

Preparation and synthesis of synthetic graphite from biomass waste: A review

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ABSTRACT

Commercial graphite is valuable products that have extensively being utilize in wide range of applications. The increase in demand, especially in customizing properties for certain utilization have led to researches on possible alternative, low-cost, and environmentally friendly synthetic graphite production. Biomass waste are among attractive carbon precursor that have been widely investigate as raw material for graphite production. The synthesis and application of biomass as carbon precursor have drawn attention due to its availability, sustainability and cost effective. In this critical review, an extensive list of production of graphite from biomass waste is presented. The effects of various process parameter on properties of synthetic graphite are also discussed. This study reviews previous study on different feasible method in synthesizing graphitic carbon.

Keywords: Preparation and synthesis. Synthetic graphite, biomass waste

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INTRODUCTION

Graphite is another form of crystalline carbon beside diamond and fullerene. It is natural occurrence mineral that naturally form in metamorphic rocks [1]. Graphite is anisotropic material, good electrical and thermal conductor within the layer (due to in-plane metallic bonding) and poor electrical and thermal conductor to the layers (due to weak van der Waals forces between the layer) [2]. Having both metal and non-metal properties making graphite as interesting material in wide application. Graphite is suitable to be used as electrochemical electrodes and brushes, as it possess good electrical conductors properties [3]. Additionally, graphite is also suitable material for casting and moulding industry due to its high melting point properties. Ability of carbon layer in graphite to slide within the layer making it convenient to be apply as lubricant and pencil material [2]. However despite all of the great properties and wide application of graphite the primary concern arise is on supply risk issues [4]. Graphite have been label has 'supply risk' material due to its vast demand and limited reserved on natural source thus synthetic graphite will be great option of filling the gap between supply and demand.

Production of synthetic graphite has attracted tremendous interest in recent years considering on increasing demand each year. Recently biomass waste has been identified as potential precursor for graphite production due to its omnipresent, environmentally benign and low cost [5]. It have the merits for being abundant, cheap and clean with high utilization potential [6]. A key aspect of graphite production is using high carbon content material as feedstock. A number of researchers have investigated on numerous numbers of biomass as precursor in graphitic carbon synthesis. To date, various approaches have also been utilised to synthesizing synthetic graphite such as laser ablation, arc discharge, chemical vapor decomposition, thermal heating, microwave heating and Joule heating. After all, not every method is suitable to be implement in biomass feedstock.

Annual production of biomass waste was about 170×10^6 t consisted of 75% carbohydrates, 20% lignin and 5% other natural products, out of this only 3.5% of

this waste were being fully utilised [7]. The usage of biomass in energy generation and another chemical production will help in economic growth for agriculture-based country. It help reducing dependency toward fossil fuel and producing more job opportunity in agriculture, forest management, oil and chemical industry [8]. Biomass play a vital role in energy supply as approximately 25% of global energy demand were generated by biomass waste [9], [10]. However, there is still an issue arise on food vs fuel controversy, the usage of edible biomass such as sugars, starches, and vegetable oil for large scale production of fuel have cause tremendous issue on food supply shortage [8].

Abundant availability of fast growth lignocellulosic biomass making it as great alternative raw material rather than food crops. Thus, most researcher focus on converting nonedible biomass (lignocellulosic biomass) to produce valuable material. Biomass, often refer to plants or plant-based material derived from nature, that can be synthesize through bio-logical photosynthesis [11]. Lignocellulosic biomass is a complex fibrous material that can be found in cell wall. It consists of three main structural unit cellulose, hemicellulose, and lignin [8], [12]. Cellulose typically accounts for 40-50% of lignocellulose source, hemicellulose 20-30% and lignin 15-25%. Lignin is the second most abundant biopolymer and most abundant aromatic-containing polymer in nature [13]. Lignocellulosic biomass is a potential sustainable feedstock in various application.

The usage of biomass in green and effective way will definitely give significant impact on environment [14]. Various process has been employed to convert biomass into fuel and chemical including gasification, pyrolysis and hydrolysis. Gasification process are used for fuel production, meanwhile another routes are used for other biomass derivative product [8]. Renewable raw material was viable alternative to produce synthetic products. If special functional properties of biomass such as biocompatibility, biodegradability and carbon contents are being utilize fully, biomass end product definitely can be utilize in wide industrial application [7].

In Malaysia, biomass waste such as palm waste were sufficient to be used as renewable energy sources. Annual global biomass production is about 146 billion tons, in

which carbon is about made up of 20 billion tons[15].Srinivasan et al. [16] have carried out research on potential application of biomass. Among the potential application discovered were biochar for soil amendment as biomass waste are rich with carbon super sorbent characteristic, energy generation due to its high calorific, filler material due to low ash and high carbon content. Srinivasan et al. also reported present of early development of crystalline structure through XRD data. High carbon content and possible development of crystalline structure making biomass as suitable precursor for development of graphitic carbon[16]. Biomass-derived carbon is one of humanmade carbon material, that are different from natural occurring carbons such as charcoal, graphite and diamond. Natural graphite and diamond are formed naturally, deposited in the crust under either metamorphic or igneous environment with high temperature and high pressure[17], [18].The application of biomass derived carbon have drawn increasing research attention due to ease of fabrication, cost effectiveness and

sustainability[19].Biomass derived carbon product usually produce by converting natural product such as plant, animal waste, via process like thermal carbonization or activation[20], [21].Although in plant biomass the carbon content usually high at (40-60%) to their elemental composition, the actual carbon yield were highly dependent on chemical composition especially mass fraction of cellulose, lignin and hemicellulose. Lignin with the highest thermal stability are measured as the major contributor to carbon content of final chars[22]. Considering on feasibility and effectiveness of using biomass as raw material for production of carbon material. This study will review on different synthetic pathway of producing graphitic carbon previously done by using different biomass waste as feedstock. The paper has been divided into a few parts starting with general method of graphite production followed by discussion on each method on specific effect of production condition. The list of carbon precursor from biomass or biomass derivative is presented in Table 2-1.

Table 2- 1:List of raw material from different agriculture waste for production of graphitic carbon

Raw material	Reference
Softwood sawdust	[23], [24]
Wood derived scaffolds	[25]
Biomass derived AC	[26], [27]
Sucrose	[28]
Sawdust	[29],[30],[31]
Green tea waste	[32]
Lignin	[33], [34],[35]
Cellulose	[5], [36],[37],[38]
Hemp grass	[39]
Seafood waste	[40]
Microalgae	[41]
Cornstalk	[42]
Chitosan	[43]
Wood	[44]
Bamboo	[45],[46],
Degreasing cotton	[47]
Coconut shell	[48], [49]
Miscanthus grass	[50]
Wheat straw	[51]
Coconut coir	[52]
Black locus seed	[53]
Wheat stalk	[54]

GENERAL PRODUCTION METHOD OF GRAPHITIC CARBON

Graphite is a mineral composed of stacked sheets of carbon atom in which arrange in hexagonal pattern[3]. Graphite have a great properties such as good electrical, good thermal conductor, and high boiling point [2].Due to it attractive properties graphite has raised great interest in various industrial application especially electrical industries

In recent years, there has been increasing interest in graphite which have led to researches on possible alternative of producing synthetic graphite. Various method can be used to prepare carbon material with graphitic framework including chemical vapor deposition, thermochemical method, arc discharge, microwave heating, and laser evaporation, but in this review the discussion is focusing only on method that are suitable for biomass raw material [55].As the main concern is on environment and minimal cost thus biomass waste are excellent choice of raw material.

One of feasible pathway to prepared carbon material is via thermal heating method[56]. Thermal heating method is the process that utilized heat to transform biomass into energy or chemical product. In thermal heating method, the process will result in most carbon stay and other element ejected. In fact most of carbon product used today was derived from carbon-rich organic precursor treated at elevated temperature in inert gas flow [57].During heat treatment process, at first stage < 100°C moisture mainly volatile, at higher temperature hemicellulose degrades easily (220-315 °C), cellulose degrades at 315-400°C while lignin cover higher range of temperature[11], [58].

In thermal heating method another route is by implying hydrothermal carbonization HTC. HTC also being employed in production of various carbonaceous material including graphitic carbon. HTC are usually done at mild processing temperature (< 300 °C), using water as carbonization medium under self-generated pressure[11], [59], [60].Hydrothermal treatment of biomass contains five procedure including hydrolysis, dehydration,

decarboxylation, polymerization and aromatization[61][82].

Microwave heating have attract lot of interest in carbonaceous material synthesis due to its rapid heating, low synthesis temperature, and environmental friendly [62]. This process used electromagnetic wave to deliver energy in form of radiation. Previous research reported that graphitic carbon from biomass can be fully synthesis via microwave assisted method. Microwave heating is new developing method that will help reducing time consumption and energy consumption. It can be considered a new energy-efficient graphitization method. Another method is ultra-sonic assisted method. Ultrasonic wave is high frequency mechanical wave that come from transducer that usually made from piezoelectric crystal [51]. Among important ultrasonic wave effect is mechanical, thermal and cavitation. The huge energy generated from ultrasonic method can cause separation of fibre, degradation and even changing crystalline degree.

In each route method selection and process condition will play a vital role in formation of synthetic graphite. Different process condition will lead to different crystallography, degree of graphitization, atomic arrangement and quality. It will affect in structural and morphology of synthetic graphite form.

1.1 Graphitization via heat treatment

Graphitization is a transformation process of disordered carbon material into three-dimensional graphite by heat treatment, when energy is provided the disordered carbon material, can be graphitized by atomic displacement [63]. Graphitization without catalyst required high temperature up to 3000 °C [64]. Thus, catalytic graphitization was introduce to accelerate the process[63].

The process of graphitization involves limited movement and rearrangement of carbon atoms which must undergo reconstructive transformation during the heat treatment process[65]. Formation of graphitic carbon from amorphous carbon precursor require movement in three dimensions by the pre-graphite matrix [65]. The degree of motion necessary is significant enough to require that the precursor substance to pass through a liquid or fluid phase at some point during heat treatment by undergoing this phase fluid macromolecules have mobility and is able to move into semi-ordered position in a pre-graphite lattice[65].

Carbon material that able to undergo temporary fluid phase are known as soft carbon. After this first organizational step occur, remaining process at high temperature heat treatment resulting in annealing of carbon into graphite lattice[65]. This step resulting in indexing graphene layers to each other. Intermediate fluid phase is known as "mesophase". During mesophase basic structure unit form and align into liquid crystal structure that will develop into graphite.

In this process carbon precursor, methods and process condition used before heat treatment and during heat treatment play an important role in determining the degree of graphitization, defect condition and crystallinity of graphite produce[34], [44], [64], [66], [67]. It will also indirectly effect the synthetic graphite properties such as thermal stability and electrical conductivity[43], [44].

Carbon precursor are among important aspect in graphite production. Generally, carbon rich material will be selected as precursor. Originally most of synthetic graphite were produce from petroleum and coal

[25][68]. However nowadays many researchers are shifting to greener option which it biomass waste as considering on it cost, environmental issue and availability[69]. The carbon source might be from natural, waste or side product of agriculture sector or industrial sector.

In this process heat treatment is among the important part as it is where transformation occur. The uses of inert gas during the process is really important to ensure no burning process occur. Gas such as N₂ and Ar are used. However, N₂ is more widely used as it can repel oxygen inside the furnace, low cost, easily available and easy to handle[70]

Heat treatment process usually occur at extremely high temperature up to 3000°C with long processing time [62]. During heat treatment usually some amount of carbon precursor will be heat up till certain temperature in inert environment. Usually graphitization process is done with aid of transition metal as catalyst to help in reduction of heat treatment temperature. Catalytic graphitization is usually carried by aid of transition-metal such as V, Zr, Pt, Ti, Al, Mn, Fe, Co or Ni or metallic compound Cr₂O₃, MnO₂, MnO₃ or Fe₃O₄. Catalytic process make it possible to transform both graphitizing and non-graphitizing carbon precursor into graphitic structure according to dissolution-precipitation mechanism[29]. There is also research done on applying rare earth element as catalyst [71]. Transition metal has been identified as good catalyst due to the capability of forming metastable (metal carbide) [5].

In graphitization process via heat treatment considerable amount of literature has published on this method. Most of researcher producing it via this typical process flow starting form raw material preparation including collecting, drying, cleaning, cutting, grinding and chemical treatment. Followed by carbonization process at lower temperature. Catalyst impregnation and finally graphitization at high temperature. However, this is not entirely the same for all researcher some prefer directly graphitize at high temperature without pre-carbonize. The basic method was altered accordingly to each preference depending on the end product desired.

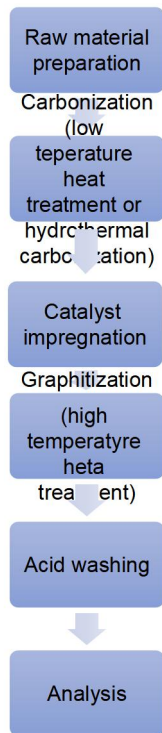


Figure 3- 1:Typical graphitization via heat treatment process flow

Graphitization can be done at different temperature, different catalyst composition and using different carbon precursor with addition of pre-treatment or activating agent [25], [44], [53]. The quality of graphite produces entirely dependent on selection of production parameter. The selection based on logical range and optimum condition will help in producing good quality synthetic graphite [72]. The summarize of process condition for graphitization process available in Table 3- 1

Table 3- 1:Process condition for graphitization via heat treatment of different biomass

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Raw material	Heat treatment temperature	Catalyst	Additional information	Reference
Softwood sawdust	800°C	Iron Nitrate	Impregnated with 100%,75%,50%,25%.10%.0% mol% Impregnated before graphitization	[23]
Softwood sawdust	750°C	Ferum	Production of nanocarbon material, graphite obtains. Using tubular reactor for pyrolysis.	[24]
Wood derived scaffolds	1000°C 1600°C	Nickel	Parameter on wood species Catalyst exposure time Pyrolysis temperature	[25]
Biomass derived AC From Zizania Latifolia Leaves	800°C to 1000°C	Nickel Nitrate	Pre-carbonized at 500°C Activated using NaOH at 750°C	[26]
Sucrose	650°C,700°C, 800°C	Iron (III) Nitrate	Molar ratio of catalyst ranging from 0.5 to 2 Regulating both molar ratio catalyst and heat treatment temperature	[28]
Sawdust	900 °C and 1000°C	Nickel (II) nitrate Ferum (III) Nitrate	2.5 or 5 mmol metal/g sawdust	[29]
Sawdust	600°C to 800°C	Iron (III)chloride	-	[30]
Sawdust of pitch pine	900 °C	-	Carbonized at 800°C Chemical treatment with sulfuric Acid or Ammonium hydroxide KOH activation	[31]
Green tea waste	700°C	-	KOH activation at 700°C Water or Hydrochloric acid treatment Carbonization at 500°C	[32]
Lignin	900°C	-	KOH or K ₂ CO ₃ activation Lignin to activator ratio 1:1 Carbonized first at 250 °C holding for 30 minute and enhancing to 900°C.	[33]

Table 3- 1:Process condition for graphitization of different biomass continued

Lignin	900°C to 1100°C	Fe (III)NO ₃ Mn (II)NO ₃ Co (II)NO ₃	Hydrothermal carbonization at 300°C,1500psi	[34]
Cellulose	500°C,600°C, 700°Cand 800°C	Fe (II)NO ₃ Co (II)NO ₃ Ni (NO ₃) ₂ Cu (NO ₃) ₂	Determination of the most active catalyst	[5]
Cellulose	800°C	Fe (III)NO ₃ Fe (III)Cl Ammonium Iron (III) citrate	Anion of Iron salt effect the extent of graphitization.	[36]
Cellulose	1500°C	Silicon dioxide	Another sample was prepared with absence of catalyst.	[37]
Cellulose	300°C to 900°C	Ni (NO ₃) ₂	Hydrothermal carbonization at 250°C	[38]
Hemp grass	800°C	-	Steam as activation agent	[39]
Seafood waste	800°C	Ferum chloride	Activation agent Zinc chloride Combining catalytic graphitization and activation.	[40]
Microalgae	1000°C	Ferrous chloride	-	[41]
Cornstalk	1100°C	Ferrocyanide	-	[42]
Chitosan	600°C,800°C,1000°C	Ferum Chloride	Nitrogen doped carbon with high degree of graphitization	[43]
Wood	1000°C,1300°C,1600°C	Ferum Chloride	3M Ferum Chloride	[44]
Bamboo	1100°C to 2100°C	-	Carbonization 800°C-1000°C	[45]
Bamboo	800°C	K ₂ FeO ₄	Carbonization at 400°C Sample pre-treated with H ₂ SO ₄	[46]
Degreasing cotton	650°C	Iron (III)acetylacetonate dissolve in DMF	Further annealed at 350°C	[47]
Coconut shell	900°C	Potassium carbonate	Carbonization at 400°C	[48]
Coconut shell	1000°C	Iron Nitrate	Carbonize at 500°C to 1000°C Ferum to Coconut shell weight ratio 1:49	[49]
Miscanthus grass	500°C,700°C,900°C	Iron Nitrate Cobalt Nitrate	Sample were also treated with mixture of Iron and Cobalt catalyst.	[50]
Coconut coir	-	-	Effect of hydrothermal carbonization on formation of curved graphite structure.	[52]
Black locus seed	800°C	K ₂ FeO ₄	K ₂ FeO ₄ used for both activating agent and catalyst	[53]
Wheat stalk	2600°C	-	Hydrothermal carbonization at 150°C Calcination at 800°C	[54]

1.1.1 Effect on type of carbon precursor used

Natural sources of carbon precursor can be divided into a few categories including plant-based, food-based, microorganism-based and animal based such as Crab shell, coconut shell, sucrose, bamboo stalk, degreasing cotton and wood sawdust [24], [28], [40], [46]–[49]. However, research attention was focusing on plant-based due to its availability, low cost, high carbon content, hierarchical nonporous structure, and heteroatom composition that are extremely beneficial. Although plant-based were favourable some researcher successfully produce graphitic carbon from animal waste, Shi et al. [40] successfully produce honeycomb-like hierarchically porous carbon with highly graphitization skeleton via combining activation and carbonization graphitization process using crab shell.

Among important factor that influenced the degree of graphitization is chemical composition of carbon sources. Selection of plant-based biomass with high lignin fraction, low cellulose fraction, low oxygen and high nitrogen content is important in producing high yield, high degree of graphitization, controllable defect and good conductivity [19]. This statements is supported by research done by Jiang Deng, Jiang Deng et al. [73] reported that after heat treatment of cellulose, hemicellulose and lignin at 900 °C, it is found that hemicellulose decomposed easily as TGA result presented no yield of product after heat treatment process. Meanwhile Cellulose and lignin yield ~9% and 39% respectively. XRD result for lignin shows narrower peak at diffraction peak 2θ 24° and 44° attribute to graphite reflection peak, suggesting higher degree of graphitization for lignin compared to cellulose [73].

Joah and team [31] investigate on graphitization of structurally separated pitch pine sawdust. Pitch pine sawdust was separated into cellulose/hemicellulose and lignin after treatment with NH_4OH . Joah Han identify that lignin forms partially graphitic structure meanwhile cellulose/hemicellulose responsible for amorphous structure. These result match with Jiang Deng finding earlier. This occur because of cellulose/hemicellulose are carbohydrate polymers consist of anhydro glucopyranose that linked by β -1-4 glycosidic linkage that considered as hard carbon meanwhile lignin is aromatic polymer made up of phenylpropane linked with β -O-4 that is potentially graphitize hydrocarbon.

Olga et al. [45] in his research demonstrated experiment of producing graphitic carbon with different raw material. They study on different biomass sources three different types of bamboo, two type of wood and petroleum coke for reference. Various temperature ranging from 800 °C to 2800 °C [45]. He reported from Raman Spectroscopy data that petroleum coke has lower I_d/I_g value with associate with lower amount of void space or defect followed by Tutul bamboo, Birch wood, Tonkin, Oak and Moso bamboo. Showing that each selection of biomass waste will undergo different degree of graphitization that depending on concentration of aromatic hydrocarbon in the precursor itself.

Overall, all the previous finding makes offer some important insight regarding information on selection of carbon precursor. It can be concluded that precursor with higher lignin content is preferable.

1.1.2 Effect of catalyst

In graphitization process many has agree that addition of catalyst in the process will enhance the overall procedure. Involvement of catalyst during graphitization help reducing activation energy during conversion of amorphous carbon to graphitic carbon. This will generally help reducing the heat treatment temperature needed to convert amorphous carbon into graphitic structure. The amount and type of catalyst added also influenced the product.

Thompson et al.[23] reported production of graphitic carbon using softwood sawdust as raw material by mixing it with Iron Nitrate solution. The mixture was then dried and undergo heat treatment in muffle furnace at 800 °C under nitrogen flow. Control sample without Iron catalyst was also prepared, from the PXRD pattern in Figure 3-2 it can be identified that sample without catalyst only shows two broad hump indicating amorphous carbon. Meanwhile sample with catalyst shows reflection peak at $2\theta = 26.6^\circ$ corresponding to graphite peak [23]. This observation also supported by Xiaoxian et. al [41] finding in which they observe microalgae precursor without catalyst is not graphitizable as no graphite lattice fringe observe in HRTEM image. From this it can be conclude that catalyst responsible for graphitic structure formation. For non-graphitizable raw material the addition of catalyst helps in lowering the temperature needed for formation of graphitic structure.

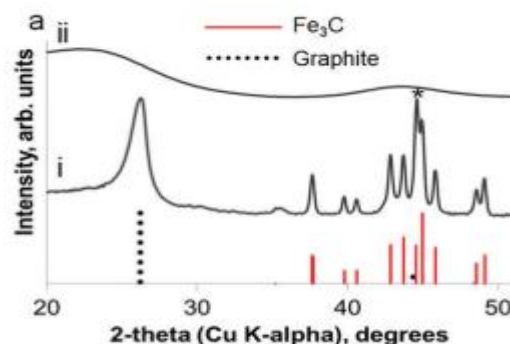


Figure 3- 2:PXRD pattern for i) iron-treated ii) controlled sample without catalyst [23]

Amount of catalyst use are also being studied. Maiké Kaarik et al [74] adding different amount of catalyst in his experiment. They suggested that according to adsorption analysis at higher amount of catalyst, the catalytic influence on the graphitization goes deeper in carbon particle causing more crystalline structure produce. This might be one of the reasons on better graphitization condition at higher amount of catalyst used. Maiké Kaarik [74] reported that Raman and XRD data shows increasing in crystallite size as concentration of catalyst increase. Jacco et al.[5]. in his research investigating on different base metal as catalyst for cellulose graphitization. Nitrate of copper, nickel, cobalt and iron were used as parameter to determine most active catalyst. Jacco found out that Iron nanoparticle are found to be most active at lowest temperature ($T \geq 715^\circ\text{C}$) and copper completely inactive, while nickel and cobalt only active at ($T \geq 800^\circ\text{C}$). This in corresponding with nickel and cobalt nanoparticle are initially encapsulated by several thin graphite-like shells (HRTEM), hence this nanoparticle have to escape from shells first before can participate in metal-induced catalytic graphitization for available amorphous carbon. Meanwhile encapsulation does not occur for iron nanoparticle. Thus making Iron directly active throughout the process[5]. This result can be supported by Sevilla et al. [29] as between Iron or Cobalt as catalyst, in their finding XRD result indicate that carbon with higher degree of structural order is produce when using Iron.

Lei Wang et. al and Chen et. al [42], [75] in their studies also reported successful production graphitic carbon nanosheets derived from biomass for using Iron catalyst this further support that Iron is among the best transition metal to be used as catalyst [42].

Another research by Jaco et.al [36] reported on effect of different Iron salt on textural properties of carbonized cellulose. Jaco loaded micro cellulose with either iron (III)nitrate, ammonium iron (III) citrate or iron (III)chloride and pyrolyze to temperature up to 800 °C [36]. Jacco et. al identify that graphitization is influenced by iron nanoparticle size distribution that affected by the anion of iron salt. For non-volatile iron salt Iron (III) Nitrate and ammonium iron (III) citrate nanoparticle are formed during heat treatment. Nanoparticle is active in catalytic graphitization process leading to formation of mesoporous materials[36]. For Iron (III)chloride large iron particle obtain due to its volatility, catalytic graphitization is restrained as no mesopores form. This research shows that different metal salt will also influence the graphitization process as suggested by Jaco et.al non-volatile iron salt is preferable.

Lignin is high-volume byproduct from the pulp and paper industry and currently burned for electric generation. Muslum and team proposing another way of transforming lignin into valuable product which is graphitic biocarbon. The lignin was first carbonized in water at 300 °C and 1500 psi for biochar production[34]. The biochar was later added with Fe (II), Co (II) and Mn (II) nitrate which then graphitized. In his research catalyst effectiveness was study, both temperature and catalyst type influence the degree of graphitization. Muslum found out that good quality graphitic structure was obtained using Mn (NO₃)₂ at 900°C and Co (NO₃)₂ at 1100°C.

Beside single catalyst some researcher also implementing Hybrid catalyst. Ian major et.[50] al introducing hybrid catalyst technique and comparing it with one catalyst technique[50]. Miscanthus grass powder were used as carbon source were firstly treated by mixing it with aqueous solution of Iron or Cobalt.7 and for mixed catalyst, the catalyst was prepared by 1:1 mixture of iron (III)nitrate moles to cobalt (II) nitrate for total 7.18×10^{-3} moles of metal. The usage of hybrid metal was done due to different reason, among it is combination of different metal can generate multi metal complexes or cluster that exhibit new catalytic activity.it is reported that sample treated with both Iron and Cobalt are twice as efficient in forming graphitic structure.

Catalytic graphitization is usually carried by aid of transition-metal such as V, Zr, Pt, Ti, Al, Mn, Fe, Co or Ni or metallic compound Cr₂O₃, MnO₂, MnO₃ or Fe₃O₄. Generally group 4 to 7 metal Fe, Co, Ni, Mn, etc are suitable to be used as catalyst because of 2 to 5 electrons in their d-shell orbitals that enable formation of strong bonds between metal carbides and carbon-based materials[76]. Among this Fe, Ni and Co have been found as effective catalyst in graphite production[77].Catalytic process make it possible to transform both graphitizing and non-graphitizing carbon precursor into graphitic structure [29]. There is also research done on applying rare earth element as catalyst [71]. Transition metal has been identified as good catalyst due to the capability of forming metastable (metal carbide)[5].

Two mechanism have been proposed to explain on catalytic graphitization (i) the dissolution-precipitation mechanism, whereby amorphous carbon is first dissolved into metal particle, then precipitate as graphite carbon and (ii) the formation-decomposition of carbide intermediates, whereby the carbon forms carbides with the metal and decomposed at certain temperature leaving graphitic structure[12], [76], [78].It can be deduce from previous research that it is notable that the usage of Iron has been successfully catalysed the graphitic structure formation and are the best metal for graphitization, anion of metal salt influenced degree of graphitization and hybrid catalyst technique are found to be twice time efficient.

1.1.3 Effect of heat treatment temperature

Heat treatment are the important part in graphitization process as it plays important role in supplying the energy for macromolecules rearrangement process. Johnson et al. [25]using wood derived scaffolds as carbon precursor at different heat treatment temperature. The research implement uses biomass waste and graphitize it at temperature between 1000 °C to 1600 °C.Based on the observation they deduces that higher heat treatment temperature more ordered graphitic carbon is produce[25].

Similarly, Liu et al in his research also studied on influence of various heat treatment temperature on degree of graphitization by using biomass-derived activated carbon AC as carbon precursor[26]. AC were first washed with HCl and dried. Then directly impregnated with 1M acetone solution of Ni (NO₃)₂ overnight. After vacuum filtration the sample inserted into tube furnace under nitrogen flow at various temperature up to 1000°C. From XRD pattern as in Figure 3-3 at lower heat treatment temperature no obvious graphite peak detected, upon heating up to 950 °C a noticeable peak around 26° was detected. As temperature increased 1000 °C the sample show extremely sharp peak. Highly porous graphitic carbon material with ultrathin graphitic structure are successfully produce via this method as chemical treatment introduce in the beginning.

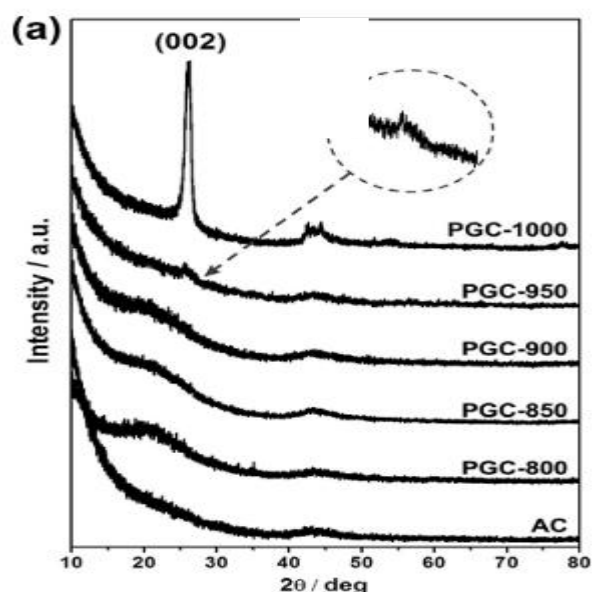


Figure 3-3: XRD pattern of AC sample prepared at different temperature[26]

Another raw material that already been employed are chitosan. Jujiao et.al[43] employed chitosan by mixing it with FeCl₃ and deionized water. The dry mixture were then undergone heat treatment under argon atmosphere at 600°C, 800°C and 1000 °C. From XRD pattern it for each sample peak at 26.4° appear, however at 800 °C and 1000 °C the peak appears narrower indicating higher degree of graphitization achieve at higher annealing temperature, the sample are then further characterize using Raman spectroscopy, spectrum of sample anneals at 1000°C, shows the lowest I_D/I_G of 0.5 indicating higher temperature of annealing leads to less disorder carbon atoms. Thus, Raman result are accordance to XRD pattern[43].

Same trend was also observed by Wu-Jun[30] using sawdust as carbon precursor. Wu-Jun sample was pyrolyzed under nitrogen atmosphere at few temperature range 600°C, 700°C and 800°C. Raman spectra shows higher I_G/I_D value of sample prepared at 800 °C, indicating greater graphitization degree[30]. This result is also further confirmed with XRD data that shows similar trend.

This observation shows agreement with observation from Yuanchao Liu [26] and Gutierrez Pardo[44] that concluded as pyrolysis temperature increased degree of crystallinity also increased, more ordered carbon structure is form. Yuanchao Liu [26] suggested that the

temperature effect might happen due to catalyst nucleate and grow into larger nanoparticle as heating temperature increased. At higher temperature upon heating process catalyst particle will quickly grow into particle with considerable size, good crystallinity, and good dispersion that can facilitate formation of shell-like graphitic nanostructure[26]. Graphite might be form either by direct precipitation from the catalyst or by the evolution of quasi-graphitic nanostructure through self-ordering process.

1.1.4 Effect of activating agent

Activating procedure were usually done in order to improve the mesoporous structure of graphitic carbon as porosity is preferable in certain industry usage. It is believed that combining thermo-chemical activation and graphitization will improve mesoporous structure, crystallinity and degree of graphitization. Yuebin Xi using enzymatic hydrolysis lignin from corn stalk waste from bio-refinery residue and alkali lignin from black liquor softwood pulping. K_2CO_3 were added as activating agent in which it is reported that it dramatically improved specific surface area and adsorption capacity which indicate present of micro- and mesopores [33]. The addition of activating agent promoting rearrangement of carbon atoms and significantly increase degree of graphitization. The result is similarly with Sun et.al [79] as it is reported that carbon source can be catalyzed using Fe component meanwhile chemical activation $ZnCl_2$ can enhance formation of porous structure, they able to produce porous graphitic structure at $700^\circ C$ and $1000^\circ C$ [79].

Youning Gong[46] introducing bamboo char as carbon precursor with addition of potassium ferrate K_2FeO_4 as both activation agent and catalyst. The sample were pyrolyzed in tube furnace at $400^\circ C$ for 2h, heating rate $5^\circ C/min$ under argon atmosphere. The dark solid produce was finally crush and ground and later dispersed in aqueous K_2FeO_4 solution with continuous stirring for 8 h and dried at $100^\circ C$ overnight. Mixture will finally be transferred into tube furnace and heated at $800^\circ C$ for 2h heating rate at $5^\circ C/min$ under argon atmosphere [46]. Youning Gong et. al in their research concluded that development of microporous structure with large surface area $1732\ m^2/g$ and high degree of graphitization is achieve with usage of K_2FeO_4 as both activation agent and catalyst. The result is also supported by the sample exhibit outstanding capacitive performance as high specific capacitance ($222.0\ F\ g^{-1}$ at $05\ A\ g^{-1}$) showing great potential as advance electrode material.

Sankar et al. in his research producing ultrathin mesoporous graphitic carbon nanoflakes from tea-wastes by combining both thermo-chemical activation and graphitization. In his research the green tea waste was first cleaned with deionized water and dried. The dried green tea waste was then carbonized at $500^\circ C$ [32]. The tea waste ash was later mix with KOH and activated at $700^\circ C$ for 2 hours. After activation the sample will then clean with deionized water for potassium compound removal [32]. The sample will then be filtered, rinsed and dried. Graphitic structure with high porosity and high conductivity was obtained after all this process. The process flow was summarized in Figure 3- 4

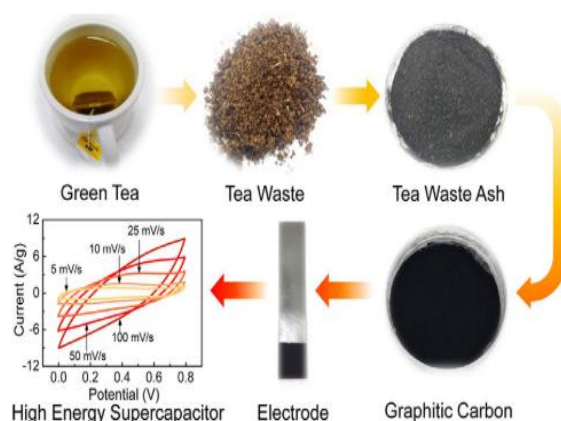


Figure 3- 4: Process flow diagram for graphitic carbon production from tea waste

Combination both catalytic graphitization as well as thermo-chemical activation procedure is an effective method to prepare graphitic porous carbon nanomaterial as concluded by previous research. The addition of activating agent definitely improves the degree of graphitization, porosity, conductivity and crystallinity.

1.1.5 Effect of pre-carbonized process before pyrolysis

Some researcher using biomass waste as carbon material by undergo catalyst impregnation and directly heat treatment process but some researcher utilised carbonization at lower temperature first before heat treatment [29], [80]. Joah Han et al. implementing carbonization and further graphitization method in his research work, pitch pine sawdust was chosen as raw material for synthesis of graphitic carbon. Similar method used by Gutierrez [44] and team using wood as raw material that firstly carbonize at $500^\circ C$ that later graphitization at $1000^\circ C - 1600^\circ C$.

Alternatively, Gabriela utilize hydrothermal carbonization followed by pyrolysis on coconut coir dust. Their study is on influence of hydrothermal carbonization on formation of graphite structure[52]. Coconut coir dust sieved 325 mesh and hydrothermally treated (HT). For hydrothermal carbonization process 1 g of coconut coir dust was dispersed in 20 mL of water for 30 minutes. The process of hydrothermal carbonization was performed in a Teflon lined stainless steel autoclave at $250^\circ C$ for 4 hours (heating rate of $10^\circ C/min$). It will later pyrolyzed for 2 hours at $1500^\circ C$ under nitrogen gas flow ($100\ mL/min$). The heating rate was made in three different steps: $10^\circ C/min$ from ambient temperature up to $1000^\circ C$; $5^\circ C/min$ from $1000^\circ C$ up to $1300^\circ C$ and $2^\circ C/min$ from $1300^\circ C$ to $1500^\circ C$ [52]. It is reported that according to HRTEM analysis sample that undergo hydrothermal carbonization shows highly curve graphite structure meanwhile sample without hydrothermal carbonization shows predominantly amorphous phase. They suggest that simple pyrolysis process is not responsible for formation and stacking of graphite, pyrolysis process act as step leading to formation of graphite in two-step process. Sample without hydrothermal carbonization or lower temperature pyrolysis do not show amorphous structure or behavior[52].

Similarly, there are another research using cellulose-derived hydrochar as carbon precursor, obtain from hydrothermal carbonization[38]. The hydrochar will

undergoes impregnation with nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in ethanol, and later undergo heat treatment under N_2 atmosphere at 900°C [38]. Lijie Hou and team also reported to successfully developing hierarchically porous and heteroatom self-doped graphitic biomass by using Black Locust seed dregs (BD) via hydrothermal carbonization [53]. The graphitic structure was developed by mixing BD with concentrated sulfuric acid and deionized water and sealed into autoclave heated to 180°C for 12h. The result carbonaceous BDC solid was filtered and washed with DI water and dried at 80°C . It will then mixed K_2FeO_4 at different mass ratio in deionized water and stirred for 8h at room temperature and dried at 100°C overnight [53]. The mixture was then annealed at 800°C for rate of $5^\circ\text{C}/\text{min}$ under N_2 atmosphere using tube furnace.

Xianyang in his research also successfully synthesis interconnected highly graphitic carbon nanosheet (HGCNS) from wheat stalk as high-performance anode materials for lithium ion batteries. HGCNS successfully synthesize via combining hydrothermal and graphitization process. The process starts with cleaning and cutting, followed by hydrothermal process. The hydrothermal process was done at 150°C in KOH solution [54]. The sample were later calcinated at 800°C and finally graphitize at 2600°C under argon atmosphere. They successfully produce ultrathin 2D nanosheet architecture carbon with high degree of graphitization with moderate mesopores [54].

Overall, from previous finding it can be conclude hydrothermal carbonization or pyrolysis at lower temperature responsible as an important step for successful graphite formation. As previous research finding that shows sample that directly undergo higher heat treatment temperature shows amorphous structure and characteristic. Numerous studies also show comparable finding as they successfully produce graphitic carbon by implementing two step method. It is also suggested that less energy is needed during graphitization when pre-carbonized material was used instead of raw biomass.

1.2 Microwave heating method

Microwave heating can be listed as potential candidate for energy efficiency graphitization methods. Several reports have reported on production of others carbon material but only two research work by Teawon Kim reported on transformation to graphitic structure. Teawon Kim et.al reported novel method of graphitization using microwave heating with catalyst and comparing it with sample prepared using conventional thermal treatment [27]. Electromagnetic waves deliver energy radiation without being dissipated through heat transfer medium, thus making microwave heating a potential method in producing carbon material. It is reported that full graphitization of amorphous carbon was achieve in shorter period as compared to normal thermal heating. Microwave heating method were more efficient in energy and time consumption.

The activated carbon powder was directly impregnated with catalyst Nickel chloride in which 6 mmol NiCl_2 were stirred with 1 gram of carbon powder for 5 hours at room temperature. The sample were later dried at 75°C for 24h. Next 1000W and 1400 W of microwave radiation was directed onto carbon sample. The reactor were kept in argon atmosphere (100 sccm) [27]. The sample were later characterize using XRD, Raman spectroscopy and transmission electron microscopy. For thermal heating lab-scale thermal furnace, Lindber blue M were utilized.

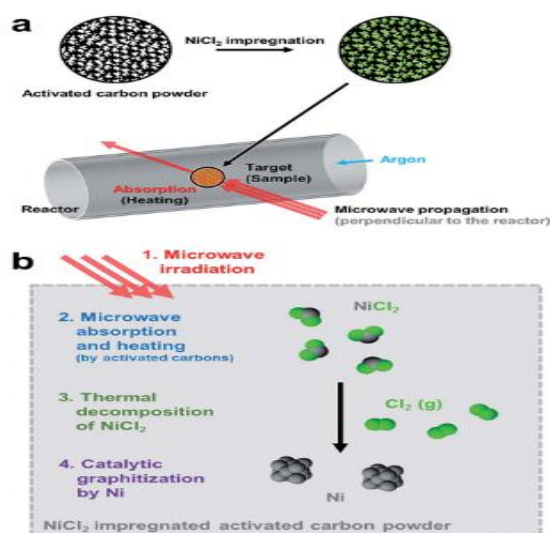


Figure 3- 5: Illustration of microwave graphitization a.) Experimental procedure b.) detail description of microwave graphitization with metal catalyst.

After microwave heating the sample was analysed. The transformation to ordered carbon were confirmed by XRD pattern by the formation of peak at angle 26.5° . With d-spacing 3.361 \AA and 3.3662 \AA , that are almost similar to reference graphite at 3.3612 . These results verify the transformation of amorphous to graphitic. From Raman spectra I_g/I_d value of reference graphite is 3.34 meanwhile the synthetic graphite was I_g/I_d 3.29 and 3.24 showing almost similar value to graphite this result is further supporting the XRD data. The benefits microwave heating is in term of time required only 5 minute meanwhile thermal heating take 1 hour and 30 minute. In other research work Teawon Kim successfully transforming activated carbon with low crystallinity to highly graphitic carbon within short period of time. They conclude that the properties of synthesis graphite is nearly identical to graphite thus suitable to be used as anode material for lithium ion batteries,

As there is limited research on microwave heating method, there is no discussion done on studying experimental parameter and process condition. The research is still on fundamental part of the process itself. However, what can be conclude is graphite can successfully synthesis by this method with aid of transition metal as catalyst. This method will have more potential in the future as short production time is the key strength of this method.

1.3 Ultrasonic-assisted method

Beside conventional thermal treatment and microwave heating another method proposed by Xu and team on producing graphite via ultrasonic-assisted method using wheat straw [51]. Ultrasonic method was proposed as considering on high pyrolysis temperature and high energy consumption on conventional method nowadays that are not suitable for industrial application. Ultrasonic-assisted method involves three main process which is degradation of lignin, graphene formation and graphitization process. The experimental part starts by cutting the wheat straw. Then raw-material will be processed using ultrasonic reactor, and ultrasonically reacted for 30 min and repeated for 3 times. Xu et al. reported that graphite material was found unexpectedly

in the ultrasonic-assisted pulp (UP) of wheat straw, as shown by X-ray diffraction as appearance of large and clear diffraction peak around $2\theta = 26.6^\circ$ attribute to graphite peak and I_d/I_g value is 1.06 indicating the present of graphite material from Raman spectroscopy [51]. Overall ultrasonic-assisted method is a novel method of producing graphitic carbon that need to be explore more especially on finding the optimum process condition. There is still too much gap on overall procedure, mechanism, product properties and experimental parameter.

1.4 Joule heating method

Feng et al introducing new method in transforming lignin-based biomass into highly crystalline graphitic carbon by Joule heating process. Joules heating method utilize the internal resistance of reduced graphene oxide GO /lignin carbon film to heat sample up to 2500K within 1h[35] Annealing of lignin at high temperature can remove impurities and intrinsic defects. The sample preparation is dissolving 20mg GO and 20mg lignin (1:1) in 20ml of deionized water then ultrasonicing for 2h to form homogenous solution. The mixed solution then pours in petri dish, water evaporated at 60°C to obtain GO-lignin film. After drying film was peeled off out of petri dish and carbonized at 873K for 2h in argon atmosphere. For Joule heating procedure the strips of carbonize GO lignin film was connected at both end to copper electrodes using conductive silver paste. Joule heating was carried out in argon atmosphere, Keithley source meter (0.314 A power 100 W) was used as external current source[35].

Result from the show that Joule heating is effective in producing graphitic carbon. Graphitic carbon produce showed ultrahigh electrical conductivity of 4500 S/cm. The HRTEM image shows both extended graphitic structure and short range ordered carbon. XRD and Raman also confirm the formation of highly crystalline structure.

The finding, of new novel pathway such as Joule heating will give great impact on industry. Variety of method with different advantage and weakness will give option and new fresh idea that is more greener and cost saving. However, many information on this method is still unknown thus extensive study should be done before this could be applied in industrial scale.

APPLICATION

The synthetic graphite form can be utilized in broad application. Sankar et al. point out that Tea waste ashes is a promising raw material for high-performance electrode material as he study found out that Tea waste ash graphitic carbon have high electrochemical performance $C_s \sim 162 \text{ F g}^{-1}$ at 0.5 A g^{-1} and high cyclic capacitance retention 121% after 5000 charge-discharge cycles[32]. Joah Han et al. also agreed the usage of biomass as energy storage material as from their finding the biomass derived graphitic carbon exhibit high specific capacitance (150 F g^{-1}) and high rate capability (91% at 50 mA cm^{-2}) both ideal quality for ultracapacitor material[81]. Those finding also corresponding with Lei Wang et al. finding that graphitic carbon from cornstalk biomass portray excellence supercapacitor properties as having excellent electrochemical capacitance up to 213 F g^{-1} at 1 A g^{-1} , high excellent cycling stability and rate performance [42]. Youning et al. also reported an excellent high specific capacitance performance up to 222.0 F g^{-1} at 0.5 A g^{-1} of biomass derived graphite.

Besides as energy storage material carbon with high degree of graphitization also suitable to be used as high performance electrocatalyst for oxygen reduction reaction. As compared from commercial electrocatalyst in term of ORR activity and durability[43]. Xiaoxian et al. reported on nitrogen doped graphitic carbon from biomass as non-noble metal catalyst for oxygen reduction reaction, by using microalgae as carbon precursor. They conclude that nitrogen doped graphitic carbon are more stable then commercial Pt/C catalyst indirectly found to be as promising candidate in fuel cell or another energy devices precursor[41].

Ji Hyun et al. in their research applying carbon from hemp stem, as anode material in lithium-ion battery. Natural hemp electrode delivers reversible capacity of 190 mA h g^{-1} at rate of 300 mA g^{-1} after 100 cycle however they found out that electrode capacity of milled hemp electrode increase suggesting that ball milling leads enhance properties for lithium storage and transport[39]. Xiangyang et al. also producing interconnected highly graphitic carbon nanosheet from wheat stalk for lithium ion battery and determine that when used as anode the graphitic carbon shows high reversible capacity (502 mA h g^{-1} at 0.1c), excellent rate capability and superior cycling performance[54].

Alternatively, another researcher applying biomass derived graphitic carbon in pollutant removal of water. Mesopores properties from catalytic process as enhance adsorption capacity of organic dyes and embedded iron carbide responsible for selective removal of heavy metal iron. Long Chen and team utilizing impregnation-carbonization method by using Iron Nitrate catalyst and cotton fabric as raw material[75].

From research done by Muslum et.al the graphitic carbon synthesize from Lignin shows high electrical conductivity due to it both micro- and mesoporous structure and it thermal stability making it suitable to be used in electric electronic industry[34].

It can be deduced that graphitic carbon derived from biomass waste can be fully utilize in either lithium ion production, ORR catalyst and even in water treatment process. The only important aspect is how the preparation and procedure enhance physical structure of the graphitic carbon to be utilize in different application. From this biomass derived graphitic carbon will be a promising natural green material in wide applicati

CONCLUSION

Graphitic carbon from biomass can be synthesis via various method including graphitization via heat treatment, microwave heating and Joule heating method. The transformation of biomass waste to valuable carbon material were successfully obtain, the addition of chemical treatment before heating process will enhance the physical structure of graphitic carbon structure depending on the application desired. Among all method microwave heating were determine as method that required less energy consumption. However, most of the researcher also successfully obtain graphitic carbon at lower temperature by introducing catalyst. Besides enhancing the process catalyst during pyrolysis can also influence in formation of mesopores that help enhancing capability both in adsorption and electron transfer. It can be concluded that biomass derived graphitic carbon is new material that can be widely utilized in different application.

6 Conclusion

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