The influence of pilot-scale pyro-gasification and activation conditions on porosity development in activated biochars

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Abstract

Few studies have examined the influence of pyro-gasification and activation conditions on porosity development in activated biochars. In this context, this study investigates the effects of pyro-gasification temperature (315, 399, and 454 °C), activation temperature (700, 800, and 900 °C), and activating agent (CO_2 flow rate: 2, 3, and 5 L min^{-1}) on porosity in materials made from wood residues (black spruce and white birch). Activated biochars were prepared in a two-step process: torrefaction/fast pyrolysis in a pilot-scale plant and activation using an in-house pilot-scale furnace. Results show that the physical properties of activated biochars improved over biochars and wood residues, with fivefold greater surface area for activated birch biochar over biochars, and threefold greater surface area for activated spruce biochars. Statistical analysis results reveal that pyro-gasification and activation temperature, CO_2 gas flow rate, and wood residue type significantly affected the porosity of activated biochars (at $p < 0.05$). The main findings are as follows: i) Torrefaction or pyrolysis pre-treatment step had less impact on the porosity of activated biochars, so lower energy expenditure is required to improve product quality, i.e., porosity; ii) Activation temperature was the major variable to optimize specific surface area; by increasing from 700 to 900 °C, the average surface area for activated biochars made from both wood residues increased to nearly 120 m^2 g^{-1}; iii) pilot-scale technologies produced porous activated biochars comparable to laboratory-scale technologies which could boost incentives to use thermochemical biomass conversion, and increase the profitability with these diversified by-products in biorefinery industry.

Keywords: Biochar, activated biochar, pyro-gasification and activation conditions, operating parameters optimization, statistical analysis

1. Introduction

Advanced biomass conversion methods (using renewable carbon sources) enable transforming low-cost waste by-products into value-added materials such as chemicals, plastics, food additives, clothing fibers, polymers, paint, heat, fuel, and electricity [1–3]. Biomass conversion is a promising research field that examines and develops sustainable, environmentally friendly products and practices. The main challenge is to produce cost-efficient materials that perform as well or better than fossil fuel-based materials [4]. Thermochemical conversion processes (e.g., torrefaction, pyrolysis, gasification) are used to convert lignocellulosic biomass into solid, liquid, and gas products at various proportions and with physicochemical properties that are significantly enhanced over those of the raw material. The solid material produced is called biochar [5], defined by the International Biochar Initiative (IBI) as a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment [6].

Recently, primary industries (e.g., agriculture, logging, forestry) have been converting biomass residues into biochar to manage the tons of waste generated daily. Biochar can then be commercialized as fertilizers for soil amendment [7–9] and as pellets for bioenergy production [10]. Recent applications reported in the literature, including carbon sequestration (climate change mitigation) and degraded site rehabilitation [11–13], have promoted advances in biochar structure and characteristics, with consequent positive impacts on agriculture and the environment [14]. Moreover, due to the higher carbon content of biochar compared to biomass and the presence of certain oxygenated groups (e.g., carboxylic, phenolic, carbonyl), biochar has been used as carbon electrode materials for application in electrochemical capacitors and supercapacitors [15–17], catalyst supports [18,19], and adsorbents [20]. However, these applications are limited by the relatively low surface area (< 200 m^2 g^{-1}) and porosity of biochars due to certain limited conditions during large-scale reactor preparation: low-temperature pyro-gasification (e.g., torrefaction at 320 °C max), short residence time (1–2 s), and high heating rate (1000 °C min^{-1}).

Activation is a commonly used method to improve the physical properties and adsorptive capacity of biochars [21]. Activation refers to chemical and/or physical treatment of biochar that maximizes the pore density as well as the surface area available for adsorption or chemical reactions. Typically, biochars are impregnated with chemicals such as H_3PO_4 or KOH and/or steam or CO_2 gas at high temperature (e.g., 900 °C), causing a selective gasification of carbon atoms [22]. During this process, low molecular weight carbon molecules are removed, generating voids in the material structure. Thus, when processed at higher temperature, activated biochar presents a better developed porous carbon structure [21]. Several biomass precursors derived from wood residues, chips and pellets, or agricultural wastes such as fruit shells, stones, husks, and hulls have been used to produce activated biochars [23]. Abundant literature have examined the influence of activation parameters (e.g., activation temperature, activation time, gas flow rate, impregnation chemical, biochar ratio) on porosity development in activated biochars [24]. The results show that processing conditions at high activation temperature (e.g., 900 °C) [25–31], high CO_2 or steam flow rate [32,33], longer residence time (e.g., 2h) [25,26,32,34–37], and high chemical impregnation ratio [38–40] produce highly porous materials. However, little attention has been paid to the different pyro-gasification (i.e., an integrative term that comprises all thermochemical processes such as torrefaction, slow to fast pyrolysis, and gasification) conditions for biochar production or how these conditions affect the porosity of activated biochars.

Biochar as a by-product of biomass conversion by pyro-gasification has also been applied as a precursor for activated biochar production. Azargohar and Dalai [41] investigated biochar activation using biochar made from wood residues produced by large-scale renewable bio-oil production, whereas Zhang et al. [42] used a pilot fluidized sand-bed reactor (7 kg h^{-1} feed rate) for fast pyrolysis of biomass wastes (oak wood, corn hulls, and corn stover) at 500 °C. For the activation procedure, the same authors used a small fixed bed reactor to produce chemically activated carbon (up to 1578 m^2 g^{-1} surface area) and a small quartz reactor to produce CO_2-activated biochar (up to 1010 m^2 g^{-1} surface area), respectively. Both activated biochars were prepared in laboratory-scale furnaces using small amounts of precursor: 20 and 0.7 g, respectively. In this case, the activation parameters were more controllable due to the small amounts of stationary precursor. Other authors have prepared activated biochars using a laboratory-scale furnace for both steps: pyro-gasification and activation [43–50]. Although a pilot-scale activation furnace that would be readily applicable for industrial-scale production of activated biochar shows great promise, few studies have investigated the processing conditions for these technologies to date.

Moreover, in response to ever stricter government regulations for pollution control, activated biochars offer an alternative material for the activated carbon market, which is projected to post $4.9 billion in revenues by 2021 [51]. For this purpose, activated biochars were prepared using pilot-scale torrefaction/pyrolysis and activation of different wood residues. The processing conditions (i.e., parameters) were optimized and statistically analyzed to assess the effects on the porosity (surface area and pore volume) of the produced materials. Using a statistical model analysis, the porosity of activated biochars was controlled by varying the processing conditions to achieve distinct porous materials for specific potential applications. An additional practical implication of this study is the reduced energy and time required to produce high-quality activated biochars from wood residues.

2. Materials and methods

2.1 Biochar preparation

Biochars were prepared from black spruce (BS) and white birch (WB) wood residues sampled from sawmills located in Abitibi-Témiscamingue, in the province of Québec, Canada. This biomass waste was selected due to its large availability in the region and its successful application as precursors for biochar production using CarbonFX technology (Airex Energy Inc., Bécancour, QC, Canada). Fig. 1 a) shows the torrefaction/fast pyrolysis plant where biomass is converted to torrefied material or biochar (at 250 to 455 °C) in an oxygen-free environment. Materials were processed in a cyclonic bed reactor enabling large-scale biochar production (250 kg h^{-1}) from a variety of feedstock, including woody biomass and agricultural waste. The biomass is first dried in a pre-drying system (100-160 ±10 °F), then transported into a conditioning chamber (900-1200 ±20 °F) connected to a combustion chamber (1200 ±20 °F), that heats the whole system. Subsequently, the biomass reaches the cyclonic bed reactor (600-900 ±20 °F) where it is converted into torrefied biomass or biochar in approximately 2 s. A panel control controls the whole system notably the following parameters: temperature process, percentage of oxygen entrance, hot air flow, and residence time in the cyclonic bed reactor. Wood residues were milled with a 6 mm Hammer Mill equipped with a screen grate (industrial grinder, Schutte Buffalo, Hammer Mills, Buffalo, NY, USA) and subsequently dried (dryer, Abri-Tech Inc., Namur, QC, Canada) to obtain a moisture content below 40% before introduction into the reactor. For each biomass waste (BS or WB), three types of biochars were synthesized by CarbonFX at three different temperatures: 315, 399, and 454 °C (600, 750, and 850 °F), respectively. The synthesized materials were designated BS315, BS399, and BS454, and WB315, WB399 and WB454, respectively.

2.2 Activated biochar synthesis

For the activation procedure, each biochar type was placed in an in-house pilot-scale furnace. Fig. 1 b) shows the 1 kg charge pilot furnace developed at the CTRI laboratory for biochar activation. It comprises three parts: 1) a feed hopper, 2) a screw conveyor tube placed in a muffle furnace, and 3) a recovery hopper. A condensation tube allows gases and organic compounds released during activation to be condensed, and additional gas inlets allow introducing nitrogen to maintain an inert system as well as CO_2 gas as the physical agent. The screw conveyor is driven by an electronic engine to transport the precursor material (milled at 1–2 mm; grinder: Ro-tap RS-29, WS Tyler, Mentor, OH, USA) from the feed hopper to the recovery hopper. Activation time was measured with a chronometer: the material took 67 min to pass through the screw conveyor to the recovery hopper. 100 g of each biochar type was processed at three different pyrolysis temperatures (315, 399, and 454 °C), activation temperatures (700, 800, and 900 ± 4 °C), and activation gas injection rates (2, 3, and 5 L min^{-1}). The highest CO_2 flow rate (5 L min^{-1}) was applied exclusively for biochar activation at 900 °C. The biochar materials BS315 and WB454, which were activated at 900 °C in the presence of CO_2 gas at 5 L min^{-1}, were designated BS315A900-5 and WB454A900-5, respectively.

2.3 Materials characterization

Before and after processing, all the materials were characterized in terms of morphology, CHNSO percentage, thermal degradation as a function of temperature, porous structure (surface area and pore volume), and surface chemistry. The morphology of wood residues, biochars, and activated biochars was investigated with a JEOL JSM-5500 (JEOL USA, Inc., Peabody, MA, USA) scanning electron microscope (SEM) after metallization (i.e., samples were mounted on gold studs). CHNS elemental analyzer (Perkin Elmer 2400 CHNS/O Analyzer; Waltham, MA, USA) was used for elemental determination of carbon, hydrogen, nitrogen, and sulfur contents by sample combustion in a pure O_2 stream. Oxygen content was obtained by calculating the difference (%O = 100 − %CHNS). Thermogravimetric analysis (TGA) using a Netzsch STA 449 F5 Jupiter instrument (Exton, PA, USA) was performed to determine thermal degradation of woody residues, biochars, and activated biochars. A 15 mg sample of each material was placed in a ceramic crucible and the temperature was then increased to 1000 °C at a rate of 10 °C/min^{-1}. Analyses were performed using He gas as a carrier at a flow rate of 50 mL min^{-1}. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Kratos AXIS ULTRA system (Wharfside, MA, UK) equipped with a channel electron multiplier detector. The X-ray source used monochromatic Al K-alpha radiation operated at 300 W under vacuum at 5×10^{-10} Torr. Binding energies for the high-resolution spectra were calibrated using C1s at 284.6 eV as a reference. The XPS core level spectra were analyzed using CasaXPS (Casa Software Ltd.).

Pore texture parameters were obtained by Kr and N_2 at -196 °C and by CO_2 at 0 °C using a Micromeritics ASAP 2460 Surface Area Analyzer (Norcross, GA, USA). N_2 was used to analyze highly porous materials (i.e., activated biochars), CO_2 to measure ultramicropores (< 0.7 nm) present in biochars and activated biochars, and Kr to analyze low porous materials (i.e., BS and WB). Wood residues and biochars were degassed under vacuum for 48 h at 80 and 100 °C, respectively. Samples after activation at 700, 800 and 900 °C were degassed under vacuum for 48 h at 250 °C prior to adsorption testing. N_2 adsorption isotherms were treated to obtain: (i) the surface area (S_{BET}, m^2 g^{-1}) calculated by the Brunauer-Emmet-Teller (BET) model applied to the nitrogen adsorption data in the appropriate relative pressure range (P/P_0) from 0.01 to 0.05 such that the BET constant (C) that provides information about the interaction of the adsorbent surface and the adsorbate was always positive [52]; (ii) the micropore volume (V_μ, cm^3 g^{-1}) determined by the Dubinin–Radushkevich (DR) equation [53]; (iii) the total pore volume ($V_{0.97}$, cm^3 g^{-1}) calculated from the amount of nitrogen adsorbed at 0.97 relative pressure [54]; and (iv) the mesopore volume (V_m, cm^3 g^{-1}) calculated as the difference ($V_{0.97} - V_\mu$). The pore size distribution (PSD) was determined by applying density functional theory (DFT) using N_2 adsorption isotherms [55]. The average mesopore diameter (d_m) was determined by applying Barret–Joyner–Halenda (BJH) analysis to the N_2 desorption branch [56].

2.4. Statistical analysis

The porosity of activated biochars [surface area (S_{BET}), total pore volume ($V_{0.97}$), micropore volume measured by N_2 and CO_2 gases (V_{μ,N_2} and V_{μ,CO_2}), and mesopore content (%)] was subjected to variance analysis with GLM using Type III procedures (partial sums of squares) [57]. GLM estimates the relative magnitude of each independent variation source: wood residue type (BS, WB), pyro-gasification temperature (315, 399, and 454 °C), activation temperature (700, 800, and 900 °C) and CO_2 gas flow rate (2 and 3 L min^{-1}). Analyses were performed using the following general linear model (Eq. 1). Only significant interactions were considered in the model, as shown in Eq. 1.

$$Y_{ijkl} = \mu + \alpha_i + \beta_j + \gamma_k + \delta_l + (\alpha\,\beta)_{ij} + (\alpha\,\gamma)_{ik} + \varepsilon \quad (1)$$

where Y_{ijkl} is the dependent variable [S_{BET}, $V_{0.97}$, V_{μ,N_2}, V_{μ,CO_2} and mesopores (%)], μ is the overall mean, α_i is the wood residue effect, β_j is the pyro-gasification temperature effect, γ_k is the activation temperature effect, δ_l is the CO_2 flow gas effect, $(\alpha\,\beta)_{ij}$ is the interaction between wood residue type and pyro-gasification temperature, $(\alpha\,\gamma)_{ik}$ is the interaction between species and activation temperature, and ε is the error term.

Data were analyzed with the PROC GLM procedure in SAS®, version 9.4 [58]. Statistical significance was determined using F-tests at $p \leq 0.05$. The assumptions of the analysis of variance (homoscedasticity and residual normality) were verified. The estimated mean and standard deviation for each activated biochar property was calculated for each wood residue, pyro-gasification temperature, activation temperature, and CO_2 gas flow rate. Tukey's studentized range (honest significant difference – HSD) was used to test significant statistical differences in activated biochar variables between wood residues (BS and WB), pyro-gasification temperatures (315, 399, and 454 °C), activation temperatures (700, 800 and 900 °C) and CO_2 gas flow rates (2 and 3 L min^{-1}). *F*-values were considered statistically significant at $p \leq 0.05$.

3. Results and discussion

3.1 Morphological, chemical, and thermal analysis

The SEM microscopic structure of BS (softwood, broadleaf, deciduous trees, or gymnosperms) and WB (hardwood, needle-leaved evergreen trees, angiosperms, or flowering plants) from the temperate part of the Northern Hemisphere is shown in Fig. 2. The SEM images show substantial differences in cellular structure between the two woods [59]. BS wood is relatively homogeneous, with a simple structure consisting primarily of overlapping tracheids (fibers) connected by bordered pits and rays. The WB wood structure is more complex: it is a diffuse-porous wood containing a relatively high proportion of fibers, vessel elements, and thin-walled ray cells. The rays are mostly homocellular and 1−3 cells wide. In addition, there are numerous extremely small and diffuse ray-vessel pits. The structural changes in biochars treated at 315, 399, and 454 °C are illustrated in Fig. 1S (Supplementary Material), showing the presence of grooves and channels. Increasing the pyro-gasification temperature from 315 to 454 °C enhances the release of low molecular weight volatiles from the matrix structure, resulting in chars with more rudimentary pores. The pores are irregular in shape and disposed in a multi-layered structure. However, no significant differences in porous structure are observed when the pyro-gasification temperature was increased from 315 to 454 °C (Fig. 1S). Fig. 2S illustrates the structure of activated biochars made from BS and WB treated at 454 °C and activated at 700, 800, and 900 °C with CO_2 at 3 L min^{-1} flow rate. The SEM images for activated biochar showed the development of narrow and larger pores structures, but no clear structural differences are seen across materials activated at different temperatures.

Weight loss (%) for the biomass, biochars (processed at 454 °C), and activated biochars (processed at 900 °C) was investigated as a function of the temperature range 30–900 °C (Fig 3 a) and b)). BS and WB showed high thermal degradation in the 100 to 500 °C range: cellulose, hemicellulose, and lignin in the wood residues were pyrolyzed via different mechanisms and reaction paths. Decomposition takes place at temperatures ranging from 240 to 350 °C for cellulose [60,61], 200 to 260 °C for hemicellulose, and 280 to 500 °C for lignin [62–64]. TGA showed that activated biochars were more thermally stable than unactivated biochars. Only 5.2% and 8.4% weight were released during thermal degradation of activated biochars prepared at 900 °C for WB and BS, respectively. This property is important for determining the ability of a given activated biochar to undergo and endure the thermal regeneration cycles when applied for contaminant sorption in water and gases [65].

The percentages of C, O, and H from several species of wood residues do not present significant differences but the percentages of cellulose, hemicellulose, lignin and extractives vary significantly. For example, the carbon content for BS and WB is 48 and 47 %, respectively, whereas the percentage of lignin in BS (25–28 %) [66] is significantly higher than in WB (17–21 %) [67]. Fast pyrolysis (at 454 °C) produced a substantial reduction in oxygen and hydrogen content and a substantial increase in carbon content compared to torrefaction (at 315 °C). The H/C and O/C ratios were used to predict the variation in biochar aromatization and polarity as a function of pyro-gasification temperature, respectively. Lower O/C ratio may result in fewer hydrophilic biochars, whereas lower H/C ratio indicates that the material presents a greater number of aromatic structures, especially for activated biochars prepared at high temperature (i.e., 900 °C). This finding suggests that torrefied wood or biochar are still far from being pure carbon so their physical or chemical modification (i.e., activation) is recommended to improve their adsorptive characteristics and applications.

XPS analysis provided information on the carbon bonding states for all materials: wood residues, biochars, and activated biochars made from BS and WB. The XPS C1s peaks were deconvoluted and used to estimate the relative proportions of the functional groups listed in Table 1S. The main peak lower than 285 eV for all materials was assigned to aliphatic/aromatic carbon (C–C, C–H, and C=C). The peaks at 285.7–287.1, 286.1−288, and 288–289.4 eV were then attached to the oxygen-containing moieties, i.e., C–O, C=O or O−C−O, and O–C=O, respectively [68]. The spectra for the biochar materials show two predominant peaks of functional groups: graphitic sp^2 carbon and the C–O bond, found in the range of 61.5−72.0% and 17.1−27.7%, respectively. The same predominant graphitic sp^2 carbon peaks seen in the biochars increased to 68.3−79.9% for the activated biochars, whereas C−O group peaks reduced to 7.1−12.8% for the activated biochars. The relative percentages of oxygenated functional groups decreased drastically at higher pyro-gasification temperature (from 315 to 454 °C) and with subsequent activation (from 700 to 900 °C). Other oxygenated groups accounted for less than 5% content for all materials, except for WB315 (i.e., 7.2% for C=O and O−C−O groups).

3.2 Material physical properties

3.2.1. Characteristics of wood residues, biochars, and activated biochars

Birch and spruce wood residues showed very low porosity, up to 0.5 $m^2\ g^{-1}$. After torrefaction/fast pyrolysis of both residues at 315, 399, and 454 °C for 2 s, materials were highly microporous, presenting ultramicropores (measured by CO_2 adsorption analysis). The final torrefied wood or biochars presented increases in surface area of 78, 136, and 177 $m^2\ g^{-1}$ for birch residues and 42, 158, and 208 $m^2\ g^{-1}$ for spruce residues at 315, 399, and 454 °C, respectively. The porosity of the biochars also increased at higher pyro-gasification temperature, as confirmed by studies that used different precursors such as debarked loblolly pine chips [69], date pits [35], or broiler litter [70]. Activated birch biochar presented a more developed porosity than activated spruce biochar, with surface area and pore volume ranging from 451 m^2 g^{-1} (WB399A700-2) to 881 m^2 g^{-1} (WB454A900-3), total pore volume of 0.20 and 0.53 cm^3 g^{-1}, respectively, and micropore volume ranging from 0.18 to 0.33 cm^3 g^{-1}. For activated spruce biochar, surface area ranged from 415 m^2 g^{-1} (BS399A900-3) to 896 m^2 g^{-1} (BS399A900-5), with total pore volume of 0.17 and 0.50 cm^3 g^{-1}, respectively, and micropore volume ranging from 0.17 and 0.34 cm^3 g^{-1} (Fig. 4).

Biochar activation involves a reaction (Boudouard reaction, Eq. 2) between the carbon present in the biochar materials and injected CO_2 ($C-CO_2$ reaction). At high temperatures, this endothermic reaction promotes the removal of carbon atoms present in the material, increasing the burn-off. The equilibrium constant of the Boudouard reaction (Eq. 2) does not favor CO production until temperatures exceed 700 °C [71]. In addition, the increased CO_2 concentration enhances the $C-CO_2$ reaction, resulting in increased pore development. It is noteworthy that, for the majority of biochars and at 900 °C, the porosity was reduced at the higher gas flow rate (5 L min^{-1}). For example, RB454CO2900-2 presented a surface area of 630 m^2 g^{-1}, which increased to 873 m^2 g^{-1} for RB454CO2900-3 but decreased to 559 m^2 g^{-1} at the highest flow rate (RB454CO2900-5) (Fig. 3S a)). Similar findings were observed for other biochar types exposed to very high flow rates [44]. The reaction between carbon and CO_2 resulted not only in the opening of blocked pores to form new micropores, but also in the widening of existing micropores by a gasification reaction, causing the formation of mesopores [72]. However, the contact time between the carbon surface and CO_2 (introduced at high velocity) may have been shortened due to the reduced diffusion into the porous structure. In addition, at longer residence times and higher CO_2 flow rate, micro- and mesopores formed during activation at high temperature (i.e., 900 °C) may be destroyed to form macropores.

$$C + CO_2 \leftrightarrow 2\ CO \qquad \Delta H = 172\ \text{kJ mol}^{-1} \qquad (2)$$

The nitrogen adsorption/desorption isotherms at -196 °C for biochars WB454 and BS454 activated at 700, 800, and 900 °C are shown in Fig. 4S a) and b). All the adsorption isotherms present a similar shape. Nitrogen isotherms are a combination of Type I and Type IV isotherms, and are characteristic of micro-mesoporous solids according to IUPAC classification [73]. However, activated biochars show the most prominent hysteresis effect at 900 °C, due to the higher proportion of mesopores compared to at 700 °C. According to their N_2 adsorption isotherms, the hysteresis loop is Type H4, which features parallel and almost horizontal branches, and is attributable to the adsorption/desorption in narrow slit-like pores [73]. The accessibility of the adsorbate molecules to the pores of the adsorbent can be affected by their shape. Therefore, the access of adsorbate molecules to the slit pores is controlled by the pore width, and is mainly restricted by the thickness of adsorbate molecules [74]. The pore size distribution shown in Fig. 4S c) and d) also confirms the presence of mesopores greater than 10 nm in diameter for activated biochars at 800 and 900 °C, whereas much lower percentages of mesopores were found for activated biochars at 700 °C. The average pore diameter data for activated birch and spruce biochars support these results. The smallest pore diameter (up to 3.7 nm) was obtained at 700 °C, whereas at 900 °C, the average pore diameter increased to up to 6.8 nm, favoring the development of mesoporosity (Fig. 3S b)).

The CO_2 adsorption isotherms at 0 °C for activated biochars made from birch and spruce are shown in Fig. 4S e) and f), respectively. At this temperature, CO_2 molecules can more easily access ultramicropores (< 0.7 nm) than N_2 at -196 °C. Activated birch biochars presented higher volume of ultramicropores (up to 0.28 $cm^3\ g^{-1}$), as indicated by the CO_2 adsorption curve compared to activated spruce biochars (up to 0.2 $cm^3\ g^{-1}$). It is noteworthy that WB454A900-3 shows high versatility: the pore size distribution comprises ultramicropores (V_{CO2} = 0.28 $cm^3\ g^{-1}$) as well as 0.33 $cm^3\ g^{-1}$ and 0.20 $cm^3\ g^{-1}$ of micro- and mesopores, respectively. The activated biochars present a variable range of pores: < 0.7 nm, from 0 to 2 nm, and mesopores (2–10 nm and > 10 nm), showing promise for a range of applications in various adsorption fields, including electrochemistry, catalysis, and contaminant sorption in water.

3.2.2 Influence of pyro-gasification and activation conditions on the porosity of activated biochars and practical implications

Means and variations in the properties of activated biochar made from both wood residues (BS and WB) are shown in Fig. 4. The analysis of variance (Table 1) shows that, for all variation sources (pyro-gasification and activation temperature, CO_2 gas flow rate, and wood residue type), most biochar porosity features were significantly affected (at $p < 0.05$). Varying the activation temperature (from 700 to 900 °C) and the CO_2 flow rate (from 2 to 3 L min^{-1}) enhanced the surface area, pore volume, and mesopore content for both BS and WB wood residues. The average surface area was 541, 557, and 660 $m^2\ g^{-1}$ at 700, 800, and 900 °C for birch, and 490, 537, and 607 $m^2\ g^{-1}$ for spruce, respectively (Fig. 4). Multiple comparison tests showed significant differences between 700 and 900 °C and between 800 and 900 °C, as indicated by different superscript letters displayed in Fig. 4. However, the differences between 700 and 800 °C were not statistically significant (except for mesopore content). This indicates that activated biochar porosity tends to increase at very high activation temperature, especially up to 900 °C. In addition, the difference between the two CO_2 flow rates (2 and 3 L min^{-1}) was significant for all porosity properties (Table 1): all porosity properties increased with increasing CO_2 flow rate (Fig. 4).

In the case of pyro-gasification temperature, the two wood residues showed different trends. Still, most of the porosity parameters (except for mesopore content) were significantly affected by increased temperature (at $p < 0.05$) (Table 1). For activated spruce biochars, the temperature increase from 315 to 454 °C enhanced the average surface area (539 to 584 m^2 g^{-1}), pore volume (0.26 to 0.30 cm^3 g^{-1}), and mesopore content (18 to 24%), as seen in Fig. 4. For activated birch biochars, most of the porosity parameters (except for mesopore content) decreased with temperature increase from 315 to 454 °C: surface area decreased from 623 to 603 m^2 g^{-1} and pore volume from 0.31 to 0.30 cm^3 g^{-1}.

Based on these findings, we may conclude that the variation due to the activation temperature exceeded the variation due to the pyro-gasification temperature and the CO_2 flow rate, as indicated by the higher F-values (Table 1). For instance, for activated spruce biochar, the surface area increased more (23.9%) with higher activation temperature (from 700 to 900 °C) compared to the increase (8.3%) with higher pyro-gasification temperature (from 315 to 454 °C) and compared to the increase (8.5%) with higher flow rate (from 2 to 3 L min^{-1}) (Fig. 4). For activated birch biochar, surface area increased by 22.0 and 9.8% with higher activation temperature (from 700 to 900 °C) and flow rate (from 2 to 3 L min^{-1}), respectively, and decreased by 3.4% with higher pyrolysis temperature (from 315 to 454 °C).

In addition, the interaction between wood residues and activation temperature was significant for most physical properties of the activated biochars, except for mesopore content (Table 1), indicating that the effect of activation temperature depends on the type of wood residue. The surface area of activated biochars made from WB and BS increases linearly with the activation temperature as shown in Fig. 5S. The variations in surface area (119 m^2 g^{-1}) and pore volume (0.11 cm^3 g^{-1}) for WB were almost the same as for BS (117 m^2 g^{-1} and 0.08 cm^3 g^{-1}, respectively) (Fig. 4). In contrast, the interaction between both wood residue types and pyro-gasification temperature was not significant for activated biochar porosity, except for mesopore content ($p = 0.0044$, Table 1), where increased pyro-gasification temperature (from 315 to 454 °C) had a greater effect on WB (6.4% increase) than on BS (1.4% increase).

Few studies have examined the effects of optimized pyro-gasification and activation conditions on the porosity of activated biochar in terms of the quality of the biomass precursor (i.e., ligno- or non-lignocellulosic) and the processing conditions (i.e., chemical or physical activation). Oh and Park [75] reported a substantial increase in surface area up to 330 $m^2 g^{-1}$ for KOH-activated rice husk biochars pyrolyzed at 700 °C ($S_{BET} = 2410 m^2 g^{-1}$) compared to 1000 °C ($S_{BET} = 2080 m^2 g^{-1}$), whereas Lua et al. [45] reported a decrease of 176 $m^2 g^{-1}$ for CO_2-activated pistachio nutshell biochars processed at 500 °C and with posterior activation at 900 °C compared to pre-carbonization at 1000 °C. Using broiler litter feedstock, the same surface area of 335 $m^2 g^{-1}$ was measured for two biochars processed at pyrolysis temperatures of 350 and 700 °C and posterior activation in the presence of steam at 800 °C [70].

Other authors have found that activation temperature was the most influential variable for changes in surface area. Azargohar and Dalai [76] used a central composite optimization design to investigate the impact of steam ratio (0.4−2), activation temperature (600−900 °C), and time (0.9−4 h) on the surface area of activated spruce biochar. Activation temperature was one of the most influential parameters for increased surface area of activated biochars. Recently, Işıtan *et al.* [29] used regression analysis to study the impact of pyrolysis and activation temperature on the surface area of activated pistachio nutshell biochar (prepared in a small-scale furnace) and found that increasing the temperature from 800 to 900 °C (in the presence of CO_2) produced a surface area increase of more than 300 $m^2 g^{-1}$ with pre-carbonization temperatures of 450, 550, or 650 °C. The regression analysis indicated that pyrolysis temperature had no significant impact on the surface area or pore volume of the activated biochars. These findings are in line with the findings of the present study on the effects of optimized pyro-gasification and activation conditions (using materials that were prepared in pilot-scale furnaces) on the porosity of activated birch and spruce biochars. Compared to activation temperature, torrefaction and pyrolysis temperature had lower impacts on the porosity of CO_2-activated biochars made from BS and WB residues.

Upscaling the production of activated biochars may reduce the efficiency of heating and mass transfer in the char bed, lowering the porosity of materials compared to other wood waste activated biochars available in the literature (S_{BET} higher than 1000 m^2 g^{-1}) [27,42,46]. These high surface areas were reached through laboratory furnaces where the conditions of temperature and flow gases were well controlled while N_2 and CO_2 were efficiently in contact with the low amount of material placed in the furnace in a static position. We have proved in this work that a pilot-scale continuous system could be an effective alternative to produce porous activated biochars having surface areas in a range of 400 and 900 m^2 g^{-1}. These materials reached surface area values and pore size distribution comparable with other agricultural waste derived-materials (i.e., pecan shells [77]; rice straw [78]; palm seed coat [79]; pistachio nut shells [45]; oil-palm shells [80]; nut waste [31]; palm kernel shells [81,82]; canola meal [83]; corn stalks [84]) prepared in small-scale laboratory furnaces. In addition, WB and BS activated biochars showed recently to be effective for the removal of phenolic compounds in synthetic and real effluents [65].

4. Conclusion

The influence of pyro-gasification temperature and activation conditions on the porosity of activated biochars made from two wood residues (black spruce and white birch) was investigated using pilot-scale furnaces for torrefaction/fast pyrolysis and activation. Pyro-gasification and activation temperature, CO_2 gas flow rate, and wood residue type significantly (at $p < 0.05$) affected most biochar porosity properties (surface area, total pore volume, micropore volume, and mesopore content). However, activation temperature accounted for more variation than pyro-gasification temperature or CO_2 gas flow rate. This means that by improving the process efficiency required for product quality, less heat or energy (at low temperatures) is expended, with no impact on the porosity of the resultant activated biochars. Further studies are needed to determine whether the statistical analysis holds true for other types of biomass residue. Comparing to small-scale laboratory furnaces, upscaling the activation furnace may reduce the efficiency of heating and mass transfer in the char bed, lowering the porosity of materials. However, porous activated biochars obtained in a range of 400 and 900 $m^2 g^{-1}$ were comparable with agricultural waste activated biochars available in the literature and produced through laboratory-scale furnaces. Therefore, the pilot-scale technologies used in this study to produce activated biochars from wood residues could boost economic incentives to apply thermochemical biomass conversion processes and to develop new and diversified products (not only biochar, bio-oil, or syngas, but also activated biochar) that would be highly profitable for the biorefinery industry.

Acknowledgments

This study was supported by Québec’s Ministry of Economy, Science and Innovation (Ministère de l’Économie, de la Science et de l’Innovation du Québec), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Research Chair Program, Abitibi-Témiscamingue College, and the Technology Center for Industrial Waste (Centre Technologique des Résidus Industriels) through its partner on this project, Airex Energy. The first author, Dr. Flavia Lega Braghiroli, sincerely acknowledges financial support by the NSERC via a Banting Postdoctoral Fellowship (2017–2019). The authors also thank Mr. Gilles Villeneuve for the assistance with both furnaces, analysis and testing in the laboratory.

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Table captions:

Table 1: Analysis of variance (GLM) with *F*-values and their significance for each source of variation in the physical properties of activated biochars

Figure captions:

Fig. 1: a) Pilot-scale fast pyrolysis unit (CarbonFX, Airex Energy); b) Biochar activation furnace developed at CTRI (Centre Technologique des Résidus Industriels – Technology Center for Industrial Waste), QC, Canada.

Fig. 2: SEM images of the two wood residues used in the present study: a) white birch (WB); and b) black spruce (BS).

Fig. 3: Weight loss as a function of the temperature range 30–900 °C (TG and DTG curves) for: a) WB, WB454, and WB454CO2900-3; and b) BS, BS454, and BS454CO2900-3.

Fig. 4: Least squares mean for biochar properties (surface area, total pore volume, micropore volume measured by N_2 and CO_2 gases, and mesopore content) for each activation temperature (700, 800, and 900 ºC) and pyro-gasification temperature (315, 399, and 454 ºC), CO_2 flow rate (2 and 3 L min^{-1}), and wood residue type (WB and BS); and multiple comparison tests. Different superscript letters (i.e., a, b, ac) displayed in the graph indicates significant difference at $p = 0.05$. Bars indicate estimated standard errors.

Table 1: Analysis of variance (GLM) with *F*-values and their significance for each source of variation in the physical properties of activated biochars

Source of variation	**Wood residues (WR)**		**Pyro-gasification temperature (PT)**		**Activation temperature (AT)**		**CO_2 Flow rate**		**WR*PT**		**WR*AT**	
df	*1*		*2*		*2*		*1*		*2*		*2*	
	F-value	*p-value*	*F-value*	*p-value*	*F-value*	*p-value*	*F-value*	*p-value*	*F-value*	*p-value*	*F-value*	*p-value*
S_{BET}	12.64	0.0012	5.56	0.0087	13.18	<0.0001	8.44	0.0067	0.63	**0.54**	4.08	0.0267
$V_{0.97}$	8.48	0.0066	7.27	0.0026	15.98	<0.0001	6.97	0.0129	0.77	**0.47**	4.27	0.0230
$V_{\mu,N2}$	8.32	0.0071	3.59	0.0395	11.43	0.0002	6.72	0.0144	0.82	**0.4483**	4.51	0.0191
$V_{\mu,CO2}$	7.07	0.0123	1.37	**0.2696**	6.64	0.0040	3.06	0.0904	0.90	**0.4173**	3.86	0.0317
Mesopore (%)	7.36	0.0108	13.47	<0.0001	16.63	<0.0001	1.51	**0.2278**	6.48	0.0044	0.67	**0.5195**

df: Degrees of freedom; Numbers in bold exceed 0.05 (*p-value*).