease in total P content of soil was observed with the increase in fly-ash concentration. Available P content of soil was found to increase with pure biochar amendment and the increase was significantly high for 450<sup>0</sup>C biochar amended soil sample than that of 250<sup>0</sup>C biochar amended soil sample. Similarly, available P content was significantly very high for 250<sup>0</sup>C thermally treated fly-ash amended soil sample than 450<sup>0</sup>C fly-ash amended soil sample. In 250<sup>0</sup>C biochar/fly-ash composite amended soil samples available P content was found to increase with the increase in fly-ash concentration whereas for 450<sup>0</sup>C biochar/fly-ash composite amended soil samples a decrease in available P was observed with fly-ash proportion (**Table-4.14**).

Micronutrient (Mn, Fe and Cu) contents from soil sample were extracted by using DTPA extractant and determined by atomic absorption spectrophotometer (AAS). In unamended soil, micronutrients were not found in a detectable range. However, fly-ash is a rich source of micro-nutrients but in the present study, fly-ash amended soil samples were found to have lower micronutrient content than biochar and biochar/fly-ash composite amended samples. Micronutrient content was found to vary with type of biochar samples prepared at 250<sup>0</sup>C and 450<sup>0</sup>C. Pure biochar amended soil samples were found to have high micronutrient content and in general, a decrease was observed with increase in fly-ash concentration. Cu was not present in detectable range in fly-ash and biochar/fly-ash composites prepared at 250<sup>0</sup>C amended soil samples, and fly-ash as well as 1:3 biochar/fly-ash composite prepared at 450<sup>0</sup>C amended soil samples, however, it was observed in biochar, and 3:1 and 1:1 biochar/fly-ash composite prepared at 450<sup>0</sup>C and biochar prepared at 250<sup>0</sup>C amended soil samples. Biochar and biochar/fly-ash composite prepared at 250<sup>0</sup>C amended soil samples were found to have higher Mn content than biochar and biochar/fly-ash composite prepared at 450<sup>0</sup>C amended soil samples. Fe content was significantly high for biochar and biochar/fly-ash composite prepared at 450<sup>0</sup>C

amended soil samples than biochar and biochar/fly-ash composite prepared at 250<sup>0</sup>C amended soil samples. A significant decrease in Fe content was observed in biochar/fly-ash composite prepared at 450<sup>0</sup>C amended soil samples with increase in fly-ash concentration. However, Fe content was not found varying significantly for biochar and biochar/fly-ash composite prepared at 250<sup>0</sup>C amended soil samples. In general, biochar from crop residue was found to increase micronutrient content of soil significantly rather than fly-ash which is considered as a good source of micronutrients. This might be due to increase in availability of micronutrient in presence of biochar in soil (**Table-4.14**).

# CHAPTER V

## DISCUSSION

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### DISCUSSION

Wheat straw pyrolysis in absence of fly-ash was incomplete resemblance to the material prepared elsewhere in literature. However, the temperature hold time had a significant impact on the lowering of the yield of biochar (Demirbas, 2006; Kim et al., 2012; Lee et al., 2013). SEM images revealed that the biochar produced at 250<sup>0</sup>C has the crystalline structure of the biomass retained to some extent, whereas upon addition of fly-ash or when thermally treated at 450<sup>0</sup>C, the structure under a complete transformation, whereby the material does not retain any significant resemblance with the biomass sample (Kim et al., 2012).

Upon addition of fly-ash the yield of the biochar increased in case of the 250<sup>0</sup>C biochar sample and decrease in case of 450<sup>0</sup>C biochar sample was observed. This is accounted to the adsorption of volatilized material at 250<sup>0</sup>C on to the fly-ash. On the contrary, the 450<sup>0</sup>C biochar composite showed an increase in the decomposition of biochar in presence of fly-ash.

H/C ratio of the biochar sample indicates a relative aromatization of the sample and this ratio was decreased with increase in fly-ash at both 250<sup>0</sup>C and 450<sup>0</sup>C treatment temperature which indicates an increased aromatization in presence of fly-ash. This increase in aromatization is responsible for the recalcitrance of the biochar and would, thus, lead to an alternative increased carbon sequestration (Bruun et al., 2011; Singh et al., 2012b)

The biochar prepared at 250<sup>0</sup>C has a slightly acidic character which is implanted by the presence of carboxylic acid functional groups at the surface of the material; however in the presence of fly-ash the pH of the composite samples prepared at 450<sup>0</sup>C had an alkaline nature (Xiao et al., 2001). This could be due to excessive formation of alkali and alkaline metal oxides at high temperature and in presence of fly-ash. Thus, the pH is dominated by the metal oxides and carbonates, which is also indicated by the alkalinity of these samples.

Biochar has a significant cation exchange property which could be modulated by fly-ash in the biochar/fly-ash composites prepared (Yuan et al., 2011). This indicates that the fly-ash trace metal leachability and phytotoxicity can be significantly be averted by using the biochar samples, which requires further investigation.

Biochar and fly-ash both has been used for a long time as a soil ameliorating agent due to their higher nutrient content, ability to maintain the pH, CEC, and improving physical characteristics like bulk density, porosity, water holding capacity, texture, etc. (Ashokan et al., 2005; Lehmann and Rondon, 2006; Li et al., 2011; Blissett and Rowson, 2012). A decrease in bulk density and porosity of soil amended with biochar, fly-ash and biochar/fly-ash composites was observed which might be due to low rate of application or the aggregation of soil particles after incorporation. The results revealed that biochar and biochar/fly-ash composites have significant effects over pH, EC, CEC, exchangeable  $Mg^{2+}$ , % OC, total K and Na contents, available P content and micronutrients contents were found significantly in biochar, fly-ash and biochar/fly-ash composite amended soil samples (Yuan et al., 2011).



# SUMMARY

## SUMMARY

Catalytic pyrolysis of wheat crop residue in the presence of fly-ash showed a significant decrease in volatilization at 250<sup>0</sup>C and an increase in the volatilization at 450<sup>0</sup>C. SEM and FTIR analyses also revealed the interaction of crop residue and fly-ash during pyrolysis leading to aromatization and deoxygenation process simultaneously. Various physico-chemical analyses results of the biochar/fly-ash composite samples ranged in between extreme ends of pure biochar and pure fly-ash resulting into a composite material which may have tuneable properties for soil amelioration and plant growth. The soil amelioration effect of the biochar and biochar/fly-ash composite material prepared at 450<sup>0</sup>C showed a significant positive effect over soil pH, EC, CEC and exchangeable cations. However, the biochar and biochar/fly-ash composite material prepared at 250<sup>0</sup>C was found to be suitable for ameliorating highly alkaline soil, because the pH of these materials was in acidic range, which has capacity to decrease soil pH after application to soil. Soil nutrient condition was found to be improved with the application of biochar, fly-ash and biochar/fly-ash composite material. Leaching studies of heavy metals after application of these composites to soil has been recommended to further support these materials as a potential soil ameliorant. On the other hand, the integrated approach of crop residue and fly-ash utilization leads to minimization of waste volume.

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