ACTIVATED CARBON FIBER - THE HYBRID OF CARBON FIBER AND ACTIVATED CARBON

Ting Lee, Chee-Heong Ooi, Radzali Othman and Fei-Yee Yeoh

[1]School of Materials & Mineral Resources Engineering, Universiti Sains Malaysia, Transkrian Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

Abstract. From application perspectives in adsorption, activated carbon fiber (ACF) is by far one of the most important carbon nanoporous materials to be considered. It has great advantages over other commercial porous storage materials. Activated carbon fiber (ACF) is a promising microporous material with a fiber shape and well-defined porous structure. In general, production of ACF can be commercially manufactured from synthetic carbon fiber (CF) with providing an additional activation process. The special characteristics of ACF include high packing density, excellent volumetric capacity, high speed adsorption/desorption and easy handling. The processing costs of ACF is a combination of fiber processing cost and activation cost which is relatively higher compared other activated carbon. Lately, production of ACF from lower costs precursors have been suggested from researcher by using agricultural wastes in activated carbon (AC) preparation. However, there were not much detail or publicly-available sources of information describing these natural fiber derived ACF, compared to synthetic ACF. The reasons include higher cost of fiber processing and difficulties of process to prepare fiber in desired shape. The background and development of carbon materials and ACF are described. In this section, topics such as raw materials, preparations, advantages and applications of ACFs will be covered.

1. INTRODUCTION

Activated carbon fiber (ACF) is thought to be one of the best absorbent in adsorption applications because of its considerable advantages over other commercial storage materials. It is an excellent microporous material with low mesoporosity and most with absence of macroporosity if it is well produced. ACF's characteristics of high packing density and excellent volumetric capacity present its importance and usefulness for adsorption applications [1,2]. Such ACF are very useful for various applications such as, heavy metal removal [3-5], biomedical applications [5-7], capacitors [5,8-11], vapor sensing [5], refrigeration [3,5], catalysis [12-15], electrochemical applications [16,17], natural gas and biogas storage [18-20]. ACF is commonly produced from carbon fiber (CF) which is not much different from the methods employed in AC production. The activation process can be described in a simple definition where an additional thermal treatment under oxidizing atmosphere on the CF in temperature range of 700 °C to 1000 °C [21].

There are differences in pores structure presented by common AC and ACF. Common AC has a ladder-like structure, adsorbate gas molecules have to pass through macropores first and mesopores for second path before entering micropores. In ACF, micropores can be reached in large amount by adsorbate gas which are directly exposed to the surface of the fibers, so this helps leading in adsorption mechanism [21]. ACF are commercially produced by the pyrolysis of carbonaceous materials
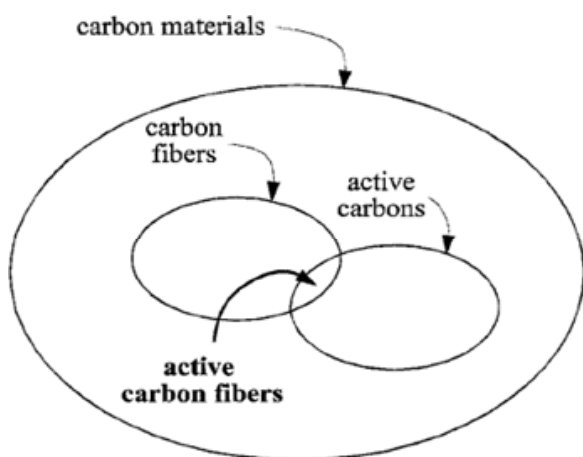
Fig. 1. Venn diagram illustrating where ACFs lie in the classification of carbon materials. Adapted from [5].

of synthetic polymers such as rayon [22-24], pitch [1,25-28], saran [29,30], polyacrylonitrile (PAN) [31,32] and phenolic resin [33,34] followed by an additional activation process. In business world, cost of processing plays an important role for the use of ACF in applications. To reduce cost of processing, some emerging studies were performed in making use agricultural by-products in biomass form as raw materials to produce cost effective ACF [35,36]. Such raw materials are ready in fiber shape naturally. Making use of such biomass as ACF materials can solve the waste disposal problem, and at the same time turning waste into wealth. Besides cost reduction, it is also considered as a green solution for ACF production to conserve a cleaner environment by reducing release of green house gasses from conventional disposal such as natural decomposition and burning as a solid fuel in a boiler. Since this is an emerging technology, existing literature about ACF production from biomass is very limited.

2. BACKGROUND OF CARBON MATERIALS

Figure. 1 illustrates the classification of ACF between two carbon materials which was recommended by International Union of Pure and Applied Chemistry (IUPAC) [5]. Essentially, ACF is the intersection of two categories of carbon materials which are carbon fibers and activated carbon, as indicated in Fig. 1. The term "activated" is sometimes substituted with "active" in some journals and books [5].

The raw materials used for preparation of ACF closely related to that of CF. In 1966, the first ACFs

were at a low yield obtained which are derived from viscose and acetate cloths (source from CF). After the first ACF production, extensive research has been carried out to produce ACF from other raw materials in order to obtain cheaper ACFs with higher yield [11]. In 1970, ACF with high yield and good mechanical properties was successful produced using lignin, polyvinychloride [29] and phenolic resin as precursors [11,37]. Since then, there were many companies commercialising ACFs from phenolic resins precursor Novolak and Kynol were the names of commercial ACF back in 1976 and 1980 respectively. It is followed by PAN- and pitch- based ACFs which were commercialized by Osaka Gas Co. Ltd in 1985 [11].

ACF can be prepared through a variety of compositions, structures and properties which depend on the raw material, method of processing and forming. It is difficult to generalise about ACF and materials based on ACF in simple words. In recent years, further research on ACF have received much attention from researchers all around the world due to its high adsorption capacities and rapid adsorption rates compared to other carbons. Various equipments and methods such as scanning electron microscopy [38,39], small angle scattering [40-42], transmission electron microscopy [43-45], X-ray diffraction [38,41,46,47], fourier transform infrared spectroscopy [48], adsorption properties [25,38,41,43,48,49], mechanical properties [43] were used in characterization to investigate the properties and improve the application performance of these popular ACF.

The current technology of ACFs is a combination of the technologies from carbon fibers and active carbons as summarized above. Detail of precursors for these carbonaceous materials such as phenolic resin, pitch and PAN is described in later part of this paper. The following section describes the detail and historical development of carbon fibers, activated carbons and activated carbon fibers respectively.

2.1. Carbon fibers

Carbon fibers, alternatively abbreviated as CFs, are carbonaceous materials in fibrous shape with diameter of 5-10 μm. The International Union of Pure and Applied Chemistry (IUPAC) defined carbon fibers as fibers, filaments, lines or reels which contain more than 92% of carbon and usually in a non-graphitic state [50]. Non-graphitic state in carbon can be described as a two-dimensional long-range order of carbon atoms in planar hexagonal networks without any measurable crystallographic order in the

Table 1. Properties of Raw Materials Used in the Manufacture of Activated Carbons. Adapted from [71].

Raw Material	Carbon (wt.%)	Volatiles (wt.%)	Density (cm^3g^{-1})	Ash (wt.%)	Texture of activated carbon	
					Hardness	Pore volume
Soft wood	40 - 45	55 - 60	0.4 - 0.5	0.3 - 1.1	Soft	Large
Hard wood	40 - 42	55 - 60	0.55 - 0.80	0.3 - 1.2	Soft	Large
Lignin	35 - 40	58 - 60	0.3 - 0.4	-	Soft	Large
Nutshells	40 - 45	55 - 60	1.4	-	Hard	Large
Lignite	55 - 70	25 - 40	1.0 - 1.35	5 - 6	Hard	Small
Soft coal	65 - 80	20 - 30	1.35 - 1.50	2 - 12	Medium hard	Medium
Petroleum coke	70 - 85	15 - 20	1.35	0.5 - 0.7	Medium hard	Medium
Semihard coal	70 - 75	10 - 15	1.45	5 - 15	Hard	Large
Hard coal	85 - 95	5 - 10	1.5 - 1.8	2 - 15	Hard	Large

third direction (c-direction) apart from more or less parallel stacking [51]. The excellent properties of carbon fibers include high stiffness, high tensile strength, light weight, high chemical resistance, high temperature tolerance and low thermal expansion. These advantages of carbon fibers attract interest from researchers in new class applications such as aerospace application in the West military in the late-1950s. CFs are also popular in civil engineering, motorsports and other competition sports [5,47,52-54].

Most commercial carbon fibers are produced from organic precursor into fiber form which involves stabilization at the initial processing steps, for example, heating PAN fiber precursor in air to temperatures up to 300 °C, then crosslinking in order to render it infusible. Finally the crosslinked precursor fiber was placed into a furnace having an inert gas atmosphere of a gas such as Argon, and heated at temperatures from 1200 °C to 3000 °C which induces graphitization of the material to drive off nearly all of the non-carbon elements, converting the precursor to a carbon fiber [5,52,53]. There are three techniques used to produce commercial fibers: melt spinning, wet spinning, or dry spinning [53]. Some of these techniques will be discussed in further section raw materials of ACF in this paper.

Certain properties are easier to develop in each carbon fiber but not available for both. Hence, the detail of raw materials and processes used to form the precursor carbon fibers are very important for structure and properties improvement. It can also help in reduction of production costs for both classes of pitch-based and PAN-based carbon fibers [53].

2.2. Activated carbons

Activated carbons, ACs, are well known porous carbonaceous materials which contain a large number of open or accessible micropores and mesopores [55,56]. The traditional term for activated carbon is activated charcoal [57]. ACs are prepared in particulate form, either as powders (particles size <100 μm, average diameter ~ 20 μm) or granules (particle size in the range 100 μm to several mm) [5]. Activated carbons can be made from nearly all carbon-rich and inexpensive precursors with a low content of inorganic substances: wood [57,58], lignite [59,60], coconut [61-65], peat [66-68], pistachio shell [69], walnut shell [70], saw dust [71], almond shell [72,73], charcoal [74], bituminous coal [75,76], brown coal [77], petroleum coke [78,79], etc.

According to T.J. Mays, (1999), the main factors of raw materials selection for production AC include cost and availability, carbon yield and inorganic matter content and ease of activation. The properties of the final AC depend on the starting material used and procedures of preparation [5]. Table 1 shows some typical materials used for AC, their properties and the type of activated carbon produced.

Traditionally, ACs can be manufactured from carbon-rich materials by carbonization followed by activation (heat treatment with an oxidizing agent), or by simultaneous carbonization-activation with presence of a dehydrating compound [50,80]. There are two main approaches to achieve activation for activated carbons via physical and chemical activation. Both activations are discussed briefly in section 4.0 - preparation of ACFs. Figs. 2 and 3 illustrate basic flow sheet for physical and chemical activation in ACs respectively [50]. Crushing and milling processes are included in the processing of
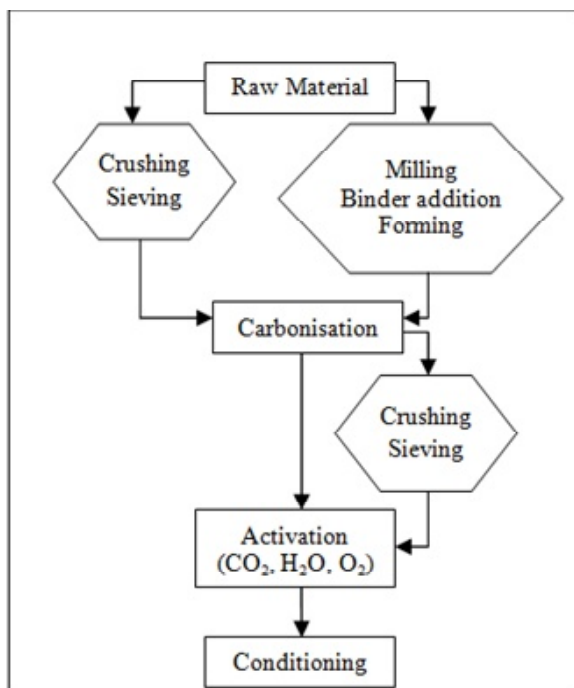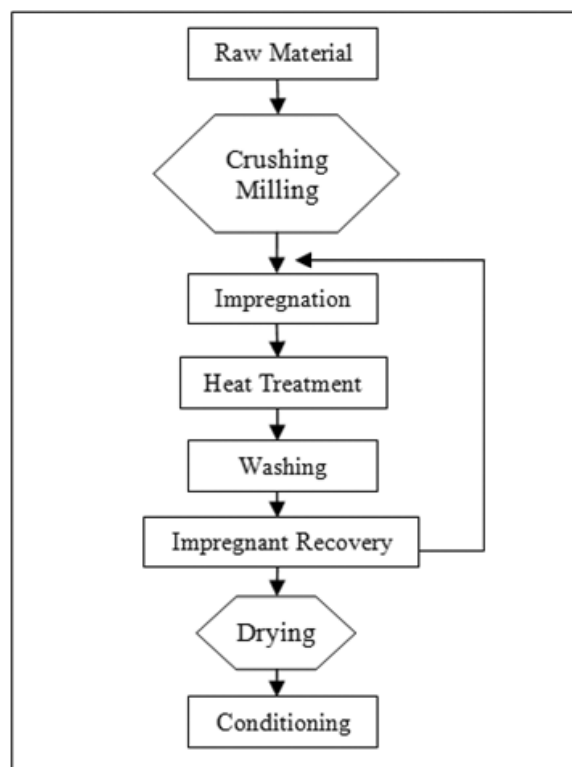
Fig. 2. Basic flow sheet for physical activation in activated carbons. Adapted from [53].

Fig. 3. Basic flow sheet for chemical activation in activated carbons. Adapted from [53].

AC. In order to produce powdered activated carbon (PAC) and granular activated carbon (GAC) with desired sizes, the produced AC is passed through crusher and tumbling machine respectively for final stage.

2.3. Activated carbon fibers

Activated carbon fibers, ACFs, are porous carbons in fiber shape with aspect ratio higher than 10 and contain a well-defined porous structure with high adsorption capacity [11, 50]. ACFs are usually prepared from general-purpose carbon fibers by a heat treatment to achieve high porosity to fulfill requirement of specific applications. One of the interesting characteristics for ACF is its extremely high surface area around 2000 m^2/g [30]. With such high surface area, ACF has been the latest additional plus point in family of porous carbon for adsorption. With this great advantage, potential adsorption applications has been widened. The understanding on ACF processing including preparation of starting precursors until derivation of final products and the characterisation of ACF in given applications are the main focuses for the researchers on development of ACFs for the past 50 years.

Fig. 4 indicates a plot of publications on ACF (combination topics of activated carbon and carbon fiber) derived from ScienceDirect as of 1980-2012. From the graph, number of publications in ACF kept increasing. By 2012, more than 160 publications about ACF in various form, *e.g.* journal papers, patents, books, *etc.*, have been published in english.

3. RAW MATERIALS OF ACFs

3.1. Synthetic raw materials

Generally, ACF can be prepared from raw carbonaceous (non-carbonized and non-activated) and synthetic fibers such as rayon [22-24], phenolic resin [33,34,81,82], polyarcrylnitride (PAN) [31,32,53,83,84] and pitch [1,25-28,46,85,86] mainly derived from petroleum products. The following sections describe selected synthetic precursor fibers utilized for the production of ACFs in the market.

3.1.1. Phenolic resins

Phenolic resin are also called as phenol formaldehyde resin (PF). These resins are synthetic polymers produced by the reaction of phenol or formaldehyde substituted phenol. A fibrous material is obtained from resin transformation after the reaction. ACFs from phenolic resin can be produced by carbonization at about 600 °C and then followed by activation with carbon dioxide (>850 °C) or steam (>700 °C) as oxidizing agent [50]. In 1891, the first true phenol-formaldehyde resin was made by
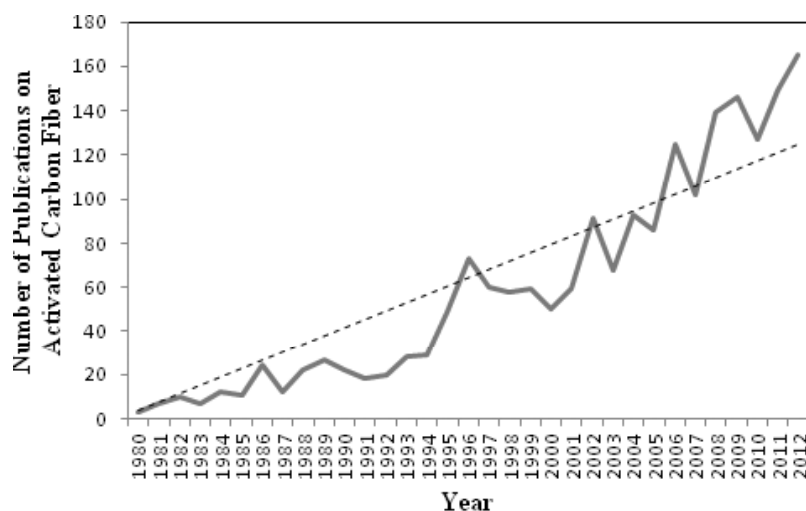
Fig. 4. Number of publications on activated carbon fibers between 1980 and 2012 steadily increase in public output. The dotted line across the plot shows the best fit in a linear trend - data derived derived from ScienceDirect as of 1980-2012.

Kleeberg [87]. Subsequently, phenolic resins were first commercialised by 1910 [82,88].

Phenolic resins are adaptable to many applications other than ACF. It is mainly used in production of circuit boards and molded products, such as laboratory countertops, pool balls and as adhesives and coatings, friction linings and oil well propants [33,82]. Some key factors that made phenolic resin maintain its commercial robustness include versatility, low cost, heat and flame resistance, durability, strength and stiffness, low toxicity, and ease of processing. Apart from these, phenolics can be formulated with excellent resistance from acids, organic solvents, and water for properties enhancement [33].

Since the phenolic resins have so much great advantages in physically properties, hundreds of technical papers and books have been written by researchers to produce ACF from phenolic resin [34,43,89,90]. A. Oya and co-workers produced ACF from phenolic resin containing cobalt as an activation catalyst and silver as an antibacterial agent. The phenolic resins were spun, stabilized in an acidic solution and follow by carbonisation at 900 °C in N_2 gas for 30 minutes. Then the ACF was obtained by activating the carbon fiber in range 750-800 °C under steam condition [34].

M.A. Daley and team worked out on adsorption of SO_2 and hydrocarbons by phenolic-based ACF. The role of pore size, pore surface chemistry, pore structure and pore volume were studied in the research for adsorption improvement. The results showed that adsorption capacity increased proportionally correlated to the amount of CO_2 evolved during heat treatment of the oxidized ACF [89,90].

3.1.2. Mesophase pitch

Raw pitch is described as a high molecular weight distillation residue produced from refining operations in petroleum or coal tar processing [91]. To obtain mesophase pitch, raw pitch is initially subjected to polymerization and condensation. This process is required to convert pitch from an originally isotropic to an anisptropic material [92]. According Brooks and Taylor, heat treatment of pitch are conducted in range 400-500 °C under inert atmosphere or vacuum for formation of aromatic hydrocarbon spheres in Fig. 5 [93,94]. Three steps are required to produce mesophase pitch from carbon fibers: melt-spinning, oxidative stabilization and carbonisation. The function of melt-spinning is to convert mesophase pitch into fiber form [92]. It is similar to the process used for many thermoplastic polymers such as nylon, olefin, polyester, saran, and sulphur [95]. Then, process is followed by oxidation which also called as stabilization. This process is carried out to improve the ultimate mechanical properties and prevent the fiber from deform during the subsequent carbonisation treatment. In general, stabilization is accomplished by heat treatment the fibers at 200-300 °C in flowing air condition. D.D. Edie and co-worker (1999) reported that the factors which affect the soaking time of heat treatment include raw materials, fiber size and the exact temperature used. The time may varies from several minutes to few hours. For carbonisation, the fibers are heated up in an inert atmosphere at temperature range 1000-1500 °C. Majority weight loss takes place in this process including liberation of CH_4, H_2, and CO_2. Subsequently, graphitisation process is carried out
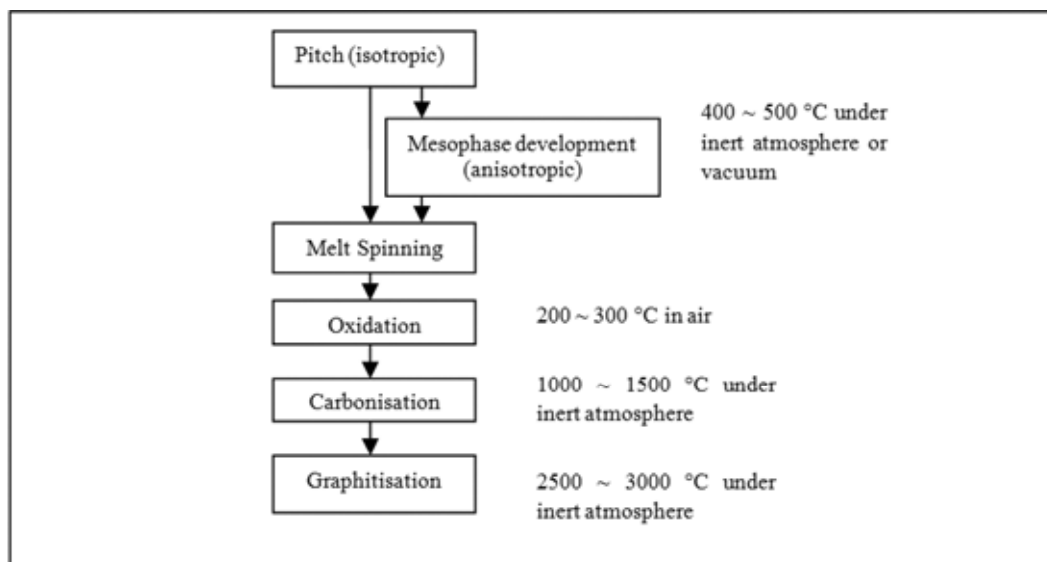
Fig. 5. Processing of carbon fiber production for Mesophase pitch. Adapted from [97].

on the fibers under inert atmosphere also but heat treatment take places at higher temperature (2500-3000 °C) to improve the strength and modulus of carbon fiber [92]. At these high temperatures, all fibers already transformed as carbon due to changes of structure. D.B. Fischbach (1971) stated that atomic diffusion and crystallite growth are occur in graphitisation process. As a result, formation of a three-dimensional graphite lattice is obtained to replace the dislocation of disorder carbon stacks [96].

Mesophase pitches are very popular raw materials used in high-modulus carbon fiber production. Mesophase pitch-based carbon fibers are also used as structural reinforcing agent in aerospace applications, *i.e.,* carbon-carbon composites. This is mainly due to its high specific strength and modulus. Apart from these, they also exhibit a high degree of anisotropy with regard to mechanical, electrical, magnetic, thermal as well as chemical prop-

erties [85]. Endo (1998) found that the texture of mesophase pitch-based carbon fibers is a direct reflection of their underlying molecular structure [85]. Therefore, the properties of mesophase pitch-based carbon fibers can vary significantly with fiber texture. Fig. 6 indicates the observed textures of mesophase pitch-based carbon fibers. Basically, there are some folding degrees observed in the crystallites, which help in resistance of crack propagation in fibers while increase its tensile strength. The properties of mesophase pitch-based carbon fibers depend on their own textures. Another example, the unique arrangement of random texture have high potential of improved compressive strengths [92].

3.1.3. Polyacrylonitrile (PAN)

The PAN-based carbon fibers exhibit their exceptional tensile strength and also represent about 90%
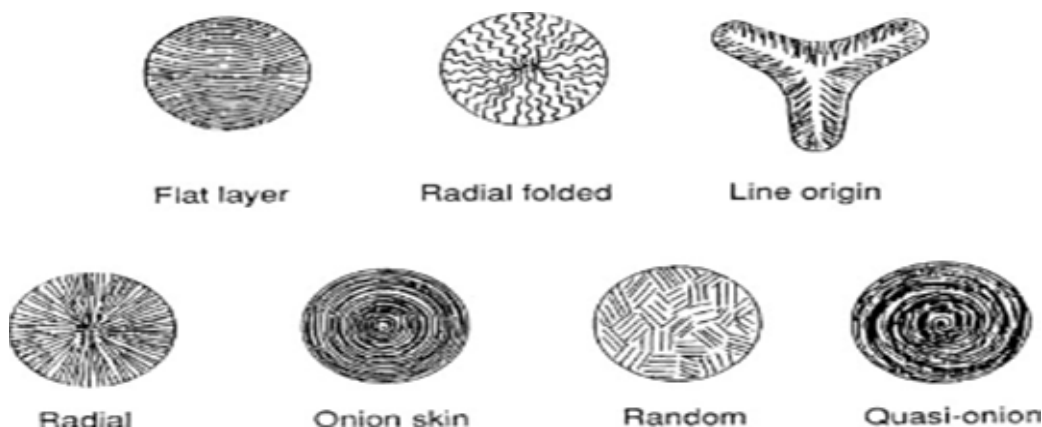
Fig. 6. Microstructures of mesophase pitch-based carbon fibers. Adapted from [30].
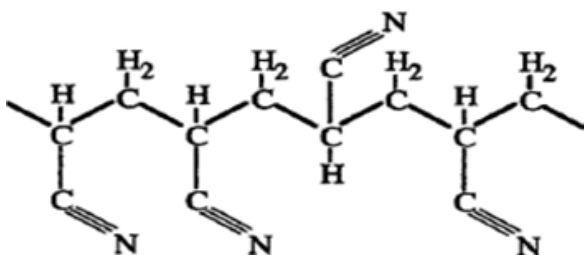
Fig. 7. The chemical repeat unit of polyacryloni-trile. Adapted from [95].

Fig. 8. Processing of carbon fiber production for activated PAN-based fibers. Adapted from [97].
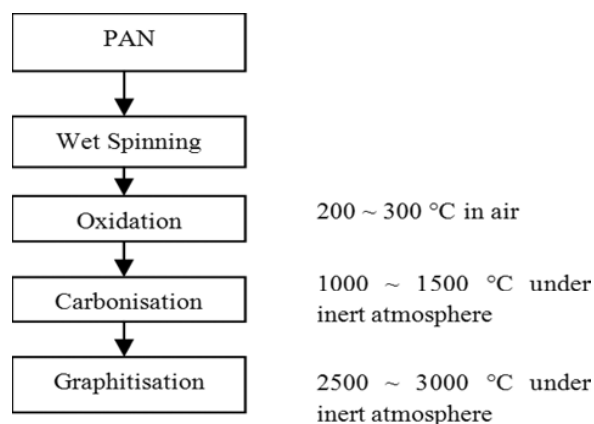
of the total production of carbon fibers. They are considered far more resistant to compressive failure than pitch-based counterparts or polymeric high performance fibers [92]. Fig. 7 shows the repeating unit of polyacrylonitrile. PAN is an atactic polymer where the nitrile groups are randomly located with respect to the polymer backbone. Extended structures of PAN molecules are formed due to high electronegativity of the nitrile group. The resulting hydrogen bonding between the polymer chains allows stronger properties of fibers to be produced in the process [97].

Fig. 8 shows flow chart of carbon fiber production for activated PAN-based fibers. PAN is generally produced into fibers via a wet spinning process due to the polymer degrades before melting. Wet-spinning process for PAN-based fibers is shown Fig. 9. The steps after wet-spinning process including oxidation, carbonisation and graphitisation are same in part of mesophase pitch. Additional info from team of Riggs, D.M., the yield of carbon fiber for PAN in carbonisation process is obtained in the range of 40-45% [98].

PAN has become an interesting starting material for the preparation of carbon fibers due to its properties of high carbon yield and high melting point. The PAN derived ACFs can be prepared by heat treatment in air at temperature 200 - 300 °C (oxygen is needed in the fiber and for structure stabilisation). After that, the carbon fiber can be carbonised and activated in the usual method [50]. Diefendorf and Tokarsky [99] have reported that a fibrillar microstructure exists in the PAN-based carbon fibers which shown in Fig. 10. Compared to mesophase pitch-based carbon fibers, PAN-based carbon fibers have higher tensile strength but lower tensile modulus which have also been reported in Matsumoto's studies [94].

3.2. Biomass raw materials

As synthetic fibers are generally derived from petroleum products, which are thought to be less envi-

ronmental friendly due to liberation of green house gases $i.e.$ CO_2 and CH_4 from fossil sources. On top of that, high burnt off percentage of such expensive raw materials eventually increases cost of ACF production. As an alternative, carbon neutral natural fiber from biomass became more popular to be used as a raw materials for ACF preparation. They include oil palm fiber [100,101], coconut fiber [102,103], hemp fiber [104], jute fiber [102], flax [105], bombyx silk [106], sisal [107], abaca [108], kenaf [109], and so forth.

For an example, millions of tonnes of biomass such as empty fruit bunch (EFB) and mesocarp fiber are generated as by-products from palm oil industry each year. Depending on locations of palm oil mills, some of such wastes generated from mills located in urban area could be sold as low grade solid fuels but most of them do not have high commercial value. They are treated as agricultural wastes dumped for decomposition. This generated a great deal of greenhouse gases e.g. methane and carbon dioxide contributing to global warming. In fact, these biomass by-products could be processed into value added products such as biochar, AC or ACF. With these advantages, conversion of waste to wealth researches have been studied by
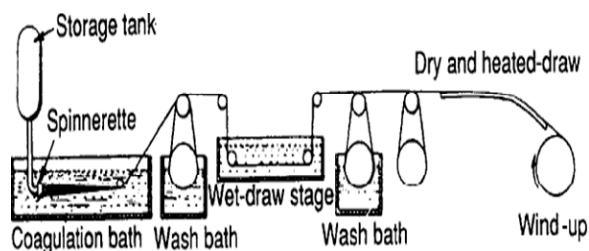
Fig. 9. Schematic of wet-spinning process used to produce PAN precursor fibers. Adapted from [95].
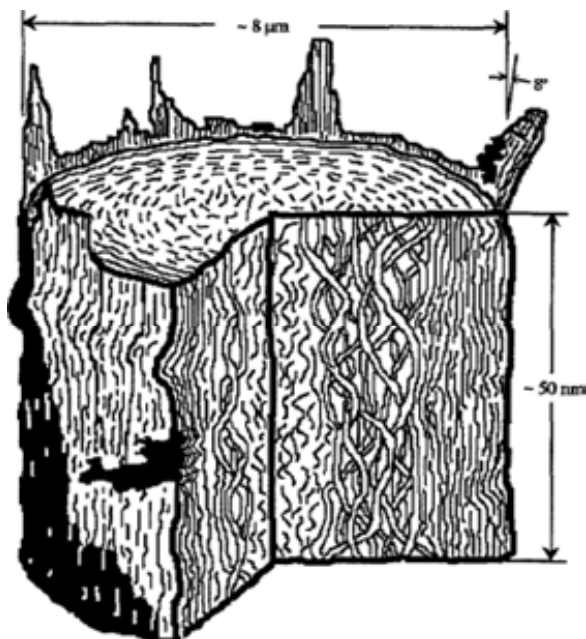
Fig. 10. Schematic model of the fibrillar texture of a carbonized PAN fiber. Adapted from [95].

many researchers using various type of agricultural by-products. The agricultural by-products also indicated as a potential materials in the production of ACFs with excellent adsorption capacity. Phan and team successfully produced ACFs from coconut fiber which present high specific surface area (1500 m^2/g) with chemical activation by phosphoric acid. The adsorption capacity are comparable to those of other commercial activated carbon fibers [102]. In addition, ACFs derived from agricultural wastes such as oil palm empty fruit bunches [110] and coconut fiber [102] exhibit good adsorption capacity of phenol and suitable for application in wastewater treatment.

According to Edie (1998) and Phan (2006), the desired properties of activated carbon fibers can be produced based on the nature of precursor used, the activating agent and the processing conditions employed [92,102]. However, application and preparation of ACF from biomass is still very limited compared to commercial synthetic ACF. So, more emphasis and resources on research works are needed to improve development of ACF production from biomass.

4. PREPARATION OF ACTIVATED CARBON FIBERS

The development of activated carbons (AC) and activated carbon fibers (ACF) are closely related to the carbon fibers (CF) (Fig. 1). The raw materials used for preparation are actually same as for CF.

Linares-Solano and his partner (2008) stated that method of activation plays an important role in determining porous structure. Activation which was introduced in process could help in increasing number of pores and continue expanding the size of the existing pores. As a consequence, porous carbon with high adsorption capacity can be produced [11].

Generally, synthesis of ACFs can be accomplished by any of the following three methods include carbonisation, physical activation and chemical activation (refer basic flow sheet for physical and chemical activation in activated carbons) in Figs. 2 and 3. However, there are also the differences in processing steps between activated carbons and activated carbon fibers derived from biomass fibers which are described as following:

(a) Crushing and milling steps are not included in the processing of activated carbon fibers. The purpose for elimination of crushing and milling from the ACF processing steps was because of the intention to maintain the fibrous shape (length-to-diameter ratio higher than 10) which exhibit better properties compared to activated carbons to fulfill requirement of certain applications.

(b) Carbonisation and chemical impregnation derived raw material for further physical and chemical activation [102, 111]

(c) Reduction in several processing costs. High electric consumption in crushing and milling activities. Sieving process is not needed after elimination of crushing and milling. Time reduction also contribute as one of the extra points in cost of the final product.

4.1. Carbonisation

In most cases, carbonisation is performed by pyrolysis under an inert atmosphere at a high temperature and nitrogen gas flow as an inert atmosphere in the process [80]. There are also some studies carried out the carbonisation process by combustion under ambient/air atmosphere at lower temperature. Presently, studies have been reported on the preparation of activated carbon products from biomass chars which can also be achieved with vacuum pyrolysis [70,80,112], summarized in Table 2. This table presents some carbonization (combustion and pyrolysis) and activation conditions of agricultural residues for porous carbon production.

During carbonization process, thermal decomposition of raw materials eliminates non-carbon elements such as oxygen and hydrogen and nitrogen and lead to a carbon skeleton (char), with a rudi-

Table 2. Carbonization and activation conditions of agricultural residues.

Two-step Process

	First Thermal Treatment (Carbonization)			Second Thermal Treatment (Char Activation)			
Material	Temperature (°C)	Duration (hr)	Atmosphere	Temperature (°C)	Duration (hr)	Atmosphere	Ref.
	Combustion Conditions			Activation Conditions			
Tires	140	360	Air	900	1	CO_2 or He	[126]
Bagasse	160	2	Air	900	1-15	CO_2	[127]
Oil Palm Wood	350-420	3-6	Air	519-806	1-3.5	Air	[56]
	Pyrolysis Conditions			Activation Conditions			
Cedar Wood	600-800	2	N_2	700-900	2-4	CO_2	[128]
Oil Palm Shell	900	1	N_2	850	1-7	CO_2	[18]
Oil Palm Stone	600	2	N_2	700-900	1	CO_2	[129]
Oil Palm Empty Fruit Bunch	700	2	N_2	750-825	1-3	CO_2	[130]
Cherry Stone	600	2	N_2	350-550	2	Air	[48]
Olive Stone/Solvent-Extracted Olive Pomace (SEOP)	800	1/6	Vacuum	800	2	Steam	[131]
Hemp fiber	60	24	Vacuum	400-550	2	N_2	[104]
Cotton Stalk	600	1/2	N_2	800-850	1/2, 1/3	Steam	[132]
Pistachio-nut Shell	350-1000	2	Vacuum	900	1/2	CO_2	[80]

One-step Process

Material	Temperature (°C)	Duration (hr)	Atmosphere	Remarks	Ref.
Banana Empty Fruit Bunch	450	1	Air	H_3PO_4 and KOH (chemical used)	[119]
Delonix regia Fruit Pod	400	1	Air	H_3PO_4 and KOH (chemical used)	[119]
Apricot/Cherry stones	800	1	Steam	-	[118]
Olive	700-800	1-2	Steam	-	[117]
Spent tea waste	600	2	Steam	-	[133]
Jute/Coconut Fiber	900	2	N_2	H_3PO_4 (chemical used)	[102]

mentary pore structure [50]. Rodríguez-Reinoso and Sepúlveda-Escribano (2001) reported that heating rate and soaking time determine the yield of the char but the characteristics of char texture are not much affected in carbonization [50]. However, the pores that are created during carbonization are very small and sometimes are blocked partially by disorganized carbon [113]. Therefore, the pores in the carbonized material have to be further developed and enhanced by second thermal treatment for activation process.

4.2. Activation

Activation can be achieved by two ways in preparation of ACF; i.e., physical activation and chemical activation. Activation is carried out to remove the disorganized carbon that blocks the pores in the activated carbon. Apart from this, it can enlarge the diameters of the pores which are formed during carbonisation process and to create some new porosity [50,113]. As a result, a well-developed and readily accessible pore structure with large internal surface area can be produced [30].

4.2.1. Physical activation

The preparation of ACFs by physical activation involves initial carbonisation of a carbonaceous material and subsequent by activation of the char under oxidizing gases such as carbon dioxide, steam, air or their mixtures in the temperature range 800 - 1000 °C [30,50,74]. To increase the efficiency of activation process, the reaction takes place inside the fibers compared to the reaction occurred outside the fibers. Higher carbon removal results better in pores development if the reaction occur inside the fiber [11]. The most common activating agents are carbon dioxide and steam, where reactions on carbon are endothermic. There are significant differences observed between these two activating agents on the porous texture and mechanical properties of the ACFs [11,114]. Virginia and Adrian (2012) found that in contrast to steam, oxidizing gases CO_2 creates final carbon product with larger micropore volume but narrower micropore size distribution [115]. According Zhang and his team (2004), CO_2 is preferably selected and used by many researchers as activation gas. The reasons includes cleanliness and easy handling of CO_2. Besides, CO_2 also helps in controlling the activation process due to the slow reaction rate at temperature around 800 °C [116].

Conventionally, physical activation is a two-step process which required both carbonisation and activation steps to produce this carbon product. Other

than that, one-step process in producing AC products also have been reported by some researchers to reduce the processing time and cost of as shown in Table 2 [117-119]. Minkova and co-workers (2007) carried out one-step pyrolysis/activation where pyrolysis of raw materials was done in a flow of steam or nitrogen at 750 °C for 2 hours [118].

Generally, the carbon products are prepared by conventional heating method for activation process. Modern developments for heating technology, microwave heating is a new approach and received great attention from many researchers. Until today, microwave activation is still being utilized at laboratory scale level for preparation of high porosity carbon products. Microwave heating is highly potential to become a feasible alternative to replace conventional heating methods in industrial production due to its number of advantages. The advantages of microwave heating over conventional heating methods include high yield of products, high heating rate, energy transfer instead of heat transfer, selective heating, better control of the heating process, lower activation temperature, smaller equipment size and less automation [120-122]. Xin-hui et al. [123] compared the AC which derived from Jatropha hull by conventional and microwave activation method. Result shown that the yield of AC is double using CO_2 as activation agent with microwave activation compared to conventional activation. The microwave activation is more cost-effective that the conventional heating due to activation temperature, activation time and CO_2 flow rate are significantly lower. Alslaibi et al. [124] reported AC production which derived from agricultural wastes by a chemical method with microwave heating exhibited higher specific surface area compared to conventional heating. The results obtained are consistent with research works from Foo and Hameed. Foo and Hammed [125] reported preparation activated carbon from oil palm empty fruit bunch by microwave-induced KOH, with the resultant adsorption capacity for methylene blue (MB) as high as 344.83 mg/g and high specific surface area.

4.2.2. Chemical activation

Chemical activation involves treatment of the starting materials with an activating agent such as zinc chloride [134], phosphoric acid [135], potassium hydroxide [136], sulphuric acid [137], hydrochloric acid [138], sodium hydroxide [139], and others. The mixture of raw material and activating agent is heat-treated under inert atmosphere at temperature ranging 400 and 700 °C. Then, the chemicals is removed

by exhaustive washing with water, followed by drying and separation from the slurry. The dried fibers are conditioned according to its application [50].

Essentially, all activation agents are dehydrating agents that inhibit the formation of tar and other by-products e.g., acetic acid and methanol. It can help in increasing above 30 wt.% of yield of carbon in this process compared to thermal activation as reported by Bansal and his partners (1988) [71]. This result is also identical with the works of Nahil and co-worker (2012) who study about preparation of ACs from cotton stalks through phosphoric acid chemical activation. Increasing the yield of activated carbon in chemical activation was due to acid activation which promotes dehydration and redistribution of biopolymers. Then, the conversion of aliphatic to aromatic compounds also took place at the same time [140].

The impregnation ratio between the mass of activating agent and the mass of raw material is one of the variables posing a great influence on the yield and porosity of the final carbon. In most studies, the impregnation ratios in the range 0.3-3 (mass of activating agent: mass of raw material) were found to be applied on various raw materials [140-143]. The yield of carbon is kept decreases when the impregnation ratio increases. More aggressive chemical reaction will results more vaporization of organic matter when larger amount of acid is applied [140]. Molina-Sabio (1995) and Nahil (2012) also worked on the impregnation ratio. Both stated that the higher the impregnation ratio brought about larger pore size in the final product [140,144]. Nahil (2012) reported that the length of polymeric species is affected by the impregnation ratio in chemical activation. At low impregnation ratios (0.3 and 0.75), the length of polymeric species might be small for narrower pores creation in micropore range. When higher impregnation ratios (1.5 and 3.0) was applied, the length of polymeric species was increased and resulted in formation of wider porosity in mesopore range [140].

Advantages of chemical activation of ACF over the physical activation also include one stage heating in chemical activation, higher yield obtained, highly microporous final products. It is more suitable for the materials which yield higher ash content. Apart from these advantages, chemical activation can assist to lower temperature for activation, shorter time for activation, and improve development of inner porosity to obtain desired result [119,145]. However, there are also disadvantages of chemical activation. Washing is needed after the heat treatment. Besides, corrosive activating agents used is also another drawback in the process [11]. Use of chemical activation agents in treatment increases cost of processing. Handling of chemical activation agents can be a dangerous and unhealthy practice. Thus, extra precautions are needed to minimise the health and safety risk.

## 5.0 ADVANTAGES OF ACTIVATED CARBON FIBERS

Activated carbon fibers are promising solid materials which exhibit excellent properties in comparison to powdered activated carbons (PAC) and granular activated carbons (GAC). Until now many researchers are interested to continue studies on ACF. The main characteristics and advantages of the ACFs are:

(a) extremely high surface area and adsorption capacity:

High adsorption capacities in ACF are due to the lack of non-adsorbing macropore and minimum mesopore spaces as described by T.J. Mays [5]. For example, T.-H. Ko and co-workers studied and reported extensively that new small pores were created in fibers due to etching of ACF surface after the activation process. Such pores (range from 10-30 nm in size) disappeared during the activation stage. Several hundred times of surface area increased after the activation process. Activation can promote enlargement of existing pores and creation of new pores. These ACF exhibit a better porous structure and capacity in basic dye adsorption than those carbon fiber that without activation [31] .

In ACF, most micropores are exposed directly to surface of fibers and to the adsorbate gas whereas in GAC, the adsorbate gas molecules have to pass through macropores and mesopores before reaching micropores. In this case, the adsorption and desorption rate of toluene on ACF are much higher than those on GAC, as reported by Manocha (2003) [30]. Of course such desorption of toluene gas can be further accelerated by raising the temperature on ACF.

A new research group worked on differences between microstructures of oil palm empty fruit bunch (EFB) precursor and EFB-based ACF. The SEM images for oil palm empty fruit bunch (EFB) precursor and EFB-based ACF are shown in Fig. 11. Referring to the SEM micrographs, new flaws and open pores are detected in cross section and surface area of EFB-based ACF which had undergone activation process. Carbon dioxide acts as an activating agent and etches the carbon basal planes of carbonised fibers in the activation process. New
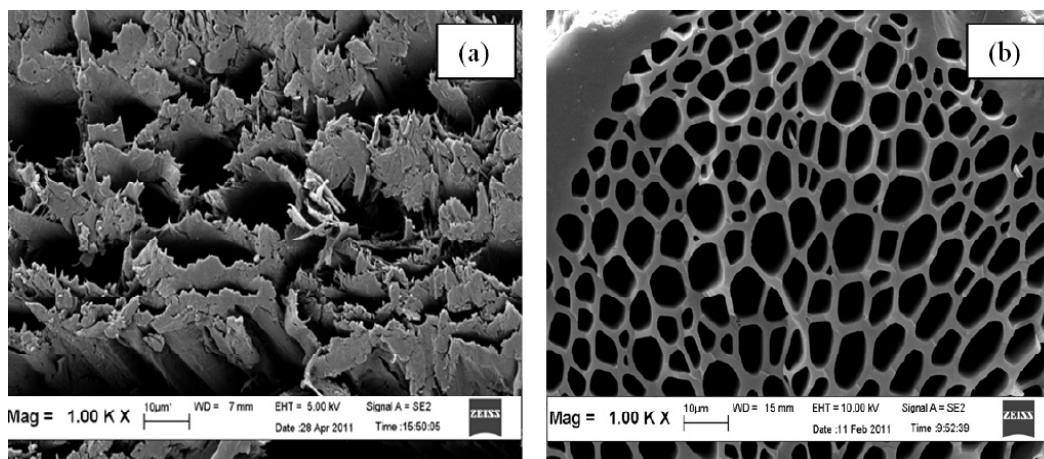
Fig. 11. (a) SEM micrograph for cross section of EFB precusor (1000x), (b) SEM micrograph for cross section of EFB-based ACF (1000x).

flaws and degradation of the fiber structures appeared after activation process. In short, high surface area and porosity of fiber product can be achieved remarkably after activation taking place [130].

(b) Fine and uniform diameter of fiber shape:

Most commercial ACFs have a small diameter in ranging between 10 and 40 μm compared to larger PAC or GAC which have ~ 100 μm and ~ 1000 μm diameter respectively. Fig. 12 shows the SEM images of a commercial activated carbon fiber.

Mays (1999) reported that fine and uniform diameter of ACF essentially eliminates limitation of mass transfer and exhibited rapid adsorption and desorption rate. It meant faster fluid transport to and from micropores and mesopores in ACF compared to other carbon materials [5]. Shmidt *et al.*(1997) reported that adsorption of methylene blue from solution in a rayon-based ACF is two orders of magnitude quicker than in a granular active carbon and one order of magnitude quicker than in a powdered active carbon at ambient temperature [147,148]. Fig. 13 illustrates the diameters range of fibers and adsorption capacities of various ACFs derived from different raw materials [88]. This is a very important characteristic for new applications which require higher packing density, *i.e.*, gas storage.

(c) Narrow and uniform pore size distribution:

The pore size of ACFs essentially build up from micropores which are narrower than 2 nm defined by IUPAC. Generally, the range of pore sizes is between 0.8 nm - 1 nm (ultra-micropore region). The range of pore size for three commercial ACFs include cellulose-based, pitch-based and PAN-based ACF is shown in Table 3 [88].

(d) Tailorability in fabrication:

ACFs are light material and have great flexibilty. They can easily proceed the product in different shape and forms of the sorbent, *i.e.*, woven clothes, nonwoven mats, papers and felts [11,30,88]. With such flexibility on these materials, the ease of handling and packing efficiency also increase directly for some specialised applications. For examples, ACFs can be used as filtration candles for small purification systems, as deodorant in defrigerators, capacitor, etc [8,30]. As revealed by Tanahashi and co-workers [8], the tailorability of ACF is greater than GAC electrodes in capacitor application. To improve robustness of material, ACF is mixed with wood pulp using paper-making technology and then continue developed as polarizable electrodes of electric double layer capacitors [8]. Problems which have been arised in the packing of the granules or powders of conventional ACs can be avoided by using ACFs [84].

## 6. APPLICATIONS OF ACTIVATED CARBON FIBERS

Today's activated carbon fibers (ACF) are advanced and versatile materials which have very great potential in large number of applications, as indicated in Table 4. In list of applications, some of them and advantages of ACF over the conventional AC will be mentioned as outlined below.

6.1. Storage of natural gas

Adsorbed natural gas (ANG) is a more preferable technology than compressed natural gas (CNG) due to its relatively safer and lower pressure (3-4 MPa) at room temperature for application of methane adsorption [18,165,166]. ANG can potentially achieve
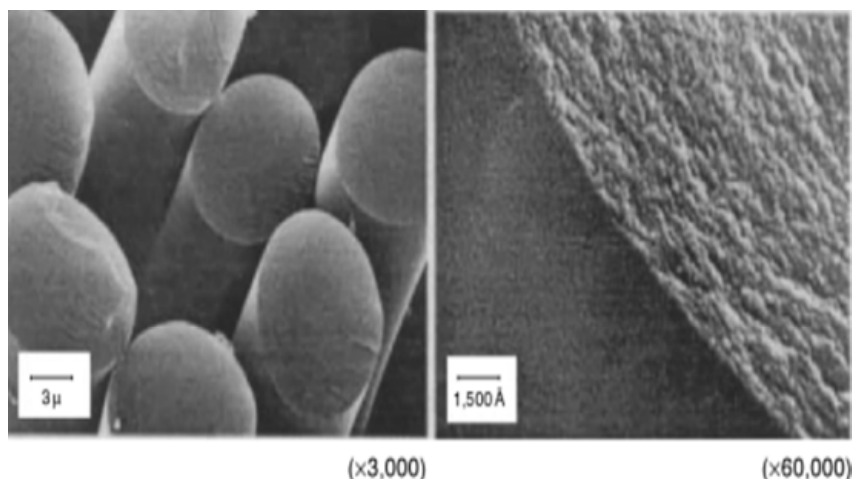
Fig. 12. Scanning electron microscope images of a commercial activated carbon fiber derived from phenolicresin fibers in 3 kX and 60 kX maginification respectively. Adapted from [91].
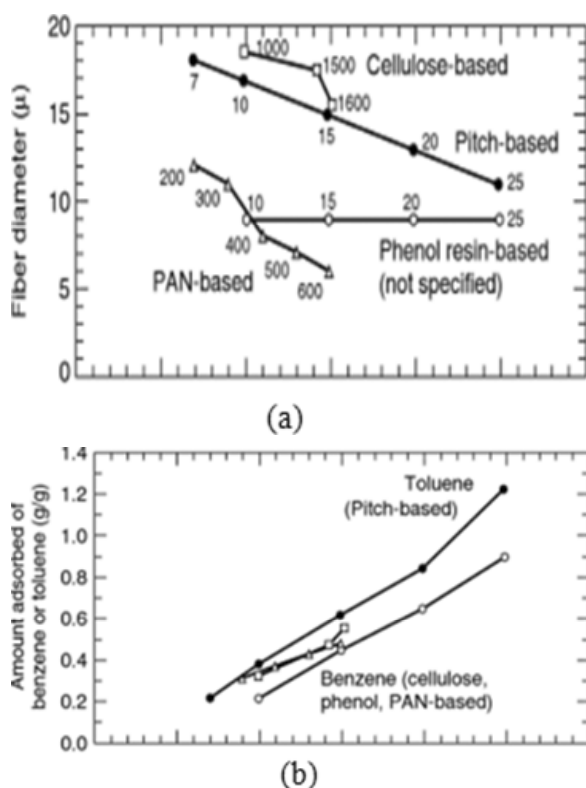
Fig. 13. (a) Diameters ranging of fibers, (b) Adsorption capacities of various ACFs include cellulose-based, pitch-based, PAN-based and phenol resin-based at 20 °C Adapted from [91].

low gas storage pressure with a single-stage compressor without sacrificing deliverable capacity [20,167]. Natural gas is usually kept in a lightweight cylinder which is filled with highly porous adsorbents in ANG technology [20]. Several studies have been carried out on methane storage focused on the preparation and characterisation of carbon-based porous materials which able to achieve an optimum methane adsorption capacities and delivery [11,149]. These works concluded that activated carbon fiber (ACF) has a considerable advantage over AC and as the best adsorbent for methane storage application.

6.2. Removal of SO_2 and NO_x

The application of ACF in SO_2 and NO_x removal have been extensively reported elsewhere after AC as a main material [150,168]. Team of Mochida *et al.* [150] have reviewed the applicability of pitch-based activated carbon fibers for the removal of SO_2 and NO_x. It was found that pitch-based ACF with heat treatment in nitrogen at temperatures ranging from 600 to 900 exhibited the highest activity for SO_2 reduction in the presence of water at temperature

Table 3. Pore sizes of ACF determined by N_2 and He adsorption. Adapted from [91].

		Cellulose-Based	Pitch-Based	PAN-Based
N_2	BET Surface Area	11.47	795	743
	Micropore Vol. (cm^3/g)	0.58	0.37	0.35
	Pore Size (Å)	10.1	9.4	9.5
He	Narrow Pore Vol. (cm^3/g)	0.54	0.42	0.32
	Wide Pore Vol. (cm^3/g)	0.04	0	0.01
	Pore Size (Å)	9.3	7.6	8.9

Table 4. Applications of activated carbon fiber produced from raw materials.

Application	Raw Material	Reference
Storage of natural gas	Pitch	[1,3]
Treatment of wastewater and air	Jute, coconut fiber, oil palm fiber	[4,5]
Removal of SO_x and NO_x	Pitch, cellulose	[6-8]
Separation of Gas	Polyimide	[9]
Purification of water	Pitch, phenolic resin, viscose	[10-13]
Removal of volatile organic compound		[14-16]
Adsorption of toxic gases	Rayon	[14,17,18]
Medication		[19,20]
Capacitor	Phenolic resin, PAN	[21-23]
Catalyst	PAN	[24,25]
Refrigeration	PAN	[26,27]

25 °C. Reduction of atmospheric NO_x to harmless N_2 was successfully achieved using pitch-based ACF through cooperation of the TiO_2 photocatalyst and urea. The ACF for NO_x removal system in the atmosphere have the potential to work effectively in urban area using method of natural wind [168]. The advantage of ACF over the conventional AC in gas-phase adsorption is their unique porous structure which support the adsorption process to perform more rapidly. Essentially, the structures of ACFs consist microporosity that is readily available to the adsorbate and absence of diffusion within meso- and macroporosity which constrain transfer limitation [11,88].

6.3. Purification of water

Water is one of the most important substances on earth. The purification of water supplies, removal of contaminants from wastewater and inhibition of bacterial growth are required to ensure water supply is in clean and good quality for use. Initially, granular activated carbon are popular to be selected as a material for water purification. However, recently some of studies have shown that ACF can be a better alternative to GAC as media for water purification [169-171]. From those studies, it can be concluded that ACF can perform better adsorption capacities and rates for low molecular weight pollutants. Besides, ACFs are easier for regeneration which is an extra advantage. However, bacteria are detected and spread easily on ACF due to its fiber structure. Presence of bacteria may cause pollution to water and affect the quality of water. To solve this problem, Oya and team were developed antibacterial activated carbon fiber with addition silver since 1993 for water treatment. Applications of these antibacterial ACF showed antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* [43,154].

7. CONCLUSIONS

Activated carbon fiber (ACF) combines the best of carbon fiber and activated carbon. Additional applications of ACF can be created from the continuous development process capitalising on advantages of these two groups of basic carbon materials. ACF is fibrous microporous carbon which have attracted the interest from many researchers in a number of advanced technologies. Advantages of ACF compared to classical active carbon include its higher adsorption capacity, higher surface areas, more rapid adsorption and desorption rates and ease of fabrication. Proper selection of precursor carbon fiber, activation method and experimental conditions could tailor pore size distribution and porous structures in the preparation of ACFs for desired specific applications. Activated carbon fibers have been utilised in number of applications to replace activated carbon as main selection of material which able exhibit better performances. Such applications include gas and liquid phase adsorption, water purification, natural gas storage, medication, capacitor, catalyst, refrigeration, etc. There is still wide scope for development of ACF in advanced technologies to construct energy sufficient, trouble free and high quality of living environment for future. Considering environmental impact of ACF production, many types of biomass have began to emerge in replacing synthetic fiber as a raw material for ACF production. Making use of biomass not only solves environmental issues, but also creating wealth from such agricultural wastes at the same time.

ACKNOWLEDGEMENTS

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