Evaluation of the Biochar Particle Size Distribution along the Sugarcane Bagasse Pyrolysis Process and Potential Applications

Nahieh T. Miranda[a,*], Rubens Maciel Filho[b], Maria Regina W. Maciel[b]

[a]Federal University of Maranhão (UFMA), Exact Sciences and Technology Center (CCET), Department of Chemical Technology, Av. Dos Portugueses, 1966 – Vila Bacanga, São Luís/MA, 65080-805, Brazil.
[b]Laboratory of Optimization, Design, and Advanced Control (LOPCA)/Laboratory of Development of Separation Processes (LDPS), School of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, Campinas, 13083-852, Brazil.
nahieh.miranda@ufma.br

The whole world has been looking for alternatives to fossil fuels, and one of the processes that has already gained great prominence is the pyrolysis process, due to its flexibility and products diversity (liquid, solid, and gas fuels). In addition to the much-investigated potentials of liquids and gases fuels, solids also have their importance, and a major highlight has been given for biochar, a product of great value, produced with high yields, which can be used in several ways (specially soil conditioner). Its applications depend on particle sizes, shape, porosity, among others. Therefore, this paper investigates the characterization of a biochar produced along a sugarcane bagasse pyrolysis plant (reported in another work), related to particle size distribution and surface area, correlating it with the operating conditions. More than one solid separator was used along the pyrolysis process. Then, 03 samples from 03 different collectors along the pilot plant were subjected to size distribution analysis of particles using a laser diffraction particle size analyzer, and the average values were decreasing along the process (273; 170; and 39 μm, respectively). Also, physical adsorption analysis (BET method) was performed, being important for the quality control when a char is applied as a soil conditioner, for example. Finally, the biochar characterization could demonstrate how it changes along the pyrolysis process, and consequently, alternative applications are demonstrated (adsorption is the most chosen).

1. Introduction

The demand for fuels and energy grows as the world population grows, and with that, there is also a concomitant increase in the need to search for alternative sources to fossil fuels. Thus, several types of biofuels have already been studied for different applications and thermochemical processes stand out, such as pyrolysis, which has been highlighted for being an efficient process when the objective is to reuse urban or forest waste. The importance of focusing on these types of processes falls mainly on the best destination given to waste, reducing pollutant emissions, and even increasing the diversity of the global energy matrix, mainly due to the capacity to generate 03 types of products: bio-oil, biochar, and gases from different types of raw materials. Biochar (char or charcoal), one of the pyrolysis products of interest, mainly from biomass, is a renewable waste (Dhyani and Bhaskar, 2018) and sustainable, reducing competition with food (Rabelo et al., 2011). Slow pyrolysis is the type of pyrolysis chosen when the objective is to produce biochar, as it provides the highest yields, while fast pyrolysis provides lower yields (Kwapinski et al., 2010). Biochar contains high carbon content (65 – 90 %), and oxygenated and aromatic compounds (Ghani et al., 2013), which prevent biological degradation (McBeath et al., 2014). Due to these characteristics and low sulfur and phosphorus content (Xu et al., 2011), biochar has several applications: it can be used as a natural fertilizer (soil additive) (Carrier et al., 2012), as a low quality solid fuel (Angin, 2013), to generate heat for various processes (Mendes et al., 2016), as activated charcoal (Suroshe and Pramanik, 2015), as an adsorbent for gas phase and liquid phase applications (Gonçalves et al., 2016), and for applications in chemical, pharmaceutical, and food industries. With this great variability of applications, biochar derived from biomass pyrolysis has gained great prominence. During the pyrolysis

process, if it is a continuous process, the produced vapors carry biochar out of the reactor. After the reactor, cyclones are generally used to separate the biochar, storing it in reservoirs (Ringer et al., 2006). Thus, in addition to the process itself, the type of biomass chosen can also favor the production of biochar. Biomass sources with high contents of fixed carbon and ash are more likely to produce more biochar (Islam et al., 2010) and different physicochemical properties of biomass affect biochar characteristics. It is recommended that smaller particle sizes should be used in the pyrolysis processes. First, the biomass surface area can be increased by using smaller particle sizes, favoring heat and mass transfer rates (Asadullah et al., 2007). Thus, increasing these rates is advantageous since the biochar insulating properties make heat transfer difficult (Varma and Mondal, 2017), which can be offset by smaller particle sizes. In addition, small particle sizes also increase the calorific value of the biochar (Sohaib et al., 2017). However, Sohaib et al. (2017) detected that increasing bagasse size (0,1 to 0,5 mm) promoted greater biochar yield. Also, biomass particle size is influenced by moisture content. Then, high moisture contents reduce the heating rates of the process, which increases the size of the biomass particles and favors high yields of biochar (Demirbas, 2004). Thus, it is noted that the type of biomass, the way it is arranged (size, humidity, composition), and the process operating conditions interfere in important characteristics of biochar. Therefore, the objective of this work is mainly to evaluate how the granulometric distribution occurs along a pyrolysis process, and to evaluate how the physical adsorption of this material occurs. These characteristics impact how biochar can be used.

2. Methodology

The biochar used in this work was obtained in a fast pyrolysis pilot plant already reported in other works (Miranda et al., 2020); (Miranda et al., 2018). The pyrolysis process of this pilot plant was carried out in a fluidized bed reactor. Then, 03 samples of the produced biochar (section 2.1) were characterized by the following analytical techniques: particle size distribution and physical adsorption (ASAP/BET – Accelerated Surface Area and Porosity/Brunauer-Emmett-Teller).

2.1 Obtaining biochar

Coupled to the pyrolysis fluidized bed reactor (Miranda et al., 2020), there is a first storage reservoir (Figure 1a) for the produced biochar (Figure 1d). The vapors produced in the reactor are sent to two cyclones (Figures 1b and 1c), which perform all the separation of solids remaining in the vapor stream. The solids carried along with vapors are collected in the 2nd and 3rd reservoirs (Biochar 2 and Biochar 3 – Figure 1e), which are located below the cyclones.

Figure 1: (a) Biochar 1 reservoir coupled to the reactor; (b) Cyclone with the respective reservoir without coating; (c) Biochar 2 and Biochar 3 reservoirs (from right to left – Biochar 1 is right below in the left of the figure); d) First biochar reservoir (Biochar 1); e) Representation of 2nd and 3rd biochar reservoirs (they are similar)

2.2 Particle size distribution

The biochar particle size distribution analysis was carried out with a particle size analyzer by laser diffraction (MASTERSIZER-S), from the brand MALVERN INSTRUMENTS, model Long Bench-MAM 5005 (Worcestershire, U.K.). The analysis was carried out in the Wet Route mode – Sample Suspension Unit, using distilled water with 4 to 6 drops of Extran, as a dispersing medium, agitation of 50 % (2,000 rpm) and pumping of 50 % (2,000 rpm). Mie's mathematical model was used, which assumes that particles are spherical and that they are not opaque. In this way, it considers the light diffraction and diffusion in the particle and medium. Section 3.1 brings the particle size results for each biochar reservoir. Each biochar sample was analyzed in 02 replicates.

2.3 Physical Adsorption (ASAP/BET)

The biochar was also subjected to physical adsorption analysis, which makes use of the surface and metal area analyzer by gas adsorption (ASAP), by Micromeritics, ASAP model 2010 (Austin, USA) and analytical balance (Bell, Umark 210A). Nitrogen gas was used. This analysis determines the surface area of the biochar; in addition to providing distribution, size, and volume of pores; and adsorption isotherms. The samples were conditioned

in an oven at 105 ºC for at least 24 hours. After equilibration at room temperature, they were weighed (0.2–0.6 g) and taken to the equipment for treatment at 300 ºC until reaching constant pressure (0.02 µmHg, lasting around 8 h). After sample treatment, the samples were analyzed with the standard method for complete analysis, obtaining partial pressures at 65 points. The results obtained are described in Table 2.

3. Results and Discussion

3.1 Particle size distribution

Over 98 % of the ground and sieved bagasse used for the pyrolysis process had particle sizes less than 1.18 mm (1,180 µm) (Miranda et al., 2020). Despite this, the sizes range was from 30 to 5,600 µm, with greater concentration in the range of 130 to 430 µm. Knowing the size of the raw material used in the process is very important, since some authors have already reported how it impacts the distribution of products and their characteristics (Sohaib et al., 2017). The produced biochar had a mean particle size between 38.82 to 272.98 µm. Table 1 brings the result-under plot (cumulative undersize), the mean particle size (volume weighted mean), and the surface weighted mean of each biochar reservoir.

Table 1: Data of particle size distribution of the 03 samples of biochar

Material	Under 10 % (µm)	Under 50 % (µm)	Under 90 % (µm)	Span	Volume Weighted Mean (µm)	Surface Weighted Mean (µm)
Biochar 1	84.39 ± 6.36	242.50 ± 13.18	510.61 ± 22.28	1.76 ± 0.03	272.98 ± 13.77	130.12 ± 6.34
Biochar 2	37.43 ± 0.33	139.86 ± 1.26	347.98 ± 4.93	2.22 ± 0.01	169.98 ± 2.42	75.43 ± 0.97
Biochar 3	6.33 ± 0.01	22.82 ± 0.05	93.29 ± 5.94	3.81 ± 0.25	38.82 ± 1.32	11.91 ± 0.01

Biochar 1 showed greater variability in the analysis, precisely because it is the first reservoir to receive the biochar that is being produced, as it is coupled to the reactor. Then, it is natural the largest particles of biochar to be held back in this reservoir. While 10 % of the Biochar 1 sample is below 84 µm, 90 % of the Biochar 3 sample is below a similar value (93 µm). The smaller biochar particles that are produced are entrained with the vapors generated in the pyrolysis process, and they are collected later after passing through two cyclones. Generally, the authors find biochar sizes in the range less than 150 to 2,000 µm (Liu et al., 2017); (Duarte et al., 2019). Figure 2 represents an average result-under plot (cumulative undersize) of the 03 biochar samples, to better exemplify Table 1.
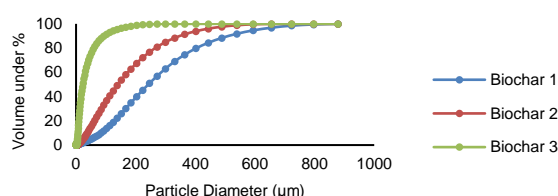

Figure 2: Average result-under plot (cumulative undersize) of the 03 biochar samples

Each biochar reservoir presents a different cumulative particle size. Biochar 1 presents 90 % of the particles under around 510 µm, Biochar 2 presents 90 % of sizes under around 350 µm, and in the third reservoir (Biochar 3), 90 % of the sample has sizes under around 90 µm. It is notorious that the variability of particle sizes is greater in Biochar 1 and 2. The curve of Biochar 3 presents a much smaller variation of size ranges, as it is the place where the last part was collected, with very small particles (roughly 38 µm). After the second cyclone, to keep acceptable levels in the atmosphere, a bag filter was used in the end of this process. Biochar 1 had the largest size in comparison to the two following reservoirs, indicating that lighter biochar is dragged through the process, being subsequently separated by cyclones in series, as already mentioned. This also indicated that the use of smaller particles really tends to be transformed into biochar, due to the ease of thermal exchange with the surface area being greater (Asadullah et al., 2007). The particle sizes of Biochar 2 and 3 decreased in size because they are the lighter solids particles, which are dragged and passed through cyclones 1 and 2, respectively. To complement the evaluation, Figure 3, in addition to presenting the accumulated volume, also shows the frequency distribution (vertical axis on the left) of the analysis.
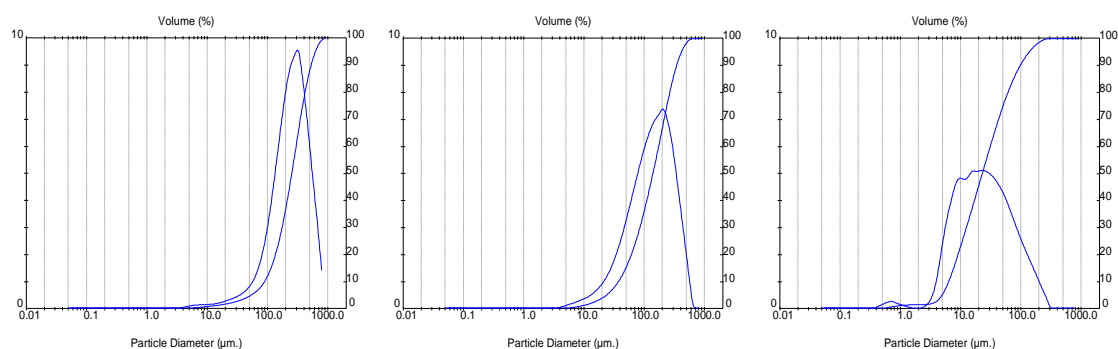
Figure 3: Particle size distribution of the 03 biochar samples (from the left to the right: Biochar 1, 2, and 3)

It is possible to verify that the sample from Biochar 1 represents the most commonly occurring particle diameter in the region from 200 to 400 μm (with a frequency of 9 %). Biochar 2, on the other hand, presents most of the particles in the region from 100 to 300 μm (with a frequency of 7 %). Finally, Biochar 3 presented a much smaller size range (10 to 50 μm – with a frequency of 5 %), but the most fluctuated size distribution curve, probably due to its fine and irregular particle shapes. Biochar 3 appeared to be the one that would have the widest range, but in fact, the other first two reservoirs have the widest range. It is also possible to verify that only the Biochar 1 sample presents particles up to 900 μm, despite being at a much lower frequency (around 1.5 %). Biochar 2 features particles up to 700 μm, and Biochar 3 has particles up to 300 μm, but all of them with a low frequency with these maximum values. If biochar is used on soils, the particles size can have a great influence either on plant or soil nutrients availability (Prasad et al., 2019). This variability in particle size facilitates the biochar application, especially for soil conditioner since it can even impact the soil physical properties (e.g., texture, pore size), affecting the capacity to hold water and the soil aeration (Kocsis et al., 2022). Smaller particles favor mixing with the soil (Blanco-Canqui, 2017). Several other applications are demonstrated: agriculture applications (like those mentioned in this article), greenhouse gas emissions control and wastewater treatment mainly through adsorption, and emerging applications (composites, construction materials) (Garcia et al., 2022).

3.2 Physical Adsorption (ASAP/BET)

Table 2 brings the results of ASAP/BET analyses of the 03 biochar samples.

Table 2: Results of ASAP/BET analyses for biochar

Material	BET Surface area (m²/g)	Langmuir Surface area (m²/g)	Pore volume (cm³/g)	Pore size (Å)
Biochar 1	17.2407 ± 0.1926	23.3956 ± 0.2151	0.027790	64.4751
Biochar 2	79.9687 ± 0.9102	108.1399 ± 1.0696	0.085610	42.8220
Biochar 3	34.9827 ± 0.1831	48.7958 ± 0.8295	0.093259	106.6346

From Table 2, Biochar 2 had the highest BET and Langmuir surface area (maximum adsorption capacity). The largest pore volume was obtained in Biochar 3, with a larger pore size as well, which is very positive for soil aeration (Kocsis et al., 2022). The surface area of the 03 biochar samples obtained was around 34 to 79 m^2/g. These differences demonstrate how the course of the process impacts on the homogeneous separation of the biochar. Pore volume ranged from 0.03 to 0.09 cm^3/g and pore size from 4.28 to 10.6 nm, characterizing them as mesopores. The last two characteristics agree to those found by Varma and Mondal (2017), who also performed pyrolysis of sugarcane bagasse. The surface area was larger than those found by these authors, and this is probably attributed to the sand content found in the used bagasse (Miranda, 2018). It can be observed that there is no growing trend in these analyses, mainly for BET, Langmuir, and pore size, since Biochar 1 showed a large variability in particle size (Table 1, Figure 2, and Figure 3), not having a certain homogeneity, meaning that there is no tendency from sample 1 to 2, but only from 2 to 3. Thus, the surface area increased from sample 2 to 3, due to the smaller particle sizes, confirming what some authors have already concluded about bagasse, mainly when using smaller bagasse sizes. Furthermore, the pore size increases with smaller particle sizes, facilitating its use in some applications, especially in adsorption. Figure 4 can demonstrate the volume adsorbed in each sample.

Biochar 1 only starts to have a better adsorption after a relative pressure of 0.8 (Figure 4), while for the other two biochar reservoirs, the adsorption has an increasing adsorption as there is a higher relative pressure, but they also show a better adsorption after a pressure relative of 0.8.
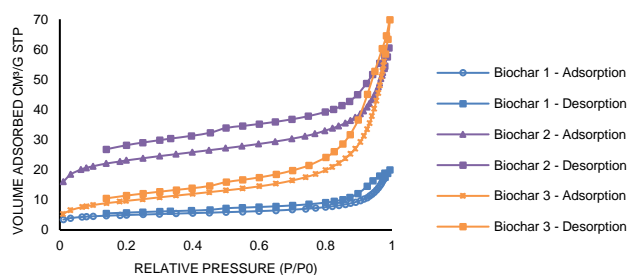
Figure 4: Adsorption and desorption isotherms obtained in Physical Adsorption

Practically all samples present type II isotherms (IUPAC nomenclature – Thommes et al., 2015), which are generally characteristic of macroporous solids. All of them present the phenomenon of hysteresis, which is the distance between the adsorption and desorption curves, which can occur for several reasons, but mainly, changes in the physical structure of the material and impurities on the surface (Rahman, 1995), corroborating with the chemical analyses carried out in another work (Miranda, 2018). These types of isotherms are reversible, and this shape indicates that there is unrestricted monolayer-multilayer adsorption up to high P/P^0 (Thommes et al., 2015). As the curvature of the curve starts early on the range of 0.0–0.2 P/P^0, it indicates that there is a significant amount of monolayer coverage overlap and a likely start of multilayer adsorption, and it is natural for this sudden increase in adsorbed volume to occur when the relative pressure approaches to 1 (Thommes et al., 2015). This type of desorption is very common in aggregated crystals of mesoporous zeolites and micro-mesoporous carbons, which is consistent with the analyzed samples, since carbon, oxygen, and silica are the main components in biochar (Miranda, 2018). The results found here agree with Moradi-Choghamarani et al. (2019).

4. Conclusions

The results show that when more than one cyclone is used in a continuous pyrolysis unit, there is going to have biochar with different sizes along the process. This is due to how the biomass particles are being broken down in the pyrolysis process itself, due to the operating conditions and the particle separation processes that the process has. The obtained different sizes biochar refer to the normal continuous process, mainly when cyclones are used since the heaviest particles tend to start to separate first, due to the gravitational force. In this type of process that was used, the largest particles already remained in the Biochar 1, due to their sizes and consequent weight. Thus, they were not dragged along with the vapors. Smaller particles rotate with the vapor and acquire angular velocity and were dragged more easily, along with the vapors, separating later (cyclones 1 and 2). This difference in particle sizes influence the fate of their uses or applications. The results (pore size, surface area, and particle size) indicated a great potential for these samples to be used as activated carbon or as an adsorbent. These applications require knowledge of this particle size and its homogeneity. Thus, the production of 03 size ranges (with particle size separators) facilitates the choice of which part of the process the biochar can be captured to be used, which can be applied in different types of adsorptions, facilitating the direct application by reducing the need for pre-treatments. Size variability also facilitates the use in burning for power generation and energy source in combustors, pyrolyzers, and gasifiers.

References

Angin, D., 2013, Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake, Bioresource Technology, 128, 593–597.

Asadullah, M., Rahman, M.A., Ali, M.M., Rahman, M.S., Motin, M.A., Sultan, M.B., Alam, M.R., 2007, Production of bio-oil from fixed bed pyrolysis of bagasse, Fuel, 86, 16, 2514–2520.

Blanco-Canqui, H., 2017, Biochar and Soil Physical Properties. Soil Sci. Soc. Am. J., 81, 687–711.

Carrier, M., Hardie, A.G., Uras, Ü., Görgens, J., Knoetze, J.H., 2012, Production of char from vacuum pyrolysis of South-African sugar cane bagasse and its characterization as activated carbon and biochar, Journal of Analytical and Applied Pyrolysis, 96, 24–32.

Demirbas, A., 2004, Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues, Journal of Analytical and Applied Pyrolysis, 72, 2, 243–248.

Dhyani, V., Bhaskar, T., 2018, A comprehensive review on the pyrolysis of lignocellulosic biomass. Renewable Energy, 129, 695–716.

Duarte, S.J., Glaser, B., Cerri, C.E.P., 2019, Effect of biochar particle size on physical, hydrological and chemical properties of loamy and sandy tropical soils, Agronomy, 9, 165.

Garcia, B., Alves, O., Rijo, B., Lourinho, G., Nobre, C., 2022, Biochar: production, applications, and market prospects in Portugal, Environments, 9, 95.

Ghani, W.A.W.A.K., Mohd, A., Silva, G., Bachmann, R.T., Taufiq-Yap, Y.H., Rashid, U., Al-Muhtaseb, A.H., 2013, Biochar production from waste rubber-wood-sawdust and its potential use in C sequestration: Chemical and physical characterization. Industrial Crops and Products, 44, 18–24.

Gonçalves, G.C., Pereira, N.C., Veit, M.T., 2016, Production of bio-oil and activated carbon from sugarcane bagasse and molasses, Biomass and Bioenergy, 85, 178–186.

Islam, M.R., Parveen, M., Haniu, H., 2010, Properties of sugarcane waste-derived biooils obtained by fixed-bed fire-tube heating pyrolysis, Bioresource Technology, 101, 11, 4162–4168.

Kocsis, T., Ringer, M., Biró, B., 2022, Characteristics and applications of biochar in soil–plant Systems: a short review of benefits and potential drawbacks, Appl. Sci., 12, 4051.

Kwapinski, W., Byrne, C.M.P., Kryachko, E., Wolfram, P., Adley, C., Leahy, J.J., Novotny, E.H., Hayes, M.H.B., 2010, Biochar from biomass and waste, Waste and Biomass Valorization, 1, 177–189.

Liu, Z., Dugan, B., Masiello, C.A., Gonnermann, H.M., 2017, Biochar particle size, shape, and porosity act together to influence soil water properties, PLoS One, 12, 6.

McBeath, A.V., Smernik, R.J., Krull, E.S., Lehmann, J., 2014, The influence of feedstock and production temperature on biochar carbon chemistry: A solid-state 13C NMR study, Biomass and Bioenergy, 60, 121–129.

Mendes, F. L., Ximenes, V.L., Almeida, M.B.B., Azevedo, D.A., Tessarolo, N.S., Pinho, A.R., 2016, Catalytic pyrolysis of sugarcane bagasse and pinewood in a pilot scale unit, Journal of Analytical and Applied Pyrolysis, 122, 395–404.

Miranda, N.T., 2018, Investigation about operational conditions for bio-oil and biochar production from sugarcane bagasse through simulation and application in pilot plant, Dissertation in Chemical Engineering (in Portuguese), School of Chemical Engineering, University of Campinas.

Miranda, N.T., Motta, I.L., Fernandes, D.S., Dianin, L.M., Maciel Filho, R., Maciel, M.R.W., 2018, Adaptation of a pilot gasification plant for the sugarcane bambasse pyrolysis process (in Portuguese), XXII Brazilian Congress of Chemical Engineering.

Miranda, N.T., Dianin, L.M., Fernandes, D.S., Maciel Filho, R., Maciel, M.R.W., 2020, Experimental Study on Sugarcane Bagasse Pyrolysis in a Thermochemical Processes Pilot Plant, Chemical Engineering Transactions, 80.

Moradi-Choghamarani, F., Moosavi, A.A., Sepaskhah, A.R., Baghernejad, M., 2019, Physico-hydraulic properties of sugarcane bagasse-derived biochar: the role of pyrolysis temperature, Cellulose, 26, 7125–7143.

Prasad, M., Chrysargyris, A., McDaniel, N., Kavanagh, A., Gruda, N.S., Tzortzakis, N., 2019, Plant Nutrient Availability and PH of Biochars and Their Fractions, with the Possible Use as a Component in a Growing Media, Agronomy, 10.

Rabelo, S.C., Carrere, H., Maciel Filho, R., Costa, A.C., 2011, Production of bioethanol, methane and heat from sugarcane bagasse in a biorefinery concept. Bioresource Technology, 102, 17, 7887–7895.

Rahman, M.S., 1995, Food Properties Handbook, 1st ed. CRC Press, Boca Raton.

Ringer, M., Putsche, V., Scahill, J., 2006, Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis, National Renewable Energy Laboratory, Tp-510-377, 1–93.

Sohaib, Q., Muhammad, A., Younas, M., 2017, Fast pyrolysis of sugarcane bagasse: Effect of pyrolysis conditions on final product distribution and properties, Energy Sources, Part A: Recovery, Utilization and Environmental Effects, 39, 2, 184–190.

Suroshe, P., Pramanik, H., 2015, Recovery of Valuable Bio-oil and Char via Pyrolysis of Sugarcane Bagasse, International Journal of Chemical and Environmental Engineering Recovery, 6, 3.

Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.W., 2015, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report) Journal Pure and Applied Chemistry, 87, 9–10, 1051–1069.

Varma, A.K., Mondal, P., 2017, Pyrolysis of sugarcane bagasse in semi batch reactor: Effects of process parameters on product yields and characterization of products. Industrial Crops and Products, 95, 704–717.

Xu, R., Ferrante, L., Briens, C., Berruti, F., Bio-oil production by flash pyrolysis of sugarcane residues and post treatments of the aqueous phase, Journal of Analytical and Applied Pyrolysis, 91, 1, 263–272.