Hydrothermal Carbonization (HTC) Hydrochar/Coal: A Review

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Abstract - *Hydrothermal carbonization (HTC), as a thermochemical process for delivering important hydrochar from different materials have acquired a ton consideration lately. The process converts biomass into a coal-like material called HTC coal by giving high temperature in a suspension with water under pressure to biomass for a few hours. This process opens up the field for utilizing distinctive feedstock to substrates with a high moisture content, for example, municipal biowaste, wet agricultural residues, fecal sludge, and so forth while pyrolysis then again is confined to biomass with dry water content. A few materials having high carbon substance can be utilized in HTC, having extraordinary application like adsorbent, catalyst support, fuel for energy preservation and now is likewise significant interest as precursors for activated carbons. Hydrothermal treatment of biomass and waste will be the ideal and supportable arrangement and furthermore the need of great importance for energy and resource recovery. A portion of the uses of activated carbon prepared from hydrochar are ecological remediation, energy stockpiling, resource recovery, and an incredible interest for activated carbon because of their exceptional properties like high density of oxygenated useful gatherings (OFGs), low degree of condensation and are effectively tunable morphological size with desired and explicit characteristics. This review is all about the application and properties of HTC coal and hydrochar. We have integrated recent advances made for the energy recovery and production of activated carbon from hydrochar, the catalysts, morphology, mechanisms, different characteristics and operating parameters are reviewed. Furthermore, the challenges and future scope for this technology and research gaps are also involved.*

Key Words: **Hydrothermal Carbonisation, hydrochar, biochar, activated carbon, coal, sustainability, biomass, waste to energy.**

1. INTRODUCTION

Energy demand keeps on expanding rapidly as the population of the world grows. The current world population of 7.5 billion is estimated to reach nearly 10.3 billion in 2040 while energy demand is assessed to reach 42 quadrillion BTU in 2040 [7]. It is a huge challenge for the current fossil energy technologies as well as the renewable and sustainable resources to fulfill such an extent of energy demand and further not contributing to global warming. In India, coal is the bulk primary energy source having 56.90% share equivalent to 452.2 Mtoe in 2018. On the other hand, Biomass is the biggest and most bountiful wellspring of renewable energy source. It contributes zero to net negative greenhouse gas (GHG) emission as plants take carbon dioxide during its growth [7]. Therefore, a less polluting coal produced by burning biomass will give a solution to this as HTC technology emits zero carbon dioxide and zero GHG. The only challenge is that biomass is wet and has is seasonally available in bulk. The technology will pre-treat the biomass for producing coal with higher density and hydrophobic feedstock which will be compatible for burning as a fuel.

Biomass, a source for sustainable development as it is recyclable and also present abundantly on the earth, can play numerous roles to replace some non-renewable sources for producing energy, carbon sequestration, and essential for producing hydrochar and activated carbon [3]. The hydrochar produced by hydrothermal carbonization of biomass has received great attention due to its attractive characteristics such as adsorption, bio-imaging, catalysis, activated carbon synthesis, [3] etc. It offers solution for solid waste management, reduction in cost of raw materials and the properties of the final product can be tailored for various applications [3]. The coal obtained is easy to handle with good dewatering properties and high calorific value when dried [44].

2. HYDROTHERMAL CARBONIZATION (HTC)

Biomass, as a non-fossil-based, feedstock has applications in numerous ventures like sustainable power sources, chemicals, farming/agriculture and pharmaceutical products. There are a few articles on thermo-chemical conversion process of biomass which refer to that gasification or direct ignition of biomass doesn't give fulfilling results attributable to properties of biomass, for example, oxygen and high moisture content. There are a few techniques for biomass pre-treatment to lessen moisture content, like torrefaction. The interaction of torrefaction produces carbonaceous material generally to be utilized in thermo-chemical processes. The limits of these techniques, for example, high moisture substance of fresh manure, leaves, organic waste, industrial waste and sewage slime from municipal sewage treatment plant, influence the effectiveness and operation cost. In a developing country like India, the measure of human waste that is untreated dung and fecal sludge from wastewater treatment processes is expanding persistently through sanitation [46].

Hydrothermal carbonization of biomass is a promising method as a solution for pre-treatment of biomass with high moisture content due to its high dewatering properties. The delivered material from HTC process, called hydrochar, is like brown coal with its elemental composition, size tunable characteristics and calorific value [19]. HTC coal can be co-fired in conventional coal plants as it has similar chemical composition as natural coal, it can be moreover can be mono-fired in combined heat and power (CHP) biomass plants [19]. The range of feedstocks fit for use as solid fuels is increased, such as sewage sludge, wet animal manure, and organic municipal solid waste as it can process wet feedstocks without energy intensive pre-drying processes. It can easily process biomass with a water content of 75-90% [19]. According to Reza et al. and Liu et al. HTC coal will in general be more positive for burning than raw biomass because of decreased slagging and fouling just as expanded most extreme weight reduction rates, higher ignition temperatures and raised combustion temperature regions [19]. HTC, for specific feedstocks can be much more appropriate for energy recuperation than anaerobic digestion [19].

2.1. Hydrothermal carbonization process

The process was explored by Friedrich Bergius in 1913 as a mean to simulate the natural coalification of organic matter in the laboratory [2,44]. The time taken naturally for coal formation obtained from decomposition of plant matter was reduced by laboratory simulation with a high process temperature, and thereby accelerating the kinetics of the chemical reactions [44]. Technically, HTC is a chemical process that converts the wet biomass in less than 12 hours of the operation into a material similar to brown coal called hydrochar. Among other thermal methods, HTC offers significant benefits for biomass conversion, for example, use of less energy for pre-treatment or drying process, high conversion efficiency, and relatively low operating temperature and cost. It operates with high moisture content biomass suspended in a pressure vessel under temperature of 180°C to 250°C and pressure between 15 to 20 bars. Also, it is an exothermic process. From the experiments we can conclude that during the carbonization process, maintaining the reactor temperature, the energy consumption is significantly low attributable to the heat emitted from the exothermic processes within the reactor [46].

A few examinations show that roughly 75-80% of carbon input was found in the solid phase, around 15-20% was dissolved in liquid phase, and the excess 5% proselytes to gas, essentially carbon dioxide. The liquid phase comprises a great deal of organic components, which are effectively degradable. This cycle is the fate of significant worry for carbon sequestration. The mass equilibrium separation worried to wet and dry biomass shows the carbon recuperation of the cycle around 90%. Additionally, by looking at the energy substance of the info and yield of materials demonstrates 60-90% of the calorific qualities accessible in hydrochar. As indicated by a few investigations, the boundaries impacting the yields of HTC measure are temperature, pressure and residence time. In which temperature has a critical impact, while pressure and residence time are dependent on temperature to enhance the hydrochar of HTC measure. In the underneath table, the impact of boundaries sorted for a few feedstocks is appeared. The outcomes showed that with temperature around 230°C and legitimate residence time, the biomass carbon yield expanded, while the H/C and O/C ratio decreased for each situation in the hydrochar [46].

Table -1: carbon % from HTC (Source: ennomotive.com)

	Solid yield db. %	C%
Biowaste		54.6
HTC 230°C, 4.5h	57	75.2
Food waste		45.7
HTC 250°C, 20h	46	75.2
Sewage sludge		51.8
HTC 230°C, 6h	51	72.6
Wood		50.3
HTC 230°C, 5min	75	56.1

2.2. Activation of Carbon precursor

Hydrothermal carbonization results in effective hydrolysis and dehydration of biomass and a hydrochar with high oxygenated functional group (OFG) content is obtained and can be effectively activated chemically [3]. Activation of suitable precursors results in formation of highly porous activated carbons, such as lignocellulosic biomass whose large surface area facilitates their performance as adsorbents [3]. This characteristic of any adsorbent is extremely desirable for enhanced performance as it facilitates high mass transfer fluxes and catalyst/adsorbate loading [3]. The application and usefulness of activated carbons have been widened due to its tailored porosity and tunable pore size distribution, for example catalysis/electrocatalysis, energy storage in capacitors, multi-sized molecules separation, electrodes and Li-ion batteries, carbon sequestration or hydrogen storage [3]. Activation methods can be briefly divided into two ways (i) physical (or thermal) activation using CO_2 or steam at 800-900 °C and (ii) chemical activation using K_2CO_3, KOH, $ZnCl_2$, citric acid, H_3PO_4, etc. in the range of 450-650 °C [17].

Ana Mestre et al. have investigated the effects and influence of precursor reactivity on the porosity of activated carbons obtained using NaOH and KOH activation [8]. The reactivity of precursors or say the OFG content in the precursor indicates at which extent obtained activated carbon is porous [8]. From recent developments, HTC has gained much importance and attention for carbon recovery due to its potential in producing hydrochar with high OFG content and its use for synthesis of desirable activated carbon [3]. Jain et al. worked with coconut shells as precursor and pre-treated hydrothermally and reported the improved reactivity and improvement in mesopore area by 67% [3,5]. They also reported enhanced growth of OFG on the hydrochar due to use od H_2O_2 and further improved porosity of activated carbons [3,6]. While Falco et al. reported increase in porosity in the carbons when it was hydrothermally carbonized in temperature from 180 to 240°C, furthermore increase in temperature lead to decrease in porosity upon KOH activation [3,10].

2.3. Hydrothermal carbonization of biomass

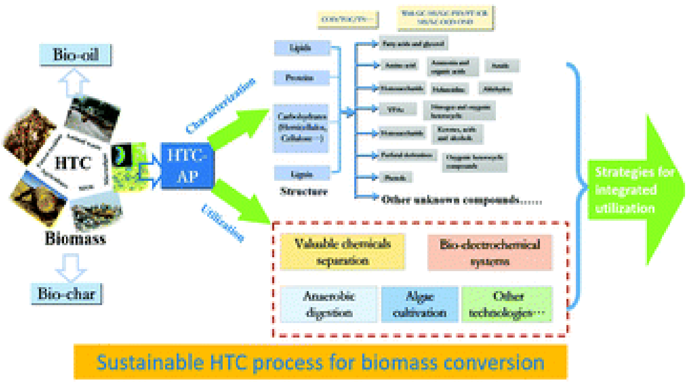

Fig -1: Conversion of biomass (Source: https://doi.org/10.1039/C8GC03957G)

Fig. 1 shows the detailed formation of different products during hydrothermal carbonization. During the process, waster acts as a solvent and also its catalyst that facilitates hydrolysis and cleavage of lignocellulosic biomass and at constant temperatures water possesses high ionization which is responsible for hydrolysis of organics and can be catalysed by acids and bases [3,18,27]. Various organic acids such as acetic, levulinic, formic and lactic acids are formed leading to decrease in pH during the process, promoting hydrolysis and decomposition of oligomers and monomers to smaller fragments. Titirici et al. investigated that the conversion of complex biomass under mild temperature conditions such as 200°C for 16h to hydrochar are chemically similar to peat or lignite depending on temperature and time [3,28]. Berge et al. investigated about the conversion of municipal waste to hydrochar and its characteristics and feasibility for large scale application [3,34]. During the process, hydrothermal liquefaction occurs in which at temperature up to 400°C with the use of catalyst, more liquid hydrocarbons and more gas is formed in the autoclave. HTC has drawn attention due to its simplicity and ability to provide hydrochar with high concentration of oxygenated functional groups (OFG) for conversion of biomass [3].

2.4. Hydrothermal carbonization application

A variety of non-traditional biomass can be processed in HTC such as human waste, municipal solid waste (MSW), wet animal waste, sewage sludge from treatment plants, and algae. Here are some applications discussed briefly.

1. Human waste/sewage sludge:

According to an article by World Economic Forum, "India's urban areas produce 120,000 tons of fecal sludge on a daily basis." Due to advantage of HTC process producing hydrochar from biomass, without giving any pre-treatment for drying, the conversion raises the carbon content, energy density and declined oxygen content of the biomass. Also, ash content can be decreased significantly by controlling the temperature. This process utilizes the energy of liquid phase in the form of methane during carbonization and the analysis shows that it is biodegradable [46].

2. Pre-treatment:

Pre-treatment, for a large portion of the thermo-synthetic cycles, is needed to annihilate the fibrous part of biomass particles, for example, entrained flow gasification. While, HTC is itself an unprecedented pre-treatment measure that raises the heating value and mechanical properties of biomass, like crushing capacity. Some particular attributes, like high ignition temperature and wide burning scope of the biomass make it fitting for boilers of warming frameworks. [46].

3. Soil amendment:

The hydrochar produced from HTC are potential for carbon sequestration in the soil, increasing the water holding capacity, boost in nutrient retention, and decreasing the greenhouse gas emissions such as CO_2, CH_4, and N_2O [46].

4. Catalyst production:

Hydrogen production was observed several times from the HTC process during catalyst production, attributable to high stability and tunable surface characteristics of hydrochar. Silvia, et.al reported HTC of algae with the point of hydrogen (H_2) production and delivered hydrochar with the catalytic ability that advanced hydrogen generation as well as flooded up phenol development in the liquid phase. Interim, acid production was restricted [46].

3. CONCLUSION & FUTURE SCOPE

Hydrothermal carbonization is an emerging technology for waste management and for production of hydrochar from biomass and has a great potential to become environment friendly and climate amicable process for variety of products. However, there are certain knowledge gaps to be attained deeply for proper application of the final products obtained from HTC. There are several aspects to be investigated before the process can be exploited and designed for production of char for specific applications. A comparative detailed study on different feedstocks used for producing hydrochar with various activating agents will contribute on a great extent to identify different features and variation in characteristics so that appropriate protocols can be developed for activated carbon production for adsorption of various contaminants and pollutants. Furthermore, a study which can provide correlation between surface characteristics and starting material and also variations in hydrothermal parameters giving difference in porosity yield which will further help in designing the HTC treatment process for the better product yield i.e., activated carbon.

Different mineral enrich waste material will give different results compared to others in view point of characteristics and porosity for example the waste enrich of high nitrogen and lignin content will be preferred over activated carbons with lesser mineral content with high porosity and less surface area. While the biomass with calcium and magnesium content will be better for supercapacitor application. Using suitable waste materials for specific energy demands will be met by HTC. At last, this data about portrayal of hydrochar as for end applications will give a manual for the clients as combination of initiated carbons is an exorbitant interaction, along these lines, data in regards to expected properties of carbons will manage us to make right determination for antecedents and will have an effect monetarily. Currently some activating agents such as K_2CO_3, KOH, $ZnCl_2$, H_3PO_4, citric acid, etc., are being used but there is scope for other alternatives which can economical and more efficient.

Also, there is potential that biomass obtained from municipal waste segregated could be taken as precursor and investigate its characteristics and scope of application for meeting energy demands. Converting residue material into hydrochar and providing zero waste residual will achieve less gap between producers, end-users and regulators of hydrochar or activated carbons and create correlation between hydrochar properties, end use application and its environmental impact. There are many experiments ongoing on pilot scale for obtaining char properties for specific applications and its benefits so that it can be replace the commercial activated carbon or char producing residues and less economical.

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