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Research article

Optimization of process parameters of self-purging microwave pyrolysis of corn cob for biochar production

John Christian C. Quillope [a], Rowena B. Carpio [a,*], Kristel M. Gatdula [a], Monet Concepcion M. Detras [a], Stephen S. Doliente [a,b]

[a] Department of Chemical Engineering, University of the Philippines Los Baños, College, Laguna, 4031, Philippines
[b] Department of Chemical Engineering, University of Bath, Claverton Down, Bath, BA2 7AY, UK

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ABSTRACT

Microwave pyrolysis offers rapid and low-cost technology to upgrade agro-forestry residues to high-value products. I-optimal experimental design was used to determine the optimal combination of microwave power and exposure time to maximize biochar yield from corn cob. A validation experiment at optimal conditions of 600 W and 6.9 min produced an average yield of 56.98% on a dry and ash-free basis, agrees with the predicted value (3.43% error) and confirms the adequacy of the model yield equation. Characterization of biochar product revealed an organized mesoporous structure with a carbon content of 62.68%, surface area of 3.05 m^2/g, pore volume of 0.003 cm^3/g, capacitance range of 27.14–53.99 μF/g, energy density range of 6.0×10^{-7} - 1.2×10^{-6} Wh/kg, and power density range of 9.4×10^{-4} – 2.49×10^{-3} W/kg. The biochar produced would require further process to be considered for various industrial applications.

1. Introduction

Carbon-based materials are becoming more important for their diverse application in various fields, such as air and water treatment solutions (Gopinath et al., 2021). Recently, a vast majority of research on renewable technology focused on developing energy storage devices, which use carbon-based electrodes to maximize the process of harnessing renewable but inconsistent energy resources such as wind and solar power. Ideally, the next-generation carbon-based materials need to be produced using renewable resources via simple, low cost and environmentally friendly methods, with controllable morphologies, rich porosity, modified surface chemistry, and appropriate functionalities (Gao et al., 2017).

The waste-to-energy initiative could help push this endeavour by using agro-industrial and agricultural wastes as raw materials, such as corn cob. Corn is a major crop planted around the world. In the Philippines, corn plant production reached 7.77 MMT in 2018 (Philippine Statistics Authority, 2019). A large volume of corn residue is generated as a waste, with corn cob accounting for 18% of the total corn production (Zhang et al., 2012). Corn plant residue is often left or burned on cultivated land to condition the soil for the next cropping season. Various literature claims that the porous solid residue of corn cob carbonization, also known as porous biochar, can be used as electrode material for a supercapacitor (Karnan et al., 2017; Qu et al., 2015; Yang and Zhang, 2018). Therefore, establishing and optimizing a cheap and environment-friendly conversion process of biomass such as corn cobs to carbon-based materials could lead to innovation in the energy storage industry.

One process that can satisfy these requirements is the microwave pyrolysis of biomass. Pyrolysis is a thermochemical conversion of organic material to a carbon-rich product without the presence of oxygen. Due to the ability of microwaves to quickly heat a material compared to other means of heating, the process currently attracts broad interest in research and development since it can produce products in a much efficient method (Adam, 2017).

Microwaves lie between infrared and radio frequencies in the electromagnetic spectrum. The two most widely used microwave frequencies are 915 MHz and 2.45 GHz (most of the domestic microwave ovens). Microwave heating works on the principle of microwave electromagnetic radiation conversion to thermal energy. Compared to conventional heating, which involves surface heating using fuels like coal, microwaves can penetrate through solid material and accomplish volumetric heating (Arshad et al., 2017). The main advantages of microwave heating over conventional heating during pyrolysis include

* Corresponding author.
E-mail address: rbcarpio@up.edu.ph (R.B. Carpio).

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the following: (1) reduced waste output and easier waste handling; (2) fast and selective heating; (3) improved system reactivity; (4) relatively easier controllability; (5) higher efficiency; (6) relative inexpensiveness; (7) cleaner energy source; and (8) portability of equipment (Mohan and Bhalla, 2016). Like conventional pyrolysis, the composition and quality of the products (particularly biochar) under microwave pyrolysis depend on the feedstock and operating parameters. Among the parameters studied in the microwave pyrolysis of biomass include particle size, reaction temperature, microwave power, microwave exposure time, and microwave absorber (Mohd, 2017). The reaction temperature is expected to affect the product composition of any thermochemical conversion process, including microwave pyrolysis. Microwave pyrolysis of coffee hulls and polypropylene showed that increasing the reaction temperature of the system decreases the biochar yield (Menendez et al., 2007; Mohan and Bhalla, 2016). The reaction temperature is directly related to the microwave power, with varying degrees of proportionality depending on the nature and the amount of the feedstock used and the presence of microwave absorbers in the system (Brewer, 2012; Januri et al., 2017). An increase in microwave power allows more heat to be transferred to the feedstock at a given time. Microwave power is also related to heating rates; a high microwave power leads to a high heating rate and reduction in heat loss to the environment. An increase in microwave power was found to increase gas and/or oil production at the expense of reduced char yield in sewage sludge, microalgae, and corn cob (Hu et al., 2012; Tian et al., 2011). The microwave exposure time has a similar effect as the microwave power during pyrolysis. An insufficient microwave exposure time could lead to partial or incomplete conversion, while excessive (or relatively longer) exposure time promotes more gas formation and lower biochar yield (Adam, 2017; Mohd, 2017).

Microwave absorbers are dielectric materials with dipolar molecules that absorb the electromagnetic waves. These materials can convert a good amount of microwave energy to thermal energy, which can be transmitted to the supported materials (Mushtaq et al., 2014). Carbon-based materials are commonly used microwave absorbers. For example, an improved conversion of waste plastic to liquid (mainly C_7 and C_{20}) and palm oil mill effluent to solid char was reported using activated carbon as a microwave absorber (Januri et al., 2017; Jing et al., 2021). Lately, conducting polymers (such as polypyrrole) are getting more attention because of their high electrical conductivity, good environmental stability, relatively easy synthesis, and redox reversibility (Hao et al., 2013). For example, a graphitic carbon from filter paper, cotton, and wood biomass precursors under microwave pyrolysis was reported using polypyrrole (Lawas et al., 2019; Wang et al., 2008). In addition, novel microwave absorbers were also developed using polypyrrole-based composites, such as polypyrrole and carbon quantum dots composites (Rahal et al., 2020).

Biochar produced from oil palm shell, maize, and sugarcane bagasse was recently reported via the conventional or microwave pyrolysis conditions using a self-purging reactor (Intani et al., 2018; Kong et al., 2019; Noor and Abdullah, 2018). Pyrolysis without using N_2 as purging gas (self-purging) reduces the production cost for biochar (Kong et al., 2019).

This work followed the parametric study conducted by Lawas et al. (2019) on the microwave pyrolysis of corn cob. Using self-purging microwave pyrolysis and polypyrrole as the absorber, the optimal settings for microwave power and exposure time were established to maximize the biochar yield from corn cob. The optimal biochar product was analyzed using scanning electron microscopy (SEM) with energy dispersive x-ray (EDX), x-ray fluorescence (XRF), Brunauer–Emmett–Teller (BET), and cyclic voltammetry (CV). By identifying the optimal conditions, the scale-up of this technology could be investigated in terms of its economic and environmental impacts (Doliente and Samsatli, 2019; Tapia et al., 2019). Accounting for these impacts is paramount in the commercial implementation of waste valorization technologies and their sustainable integration into biomass supply chains in both developed and developing countries (Doliente et al., 2020; Tapia et al., 2019).

An optimal design, such as the I-optimal and D-optimal, is an alternative experimental design when the classical/standard approaches, such as response surface methodology (RSM), are not appropriate or impractical to use. In this study, the limitation set by the microwave source, where the output power can only be chosen from the following: 100 W, 300 W, 450 W, 600 W, 700 W, and 800 W makes the RSM unsuitable. The I-optimal design was chosen in the study because it can flexibly accommodate constraints while it also determine the main effects, two-factor interactions, and precise predictions of the response variable (Smucker et al., 2018). Also, the I-optimal was suggested over D-optimal when a possible curvature is suspected as I-optimal forces midpoints into the experimental design (Worley, n.d.). To date, this is the first optimization study on self-purging microwave pyrolysis of corn cob using the I-optimal experimental design.

2. Materials and methods

2.1. Materials and sample preparation

The corn cob wastes were purchased and collected from the public market of Los Baños, Laguna, Philippines. All reagents and sample preparation methods are the same as described in the parametric study previously conducted by Lawas et al. (2019). The $FeCl_3{\cdot}6H_2O$ (analytical grade) and pyrrole monomer (98% pure) were purchased from Sigma-Aldrich, and the silica gel (self-indicating, 5–10 mesh) was from LABCHEM.

Sample preparation was first employed by a series of steps: washing, air drying (7 h/day, for 1 week), and size reduction of the raw corn cob samples. Size reduction was performed initially using a knife and then using a domestic blender. Finally, the corn cob chips were collected after passing through a Tyler no. 4 screen (4.76 mm opening size). The characteristic of the raw corn cob and prepared corn cob chips are presented in Table 1.

A pyrrole concentration of 0.1 M and a catalyst concentration of 0.1 M were prepared in a 500-mL volumetric flask by adding an appropriate amount of pyrrole and $FeCl_3{\cdot}6H_2O$ in distilled water, respectively. To prepare the biomass/absorber feed mixture, 5 g of the biomass feedstock was placed in a 250-mL Erlenmeyer flask. Then, 50 mL of the 0.1 M pyrrole solution was poured into the flask and left to stand for 2 min to ensure contact between the biomass and the microwave absorber. Then, 50 mL of the 0.1 M $FeCl_3$ solution was added, causing the solution to darken, signifying the polymerization of pyrrole to polypyrrole. Lastly, the feed mixture was covered with aluminum foil and allowed the polymerization for 24 h.

The resulting mixture was washed several times with distilled water (total of 200 mL) until a clear solution was obtained to remove the excess polypyrrole and $FeCl_3$ from the corn cob chips. Washing was employed to avoid overheating, ensure uniform heating of the biomass, and prevent the interference of $FeCl_3$ with the heating process.

The excess water was squeezed out from the samples using a cheesecloth. Afterwards, the wet biomass was placed inside a microwavable container and put inside a zip lock bag along with silica gel. The bag was then sealed and left under the sun for three days to dry. Finally, the dried biomass was stored in a sealed container until use.

Table 1. Characteristic of corn cob biomass.

Type	Moisture (% w/w)	Ash (% w/w)	Particle size (mm)
Raw corn cob	9.42	1.67	-
Prepared corn cob chips[1]	4.92	0.90	≤0.4.76

[1] The actual biomass feedstock used in the experiment.

2.2. Experimental setup

Figure 1 shows the microwave pyrolysis set-up used in the study. The set-up has three major components: a microwave oven (modified Samsung ME711K), a condenser tube (300 mm jacket length), and a quartz boiling flask (50 mL capacity). The condenser tube was connected perpendicular to the microwave source through a hole at the ceiling of the oven. The microwave pyrolysis experiments were performed under self-purging conditions (Intani et al., 2018; Kong et al., 2019; Yek et al., 2017). This approach uses its gaseous pyrolysis product instead of using N_2 gases supplied from an external source as the purging gas (Kong et al., 2019). Thus, no initial purging with N_2 was employed. The connection between the oven and the condenser was sealed using silicone glue. For every run, 1.5 g of the dried sample is placed in the quartz boiling flask (reactor). The reactor was securely attached and sealed to the condenser inside the microwave oven using high-temperature silicone tape to prevent air from leaking into the reactor during microwave heating. Afterwards, appropriate microwave power (450 and 600 W) and exposure time (5–10 min) were set for the microwave pyrolysis by adjusting the control knobs of the equipment. A digital timer monitors the required exposure time. The biochar yield was determined by gravimetry and expressed as percent weight on a dry-ash-free (% daf) of the biomass feedstock using the following equation:

$$Biochar\ yield\ (\%\ daf) = \frac{m_{bc} * (1 - A_{bc})}{m_f * (1 - M - A)} \times 100 \quad (1)$$

where, m_{bc} is the mass of biochar obtained, A_{bc} is the mass fraction of ash in the biochar, m_f is the mass of corn cob feedstock used, M and A are the mass fraction of moisture and mass fraction of ash, respectively, in the corn cob feedstock. All gaseous products (condensable and non-condensable) were allowed to escape through the condenser tube.

2.3. Design of experiment

This work builds upon the parametric study conducted by Lawas et al. (2019), which determined the microwave power and exposure time as significant factors in biochar production using corn cob. Before the experiment, the results from the said study were first validated through a series of verification runs. To predict the optimized conditions using an experimental design software, Design Expert (version 11.0.05), the two resulting significant factors (microwave exposure time and output power) were kept in range. The remaining factors that were reported insignificant by the parametric study (polymerization time, catalyst concentration, and pyrrole concentration) were then examined and adjusted several times, resulting in the predicted optimal conditions presented in the **Supplementary data.**

In Design Expert, the goal set for the biochar synthesis was to achieve the maximum yield. Upon examination and manipulation through the software, the pyrrole concentration and polymerization time were recommended to be kept at their maximum values – 0.1 M and 24 h, respectively – to maximize biochar yield. As for the catalyst concentration, a slight deviation from the minimum value was recommended, thus reaching a concentration of 0.105 M. At these recommended conditions, an optimal biochar yield of 55.62% with a 95% confidence interval was estimated using the software.

Upon validating the parametric model, the I-optimal design was then employed in this experiment. Using Design Expert, Table 2 shows the experimental design generated for the optimization of biochar yield. The high and low values considered are within the range of values used by Lawas et al. (2019). After determining the optimal microwave power and

Table 2. I-optimal experimental design for the optimization of biochar yield.

Randomized Run	Parameters	
	Exposure Time, min	Output Power, W
1	8.1	600
2	10.0	600
3	9.3	600
4	10.0	450
5	6.3	450
6	7.5	450
7	8.8	450
8	5.7	600
9	7.5	450
10	6.9	600
11	5.0	450
12	5.7	600

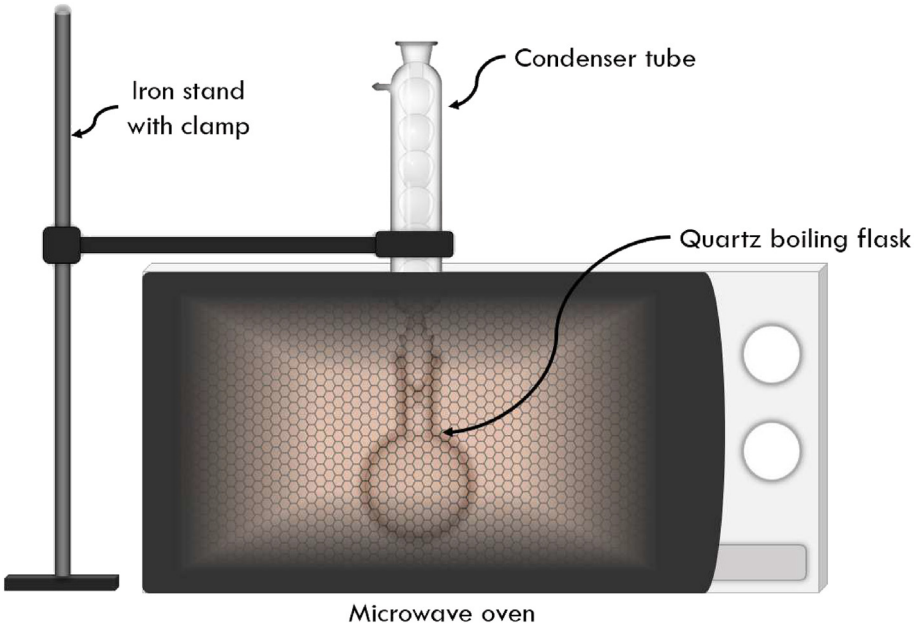


Figure 1. Experimental setup for pyrolysis experiment.

exposure time setting, five (5) additional runs were conducted under this condition for validation.

2.4. Analysis

The moisture and ash content of the raw corn cob and biochar product were measured based on NREL/TP-510-42621 (Sluiter et al., 2008) and ASTM E1755-01(2015) (ASTM, 2015), respectively. The biochar products derived at optimal conditions were then mixed at equal proportion to form a composite sample and subjected to different characterization. SEM-EDX analysis was conducted using the Phenom XL Scanning Electron Microscope. The surface area and pore volume were determined using a BET analyzer wherein the sample was degassed in a vacuum for 12 h at 100 °C before analysis. The inorganic composition was determined by XRF using EDX-7000. The electrochemical properties (e.g., specific capacitance, specific energy density) of the biochar were analyzed using cyclic voltammetry using two mass loadings (75 and 100 mg) at varying scanning rates (10, 25, 50, and 100 mV/s) based on the method described by Dehkhoda (2016). The FTIR analysis of biochar was performed using Thermo Scientific Nicolet 6700.

3. Results and discussion

3.1. Effect of microwave power and exposure time on biochar yield

Figure 2 summarizes the behavior of the biochar yield with 450 W and 600 W microwave power and different exposure time. Figure 2 was divided into four regions: Regions 1 and 2 represent the sudden decrease and gradual increase of the biochar yield at 450 W, respectively, while Regions 3 and 4 illustrate the sudden increase and decrease of biochar yield at 600 W, respectively. The opposite trends of the response with 450 W and 600 W appear to be primarily due to their subsequent reaction temperatures. Unfortunately, the temperature during the reaction was not measured. Thermocouple was not used for temperature measurement because it could locally distort the electromagnetic field, conduct heat away from the sample, induce thermal instabilities, damage the reactor and microwave oven, and lead to measurement error (Pert et al., 2001), caused by sparks or electric arcs commonly encountered in microwave-metal interactions (Arshad et al., 2020; Fernandez et al., 2011). Also, alternative temperature probe such as IR optical pyrometer was not utilized due to funding limitations. However, the reaction temperature of a system subjected to microwaves is directly proportional to its microwave power (Anis et al., 2017; Menendez et al., 2007). The reaction temperature influences the pyrolysis products' distribution and composition, including biochar (Menendez et al., 2007). Since the power controller served as the temperature controller for the system, it can be considered that the difference in microwave power levels between the two sets of runs significantly affects the biochar yield through its proportional effect on the temperature of the system (Anis et al., 2017). Nevertheless, this assumption needs to be verified in future work because there can be a non-thermal effect that could contribute to microwave pyrolysis.

To fully understand the trends observed in the results, the effects of moisture and ash contents of the biomass were first assessed. Before pyrolysis, the treated biomass was dried only at its equilibrium moisture content. This eases the production of biochar as its own moisture could serve as an effective microwave absorber. Hence, as the moisture absorbs microwave radiation, it increases the amount of heat generated by the system, increasing or decreasing the biochar yield depending on the initial temperature/microwave power employed (Adam, 2017; Shrestha et al., 2011). However, this effect is only temporary since moisture was assumed to be easily removed within the time and power range employed in this study. On the other hand, ash formation in pyrolysis processes may slow down the gasification of biochar, which increases the char content since it also prevents the solids from reacting with the gases by creating a protective barrier between the solids and the atmosphere (Strandberg et al., 2017).

The drastic decrease in biochar yield within Region 1 could be attributed to the high amounts of moisture and low ash formation within the system. The treated (prepared) biomass has an average moisture content of 4.92% (see Table 1). Upon pyrolysis, the biochar products were found to contain moisture ranging from 0.03% to 4.44%. Even though the moisture content could be removed fairly easily, the sample could still take more time to dry. The remaining moisture in the sample acts as a microwave absorber, which further assists biomass conversion to both char and ash, and char to gases (Menendez et al., 2007; Shrestha et al., 2011). Another important point to focus on in this region is the conversion of the volatile matter into condensable and non-condensable gases. Following the mechanism proposed by Huang et al. (2013), the microwave pyrolysis process is at its first stage at Region 1, where a system consisting of intermediate solids surrounded with condensable and incondensable gases can be observed. The incondensable gases could easily escape from the system while the condensable gases could not condense back to the system and proceed to repolymerization reaction due to the short exposure time and relatively low microwave power in this region. Additionally, it is also possible that the ash formation in this region is still low enough to form a barrier that prevents the gasification of the biochar product. Region 2, on the other hand, represents the same system, but at a longer exposure time, this starts at the minimum yield obtained, where the moisture of the system is assumed to have been

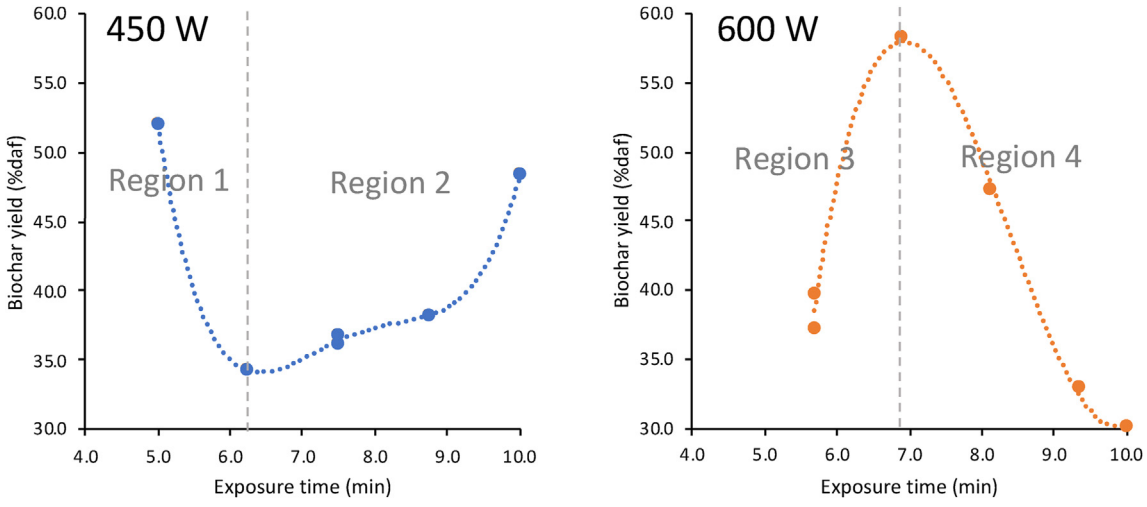


Figure 2. Effect of increasing exposure time on the biochar yield at 450 W and 600 W output power.

Table 3. Fit analysis for the optimization of biochar yield.

Source	Value	Source	Value
Standard Deviation	1.486×10^{-6}	R^2	0.9930
Mean	40.9347	Adjusted R^2	0.9742
Coefficient of variance	8.32	Predicted R^2	0.9286
		Adequate precision	24.070

Source: Design Expert Version 11.

Table 4. Summary of the results of the verification runs conducted for the optimization of biochar yield.

Run	Biochar yield (%)	Average yield (%)	Upper limit at 95% CI (%)	Lower limit at 95% CI (%)	Standard deviation (%)
1	64.41	56.98	61.88	55.99	4.47
2	51.27				
3	55.15				
4	57.19				
5	56.85				

depleted. This region also represents the continuation of the reaction model proposed by Huang et al. (2013), wherein intermediate solids are further broken down into solid residues and incondensable gases. The relatively low reaction temperature caused by the low microwave power (450 W) builds up a relatively lower pressure within the system. The low pressure exerted by the gases produced, combined with the prolonged exposure of the gases to the condenser tube and large temperature difference between the top and bottom of the condenser tube, induce reflux that forms bio-oil within the condenser, which was observed to drop back to the solids. As the reaction progresses, the bio-oil and biochar may undergo secondary reactions that cause the polymerization of molecules (Miura et al., 2004). These may explain the gradual increase in the biochar yield in Region 2. The lowest biochar yield obtained in this region (34.24% daf) compared to the typical fixed carbon content of corn cob of 11.31–24.6% daf (Anukam et al., 2017; Demiral et al., 2012; Demirbas, 2004; Shariff et al., 2016) supports this idea.

Region 3 represents the initial phase of the experimental runs conducted at a microwave power of 600 W. In this region, a steadily increasing trend was observed; the higher heating rate caused by a higher output power probably removed the moisture from the system, and the subsequent formation and melting of ash also occurred. Even with a higher heating rate, the tendency of the converted biochar to undergo gasification is lowered by the efficient formation and possible melting of ash (Strandberg et al., 2017). Thus, the conversion of the biomass to biochar becomes more efficient until the ash formation reaches a certain point where the depletion of the fixed carbon decreases the biochar yield.

Lastly, Region 4 represents the subsequent decrease in biochar yield at 600 W. At this phase, the higher heating rate caused by the high output power and longer exposure time could induce self-gasification in the presence of a particular inorganic element, such as potassium, which acts as a catalyst (Menendez et al., 2007). During microwave pyrolysis, the char is at a much higher temperature than the surrounding atmosphere. Therefore, relatively higher microwave power and long exposure time could produce numerous tiny sparks or "microplasma". In this situation, a heterogeneous reaction between the solid and gases produced may be expected where gasification reaction (e.g., reaction of CO_2 and C) may occur even at relatively low temperatures during pyrolysis (Menendez et al., 2007).

The ANOVA result revealed that only the microwave power output and its interaction with exposure time have significant effects ($p < 0.05$) on the biochar yield. This is in contrast to the study by Lawas et al. (2019), which reported that both factors and their interaction to be significant. The model generated is presented by the following equation:

$$(Biochar\ yield)^{-3}(\%\ daf) = -7.55\ x\ 10^{-7}(A) - 8.107\ x\ 10^{-6}(B) + 8.939\ x\ 10^{-6}(AB) + 4.395\ x\ 10^{-6}(A^3) - 6.164\ x\ 10^{-6}(A^3B) \quad (2)$$

where A and B represent the coded values of exposure time (min) and microwave power output (W), respectively. The positive and negative sign in the model equation indicates the synergic and antagonistic effects,

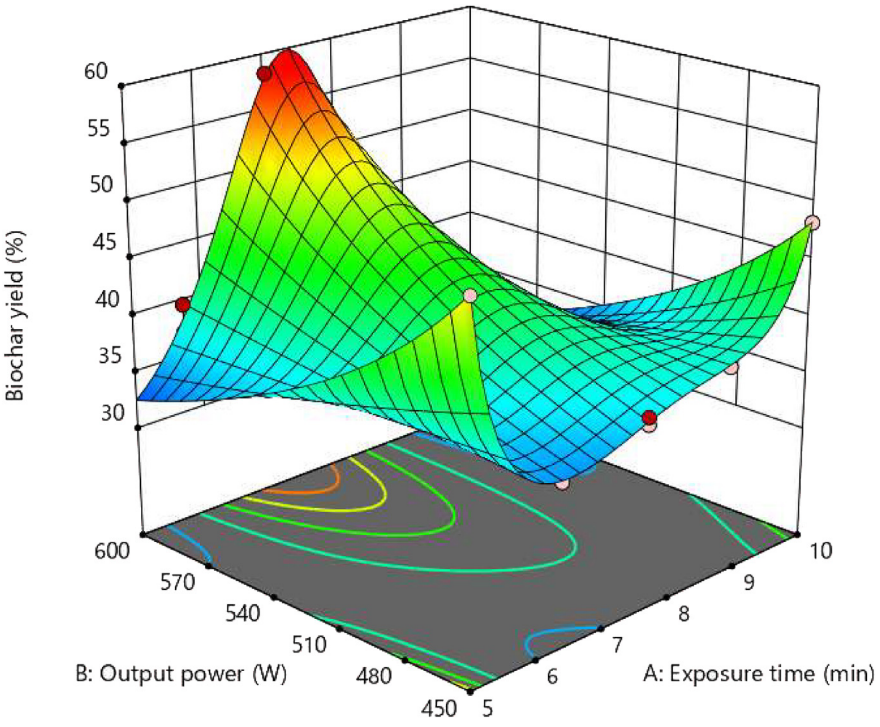
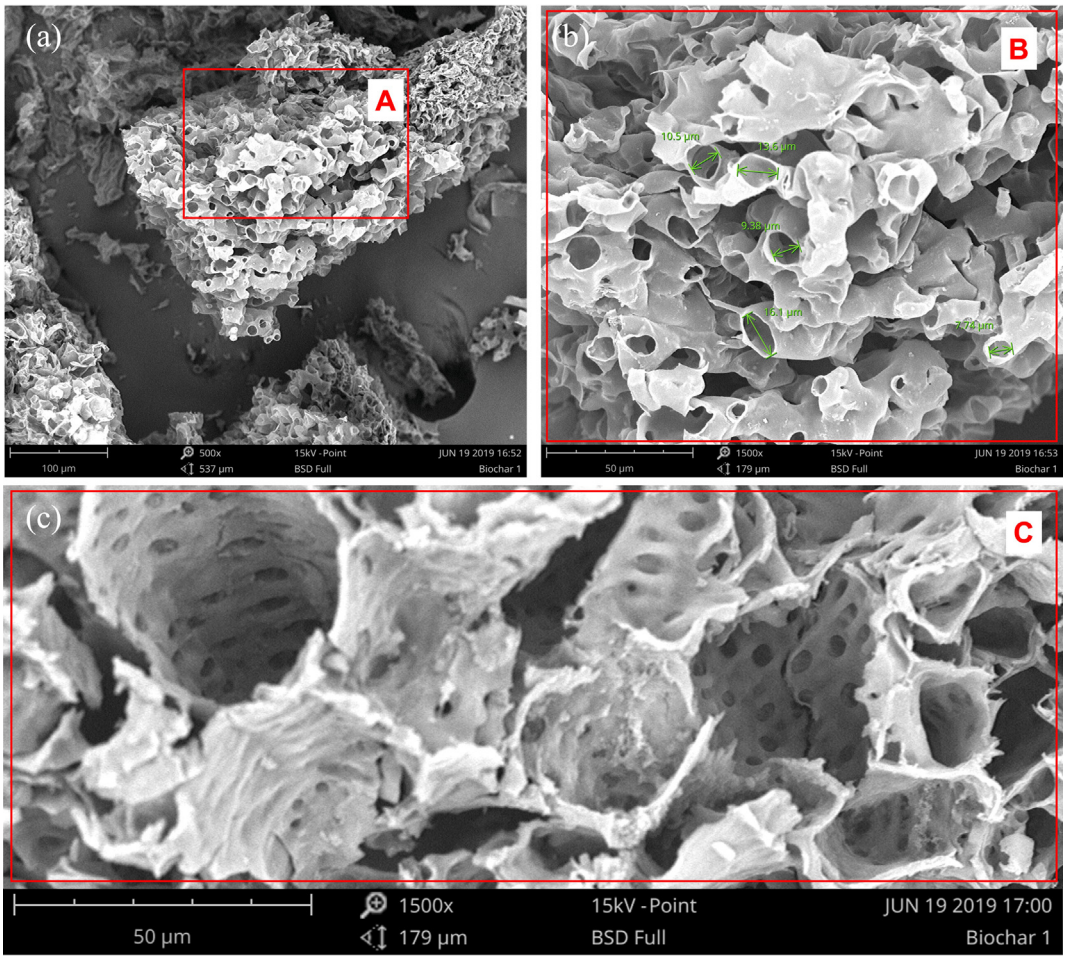


Figure 3. 3D-Surface plots of biochar yield as a function of microwave output power and exposure time.



Region	EDX Analysis			Average % C
	% C	% O	% Cl	
A	61.85	38.15	0	
B	61.96	38.04	0	62.68
C	64.22	33.29	2.49	

Figure 4. SEM images with EDX analysis of the optimized biochar product at different magnifications: 500x (a), 1500x (b and c). The red box enclosures (A, B, C) are the regions selected for EDX analysis.

respectively. The fit analysis of the model is summarized in Table 3. The model has an R^2 and adjusted R^2 value of 0.9930 and 0.9742, respectively, indicating a good fit for prediction as it indicates both acceptability and precision. Furthermore, the difference between the adjusted and predicted R^2 is within the maximum allowable value of 0.2; thus, no model reduction is required. Lastly, the model's adequate precision of 24.070 indicates that interpolation is possible within the range of the exposure time and microwave power used in the study.

3.2. Numerical optimization and validation of results

The numerical optimization of biochar yield using microwave output and exposure time by I-optimal design generated 68 solutions (see **Supplementary data**). Due to the limitation imposed by the controller for the microwave output power at discrete values, only the first solution with desirability = 1.000 was considered to be realistic in practice. The result suggests that a microwave power output of 600 W and an exposure time of 6.9 min be sufficient to produce an optimum biochar yield of 58.94% daf. After performing five (5) validation experiments of the optimized process conditions, the results are shown in Table 4. The standard deviation of less than 5% indicates a replicable method. The average value on biochar yield recorded (56.98%) sufficiently agrees with the predicted value (3.43% error). This validation confirms the adequacy of the model equation developed for biochar yield.

Figure 3 shows the 3-D surface model of biochar yield with respect to microwave power output and exposure time. The presence of the red portion of the curve indicates that the optimal condition is contained within the range of values in the surface model. A favorable response can be observed at higher output power and intermediate exposure time. However, the biochar yield tends to decline at both upper and lower limits of exposure time, mainly due to the varying contact time between the converted char and the by-products of the process. The presence of potentially rising biochar yields at regions where the output power is less than 450 W could be further explored; however, the resulting heating rate may be too low to convert the sample into biochar efficiently. The response behavior can still be studied for future research since the lower

Table 5. Inorganic composition, surface and electrochemical analysis of optimized biochar.

Property	Value
Ash (% w/w)	1.16
Ash composition (% w/w)	
Na_2O	2.795
SiO_2	2.525
Cl	2.388
Fe_2O_3	0.791
P_2O_5	0.588
SO_3	0.566
TiO_2	0.205
K_2O	0.097
CaO	0.039
Cr_2O_3	0.016
CuO	0.012
MnO	0.004
ZnO	0.002
BET surface area (m^2/g)	3.05
Pore volume (cm^3/g)	0.003
Specific capacitance (μF/g)	27.14 – 53.99
Energy density (Wh/kg)	$6.0 \times 10^{-7} - 1.2 \times 10^{-6}$
Power density (W/kg)	$9.4 \times 10^{-4} - 2.49 \times 10^{-3}$

heating rate offered by the 450-W power can be compensated by a longer exposure time. Furthermore, the rising behavior of the yield may imply that an optimal point may also be found beyond the range used in this study.

In general, the behavior of the biochar yield based on the surface model reflects the behavior of the biochar yield in the parametric study of Lawas et al. (2019). A lower heating rate caused by the low output power gives the biochar yield a dynamic behavior and this behavior largely depends on the extent of carbonization that can be manipulated by adjusting the exposure time. Thus, this coherence between the parametric study and the optimization study can be considered as a manifestation of the method's replicability to optimally produce biochar through microwave pyrolysis.

3.3. Characteristics of optimized biochar

The SEM images and EDX analysis of the biochar sample from the optimized condition are shown in Figure 4. The images show pores ranging from 1.83 to 43.4 μm. Macropores were easily identified within the biochar sample, whereas micropores were not easily spotted. The formation of pores is due to the release of volatile gases within the biomass by the effect of microwave heating. Due to the outward heat flow within the material, larger pores are more developed in biochar products from microwave pyrolysis (Adam, 2017). The defined structures at the inner part of the structure can be attributed to the radial flow of heat due to microwave pyrolysis. The EDX results reported in Figure 4 show a similar carbon content value, with an average of 62.68%, from three different regions selected. It means that the conversion of carbon within the material is uniform. However, EDX only provides and approximate the surface carbon content; it is suggested to determine the actual carbon content using elemental analysis. The estimated carbon content of the biochar produced is comparable to lignite (60%–70% carbon), a low-rank type of coal (King, n.d.)' and relatively lower compared to the 65%–93% carbon reported by Qu et al. (2015) for the corn cob biochar produced via conventional pyrolysis. It is also lower than the carbon materials used for energy storage devices, such as commercially available activated carbon, graphene, graphene oxide and carbon nanotubes (Mensah-Darkwa et al., 2019; Yang et al., 2019).

Table 5 shows the inorganic composition, surface and electrochemical analysis of optimized biochar. The inorganic composition of the biochar product based on the XRF analysis revealed the main inorganic (ash-forming) elements are Na, Si, and Cl (concentration >2.3%). Other species such as Fe, P, S, Ti, K, Ca, Cr, Cu, Mn, and Zn were also detected at concentration <1%. The presence of Cl in the biochar produced may also account for any residual Cl from the pretreatment of the corn cob. The presence of certain elements such as Si, P, K, and Ca affects the formation of the pyrolysis products (Strandberg et al., 2017). Moreover, some metals can cause biomass to self-activate (Herou et al., 2018). It is reported that the formation of K and SiO_2-rich ash can encapsulate the converted solids through ash formation at high temperatures (Strandberg et al., 2017). The relatively high amounts of these elements in the biochar support the assumption that ash melting could be the possible explanation behind the immediate increase in the biochar yield observed at 600 W in Region 3 (see Figure 2). On the other hand, the significantly lower amount of Ca present in the sample may explain the gradual increase in the biochar yield at the 450 W curve in Region 2 (see Figure 2). In general, Ca tends to increase the melting temperature of potassium and silica-rich ash (Strandberg et al., 2017). However, since Ca is relatively lower than the other metals present in the sample, the melting temperature of the ash likely remained relatively stable. When the ash melt, it could encapsulate the converted solids and prevent further gasification; this could explain the increasing biochar yield at the latter part of the 450 W runs.

The BET surface area and pore volume of the optimized biochar product are 3.05 m^2/g and 0.003 cm^3/g, respectively. The low surface area and pore volume may be due to some formed pores being closed off due to ash melting (Yu et al., 2010). The surface area obtained is much lower than a typical activated carbon but is within the range (0.71–27 m^2/g) reported for some microwave pyrolysis-derived biochar (Nzediegwu et al., 2021; Yu et al., 2010).

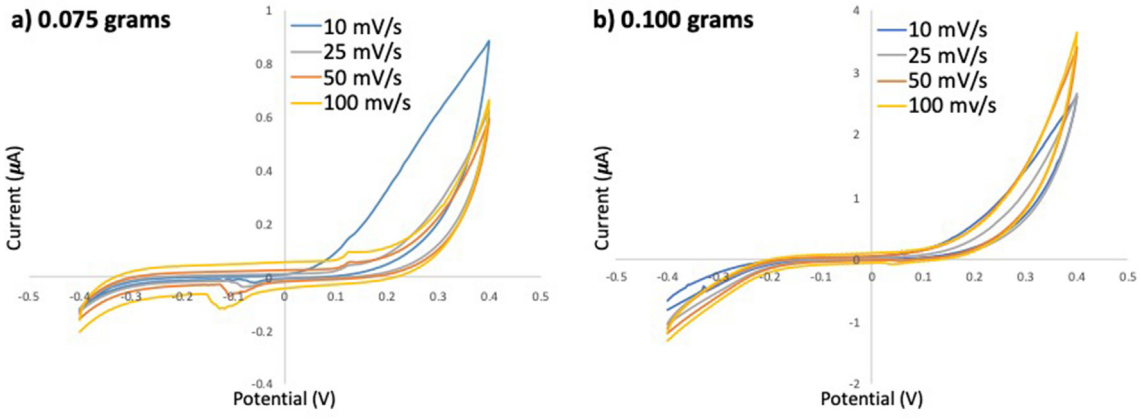


Figure 5. Cyclic voltammograms of the a) 0.075 g and b) 0.100 g biochar-electrolyte dispersion at scanning rates of 10, 25, 50, and 100 mV/s.

The average specific capacitance, specific energy density, and power density of the biochar sample calculated from cyclic voltammograms (see Figure 5) are in the range of 27.14–53.99 μF/g, $6.0 \times 10^{-7} - 1.2 \times 10^{-6}$ Wh/kg, and $9.4 \times 10^{-4} - 2.49 \times 10^{-3}$ W/kg, respectively. These results revealed a poor electrochemical property of the optimized biochar compared to carbon-based material used for energy storage systems. For example, conventional capacitors supercapacitor and batteries which have values of capacitance in the range of 3.4–763 F/g (Herou et al., 2018), energy density of 3–275 Wh/kg (Jian et al., 2016; Thomas et al., 2019), and power density of 1–15 kW/kg (Jian et al., 2016).

The surface and electrochemical properties of the optimized biochar product can be improved by activation pretreatment of corn cob and post-treatment of the biochar product. Elgrishi et al. (2018) reported that chemical activation through the addition of KOH can significantly improve the surface area of the biochar product that can reach values as high as 2720 m^2/g.

4. Conclusion

Optimization of the microwave pyrolysis parameters (microwave exposure time and power) determined a maximum yield at an exposure time of 6.9 min under 600 W microwave power. The model-predicted value of maximum yield (58.94%) agrees well with the experimental values, with an average yield of 56.98% daf. Successful carbonization of the corn cob chips was observed from the EDX analysis of the optimized biochar product. The biochar produced is 62.68% carbon, comparable to lignite. SEM micrographs of the biochar sample showed an interesting result. Mesopores systematically arranged at the inner surface of the biochar product could aid in the efficient transfer of ions and charges for energy storage applications. Futher studies on various activation methods are highly recommended to improve the product's surface and electrochemical properties.

Declarations

Author contribution statement

John Christian C. Quillope: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Rowena B. Carpio & Stephen S. Doliente: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Kristel M. Gatdula & Monet Concepcion M. Detras: Conceived and designed the experiments; Analyzed and interpreted the data.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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