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Carbon Functional Produced By Hydrothermal Carbonization of Wet and Lower Value Biomass. A Review

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ABSTRACT
Hydrothermal carbonization (HTC) is an active area of research in synthesizing carbon-rich materials from low cost and wet biomass. HTC processes is to fulfil the environmental and sustainable organic wastes. Carbon-rich materials have received a great deal of attention because carbon-rich materials were used as raw material for several industrial products, such as adsorbents, catalysts, capacitors, energy storage and solid fuels. Hydrochars produced from HTC havelower surface area and poor morphology properties, that needs another treatment to improve thus properties of the carbon materials. Increased the properties of hydrochars needs activation, especially increase the surface area and pore development.The treatment involved physical and chemical. HTC can synthesis micro-or nano-scale carbon spheres environmentally friendly without employing organic solvents, surfactants, or catalysts. The carbon functional with high surface area will meet the requirement of useful carbon functional. For adsorbent beside have high surface area, appropriate pore size will meet the requirements. It has been possible to create materials with well-defined nanostructures, morphologies and tuneable surfaces. Synthesis of carbon functional is still relies on artful manipulation of synthesis parameters.

Key words: biomass, HTC, carbon functional, activation, surface area

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I. INTODUCTION

Hydrothermal conversion is a thermo-chemical conversion technique which uses liquid sub- and 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.[1]The complex reaction chemistry of HTC offers a huge potential for producing a variety of products, from fuel to super-capacitors, from carbon nano-sphere to low cost adsorbents, from fertilizers to soil amenders.

It is performed in a closed reactor at a temperature range of 180 – 280 ^{o}C under pressure of 2-6 MPa for 5 to 240 mins. [2] The primary product of hydrothermal carbonization is a coal-like product called hydrochar and also produces aqueous, and gas phases.[3] The mechanism for this process mainly entails decarboxylation, dehydration and polymerization.[4] 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 catalysts at temperature between 200^{o}C and 280 ^{o}C because its ionic product is maximized. At this temperatures the dielectric constant of water is reduced so it acts more like a nonpolar solvent.[5]Hydrocharhas further treatment to get quality of a carbon functional.

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).A simple energy balance of this process indicates that it is exothermic, during the reaction energy is released. The detailed nature of these reaction pathways is not well known and depends on the type of feed.[4]During chemical dehydration, the biomass is carbonized significantly by lowering the H/C and O/C ratios. The dehydration of glucose was formulated by Titirici[6],as shown in Fig.1

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{HTC}} \underset{\text{HTC-Biochar}}{C_6H_4O} + \underset{\text{water}}{4\,H_2O} \quad \underset{\text{Heat}}{-1040\ \text{kj/mol}}$$

Figure 1. Simple mechanism of carbohydrate dehydration

Hemicelluloses degrade much faster than cellulose, the activation energy is lower for hemicelluloses than cellulose.[7] Biomass is degraded in HTC resulted three phases, firstly, residual solid is called hydrochar, secondly, liquid phase, thirdly, liquid phase is further degraded into gas.[4] Degradation pattern was proposed by Lucian[8], as shown in Fig.2. Biomass was degraded resulted residual solid, liquid and gas.

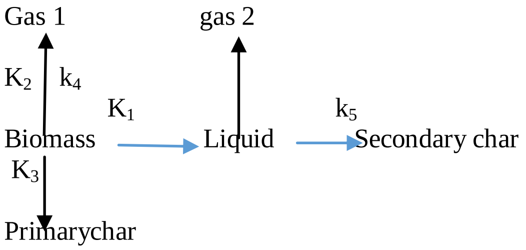

Figure 2. The lumped model used to describe HTC reaction paths.

From the figure 2. The first reaction step is reaction 1. (Biomass → liquid) represents the hydrolysis and dissolution processes.[4] These liquid products can undergo further reaction and form stable liquid compounds or highly reactive intermediates-especially 5-HMF.[4,9] These reactive intermediates can back polymerize producing a solid residue named "secondary char" (reaction 5, Liquid → Secondary char).[10]

II. HTC PROCESSES

II.1. Temperature

The hydrothermal process, temperature is a vital factor as it is a key factor of water properties which initiates an ionic reaction in the subcritical regimes. The reaction mechanism shifts from ionic reactions to free radical reactions in the supercritical region.[11] In the ion led hydrothermal reaction, the increasing temperature changes in viscosity of water, allowing for easy permeation into the porous media, therefore the biomass is further degraded.[4]

Temperatures approaching a definite reaction concentration have a conclusive impact on the hydrolysis reaction of biomass, and the higher temperatures can lead to dehydration, decarboxylation, and condensation simultaneously. At higher temperatures, with adequate time, it may prompt a higher degree of intermediary dissolution and consequent transformation via polymerization and secondary char formation.[12]

Colloidal carbon sphere were usually generated by the HTC of glucose as a temperatures of 170-260 ^oC. The minimum temperature for the hydrothermal carbon formation from glucose was 160 ^oC, and HTC did not take place below 160 ^oC, resulting in almost no silidresidue.[13] At 180 ^oC HTC carbons formed were rich in carbonyl functionalities.[14] 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 ^oC, had diameters of about 0.4, 0.44, 1.2, 1.2 and 1.4 µm, respectively.[13] Above 280 ^oC, only a very small fraction of carbon microspheres higher than 260 ^oC.[15] 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.[14]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.

II.2 Pressure

The hydrothermal pressure impacts to the network of reaction. At a higher pressure, it can be simply determined that both dehydration and decarboxylation as the main general reactions. This outcome has been proven by experiment and demonstrated to lowly effect both the HTC and natural coalification.[16,17] The hydrothermal reaction pressure increases isotropically with the increase in temperature or by adding liquids.

II.3. Residence Time

The residence time of hydrothermal reaction is one of the important factors for carbon-rich materials formation. Exact residence time cannot be determined since reaction rates remained largely unknown, but typical published experiment residence time varied between 1 and 72 h.[4] 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 ^oC, 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.[18] If the reaction was too long, the produced carbon spheres fused, giving rise to particles with irregular shapes.[19]

Exact residence time cannot be given accurately.[20] HTC experiments were carried out at a constant concentration of 10 wt% glucose and 180 °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 colour 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.

II.4. Percursor Concentration

The concentration of glucose increased from 0.5 to 1mol/L, the diameter grew from 1.2 to 1.4 µm, if the HTC experiments were carried out at a constant temperature of 190 °C and dwell time of 4.5 h.[13] When the concentration of sugar increased from 1.5 to 3.0 mol/L, the average diameters in two samples were all 5 µm.[21]

HTC has a wide range of possible sources such as carbohydrate (glucose, fructose, xylose, sucrose, cellulose, and starch),[13] biomass,[4] sewage sludge, animal manure, municipal solid waste,[22] agricultural residues and algae.[9] Carbohydrate have been ideal starting materials for preparing carbon sphere, because they were cheap and favoured in the dehydration process.[23] Under similar operational conditions, the diameters of carbon microspheres depended on the type of saccharides used. The average diameter of carbon microspheres derived from different carbohydrates had a sequence of sucrose > starch > glucose.[13] The acidic condition tended to increase the reaction rate in HTC, because the hydronium ions generated from these acids catalyzed dehydration and further polymerization of HMF.[24] A pH of 1.5 solution could increase glucose destruction.[25]

III. **Hydrothermal Carbonization**

Hydrothermal carbonization of lingo-cellulosic biomass is an environmental process where biomass is treated in hot compressed water. It is a convenient way to convert biomass into carbonaceous materials under moderate conditions. Degradation of biomass waste in HTC resulted three phases such as gas, liquid and residual solid that rich carbon materials.[4] Carbon material produced from HTC is called hydrochar and further treatment to fulfil the requirement as carbon functional, such as carbon microsphere, adsorbent, catalysts and capacitors.[26]

Camellia oleifera shells can be used to produce hydrochars via HTC. Increase the temperature the mass yield of hydrochars decreased.[27] Macadamia nut shell was proceeded in HTC to produce hydrochars. Increase in HTC temperature and residence time decreased the mass yields of hydrochars and increased the HHV value.[28] Wetland biomass was produced by HTC produce carbonaceous materials. They shows that wetland biomass has great potential for the productionof HTC-biochar.[29]

Liqnocellulosic biomass has been a great interest as precursor for the preparation of carbon-rich materials because of their low cost and due to environmental concern.[30]*Cattail* leave also used to produce hydrochar. Increased the temperature and time resulted in the decomposition of hydrochar gradually, increased amorphous carbon and aromatic groups on surface of hydrochar.[31]Hydrochar resulted from HTC process has surface area very low, indicated that porous structure was not develop during treatment.[32]

Nizamuddin[33] produced hydrochar from oil palm shell by HTC resulted surface area 12.6 m^2/g at temperature of 260 °C.Wang[34] produced hydrochar from organic sludge by HTC resulted of surface area from 26.5 to 35.4 m^2/g. Coconut shell was hydrothermally at temperature of 300 – 500 °C, successfully produced a hydrochar-derived adsorbent with 308 m^2/g surface area.[35]Titirici[6] reported that they prepared the carbonaceous nanostructures using plant materials. They found that the present of metal ion can effectively accelerate the hydrothermal carbonization process. They have also reported that from soft biomass hydrophilic and water dispersible carbonaceous nanoparticles are formed in the range of 20-200 nm. These particles are in a spherical structure which indicates biomass is first liquefied and then carbonized. The hydrothermal carbonization process not only produces carbonized materials from biomass but also forms useful nanostructures.

III.1. Mechanism of Hydrothermal Carbonization

Information about the fundamentals of the hydrothermal carbonization model system have been studied using model carbohydrate precursors (e.q. D-Xylose and D-Glucose) and their decomposition products (e.q. furfural and HMF).[36] It was demonstrated that under hydrothermal conditions all hexose become sugars, regardless of their complexity, degrade to a HMF intermediate, which finally condenses to a carbon-like materials having similar morphologies and the same chemical and structural composition, independent of the starting precursor. By contrast, D-xylose dehydrates to furfural, which in turn reacts to provide carbon structures very similar to those obtained from using a pure furfural precursor, which are importantly different from materials derived from the hexose.[37] The hydrothermal carbonization reaction essentially proceeds via three important steps:Dehydration of the carbohydrate to HMF or furfural, Polymerization towards polyfurans, and carbonization via further intermolecular dehydration

Hu[38] reported that in direct hydrothermal carbonization biomass compounds were heated in sealed autoclaves in the presence of citric acid at 200 °C for 16 hours. Interestingly they found two types of carbonaceous materials: soft tissues and hard plant tissues. Soft plant tissues were without extended crystalline cellulose scaffolds of spherical carbonaceous nanoparticles of a very small size and porosity. Hard plant tissues are with structural crystalline cellulose scaffolds, however, they can preserve the shape and large scale features on a macro and micro scale; as a result of considerable mass loss, there arises a significant structural change on a nano-scale resulting in a sponge like continuous carbon network with well-defined mesoporous structures.

In the catalytic hydrothermal carbonization process, catalysts are used to accelerate the carbonization process. Recently, Yu[39] reported that the present of metal ions can effectively accelerate hydrothermal carbonization of starch, which reduces the reaction time but also directs the synthesis towards various metal-carbon nano-architectures such as carbon nanocables, nanofibres, and spheres. They also reported that iron ions and iron oxide nanoparticles were shown effectively to improve the hydrothermal process.[6]

IV. ACTIVATED CARBON

Activated carbon have very high porous structure with a large internal surface area around 500-2000 m^2/g and have good adsorption capacities. It has application in removing a wide variety of pollution including organic and inorganic substances from liquid or gas phase.

Physical activation is a process in which the precursor is developed into activated carbon using gases and generally carried out in two steps. Carbonization is the first step which involves conversion of the precursor into carbon, which is generally nonporous. Activation is the second step and involveds contacting char with oxydixing gases such as steam or CO_2 in the temperature range of 600 – 1200 °C. During this reaction disordered carbon atoms are removed, which results in the formation of a well-developed micropore structure.[40]

Chemical activation is a single step process for preparation of activated carbon where carbonization of the precursor in the presence of a chemical agent takes place. Chemical activation involves impregnation of the precursor with chemical such as H_3PO_4, KOH, $ZnCl_2$, and NaOH followed by heating under inert atmosphere at temperatures in the range 450 – 900 °C, depending on the impregnation used. The activating agents function as dehydrating agents have influence the carbonization process by inhibiting tar formation and thereby enhancing carbon yield. This method leads to high micropore volumes and wider micropore sizes. Therefore these materials are preferred for liquid phase application.[41]

The process to employed to increase surface area and porosity in the materials obtained from a carbonized organic precursor is referred to as “activation” and the resulting broad group of materials are referred to as “activated carbon”. Carbon chars, a carbonized organic precursor, usually have a relatively low porosity and their structure consists of elementary crystalline with a large number of interstices between them. The interstices tend to be filled with “disorganized” carbon residues (tars) that block the pore entrances. Activation opens these pores and can also create additional porosity. Varying the carbon precursor and activation conditions allows some control over the resulting porosity, pore size distribution, and the nature of internal surface.

The activation process can be divided into two general categories, thermal and chemical activation. Thermal activation entails the modification of a carbon char by controlled gasification, and is usually carried out at temperature between 700 and 1000 °C in the present of a suitable oxidizing gas (e.q. steam, carbon dioxide, and air). During gasification, the oxidizing atmosphere increases the pore volume and surface area of the material through a controlled carbon “burn-off” and the elimination of volatile pyrolysis products.

Chemical activation is usually carried out at slightly lower temperature(400 – 700 °C) and involves the dehydrating action of certain agents such as phosphoric acid, zinc chloride and potassium hydroxide. Experimentally high surface area materials (> 2500 $m^2\ g^{-1}$) heve been prepared using potassium hydroxide activation technique.[42]

IV.1. Chemical modifications

The introduction of heteroatoms into carbon materials, also known as “doping”, is useful method of altering their physical, electronic and chemical properties. Successful work so far includes the superior performance of doped carbons in applications such as electrode materials for catalysis[43]or energy storage,[44] stationary phases,[45] chemo selective adsorption[46] and many others. The majority of research in this field has focused on nitrogen doping, which is known to induce favourable changes in the carbon materials, e.q. increased conductivity[47] and high activity in the oxygen reduction reaction.[43]

The synthesis of nitrogen doped carbons has been achieved via variety of pathways, such as post treatment of carbon with ammonia,[48] pyrrol,[49] polyacetonitrile[47] or polyaniline[50] as starting compounds. Sulfur is also receiving attention in current carbon materials research. In contrast to nitrogen which is often used to alter electronic properties of the carbon materials, sulfur has been used more for the alteration of physical properties and for applications where its easily polarizable lone pair are importance.

Sulfur doped carbon materials have, for example shown beneficial effects on the selective adsorption of waste metals,[46] and the desulfurylation of crude oil.[51] The synthesis of these sulfur doped materials generally involves the pyrolysis of sulfur containing, polymer based carbons.[52]

Hydrothermal carbonization (HTC) is an attractive alternative for the synthesis of doped carbon materials. Nitrogen doped carbon microsphere were obtained by hydrothermally treating naturally occurring, nitrogen containing compounds, such as glycine,N-acetyl glucosamine or chitosan.[53] Albumin, a glycoprotein was used as structure directing additive in the HTC of glucose to produce nitrogen doped carbon aerogels.[54] In order to extend the possibilities of HTC derived products, it is of interest to investigate the incorporation of other heteroatoms such as sulfur.

Hydrochars produced from HTC has very low of surface area, indicating that porous structure was not development during treatment.[32]Hydrochar was obtained from *chickpea* stalk by HTC method, then activated carbon was synthesized by chemical activation using $ZnCl_2$ activator. The BET surface area of the activated carbon with higher iodine number was determined as 572 m^2/g.[55]Hydrochars derived from hickory wood and peanut hull through HTC were activated with H_3PO_4 and KOH to improve their performance as a volatile organic compound (VOC) adsorbent. The VOC adsorptive capacities of the activated hydrochars (50.57 – 15966 $mg.g^{-1}$) were greater than of the non-activatedhydrochars (15.98 – 25.36 $mg.g^{-1}$).[56]Hydrochar was used to produce activated carbon via phosphoric acid activation. Results showed that the specific surface area and total pore volume of activated carbon were increased to 2192 m^2/g and 1.269 cm^3/g.[57] Activator KOH increased the sorption capacity of hydrochar from 27.8 $mg.g^{-1}$ up to 137 $mg.g^{-1}$.[58]Hydrochars from HTC process activated with KOH increased the good mesoporosity, with a methylene blue number of 385 mg/g, and a well-development micropore structure, with iodine number of 747 mg/g.[59]

IV.2 Thermal modifications

HTC may be classified into two main regimes (1) low temperature regime, which proceeds below 300 °C. Functional carbonaceous are obtained via dehydration and polymerization schemes. (2) high temperature regime which proceeds between 300 °C and 800 °C. HTC in low and high temperature regimes give rise to very different materials. In low HTC results in carbonaceous materials(carbon content of 60wt %) with abundant oxygen-containing functional groups, whereas in high HTC generally results more graphitic structures with high carbon contents.[38]

High HTC carried out under supercritical water conditions. Supercritical fluids have transport properties that similar to those of gas (low viscosity, high diffusivity, low surface tension) but solvating powers similar to those of liquids. Supercritical water has low dielectric constants that are in the range of that for common organic solvents. Supercritical water behaves like a non-polar solvent which can dissolve organic molecules and precipitate salts.[60] This makes it a suitable medium for a wide range of reactions, such as hydrolysis, hydrations, dehydrations and oxidations.[61]

V. NANOCASTING

Porous carbon represent high surface area and high porosity, synthesis still relies on artful manipulation of synthesis parameters and not so much on design principles by which a more detailed adjustment of the properties of the materials was possible in terms of control in surface area, porosity, pore size and so on. More precise manipulation has been demonstrated via “nanocasting” approaches for the synthesis of porous inorganic materials, organic materials and carbon materials.[62]When the templates are used in the synthesis of porous solids, two different modes in which the template can be distinguished, namely soft-templating and hard-templating.

V.1 Soft-templating

Soft templating creates voids in a solid by inclusion of molecular or supramolecular templates species (e.g. surfactants or block copolymers) which accupies a specific void space around which the growing solid phase is built. If afterwards the template is removed, the space is made accessible and a pore system develops. The sizes of the voids can range from the molecular scale, where molecules are used as templates, to the macroscopic scale. The mechanisms by which the pore system develop are diverse. However, it is clear that there needs to be a favourable interaction between the templating species and solid to be template (e.g. hydrogen bonds or ionic interactions).

The two major discoveries in developing porous solids via soft-templating approach are zeolites and mesoporous silica materials. In zeolite synthesis, structure-directing agents are templated with an alumina source and a silica source to form crystalline micro-porous aluminosilicate.[62,63] This is a molecular templating, where one molecular / ion occupies one space and then after template removal generates a pore with diameter at the molecule scale (e.g. 0.1 - 2 nm). The formation mechanism is somewhat controversial and there are several roles of template species suggested:

- The framework forms around the template molecule which determines the shapes and size of the later voids in structure.
- Template species can just be a space filler which occupies the voids between the framework constituents ann thus contributes to the energetic stabilization of a more open structure compared to the denser structure.
- It may control the equilibrium in the synthesis mixture, such as pH value or complexation structure.
- It can pre-organise solution species to favour nucleation of a specific structure.

Synthesis of mesoporous materials such as mesoporous silica involves templating species such as surfactant micelles or block copolymer molecules, whereby the polymers act as true templates, as the Iyotropic ordered phase of those structures essentially directs the pore structure of the final mesoporous materials.

V.2. Hard Templating

Hard templating a pore structure of a preformed rigid porous solid is replicated by an added/ infiltrated liquid or gaseous precursor species. Typically, the precursor can be incorporated into the pores by sorption, phase transition, ion exchange, complex or covalent grafting. Upon heat treatment, the precursors are thermally decomposed and a composite of a template and a forming solid spesies is formed. The hard-template can be then removed mainly by acid etching to give a negative replica of a template structure. This method, in particular, allows the synthesis of different types of structures depending on those of performed porous solids such as mesoporous silica and zeolite and is very versatile.[64]

For example sucrose was used as an efficient carbon precursor and could be completely incorporated into the channels of mesoporous silica templates by a controllable two-step incorporated into the channels of mesoporous silica templates by a controllable two-step impregnation process.

The hard templating method in principle allows precise control of pore volume and pore size, but compared to the soft-templating method, this application approach is technically complicated requiring the synthesis of the inorganic hard-template initially and also a highly acidic solution such as HF for the removal of inorganic templates, making the overall process relatively resource consumptive.

VI. CARBON FUNCTIONAL AND APPLICATION

Functional carbonaceous materials can be produced via dehydration and polymerization reactions in the low-temperature HTC, below 300 ^{o}C. The carbon content is increased during the carbonization phase. HTC appears more appropriate to less-valuable organic residues. HTC with higher temperature and longer time, hydrochar tended to become darker in colour.[65] The content of C element in hydrochar is usually greater than 60%, and the other elements contained in it are mainly H,O,N,S.[66] The hydro-char, rich in carbon, can be utilized as fuel, enrichment, or as an adsorbent or precursor for activated carbon.

Carbon materials have attracted interests as electrode materials for electrochemical capasitors, because their high surface area, electrical conductivity, chemical stability and low cost. Activated carbons produced by different activation processes from various precursors are the most widely used electrodes.[67]The activity in materials science is the development of new materials for many purposes. This includes high-performance materials with specific characteristics, for example employed as electrode materials for lithium-ion batteries and supercapacitors, in fuel cells, and as host materials for hydrogen storage. Carbons have previously been utilized in various electrochemical energy storage system.[68] Materials carbon can be produced by pyrolysis or hydrothermal carbonization.

HTC is a convenient way to convert wet biomass at rather moderate conditions into carbonaceous nanostructure, meso-porous network structure. Among various forms of carbon materials, carbon microspheres (CMSs) have attracted substantial attention due to their particular physical properties, including minimal surface area, controllable sized, and diverse morphologies.[69] Carbonaceous materials have been widely used in diverse industries due to their superior properties such as good electrical, high surface area and porosity, and their specific surface chemistry.[38] Specialty carbon sphere have received growing research attention due to their porous structure,[70] high electrical conductivity,[71] and excellent chemical stability,[72] which exhibit potential application in super-capacitors,[73] catalyst supports,[74] and adsorbents.[27] The physical and chemical properties as well as the structure of formed carbon are affected by both reaction conditions and the feed stock.

Preparing CMSs its depend on the type feedstock, temperature and longer reaction time and precursor sources. Carbon sphere with regular shapes (φ 300 – 1200 nm) were prepared by a simple glucosehydrothermal process.[75] Carbon sphere obtained from hydrothermal carbonization of xylose, glucose, sucrose and pine wood. HTC of xylose showed uniform spherical particles with diameters around 80 μm. While carbon nanospheres obtained from glucose, sucrose and pine-derived saccharides had particle size in the range of 100-150 μm, 300-400 μm, and 50-100 μm, respectively.[76]

Using citric acid is used as a catalyst, Sulistya[77] conducted sucrose as a carbon source found that size of CMSs increased with increasing concentration of citric acid. Concentration of citric acid between 0 and 5wt%, The CMSs size increased from 3.12 to 11.2 μm. Faradilla[78] used nanoscale cellulose as a carbon sources and citric acid as catalyst, they found that without presence of citric acid resulted the biochar lacked several of the spherical dimensions, unfortunately, the stable and high surface area when the hydrochar was rinsed with acetone.

VI.1 Carbon materials for Adsorbents

Pari[79] used cassava and tapioca flour through hydrothermal carbonization and KOH as an activation obtained carbon sphere shape, BET area of 986 m^2/g, and total pore volume 0.57 cc/g. Borax also used for additive, borax could catalytically transform the starch into hydroxymethylfurfural (HMF) and favouring the rapid nucleation and slow growth of particle.[80]

Hydrocharprepared from palm kernel shells by hydrothermal carbonization and activated in nitrogen flow had amesoporous structure with homogeneous pore distribution and the specific surface area of 131 m^2g^{-1}.[81]Hydrochar produced from Grape Seed by hydrothermal carbonization and activated by chemical agents of KOH,$FeCl_3$ and H_3PO_4, resulted with KOH led to highly porous carbons with around 2200 $m^2.g^{-1}$, obtained with $FeCl_3$ (321-417 $m^2.g^{-1}$) and H_3PO_4 (590-654 $m^2.g^{-1}$).[82] Activated carbon from hydrochar produced by HTC of wastes. KOH as an activation agent resulted meso-porosity with amethylene blue number of 385 mg/g, and micropore with iodine number of 747 mg/g.[59]Hydrochar activated with phosphoric acid resulted the specific area and total pore volume of 2192 m^2/g and 1.269 cm^3/g.[57]Hydrochar was obtained from *chickpea stalk* by hydrothermal method. Hydrochar was activation using $ZnCl_2$ activator. It was determined that the highest iodine number of activated carbon was 734 mg/g, the highest iodine number was determined by BET surface area of 572 m^2/g.[55]Hydrochars derived from *hickory* wood and peanut hull through HTC were activated with H_3PO_4 and KOH. The volatile organic compound (VOC) adsorptive capacity of the activated hydrochars of (50.57-159.66 mg/g) were greater than that of the non-activated hydrochars of (15.98-25.36 mg/g).[56]Hydrochar was produced from *Phoenix dactylifera* palm leaves by hydrothermal carbonization, and chemically modified with H_2O_2. The adsorption capacity of activated hydrochar was 74.5 mg/g increased with non-activated hydrochar of 17.8 mg/g.[83]Hydrochar produced from grape pomace by HTC. Hydrochar was chemically modified using 2 M KOH solution. Results showed that the KOH treatment increased the sorption capacity of hydrochar from 27.8 mg/g up to 137 mg/g.[58] Pari[79] used cassava and tapioca flour produce sphere carbon and activated using KOH as chemical agent. The process resulted the carbon predominantly in sphere shape, exhibited the BET area of 986 m^2/g, total pore volume of 0.57 cm^3/g, micropore volume of 0.46 cm^3/g, pore diameter of 1.6 nm, and electrical resistance lower than 0.01 ohm.

VI.2 Carbon materials for Energy storage

Energy storage is one of the important technologies for a sustainable future of our society. Area of activity in materials science is the development of new materials for energy application. This includes high-performance materials with specific characteristics, for example as host materials for hydrogen storage.[68] Surface area is important to increase the storage capacity. Pore size is more important because pore size used transport solute to inside to outside the particles. Activated carbons prepared by KOH activation and using a single stage activation process have reached very high values of methane storage (155 V/V).[84]

VI.3 Carbon materials for Capasitors

Activation of hydrochars is important ways to get carbon functional that meets the requirement and desired characteristics. High surface area and capacitance are required for the electrochemical capacitance.[85] Carbon from xylose prepared by hydrothermal synthesis and chemical activation with KOH. The largest surface area of the activated carbon which is calculated by BET method is about 3500 m^2/g, specific capacitance reaches 340 F/g at current density of 0.5 A/g.

Beside high surface area of engineering nanostructured materials for high end application, some of the most important factors concerning material properties are; surface area almost all application, chemical inertness for support materials, high conductivity for electronic application, and surface functionality for adsorption, and acid/base catalysts.

VII. CONCLUSION

Hydrothermal carbonization is a promising tool to prepare hydrocharpercursors with high potential for the activated carbon synthesis. Hydrochars produced from HTC process can be further treatment become carbon functional that can be used in industrial purposes, such as adsorbents, capasitors, energy storage, and solid fuels. The preparation of suitable hydrochar for carbon synthesis which is governed by properties of hydrochar, particularly oxygenated functional groups, which evolves with the variation in parameters, particularly produce activated carbons with specific and desired characteristics. The hydrothermal carbonization process in the preparation of hydrochar with turned surface chemistry that improve hydrochar characteristics.There were many ways to activate the hydrochar into carbon functional, such as chemical thermal modifications. There are a lot of chemical agents that used as agent, such as KOH, $FeCl_3$, H_3PO_4, KOH led to give highly surface area. More precise manipulation has been demonstrated via nanocasting.

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