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UTILIZATION OF CARBONIZED WOOD FROM TROPICAL FAST-GROWING TREES FOR FUNCTIONAL MATERIALS

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ABSTRACT

Establishment of fast-growing tree species plantations in tropical areas generate wood biomass residue in which some of them are currently utilized for heating fuel and some others are used for charcoal production with limited purposes. The development of functional materials for engineering applications utilizing carbonized wood from fast-growing trees species have to consider the microstructure and pore structure in carbonized wood which has a relationship to the carbonization conditions. This review covers the current researches on progress in the carbonization of wood from tropical fast-growing trees, mechanism of the microstructure and pore structure development in carbonized wood during carbonization, proper utilizations of the microstructure and porosity in carbonized wood for the development of functional materials and efforts and enhancing the development of functional materials using carbonized wood from tropical fast-growing trees.

Keywords: *carbonized wood, functional materials, fast-growing trees, carbonization*

INTISARI

Pembangunan hutan tanaman dari jenis-jenis cepat tumbuh di kawasan tropis menimbulkan limbah biomassa kayu yang sebagian saat ini digunakan untuk kayu bakar dan sebagian lain digunakan untuk produksi arang dengan tujuan penggunaan yang terbatas. Pengembangan material-material fungsional untuk berbagai aplikasi teknik dengan memanfaatkan arang kayu dari jenis pohon cepat tumbuh harus mempertimbangkan struktur mikro dan struktur pori dalam arang kayu yang berhubungan dengan kondisi karbonisasi. Ulasan ini meliputi kemajuan penelitian-penelitian saat ini pada karbonisasi kayu dari pohon cepat tumbuh tropis, mekanisme perkembangan struktur mikro dan struktur pori dalam arang kayu selama karbonisasi, pemanfaatan yang tepat dari struktur mikro dan porositas dalam arang kayu untuk pengembangan material-material fungsional serta usaha dan peningkatan pengembangan material-material fungsional menggunakan arang kayu dari pohon cepat tumbuh tropis.

Katakunci: *arang kayu, material fungsional, pohon cepat tumbuh, karbonisasi*

INTRODUCTION

The used of carbonized wood for functional materials in the engineering applications is now being considered owing to the recent discovery that it can be used for gas and heavy metal adsorbers, activated carbon, textiles, composite materials, fire retardant wood products, fuel, deodorant and electromagnetic shielding, electrical and thermal conductors and also thermal management material (Pulido *et al*., 2001; Byrne & Nagle, 1997; Demirbas, 2001; Oya&Iu, 2002; Wang & Hung, 2002; Subyakto *et al*., 2004; Sulistyo *et al*., 2009; Sulistyo *et al*., 2010). Carbonized wood which is produced by the thermal degradation of wood materials in an inert atmosphere consist of porous carbon with turbostratic microstructure in which carbon graphitic crystallites have a disordered arrangement. Pores in carbonized wood consist of gaps between elementary graphitic crystallites (Rodriguez-Reinoso & Molina-Sabio, 1992). The arrangement and growth of carbon crystallites correspond to development of pore structure during the carbonization of wood. The porous nature in carbonized wood is useful in the adsorption of heavy metals from aqueous solution (Pulido *et al*., 2001). In addition, as turbostratic carbon with porous structure, carbonized wood which provides higher reactivity than graphite has attracted for production carbide ceramics for applications such as high temperature filter, catalyst for bioengineering process (Greil, 2001) and thermoelectric materials (Fujisawa *et al*., 2008).The microstructure and pore structure in carbonized wood are considered to be important in the development of functional materials.

Currently fast-growing tree species plantation has been intensively established in the tropical countries including Indonesia to meet the increase demand of wood material. Wood materials from fast-growing trees plantation, for example jabon (*Antocephalus cadamba*), is generally utilized for wood panels, floorings, furnitures and others (Risnasari *et al*., 2011). The wood biomass residue which is generated from logging activities and processing is utilized for fuelwoods and cookings. Recently, biomass residues of fast-growing tree species has been carbonized for limited applications such as for heating, cooking, activated carbon and also was proposed for carbon sequestration (Kataki & Konwer, 2002; Maniatis & Nurmala, 1991; Marsoem *et al*., 2004; Ogawa *et al*., 2006).The current utilizations of carbonized wood biomass from tropical fast-growing trees only considered the physical and chemical properties and the pore structure of carbonized wood. This review covers the current researches on the progress in the carbonization of wood from tropical fast-growing trees, mechanism of the microstructure and pore structure development in carbonized wood during carbonization and proper utilizations of microstructure and porosity in carbonized wood for the development of functional materials and efforts enhancing the development of functional materials of carbonized wood from tropical fast-growing trees.

Progress in the carbonization of wood biomass from tropical fast-growing trees

Studies have been conducted in carbonization of wood from tropical fast-growing trees. These studies are divided into three topics i.e. characterization of wood materials particularly for fuel wood, development of wood carbonization method and charcoal production, also characterization and utilization of carbonized wood related to the carbonization conditions.

In an effort to choose tree species for fuel wood, the wood from fast-growing trees were characterized their physico-chemical properties and calorific value. Kumar & Gupta (1992) analyzed chemical content of

Acacia nilotica wood which showed that it contains 85,0 % of volatile matter, 1,03 % of ash and 14,97 % of fixed carbon. Other workers characterized the calorific value of various wood species which was found that *A. nilotica*, *A. auriculiformis* and *A. mangium* possess better fuel wood characteristics than other species, with value of 20,44, 19,67 and 18.86 kJ/kg, respectively (Kataki & Konwer, 2002; Shanavas & Kumar, 2003).They concluded that these acacia species may be considered for inclusion in energy plantation program. *Acacia mangium* and *A. crassicarpa* grown naturally in Merauke also showed good properties for fuelwood with characteristic of 85 and 83% of volatile matter, 0,24 and 0,24 % of ash, 14 and 17 % of fixed carbon and 4,066 and 4,701 cal/g, respectively (Wahyuni & Sulistyo, 2013).

In Indonesia, carbonized wood or wood charcoal is mostly produced by traditional methods including pit kiln, earth mound kiln, brick kiln and metal drum kiln (Marsoem *et al*., 2004). The improvements of wood carbonization methods have been introduced by developing various types of charcoal kilns. Nurhayati *et al*., (2006) built various integrated charcoal kilns to produce charcoal and wood vinegar as by products. These kilns carbonized acacia wood at temperature under 400 ºC and yielded charcoal around 23-35 wt.%. Marsoem *et al*., (2004) developed a movable kiln with a double layer wall which was composed of double stainless steels and a heat insulator filling up the space between the stainless steel layers. The yield of charcoal in the production by using a double layer wall of movable kiln was about 31 %. The same result was obtained by other workers which was carbonized acacia wood by using traditional earth mound and metal kiln (Khristova & Khalifa, 1993).The acacia wood conversion to carbonized wood or wood charcoal increases the calorific values from 18.07 to 520 kJ/kg.

Intensive studies on carbonization conditions related with charcoal properties were done by two research groups i.e. Kumar *et al*., (1992, 1993 & 1999) and Kumar & Gupta (1992-1994). The carbonization of *A. nilotica* was conducted at various temperature ranges from 400-1200 ºC, with various reaction time range from 1 to 5 h and using slow heating (4 ºC/min) and flash heating. The charcoal properties such as proximate and ultimate analyses, calorific value, reactivity, electrical resistivity, strength, etc. were measured in order to determine the carbonization condition which could obtain wood charcoal or carbonized wood for reductant material of iron-making. Kumar *et al.,* (1993, 1995) also investigated the effect of carbonization on morphology and crystalline structure of wood carbon by using SEM and XRD. They found that these wood charcoal properties were strongly influenced by carbonization temperature, heating rate and reaction time (Kumar et al., 1992, 1993 & 1999; Kumar & Gupta, 1992-1995). Summary of their results are as followed:

- When the carbonization temperature and reaction time increase, the fixed carbon and ash content increase from 73.85 to 88.64 % and 2.95 to 4.46 %, respectively while volatile matter content decrease from 23.20 to 6.90 %, the carbon element increase whereas the hydrogen decrease (Kumar *et al*., 1992).
- Study using SEM shows that fibrous structure of wood is conserved during slow carbonization up to temperature of 1200 ºC, while the rapid carbonization at temperature above 600 ºC breaks the fibrous structure (Kumar & Gupta, 1995).
- X-ray diffraction pattern presents broad profiles which is characteristic of a hard carbon. This

indicates that the wood chars compose of graphite-like plane arranged turbostratically. The apparent interlayer spacing (d_{002}) decrease slightly while microcrystallite diameter (L_a) increase markedly with increasing carbonization temperature and reaction time (Kumar *et al*., 1993).

- The crushing and impact strength of acacia wood chars decrease with increase of carbonization temperature up to 600 ºC follow by an increase thereafter. In contrast with slow carbonization (4 ºC/min), rapid carbonization (30 ºC/min) yields carbonized wood or wood charcoal of lower crushing strength (Kumar *et al*., 1999).
- Wood charcoal shows an abrupt decrease in their electrical resistivity value with increasing carbonization temperature up to about 800 ºC, followed by a slight decrease with further rise of temperature up to 1200 ºC. Increasing reaction time up to about 3 h influences on decreasing of the electrical resistivity value (Kumar & Gupta, 1993).
- Increasing of carbonization temperature produce a decrease in the CO_2 reactivity of resulting charcoal. Charcoal prepared under rapid carbonization exhibits significantly higher reactivity compared to those prepared under the slow one. Prolonged reaction time during slow carbonization of wood yields charcoal having lower reactivity (Kumar & Gupta, 1994).

Summary of the researches on carbonization of wood from tropical fast-growing trees which has been performed in the following conditions:

- The carbonization has been conducted at limited and uncontrolled heating conditions
- Thermo chemical conversion mechanism of wood and chemical structure change during carbonization process was still unknown
- Graphitization behavior of carbonized wood or charcoal was unknown yet
- The microstructure and pore structure development in wood carbonization is not well understood
- Only limited charcoal properties information was provided.

Mechanism of the microstructure and pore structure development in carbonized wood during carbonization

Figure 1 shows the turbostratic microstructure and pore structure in carbonized wood. The graphitic crystallites are arranged disorderly in the microstructure of carbonized wood. The gaps between the graphitic crystallites are pores with the molecular dimension and continuous network. There are cross-linking chains between graphitic crystallites in the microstructure of carbonized wood. The cross-linking influences the graphitic crystallites in the position near each other and the same time determine the hardness of carbonized wood. The cross-linking chains also preserve the morphology of wood during carbonization. Ishimaru *et al*., (2007) confirmed the cross-linking chains of ether bridges in carbonized wood by Fourier transform infrared spectroscopy.

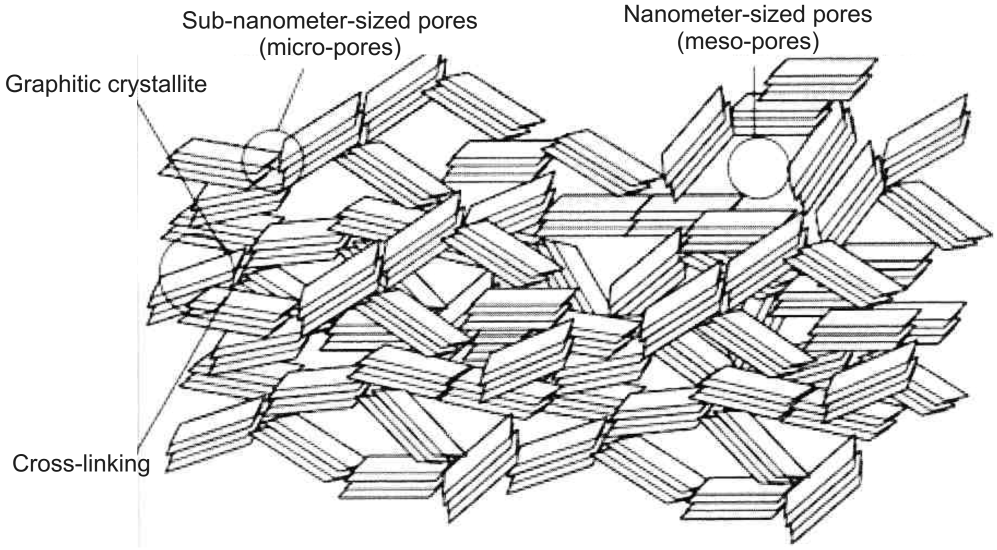

Fig. 1.Turbostratic microstructure with random orientation of graphitic crystallites and pores as the gap between graphitic crystallites in carbonized wood (Fumio Kurosaki – Kyoto University).

The microstructure and pores in carbonized wood are determined by the heat treatment conditions, including temperature, reaction time and heating rate. In the early stages of carbonization, which occur at temperatures between 307 and 347 ºC, the crystal structures of cellulose microfibrils are completely degraded and an isotropic material forms that is less crystalline (Paris *et al*. 2005). Transmission electron microscopy observations confirmed that the heterogeneity of wood cellulose disappeared during carbonization (Ishimaru *et al*., 2007). Heat treatment in the range 300 – 1400 ºC causes carbon crystallites to grow and increase the ordering in the microstructure of the carbonized biomass (Paris *et al*., 2005). This study is appropriate with the study on the chemical structure of carbonized wood by Nishiyama *et al*., (1998) which showed that the carbon double bound and aromatic rings were seen to form at a carbonization temperature of about 600ºC, whereas the ratio of aromatic carbons increased in the temperature range 800-1000 ºC. Micropores having substantial volumes have developed by 500 ºC and they increase in number with further heat treatment up to 900 ºC (Mackay & Roberts, 1981). A reaction temperature at 800 ºC resulted in carbonized wood with pores ranging from micropores to macropores (Gomez-Serrano *et al*., 1993).

Kercher and Nagle (2003) developed a “quasi-percolation model” for the microstructural and pore development in carbonaceous material above 327 ºC. This model assumes that turbostratic crystallites coexist with low-density disordered carbon. As the carbonization temperature increased above 600 ºC, the large turbostratic crystallites grew very little, but the graphene sheets grew substantially. Volumetric shrinkage suggested that turbostratic crystallites were drawn closer together as the low-density disordered carbon was converted intohigh-density graphene sheets. At approximately 900 ºC, the large graphene sheets and the large turbostratic crystallites significantly impinged on each other. This leads eventually to the formation of nanopores due to local incorporation of low-density disordered carbon into the high-density turbostratic crystallites.

Proper utilizations of microstructure and porosity in carbonized wood for the development of functional materials

In activated carbon production, the volume, structure and adsorption capacity of pores in carbonized wood are increased by activation process. The pores in carbonized wood are utilized to infiltrate the activation agents and then to be oxidized or to react with the carbon atom in the surface of the pores to create new porosity. In a physical activation process, carbonized wood is subjected to a partial and controlled gasification at high temperature with steam, carbon dioxide, air, or a mixture of these. This gasification selectively eliminates first the more reactive carbon atoms of the structure generating the porosity; further gasification will produce the final carbon with the pore structure sought (Rodriguez-Reinoso & Molina-Sabio, 1992). In a chemical activation process the lignocellulosic precursor is mixed with a chemical restricting the formation of tars (ZnCl,H_2PO_4, etc.) and, after kneading, carbonized and washed to produce the final activated carbon. The chemical incorporated to the interior of the precursor particle reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinking of the particle; in this way, the conversion of the precursor to carbon is high, and once the chemical is eliminated after the heat treatment, a large amount of porosity is formed (Rodriguez-Reinoso & Molina-Sabio, 1992).

The microstructure of carbonized wood is considered to be an important in controlling wood based carbon materials processing (Ishimaru *et al*., 2007). Since the porosity and turbostratic structure of carbonized wood are preserved at high temperature, there is considerable interest in using carbonized wood to produce engineering carbonized wood based ceramics. The conversion of carbonized wood into non-oxides ceramics such as silicon carbide (SiC) may involve infiltration and reaction with Si or gaseous SiO or liquid SiO_2. Carbonized wood serves as a host for a fluid or gas medium, which reacts with carbon to form a carbide phase (Greil, 2001). The infiltration of the porous precursor structure with a fluid medium is essential in the manufacturing of SiC ceramics. Conversion of carbonized wood into SiC offers several attractive properties, including high thermal conductivity, corrosion resistance, high strength and high wear ability (Cheung & Ng, 2007; Parneva *et al*., 2006). Numerous applications have already been proposed for these materials, including car brake systems, heating elements and aerospace components (Zollfrank & Sieber, 2005; Varela-Feria *et al*., 2008).

Efforts enhancing the development of functional materials using carbonized wood from tropical fast-growing trees

As discussed previously, the structural arrangement and growth of carbon crystallites during carbonization correspond to the pore development in carbonized wood. It is well known that the graphitization in the microstructure of a carbon material has great influence on its properties in particular the electrical, magnetic, frictional, and thermal properties (Wang & Hung, 2002). Therefore the development of microstructure and porosity in carbonized wood from tropical fast-growing trees is required to be clarified and has to be considered in relationship to the carbonization conditions such as temperature. For example, Sulistyo *et al*. (2011) reported that the degree of order of the microstructure of carbonized wood produced by traditional methods was lower than that prepared at 700 ºC. It is necessary to improve the traditional charcoal production methods that are mostly conducted at low temperature of carbonization. The clarification of the relationship between microstructure and pore structure development in carbonization of wood from tropical fast-growing trees needs to be followed by the exploitation of the microstructure and porosity in carbonized wood for the development of functional materials.

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