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# Effects of temperature on the physicochemical characteristics of fast pyrolysis bio-chars derived from Canadian waste biomass

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## HIGHLIGHTS

- Physico–chemical studies of bio-chars produced from waste biomasses at 400–550 °C.
- Abundant alkaline elements in biochars showed their potential for soil application.
- All biochars, except poultry litter-based are suitable precursors for activated carbon.
- Larger carbon content and compact aromatic structure in biochars produced at 550 °C.
- Biochars prepared at 550 °C have better potential for soil application.

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## ABSTRACT

Bio-chars are produced by means of a mobile pyrolysis unit from fast pyrolysis of different types of Canadian waste biomass including agricultural waste (wheat straw and flax straw), forest residue (sawdust) and animal manure (poultry litter). They were analyzed for their physicochemical changes with pyrolysis temperature (400–550 °C). To study the chemical nature of bio-char samples, analyses such as XRD, FTIR, Raman spectroscopy, XPS, SEM, ICP, TGA and electrical conductivity measurements were performed. ICP-MS analysis showed that poultry litter-derived bio-char had the largest concentration of inorganic elements (~200,000 ppm) followed by wheat straw, flax straw and sawdust derived bio-chars. In addition, the alkaline elements were 4–14 times that of essential elements (Fe and P) and 18–57 times that of heavy elements. Electrical conductivity of bio-chars, a measure of their salinity, was maximum for all samples prepared at 400 °C. SEM showed that sawdust derived bio-chars retained relatively less dissociated surfaces compared with other bio-chars. XRD confirmed the presence of sylvite, dolomite and quartz in the bio-chars. The deconvoluted XPS spectra indicated that for all precursors except poultry litter, aromatic/aliphatic carbon portion increased in the corresponding bio-char with the pyrolysis temperature. For all precursors, O/C mass ratio decreased with an increase in the pyrolysis temperature due to the development of compact aromatic structure in bio-char. This result was confirmed by a drastic increase in $I_D/I_G$ (defect to graphitic carbon) ratio of bio-char samples produced at 550 °C from the deconvolution results of Raman spectroscopy. Thermogravimetric analysis showed that biomass decomposition started at lower temperatures for the following order: poultry litter, wheat straw, flax straw and sawdust.



## 1. Introduction

Biomass is a promising alternative renewable source for energy and chemical feedstock. Non-food biomass has a great potential to produce bio-energy and bio-chemicals. In addition, use of biomass as a feedstock for energy sector is one of the most effective solutions for global problems such as increase in greenhouse gases emissions, increasing energy demand and dependency on fossil-fuel. About 561 million dry tones of biomass is available in Canada that has great potentials for bio-energy and bio-chemicals production [1]. Thermo-chemical processes such as pyrolysis, gasification and liquefaction are the most common techniques used for production of bio-fuels and bio-char. Pyrolysis needs oxygen deficient condition at elevated temperatures to produces pyro-gas, bio-oil and bio-char. These products can be used directly or after

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processing as fuel. Bio-char and bio-fuel not only have some fuel applications but also can be used as a source for chemicals and value-added products. Physical and chemical properties of bio-char depend on the type of feedstock and operating conditions used for pyrolysis. During recent years, environmental, agricultural and industrial applications of bio-char have attracted the attention of scientific community.

Bio-char is mostly formed from carbon and has various applications for soil amendment [2], removal of toxic materials [3] and production of value-added products [4]. To evaluate each type of bio-char for any particular application, the bio-char should be characterized for its composition, porous structure and surface chemistry. From agricultural point of view, bio-char has a great potential to improve the soil productivity [2]. Improvement of soil properties depends on the mineral content of bio-char, its composition and structure as well as bio-char stability and surface chemistry. Degree of carbonization of bio-char plays an important role for adsorbing organic or metallic contaminants [5]. Bio-char can be used for production of value-added products such as activated carbons. The quality of activated carbon for its especial application strongly depends on the composition and structure of precursor as well as type of activation process.

For the present study, pinewood sawdust (forest residue), wheat straw and flax straw (agricultural residues) and poultry litter (livestock manure) were used as precursors for pyrolysis. These biomass precursors are abundant across Saskatchewan and Canada. For example, 9.5 million tons of wheat and 0.3 million tons of flax were produced in 2010 in Saskatchewan [6,7]. Pinewood sawdust is a forest residue and harvesting pinewood will not exceeding Canada's sustainable forestation limits. Use of poultry litter for pyrolysis is an effective solution for its disposal as it is one of the main problems for the world poultry farming industry [8,9]. A recent study by Azargohar et al. [10] describes the physico-chemical characteristics of biomasses used in this research. In addition, investigations by Nanda et al. [11] on wheat straw and pinewood sawdust, Naik et al. [12] on flax straw and Das et al. [13] on poultry litter also intensely discuss the physical and chemical properties of these waste biomasses. These studies help to understand the feedstocks and their potentials for biofuel (e.g., bio-oil) and biomaterial (e.g., bio-char) production through pyrolysis. However, the current study is focused on determining the nature of their bio-chars for potential environmental and industrial applications. Inorganic elements' concentration measured by ICP-MS is used to evaluate nutrients present in bio-char which are useful for soil amendment. Electrical conductivity presents an estimation of salinity of bio-char which is a critical criterion for bio-char incorporation in soil. Raman spectroscopy determines the extent of formation for compact aromatic structures in bio-char. Formation of such structures in bio-char results in their long-life span in soil compared with that for waste biomass. FTIR and XPS show how surface and structural properties of bio-char are different from those for parent lignocellulosic material. Changes in the surface chemistry of bio-chars can be determined by FTIR and XPS. In addition, XPS is able to quantify this change in surface functional groups. Surface chemistry of bio-char affects its performance in soil incorporation and any adsorptive properties of bio-char for environmental applications. The surface morphology of char is studied using SEM. Suitable bio-char for activated carbon production needs to have low ash content and large carbon content. Characterization techniques such as XPS, TG/DTA and Raman as well as plots such as Van Krevelen plot provide enough information regarding structural change and elements' concentration change in the organic part of bio-char with a change in pyrolysis temperature. For agricultural application, characterization techniques such as ICP-MS, electrical conductivity, XRD, Raman and XPS are useful. Large portion of alkaline elements, lower EC, more number of minerals and highly developed aromatic structure are necessary for agricultural application of bio-char.

This study shows the effects of pyrolysis temperature (400, 475 and 550 °C) on the characteristics of bio-chars produced by means of fast pyrolysis in a mobile pyrolysis unit. Use of mobile pyrolysis unit in rural area provides great opportunities to decentralize energy sources for farmers or small communities with the ability to self-sufficiently produce fuels for heating purposes and bio-chars for soil amendment from processing common wastes such as agricultural wastes and litters found in farms. Spectroscopic techniques, thermogravimetric analysis and X-ray scattering techniques were used for this study.

## 2. Experimental

Feedstock and pyrolysis process: wheat straw (WS), sawdust (SD), flax straw (FS) and poultry litter (PL) collected in Saskatchewan (Canada) were used as the feedstock for the pyrolysis process. Pyrolysis of these four different precursors was performed at the Saskatchewan Research Council (Saskatoon, Canada) using a mobile pyrolysis unit made by ABRI Tech Inc. (Quebec, Canada) at three different temperatures in the range of 400–550 °C. Vapor residence time was ~1 s. Bio-char residence time was ~15 min. Pyrolysis time for each run was 8 h and an average feedrate of 200 g/min was used for pyrolysis runs. System works under atmospheric pressure condition. Details of mobile pyrolysis unit are mentioned elsewhere [10]. The bio-chars produced at 400 °C are denoted as SD-400, WS-400, FS-400 and PL-400 based on the corresponding precursors. Similarly, the bio-chars produced at 475 and 550 °C were denoted as SD-475, WS-475, FS-475, PL-475 and SD-550, WS-550, FS-550, PL-550, respectively.

Characterization methods: The Inductively coupled plasma-mass spectrometry (ICP-MS) analysis of bio-char samples was performed using a Sciex Elan 5000 ICP-MS (Perkin Elmer, USA).

The IR spectra of bio-char samples were obtained using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Samples were scanned and recorded using a Spectrum GX spectrometer (Perkin–Elmer, USA) for an average of 256 scans at a resolution of 4 $cm^{-1}$ and in the wave number range of 400–4000 $cm^{-1}$.

A Renishaw inVia Raman microscope was used for Raman spectroscopy of bio-chars with back scattering configuration. The source of radiation was a laser operating at a wavelength of 514 nm. Bio-char pellets were prepared for analysis under the laser. The spectral resolution was 4 $cm^{-1}$ with 10% laser power and 10 s of exposure time along with a total of 15 acquisitions. The Raman spectra between 1100 and 1800 $cm^{-1}$ were curve-fitted using the WiRE Raman software (version 3.2).

Standard X-ray photoelectron spectroscopy (XPS) measurements using an Omicron monochromatized Al K$\alpha$ source ($h\nu$ = 1486.7 eV) and Sphera EA125 hemispherical electron energy analyzer were carried out in the Surface Science Facility located at the Resonant Elastic and Inelastic Soft X-ray Scattering (REIXS) beamline of the Canadian Light Source (Saskatoon, Canada). The survey scan spectra were collected in the 1200–0 eV binding energy range in 0.5 eV steps with a pass energy of 50 eV. High resolution scanning of the C1s region was also conducted in 0.1 eV steps with a pass energy of 25 eV. An accelerating voltage of 15 kV and an emission current of 20 mA were used for the analysis. The operating vacuum pressure was less than $2 \times 10^{-10}$ mbar. Peak deconvolutions of high resolution C1s spectra were accomplished using the CasaXPS software (version 2.3.16 PR 1.6).

Thermogravimetric analysis (TGA) was used to determine the devolatilization characteristics of feedstock and bio-chars using a Pyris Diamond TG/DTA instrument (PerkinElmer, USA). The