Program Digest, 2019 IEEE International Ultrasonics Symposium (IUS)
Glasgow, Scotland, October 6-9, 2019

Enhancing Surface Properties of Softwood Biochar by Ultrasound Assisted Slow Pyrolysis

Aneeshma Peter, Bruno Chabot, Eric Loranger*
I2E3 – Institut d'Innovations en Écomatériaux, Écoproduits et Écoénergies à base de biomasse
Université du Québec à Trois-Rivières (UQTR)
Trois-Rivieres, Québec, Canada
*Eric.loranger1@uqtr.ca

Abstract— **In recent decades, biochar, by virtue of its exceptional properties of surface functionalisation, easy availability and low-cost processability, has been extensively applied in adsorption chemistry and major industrial sectors such as biofuels, pulp and paper, biorefineries, etc. Studies on biochar derived from softwood have revealed its efficient physicochemical properties. These properties depend on different parameters such as biomass feedstock, different processing methods and pyrolysis conditions. Application of ultrasound in lignocellulosic materials is a developing area of research, which implement the effect of cavitation bubbles. Herein, we introduce ultrasonication as a tool to enhance the physical properties of the softwood-derived biochar and a feasible processing technique for potential application of biomass feedstock, thus expanding its application in industrial level. Biochar used in this work was synthesized using a laboratory scale slow pyrolysis. A detailed investigation on the ultrasonic pre-treatment effects on the overall structure of biochar has been done. The mechanical and sono-chemical effects were studied with different combination of frequency and power at bath temperature of 80 ºC for 2-hours exposure time.**

Keywords— Softwood chips, Biochar, Ultrasound pre-treatments, Pyrolysis, Physio-chemical properties

I. Introduction

The history of carbon materials began at *terra preta* times, from which evolved diverse forms of charcoal. The potential application of these eco-friendly materials in different sectors of day-to-day life increased rapidly because of the environmental issues arose especially after the green revolution. The physicochemical properties of carbon-based materials like biochar has motivated many researchers to investigate the benefit in terms of mitigating global warming, soil amendment, enhancing crop yield, adsorption of contaminants and carbon capture. The unique properties of biochar, such as large specific surface area, porosity, mineral components along with enriched surface functional groups and ion exchange capacity makes it interesting over activated carbon [1]. There are studies to prove that these properties can be facilitated by controlling the choice of biomass feedstock, pyrolysis conditions and different processing techniques [2-3]. Studies with wood biochar is getting considerable attention in Canada, especially in Quebec where most of the forest trees are softwood. They are mostly processed into lumbers for the construction industry, leaving large volumes of biomass in the form of wooden chips. These wood chips come under the tertiary level of biomass processing which is post-consumer residues of feedstock. These biomass residues are challenging to handle because of the hygroscopic nature and heterogeneity in physical and chemical properties that arises from cellulose, hemicellulose and lignin components. An efficient method of processing techniques is required in order to overcome the challenges related to material quality and convert them into a usable form of energy. Various pre-treatment methods can be adopted and employed at the level of moisture management, density management and physical property management.

Application of power ultrasound in biomass is a recently developed area of research. It has been shown that ultrasound pre-treatment is an effective technique to modify the physicochemical structure of the biomass [4], increasing the stability [5] and mostly, contributing to the pyrolysis product yields [6]. Ultrasonication makes use of the effect of cavitation and the bubbles collapsing near the solid surfaces disrupts the spherical shape and induces the formation of microjets, which can impact the surfaces. For this reason, ultrasound has been used to explore hard-to-reach surfaces [7]. In the same perspective, cavitation effects can be utilized to modify the surface morphology of biochar to have improved physicochemical properties. Ultrasound enhanced activation and organic functionalisation are one of the very recent developments in biochar research [8-9].

Understanding the ability of ultrasound to promote chemical and thermal decomposition reactions during pyrolysis with better efficiency in terms of product yield and physicochemical properties will be a key step to introduce ultrasound in industrial level of feedstock processing. Introducing ultrasound transducers into a pyrolysis reactor is not a feasible idea in this scenario. However, it is possible to incorporate ultrasound prior to the use of the pyrolysis reactor, as a pre-treatment. The balance between the mechanical and sono-chemical effect in different combinations of frequencies, power, exposure time and bath temperature may have a different attack mechanism on biomass, hence could lead to different biochar properties. The current study is economic

and practically feasible since the biochar being a byproduct during bio-oil production by lab-scale slow pyrolysis in a temperature range of 500-550 ºC. To the best of our knowledge, this work is unique in terms of ultrasound pre-treatment effect on biochar surface morphology.

TABLE I
LIST OF PRE-TREATMENTS PERFORMED ON WOOD CHIPS

Sample	Frequency (kHz)	Power (W)	Temp (º C)	Time (Hour)
UST-1	40	1000	80	2
UST-2	40	250	80	2
UST-3	170	1000	80	2
UST-4	170	250	80	2

II. Experimental Section

A. Biomass Feedstock

The biochar used in this project were obtained from softwood chips (mix of spruce, fir, pine and larch) provided by an eastern Canadian pulp and paper mill. Wood chips were washed to remove impurities, dried in air and then grinded to 5 mm by 5 mm sized needles prior to the experiments. The wood chips were then dried in an oven at 105 °C for at least 24 hours before being used in the pyrolysis reactor (48 hours for ultrasound treated samples).

B. Ultrasonic pre-treatments

Ultrasonic treatments were performed in a 34 L ultrasonic bath, model BT90 from Ultrasonic Power Corporation (USA), made of 316 L stainless steel, equipped with 12 transducers located below the bottom plate of the bath. Commercially available frequency generators of 40 and 170 kHz were used to produce between 250 and 1000 W of nominal ultrasonic energy to study the mechanical and sono-chemical effects, respectively. The exposure time was fixed for 2 hours at a bath temperature of 80 ºC (Table I). For each treatment, 200 g of wood chips were dipped into 4 L of deionized water in a weighed mesh bag, to ensure that the wood chips are completely submerged in water and homogenously treated by ultrasound.

C. Lab-scale Pyrolysis

The pyrolysis was performed using method previously reported by Loranger *et al*. [10] and as explained in Cherpozat *et al*. [6] At least three trails were performed to confirm the average yield of biochar and other pyrolysis products. The biochar was cleaned from tar and was stored in plastic bags. Prior to each analysis, prepared biochar was dried at 105 °C for at least 12 hours and stored in desiccator.

D. Chemical and Physical Characterisations

The elemental composition of C, H and N were analyzed using elemental analyzer, EA 1108 Fisons, CHNS instrument. The oxygen content was determined by mass difference. Proximate analysis (Ash, moisture and volatile content) were performed using the method described by American Society for Testing and Materials D1752-84, which is recommended by the International Biochar Initiative. pH of the material was measured using Accumet XL20, Thermo Fisher Scientific pH-meter in deionized water at 1:2 weight by volume ratio after stirred at room temperature for two hours. Conventional back titrations were performed using 0.05M NaOH and 0.05M HCl to understand the nature of functional groups, keeping the Boehm assumption in mind, which proves that the NaOH will neutralize the acidic carboxylic, lactonic and phenolic functional groups present on the biochar surface [11]. Zeta Potential of untreated and ultrasound pre-treated wood biochar was measured for a suspension of biochar powder in deionized water with pH 6.14 using Zetasizer-nano series from Malvern Instruments. Infrared spectra of each prepared biochar and untreated wood were obtained in Nicolet iS10 Smart iTR Infrared Spectroscopy instrument at room temperature using biochar mixed with spectroscopic grade pre-dried KBr pellet. The spectra were obtained in reflection mode in the range of 400-4000 cm^{-1} for a minimum of 16 scans with 1 cm^{-1} resolution. To understand the thermal stability of the material, Thermogravimetric Analysis (TGA) was performed on Mettler Toledo TGA 2. Samples were heated under nitrogen to provide inert atmosphere and prevent combustion of the samples. The sample was heated from room temperature to 100 ºC by ramping at 20 ºC/min, and then heated to 700 ºC. Scanning Electron Microscopy (SEM) images were captured using Hitachi SU1510 instrument to understand the changes in biochar surface. Energy Dispersive X-ray Spectroscopy (EDX) was obtained with X-Max, Oxford instrument to verify the surface carbon and oxygen content. Surface area was measured via the Brunauer, Emmett and Teller (BET) method that measures N_2 gas sorption (0.162 nm^2) at 77 K. Approximately 100 mg of biochar was outgassed at 200 °C (16 hours) and then analyzed on an Autosorb-1 Surface Area Analyzer (Quantachrome Instruments).

E. Adsorption of Cu using biochar

Adsorption of metal is an efficient method to understand the surface property of the material. Cu (II) has been selected for the batch adsorption tests, as it is easily available and less toxic heavy metal. 100 ppm solution of Cu (II) was prepared from stock $CuSO_4$ solution. 5 g/L adsorbent was added to metal solution and then the mixture was agitated on a reciprocating shaker at room temperature. The kinetics of the material were studied from 0.5 hours to 24 hours. Samples were taken at desired intervals and subsequently filtered with Whatman No. 1 filter paper. The filtrates were analyzed for residual heavy metal concentration in the solution [12]. Pseudo first order and Pseudo second order kinetic models were examined by linearizing the experimental data.

III. Results & Discussion

The pyrolysis product yield exhibited the common trend, which is dependent on pyrolysis temperature and reaction time. However, a small decrease in yield was observed for ultrasound pre-treated samples which could be happened to adjust with the mass balance between bio-oil and

syngas. Chemical and physical characterisations are performed to understand the pre-treatment effect of ultrasound on material properties.

A. Chemical Characterisation of biochar

Proximate and ultimate analysis of biochar were performed and summarized in Table II. Proximate analysis results indicated the stability of biochar produced during pyrolysis at a given temperature range. Dry biomass feedstock contains around 46 percent of carbon. The pyrolysis temperature range for all the experiments performed is responsible for different dehydration and decarboxylation reactions and increases the degree of carbonization with a subsequent decrease in hydrogen and oxygen content. It is clear from the result that the biochar is rich in carbon which is an indication of increase in aromaticity hence the properties could be similar to activated carbon. The biomass contains rapidly reacting oxygen fractions which are lost after the initial heating and reluctant oxygen which will retain in the matrix of the final product. This can be responsible for the ten percent oxygen in the synthesized samples.

TABLE II
PROXIMATE AND ULTIMATE ANALYSIS OF BIOCHAR

Weight %	Biochar	Feedstock
Moisture	4	-
Volatile	23	-
Ash	< 1	-
C	86.5 ±1.09	46.7
H	2.7 ±0.1	6.4
N	0.05 ±0.02	0.04
O*	10.7	46.9

*Oxygen content was determined by mass balance

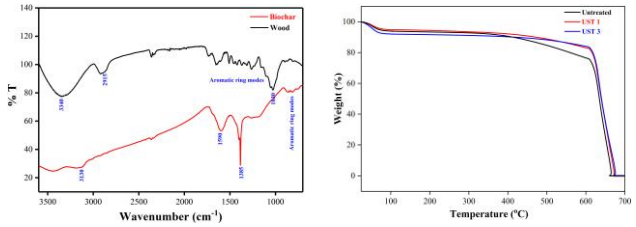
To confirm the presence of oxygen contained functional groups on the biochar surface, the acidic sites are determined by conventional back titration method. The back titration determines the total concentration of phenolic, lactonic and carboxylic functional groups on the surface. The results (Table III) indicated that the approximate ten percent oxygen content in the biochar is from the functional groups present on the carbon surface which are impervious to different reaction mechanisms during the pyrolysis. Zeta potential of biochar (Table III) in water also confirmed that the surface of biochar is negatively charged. The surface functionality makes biochar different and preferred over activated carbons since the oxygen sites could be utilized for different ionic interactions.

TABLE III
SURFACE CHARGE NATURE OF BIOCHAR

pH*	6.14
Zeta Potential (mV)	-2.63
Acidic sites (mmol/g)	1.27

* pH of deionized water: 5.92

The infrared spectra of the base wood and ultrasound pre-treated wood biochar samples were analysed and compared with base activated biochar to confirm the different functional groups present. The adsorption bands were less intense for the biochar samples (Figure 1.a). It was interesting to note that the spectral pattern for all ultrasound treated or untreated biochar were similar except slight intensity changes due to the pyrolysis temperature difference. O-H peak at 3340 cm^{-1} was almost disappeared which clearly represents the oxygen content loss during carbonization. Observed aromatic C-H stretching at 3130 cm^{-1}, aromatic C=C stretching and CH_2 bending vibrations at 1500-1300 cm^{-1}, and aromatic C-H out of plane vibrations at the range of 800 to 700 cm^{-1} are characteristic bands for conjugated aromatic rings. At the same time, carbonyl C-O band around 1600 cm^{-1} was very less intense which explains the low oxygen content in biochar samples.



a) b)

Fig. 1. a) Infrared spectra of feedstock and biochar derived. b) Thermogravimetric analysis of ultrasound untreated and pre-treated wood biochar

TGA analysis shown that the samples are thermally stable up to 600-650 °C (Figure 1.b). It was well observed that the ultrasound pre-treated samples are structurally more stable than the untreated.

Chemical characteristics of synthesized biochar verified the efficiency of laboratory scale pyrolysis to produce biochar with good material quality. The chemical characteristics remained consistent and identical for all ultrasound pre-treated wood biochar. Thus, the pre-treatment with ultrasonication is confirmed to be physical phenomenon which does not affect the chemical structure and composition of feedstock. Since pyrolysis does not affect the physiology of the wood, the effect of ultrasound pre-treatments is expected to be evident in physical characteristics and surface morphology.

B. Ultrasonic pre-treatment effects on surface morphology

To understand the physical effect of ultrasound pre-treatment, surface morphology studies has been performed using SEM images and metal adsorption studies. Figure 2 shows the comparison image for ultrasound pre-treated and untreated wood biochar. It was observed that unlike the untreated wood biochar, in all the ultrasonic conditions, the slit like channels on the wood surface were cleaned from different attachments. As expected, the mechanical effect on surface of biochar were more evident in 40 kHz samples. The surface ruptures were less apparent in 170 kHz treated samples though the channels were clean from the microfibers.

The specific surface area of UST-1 is slightly increased compared to the untreated one but there is a significant decrease in the case of UST-3 (Table IV).

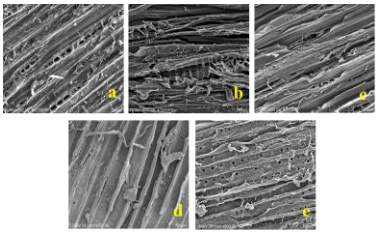


Fig. 2. SEM images of biochar derived from ultrasound pre-treated wood chips. a) Untreated b) UST 1 c) UST 2 d) UST 3 e) UST 4

In higher frequency ultrasound, even though the microchannels were smoothened, it could happen that the surface sites were blocked because of the breaking down of microparticles or structural rearrangement.

TABLE IV
ADSORPTION KINETICS OF BIOCHAR

Adsorbent	BET-N_2 Specific Surface Area (m^2/g)	Pseudo Second order		
		Q_e	k	R^2
Untreated	10.48	1.09	0.051	0.993
UST 1	12.40	1.542	0.022	0.987
UST 2	nd*	1.539	0.040	0.988
UST 3	3.31	0.739	0.042	0.911
UST 4	nd*	0.729	0.22	0.992

*nd: not determined

Adsorption experiments provided a better understanding about the surface change on biochar. Figure 3 is an example for the effect of contact time of Cu (II) on biochar. Almost 80 percent adsorption occurred in the first 4 hours and then a slow approach to the equilibrium over 24 hours. This trend was visible for ultrasound untreated and pre-treated samples. The adsorption kinetics was fitted to pseudo second order model only, indicating that the adsorbate-adsorbent interaction follows physisorption. The adsorption capacity at equilibrium and rate constant were calculated by linearizing the experimental data (Table IV). The regression coefficient R^2 indicates the fit of experimental points to the pseudo second order model.

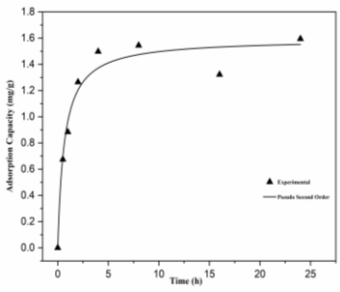


Fig 3. Pseudo second order kinetic model for ultrasound pre-treated wood biochar UST-1

The 40 kHz pre-treated samples showed better adsorption of Cu (II) on biochar surface. The 170 kHz samples were shown almost half less adsorption than 40 kHz samples. This was also evident in the BET surface area. The low frequency ultrasound alters the surface by exposure of the material to the treatment solution and enhances its accessibility by generating collapses. On the other hand, it could happen that the high frequency smoothened the microchannels but also decreased the accessibility of the pits which resulted in significant decrease of the adsorption capacity.

IV. Conclusion

Ultrasound pre-treatments affects the surface morphology of biochar without changing the chemical characteristics. Low frequency ultrasound generates collapses, break down the pits and open up the microchannels which positively affects the adsorption behaviour of the material. It can be an effective method to process biomass feedstock at the property management level, thus leads to potential application of derived products by tuning the physical morphology. However, detailed comparison studies must be done in order to explore the effect of each ultrasound pre-treatment conditions.

Acknowledgment

The authors gratefully acknowledge all the members of I2E3 for their great support and help during the period of this work. Financing was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) and by Queen Elizabeth *II* Diamond Jubilee Scholarship.

References

[1] F. R. Oliveira, A. K. Patel, D. P. Jaisi, S. Adhikari, H. Lu and S. K. Khanal, Environmental application of biochar: Current status and perspectives, *Bioresource Technol*., 2017

[2] Y. Sun, B. Gao, Y. Yao, J. Fang, M. Zhang, Y. Zhou, H. Chen and L. Yang, Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties, *Chem. Eng. J*., 2014, 240, 574-578

[3] S. Jiang, T. A. Nguyen, V. Rudolph, H. Yang, D. Zhang, Y. S. Ok and L. Huang, Characterization of hard-and softwood biochars pyrolyzed at high temperature, *Environ. Geochem. Health*, 2017, 39, 403-415

[4] Z. He, Z. Wang, Z. Zhao, S. Yi, J. Mu and X. Wang, Influence of ultrasound pretreatment on wood physiochemical structure, *Ultrason. Sonochem*., 2017, 34, 136-141

[5] S. Qiu, Z. Wang, Z. He and S. Yi, The Effect of Ultrasound Pretreatment on Poplar Wood Dimensional Stability, *BioResources*, 2016, 11, 7811-7821.

[6] L. Cherpozat, E. Loranger and C. Daneault, Ultrasonic pretreatment effects on the bio-oil yield of a laboratory-scale slow wood pyrolysis, *J. Anal. Appl. Pyrolysis*, 2017, 126, 31-38

[7] T. Leong, M. Ashokkumar and S. Kentish, The fundamentals of power ultrasound-A review, 2011

[8] R. Chatterjee, B. Sajjadi, D. L. Mattern, W.Y. Chen, T. Zubatiuk, D. Leszczynska, J. Leszczynski, N. O. Egiebor and N. Hammer, Ultrasound cavitation intensified amine functionalization: A feasible strategy for enhancing CO_2 capture capacity of biochar, *Fuel*, 2018, 225, 287-298

[9] B.Sajjadi, J. W. Broome, W. Y. Chen, D. L. Mattern, N. O. Egiebor, N. Hammer and C. L. Smith, Urea functionalization of ultrasound-treated biochar: A feasible strategy for enhancing heavy metal adsorption capacity, *Ultrason. Sonochem.*, 2019, 51, 20-30.

[10] É. Loranger, A.-O. Piché and C. Daneault, Ultrasonic pre-treatments of wood chips used in a conventional pyrolysis and their effect on bio-oil composition and calorimetry, *SAMPE Conference Proceedings*, 2016.

[11] H. P. Boehm, Chemical identification of surface groups: Advances in catalysis, Elsevier, 1966, 16, 179-274.

[12] X. Chen, G. Chen, L. Chen, Y. Chen, J. Lehmann, M. B. McBride and A. G. Hay, Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution, *Bioresource Technol.*, 2011, 102 ,8877–8884