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The Pharma Innovation

ISSN (E): 2277- 7695
ISSN (P): 2349-8242
NAAS Rating: 5.03
TPI 2018; 7(4): 1132-1136

www.thepharmajournal.com
Received: 08-02-2018
Accepted: 10-03-2018

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Hydrothermal carbonisation of biomass and its potential applications in various fields

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Abstract
Hydrothermal carbonization is a thermo chemical process for converting moist biomass feedstock to a homogeneous carbon-rich solid, a high-strength process liquid, and a gaseous product mainly consisting of CO_2. Hydrolysis, dehydration, decarboxylation, aromatization, and condensation-polymerization are the main HTC reactions. The fibrous components degrade into liquid intermediates, followed by liquid biocrude and solid hydrochar by means of liquid-liquid, solidliquid and/or solid-solid reactions. The primary HTC process variables are reaction temperature, reaction time, and pressure as well as the feedstock itself. Many studies have suggested that hydrothermal carbonization (HTC) has been considered as an alternative method of processing biomass for value-added products. The HTC is known to have several advantages such as lower energy consumption and less emission over pyrolysis. Hydrochar and its derivatives are promising materials that has huge potential to be used in a range of applications. Most of the efforts of this review are on reviewing the potential applications of hydrochar in various fields including agriculture, environment, energy, adsorbent and medical applications. Hydrochar has gained global attention as soil amendments to potentially improve soil quality because they contain a variety of organic structures. The HTC process is a promising one for the ecofriendly waste management.

Keywords: Hydrochar, HTC etc.

Introduction

The biomass is the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. It has been assigned many roles to play in strategies for sustainable consumption. In addition, being a food source and renewable raw material (Perlack *et al.*, 2005) [27], it can be used for energy production (Kaltschmitt *et al*.,, 2009 and Laikum, 2010) n [13, 19] carbon sequestration (Pratt and Moran, 2010 and Whitman and Lehmann, 2009) [28, 21, 41] and, finally, as an essential element to increase soil fertility (Lehmann and Joseph, 2009) [21]. A major disadvantage for almost all applications is the high degree of heterogeneity in the form, composition and water content of biomass. Therefore, drying and/or conversion processes are usually required to improve material properties for easier handling, transport and storage of such materials. A variety of thermo-chemical or biological processes can be used to convert biomass in the absence of oxygen to products with higher degrees of carbon content than the original biomass. An alternative to slow-pyrolysis is a relatively new process called hydrothermal carbonization (HTC) or hydrous pyrolysis of biomass, where the biomass is treated with hot compressed water instead of drying, has shown promising results. The HTC process offers several advantages over conventional dry-thermal pre-treatments like slow-pyrolysis in terms of improvements in the process performances and economic efficiency, especially its ability to process wet feedstock without pre-drying requirement (Singh and Dutta, 2015). Hydrochar (HTC char) is a valuable resource and is superior to biochar in certain ways. This opens up the field of potential feedstocks to a variety of nontraditional sources: wet animal manures, human waste, sewage sludges, municipal solid waste (MSW), as well as aquaculture and algal residues. These feedstocks represent large, continuously generated, renewable residual streams that require some degree of management, treatment and/or processing to ensure protection to the environment. In recent years, hydrothermal carbonization (HTC) has been considered as an alternative method of processing biomass for value-added products (Stemann *et al.*, 2013) [34]. The solid product created during HTC is called hydrochar in order to distinguish it from biochar. During HTC, biomass is heated in an oxygen free environment in the presence of subcritical water and autogenous pressure in the range of 2-10 MPa (Mumme *et al.,* 2011) [26].

The HTC is known to have several advantages such as lower energy consumption and less emission over pyrolysis. The feedstocks with a high moisture content yield low amounts of solid material after drying, which makes them insufficient sources for pyrolysis (He *et al.,* 2013) [11]. Therefore, a greater variety of feedstocks could be considered for processing into hydrochar since drying the feedstock is not necessary for HTC (Kambo and Dutta, 2015) [14]. Another advantage is that HTC yields higher amounts of char and uses lower amounts of energy than pyrolysis. This is partially due to the fact that the feedstock does not need to be dried, as well as lower operating temperatures for HTC compared to pyrolysis (Libra *et al*., 2011) [22]. The HTC and pyrolysis generally use temperatures between 200-300 ^{0}C and 300-600 ^{0}C, respectively (Takaya *et al.,* 2016) [37]. The lower operating temperature of HTC is due to the activation temperatures of the chemical reactions that occur when the biomass is heated in the presence of liquid. When biomass is heated during HTC or pyrolysis, the physical structure is altered through reaction mechanisms such as hydrolysis, dehydration, decarboxylation, aromatization and re-condensation (Funke and Zeigler, 2010) [10]. While these reactions occur during both pyrolysis and HTC, hydrolysis is the predominant reaction during HTC, which has lower activation energy than the other decomposition reactions (Libra *et al*., 2011) [22]. During the hydrothermal carbonization (HTC), biomass undergoes structural rearrangement by degrading into solid, liquid and gaseous products (Lu *et al*., 2015) [23]. The compounds created during the previously described mechanisms can undergo re-condensation if they are highly reactive. Lignin fragments are highly reactive and condense easily, as well as aromatized polymers from cellulose degradation (Islam *et al.*, 2015) [25]. The re-condensation of HTC degradation products leads to the formation of hydrochar (Libra *et al*., 2011) [22]. Degradation products from hemicellulose, however, stabilize lignin fragments and slow down condensation reactions significantly (Funke and Zeigler, 2010) [10].

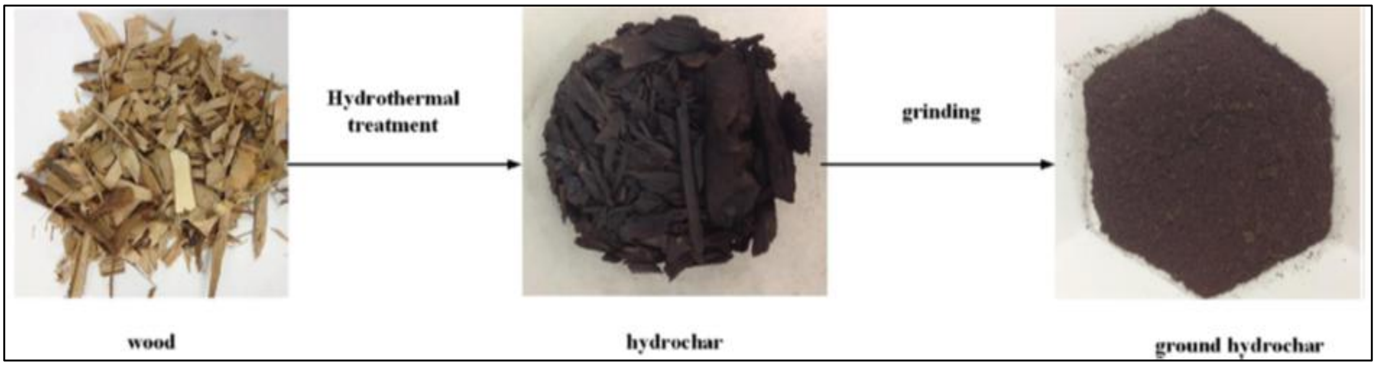

Fig 1: hydrochar produced from wood sample (Fang *et al.,* 2018) [7]

Hydrothermal processes

In hydrothermal processes, the solid material is surrounded by water during the reaction, which is kept in a liquid state by allowing the pressure to rise with the steam pressure in (high)-pressure reactors. With process temperatures of up to 220°C and corresponding pressures up to approximately 20 bar, very little gas (1-5%) is generated, and most organics remain as or are transformed into solids. At higher temperatures, up to approximately 400°C, and with the use of catalysts, more liquid hydrocarbons are formed and more gas is produced. This so called ‘hydrothermal liquefaction’ has drawn some interest, although most liquefaction work is performed using organic solvents instead of water (Behrendt *et al*., 2008) [3].

Feedstocks

Potential feedstocks for wet hydrolysis span a variety of nontraditional, continuously generated and renewable biomass streams: wet animal manures, human waste (i.e., excrements and faecal sludges), sewage sludges, MSW, as well as aquaculture residues and algae. These feedstocks usually require some degree of management, treatment and/or processing to ensure protection of the environment. Many of these streams (e.g., human waste and MSW) already have substantial collection and treatment costs associated with them. Carbonization of biomass has a number of advantages when compared with common biological treatment. It generally takes only hours, instead of the days or months required for biological processes, permitting more compact reactor design. In addition, some feedstocks are toxic and cannot be converted biochemically. The high process temperatures can destroy pathogens and potentially organic contaminants such as pharmaceutically active compounds (Bridle *et al.,* 1990 and Sutterlin *et al*., 2007) [4, 36]. Furthermore, useful liquid, gaseous and solid end-products can be produced (Seki, 2006) [31, 32], and at the same time contribute to GHG mitigation, odor reduction and additional socio-economic benefits.

Agricultural residual feedstocks

It includes crop residues, grains for ethanol production, corn fiber, MSW and animal manures.

Human waste & sewage sludge

The amount of human waste (untreated excrement and faecal sludges) and sewage sludges (primary and secondary sludges from wastewater treatment processes) is continuously increasing, not only through the installation of new sanitation facilities in developing countries, but also through intensified wastewater treatment in developed countries (Le Blanc *et al*., 2008) [20].

Municipal solid waste

Municipal waste-generation rates vary with location and have been shown to correlate with average income. MSW is broadly defined as wastes originating from residential (i.e., product packaging, newspapers, magazines, food waste, grass clippings, yard waste and recyclables), institutional (i.e., schools and prisons), and commercial sources (*i.e*., restaurants). Construction and demolition debris and combustion ash are not generally characterized as MSW. For the purposes of this review, industrial and municipal wastewaters are not classified as MSW. Thermochemical processing of MSW has the potential to reduce GHG emissions associated with current waste management techniques (*i.e*., landfilling and composting), while producing value-added products, such as activated carbon.

Chemical composition of Hydrochar

The hydrochar has a higher proportion of carbon (C) and lower proportion of oxygen (O). It is mainly the result of dehydration and decarboxylation processes, which remove hydrogen (H) and O from the solid in the form of H_2O and CO_2 (Sun *et al*., 2014) [35]. In addition, the type of C found in hydrochar is also different from that of the raw biomass. Hydrochar contains more aromatic C than the raw biomass because dehydration and decarboxylation during HTC leads to the formation of aromatic C in the biomass (Libra *et al.,* 2011) [22]. Many types of hydrochar may have lower ash content than biomass because the inorganic elements are released during biomass degradation and dissolved in the processing liquid during HTC (Fuertes *et al.,* 2010) [9]. Sulfur (S) and nitrogen (N) contents are also lower in hydrochar because the nitrogen and sulfur oxides formed during HTC are dissolved in the processing liquid (He *et al.,* 2013) [11].

Properties of Hydrochar

Hydrochar is having lower C and ash content. It's a desirable character when it is used as a fuel. Although high surface area and pore volumes are correlated with increased sorption ability, the lower ash content of hydrochar means that it may be a more suitable precursor for activated carbon. Hydrochar may be used to decrease the pH of soils with high basicity.

Potential uses of hydrochar

1. Soil amendment and a nutrient source

It promotes sequestration and reduces green house gas emission and helps to mitigate global warming. Although most types of hydrochars, especially the ones derived from plant biomass, have a low nutrient content and cannot be used as a fertilizer by itself, it may be added to soil to enhance the effects of fertilizer by reducing the amount of fertilizer that is lost through surface run-off (Beck *et al*., 2011) [2]. The nutrients are sorbed into the pores on the surface of the char material, which then slowly release the nutrients into the soil over time for plant uptake (Yao *et al.*, 2013) [42]. In general, chars from the wet and dry pyrolysis of waste feedstocks retain high levels of calcium, potassium and phosphorous. This was seen in animal manures (Ro *et al*., 2010 and Kim *et al.*, 2009) [30, 15] and with sewage sludge (Hossain *et al.*2010) [12]. In HTC, dissolution of water-soluble minerals can be significant; however, the nutrient content will also depend on the technique for dewatering the solid conversion product. aHydrochar will affect soil properties based on the same basic principles, 'soil physics and chemistry', 'water', 'nutrients' and 'microbial activity'. It will very likely reduce the tensile strength, increase the hydraulic conductivity and enhance the soil WHC. It can theoretically increase the CEC of soils, improving 'nutrients.' Hydrochars often exhibit higher labile carbon fractions such as carbohydrates and carboxylates than biochars (Cao *et al.*, 2011) [5]. Labile carbon in hydrochars could thus initially induce nitrogen deficiency by nitrogen immobilization, particularly in chars from nitrogen-poor feedstock. Conversely, the large labile carbon fraction may initiate microbial growth and stimulate soil-char nutrient cycling after a lag phase (Kolb *et al*., 2009) [16]. With freshly produced hydrochars mixed with soil, we observed a preferential growth of fungi (basidiomycetes); Rillig *et al.*(2010) [29] recently described a strong stimulation of arbuscular mycorrhizal root colonization. Hence, depending on the type of fungus it may thus be possible to create purpose-optimized 'designer hydrochars' that, for example, stimulate symbiotic fungi to help establish young trees after planting. However, experimental data are currently lacking. Hydrochar, with its lower production temperature, may retain more nutrients in a plant-available form, either in the hydrochar itself, or in the aqueous phase. In the face of declining phosphorus deposits worldwide, the conservation of plant nutrients from residual materials for agricultural use may become one of the most interesting features of char in soil applications. In the current quest for the most beneficial SOC and fertility increasing management practices (Lal, 2004) [17], it may be highly promising to consider SOC increasing soil additives such as chars (Lal, 2009) [18].

Soil application of hydrochar

The hydrochar is wet when it leaves its production process; therefore, it may be easier to apply to soils without dust losses. However, it may be necessary to find a 'water content window' (probably between 10 and 15% water content) where the hydrochar is neither at risk of dust formation nor quick fungal degradation. To date, no guidelines or experiences towards the water content of hydrochar for storage, handling and field application exist.

2. Water retension

Adding hydrochar to soil increases the amount of water that can be retained by the soil, although this improvement is observed only in sandy soils. Soils with high AWC such as those with high organic matter content did not show as dramatic improvement in their physical properties. The addition of hydrochar to soil decreases the bulk density of soil and increases total pore volume, allowing more water to be retained by soil (Abel *et al.*, 2013) [1].

3. Energy from hydrochar

The HTC can be used to produce gas, liquid, and solid fuels from biomass for energy purpose (Libra *et al.,* 2011) [22]. Hydrochar thus can be used directly as a solid fuel that can be burned for energy.

4. Low cost adsorbent

Hydrochar has been found to be a low-cost adsorbent for contaminants in aqueous solutions, and a range of sorption ability has been found for it.

5. Heavy metal removal

The modifying hydrochars with chemicals was shown to improve their sorptive abilities for a variety of heavy metals (Spataru *et al*., 2016) [33].The saw dust hydrochar were found to be effective for sorption of cadmium in aqueous solutions.

6. Organic pollutant removal

Hydrochar has been tested for its ability to adsorb organics ranging from dyes, pharmaceuticals, and pesticides (Fernandez *et al*., 2015) [8].

7. Pathogen removal

Most studies on the usage of hydrochar for contaminant remediation are conducted on organics and heavy metals, although a few have been conducted on pathogens (Chung *et al.*, 2015) [6].

8. Generation of nano structured materials

The HTC process allows the generation of a variety of nanostructured carbon materials designed to fulfill a specific function. The structure, size and functionality of the hydrochar can be varied by changing the carbonization time, feedstock type and concentration, as well as by using additives and stabilizers. Soluble, nonstructural carbohydrates produce micrometer-sized, spherically shaped particles with numerous polar oxygenated functionalities from the original carbohydrate or additives. The presence of such surface groups offers the possibility of further functionalization and makes the materials more hydrophilic and highly dispersible in water (Titirici *et al*., 2008) [39]. Through the choice of feedstock or addition of certain compounds (so-called 'doping'), the type of functional groups on the hydrochar can be controlled. For biomass without structural crystalline cellulose scaffolding, hydrophilic and water-dispersible carbonaceous spherical nano particles in the size range of 20-200 nm were obtained (Titirici *et al*., 2007) [40]. Such carbon nano particles might represent an alternative to the current carbon blacks, or end up in novel applications, such as reinforcement in concrete or pavements. For biomass made from crystalline cellulose, an 'inverted' structure was found, with the carbon being the continuous phase, penetrated by a sponge-like continuous system of nanopores (representing the majority volume). In addition, these products are hydrophilic owing to the presence of approximately 20 weight% functional oxygenated groups, and can be easily wetted with water. Such structures are ideal for water binding, capillarity, and ion exchange (Titirici *et al*., 2007) [40].

Coclusion

The hydrochar and its derivatives are promising materials that has huge potential to be used in a range of applications. So it can be beneficial for agriculture, medical, technological as well as industrial fields. Carbonization of biomass residue and waste materials has great potential to become an environmentally sound conversion process for the production of a wide variety of products. However, process and product developments are still in their infancy for these feedstocks, and, accordingly, there are many aspects that require additional research. Filling the current research gaps is necessary before the process can be designed and exploited

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