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Hydrochars Produced By Hydrothermal Carbonization Of Lower Value And Wet Biomass Used For Soil Amendment To Sustainable Agriculture: A Review

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--***ABSTRACT***--
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Hydrochar can be used in many application such as of soil amendment, energy purposes, activated carbon adsorbent and nanostructured materials. Hydrochar has high stability buried in the soil, that can stand hundred or thousand years buried as a carbon sequestration. Additional hydroochar in soil gave many benefits that increased the crop yield. Hydrochar is porous material that absorb minerals and retain water, for sustainability supply of water. Addition hydrochar to the soil reduced the need of chemical fertilizer, resulting in reduced emissions from fertilizer production. Hydrochar increases the soil microbial life. Hydrochar retain of nitrogen, it will reduce nitrous oxide emissions. Turning agricultural waste into hydrochar, it will reduce methane generation by the natural decomposition of the waste. Hydrochar can neutralize the soil, but if the pH of soil already high addition of hydrochar increased the soil pH. Hydrochar contains a lot of nutrients that benefit to the crops. The surface hydrochar structure are not built perfectly to porous shape. It seems to be spon that retain water. If hydrochar added to sandy soil, it will help the retain of water, if hydrochar added to the clay soil, it will help to reduce the soil compaction. The porosity of hydrochar as a good place for microbial growth, such as rhizobia and mycorhizal those are microbials for nitrogen fixation. Paddy rice production also increased when hydrochar added to the soil. Hydrochar have negative effects in the begin of addition, there are any changing of pH soil, hydrochar still has volatile matter, and suddenly changing of nutrients concentration.

Key words*: hydrochar, soil, adsorb, nutrient, crop yield*

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I. INTRODUCTION

Hydrothermal carbonization is promising technology for converting high-moisture waste biomass into residual solid rich carbon that is called hydrochar. Hydrochar differentiates from biochar, because it is produced in a aqueous environment, at lower temperatures and longer retention times. Hydrochars were obtained at 200 ^{o}C and 300 ^{o}C and residence times ranging from 2 to 16 h.[1]

The general sources of biomass are agricultural (food grain, straw, seed hulls, corn stalks, cattle manure, and poultry waste), forest (woody waste, bark or wood, trees, mill scrap, and sawdust), municipal (paper waste, sewage sludge, and food waste), energy (swith grass, willow, poplars, corn, canola, soybean, and other plant oils), and biological (animal waste, biological waste, and aquatic species).[2] Wetland biomass also converted into hydrochar in hydrothermal carbonization, such as reed, typha, juncus and carex,[3] rice husk.[1] Biomass can be broadly classified into three groups: terrestrial biomass (forest, grassed, crops), aquatic biomass (algae, marine plants), and waste biomass (municipal solid waste, agricultural waste, forestry residue).[4]

Environmental issues, sustainability, declining fossil fuels, and energy security concerns have led the world to explore alternative, clean, cheap and renewable energy resources. Biomass is one of the options for renewable and sustainable energy, as it is the world's fourth largest energy source worldwide following coal, oil and natural gas. Biomass being abundant, carbon natural, environmentally benign, sustainable, and a potential renewable to replace the fossil fuels.

Hydrothermal conversion is a thermo-chemical conversion technique which uses liquid sub-critical water as a reaction medium for conversion of wet biomass and waste stream. For wet biomass conversion, processes which do not require water evaporation are desired. Hydrothermal carbonization (HTC) is a thermo-chemical pretreatment process is treated under hot compressed water to produce hydrochar. Hydrochar is a stable, hydrophobic, friable solid product.[5] The complex reaction chemistry of HTC offers a huge potential for producing a variety of products, from fuel to super capacitors, from carbon nanosphere too low cost adsorbents, and fertilizers to soil amenders.

Hydrothermal carbonization is a thermochemical process for the pretreatment of high moisture content biomass under hot compressed water, making it applicable for diversified purposes. It is performed in a closed reactor at a temperature range of 180 – 280 ^oC under pressure of 2-6 MPa for 5 to 240 mins.[6] The primary product of hydrothermal carbonization is a coal-like product called hydrochar and also produces aqueous, and gas phases.[7] The mechanism for this process mainly entails decarboxylation, dehydration and polymerization.[8] The water content in the wet biomass is an excellent solvent and reaction medium. Water can act as a base as well as an acid at temperature between 200 ^oC and 280 ^oC because its ionic product is maximized. At this temperatures the dielectric constant of water is reduced so it acts more like a nonpolar solvent .[9]

The advantage of hydrothermal carbonization is that, without an energy-intensive drying method, the biomass can be transformed to carbonaceous solids. During the HTC phase, toxic organic molecules and residual micro pollutants are also degraded.[10] Reaction temperature, pressure, and time are the important factors that influences the process of hydrothermal carbonization, whereas the type of biomass used affects the products of HTC.

Hydrothermal carbonization is understood to be coalification of organic material in aqueous phase under applied high temperature and pressure. Hydrothermal carbonization is based on a single chemical process, namely the splitting of water from carbohydrate (dehydration). HTC is a mimicry of the natural coal formation.[11]

$$\underset{\text{Carbo Hydrate}}{C_6H_{12}O_6} \xrightarrow{\text{HTC}} \underset{\text{HTC-biochar}}{C_6H_2O} + \underset{\text{water}}{5\ H_2O} + \underset{\text{Heat}}{-950\ \text{kj/mol}}$$

A simple energy balance of the process already indicates that it is exothermic, during the reaction, energy is released.[12]

A further advantage of HTC is that the liquid phase can be separated considerably more efficiently from HTC-biochar than from original biomass. Reaction takes place in the HTL is hydrolysis and further reaction of dehydration and decarboxylation.[5] Several reviews of the HTC process show that biomass with a low calorific value and high water content can be upgraded to a valuable carbon-rich solid, lignite-like fuel.[8,13] Wetland biomass has great potential for the production of HTC-char.[3] Hydrochars produced from HTC of biomass have many application such as soil amendment, slow-release fertilizers, adsorbents, and energy sources.[14] Hydrochar has higher carbon content, heating value, and energy density and the lower inorganic matter, improved hydrophobicity, and modified micro cryatalline structure and morphology as compared to raw biomass could lead to the broad application of hydrochar in various fields, including the energy, catalyst, adsorbent and medical field.[15,16]

II. PROCESSES AND PRODUCTS OF HTC

HTC products depend on the type of biomass, temperature, pressure, catalysts used, residents time of reaction and biomass water ratio. Utilization of biomass for production of biofuels reduces greenhouse gas emissions, improves air quality, and helps to achieve energy independences as well as energy security.[17] The advantages of hydrothermal carbonization such as:

1. Low carbonization temperature
2. Aqueous phase system
3. Inexpensive renewable precursors (eq. carbohydrate, their hydration derivatives or raw biomass) used as carbon sources.
4. Simple one pot ability to incorporate other important chemical structure such as nanoparticles or functional monomers.
5. Easy access to material with useful, easily transformable functional surface (eq. hydroxyl, carbonyl, carboxyl, lactone, and olefinic groups), allowing simple post-chemical modification (eq. functional polymers).

The higher carbon content, heating value, and energy density an inorganic matter, the lower inorganic matter, improved hydrophobicity, and modified microcrystalline structure and morphology as compared to raw biomass could lead to the broad application of hydrochar in various field, including the energy, catalyst, and medical fields.[15,18]

II.1 Temperature

Operating temperature is the primary control parameter of the HTC process. To investigate the effect of reaction temperature on the bio-oil yield and residual solid like carbon or hydrochar, experimental runs are performed at different temperatures. The yield bio-oil strongly depends on the reaction temperature, the yield of bio-oil is increased with increasing reaction temperature and then decreased with a further increasing temperature.[19] It is evident that the solid yield decreased by 2-5% as the reaction temperature increased from 180 ^{o}C to 200 ^{o}C. On the other hand , the liquid yield continued to increase by 2-6% with the increased in the reaction temperature from 180 ^{o}C to 200 ^{o}C.[4] Like the solid yields, the mass yield of the hydrochar, reduced as the temperature was increased. A higher temperature in the HTC process triggers the decomposition of different biomass component, causing a lower solid yield and higher liquid yield.[20]

It is evident that the solid yield decreased by 2-5% as the temperature increased from 180 to 200 ^{o}C, the liquid yield continued to increase by 2-6%.[4] The higher heating value (HHV) of the hydrochar samples increased with an increase in reaction temperature and time. Decrease in volatile matter caused by chemical dehydration and decarboxylation reaction, an increase in carbon content resulted in hydrochar with higher heating value.[21, 22]

Colloidal carbon sphere were usually generated by the HTC of glucose as a temperatures of 170-260 ^{o}C. The minimum temperature for the hydrothermal carbon formation from glucose was 160 ^{o}C, and HTC did not take place below 160 ^{o}C, resulting in almost no solid residue.[23] At 180 ^{o}C HTC carbons formed were rich in carbonyl functionalities.[24] Increasing the HTC temperature led to hydrothermal carbons with a higher degree of aromatization. HTC of carbon spheres, which were derived from 0.5 mol/L pure glucose solution for 4.5 h at different temperatures of 170, 180, 190, 210, and 230 ^{o}C, had diameters of about o.4, 0.44, 1.2, 1.2 and 1.4 μm, respectively.[23] Above 280 ^{o}C, only a very small fraction of carbon microspheres higher than 260 ^{o}C.[25] The processing temperature affected both the average diameter of carbonaceous particles and the size distribution. Higher temperatures led to uniform particle diameter and a more homogeneous average size.[24] When temperature was relatively low, glucose decomposed slowly. New nuclei may just form while the former nuclei already started carbonization, resulting in different growing time. So, under lower temperature, the size distribution was wider. When temperature was relatively high, glucose can decompose completely very fast. All nuclei occurred at same time, which led to a more homogeneous average size. But if the processing temperature was too high, formed microsphere had a risk to fuse together and become larger. Increase of temperature resulted the residual solid/hydrochar was decreased.[1] The hydrochar obtained at 300 ^{o}C and 6 hours resident times showed a predicted higher heating value of 17.8 MJ/kg.

II.2 Residence Time

Exact residence time cannot be determined since reaction rates remained largely unknown, but typical published experiment residence time varied between 1 and 72 h.[8] A longer residence time led to higher reaction severity and less organic loss in the sugar solution. When HTC were carried out at a constant concentration of 0.5 mol /L glucose and 160 ^{o}C, as the residence time increased from 2 to 4,6,8 and 10 h, the diameters grew from 200 to 500, 800, 1100 and 1500 nm.[26] If the reaction was too long, the produced carbon spheres fused, giving rise to particles with irregular shapes.[27]

The HTC process with residence was observed by Titirici.[28] HTC experiments were carried out at a constant concentration of 10 wt % glucose and 180 ^{o}C, during the first 2 h, no solid residues were observed, and glucose was dehydrated and decomposed into small soluble organic molecules. After 4 h, the color of the solution became dark orange suggesting that a polymerization /aromatization occurred, called polymerization step, past 5 h the first solid precipitated out of the aqueous solution. After 8 h, a brown colloidal dispersion was formed. The black-brown solid formed spherically shaped particles of around 500 nm, aggregated together in 12 h. The growth process kept continuing, and the particle size increased to around 1.5 μm until all HMFs have been consumed.

III. HYDROCHAR AS A SOIL AMENDMENT

III.1 Hydrochar properties

Hydrochar is brown carbon material produced from the decomposition of plant-derived organic matter in a low oxygen environment to release energy-rich gases which are then used for producing liquid fuels.[29] The carbon atoms in hydrochar molecules are strongly bound to one another, and this makes hydrochar resistant to attack and decomposition by micro-organisms. The carbon in most organic matter is rapidly (between 1 and 5 years) returned to the atmosphere as CO_2 through respiration. Aromatic black carbon persist in the environment longer than any other form of organic carbon. Hydrochar is typically older than any other form of carbon in soils.[30] Despite this high level of resistance we know that hydrochar will ultimately be mineralized to CO_2; otherwise, soil organic matter would be dominated by hydrochar accumulated over geological time scales.[31] Very little is known about the haft life of hydrochar for two reasons, first, the recalcitrance of hydrochar greatly depends on a multitude of factors, including the type of biomass to be processed, the production condition, soil properties and climate.[32] Some hydrochar may decompose relatively rapidly in soils, while others persist for millennia.

Hydrothermal carbonization (HTC) is great importance because it can generate chars that are rich in organic carbon from biomass with high water content; these chars have the potential to be used in a wide range of applications, such as energy purposes, soil amendment processes, also producing activated carbon adsorbents, catalysts, and nanostructured materials.[6] The HTC-chars were found to contain around 53 to 60% of the carbon originally present in the biomass,[3] and HHV value of 17.8 MJ/kg.[1] HTC process to convert biomass that uses water as the reaction medium, which does not have any toxicity and categorizes the method as an environmentally friendly process. The solid product obtained by this process is commonly called hydrochar. Hydrochars are mainly used as soil amendments due to their high content of phosphorus and nitrogen.[33]

III.2 Nutrient retention

Nutrients are retained in soil and remain available to plants mainly by adsorption to minerals and organic matter. While we are usually unable to change the mineralogy of a given soil, we can change the amount of soil organic matter. Applying hydrochar to soil can have multiple benefits, such as the carbon sinks and soil additives to increase plant productivity. Hydrochar is used as an amendment in agricultural soils due to many interesting characteristic, including high carbon content, high pH, high stability, high porosity, and high surface area. It was reported that hydrochar can improve soil's chemical, physical and biological properties, resulted increasing crop productivity.[34]

Hydrochar sinks in the soil can be amendment the soil. Hydrochar stayed in the soil longer compared to the compost resulted to the anaerobic digestion.[35] In the soil hydrochar have function of water retention, to retain nutrition from erosion, increase the microbial activities, and the resulting is increasing the growth of plantation.[36,37] The growth biomass plantation increased 189% in the addition of hydrochar of 23.2 ton per hectar. Paddy rice production also increased when hydrochar added to the soil.[38] Hydrochar have negative effects in the begin of addition, there are any changing of pH soil, hydrochar still has volatile matter, and suddenly changing of nutrients concentration.[39] The qualities of hydrochar include the capacity of adsorbs, the capacity of ion exchange, and has little movable ingredient such as tar, resin, and volatile. In the process adsorption capacity reduces, and ion exchange capacity increased.[40]

Hydrochar is a desirable soil material in many locations due to its ability to attract and retain water. This is possible because of its porous structure and high surface area. As a result, nutrients, phosphorus, and agrochemical are retained for the plant benefit. Plants therefore, are healthier and fertilizers leach less into surface or ground water. Addition of hydrochar increased the PO_4-P and K contents. Hydrochar addition did not inhibit seed germination at any rate, and showed no significant impact on plant growth in any soil, despite improved soil conditions.[41]

III.3 The benefits of hydrochar to increase the fertility of soil

Hydrochar offers potential as a soil amendment and can be used to improve various soil properties including physical, chemical and biological properties. Hydrochar added to soil Increase the soil pH. The pH of hydrochar around 9, if the soil pH is acidic, hydrochar can neutralize the soil. But if the pH of soil already high addition of hydrochar increased the soil pH. Hydrochar added of nutrients to the soil. Hydrochar contain a lot of nutrients that benefit to the crops, but nutrient in the hydrochar can stands in short time. After hydrochar wash out with water the nutrients in the hydrochar decrease and will disappear. Hydrochar produced from pig manure a lot of contain nitrogen and heavy metal such as Cu, Zn, Cr, and As.[42] Hydrochar produced from sewage sludge contain phosphorous.[43]

The hydrochar stable in the soil for a hundred years. Hydrochar has low density and porous materials. It's seems to be spoon that can retain water, water can deliver in the dry season. If hydrochar added to sandy soil, hydrochar will help the retain of water, if hydrochar added to the clay soil, hyochar will help to reduce the soil compaction.[35,44] The porosity of hydrochar as a good place for microbial growth, such as *rhizobia* and *mycrorhizal*, those are microbials for nitrogen fixation.[45] Hydrochar more stable than compost or animal waste.[46] Hydrochar improve soil fertility by increasing microbial activity, nutrient availability, and reducing alumonium toxicity. Hydrochar can help retain nutrients in the soil due its charged surface and high surface area which allow it to adsorb nutrients like nitrogen, phosphorus, and carbon.[47]

Additional effects from adding hydrochar to soil can further reduce greenhouse gas emissions and enhance carbon storage in soil.

- Hydrochar reduces the need for fertilizer, resulting in reduced emissions from fertilizer production.
- Hydrochar increases soil microbial life, resulting in more carbon storage in soil.
- Because Hydrochar retain nitrogen, emissions of nitrous oxide may be reduced

• Turning agricultural waste into hydrochar reduced methane generated by the natural decomposition of the waste.

There are additional pathways to reduced emissions that may result when hydrochar is added to soil. These include savings in energy and emissions from fertilizer production as the need for fertilizer is reduced and potential reductions in methane emissions when biomass is charred rather than allowed to decompose. The influence of hydrochar amendment reduced the greenhouse gas emissions.[48]

Hydrochar addition evidently increased rice yield in low fertility soils and decreased greenhouse gas emissions.[49] Hydrochar from sawdust and straw could increase rice yield and nitrogen uptake.[50] Hydrochar exhibits biological activity and high content in organic C, Ca and other micronutrients Mg,Zn,Cu,Na,Cl.[51] Maize developed was better in anthropogenic soil compared to soil that received hydrochar.[52] Hydrochar is expected to adsorb P and N efficiently, due to its great cation exchange capacity. Hydrochar has the maximum N adsorption of 11.73 mg/g, but it showed limited PO_4-P adsorption.[53]

IV. CONCLUSION

Converting lower value and wet biomass into hydrochar benefits to environmental issue, sustainability, energy security concern, prepared soil amendment and also help mitigation of climate change. Biomass being abundant, carbon neutral, environmentally benign, sustainability, and potential renewable to replace the fossil fuels. There are many sources of biomass that spread out on the surface of the earth, can be classified into three groups; terrestrial, aquatic and biomass waste. Hydrothermal carbonization (HTC) is a thermo-chemical pretreatment process that is treated under hot compressed water to produce hydrochar. The hydrochar products qualities are depend on the raw materials used and operation conditions of HTC.

Applying hydrochar to soil can have multiple benefits, such as carbon sinks and soil additive to increase crops productivity. Hydrochars offers potential as a soil amendment and can be used to improve soil properties. Physical properties it's capacity of water holding and soil structure. Chemical properties it's included pH buffering and the capacity to hold exchangeable cations. Biological properties it's included microbial activity and carbon and nutrient cycling. Additional hydrochar increased crops yield and reduced greenhouse gas emissions.

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