CHARACTERIZATION AND GAS ADSORPTION PROCESS OF POLYACRYLONITRILE-BASED CARBON FIBERS

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CHARACTERIZATION OF POLYACRYLONITRILE-BASED CARBON FIBERS FOR GAS ADSORPTION PROCESS

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Dedicated to my beloved parents
(*Yusof bin Omar and Rahidah binti Daud*)
my husband
(*Mohizan bin Moktar*)
My daughter
(Nur Hana Arissa)
my siblings
(*Suai, Izah, Nazmi, Nazri*)
and friends who give me inspiration, encouragement and endless support throughout the success of my study.
May this thesis be an inspiration and guidance in the future.

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ABSTRACT

Polyacrylonitrile (PAN) has been found to be the most suitable precursor for producing carbon fibers (CFs) for gas adsorption because of its advantages such as high thermal stability, high specific surface area and high adsorption properties. The objectives of this study were to prepare and characterize polyacrylonitrile (PAN)-based carbon fibers (CFs) prepared via solvent-free coagulation process and study the influence of heat treatment process parameters on its morphological structure and gas adsorption properties. The factors considered in this study were polymer PAN concentration (10 wt. % - 18 wt. %), effects of acrylamide (AM) addition (0 wt. % - 7 wt. %), the stabilization temperatures (200 °C – 300 °C), and also the activation temperatures (600 °C – 900 °C). The PAN precursor fibers were produced via solvent-free coagulation process. The coagulated PAN fibers were then collected and dried under stress in oven for three hours before being post-treated with $KMnO_4$. The treated PAN fibers were then subjected to heat treatment process which involved stabilization, carbonization and activation steps up to 900 °C. The PAN fibers were characterized using scanning electron microscopy (SEM), Fourier transform infra-red (FTIR), x-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetry analysis **(**TGA), X-ray photoelectron spectroscopy (XPS), Vario elemental analyzer, tensile testing machine, and Nitrogen Adsorption at -196.15 °C. Experimental results showed that PAN fibers containing 5 wt. % AM has the best mechanical properties as compared to those fabricated from pure PAN and PAN/ AM with 2 wt. % and 7 wt. % of AM with the Young Modulus of 5.54 GPa. In addition, the PAN fibers with 5 wt. % AM exhibited superior exothermic trend with the lowest initiation stabilization temperatures. The best stabilization temperatures were found to be at 275 °C in air atmosphere with the Young Modulus of 7.50 GPa. Meanwhile 600 °C were the best moderate carbonization temperatures for preparing the activated carbon fibers (ACFs). The activated carbon fibers prepared at 900 °C (ACFs 900) showed the best adsorption properties compared to the other ACFs with 626.94 m^2/g specific surface areas and the average pore diameter of ACFs 900 is in the microporous range (18.6 Å). In conclusion, the PAN based CFs for gas adsorption processes were successfully prepared via environmentally friendly solvent-free coagulation process and suitable heat treatment processes.

ABSTRAK

Poliakrilonitril (PAN) telah dikenal pasti sebagai prapenanda yang paling sesuai untuk menghasilkan gentian karbon (CFs) untuk penjerapan gas kerana beberapa kelebihannya seperti, kestabilan terma yang tinggi, kawasan pemukaan spesifik yang tinggi dan sifat kebolehjerapan yang tinggi. Tujuan kajian ini adalah untuk menghasilkan dan mencirikan gentian karbon (CFs) dari poliakrilonitril (PAN) dengan menggunakan pengentalan dalam takungan bebas pelarut dan mengkaji kesan pemanasan ke atas struktur morfologi dan kebolehjerapan gasnya. Terdapat beberapa faktor yang dikaji dengan teliti dalam kajian ini termasuk kepekatan larutan polimer (10 berat % - 18 berat %), kesan penambahan akrilamid (AM) (0 berat % - 7 berat %), suhu semasa penstabilan (200 ^{o}C – 300 ^{o}C), dan juga suhu pengaktifan (600 ^{o}C – 900 ^{o}C). Gentian prapenanda PAN dihasilkan menerusi teknik pengentalan dalam takungan bebas pelarut. Kemudiannya, gentian tersebut dikumpul dan dikeringkan di bawah tekanan dalam ketuhar selama tiga jam sebelum dirawat menggunakan $KMnO_4$. Gentian PAN terawat kemudiannya menjalani langkah-langkah pemanasan yang melibatkan proses penstabilan, pengkarbonan dan pengaktifan sehingga 900 ^{o}C. Gentian PAN dicirikan menerusi imbasan elektron mikroskopi (SEM), infra-merah pengubahan Fourier (FTIR), teknik pembelauan sinar-X (XRD), pemeteran kalori pengimbasan kebezaan (DSC), analisis gravimetri haba **(**TGA), spektroskopi electron-foto sinar-X (XPS), penganalisis elemen Vario, mesin pengujian tegangan dan penjerapan nitrogen pada suhu -196.15 ^{o}C. Hasil kajian menunjukkan gentian PAN yang mengandungi 5 berat % AM adalah terbaik dari segi ciri mekanikal berbanding gentian PAN asli dan gentian PAN yang mengandungi 2 dan 7 berat % akrilamid dengan nilai modulus Young 5.54 GPa. Tambahan pula, ciri eksotermik bagi PAN yang mengandungi 5 berat % AM juga adalah yang terbaik dengan permulaan suhu penstabilan terendah. Suhu 275 ^{o}C dalam persekitaran udara didapati adalah suhu terbaik untuk proses penstabilan dengan nilai modulus Young 7.50 GPa. Manakala suhu 600 ^{o}C adalah suhu terbaik untuk proses pengkarbonan sederhana bagi penyediaan gentian karbon diaktifkan (ACFs). Gentian karbon diaktifkan pada suhu 900 ^{o}C (ACFs 900) pula menunjukkan sifat kebolehjerapan paling baik berbanding gentian karbon diaktifkan (ACFs) yang lain dengan kawasan permukaan spesifik 626.94 m^2/g dan diameter purata liang berada dalam julat bahan berliang mikro (18.6 Å). Kesimpulannya, gentian karbon (CFs) berasaskan PAN untuk tujuan proses penjerapan gas telah berjaya dihasilkan melalui proses pengentalan di dalam takungan bebas pelarut dan proses pemanasan yang sesuai.

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LIST OF ABBREVIATIONS

AC	–	Activated carbon
ACFs	–	Activated carbon fibers
ACFs 600	–	Activated carbon fibers at 600 ^{o}C
ACFs 700	–	Activated carbon fibers at 700 ^{o}C
ACFs 800	–	Activated carbon fibers at 800 ^{o}C
ACFs 900	–	Activated carbon fibers at 900 ^{o}C
AFM	–	Atomic force microscopy
AM	–	Acrylamide
ANG	–	Adsorbed natural gas
C	–	Carbon
CFs	–	Carbon Fibers
CH_4	–	Methane
CNG	–	Compressed natural gas
CNTs	–	Carbon nanotubes
CO	–	Carbon monoxide
CO_2	–	Carbon dioxide
DMAc	–	Dimethylacetamide
DMF	–	Dimethylformamide
DMSO	–	Dimethylsulfoxide
DSC	–	Differential scanning calorimetry
EDS	–	Energy dispersive spectrometer
FTIR	–	Fourier transform infrared spectroscopy
GPa	–	Giga Pascal
HCN	–	Hydrogen cyanide
HTT	–	Heat treatment temperature

IA	–	Itaconic acid
IM	–	Intermediate modulus
IR	–	Infrared
$KMnO_4$	–	Potassium permanganate
LNG	–	Liquefied natural gas
MA	–	Methacrylic acid
Mn	–	Manganese
NA	–	Not available
N_2	–	Nitrogen
NG	–	Natural gas
NGV	–	Natural gas vehicle
PAN	–	Polyacrylonitrile
PFs	–	Precursor fibers
SEM	–	Scanning electron microscopy
SFs	–	Stabilized fibers
TGA	–	Thermogravimetry analysis
WAXD	–	Wide angle X-ray diffraction
XPS	–	X-ray photoelectron spectroscopy
XRD	–	X-ray diffraction
YM	–	Young Modulus

LIST OF SYMBOLS

$ – Dollar

% – Percent

$\AA$ – Angstrom

A_a – Amorphous area

A_c – Crystalline area

E_c – Elastic modulus of carbon fibers

E_p – Elastic modulus of precursor fibers

$\mathrm{L_c}$ – Stacking size

MW – Molecular weight

nm – nanometer

P_x – Stress

θ – Angle

$\mathrm{R_a}$ – Mean surface roughness

$\mathrm{T_g}$ – Glass transition temperature

$\mathrm{T_m}$ – melting point temperature

v/v – Volume per volume

V – Velocity

wt. % – Weight percent

β – Width in degree of the half-maximum intensity

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CHAPTER 1

INTRODUCTION

1.1 PAN Based Carbon Fibers

Carbon fibers can be made from various types of precursors such as pitch, polyacrylonitrile (PAN), coal, rayon and the latest development is through vapor grown fibers. However, the commercial production of vapor grown fibers is still in its infancy. The two most dominant classes of precursor fibers ar+e polyacrylonitrile-based (PAN-based) and pitch-based carbon fibers. Established study recently shows that PAN-based carbon fibers are the most suitable and widely applied for making high performance carbon fibers (Farsani *et al.*, 2007; Huang, 2009; Rahaman *et al.*, 2007). Although carbon fiber can be made from pitch precursor, the processing cost and purifying it to the fiber form is very expensive compared to PAN precursor fibers (Chung, 2001).

Carbon fiber is a new breed of ideal engineering fiber that can be produced from many different types of precursor but about 90 % of world’s total carbon fiber productions are polyacrylonitrile (PAN)-based (Sánchez-Soto *et. al.*, 2001; Huang, 2009; Morgan, 2005; Donnet, 1998; Sutasinpromprae *et. al.*, 2006; Yusof and Ismail, 2012a). As the performance of carbon fiber composites highly depends on its precursor and good precursor should have high carbon content (Ko *et al.*, 1992b), high molecular weight (Hou *et al.*, 2006; Sawai *et al.*, 2006) and also high degree of molecular orientations (Sawai *et al.*, 2006; An *et al.*, 2006; Jie and Wangxi, 2005), PAN-based carbon fibers seems to satisfy all of these requirements.

Commercially, carbon fibers for composites materials are divided into general purpose such as for sporting goods and high performance carbon fibers e.g. in aerospace and aircraft industries (Chung, 2001). The general purpose type is characterized by an amorphous and isotropic structure, low tensile strength, low tensile modulus and low cost. Meanwhile, high performance type is characterized by relatively high in strength, stiffness and modulus which are the most important characteristics of an ideal engineering material. The urgency of structural requirement for the aircraft and aerospace industry led to improved high strength and high modulus fiber and their composites. Carbon fibers are seldom used alone but widely used as reinforcement with other matrices in composite materials such as carbon fiber reinforced plastics, carbon fiber reinforced ceramics, carbon–carbon composites and carbon fiber reinforced metals, because of their high specific strength and modulus (Donnet *et al.*, 1998).

Carbon fibers which are reinforced with other matrix, exhibit the highest specific stiffness. This will serve to transmit load from the point of impact further into the structure so that higher load can be absorbed without permanent damage (Savage *et al.*, 2004). Using carbon fiber-reinforced plastics in automobiles which replace half the ferrous metals in current automobiles would greatly reduce weight, emissions, and fuel consumption (Caprino *et al.*, 2004). Although the majority of fiber reinforced resins contain glass-fibers, the attractive properties like high strength and modulus makes carbon fibers useful as a reinforcement for polymers, metals, carbons, and ceramics, even though they are brittle (Chung, 2001).

Latest advanced in commercial applications include carbon-fiber flywheels as energy storage devices in electric powered automobiles (Blankinship, 2007, Gupta, 1996). Another important application of carbon fiber is for compressed natural gas (CNG) pressure vessel. The CNG storage tanks usually made from pressure vessels and are therefore constrained in their geometry, which are typically cylindrical, and are also rather heavy more than 1 kg/ L for steel tanks. Moreover, attainment of pressure higher than 20.7 MPa (3000 psi) pressure requires costly multi-stage compression facility (Menon and Komarneni, 1998). The major challenges for CNG vehicles are to have pressure vessel that have high pressure strength, lightweight, high temperature resistance and high corrosive material resistance. The best way to meet the above demand is by selecting carbon fiber CNG vessel.

Carbon-fiber composites are lighter, stronger and safer than massive steel flywheels. This enables more energy to be stored in a smaller, lighter package, eliminating much of the footprint and weight issues of conventional flywheels (Blankinship, 2007). Carbon fibers could be categorized in three categories which are, low modulus, intermediate modulus (IM) and high modulus (HM) types. The strength and the modulus of each type are listed in Table 1.1. High modulus (HM) types carbon fibers have high modulus, thus they have a low strain to failure. When incorporated into structures, they give the highest stiffness per unit weight (Donnet *et al.*, 1998). Intermediate modulus (IM) type carbon fibers, which are heat-treated to a lower temperature, have a medium modulus but a very high strength. Meanwhile, low modulus carbon fibers have quite low elastic modulus and low tensile strength.

Today, carbon fiber composite products are widely used. Although the worldwide production of carbon fiber has increased rapidly, it remains less than 30 million pounds/year (Kadla *et al.*, 2002). The cost of carbon fiber production and demand limits its widespread use. The basic difficulty is the combined result of precursor cost, yield, processing cost and the like. Thus, there is a lot room for improvement in the properties and production of precursor carbon fibers via solvent free coagulation process that is employed in this work since it does not involve solvent in its coagulation bath. The use of organic solvent in the conventional coagulation bath requires additional production cost and very carcinogenic. However, the solvent in the coagulation bath play an important role in controlling the counter-diffusion of solvent and non-solvent (Bajaj *et al.*, 2002). Thus, the main challenge for precursor fibers produced from solvent-free coagulation process is to have good and comparable mechanical properties of fibers with the absence of solvents in the coagulation bath

Table 1.1 : Classification of carbon fibers based on Heat Treatment Temperature (Donnet and Bahl, 1987)

Carbon Fiber category	HTT (°C)	Tensile Strength (GPa)	Young's Modulus (GPa)
Low Modulus Type	1000	1.72-2.41	138-172
Intermediate Modulus (IM) Type	1500	3.45-4.13	241-276
High Modulus (HM) type	2500	2.41-2.76	345-482

1.2 PAN Based Activated Carbon Fibers for Gas Adsorption

In addition to its well known application as an excellent reinforcer for composites, PAN-based activated carbon fibers have also been receiving increasing attention in recent years as adsorbent for gas adsorption application and water treatment (Brasquet *et. al.,* 2000; Sánchez-Soto *et. al.,* 2001; Huang, 2009). An important and significant application for activated carbon fiber is as adsorbent media for low pressure natural gas storage. Burchell (2002) reported that natural gas can be stored at an adsorbed state of 3.5 MPa (500 psi) by using activated carbon fiber as the adsorbent media compared to conventional pressure requires in compressed natural gas storage vessel at pressure more than 20.7 MPa (3000 psi).

As the source of fossil fuel (gasoline and diesel) is now decreasing, natural gas (NG) is definitely an attractive alternative fuel for vehicles as it is a relatively clean burning fuel compared with gasoline. It burns cleanly and efficiently, with very few non-carbon emissions (Alcaniz-Monge *et al.,* 1997; Yusof *et al.,* 2012c). The combustion products of gasoline (petrol), diesel, and kerosene vehicles cause serious health and environmental problems. In addition, NG is much cheaper than conventional petroleum-based gasoline (Shao *et al.,* 2007). Unlike oil, gas requires limited processing to prepare it for end-use. These favorable characteristics have enabled natural gas to penetrate many markets, including transportation sectors.

However, there are difficulties in the use of natural gas especially in transportation and storage issues. This is because of its limited driving range as a result of its low volumetric energy density and gaseous form (Menon and Komarneni, 1998; Wang *et al.,* 2010) and also public safety concerns. Therefore, many researchers attempt to make natural gas vehicles competitive with current ones using conventional fuels (Alcaniz-Monge *et al.,* 1997; Shao *et al.,* 2007). Natural gas for vehicular (NGV) application depends on the storage capacity in an onboard fuel tank.

Current gas vehicles employ storage vessels at very high pressure (~20 MPa) by compressed natural gas (CNG) method. Although CNG is less expensive than gasoline on an energy basis, use of CNG requires significant additional upfront vehicle costs, mainly the cost of onboard CNG storage. The key factor in CNG vehicle market penetration is the payback period of the higher cost of a CNG vehicle with lower-priced natural gas. The high pressure involves in CNG method also contributes to the slow market of CNG vehicles because of the safety issue.

Compared with the compressed natural gas (CNG) method, adsorbed natural gas on a suitable microporous adsorbent offers a promising opportunity for natural gas vehicles (NGV) technology. Natural Gas stored as an adsorbed phase in porous material is referred to as Adsorbed Natural Gas (ANG) (Menon and Komarneni, 1998). The adsorbed natural gas (ANG) requires lower storage pressure at 4 MPa compared to pressure requires ~20 MPa in compressed natural gas storage vessel at pressure (Burchell, 2002; Vasiliev *et al.,* 2003). Furthermore, ANG technology can provide a satisfactory energy density at a moderate pressure 4 MPa and room temperature which presents a perspective in transport and other application (Shao *et al.,* 2007). In addition, a low pressure ANG storage tank can be filled with natural gas from a domestic pipe-line using an inexpensive single-stage compressor.

1.3 Adsorbed Natural Gas Application

Microporous materials are widely used as adsorbents for various applications such as gas separation and purification, catalysis support, and gas storage. The use of adsorbent materials for storing natural gas is another application attempting to make natural gas vehicles (NGVs) competitive with current vehicles using conventional fuels. Adsorbed natural gas (ANG) uses adsorbents, such as activated carbons (ACs), activated carbon fibers (ACFs), silica gels, and zeolites to store natural gas at moderate pressures, (35 bars), compared to the high-pressures (200 bars) for current compressed natural gas (CNG) technology.

ANG provides a method of storing gas at a substantially higher concentration that can be achieved with simple compression. Although not attaining the density typically found with method such as liquefied natural gas (LNG), it is potentially much simpler and not requiring the use of refrigerator method or significantly ancillary equipment. Although adsorption on carbon materials develop to date produces its greatest absolute enhancement at pressures around 35 bars, higher relative gains are obtained in the 3-10 bar range more appropriate to local storage and distribution systems. Thus ongoing researches are focusing on developing carbon materials to be used as adsorbent media in ANG technology at lower pressure.

Activated carbonaceous adsorbents have drawn great attention for their strong adsorption capacities. The activated carbon fibers are characterized by the presence of a large number of micropores, which act as adsorption sites (Chung, 2001). Of the activated carbonaceous adsorbent, activated carbon fibers (ACFs) have attracted considerable concerns because of their high adsorption properties (Lee *et al.*, 2004; Zaini *et al.*, 2010), ease of synthesis (Lu and Zheng, 2001), and wide applicability (Brasquet et. al., 2000; Shao et al., 2007). As compared to the conventional activated carbons (AC), ACFs have very fast adsorption/ desorption rates in gas and liquid filtration (Lu *et al.*, 2001). Moreover, ACFs are also easy to handle and avoid problems arising from the packing of granules or powders of activated carbons (Lu and Zheng, 2001).

Therefore, current developing technology involves adsorbed natural gas (ANG) storage on a suitable micro-porous material such as activated carbons and activated carbon fibers (ACFs) (Menon and Komarneni, 1998; Wang *et al.*, 2010; Yusof and Ismail, 2012a). The main requirement for adsorbent media is it has to be predominantly microscopic. The optimal storage capacity will be obtained when that fraction of storage volume that is micropore is maximized with no void or macropore volume (Menon and Komarneni, 1998; Shao *et al.*, 2007). In addition, the adsorbents must have high surface area and high packing density. The porous texture of the fibers is strongly depends on the activation process and carbon precursor. In order to successfully achieve this requirements, the fabrication of carbon fiber plays a major part in obtaining fiber that have high surface area, no macrovoids and high packing density which will then be activated.

One of the biggest challenges of adsorption process is to obtain good adsorbent for specific applications. Those with well-controlled properties and can be produced in large quantities are more preferable but to be selected as a good adsorbent, it should be high packing density, high adsorptive capacity, high adsorption rate with maximum desorption capability. Methods of evaluating adsorbent effectiveness vary that involve either by measuring of gas adsorption capacity, adsorption isotherm, heat of adsorption, kinetics of adsorption, adsorbate-adsorbent interaction using FTIR or NMR spectroscopy, or pore characteristics using SEM or AFM observations (Cracknell *et al.*, 1993; Lozano-Castello *et al.,* 2002; Hadjiivanov *et al.,* 2003).

1.3.1 The Adsorbed Natural Gas Technology

Adsorption is the adhesion of molecules of liquids, gases, and dissolved substances to the surface of a solid. The ability of a solid to adsorb depends on the chemical makeup of the solid and its physical structure. Activated carbon fibers (ACFs), for example, have a very large surface area because of its porous nature. This gives it the ability to adsorb large quantities of natural gas. In a conventional high-pressure CNG tank, gas is forced into the tank under pressure. The greater the pressure, the greater the volume of gas stored in the tank. The maximum pressure, and therefore volume of gas held in the tank, is limited by the physical properties of the tank and its valve. The addition of a microporous material into the tank, such as activated carbon fibers, makes it possible to store a larger volume natural gas in the tank at relatively lower pressure and at room temperature.

There are various types of pores in the ACFs in ANG technology as shown in Figure 1.1. Referring to Figure 1.1, the ACFs are the adsorbent and the adsorbates are methane molecules, the major constituent of natural gas. Therefore, it is important to realize that the accessibility of gases (adsorbates) to the adsorption sites depends on the pore system and the pore size. Macropores (>50 nm) have small specific surface area and are thus insignificant to adsorption; however, these pores control the access of adsorbate and also serve as the space for deposition.

Mesopores (2-50 nm) provide channels for the adsorbate to the micropores from the macropores. Special methods are required to create mesopores and micropores such as optimum activation temperature, optimum activation time, specific heating speed, and flow rate of activation agent. As reported in the literature, mesopore can function as capilary condensation, thus it is indispensable for the adsorption of liquid and gas. Micropores (<1 nm) determine the adsorption capacity of the activated carbon. They have large specific surface areas and take the largest fraction of the adsorbed mass and act as the major adsorption sites. Therefore, micropores are the major area of interest in the research of activated carbon fibers.

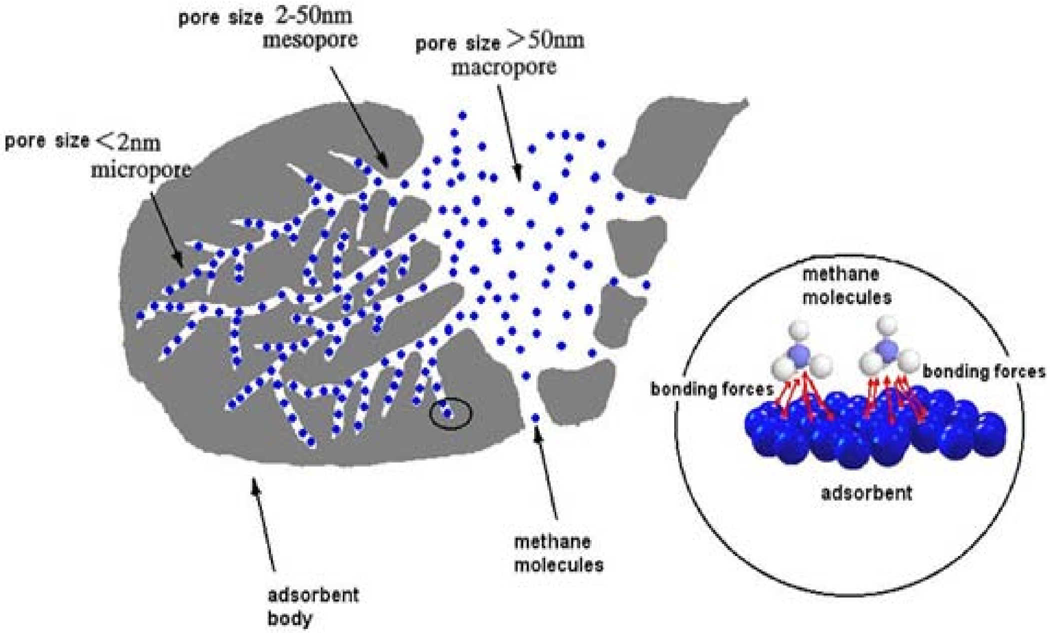

Figure 1.1 The pore structure of activated carbon fibers in ANG technology (Mochida *et al.*, 2000)

1.4 Fabrication Processes

Producing a high performance PAN-based carbon fibers and activated carbon fibers is not an easy task, since it involves many steps that must be carefully controlled and optimized. Such steps are the dope formulation, spinning and post spinning processes as well as the pyrolysis process as depicted in Figure 1.2. At the same time, there are several factors that need to be considered in order to ensure the success of each step. However, amongst all steps, the pyrolysis processes are the most important step and can be regarded as the heart of the carbon fibers and activated carbon fibers production. Pyrolysis processes involve stabilization, carbonization and activation steps that need to be optimized in order to get the suitable microporous carbon materials to be used as adsorbent media for gas adsorption.

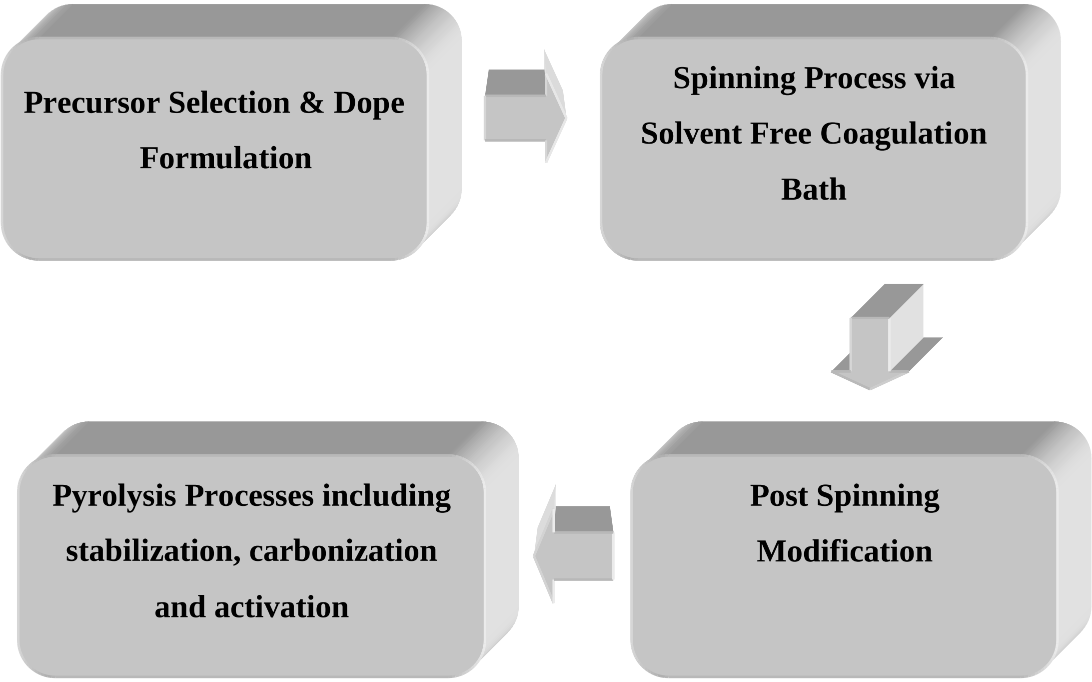

Figure 1.2 General fabrication processes of carbon fibers and activated carbon fibers

1.4.1 Precursor Selection and Dope Formulation

Precursor fibers play a main role in carbon fiber quality as carbon fibers inherited characteristic of precursor fibers. The most widely employed carbon fibers precursor is PAN fibers due to their high carbon yield and high performance of the resultant carbon fibers. The polymer concentration in the spinning solution significantly influences the fiber morphology and density. Thus, in this research, optimum polymer concentration was investigated thoroughly. In addition, numerous studies reported that addition of co-monomers, i.e. itaconic acid (IA) methacrylic acid (MA), and acrylamide (AM) in precursor fibers are beneficial in the stabilization of the fibers by lowering the stabilization time and extending the thermal degradation (Wangxi *et al.*, 2003; Bajaj *et al.*, 2001; Funk, 1990; Mittal *et al.*, 1997b). The optimum amount of co-monomers should be used in order to obtain the best quality of carbon fibers (Chand, 2000).

Nevertheless, there are still few reports on the effects of acrylamide loading in the overall mechanical and thermal properties of Polyacrylonitrile (PAN)/ acrylamide (AM)-based carbon fibers. Therefore, one of the objectives of this study is to investigate the manipulation of AM content in PAN fiber and studying its mechanical and thermal properties. However, the production of a high quality carbon fiber precursor via solvent free coagulation process is fairly new and a lot of new information is yet to be discovered. This process may involve many steps that must be controlled and optimized in this research work to provide an avenue in enhancing the performance of PAN/AM-based carbon fibers using solvent-free coagulation bath in the future.

1.4.2 Spinning Method and Solvent-free Coagulation Process

Spinning is the second step for making carbon fibers. Spinning can be defined as the transformation of a liquid material into a solid fiber (Ferguson, 2001). Dry spinning, wet spinning, melt spinning and dry-jet wet spinning are all referred to as solution spinning, as they all use a polymer solution, which is also known as dope. Wet spinning is the standard method for spinning PAN fibers. Dry and wet spinning can be combined to form a process known as dry-jet wet spinning. In brief, during dry-jet-wet spinning process, polymers dissolved in a suitable solvent is extruded into an air gap before entering a coagulation bath that is miscible with the solvent but not with the polymer. A phase inversion process takes place producing a solid fiber.

Dry-jet-wet spinning is recently replacing wet spinning as it yields fibers of better mechanical properties and controlling noncircular cross sections. Through the dry-wet spinning process, the dope is extruded into an air gap of less than one cm and followed by a conventional coagulation process. This will help in allowing the extruded dope to cool to a certain extent in the air gap before reaching the coagulation bath and to relax the high stresses develop inside the spinneret assembly (Bajaj *et al.*, 2002). The air gap has been shown to produce fibers that are stronger and more extensible than fiber produced from the wet jet spinning method (Ferguson, 2001).

In the air gap, the extruded dope is allowed to cool to a certain level before reaching the coagulation bath. It will also provide relaxation towards the high stresses developed in the spinneret assembly. The dry-jet-wet spinning actually cleverly combines the advantage of dry spinning as well as the wet spinning. In example, it possesses the advantages of high speed of formation, high concentration of dope, and high degree of jet stretch that usually characterize the dry method of spinning. However, it still retains the capability of controlling the structure of as-spun fibers by adjustment of spinning bath parameters.

Conventionally, the coagulation bath contains solvent and non-solvent. The common non-solvent used is water. Meanwhile, the solvent used for controlling the mass transfer in the coagulation bath are sodium thiocyanate, dimethyacetamide (DMAc), nitric acid, ethylene glycol and dimethylformamide (DMF) (Edie, 1998). The solvent in the coagulation bath acts as a resistance to the solvent inside the as-spun fibers from diffusing into coagulation bath and sequentially reduces the possibilities of instantaneous coagulation. This reduces the formation of micro-pores in the cross section of PAN fiber (Rahman *et al.*, 2007). Usually the solvent used for controlling the mass transfer in the coagulation bath is similar with those uses in spinning dope (Funk, 1990).

Recently, interest on environmental issue has brought to the development of carbon fiber fabrication in solvent-free coagulation process using pure water in the coagulation bath (Ismail *et al.,* 2008; Rahman *et al.*, 2007; Yusof and Ismail, 2011; Yusof and Ismail, 2012b). The organic solvents such as dimethylformamide (DMF) which was normally employed in the conventional coagulation bath in the fabrication of PAN fibers could cause cancer for a long period of exposure due to its carcinogenic effects (Ismail *et al.,* 2008; Yusof and Ismail, 2011). Therefore, in an attempt to reduce the carcinogenic effects during fabrication of carbon fibers, we investigated the properties of PAN precursor fiber develop using solvent-free coagulation bath. It is believed that it will benefit in creating safer environment for human healthiness.

Solvent-free coagulation process using multihole spinneret was employed in this research with 100 percent pure water in the coagulation bath. In order to compensate the absence of solvent, other spinning parameters e.g. residence time and coagulation bath temperature need to be optimized. Coagulation bath temperature is responsible for controlling the mass transfer and the counter-diffusion of the solvent and non-solvent thus influences microscopic and morphological structures as well as the mechanical properties of PAN-fibers (Rahman *et al.*, 2007).

1.4.3 Pyrolysis Processes

Although the manufacturing processes for various precursors are different in details, all of them still follow same basic sequences which involve polymerization of precursor, spinning, stabilization, carbonization, graphitization, and surface treatment or sizing to facilitate handling (Luo, 2006). Carbon fibers contain at least 90 % carbon by weight obtained by pyrolysis of an appropriate precursor fiber. In the first pyrolysis process known as stabilization, the fibers are treated under tension condition in an oxidizing atmosphere at typical temperatures between 200 ^{o}C and 300 ^{o}C. This important step is conducted to prepare the fibers so that they can withstand higher temperatures during the carbonization treatment (Flock *et al.*, 1999).

Although at this stage, the fibers are not yet transformed into carbon fibers, oxidation stabilization is the most essential process since it allows the subsequent polymer degradation reactions during carbonization to proceed without collapse of the fiber or loss of orientation (Savage, 1993). In the step of oxidative stabilization, PAN fibers are heated in an oxygen-containing atmosphere to further orient and then cross-link the molecules, such that they can survive higher temperature pyrolysis without decomposing (Farsani *et al.*, 2007).

Meanwhile, in carbonization step, fibers are treated at high temperatures in inert condition between 600^{o}C and 800^{o}C to remove the non-carbon elements as volatile gases. During this step, most of the non-carbon elements within the fiber are volatized in the form of methane, hydrogen, hydrogen cyanide, water, carbon monoxide, carbon dioxide, ammonia and various other gases (Edie, 1998). The carbonized PAN-based carbon fibers will undergo subsequent pyrolysis process to get graphitized carbon fiber or activated carbon.

Carbonized PAN fibers will be activated subsequently by heating process for one minute to one hour with the introduction of moisturized carbon dioxide gas. Activation is done to create porous structure in ACFs for adsorption purposes, at which carbonized fiber is subjected to a heat treatment temperature (HTT) in a temperature range of 600 to 1200^{o}C (Burchell, 2002). The resulting PAN-based activated carbon fibers are suitable for use as adsorption materials (Ko, 2000). The activated carbon fiber provides excellent gas-solid contact efficiency and high adsorption capacity, more importantly it can be fabricated in any shape owing to a good mechanical strength (Lee *et al.*, 1997).

1.5 Problem Statements

Nowadays, nearly all vehicles run on either gasoline or diesel fuel, which contribute to global warming effects as green house gases were discharged continuously. Natural gas is definitely an attractive fuel for vehicles as it burns cleanly and efficiently, with very few non-carbon emissions compared to gasoline. Natural gas possesses remarkable qualities whereby it emits the lowest carbon dioxide per unit of energy generated than other fossil fuels. However, there are difficulties in the use of natural gas especially in transportation and storage issues because of its low energy density and gaseous form. The development of PAN-based activated carbon fiber as the precursor for natural gas storage is beneficial to overcome the environmental problem that has become a huge global issue nowadays.

Unfortunately, high production costs, up to $20 per pound have limited the widespread use of carbon fibers. The price of carbon fibers is high mainly because of two reasons which are the high price of precursor PAN fibers and the high cost of production (Farsani *et al.,* 2007). In order to suppress this drawback, the local PAN-based carbon fiber being developed with the condition processes of producing carbon fiber are to be optimized. In addition to its environmental unhealthy issue, the high amount of solvent usage in conventional coagulation bath contributed to the increase of the production cost (Ismail *et al.,* 2008). The use of solvent-free coagulation bath is believed able to produce precursor PAN fibers in huge amount with low in cost that make it feasible to be used as adsorbent media for natural gas storage.

Furthermore, in responds to environmental concerns, the free-solvent coagulation bath will be employed to decrease the impact of solvent usage to environment. However, as it had already known, solvents play important role in controlling the mass transfer as well as acts as a resistance to solvent inside the as-spun fibers from diffusing into coagulation bath and sequentially reduces the possibility of instantaneous coagulation. Therefore, several strategies need to be employed in order to compensate the absence of the solvent in coagulation bath such as optimizing the residence time during fabrication process and also decreasing the coagulation bath temperature. The other fabrication process parameters namely spinning dope temperature, amount of additives and polymer concentration will also being taken into consideration to find the optimum condition of fabrication high performance carbon fibers in solvent-free coagulation process.

Meanwhile, in order to produce a good adsorbent media for gas adsorption, the suitable activation temperatures are needed. Thus, in this study the thorough investigation on finding the optimum activation temperatures is the main focusing area of study. In this study, the aim is to locally produce high performance and low cost polyacrylonitrile-based carbon fibers via solvent-free coagulation process using dry-jet-wet spinning method. Later on, the carbon fibers produced are meant to be used as precursor for natural gas storage either material for carbon fiber composites pressure vessel for compressed natural gas (CNG) or as adsorbent media for adsorbed natural gas (ANG).

1.6 Objectives of the Study

Based on the research background and the problem statements, therefore the research objectives were outlined as below:-

(a) To prepare and characterize PAN fibers as a precursor for PAN-based carbon fibers and PAN-based activated carbon fibers via solvent free coagulation process

(b) To study the influence of heat treatment process parameters on the morphological structure and mechanical properties of carbon fibers.

(c) To study the influence of heat treatment process parameters on the morphological structure and adsorption properties of activated carbon fibers.

1.7 Scopes of the Study

In order to accomplish the objectives, the following scopes of work have been drawn:-

a) Preparing the polymer solution formulation for the fabrication of PAN-based carbon fiber based on data available in the open literatures.

b) Fabricating PAN precursor fibers via solvent-free coagulation process by using dry-jet-wet spinning methods.

c) Characterizing the thermal and mechanical properties of PAN precursor fibers using Scanning Electron Microscopic (SEM), Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (FTIR–ATR), Wide Angle X-ray diffraction (WAXD), Differential Scanning Calorimetric (DSC), thermal gravimetric analysis (TGA) and tensile testing machine.

d) Studying the effect of stabilization conditions of the PAN fibers at 200-300 °C in an oxygen-containing environment on mechanical and thermal properties of the resultant carbon fibers.

e) Studying the effect of carbonization conditions of the PAN stabilized fibers in an inert environment on mechanical and thermal properties of the resultant carbon fibers.

f) Studying the effect of activation conditions on the PAN-based carbon fibers in carbon dioxide gas on thermal and adsorption properties of the resultant activated carbon fibers (ACFs).

g) Characterizing the pore structure and adsorption properties of PAN-based activated carbon fibers using Scanning Electron Microscopic (SEM), Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (FTIR–ATR), Wide Angle X-ray diffraction (WAXD), Differential Scanning Calorimetric (DSC), Nitrogen Adsorption Isotherm using BET method.

1.8 Significant of the Study

This study is expected to suppress the drawbacks of high manufacturing production cost of carbon fibers and activated carbon fibers precursor. In addition, the free-solvent coagulation bath that was employed in this study is able to decrease the impact of solvent usage to environment. Furthermore, this is a new fabrication technique to produce polyacrylonitrile-based activated carbon fibers via solvent-free coagulation process, to be used as a natural gas adsorbent media. In addition, this study represents the first reported data on adsorption characteristics of polyacrylonitrile-based activated carbon fibers prepared via solvent-free coagulation process, intended to be used as a natural gas storage media in the open literature. Hence, the issue on natural gas storage problem because of its low density can be solved.

1.9 Thesis Outline

This thesis aims to establish a thorough analysis for PAN-based carbon fibers and PAN-based activated carbon fibers prepared via a solvent free coagulation process. The major part of this thesis concentrates on the precursor fibers preparation and heat treatment steps including stabilization, carbonization and activation at various conditions involved during the fabrication of PAN-based carbon fibers and activated carbon fibers. To date, there is no systematic study on the effects of using solvent-free coagulation process to the PAN-based carbon fibers properties and its structure evolution during stabilization, carbonization, and activation.

Chapter 1 explores the background information regarding to PAN-based carbon fibers and activated carbon fibers, spinning methods and also the novel solvent-free coagulation process. The details of problem statements, objectives and scopes of this research also have been discussed thoroughly in this chapter. Chapter 2 contains background information relevant to a review of precursor selection and steps involved in the fabrication of PAN-based carbon fibers. The spinning method using solvent-free coagulation process, post spinning activities and pyrolysis process involved were discussed in detail together with the results obtained from previous researches using conventional coagulation bath.

Chapter 3 focuses on the experimental methods as well as the characterization tools which were utilized during the course of this research. In order to clearly elucidate the thermal behavior, structure properties, mechanical properties and adsorption properties of the PAN-based activated carbon fibers, a meticulous investigation using DSC, TGA, FTIR, SEM, XRD, Nitrogen Adsorption Isotherm, Vario Elemental

Analyzer, AFM, XPS and tensile testing machine is presented. Chapter 4 described in detail the influence of PAN composition and acrylamide addition on the fibers properties of the prepared PAN/AM based carbon fibers prepared via solvent free coagulation process. The results obtained are compared with the carbon fibers prepared using conventional coagulation bath.

Chapter 5 presents the microstructure properties, thermal and mechanical properties of PAN/AM-based carbon fibers prepared at different stabilization and carbonization conditions. The effects of activation process parameters are covered in Chapter 6. The activation temperature is varied systematically in order to investigate the optimum activation temperature for activation process. Meanwhile, Chapter 7 provides the summary, conclusions and recommendations drawn from this study. The future directions of the activated carbon fiber in industrial application were also provided.

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