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The Production of Engineered Biochars in a Vertical Auger Pyrolysis Reactor for Carbon Sequestration

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Abstract: Biomass pyrolysis and the valorization of co-products (biochar, bio-oil, syngas) could be a sustainable management solution for agricultural and forest residues. Depending on its properties, biochar amended to soil could improve fertility. Moreover, biochar is expected to mitigate climate change by reducing soil greenhouse gas emissions, if its C/N ratio is lower than 30, and sequestrating carbon if its O/C_{org} and H/C_{org} ratios are lower than 0.2 and 0.7, respectively. However, the yield and properties of biochar are influenced by biomass feedstock and pyrolysis operating parameters. The objective of this research study was to validate an approach based on the response surface methodology, to identify the optimal pyrolysis operating parameters (temperature, solid residence time, and carrier gas flowrate), in order to produce engineered biochars for carbon sequestration. The pyrolysis of forest residues, switchgrass, and the solid fraction of pig manure, was carried out in a vertical auger reactor following a Box-Behnken design, in order to develop response surface models. The optimal pyrolysis operating parameters were estimated to obtain biochar with the lowest H/C_{org} and O/C_{org} ratios. Validation pyrolysis experiments confirmed that the selected approach can be used to accurately predict the optimal operating parameters for producing biochar with the desired properties to sequester carbon.

Keywords: pyrolysis; auger reactor; engineered biochar; forest residues; agricultural biomass; response surface methodology

1. Introduction

In 2014, the Intergovernmental Panel on Climate Change reported that "global emissions of greenhouse gas (GHG) have risen to unprecedented levels despite a growing number of policies to reduce climate change" [1]. GHG emissions need to be lowered by 40% to 70% compared to the 2010 values by mid-century, and to near-zero by the end of the century, if we are to limit the increase in global mean temperature to two degrees Celcius [1].

Pyrolysis, the thermochemical decomposition of biomass under oxygen-limiting conditions at temperatures between 300 and 700 °C, can be a sustainable management solution for agricultural and forest biomasses, and is proposed as a strategy to mitigate climate change. The resulting co-products of pyrolysis are: a liquid bio-oil, non-condensable gases, and a solid biochar. The yields and characteristics of the products depend on pyrolysis operating parameters and biomass feedstock properties. Non-condensable gases are generally used to heat the pyrolysis unit. Bio-oils have heating values of 40%–50% of that of hydrocarbon fuels [2], and could be used to replace fossil heating oil. Biochar can be used as a soil amendment to improve soil fertility and has been proposed as a tool for mitigating climate change [3], because of its potential for carbon (C) sequestration. When biomass is converted into biochar and is applied to soil, C can be stored for more than 1000 years [4,5]. In other words, biochar production is a way for C to be drawn from the atmosphere, and is a solution for reducing the global impact of farming [6]. Woolf et al. [7] reported that biochar and its storage in soil can contribute to a reduction of up to 12% of current anthropogenic CO_2 emissions. Moreover, there is evidence that biochar amendment to soil can help reduce GHG emissions, and particularly N_2O [8], a powerful GHG, with a global warming potential of 298 [9]. Specifically, agriculture is a major source of N_2O, contributing approximately 70% of Canadian anthropogenic N_2O emissions. Agricultural soils contribute to about 82% of these emissions [10]. Despite the many potential benefits of soil amendment with biochar, special attention must be paid to the negative side effects. For example, heavy metals (e.g., Cu, Zn, and Mo) could be found in biochar and accumulate in soil, leading to phytotoxicity problems.

The yield and characteristics of pyrolysis products are influenced by different factors, including biomass feedstock and pyrolysis operating parameters (solid residence time, vapor residence time, temperature, heating rate, and carrier gas flowrate). Thus, not all biochars are created equal and biochars should be designed with special characteristics for their use in environmental or agronomic settings [11,12]. Biochars with a low N content, and consequently a high C/N ratio (>30), could be more suitable for the mitigation of N_2O emissions from soils [8,13]. Moreover, biochars produced at a higher pyrolysis temperature and with an O/C_{org} ratio < 0.2, H/C_{org} ratio < 0.4, and volatile matter below 80%, may have a high C sequestration potential [13]. In fact, a H/C_{org} ratio < 0.4 would indicate a BC_{+100} of 70% (i.e., at least 70% of the C in biochar is predicted to remain in soil for more than 100 years), as an H/C_{org} ratio in the range 0.4–0.7 would indicate a BC_{+100} of 50% [14].

It is also important to select the proper pyrolysis technology to obtain the desired yield and properties of the product. Among all the existing pyrolysis technologies, the auger reactor is one of the most attractive designs that has been developed [15]. It enjoys some popularity because of its simplicity of construction and operation [16]. In an auger reactor, biomass is continuously fed to a screw, where it is heated in oxygen-free conditions, and then the auger rotation moves the product along the auger axis to the end of the reactor. The gases and organic volatiles leave the reactor at the end of the reactor, and the biochar is collected at the bottom. Gas exits may also be performed along the auger reactor wall, in order to decrease the vapor residence time. The yield of bio-oil (condensed gases) in auger reactors is variable, depending on the operating parameters, but is typically in the range of 40 to 60 wt % of the feedstock, which is lower than what is normally achieved with fluidized-bed reactors. This is because the heat transfer in an auger reactor is lower. Therefore, small-diameter reactor tubes which have a limited distance between the inner reactor tube surface and the internal auger shaft, are needed. In order to increase the heat transfer, some auger reactors combine a small inert solid particulate heat carrier (usually sand or steel shot) with relatively small particles of biomass (1 to 5 mm). The residence time of the vapors is much longer in auger reactors than in fluidized beds, which increases the likelihood of secondary reactions and consequently increases the yield of char [16].

The hypothesis of this research project is that it is possible to produce a biochar with beneficial characteristics from an environmental perspective, when pyrolysis operating parameters are suitably selected in a vertical auger reactor. Thus, the main objective was to validate a response surface methodology approach used to identify the optimal pyrolysis operating parameters (temperature, solid residence time, and nitrogen flowrate), in order to produce engineered biochars with the ideal characteristics for C sequestration.

2. Materials and Methods

2.1. Description of the Response Surface Methodology Approach

2.1.1. Development of the Statistical Models

Response surface methodology (RSM) was selected as an approach to determine the optimal pyrolysis operating parameters, in order to produce engineered biochars that can be used to sequester carbon. RSM is a collection of statistical and mathematical techniques for developing, improving, and optimizing processes [17], and is used to illustrate the relationship between the response variables (dependent variables) and the process variables (independent variables). In this study, the selected independent variables were the pyrolysis temperature, solid residence time in the heater block, and N_2 flowrate, which are three parameters known to influence the yields and characteristics of products in an auger pyrolysis reactor [18]. The biochar yield and three indicators of biochar potential for climate change mitigation (C/N, H/C_{org}, and O/C_{org} ratios), were the response variables studied. Biochars with the highest C/N ratio are expected to reduce soil GHG emissions, and those with the lowest H/C_{org} and O/C_{org} molar ratios are expected to have a high C sequestration potential [13].

The Box-Behnken design was selected for collecting data. For an experiment of three factors, this incomplete factorial design requires three evenly spaced levels for each factor, coded −1, 0, and +1 (Table 1). Two variables (−1 and +1 levels) are paired together in a 2^2 factorial, while the third factor remains fixed at the center (level 0). A total of 15 experiments run in a random order are necessary, including three repetitions of an experiment, with the three independent variables fixed at their central point.

The method of least squares from the RSREG procedure of SAS [19] was used to estimate the parameters of the quadratic response surface regression models (Equation (1)), fitted to the experimental data obtained from the Box-Behnken design:

$$Y = \beta_0 + \beta_1 T + \beta_2 R + \beta_3 N + \beta_4 T^2 + \beta_5 (R \times T) + \beta_6 R^2 + \beta_7 (N \times T) + \beta_8 (N \times R) + \beta_9 N^2 \tag{1}$$

where *Y* is the studied response variable (biochar yield, C/N, H/C_{org}, and O/C_{org} ratios); $\beta_0, \ldots \beta_9$ are the regression coefficients to be estimated; and *T*, *R*, and *N* are the values of the independent variables (temperature, solid residence time, and N_2 flowrate, respectively). The significance of each independent variable was determined by the analysis of variance (ANOVA). A lack of fit test was performed to check the adequacy of the model.

2.1.2. Determination of the Stationary Points

A canonical analysis [19] was used to determine the nature of the stationary point (or the point on the surface where the partial derivatives are equal to zero), which can be a point of maximum response, a point of minimum response, or a saddle point. In the case of a saddle point, a RIDGE statement [19] was used to indicate the direction in which further experimentation should be performed, to produce the fastest decrease or increase in the estimated response, starting at the stationary point.

2.1.3. Validation of the Statistical Models

In order to validate the quadratic response surface regression models, a biochar was produced with the pyrolysis operating parameters determined from the response surface analysis, for producing a biochar with the optimal properties to maximize C sequestration (i.e., the lowest O/C_{org} and H/C_{org} ratios). A second biochar with the opposite characteristics (highest O/C_{org} and H/C_{org} ratios) was produced from each biomass. Predicted values from the response surface models vs. the actual values of the O/C_{org}, H/C_{org}, C/N ratios and yield, were compared using linear regression.

2.2. Pyrolysis Experimental Setup and Procedure

2.2.1. Description of the Vertical Auger Pyrolysis Reactor

In order to validate the selected approach, pyrolysis tests were carried out in a vertical auger pyrolysis reactor (Patent CA 2830968), developed by the *Institut de recherche et de développement en agroenvironnement* (IRDA) in collaboration with the *Centre de recherche industriel du Québec* (CRIQ). The pyrolysis unit (Figure 1) was installed at the IRDA research facility (Deschambault, QC, Canada). It included a hopper, a horizontal feed screw, a vertical screw passing through a 25.4 cm long heater block, a canister for the biochar recovery, and a condensation system. The feedstock in the hopper was fed to the heater block by a horizontal and vertical feed screw in a 2.54 cm diameter steel tube. The rotation speed of the two screws was controlled separately by gear motors, thus controlling the biomass flow rate. An agitator was installed and fixed at the hopper lid in order to facilitate and ensure the supply to the horizontal screw when using materials with a low density. Then, the feedstock was transported through the 25.4 cm long reactor within the vertical screw. The feedstock residence time in the reactor was set by controlling the rotation speed of the vertical screw, and was calculated in relation to the pitch of the screw (3.8 cm). Thermal power was supplied by two heating elements of 1500 Watts, inserted in a copper block surrounding the tube in the reaction zone. A thermocouple inserted in the middle of the cooper block registered the outside tube temperature and was used as the set point to control the heating elements. Temperatures were acquired every 10 s by a data logger (CR10X, Campbell Scientific, Edmonton, AB, Canada). At the exit of the vertical screw, the solid product of the pyrolysis (char) dropped into the canister (31.4 cm high and 16.8 cm diameter). A pot (15.2 cm high) was placed into the canister in order to recover the accumulated char. A flange at the bottom of the canister gave access to the pot. Moreover, the fine particles were separated from the gas by an inner baffle (10.2 cm diameter and 10.5 cm long) placed at the exit of the vertical screw. The gas was evacuated by an opening in the upper part of the canister and was directed to the condensation system. Every flange was tightened with a high temperature graphite gasket (1034 kPa) in order to prevent the entry of oxygen into the system. The air flowing into the system was purged with nitrogen, which was injected from the hopper's lid at volumetric flowrates ranging from 1 to 5 $L \cdot min^{-1}$, controlled by a flowmeter (Aalborg Instruments, New York, NY, USA; accuracy ±2%). While the nitrogen flow ensured that the pyrolysis reaction occurred in a non-oxygen environment, it also helped to evacuate the pyrolysis gas.

2.2.2. Biomass Selection and Analysis

The type of feedstock utilized for pyrolysis (e.g., woody biomass, crop residues, grasses, and manures) influences the yield and characteristics of the biochar, including the concentrations of elemental constituents, density, porosity, and hardness [20]. Moreover, the yield of the biochar from biomass can be influenced by its lignin, holocellulose, and extractives contents [21]. Three biomasses with different physico-chemical properties were selected for the pyrolysis experiments: wood pellets made from a mixture of Black Spruce (*Picea mariana*) and Jack Pine (*Pinus banksiana*), the solid fraction of pig manure (SFPM), and switchgrass (*Panicum Virgatum* L.). In Canada, forest biomass residues such as logging residues are present in large quantities. Moreover, forest biomass is the most common feedstock used for pyrolysis. Woody biomass has a high C content and low N content, which can lead to a biochar with a high C/N ratio. Switchgrass, a perennial grass, shows great characteristics for bioenergy production, because of its medium to high productivity (8 to 12 t $DM \cdot ha^{-1} \cdot yr^{-1}$), its sustainability, its great ability to use water and nutrients, its adaptation to the climate of Eastern Canada, and its relatively high gross calorific value (GCV), of between 18.2 to 19.1 $MJ \cdot kg^{-1}$ [22]. SFPM was selected because pyrolysis could be a sustainable management solution for the surplus of pig manure in some regions, where phosphorus (P) spreading in fields is restricted by regulations. Pyrolysis of the solid fraction of pig manure concentrates P in biochar [23], which facilitates its exportation outside of the region in surplus.

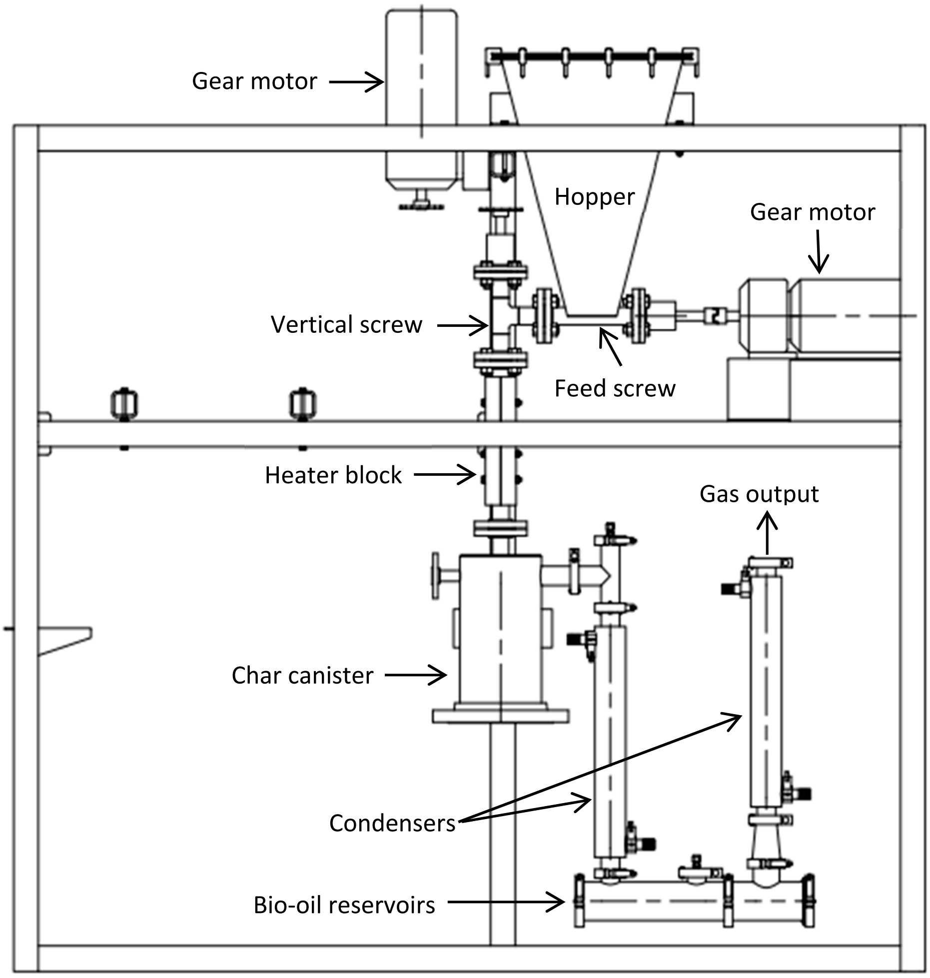

Figure 1. Schematic view of the vertical auger pyrolysis reactor.

All biomasses were ground and sieved to a particle size between 1.0 and 3.8 mm, prior to pyrolysis. The chemical properties of biomasses (proximate and ultimate analysis) were analysed at the IRDA laboratory (Quebec City, QC, Canada). The C, H, N, and ash content of the biomass were evaluated by dry combustion (Leco TruSpec, St. Joseph, MI, USA). The O content was calculated by subtracting the C, H, N, and ash contents from 100 wt %. Chlorine (Cl) extraction with water and dosage by titration with silver nitrate ($AgNO_3$) was used to determine the Cl content. Cellulose, hemicellulose, and lignin contents were analysed according to the AFNOR method [24].

2.2.3. Pyrolysis Experiments

Preliminary pyrolysis tests and a review of the literature were carried out in order to identify the range of pyrolysis operating parameters needed to obtain typical biochar yields in the pyrolysis auger reactor, ranging from 15% to 45%. For the three selected biomasses, the range of the N_2 flowrate selected was between 1 and 5 $L \cdot min^{-1}$, and the range for the solid residence time was between 60 and 120 s. The range of the pyrolysis temperature found for wood and SFPM was between 500 and 650 °C, and between 450 and 600 °C for switchgrass. For the selected solid residence times, the biomass flowrate in the pyrolysis reactor depended on the biomass properties, and varied from 0.61 to 1.08 $kg \cdot h^{-1}$ for wood, from 0.42 to 0.8 $kg \cdot h^{-1}$ for SFPM, and was fixed at 0.57 $kg \cdot h^{-1}$ for switchgrass.

The Box-Behnken design was carried out for each biomass with the defined range of pyrolysis operating conditions (Table 1), for a total of 45 experiments (Tables A1–A3).

Table 1. Box-Behnken design: list of independent variables and levels.

Independent Variable	Biomass	Values of the Coded Levels		
		−1	0	+1
Temperature (°C)	Wood	500	575	650
	SFPM	500	575	650
	Switchgrass	450	525	600
Solid residence time (s)	Each biomass	60	90	120
N_2 flowrate (L·min^{-1})	Each biomass	1	3	5

2.2.4. Products Yield and Biochar Characteristics

Bio-oil (Equation (2)) and biochar (Equation (3)) yields were calculated on a wet biomass basis, the non-condensable gas (Equation (4)) yield was calculated by the difference, and the liquid organic yield (Equation (5)) was calculated by subtracting the water content from the bio-oil yield:

$$Yield_{bio-oil}(\text{wt }\%) = \frac{m_{B1} + m_{B2}}{m_f} \times 100 \quad (2)$$

$$Yield_{biochar}\ (\text{wt }\%) = \frac{m_{Biochar}}{m_f} \times 100 \quad (3)$$

$$Yield_{gas}(\text{wt }\%) = \frac{m_f - m_{Biochar} - m_{B1} - m_{B2}}{m_f} \times 100 \quad (4)$$

$$Yield_{liquid\ organics}(\text{wt }\%) = \frac{100 - water\ content}{100 \times yield\ bio-oil} \quad (5)$$

where m_{B1} is the mass of bio-oil produced in the first condenser (g), m_{B2} is the mass of bio-oil produced in the second condenser (g), $m_{biochar}$ is the mass of biochar collected in the canister (g), m_f is the mass of feedstock pyrolysed (g), and the water content is the water content of bio-oil (wt %) measured following the Karl-Fischer titration method [25].

Biochar samples were analysed for moisture, volatile matter, and ash contents, based on the ASTM D1762-84 standard [26]. The organic carbon (C_{org}), total carbon (C_{tot}), hydrogen (H), nitrogen (N), and oxygen (O) were also analysed, using the same method as that employed for the analysis of biomasses.

3. Results and Discussion

3.1. Analysis of Biomass

The physicochemical properties of wood, SFPM, and switchgrass, are presented in Table 2. An ultimate analysis (C, H, N, O) shows large variations between the biomasses. The C content of wood is the highest, at 47.7%, and is the lowest for SFPM (40.0%). This is inversely proportional to the ash content, which is highest for the SFPM (11.5%), and lowest for wood (0.57%). SFPM has high N and Cl contents (2.96% and 3609 mg·kg^{-1}, respectively) when compared to wood and switchgrass. The O content is low for SFPM (28.2%), when compared to wood (40.0%) and switchgrass (42.5%). The H content ranges from 3.23% (switchgrass) to 6.39% (wood). The water content of SFPM (13.0%) is higher than switchgrass (7.2%) and wood (6.5%).

Based on an analysis of the lignocellulosic components, wood could necessitate a higher temperature to decompose because its lignin content (24%) is higher than that of SFPM and switchgrass (12.9% and 11.2%, respectively). In fact, the proportion of cellulose, hemicellulose, and lignin in biomass, will influence the degree to which the physical structure is modified during processing [27]. Hemicellulose and cellulose, which are more volatile during thermal degradation [28], are degraded at 200–300 and 300–400 °C, respectively, and lignin is degraded between 200–700 °C, representing a wide range in temperatures [29].

Table 2. Biomasses physicochemical properties.

	Unit	Wood	SFPM	Switchgrass
C_{tot}	wt %	47.7	40.0	45.8
N	wt %	0.128	2.96	0.425
O	wt %	40.0	28.2	42.5
H	wt %	6.39	5.85	3.23
Water content	wt %	6.5	13.0	7.2
Ash	d.b.%	0.57	11.5	1.6
Cl	mg·kg^{-1}	10	3 609	28
Lignin	wt %	24.0	12.9	11.2
Cellulose	wt %	30.4	11.9	42.9
Hemicellulose	wt %	29.9	22.0	30.1

3.2. Response Surface Models

3.2.1. Biochar Yield

The yields of products from the 45 pyrolysis tests carried out following the Box-Behnken design, are presented in Appendix A for wood (Table A1), switchgrass (Table A2), and SFPM (Table A3). The highest bio-oil yields were obtained from wood (48.6% to 63.6%) and switchgrass (44.8% to 61.4%), and pyrolysis of these materials was associated with low biochar yields (17.5% to 31.2% and 16.8% to 26.4%, respectively). Conversely, the pyrolysis of SFPM produced lower yields of bio-oil (38.3% to 46.7%) and higher yields of biochar (32.1% to 40.4%). The canonical analysis indicated that the stationary points of the three response surface models are saddle points. Thus, results from the RIDGE analysis, indicating the direction toward which further pyrolysis experiments should be performed, in order to obtain the minimal and maximal estimated values of biochar yield, are presented in Table 3. It is known that biochar yield decreases as pyrolysis temperature increases [30]. Based on the results of the analysis of variance for the models, the biochar yield is significantly dependent on the pyrolysis temperature for the three biomass feedstocks ($Pr < 0.05$; Appendix B), as the solid residence time is only significant for the switchgrass biochar. In contrast to what is reported in some studies [18,31], the biochar yield was not significantly influenced by the N_2 flowrate, which influences the vapor residence time. The predicted biochar yield is the highest for the pyrolysis of SFPM (maximum of 40%), due to the high ash content of the feedstock, which is found in biochar after pyrolysis. The biochar yield from switchgrass and wood pyrolysis are similar. However, the predicted highest value for wood (27.8%) is higher than for switchgrass (25.2%), despite the highest pyrolysis temperature being demonstrated for wood. It reflects the higher lignin content of wood, which preferentially forms char during pyrolysis [21].

Table 3. Estimated values of biochar properties and estimation of optimal pyrolysis operating parameters from the response surface models.

	Biochar Yield (wt %)		H/C_{org}		O/C_{org}		C/N	
Wood	Min	Max	Min	Max	Min	Max	Min	Max
Estimated value	17.2	27.8	0.54	0.81	0.14	0.25	477	539
Temperature (°C)	646	507	646	515	642	517	639	522
Residence time (s)	89	79	99	79	103	80	75	90
N_2 Flowrate (L·min^{-1})	3.6	3.4	2.9	3.9	2.8	4.1	2.8	4.4
Switchgrass								
Estimated value	17.4	25.2	0.47	0.77	0.10	0.23	100	108
Temperature (°C)	593	451	588	456	594	462	588	466
Residence time (s)	78	88	106	80	102	75	74	72
N_2 Flowrate (L·min^{-1})	3.3	2.8	3.1	3.4	2	3.4	3.3	3.1

SFPM								
Estimated value	32.2	40	0.66	0.90	0.14	0.21	11.5	12.8
Temperature (°C)	649	507	628	508	631	543	594	614
Residence time (s)	95	79	94	79	94	73	84	103
N_2 Flowrate ($L \cdot min^{-1}$)	3	3.4	1.6	3.6	1.7	4.4	4.9	1.5

3.2.2. H/C_{org} and O/C_{org} Ratios

The minimum values of H/C_{org} and O/C_{org} indicate a high biochar C stability [32–35], and thus, a maximum potential for C sequestration. H/C_{org} and O/C_{org} ratios of biochars produced from the 45 pyrolysis tests significantly varied for a single biomass, depending on the pyrolysis operating parameters (Tables A1–A3). The response surface models demonstrated that the biochar produced from the three biomasses only demonstrates a good potential for C sequestration if the operating parameters are properly selected. A minimum stationary point was only found for the O/C_{org} molar ratio of biochar made from switchgrass; otherwise, saddle points were found. Minimum and maximum values of H/C_{org} and O/C_{org}, predicted from the RIDGE analysis, are presented in Table 3. The minimum predicted H/C_{org} ratios are 0.47, 0.54, and 0.66 for biochars produced from switchgrass, wood, and SFPM, respectively. This means that, for the optimal pyrolysis operational parameters, at least 50% of the C in biochar is expected to remain in the soil for more than 100 years [14]. The predicted minimum O/C_{org} ratio below 0.2 (0.10, 0.14, and 0.14 for switchgrass, wood, and SFPM, respectively) confirms the C sequestration potential of biochars produced with similar pyrolysis operating parameters. In fact, the pyrolysis operating parameters needed to obtain the minimum H/C_{org} and O/C_{org} ratios for each biomass, are similar. Conversely, the maximum predicted H/C_{org} and O/C_{org} values for the three biomasses are always above 0.7 and 0.2, respectively. Harvey et al. [36] found that pyrolysis conditions are the primary factors controlling the thermal stability of the resulting biochar. More specifically, Zhao et al. [37] demonstrated that biochar recalcitrance (i.e., its ability to resist decomposition) is mainly determined by pyrolysis temperature. The ANOVA analysis confirmed this fact: the pyrolysis temperature always significantly influenced ($Pr < 0.05$) the H/C_{org} and O/C_{org} ratios (Tables A4–A6). Moreover, the solid residence time significantly impacted the indicators of C stability for the pyrolysis of switchgrass: as the residence time increased, the H/C_{org} and O/C_{org} ratios decreased. Di blasi [38] also reported that the solid residence time has an influence on the physical and chemical characteristics of biochar. The addition of a heat carrier material in an auger reactor could decrease the solid residence time required to provide sufficient reaction heat and time [18]. Finally, Antal and GrØnli [21] reported that biochar characteristics can also be modified with a change in the sweeping gas flow rate, which has an impact on the vapor residence time. Statistical analysis revealed that the N_2 flowrate has a significant impact on the O/C_{org} ratio of SFPM and wood biochars. A lower O/C_{org} ratio is obtained with lower N_2 flowrates.

3.2.3. C/N Ratio

Biochars with a C/N ratio higher than 30 could help in decreasing the N_2O emissions from soil [13]. Results of the experimental Box-Behnken design showed that the C/N ratio markedly varies among biomasses, from 430 to 541 for wood, 95 to 115 for switchgrass, and 11.0 to 13.0 for SFPM. The Canonical analysis of the response surface models shows that a maximum stationary point was found for the C/N ratio of wood biochar, and that saddle points were identified for switchgrass and SFPM biochars. The minimum and maximum values estimated from the RIDGE analysis are presented in Table 3. The ANOVA (Tables A4–A6) showed that none of the pyrolysis operating conditions significantly influenced the C/N ratio of biochar. In fact, because the N content of biomasses is low, particularly for wood and switchgrass (0.128% and 0.454%), the impact of pyrolysis operating parameters on the N content of biochar, and consequently on its C/N ratio, is low. Even if the C/N ratio for a single biomass does not significantly vary, depending on the pyrolysis operating parameters, there are large variations among the biomasses. In the literature, it was found that the C/N ratio is highly dependent on the type of biomass feedstock used for pyrolysis [8,39]. In the present study, the biomass C/N ratio (13.5, 108, and 372 for SFPM, switchgrass, and wood, respectively) is similar to the C/N ratio of biochar produced from the corresponding biomass, and the C/N ratios of biochars produced from wood pyrolysis are the highest (430 to 565), and ranged from 95 to 115 for switchgrass pyrolysis. Thus, based on their chemical composition, biochars made from these two biomasses have the potential to mitigate N_2O emissions from soil. Biochars produced from the pyrolysis of SFPM have a C/N ratio lower than 30 (11.0–13.0) and could potentially increase N_2O emissions from soil, due to their high N content [39] and low C content.

3.3. Experimental Validation of the Models

In order to validate the quadratic response surface regression models, two biochars were produced from wood (B1 and B2), switchgrass (B3 and B4), and SFPM (B5 and B6) (Table 4). B2, B4 (two replicates), and B6 were produced with the pyrolysis operating parameters (temperature, residence time, and N_2 flowrate) determined from the response surface analysis for producing a biochar with the optimal properties in order to maximize the C sequestration potential (i.e., the lowest O/C_{org} and H/C_{org} ratios). B1, B3, and B5 were produced using the optimal parameters for producing a biochar with the opposite characteristics (highest O/C_{org} and H/C_{org} ratio). In fact, because the predicted optimal pyrolysis parameters needed to obtain the optimal O/C_{org} and H/C_{org} ratios are similar, the selected temperature, residence time, and N_2 flowrate, were average values. For example, the lowest H/C_{org} and O/C_{org} ratios predicted for wood biochar would be obtained at 646 °C and 642 °C, respectively (Table 3). Thus, the selected temperature for the production of biochar with the best C sequestration potential was 644 °C (Table 4). The pyrolysis operating parameters for biochar production that were used to validate the models, and the corresponding yields and properties of the resulting biochars are presented in Table 4. B2, B4, and B6 were produced at a higher temperature, during a longer residence time, and with a lower N_2 flowrate than B1, B3, and B5, respectively. Their ash contents are higher, whereas their H and O contents are lower. Moreover, the C and N contents of B2 and B4 are higher than B1 and B3, respectively. The water content is always low (about 1%), whereas the biochars produced at higher temperatures are more alkaline.

Table 4. Products yields and physicochemical properties of biochars produced with optimal pyrolysis operating conditions.

	Unit	B1	B2	B3	B4 [1]	B4 [2]	B5	B6
Pyrolysis parameters								
Biomass		Wood	Wood	SG [3]	SG	SG	SFPM [4]	SFPM
Temperature	°C	516	644	459	591	591	526	630
Res. time	s	80	101	78	104	104	76	94
N_2 flowrate	$L \cdot min^{-1}$	4.0	2.9	3.4	2.6	2.6	4.0	1.7
Products yields								
Biochar	% (w.b.)	26.4	18.5	26.9	18.9	18.6	46.4	34.9
Bio-oil	% (w.b.)	58.2	51.5	60.2	49.4	49.0	37.9	41.5
Biochar properties								
C_{total}	% (w.b.)	71.6	80.0	67.1	79.5	80.2	51.5	49.2
C_{org}	% (w.b.)	70.7	76.0	64.9	79.1	79.9	47.4	45.2
H	% (w.b.)	4.8	3.73	4.85	3.36	3.35	3.73	3.36
O	% (w.b.)	21.6	13.4	22.9	10.0	9.59	15.6	13.7
N	% (w.b.)	0.141	0.166	0.641	0.828	0.780	4.40	4.05
$P_{soluble}$	$mg \cdot kg^{-1}$	13.7	7.16	109	26.7	32.1	165	55.7
Water content	% (w.b.)	0.9	1.2	1.5	1.0	1.8	0.9	0.9
Ash (750 °C)	% (d.b.)	1.4	2.1	4.1	5.6	5.4	23.6	28.1
pH		6.8	7.6	6.4	8.7	8.9	8.6	9.3

[1] First pyrolysis test for B4 production; [2] Second pyrolysis test for B4 production; [3] Switchgrass; [4] Solid fraction of pig manure.

The observed vs. predicted values for the biochar yield, C/N, H/C_{org}, and O/C_{org} ratios, are illustrated in Figure 2. A comparison of the linear regressions with the 1:1 line indicates that the models fit the experimental data for the yield (R^2 = 0.97), C/N (R^2 = 1.0), H/C_{org} (R^2 = 0.88), and O/C_{org} (R^2 = 0.73). B2 and B4 are expected to have a better potential for mitigating climate change, have a high C sequestration potential (H/C_{org} < 0.7; O/C_{org} < 0.2), and have the potential to reduce soil GHG emissions (C/N ratio > 30).

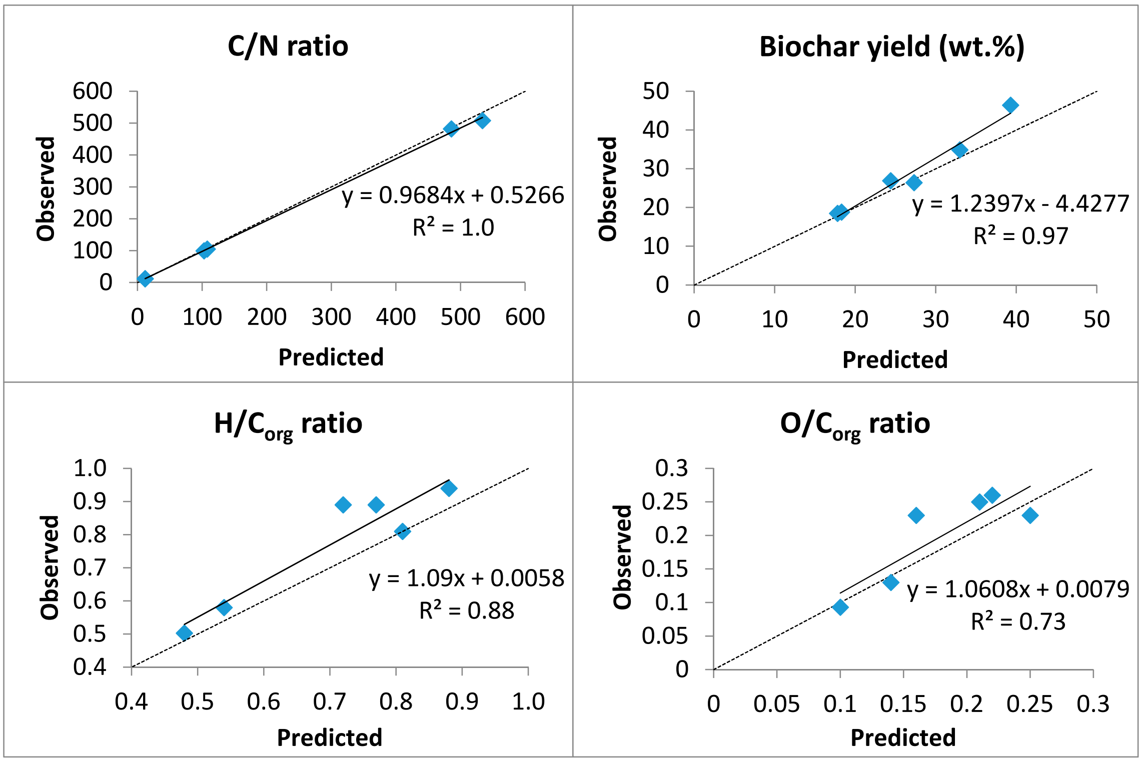

Figure 2. Biochar yield, C/N, H/C_{org}, and O/C_{org} ratios: observed vs. predicted values.

4. Conclusions

Results from this study demonstrated that the response surface methodology approach can be used to accurately predict the optimal operating parameters of a vertical auger reactor (temperature, solid residence time, and nitrogen flowrate), required to produce engineered biochars with specific characteristics for C sequestration. It was highlighted that the pyrolysis products' yields and biochar characteristics highly depend on the pyrolysis operating conditions and biomass feedstock. Biochar produced from wood and switchgrass can only present a high potential for C sequestration if the pyrolysis operating parameters are properly selected. In fact, the minimum H/C_{org} and O/C_{org} ratios predicted from the response surface models reached values lower or equal to 0.54 and 0.14, respectively, for a pyrolysis temperature ranging from 588 to 646 °C, a solid residence time from 99 to 106 s, and a N_2 flowrate from 2.0 to 3.1 L·min^{-1}. Moreover, regardless of the pyrolysis operating conditions, the biochars produced from the pyrolysis of wood and switchgrass could help to decrease soil N_2O emissions, because their C/N ratios are higher than 30. Further experiments have to be carried out with the produced biochars, in order to evaluate their effect on soil GHG emissions and C sequestration, and to validate the hypothesis made in this study.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A. Experimental Data: Box-Behnken Design

Table A1. Pyrolysis of wood—Experimental data.

Operational Parameters			Products Yields				Biochar Properties		
T	Res. Time	N_2	Bio-Oil	Liquid Organics	Biochar	Syngas	C/N	H/C_{org}	O/C_{org}
°C	s	$L{\cdot}min^{-1}$	%		%	%			
500	60	3	57.6	39.0	31.2	10.9	517	0.84	0.25
500	90	1	61.9	39.9	24.6	13.2	491	0.68	0.19
500	90	5	55.2	36.3	30.2	14.2	531	0.92	0.29
500	120	3	63.6	41.9	23.4	12.4	541	0.68	0.19
575	60	1	49.1	31.8	22.6	28.0	483	0.68	0.19
575	60	5	56.8	37.8	22.2	20.5	512	0.74	0.22
575	90	3	60.0	38.1	20.7	18.8	565	0.65	0.19
575	90	3	60.6	40.6	20.6	18.2	487	0.65	0.18
575	90	3	61.5	39.4	20.2	17.8	504	0.62	0.17
575	120	1	58.8	34.4	21.2	19.6	503	0.60	0.15
575	120	5	54.4	35.2	19.9	25.2	500	0.63	0.18
650	60	3	56.0	36.8	18.3	25.2	430	0.59	0.16
650	90	1	52.4	31.3	18.0	29.0	491	0.51	0.13
650	90	5	48.8	27.8	17.5	33.1	497	0.57	0.15
650	120	3	48.6	27.4	17.6	33.3	466	0.53	0.13

T: temperature; Res. Time: solid residence time; N_2: Nitrogen flowrate.

Table A2. Pyrolysis of Switchgrass—Experimental data.

Operational Parameters			Products Yields				Biochar Properties		
T	Res. Time	N_2	Bio-Oil	Liquid Organics	Biochar	Syngas	C/N	H/C_{org}	O/C_{org}
°C	s	$L{\cdot}min^{-1}$	%	%	%	%			
450	60	3	57.8	35.4	25.6	16.4	114	0.81	0.25
450	90	1	59.2	34.3	26.4	14.0	106	0.77	0.21
450	90	5	60.1	37.1	24.9	14.4	102	0.82	0.24
450	120	3	59.4	34.1	24.4	15.9	101	0.69	0.19
525	60	1	61.4	34.7	20.5	17.9	100	0.64	0.18
525	60	5	55	33.4	19.9	24.5	105	0.72	0.21
525	90	3	58.3	37.2	20.2	21.2	115	0.60	0.16
525	90	3	58.5	31.0	21.3	19.9	95	0.61	0.16
525	90	3	59	30.8	20.0	20.6	99	0.58	0.14
525	120	1	56.8	42.3	21.9	21.1	102	0.57	0.14
525	120	5	54.5	27.9	20.9	24.1	103	0.54	0.14
600	60	3	51.5	30.8	16.8	30.5	98	0.58	0.15
600	90	1	48.9	21.3	18.7	31.9	105	0.48	0.10
600	90	5	44.8	20.4	17.3	37.2	99	0.49	0.11
600	120	3	48.1	21.8	18.5	32.9	102	0.46	0.10

T: temperature; Res. Time: solid residence time; N_2: Nitrogen flowrate.

Table A3. Pyrolysis of SFPM—Experimental data.

Operational Parameters			Products Yields				Biochar Properties		
T	Res. Time	N_2	Bio-oil	Liquid organics	Biochar	Syngas	C/N	H/C_{org}	O/C_{org}
°C	s	$L \cdot min^{-1}$	%	%	%	%			
500	60	3	42.8	12.5	41.6	14.9	11.6	0.92	0.21
500	90	1	45.7	12.4	38.8	15.1	12.4	0.80	0.16
500	90	5	39.3	10.6	40.4	19.5	12.0	0.91	0.21
500	120	3	41.7	10.8	39.6	17.0	12.5	0.85	0.18
575	60	1	46.7	10.8	36.7	15.0	12.3	0.75	0.16
575	60	5	40.1	11.7	38.5	20.6	11.5	0.85	0.23
575	90	3	42.3	11.7	35.8	21.0	12.7	0.78	0.18
575	90	3	43.7	12.1	36.0	19.4	12.4	0.76	0.16
575	90	3	43.6	11.9	34.8	19.8	11.4	0.74	0.17
575	120	1	45.7	12.0	34.7	17.7	12.9	0.65	0.14
575	120	5	38.6	9.2	35.9	24.5	12.1	0.72	0.16
650	60	3	42.7	10.5	33.8	21.8	12.6	0.66	0.14
650	90	1	44.0	7.7	32.4	22.8	13.0	0.61	0.13
650	90	5	38.3	9.3	32.1	28.8	11.0	0.74	0.18
650	120	3	39.1	8.5	32.6	27.2	12.8	0.68	0.14

T: temperature; Res. Time: solid residence time; N_2: Nitrogen flowrate.

Appendix B. ANOVA Tables

Table A4. ANOVA for the model of wood biochar.

Wood	Factor	DF	Mean Squares	F Value	Pr > F
Yield	Temperature	4	53.001	29.96	0.0011 *
	Res. time	4	8.0950	4.580	0.0632
	N_2 flowrate	4	2.9350	1.660	0.2936
H/C_{org}	Temperature	4	0.0287	18.78	0.0033 *
	Res. time	4	0.0063	4.120	0.0763
	N_2 flowrate	4	0.0070	4.580	0.0631
O/C_{org}	Temperature	4	0.0043	22.04	0.0022 *
	Res. time	4	0.0010	4.930	0.0552
	N_2 flowrate	4	0.0014	7.430	0.0247 *
C/N	Temperature	4	1452.1	1.250	0.3972
	Res. time	4	471.35	0.410	0.7982
	N_2 flowrate	4	304.41	0.260	0.8904

DF: Degrees of freedom; Res. Time: solid residence time; * Significant at Pr < 0.05.

Table A5. ANOVA for the model of switchgrass biochar.

Switchgrass	Parameter	DF	Mean Squares	F Value	Pr > F
Yield	Temperature	4	29.441	87.23	<0.0001 *
	Res. time	4	0.8077	2.390	0.1822
	N_2 flowrate	4	0.7911	2.340	0.1876
H/C_{org}	Temperature	4	0.0368	45.51	0.0004 *
	Res. time	4	0.0083	10.30	0.0124 *
	N_2 flowrate	4	0.0014	1.700	0.2847
O/C_{org}	Temperature	4	0.0061	72.32	0.0001 *
	Res. time	4	0.0017	20.26	0.0027 *
	N_2 flowrate	4	0.0003	3.000	0.1298
	Temperature	4	29.954	0.530	0.7194

C/N	Res. time	4	21.608	0.380	0.8125
	N_2 flowrate	4	2.1106	0.040	0.9964

DF: Degrees of freedom; Res. Time: solid residence time; * Significant at Pr < 0.05.

Table A6. ANOVA for the model of SFPM biochar.

SFPM	Parameter	DF	Mean Squares	F Value	Pr > F
Yield	Temperature	4	27.624	96.31	<0.0001 *
	Res. time	4	2.7895	9.730	0.0141 *
	N_2 flowrate	4	0.8267	2.880	0.1381
H/C_{org}	Temperature	4	0.0207	18.07	0.0036 *
	Res. time	4	0.0030	2.630	0.1592
	N_2 flowrate	4	0.0054	4.680	0.0606
O/C_{org}	Temperature	4	0.0009	5.020	0.0533 *
	Res. time	4	0.0008	4.470	0.0661
	N_2 flowrate	4	0.0014	8.040	0.021 *
C/N	Temperature	4	0.2138	0.850	0.5509
	Res. time	4	0.1987	0.790	0.5793
	N_2 flowrate	4	0.6988	2.770	0.1466

DF: Degrees of freedom; Res. Time: solid residence time; * Significant at Pr < 0.05.

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