

Synthesis of Carbon-Based Materials by Microwave Hydrothermal Processing

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1. Introduction

The conventional methods of converting biomass into renewable energy are based on thermal, biochemical or physical processes. Carbonization is one of the possible thermochemical conversion of biomass into energy, where a solid residue known as charcoal is produced through a slow process of partial thermal decomposition of wood in the absence or controlled presence of oxygen (Bridgwater, 2003).

Each temperature range in carbonization is responsible for a product or byproduct. Both temperature and the raw material influence the quality of the obtained charcoal and they play a key role in several reactions that occur in the carbonization process used to produce compounds with different physical and chemical properties.

In Brazil, the conventional charcoal production consists in cycles of 8-10 days to produce 20 m³ of charcoal, depending on the oven type. Furthermore, the carbonization process generates byproducts such as carbon dioxide (60%), carbon monoxide (30%) among others (Trugilho & Silva, 2001).

These facts raise concern about global warming and environmentally friendly processes of energy production, and the need for research that aims to develop clean technology or green chemistry, new energy production routes that reduce waste and pollutants.

The use of renewable energy has been widely discussed as an alternative to fossil fuels. The biomass, consisting mainly of agricultural and forestry waste, can be regarded as a renewable energy source with potential to supply the global energy demands. Moreover, the use of biomass contributes to reduce the greenhouse effect.

The discussion on biofuels and renewable energy sources became a relevant topic both in academia and industry. The development of new technologies that leads to new and more products with specific applications and economically feasible is a challenge for scientific and technological advances.

A great contribution to environmentally sustainable processes was the development of a carbonization method that uses aqueous media, the hydrothermal carbonization (HTC). Hydrothermal carbonization is a thermochemical process for biomass conversion to produce a solid material, named "hydrochar". In this chapter, authors feature the use of microwave energy in hydrothermal carbonization of lignocellulosic materials as an innovative process and discuss the potential of this technique in biochar production.

2. Hydrothermal carbonization

There are many methods to produce advanced materials. One of them is hydrothermal processing. This technique enables the production of complex materials with interesting physicochemical properties. A wide range of materials such as metals, oxides, hydroxides, silicates, carbonates, phosphates and sulphates are being produced by this technique as nanostructured particules (nanotubes, nanowires, nanospheres). It is also a method used to produce carbonaceous materials with both sp^2 and sp^3 hybridization type.

According to Yoshimura and Byrappa (2008), a hydrothermal process can be defined as any homogeneous or heterogeneous chemical reaction in the presence of solvent (whether aqueous or non-aqueous) above room temperature and at pressure greater than 1 atm in a closed system. As previously mentioned, the hydrothermal carbonization (HTC) is a thermochemical conversion process of biomass or lignocellulosic raw materials that yields a solid product, known as hydrochar. HTC has been widely used to simulate the coalification in laboratory (Funke and Ziegler, 2010). Due to increasing demand for efficient biomass conversion technologies, hydrothermal carbonization has attracted much attention as a promising large scale application.

Several studies have already been published reporting on hydrothermal environment to carbonize materials like cellulose (Sevilla & Fuertes, 2009; Inoue et al., 2008), switchgrass and corn stover (Kumar et al., 2011), wood (Liu et al., 2010), microalgae (Heilmann et al., 2010), swine-manure (Cao et al., 2010) and sugars such as xylose (Ryu et al., 2010), glucose (Mi et al., 2008), sucrose and starch (Sevilla & Fuertes, 2009).

Basically, the method consists of heating the biomass in the presence of a catalyst in a closed vessel under pressure, at temperatures ranging from 180 to 300°C, with reaction times between 1 and 48 h. Thus, the hydrothermal carbonization allows the use of stored energy in biomass more efficiently. Figure 1 shows a simplified scheme of energy comparison of HTC with the most common methods for processing biomass (adapted from Titirici et al., 2007).

Theoretically, 15% of the energy stored in biomass is already lost when the carbohydrates are converted into alcohol, for example, and two of six carbon atoms are released as CO_2 , generating a carbon efficiency of 0.66 or 60%. The carbon conversion efficiency (CE) can be defined as the amount of carbon derived from biomass, which remains linked to the final product after processing. In the anaerobic conversion, about 18% of energy is lost and 50% of carbon is released as CO_2 (CE=50%). In the HTC process, the carbon efficiency is very close to 100, *i.e.* almost the carbon from biomass is converted into carbonized material, without generating CO and CO_2 (Titirici et al., 2007).

HTC is one of the most advanced technologies to convert biomass and waste with high moisture levels, because it eliminates the drying step. In addition, HTC efficiently decomposes the carbohydrates in biomass, such as cellulose and hemicellulose by hydrolysis, to produce sugars and other decomposition byproducts, *i.e.* organic acids and aldehydes (Mochidzuki et al., 2003; Fujino et al., 2002).

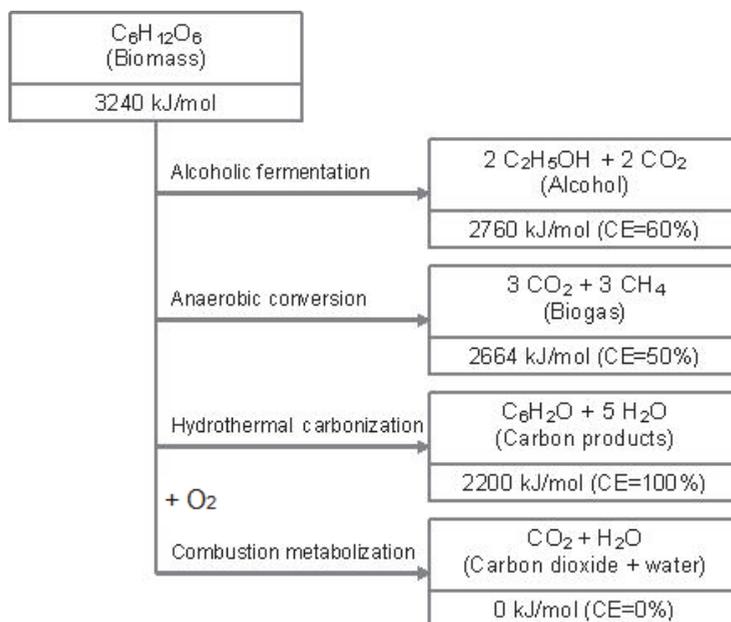


Fig. 1. Simplified diagram comparing different processing of biomass conversion.

Water acts both as reagent and reactive environment, which aids the hydrolysis, depolymerization, dehydration and decarboxylation reactions. However, these conventional hydrothermal processes need special systems that support pressure, temperature (usually an autoclave with pressure safety device), and reaction times ranging from hours to days, making them expensive and time consuming. Another inconvenience is the low selectivity, generating by products in the same reaction.

3. Microwave-assisted hydrothermal carbonization

3.1 Microwave in materials processing

Microwaves are electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz and wavelengths between 1 m and 1 mm. Originally, microwaves were used in telecommunications, such as radar and telephone technology. Only during World War II, Percy Spencer discovered that microwaves had the ability to heat food, based on the fact that the wave energy in this range of electromagnetic spectrum matches the energy of the rotational movement of some dipolar molecules like water, fats and sugars (Spencer, 1941). Thereafter, microwaves have been used in several applications like as civil aviation radars, cellphones and especially in domestic ovens.

From the physicochemical point of view, heating by microwave radiation is a result of the interaction of electromagnetic wave with the electric dipole of the molecule.

Food heating and cooking in a microwave oven, for example, takes place because food contains water, which is formed by polar molecules able to align with the microwave electric field, as shown in Figure 2 (adapted from Titirici et al., 2007).

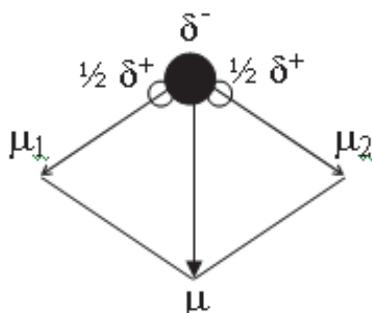


Fig. 2. Electric dipole of the water molecule. δ^- and δ^+ are the negative and positive partial charges of oxygen and hydrogen, respectively; μ_1 and μ_2 are the dipole moments of the water molecule and μ matches to the resulting dipole moment.

In chemistry and materials science fields, application of microwave technology has attracted special interest in the synthesis of organic and inorganic compounds and heat treatment of materials (drying and sintering).

Microwave radiation has been used in material processing and synthesis reactions, such as the synthesis of advanced ceramic materials (Keyson et al., 2006), carbides (Rambo et al., 1999), oxide nanoparticles (Palchik et al., 2000), synthesis from catalytic reactions (Balalaie et al., 2000) and recycling plastics (Lulow-Palafox & Chase, 2001) in addition to use in organic synthesis with organic solvents (Nücher et al., 2004) and in the absence of solvents (Caddick, 1995).

In contrast to conventional ovens, the material processed in a microwave oven interacts with electromagnetic radiation and not with the radiant energy. Due to the heat being generated by the material itself in its bulk, the heat reaches the entire volume and can be much faster and selective. These characteristics, when properly monitored, result in a homogeneous material, with faster production, while providing a significant reduction in energy losses (Clarck & Sutton, 1996).

All this set of benefits even leads to the greatest: the economic. Furthermore, the use of microwaves in a process is classified as clean technology, following the global trend towards the use of alternative environmentally friendly methods.

The use of microwaves on hydrothermal carbonization contributed to simplify and accelerate the process, since the reaction time was decreased compared to conventional hydrothermal carbonization and the obtained products are usually homogeneous. The main difference between the conventional and microwave heating is how the heat is generated. In the conventional process, energy is transferred to material by convection, conduction and radiation of heat from the material surface.

On the other hand, microwave energy is derived directly from the material by molecular interactions with electromagnetic waves. The material is processed rapidly, with selective power, homogeneous heating and energy conservation. These factors contribute to the improvement of the properties of the final products and enable the synthesis of new materials that could not be obtained by conventional methods (Yang et al., 2002).

The use of microwaves in the carbonization process have been intensively investigated over the last decade with different raw materials like wood (Wan et al., 2009; Miura et al., 2000), corn stover (Wan et al., 2009), grass (Orozco et al., 2007) in addition to some sugars

like as glucose and fructose (Qi et al., 2008) and activated carbons (Deng et al., 2010; Franca et al., 2010, Xin-hui et al., 2011)

The innovative process discussed in this chapter depicts the use of microwave heating in the biomass hydrothermal carbonization, which is named microwave-assisted hydrothermal carbonization (MAHC) (Guiotoku et al., 2009).

The method is based on previous work conducted by Antonietti and co-workers (2006), and uses pine sawdust and α -cellulose as raw material, water (hydrothermal environment), mild temperature (200°C) and citric acid as catalyst. The experiments were carried out using a microwave oven Millestone (Ethos Plus) suitable for sample digestion. The device frequency used was 2.45 GHz, 12.25 cm wavelength and 1000 W power supply. Figure 3 illustrates a simplified scheme of the microwave oven chamber (adapted from Walter et al., 1997).

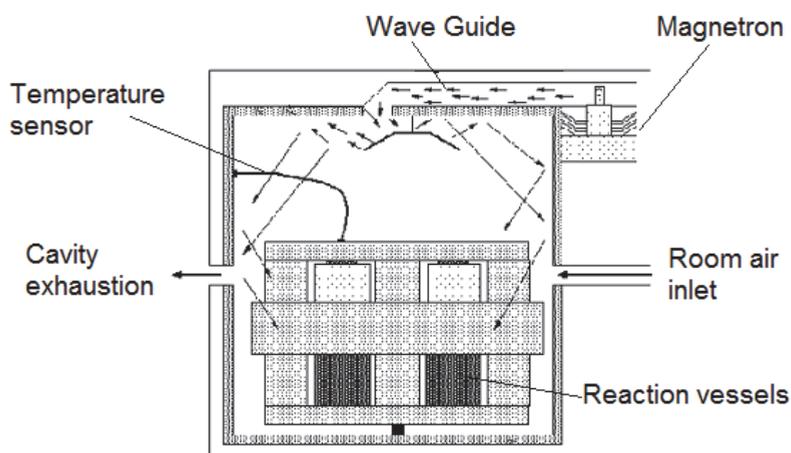


Fig. 3. Typical laboratory cavity-type microwave system . TFM™, a modified polytetrafluoroethylene, reaction closed vessels with 100 mL volume were used in the carbonization process. These vessels withstand temperatures up to 300°C and the pressure inside may range from 80 to 100 bar.

Different catalyst concentrations were tested with pine sawdust (PS) as raw material. Figure 4 illustrates the experiments (Guiotoku, 2008).

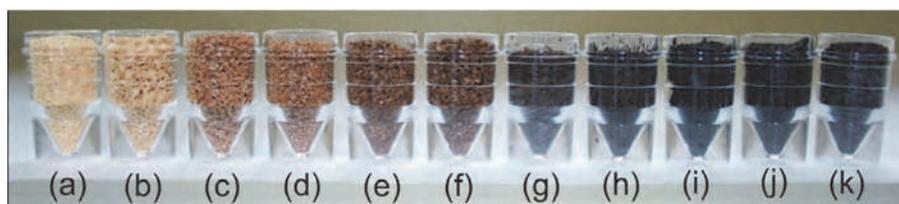


Fig. 4. Pine sawdust samples (a) in natura; hydrothermally carbonized during 30 minutes with different catalyst concentration: (b) 0.00; (c) 0.10; (d) 0.15; (e) 0.25; (f) 0.5; (g) 1.0; (h) 1.5; (i) 2.0; (j) 2.5 and (k) 3.0 mol·L⁻¹.

The color in the carbonized pine sawdust samples depends on the catalyst concentration. As the acid concentration increases, the samples become darker. The catalyst concentration chosen to conduct the experiments was $1.5 \text{ mol}\cdot\text{L}^{-1}$. The changes caused during the cellulose heating in water are predominantly determined by hydrolytic reactions and especially in this case, by acid hydrolysis reactions.

The key factor that influences the acid hydrolysis reaction is the way in which it takes place, since the most important reaction in cellulose occurs in heterogeneous phase: solid polysaccharide in acid media.

3.1.1 Energy assessment

When subjected to carbonization or conventional pyrolysis lignocellulosic material generally undergoes thermal decomposition of their components - hemicellulose, cellulose and lignin - under inert or oxygen restricted atmospheres. Each component volatilizes more intensively at specific ranges of temperature: hemicellulose at $200 - 300^\circ\text{C}$, cellulose at $240 - 350^\circ\text{C}$ and lignin at $350 - 500^\circ\text{C}$. The decomposition products are basically oil, gas and solid products (charcoal).

In order to evaluate the energetic potential of pine sawdust (PS) and α -cellulose (C), proximate analysis and gross calorific value were carried out as shown in Table 1 (Guiotoku, 2008). The samples were hydrothermally carbonized in a microwave oven at 200°C for 60, 120 and 240 min with 10 mL of $1.5 \text{ mol}\cdot\text{L}^{-1}$ catalyst solution.

Sample	Time (min)	% VM ^a	% Ash	% FC ^b	HGC ^c (MJ/kg)
PS60	60	61.41	0.20	38.39	22.60
PS120	120	55.14	0.20	44.66	24.22
PS240	240	50.94	0.21	48.85	25.42
C60	60	53.37	0.25	46.38	21.62
C120	120	51.36	0.28	48.36	24.91
C240	240	48.05	0.21	51.74	27.12

^aVolatile matter; ^bFixed carbon; ^cHigh gross calorific value.

Table 1. Proximate analysis and calorific values of pine sawdust (PS) and α -cellulose (C) samples carbonized in MAHC for 60, 120 and 240 min.

In the proximate analysis properties such as volatile matter, ash and fixed carbon were determined. There is a small decrease in volatile matter with increasing carbonization time, due to volatilization of low weight molecules during longer reaction times. The fixed carbon is intrinsically linked to high gross calorific values and their values increases with the MAHC reactions times, indicating that more carbonized material was generated.

Figure 5 shows the low gross calorific values (LGC) for some solid and liquid fuels. Hachured bars correspond to the MAHC materials (adapted from Ministério de Minas e Energia, 2007). LGC values may be calculated from equation (1):

$$\text{HGC} = \text{LGC} + m(c \cdot \Delta T + L) \quad (1)$$

where HGC = high gross calorific value; m = water mass combustion; c = water specific heat; ΔT = difference between ambient and equilibrium temperature before condensation, and L = condensation latent heat of water vapor.

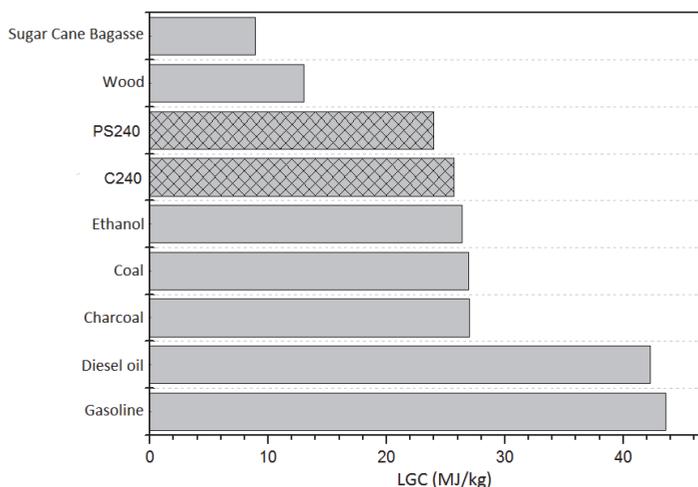


Fig. 5. Low gross calorific values for solid and liquid fuels. P240 and C240 are the MAHC samples.

Gross calorific values of MAHC products are comparable to a fossil fuel (coal), charcoal and ethanol. However, gross calorific values found for petroleum-based fuels, such as gasoline and diesel oil are 48% higher than the carbonaceous materials obtained in MAHC process. Thermogravimetric analysis (TGA) provides information about the thermal stability of carbonized materials. Figure 6 shows the weight loss curves for the pine and α -cellulose samples under argon atmosphere.

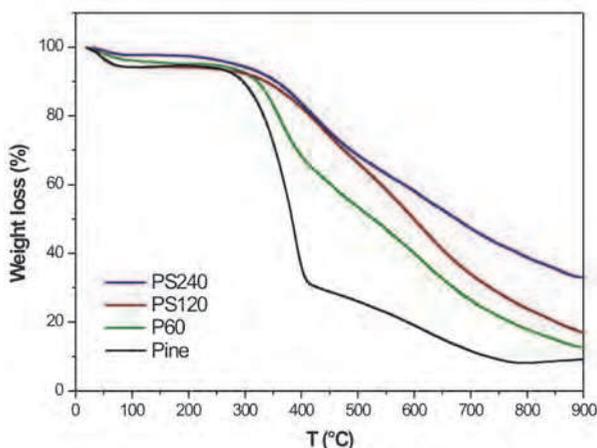


Fig. 6. Thermogravimetric curves of pine sawdust samples *in natura* and MAHC pine sawdust samples (PS) carbonized in microwave for 60, 120 and 240 min.

TG curves for pine samples reveal three weight loss stages, the first matches the moisture loss and occurs at 95 to 110°C, the second stage at 300 to 470°C is assigned to the cellulose

thermal decomposition with cellulose macromolecule breakdown. The third weight loss at 470 to 740°C, is assigned to thermal degradation of lignin. The α -cellulose samples showed similar trends.

Thermogravimetric analysis showed that the carbonization time was not enough to promote complete carbonization. These results were confirmed by elemental analysis of MAHC charcoals and raw materials (Table 2) (Guiotoku et al., 2009). Elemental analysis data from α -cellulose carbonized in a tubular furnace at 900°C, for 3 h, under nitrogen atmosphere, was used as reference material to complete carbonization.

Time	C (wt.%)	H (wt.%)	N (wt.%)	O ^a (wt.%)	Atomic ratio	
					H/C	O/C
<i>Pine sawdust</i>	45.45±0.06	6.22±0.09	0.02±0.01	48.31±0.16	1.16	0.79
0	60.01±0.15	5.51±0.00	0.02±0.00	34.46±0.16	1.10	0.43
60	64.74±0.15	5.29±0.18	0.04±0.01	29.93±0.35	0.98	0.35
120	63.54±0.12	5.19±0.10	0.71±0.01	30.56±0.20	0.98	0.36
<i>α-cellulose</i>						
0	40.5±0.15	6.43±0.02	0.09±0.06	52.98±0.11	1.90	0.97
60	63.11±0.08	4.74±0.007	0.26±0.05	31.89±0.13	0.90	0.38
120	63.63±0.00	4.64±0.03	0.06±0.02	31.67±0.06	0.87	0.37
240	63.75±0.09	4.50±0.04	0.46±0.01	32.19±0.10	0.85	0.37
<i>α-cel charcoal</i>	91.08±0.12	1.33±0.05	0	7.59±0.08	0.17	0.06

Table 2. Elemental analysis for pine sawdust and α -cellulose at different times of MAHC and α -cellulose charcoal (Guiotoku et al., 2009). ^a The oxygen content was determined by mathematical difference [100% - (C% + H% + N%)].

Compared with their respective raw materials, the samples subjected to the microwave-assisted hydrothermal carbonization process had their carbon content increased by 40% and 57% for pine sawdust and α -cellulose, respectively. In contrast, the amount of O and H decreased in all carbonized materials, which suggests aromatization process.

In order to evaluate qualitatively the carbonization process, H/C and O/C molar ratios were plotted using the van Krevelen diagram, which provides information about the changes in chemical structure after carbonization, as seen in Figure 7. The van Krevelen diagram is widely used in study and classification of kerogen, which is a mixture of organic chemistry compounds modified by geological actions that originates the most of fossil fuels such as oil, gas and coal. This classification is basically provided by analysis of H/C and O/C molar ratios (van Krevelen, 1950).

In the diagram, H/C and O/C ratios of carbonized materials decrease when compared to their natural samples, suggesting that changes in the materials were taking place. The loss of H and O occurred by dehydrogenation, deoxygenation and dehydration processes.

However, as seen in TGA curves, the products are not completely carbonized, since they are in the center of diagram, between the raw material and α -cellulose charcoal. Such partially carbonized materials are commonly obtained by hydrothermal carbonization and their chemical structure can be described as amorphous aromatic carbon -OH and -COOH substituted (Titirici et al., 2007a).

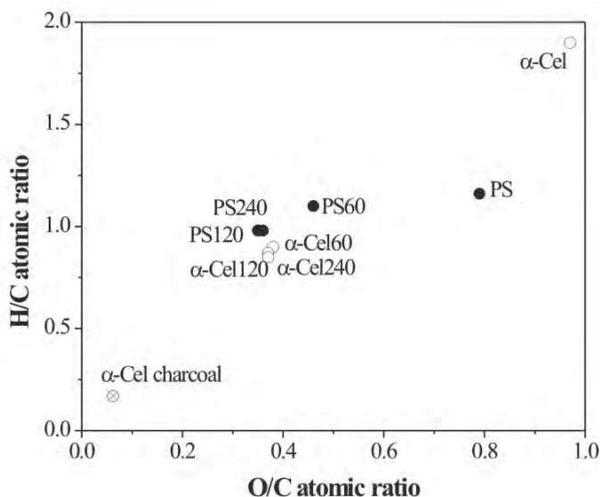


Fig. 7. The van Krevelen diagram for pine sawdust (●), α -cellulose (○) and α -cellulose charcoal (⊗) (Guiotoku et al., 2009).

SEM (Scanning Electron Microscopy) micrographs of pine sawdust and α -cellulose both *in natura* and in carbonized form are depicted in Figure 8.

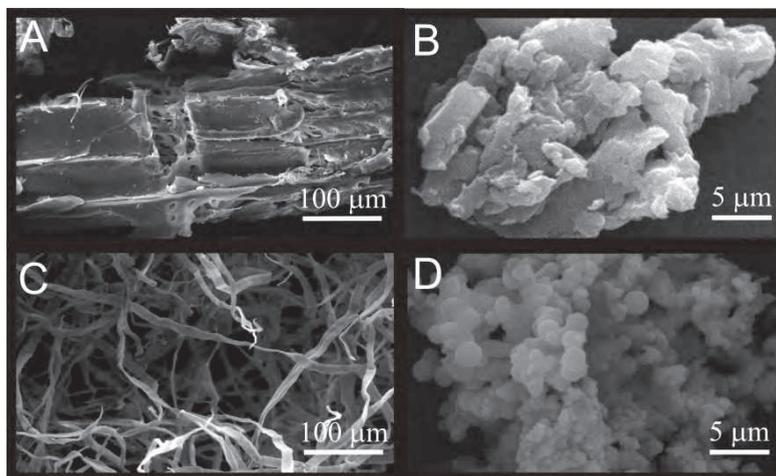


Fig. 8. SEM micrographs of pine sawdust (A) and α -cellulose raw material (C); hydrothermally carbonized in microwave oven pine sawdust (B) and α -cellulose (D) (Guiotoku et al., 2009).

Carbonized pine sawdust apparently maintained its micro-morphological features after hydrothermal carbonization (Fig. 8B). In contrast, the carbonized α -cellulose is characterized by a noticeable morphological change after the MAHC process (Fig. 8 C and D). α -cellulose exhibits a fibrous aspect (Fig. 8C). After carbonization the fibers changed to spherical particles, with sizes of approximately 1.5 μm in diameter (Fig. 8D).

3.1.2 Chemical characterization

To better understand the molecules breakdown mechanism under microwave-assisted hydrothermal carbonization, Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS) analysis were carried out in order to identify and quantify the carbonized compounds.

A list of compounds identified by Py-GC-MS and total ion current (TIC) is shown in Table 3. Carbonized products were divided into five classes: (A) alkyl furans, (B) oxygen-functionalized furans, (C) benzenoids, (D) benzofurans and (E) unknown compounds. Only compounds with total percentage area higher than 1.0% had their spectra analyzed (Guiotoku et al., submitted).

Eight chromatographic peaks, 27.2% of total area, did not provide pure compounds. For this reason their mass spectra were not useful for interpretation. Major classes identified in the hydrochar were benzofurans followed by oxygen-functionalized furans, which correspond to 32.1% and 24.3%, respectively. The minor classes were alkyl furans and benzenoids.

RT (min)	Compound	Class	MW	Fragment ions	%
2.18	2,5-dimethyl-furan	A	96	43, 53, 81	2.45
2.73	<i>impure</i>	?	-	-	1.33
3.20	methyl-benzene	C	92	65, 91	1.29
3.85	2,3,5-trimethyl-furan	A	110	43, 67, 95	1.12
4.44	?-methyl-phenol	C	108	77, 107	1.07
4.51	2-ethyl-furan	A	96	53, 81	1.82
5.22	<i>impure</i>	?	-	-	2.65
6.03	2-acetyl-furan	B	110	67, 95	3.1
6.75	2,3-dihydro-furfuryl-ethanol	B	114	53, 68, 96, 113	21.25
7.06	<i>impure</i>	?	-	-	2.01
7.56	trimethyl-benzene	C	120	77, 105	2.52
8.10	<i>impure</i>	?	-	-	3.42
8.39	<i>impure</i>	?	-	-	5.57
8.96	<i>impure</i>	?	-	-	2.13
9.49	<i>impure</i>	D	-	-	7.38
9.55	methyl-benzofuran	D	132	77, 103	2.57
15.24	methyl-2-ethyl-benzofuran (probably)	D	160	77,103, 131	10.82
18.70	<i>impure</i>	?	-	-	2.73
20.81	dimethyl-2,3dihydro-2-acetyl-benzofuran	D	190	91, 119, 147, 175	18.71

Table 3. Identified compounds and their relative distribution in Py-GC-MS data of microwave assisted hydrothermal product of cellulose (hydrochar).

The most pyrolytic furan-like and benzenoids compounds present in the hydrochar are detected in Py-GC-MS analysis of raw materials and carbonized cellulose, A and B classes (Pastorova et al., 1994). However, levoglucosan, the main product detected by pyrolysis analysis of raw cellulose, and other sugar markers (*e.g.* pyranones) were not identified in the hydrochar, indicating that all original material was modified during the hydrothermal treatment.

Furthermore, condensed aromatic compounds (*e.g.* naphtalene and phenantrene) usually present in the macromolecular structure of carbonized cellulose were also not detected. Therefore, apparently the hydrochar material did not preserve the oligosaccharide structure

of the started material in spite of low temperature used, and no strong evidence of the cellulose charcoal was detected in the final hydrochar product.

The solid state ^{13}C NMR spectrum of hydrochar is showed in Figure 9 and is characterized by the presence of two broadened peaks centered at 25 and 125 ppm.

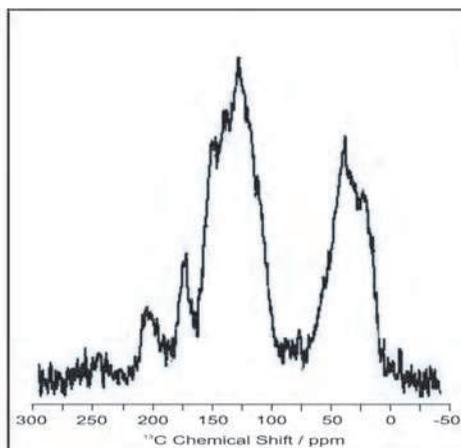


Fig. 9. Solid state ^{13}C NMR spectrum of hydrothermally carbonized on microwave cellulose (hydrochar) (Guiotoku et al., submitted).

Contribution of aliphatic groups can be observed between 10 and 60 ppm, with methylene resonance contribution ranging from 20 to 40 ppm. The peak at 125 ppm is typical of charred residues due to polycyclic aromatic structures. Other peaks of low intensities appear at 175 and 205 ppm, and they are consistent with the presence of carboxyl and carbonyl functional groups, respectively (*i.e* aliphatic carboxylic acids - 175 ppm and aldehydes and ketones - 205 ppm).

Results of the NMR and Py-GC-MS analyses confirmed that the hydrochar product contains an intermediate polymer composed of mainly furan elements. A strong cellulose signal is also absent in the NMR spectrum, since signals around 75 ppm, indicative of the presence of hydroxylated methylene groups, were not prominent. The same results were observed in the pyrolysis analysis.

Interestingly, NMR spectra provided information on the nature of aromatic carbons (129 ppm), which may be interpreted as a graphite-like structure (Jiang et al., 2002). Py-GC-MS analysis provided a more detailed view of the aromatic structure, suggesting that aromatic monomers of hydrochar polymer are built on benzofuran-like components.

According to a study about hydrochar production from cellulose, the carbon-rich production from cellulose takes place via: (i) hydrolysis; (ii) dehydration and fragmentation of sugars; (iii) polymerization or sugar derivatives condensation, and (iv) aromatization (Sevilla & Fuertes, 2009). Similar mechanism should occur in hydrochar production by microwave hydrothermal carbonization, leading to partial oxygenated and aromatic products.

Hydrothermal carbonization is a novel route to produce carbon-rich material, and its use as a soil additive should be considered, mainly due to its specific properties like a functionalized chemical nature structure (hydrochar). In contrast to several biochar

agronomic studies (Sohi et al., 2010 and references therein), only preliminary studies using hydrochar have been carrying out.

4. MAHC and biochar

Biochar is any source of biomass previously heated under low or absence of oxygen supply – a carbonization process – whose purpose is to be applied to soil in order to improve its agronomic and environmental quality. This process results in a very stable carbon-rich material not only capable of improving physical and chemical soil properties, and therefore soil productivity, but also of increasing soil carbon storage on large scale and for a long period of time (Sohi et al., 2010).

Biochar application to soil involves a combination of biological and physico-chemical routes to reduce atmospheric greenhouse gas levels, but its behavior in soil needs to be deeply evaluated for large scale use (Hammond et al., 2011). Nevertheless, there are few alternatives of carbon-neutral or carbon negative technologies, with great economic viability and low cost, leading to significant changes in the global carbon balance, such as that can be expected by adopting the currently technology known as biochar.

Usually, biochar is obtained from the partial transformation of biomass in to coal-like material by thermal decomposition under low oxygen atmosphere, resulting in partial degradation of cellulose into smaller molecules. This material is characterized by condensed aromatic structures with no functional groups (e.g. alcohol and organic acids), which are very important for reactivity and soil fertility when used as an additive. Therefore, methods for production and conversion of lignocellulosic biomass waste into highly functionalized biochar have emerged as a major challenge.

Soil fertility, especially in tropical soils, is substantially influenced by soil organic matter contents and its physical and chemical properties. Soil organic matter (SOM) is a complex mixture of organic compounds, of plants and animals origin, in gradual decomposition stage due to chemical or biological transformation. Pyrogenic carbon is the most recalcitrant fraction of SOM and, according to Seiler & Crutzen (1980), it can be described as “a continuum from partly charred plant material, through char and charcoal, to soot and graphite particles without distinct”.

Pyrogenic carbon is derived from partial carbonization mainly of lignocellulosic materials resulting in different sizes of condensed polyaromatic units, hydrogen and oxygen deficient. Soot particles that condense from gas phase typically develop as concentric shells of graphene stacks (“onion-like” structure) (Preston & Schmidt, 2006). Pyrogenic carbon is highly resistant to thermal, chemical and photo degradation, excellent characteristics for soil carbon sequestration (Glaser et al., 2001; Masiello, 2004). However, partial oxidation of peripheral aromatic units may produce carboxylic groups that elevate the total acidity of SOM and, therefore, the cation exchange capacity (CEC) and soil fertility (Novotny et al., 2009). This effect is demonstrated in Figure 10 where the ^{13}C NMR spectra of charcoal before and after chemical oxidation is shown (Novotny et al., 2007).

The use of biochar as a soil conditioner and several scientific publications can be found from the beginning of the 20th century. Nevertheless, recent studies about Amazonian Dark Earths, known as *Terras Pretas de Índios* (TPI), renewed the scientific interest on pyrogenic carbon in soils. TPI are anthropogenic dark earths which surface horizons of variable depth enriched in organic matter (OM), pottery shards lithic artifacts and other evidences of human activity (Kämpf et al., 2009).

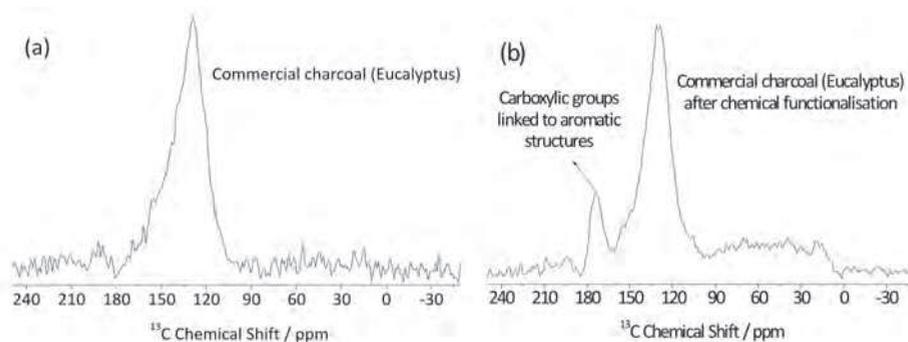


Fig. 10. Solid state ^{13}C NMR spectra of charcoal (a) before and (b) after chemical oxidation (Novotny et al., 2007).

These archeological Amazonian sites are highly fertile, very unusual among Amazonian soils, typically of low fertility, highly weathered and very acid. TPI soils have carbon content up to $150 \text{ g}\cdot\text{kg}^{-1}$ of soil, compared with 20 to $30 \text{ g}\cdot\text{kg}^{-1}$ in adjacent soils (Novotny et al., 2009). This additional carbon is present mainly in the pyrogenic form, which is more stable than other carbons forms (Glaser et al., 2001), distributed along the whole soil organic profile, which can reach up to 200 cm deep, averaging from 40 to 50 cm, while surrounding soils are limited from 10 to 20 cm. Therefore, carbon stocks in TPI can be an order of magnitude higher than in surrounding soils.

Humic acids extracted from TPI and analyzed by ^{13}C NMR spectroscopy, revealed that this fraction is rich in condensed aromatic structures and functionalized with carboxylic groups linked directly to the recalcitrant polyaromatic rings. In contrast, humic acids from adjacent non-anthropogenic soils have a higher content of labile compounds, such as carbohydrates and aminoacids. Once in soil biochar increases the pyrogenic fraction and the stable carbon pool. Besides carbon sequestration, biochar can provide other benefits such as: enhancing productivity (from 0 to 300%); decreasing emission of methane and nitrous oxide (up to 50% estimations); decreasing nutrients leaching and enhancing water holding capacity (Gaunt & Lehmann, 2007).

The success in obtaining functionalized materials by MAHC leads to new perspectives for the application of spherical carbonaceous particles, as soil amendments. Although soil pyrogenic carbon is rich in condensed polyaromatic compounds of low H/C and O/C ratios, chemical characteristics which provide high recalcitrant, resilience and resistance to thermal, chemical and photo degradation (Seiler & Crutzen, 1980), as a soil organic matter component, the presence of functionalized groups as carboxyls and hydroxyls is desirable to improve cationic exchange capacity (CEC). Charcoal is an efficient material for carbon sequestration (half-life ranging from decades to millennia), but it does not contain carboxylic groups that could improve its reactivity and CEC. Functionalization of the aryl backbone can be naturally obtained, slowly, or through chemical, thermal or biological oxidation like MAHC.

Hydrothermal carbonization produces carbonaceous materials under milder conditions than other carbonization processes. The structure of the hydrochar produced is basically an aromatic nucleus with hanging functional groups such as hydroxyl (-OH), carboxyl (-OOH) and carboxylic acids (-COOH), making it hydrophilic and less graphitized as compared with conventional charcoal (Rillig et al., 2010).

Conventional pyrolysis results in graphite-like structures with low O/C and H/C ratios and, therefore, few functional organic groups. Due to its polar structure, hydrochar is especially interesting as a soil conditioner, since it can play an active role in soil CEC and reactivity.

Biochar has been considered a very promising technology around the world mainly because it perfectly fits in the bioenergy sector as a solution for mitigation of greenhouse gas emissions. Scientific evidences indicate that biochar improves soil biodiversity, enhances soil performance, and reduces its susceptibility to weathering and its fertilization input. With the additional suppression of trace gas emission, a biochar-to-soil strategy based on agricultural waste streams offers a sustainable, carbon negative energy production by cutting farming's carbon footprint, and offering to the society a rare win-win option for combating climate change (Sohi et al., 2010).

Some of the benefits of biochar with respect to biomass are low moisture retention, high gross calorific value (and consequent reduction in transportation costs), ease of handling, it non perishability and long term storage ability. The acceleration of biomass carbonization by a factor of 10^6 to 10^9 by microwave hydrothermal reaction can be considered promising technology.

Despite these advantages of MAHC, further studies are still needed, in order to evaluate the viability of the wide range of possible applications. Considering its potential, the microwave-assisted hydrothermal carbonization is a new thermochemical conversion technology that should be seriously considered among biomass conversion technologies for the near future.

5. Research challenges and perspectives

Brazil is now the world's largest exporter not only of coffee, sugar, orange juice and tobacco but also of ethanol, beef and chicken, and the second-largest source of soybean products (The Economist, 2010). With this huge agricultural production, the first challenge is exactly the large variety of biomass source available to char. Each biomass source is physically and chemically different and has specific ideal conditions to char, and different soil responses. Besides, the large climate variation of the country also contributes to the variety of biomass and soil. With all these possibilities, it is necessary to prioritize the biochar research on certain biomass sources. At the moment, the natural trend seems to point to Brazilian energetic matrix, which is based in renewable sources (45% compared with a world average of 15%), from which 27.2% is supplied by biomass (Lora & Andrade, 2009). The Brazilian agro-energy chain involves 121.15 million tons of bagasse from sugar cane industry, although others sources of wasted biomass are currently in the biochar research agenda. As for MAHC procedures, the challenge is even larger since as a biochar making technique, is barely studied.

6. Conclusions

The purpose of this chapter was to demonstrate how the use of microwaves in an already well established process such as the hydrothermal, can produce materials with several interesting physico-chemical properties. As this process has been recently developed, there are no sufficient studies for material comparison and the discussed results during the chapter was based on the work of the authors research group. However, the authors hope

that the disclosure of this book may inspire further studies and applications for microwaves on carbonaceous materials in all fields of knowledge, such as materials engineering, chemistry, physics, biology, agronomy and others.

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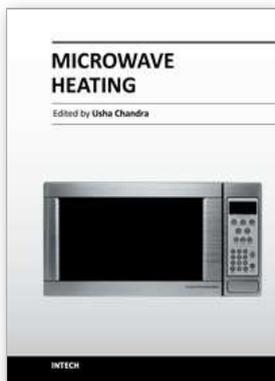
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