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Synthesis of High-Surface-Area Biochar Particles Using Microwave Pyrolysis Technique

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ABSTRACT Biochar was produced via microwave-assisted pyrolysis, performed on different biomass feedstocks. Two feedstocks were wood-based, namely maple and spruce, due to the significant forestry industry in New Brunswick and the potential for utilization of waste. Switchgrass, an agricultural biomass, was the third feedstock, and was chosen for comparison purposes as well as its popularity. MW pyrolysis process parameters were kept constant for all experiments, which allowed proper comparison of products of different pyrolyzed biomass. Process parameters included: MW power level of 500 W, reaction temperature of 700˚C, and residence time of 60 minutes. A carbon microwave absorber was employed for all experiments at 10 wt. % in order to catalyze the reaction; already produced biochar acted as a cost effective absorber. Biochar characterization was the focal point of this research, with an emphasis on porosity and surface area properties. Properties used for characterization included: BET surface area (m^2/g), porosity distribution (cc/g), scanning electron microscopy (SEM), elemental analysis, and ash content. Pyrolysis experiment data was also

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discussed including: temperature profiles, heating rates (˚C/min), maximum temperatures (˚C), and biochar yields (wt. %). Wood-based feedstocks performed favorably compared to switchgrass in all categories, with spruce (softwood) having exceptional properties. Spruce biochar showed a BET surface area of 204 m^2/g, followed by maple at 155 m^2/g and switchgrass at 116 m^2/g. Porosity distributions showed similar profiles for all feedstocks, where peak values followed the same trend as surface areas, with spruce at 12.12 x 10^{-2} cc/g; SEM images showed unique honeycomb-like structure of produced biochars. Wood-based biochar showed higher carbon content and lower ash content, yielding a more refined product. Temperature profiles were similar for all feedstocks, with wood showing higher heating rates, in the vicinity of 150˚C/min.

Keywords: Biochar, Microwave Pyrolysis, Surface Area, Porosity

INTRODUCTION Renewable energy, and value-added products, produced via biomass conversion has gained significant interest in recent years. Concerns related to global warming, as well as declining fossil fuel reserves, have acted as a catalyst to promote studies and expand the research field. CO_2, the most prevalent greenhouse gas, has experienced an increase in atmospheric concentration from 280 to 396 ppmv, from pre-industrial to current levels, respectively. Greenhouse gas emissions, if not acted upon, will raise atmospheric temperatures substantially, yielding irreversible damage to the environment and human livelihood. With knowledge of environmental issues, as well as an understanding that they will only continue to grow, scientists and engineers are urged to begin to develop products that are not only functional, but also sustainable (Li et al., 2016).

Several strategies have been investigated for conversion of biomass into fuels, and value-added products. These can be divided into two major categories: thermochemical and biochemical conversion. Biochemical processes, in general, use various microorganisms (bacteria, yeast, etc.) to convert biomass into value-added fuels, chemicals, and gases. Thermochemical conversion groups together a set of processes, including torrefaction, pyrolysis, and gasification, that use heat to thermally degrade the biomass into a solid, liquid, and gaseous product. Related to biomass conversion, the three outputs of thermochemical conversion are called biochar, bio-oil, and syngas, respectively. The processes differ in their operating conditions, which primarily consist of reaction temperature, residence time, and quantity of oxygen present. Torrefaction uses lower reaction temperatures (< 300˚C) and longer residence times, in the absence of oxygen, to produce higher biochar yields. Gasification uses higher reaction temperatures (> 1000˚C) and short residence times, with some oxygen present, to produce higher syngas outputs. Pyrolysis falls between these two processes, using reaction temperatures between 300˚C – 1000˚C, with no oxygen present, to produce approximately equal parts of each of the outputs. Bio-oil and syngas require further upgrading to be then used as fuel, or valuable chemicals can be extracted from the bio-oil through further processing.

Biochar is a versatile carbonaceous material, which has established value in numerous application routes. The most prominent include: soil amendment, carbon sequestration, and contaminant remediation (Das et al., 2015). While these are the most notable, several other applications exist and new ones are continuously emerging. Biochar has a highly porous, honeycomb-like structure, which is highly thermally stable. When mixed with soil, the unique structure allows it to retain a high quantity of nutrients and water, making it effective for enhancing soil quality. The high stability of biochar enables it to resist microbial degradation and mineralization, allowing it to remain in soil for hundreds, and even thousands of years. This allows it to be an effective method for carbon sequestration. While the biomass was growing as an agricultural crop, for example, it absorbed CO_2, but since it was converted to stable biochar it did not release CO_2 back to the atmosphere; this creates a carbon negative process. Contaminant remediation is achieved through the high specific surface area (SSA) and porosity of biochar. These properties allow it to absorb organic and inorganic contaminants from a contaminated media, restoring it to its original composition (Srinivasan et al., 2015). The high porosity and surface area of biochar is what has enabled it to be successful in the aforementioned applications. This unique structure is produced at high reaction temperatures, in the absence of oxygen, due to rapid release of volatiles. Therefore, pyrolysis is the optimal process for producing considerable quantities of highly porous, high surface area biochar.

Conventional pyrolysis uses electrical heating to heat the outer surface of the reactor, and then through conduction and convection, the heat is transferred to the biomass within the reactor. A novel, emerging technique is to utilize microwaves as the heating mechanism, which has shown several advantages. Microwave heating is a subclass of dielectric heating, which uses a high-frequency alternating electric field to cause molecular dipole rotation. Friction and collision generated by the molecular rotation and movement results in microwave heating. Microwave pyrolysis has several advantages, including: fast heating rates, selective and uniform heating, and instantaneous on/off control. Therefore, microwave pyrolysis has much quicker startup and shutdown times, resulting in significant energy and economic savings. Moreover, pre-treatment, such as drying and size reduction, are not necessary in microwave heating processes, resulting in further economic savings. Studies have also shown that a higher quality biochar is produced from microwave pyrolysis, with higher surface area and porosity; this is due to high heating rates and the quick release of volatiles (Luque et al., 2012).

MATERIALS AND METHODS

Biomass Collection Biochar was produced from three biomass feedstocks obtained by available resources in New Brunswick. Two of the three feedstocks were wood-based, namely maple, a hardwood, and spruce, a softwood. Wood-based feedstocks were given priority due to the significant forestry industry in New Brunswick. An ample amount of waste wood is produced annually, and therefore could be obtained at minimal cost to be converted to value-added products. Moreover, from literature review, it was seen that wood produced a biochar with more optimal properties, including lower ash content and higher specific surface area (SSA). The last feedstock, switchgrass, is an agricultural feedstock that has been highly investigated in pyrolysis studies. This is due to its ability to be grown on low-quality land with minimal supervision, while being harvested multiple times per year (Zhou et al., 2013, Mohamed et al., 2016). It was chosen for comparison purposes, as an agricultural feedstock versus other wood-based feedstocks. Figure 1 shows the raw biomass that was collected, from left to right: maple hardwood, spruce softwood, and switchgrass.

Figure 1. Raw biomass used for microwave pyrolysis experiments (right to left: maple hardwood, spruce softwood, and switchgrass).

Feedstock Preparation Prior to experiment, biomass was compacted into briquettes of 25 grams each, through the use of a hydraulic press. Biomass briquetting was performed to enable more accurate temperature measurement via a high-grade thermocouple. A hole was made in a single briquette and the thermocouple was inserted to capture material temperature; the briquette was located in a consistent position of the reactor for each experiment. This method ensured that the thermocouple was fully contacting the biomass during pyrolysis, instead of having partial contact, which would have been the case with loose biomass.

Microwave Processing Microwave pyrolysis was performed at constant parameters while the feedstock source was varied. This enabled accurate comparison of the biochars produced from different biomass sources: maple, spruce and switchgrass. Table 1 shows the pyrolysis parameters that were employed. A total of ten microwave pyrolysis experiments were carried out for each feedstock, and the data presented represents average values and trends observed.

Table 1. Experiment parameters used in microwave pyrolysis.

Raw Biomass	CMWA	Microwave Power	Reaction Temperature	Residence Time
100 g	10 g	500 W	700˚C	60 min

Reaction temperature is a dependent variable, based on the power level and amount of microwave absorber used. Therefore, 700˚C is an average value with +/- 50˚C, during the duration of the pyrolysis experiment. Previously produced biochar was used as the carbon microwave absorber (CMWA) at a loading rate ten percent (wt. %). The experiment setup is shown below in Figure 2.

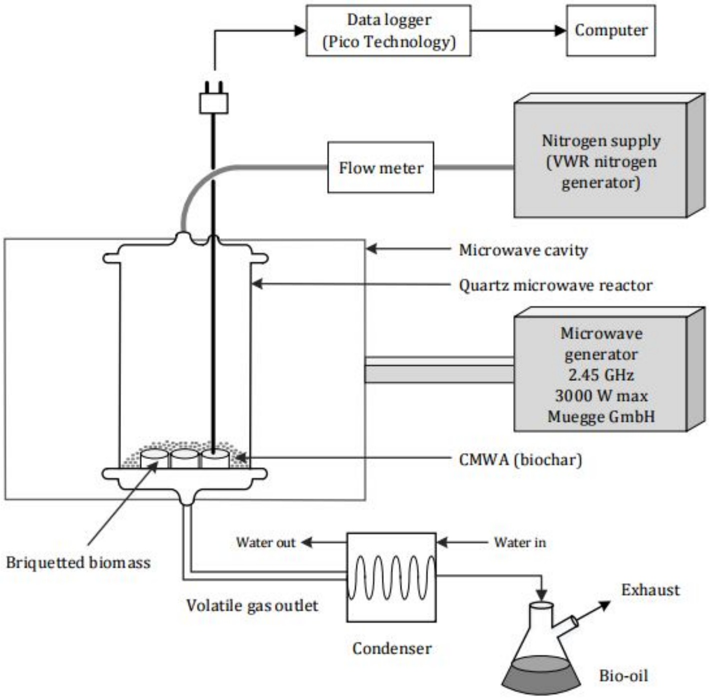

Figure 2. (a) Microwave pyrolysis system with process flow, and (b) reactor used in experiments.

Characterization of Solid Residues Based on literature, common biochar characterization tests were performed to determine quality of the produced biochars. Elemental analysis employed the use of a CHN Elemental Analyzer, and tests were performed according to ASTM D5373. The moisture and ash (dry-basis) contents were measured following the ASTM D1762-84 protocol, employing the use of a muffle furnace.

Porous properties of interest included: porosity distribution (cc/g) and BET surface area (m^2/g). These were obtained from nitrogen absorption isotherms at 77 K, using a physiosorption analyzer (Autosorb 1) in the Chemistry Department at the University of New Brunswick (UNB). Further study of the biochar structure utilized SEM imaging (scanning electron microscopy); JEOL JSM 6400 model was used in the Microscopy and Microanalysis Facility at UNB.

RESULTS AND DISCUSSION

Biochar Production As biomass is a low microwave absorber, a high microwave absorber was needed to help catalyze the reaction. Carbon based materials are strong candidates for microwave absorbers (CMWA) since their dielectric loss tangent parameter (DLTP) is much higher than raw biomass; the DLTP of a material represents its inherent dissipation of electromagnetic energy into heat. Therefore, produced biochar from microwave pyrolysis was recycled into the system to act as a cost effective microwave absorber. The reaction temperature was dependent on both the microwave power level and the ratio of microwave absorber to raw biomass. Using a power level of 500 W and 10% CMWA, reaction temperatures in the vicinity of 700˚C were obtained. Figure 3 shows a comparative graph of microwave pyrolysis temperature profiles from different feedstock.

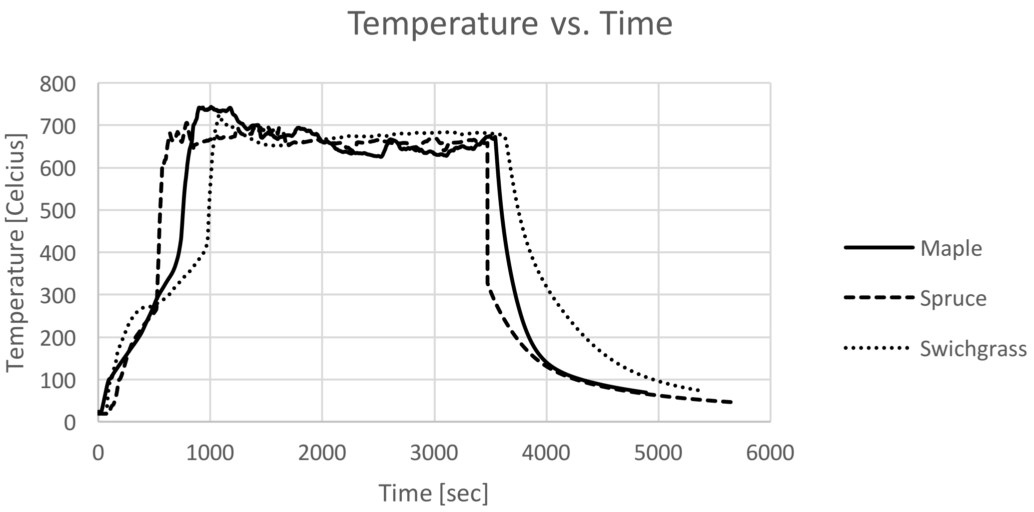

Figure 3. Sample temperature profiles observed in microwave pyrolysis experiments for different feedstocks.

As evident, all of the three feedstocks performed well under microwave pyrolysis. Reaction temperatures in the vicinity of 700˚C were reached and maintained for the duration of the conversion process. As shown earlier in Figure 1, the maple chips and switchgrass were in their raw form obtained from local resources, while the spruce wood had been shredded and sieved to a <2 mm particle size. Feedstocks were then briquetted and pyrolyzed. Regardless of size reduction, both feedstocks reached desired temperature and were pyrolyzed effectively. These experiments validated the ability of microwave pyrolysis to process biomass well, regardless of pre-treatment. In conventional pyrolysis, size reduction is a necessary step and has a significant economic footprint.

From Figure 3, the steep initial ascent of the temperature profiles consisted of two sections. The initial slope is smaller, which is correlated with the low microwave absorption of the raw biomass. During this part of pyrolysis, the CMWA is absorbing microwaves and then heating the raw biomass through conduction. This period is short due a series of reactions occurring rapidly, which change the physio-chemical properties of the biomass. After the primary volatiles are released, the charcoal begins to be formed. Due to biochar beginning to be formed, the slope of the curve increases and the reaction is accelerated; this defines the second slope of the initial temperature rise. The curves then peak at a maximum temperature, slightly fall and remain at an approximately constant reaction temperature. The temperature decrease, after reaching a maximum, can be attributed to the increased temperature difference between the sample and the reactor and ambient, which led to heat loss until steady state. Similar temperature profiles and phenomenon have been observed in previous studies (Mohamed et al., 2016, Wang et al., 2015). Table 2 shows the max temperatures and heating rates observed in microwave pyrolysis for each of the feedstock.

Table 2. Average values of heating rate and max temperatures during microwave pyrolysis.

Biochar Feedstock	Heating Rate (˚C/min)	Max Temperature (˚C)
Spruce	150.2	744
Maple	135.6	783
Switchgrass	122.4	761

Heating rate was observed to vary with feedstock, with spruce performing the best at 150˚C/min. According to prior literature, for a power level of 500 W, heating rates have been observed in the range of 98-140˚C/min for different feedstocks (Huang et al., 2016). These results were primarily related to agricultural and grassy biomass, where the switchgrass results fall in mid-range. As evident, woody biomass proves to have enhanced heating performance in microwave pyrolysis. Table 3 shows the reaction temperatures, which is calculated as the average during the stable section, as well as the biochar yields in weight percent.

Table 3. Average value of reaction temperature and biochar yields during MW pyrolysis experiments.

Biochar Feedstock	Reaction Temperature (˚C)	Avg. Biochar Yield (wt. %)
Spruce	670	22.2
Maple	680	22.0
Switchgrass	690	24.4

Biochar yield is dependent primarily on the reaction temperature during the pyrolysis process. Higher reaction temperatures favor higher gas yields and lower char yields. Since high porosity biochar was the objective of this study, which occurs at higher temperatures, the intermediate temperature of approximately 700˚C was employed. This would allow significant production of biochar with desired properties. Reaction temperatures were extremely close for each of the feedstocks, which produced similar biochar yields in the range of 20-25%. For this temperature range, biochar yields were produced as expected (Li et al., 2016, Zhou et al., 2013, Wang et al., 2015).

Biochar Properties The primary goal of elemental analysis, related to biochar characterization, is to determine the carbon content. Higher carbon content depicts a higher quality, and more refined biochar. Wood-based biochars produced the highest carbon contents of 80 wt. %. Switchgrass had a significant lower carbon content of 69 wt. %. Ash content is an additional pertinent biochar property, where higher ash content portrays a more brittle biochar. Wood-based biochars had exceptionally low ash contents in the vicinity of 1 wt. %. Switchgrass showed a sizeable difference, exhibiting an ash content 9.50 wt. %. Table 4 presents the complete results for elemental analysis and ash determination. Previous studies confirm these results, showing higher carbon and lower ash content for woody feedstocks, compared to grassy and agricultural biomass (Huang et al., 2008, Wang et al., 2009). Moisture content was observed to be low for all produced biochars, with wood-based biochars being exceedingly low of less than 1 wt. %.

Table 4. Elemental analysis and ash content of microwave pyrolysis biochars

Biochar Feedstock	C	H	N	O*	Ash Content (wt. %)
Spruce	80.1	2.90	.03	16.0	0.98
Maple	79.5	3.37	.04	15.5	1.56
Switchgrass	69.6	2.36	.05	18.5	9.50

*Calculated by difference

The main focus of this study was to analyze the highly porous, honeycomb-like structure of the biochars, which has enabled its success in various application routes. It was of interest to accurately visualize the porous biochar structure. Therefore, various SEM images of samples were taken, and are presented below in Figure 4. Below, rows identify the feedstock source, while the columns indicate the magnification level. Spruce, maple, and switchgrass biochar SEM images are given by column one (images 'a' and 'd'), column two (images 'b' and 'e'), and column three (images 'c' and 'f'), respectively. Row one consists of images of magnification 2000x, while images in row two were taken at 1000x magnification. As evident, all biochar structures are highly porous, but contain significant variation in pore sizes. Biochar produced from maple showed the cleanest pores, being almost free of carbon-like adhesives; these results agree with SEM biochar structures seen in a study performed on cylindrical wood blocks (Miura et al., 2004). Spruce images showed, on average, smaller pores but in a higher quantity.

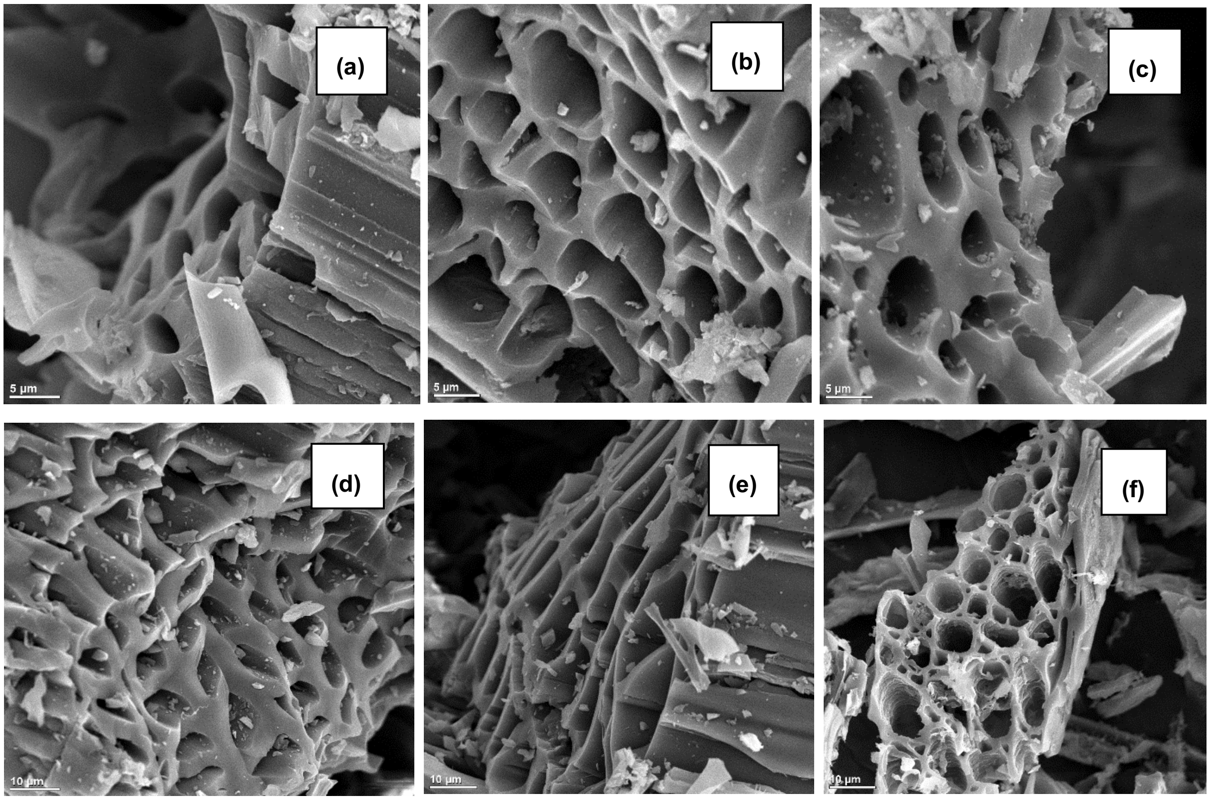

Figure 4. SEM micrographs taken for spruce, maple, and switchgrass biochar structures at 1000x and 2000x.

The BET surface area and porosity distribution of biochars were found through physiosorption analysis, and are shown in Table 5 below. As evident, biochar from spruce wood (softwood) showed the most promising results with a surface area of 200 m^2/g. Hardwood followed with a result of 150 m^2/g, and switchgrass showed the lowest of 116 m^2/g. Previous studies showing surface area results have shown a very wide range of values, with common results in the range of 0-50 m^2/g, and high outliers in the range of 200-400 m^2/g. Moreover, woody-based feedstocks have performed better than grassy and agricultural residues (Wang et al., 2009, Miura et al., 2004, Zhao et al., 2012, Salema et al., 2017). This study is the first one, to the researcher's knowledge, that compares woody feedstocks with grassy biomass under the same microwave configuration.

Table 5: Pore volume and BET surface area of pyrolysis biochars.

Biochar Feedstock	Pore Volume ($x10^{-2}$ cc/g)	BET Surface Area (m^2/g)
Spruce	12.12	203.9
Maple	7.712	155.7
Switchgrass	5.394	116.5

Porosity distribution agreed with surface area results, with spruce being the highest performer, followed by maple and switchgrass. The steady state value of pore volume (cc/g) is shown in Table 4, while the complete distributions are presented below in Figure 2. Cumulative porosity distribution represents the amount of nitrogen absorbed in pores of increasing magnitude, during physiosorption analysis. As evident, the vast majority of pores fall below 50 angstroms (5 nanometers), with the profiles reaching near steady state by 100 angstroms (10 nm).

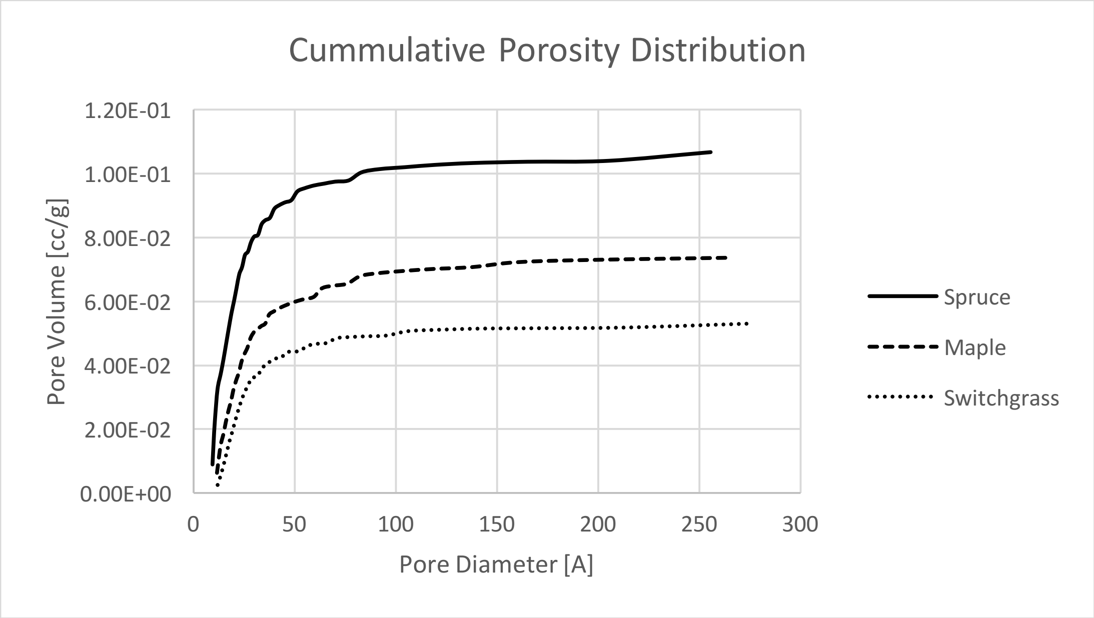

Figure 2. Cumulative porosity distributions for spruce, maple, and switchgrass biochars produced via microwave pyrolysis.

CONCLUSIONS Porous properties of the MW pyrolysis biochars were the primary focus of this research, and extremely promising results were obtained. Wood-based biochars showed more optimal results when compared to the agricultural feedstock, switchgrass. BET surface area of 204 m^2/g, and specific porosity of 12.12 x 10^{-2} cc/g, were achieved for spruce biochar. SEM imaging showed the porous, honeycomb-like structure of all produced biochars. High porosity is attributed to high reaction temperatures and heating rates of MW heating, enabling the rapid release of volatiles. Moreover, biochar quality was defined by elemental analysis and ash content. Wood-based feedstocks showed exceptional results, with carbon contents above 80 wt.% and ash contents around 1 wt.%, while switchgrass showed carbon contents below 70 wt. % and ash contents of approximately 10 wt. %. Heating performance and yields of different feedstocks during microwave pyrolysis were also investigated. Biochar yields and reaction temperatures were similar for all feedstocks, at 700˚C and 20-25 wt.%, respectively. High heating rates were attained in microwave heating, as expected, with spruce heating at 150˚C/min.

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