CHAPTER I
INTRODUCTION AND SCOPE OF WORK

1.1 The Element Carbon and Various Forms

The name “CARBON” is derived from the Latin word carbo or carbonis. Carbon is the lightest member of the IVA family of the periodic table it has atomic number 6 and electronic configuration is 1s²2s²2p². Carbon is an amazing element; more than 90 per cent of all known chemical substances are built around it. Carbon is well-studied as scientific discipline and organic chemistry, are based on it. Carbon is also at the center of the fuels that support the present economy of the world. Carbon is the 19th most abundant element in the earth's crust. The element has the highest melting point about 3550°C and the boiling point about 4500°C, so it is very stable. Carbon is an element with different types of allotrops via sp³ (Diamond), sp² (Graphite), sp (carbines) and spⁿ (fullerene) hybridization. Figure.1.1 shows the structure of these forms of Carbon. In diamond, each carbon atom is bound to four other carbon atoms in a pattern of tetrahedrons. This structure makes diamond extremely hard. In graphite, the carbon atoms form sheets of linked hexagons. Each carbon atom within a sheet forms strong bonds to three other carbon atoms, but the stacked sheets are only held together by weak bonds. This means that the sheets can slide past each other, giving graphite its soft and greasy feel. The valancy of carbon is four, so that the resulting structure is of different types like chain, rings and in network form. Carbon is not black, or transparent, or soft, or hard, or a conductor, or a nonconductor, it all depends on structure. Among all the naturally abundance carbons the most stable isotopes is C¹², which is 98.90%. An important product of carbon is carbon fibers. It is obtained by pyrolysis at 1500°C or above of oriented organic
polymer fibers like polyacrylonitrile, polyacrylate, esters or cellulose. These fibers when incorporated into plastics, the reinforced materials called composites are light and of great strength.

Elemental carbon in the sp² hybridization can form a variety of amazing structures [1]. Apart from the well-known graphite, carbon can build closed and open cages with honeycomb atomic arrangement. The first such structure to be discovered was the C60 molecule (Fullerenes) by Kroto et al. [2]. All the carbons of C60 are equivalent and sp2 hybridized. Each carbon atoms simultaneously belongs to one five-membered ring and two benzene like six membered rings. Although various carbon cages were studied, it was only in 1991, when Iijima [3] observed for the first time tubular carbon structures. The nanotubes consisted of up to several tens of graphitic sheets (so called multi-walled carbon nanotubes (MWNT)) with adjacent shell separation of ~0.34 nm, diameters of ~1 nm and high length/diameter ratio. Two years later, Iijima and Ichihashi and Bethune et al.[3,4,5] synthesized single-walled carbon nanotubes (SWNT). Various methods are used for the synthesis of carbon nanotubes like, Arc Discharge [1,3], Laser ablation [6], Chemical vapour deposition (CVD) [7,8]. Due to attractive properties, these are used in various applications like, carbon nanotubes composites, electrochemical devices, Hydrogen storage, Field Emission devices, nanometer sized electronic devices, sensors and probes.
Figure 1.1. Structure of different allotropes of carbon
1.2. Pitches as Carbonaceous Precursor for Carbon Fibers

Carbon is mainly derived through pyrolysis of carbonaceous organic materials such as natural precursor like wood, thermosetting resins, pitches and hydrocarbons. For most of the applications, pitches are often used as precursors for production of the carbonaceous materials. Pitches are complex mixture of polynuclear aromatic hydrocarbons and are thermoplastic in nature. Pitches are prepared from coal and petroleum sources. Pitches are different low molecular and high molecular weight carbonaceous materials derived from organic precursors by relatively low temperature process. Pitch is an essential precursor in the manufacture of a wide variety of granular engineering carbon and graphite materials such as large scale graphite electrode for the electric arc furnaces, anode and cathode for aluminum smelting, nuclear graphite, electrical brushes and carbons for activated carbons, mesocarbon microbeads, carbon fibers, carbon-carbon composites [9-14], carbon foams and high temperature lubricants, mechanical and wear applications. In terms of consumption, graphite electrode industry is the main consumer of pitches. Two types of pitches, binder and impregnated are used in the fabrication of carbon products. Binder pitches are used to hold carbon aggregates together during molding and baking. Impregnating pitches are very specialized product and are used to reduce porosity and increases the density of baked carbon body prior to graphitization. The continued development of carbon products requires a sound scientific understanding of the physical and chemical properties of the pitch like precursors used in their production process.
1.2.1 Types of Pitches

1.2.1.1 Coal-Tar Pitch

Coal tar is a by product obtained during coking of bituminous coals pitches. These are obtained from the coal tar by distillation and heat treatment process. Figure 1.2 shows the diagram for the preparation of coal tar pitch. These are complex mixtures containing a range of aromatic and heterocyclic organic compounds consisting predominantly of carbon and hydrogen with small amounts of nitrogen, oxygen, and sulphur in specific cases. The precise composition and properties vary according to the source of the tar and the method of removal of low molecular weight fractions.

1.2.1.2 Petroleum Pitch

Petroleum pitch is obtained from the residues at the bottom of catalytic crackers of naphtha, crude oil distillation plants or refineries by distillation, heat treatment or oxidation or by a combination of these processes. Figure 1.3 shows the preparation of petroleum pitch. Like coal tar pitch, the chemical and physical characteristics of these pitches are dependent on the source of the petroleum crude and processing conditions. Primarily, the pitches are characterized by coke yield and coke structure produced from the crude petroleum, which in turn depend on the aromaticity or C/H ratio of the pitches. Coal tar pitches are usually more aromatic than petroleum pitches. However, from the point of view of fundamental understanding of the pitch processing, its chemical characteristics and their influence on pyrolysis behavior, solvent fractionation has widely been used to divide the pitch in to a broad range of constituents. Though, coal tar and petroleum industries have tended to use different solvents and nomenclature,
1.2.1.3 Synthetic Pitch

Pitches are complex mixtures of many organic compounds with a high aromatic character. They are usually derived from coal-tar or from petroleum residues and are regarded as byproduct of the parent industry. These create problems of reliability for the carbon manufacture. In addition, when these precursors are used in the fabrication of advanced carbon products like fibers and carbon-carbon composites, there is a need for improved processing characteristics as well as increased reliability. This had led to the development of specialty pitches designed specially for these industries, some of which are synthesized from various synthetic compounds like poly vinyl chloride, aromatic hydrocarbon such as naphthalene, methyl naphthalene and biomass. These types of pitches are called synthetic pitches. Mochida et.al [15-19] have done lots of work on synthetic isotropic and mesophase pitches. The pitches were prepared from aromatic hydrocarbons such as naphthalene, methyl-naphthalene by the aid of super catalysts HF/BF$_3$. 
Figure 1.2 Coal tar Pitch Preparation Process diagram
Figure 1.3  Petroleum Pitch Preparation Process diagram
1.2.2 Mesophase Pitch

Pitch can be produced either by the distillation of coal tar or from the high molecular weight residues produced during the distillation of crude oil. All pitches consist of a wide range of polyaromatic and cyclic aliphatic hydrocarbons, containing linear aliphatic side chains. All of the compounds in pitch have not yet been identified. The molecular weight of the polyaromatic compounds vary from 200 to 1000. Because of this variation in molecular composition and evaporation, melting occurs over a wide range of temperature.

A mesophase can be formed by the thermal or catalytic polymerization of a suitable petroleum or coal tar pitch. In fact, the reaction occurs by a classic free radical mechanism. Thus, when a highly aromatic pitch is heated to temperatures of 400-450°C for extended periods, an optically anisotropic material, mesophase is formed. The mesophase formation reaction depends on the temperature and the carbon-to-hydrogen ratio of the aromatic during this heat treatment.

Initially, small spheres of mesophase are formed, with the polyaromatic layers arranged. As they grow larger, the spheres coalesce to form large spheres. Insoluble impurities in the molten pitch will inhibit coalescence and, therefore hinder the formation of extended areas of anisotropy. The first step in mesophase production involves the removal of light molecular weight species. This happens in conjunction with the free radical reaction of small aromatics to form polyaromatic molecules with molecular weights of about 1200, suitable for the formation of mesophase. The evaporation of the volatiles is important since they interfere with the formation of mesophase. When the isotropic phase has passed, the mesophase will react. All the...
existing methods of purification merely depend on the extraction. Successive extraction with solvents such as toluene, quinoline and hexane remove the soluble fraction, and ultimately the insoluble fraction is used to form mesophase. Figure 1.4 shows the schematic diagram for the preparation of mesophase pitch [13].

1.2.3 Chemical Composition of Pitches

The chemical composition of pitches is difficult to analyze. The composition and properties of pitches varies according to the source and the method of removal of the low molecular weight species. In pitches different aromatic hydrocarbons and aliphatic hydrocarbons are presents in various forms. It also contain nitrogen, sulphur, oxygen, -OH etc. Various types of hydrocarbons present in the pitches are shows in the flow chart in Figure 1.5.
Figure 1.4 Schematic diagram of Mesophase pitch preparation
Figure 1.5 Chemical constituents of pitches

Hydrocarbons

Alkanes
e.g. Methane,

Arenes
e.g. Benzene, Toluene, o,m,P Xylene, Naphthalene, anthracene, Phenanthrene

Alkenes
e.g. Methene, Ethene, Propene

Alkynes
e.g. Methylene, Ethylene
In pitches various gases are present like methane, ethane, carbon monoxide, H₂, O₂, N₂, CO₂ etc. It may be anhydrides, ether, ketone, alcohols, aldehyde etc. The oxygen containing compounds like carboxylic acid, phenol, acetone, fatty acid, chloroform, diethyl ether, N-hexane, tars, cyclohexane etc. are also present. Pitches also contain sulphur containing compounds like thiofin in very less amount, mercapton like organic compounds and nitrogen containing compounds such as pyridine, pyrole, quinoline etc.

1.2.4 Solubility of Pitch

Solubility has widely been used as a method of characterization of insoluble content present in the pitch. In recent development it has been effectively used as a method of modifying the chemical structure of pitch prior to and during the processing of fibers. In general pitch is specified only in terms of solubility in selected solvents such as hexane, toluene, pyridine and quinoline. It is however, possible for different pitches to have similar toluene and quinoline insoluble fractions and yet have quite different molecular weight distributions and rheological properties.

The petroleum industry had defined the following species,

(i) Carboids – Insoluble in CS₂

(ii) Carbenes – soluble in CS₂ but insoluble in CCl₄

(iii) Asphaltenes- Insoluble in light paraffinic hydrocarbons such as N-pentene but usually soluble in CS₂, CCl₄, and C₆H₆.
(iv) *Pre-asphaltenes*- A term sometimes used to describe the fraction insoluble in solvents such as benzene but soluble in pyridine.

The coal tar pitches used in the carbonization industries are often fractionated using the following solvents.

(i) *Quinoline of Pyridine*- Insoluble in quinoline or pyridine are the pitch components very high molecular weight aromatic compounds are solid impurities, known as C1 component of α-resins.

(ii) *Benzene of Toluene*- Pitches components insoluble in Benzene and Toluene are soluble in quinoline or pyridine known as the C2 component or β-resin.

(iii) *Petroleum ether and n-hexane*- Insoluble content which is soluble in benzene or toluene is some times known as “resinoid” fraction identifies with asphaltenes, whilst the soluble materials is the “crystalloid” fraction.

1.2.5 *Pyrolysis of Pitch*

The pitches convert to carbon by pyrolysis process. During the pyrolysis process evaporation of low molecular weight species take place. As the temperature is progressively raised, low molecular weight components get volatilized. It depend on the surface evaporation rate as determined by the temperature, pressure, gas phase and liquid phase composition and the kinetics of diffusion of the volatile species on the surface. In the pyrolysis of pitch bonded system, the weight loss as a function of temperature depends upon its dimensions as well as the factors listed above. For the production of mesophase precursor for fabrication of advanced carbon such as fibers,
it is common practice to use gas purging and vigorous stirring conditions to facilitate
the removal of the volatile species.

Other main factor is cracking reactions carried out followed by evaporation of
volatile fragments. This takes place at higher temperature about 350-400°C. The
fragments mainly result from the thermal scission of aliphatic side chains to
polycondensed aromatic ring structures. The polynuclear aromatic radicals produced
are quite reactive and combine to produce planar aromatic ring structures of even
higher molecular weight and greater aspect ratio. These remain in the melt, altering its
physical characteristic quite markedly when this stage is operative, the average
molecular weight of the volatile species decrease as there is a change in the proportion
of volatile emanating from unreacted volatile molecules and low molecular weight
products of the cracking reaction. An important criterion in selecting a pitch precursor
for carbon manufacture is the carbon yield. This depends on the composition of the
precursor pitch but also it is strongly influenced by the pyrolysis conditions.
Increasing the heating rate, the pressure and the volume to surface ratio all tend to
increase the carbon yield by restricting the evolution of volatile molecules present in
the original pitch. The reaction of these species in the carbonizing liquid as the
temperature is raised allows them to participate in cracking reactions and in molecular
growth processes.

1.2.6 Modification of Pitches

1.2.6 (A) Thermal Modifications

Commercially available pitches are low softening point and low carbon yield
which induce problem during the processing. It has a very low carbon yield around
35-45 % so it results ultimately in to porous carbon. Modification of pitches is the
effective way to increase the softening point and carbon yield with improve properties.

Thermal modifications of pitches are generally carried out in presence of air or nitrogen or combination of air and nitrogen [13, 20-22]. Pitch based carbon fibers prepared from isotropic pitches have been recognized as a high performance and low cost materials. However, the slow stabilization due to the lower softening point of the precursor pitches increases their manufacturing cost. Hence, suitable procedure to raise the softening point of such precursor allows a higher temperature at stabilization and it shorten the stabilization periods. The controlled heat treatment in air and nitrogen allows controlling the viscosity and softening point of the pitch [22]. The thermal modification results in excellent spinnability of this material that can be easily carbonized with intermediate step of stabilization. Pitch modified by heat treatment undergoes polymerization and ultimately raise the softening point and carbon yield. Modification by air blowing promotes the cross-linking between adjacent aromatic molecules; suppress the evaporation of light fraction and stacking of large aromatic molecules, thus retarding the formation of liquid crystalline mesophase.

1.2.6 (B) Solvent Modification

Solvent modification of pitch is currently being investigated as a possible technique in the production of high quality mesophase pitch from coal tar and petroleum pitches. Mesophase pitch is used to make high technology products, such as carbon fibers. The conventional production of mesophase pitch initially involves the removal of low molecular weight species from coal tar and petroleum pitches. The remaining residue is then transformed into a mesophase pitch through polymerization
process. Various solvents are used for the modification of pitches like toluene, heptane, pentane and methanol. Mesophase pitch are produced using a supercritical extraction (SCE) technique. The SCE unit consists of a continuous-flow apparatus and uses near critical of supercritical toluene to fractionate isotropic petroleum pitches. A 50/50 by weight mixture of isotropic pitch and toluene, is pumped continuously in to the system using a high-pressure cylinder. Pure toluene is also continuously pumped seperately at a predetermined flow rate to achieve a desired solvent-to-pitch ratio. The two streams are preheated, mixed in a mixing ‘tee’ and then further mixed using coiled tubing before reaching the equilibrium cell. This equilibrium cell functions as liquid-liquid steps are all performed in an isothermal nitrogen bath. The heavy and light liquid phases separate in the cell by gravity and are collected independently through lines at the bottom exit and top of the cell, respectively. The lighter liquid (Top phase) consists mainly of toluene (~80% by weight) and the lower molecular weight fraction of the pitch, while the heavier liquid (bottom phase) consist of mesophase pitch and ~20 wt% toluene. The bottom phase is then dried under vacuum to remove the toluene [23-25].

1.2.6 (C) Chemical Modification

Development of high softening point pitch by chemical treatment with bromine, iodine, benzoquinone or some oxidizing agent like HNO₃, H₂O₂, H₂SO₄, and H₃PO₄, and also with addition of polymer like PVC, melamine formaldehyde, benzoquinone to enhance the physical and mechanical properties of carbon materials. The chemical modification method is the easiest method for the improve properties of pitches. Various oxidizing agent and polymerization agents are used for the modification of pitches. During the chemical modification, dehydrogenation process
takes where as in some cases polymerization takes place in presence of croslinking agent [18,19,26,28,29].

1.2.6 (D) Catalytic Modification

Generally the catalytic modifications are carried out for the preparation of synthetic pitches from naphthalene and methyl naphthalene in presence of HF/BF₃ or AlCl₃ catalyst. Using this catalyst, Mitsubishi Gas Chemical Company produced pitch on large scale. Mochida et al. [19] reported various work on the catalytic modification of pitch and synthesis of pitches from hydrocarbons. Modification of coal tar pitch with divinyl benzene (DVB) as a croslinking agent in the presence of p-toluene sulfonic acid (PTS). It shows the catalytic modified of pitch enhance the liquid crystal formation.

1.3. Carbon Fiber

1.3.1 Historical Perspective

Carbon fibers, though known since Thomas Edison's development of the incandescent light in the 1870s, were not made in large quantities until the late 1960s. Thomas Edison who purposely took carbon fibers and later bamboo and converted them in to carbon fiber in his quest for incandescent lamp [1,8]. Interest in carbon fibers was renewed in late 1950’s when synthetic rayon in textile form was carbonized to produce carbon fibers for high temperature applications [30,31]. The technical and commercial breakthrough for high-performance carbon fibers started in the late 1960s after introduction of the PAN process, which turned out to be more economical due to higher carbon yields, which is 50% against 30% for rayon, and
simpler fabrication process [32]. PAN based fibers also had superior physical properties compared to rayon based fibers [3]. Mainly, PAN fiber is today recognized as the most important and promising precursor for manufacture of high strength carbon fibers. Later, carbon fibers were also prepared from pitch, a very cheap precursor. The most commonly used pitches are those obtained from petroleum, asphalt, coal tar, and PVC. The properties of pitch carbon fibers are generally inferior to PAN carbon fibers because, if not specially treated, the pitches are usually isotropic before pyrolysis, and the isotropy is maintained in the fibers unless the orientation of the larger planes is carried out under tension during the high temperature treatment, between 2000 and 3000°C. Although this process gives the carbon fibers excellent performance properties, it is very expensive [2]. This expensive stretching treatment can be avoided by using mesophase pitches, which are liquid crystalline in nature. The high degree of molecular orientation of as-spun mesophase pitch fibers allows it, unlike PAN, to develop a truly graphitic crystalline structure during the carbonization/graphitization step [3]. Hence ultra high modulus carbon fibers are now produced from mesophase pitches.

Numerous other precursors have been tried to produce carbon fibers. Cellulosic precursor fibers such as cotton, linen, ramie, sisal, heme, and flax, although of considerable historical significance, are no longer an important source of carbon fibers. Polynosic fibers have been suggested, but they do not provide any real advantage over regular rayon fibers [2].

More recent investigations into the production of carbon fibers from cellulosic fibers are concentrated toward modifying the degradation mechanism so that carbon
yield can be enhanced. The possibility of converting nonheterocyclic aromatic polymers such as phenolic polymers [30-35], phenol formaldehyde resin [35–38], polyacenaphthalene [39,40], polyacrylether [41], polyamides [42-45], and polyphenylene [46,51] into carbon fibers have also been investigated. These substances have several advantages, such as easy cyclization into a graphitic structure, easy elimination of non-carbon atoms, and a greater carbon yield, but no breakthrough in fiber properties has been observed. Some of heterocyclic high temperature-resistant organic polymers such as polyimides [42–44], polybenzimidazole [45,42], polybenzimidazonium salt [45], polytriazoles [51] have been successfully converted into high modulus carbon fibers with unique mechanical properties and a carbon yield of as high as 90% in some cases [45]. The only drawback of these polymers is their high cost. Certain linear thermoplastic polymers such as polyethylene, polypropylene [52], polyvinyl chloride [53,54], polyvinyl alcohol [55, 56], and polyvinylacetate [55] have also been well investigated for their conversion into carbon fibers, but have shown poor mechanical properties and very low carbon yields. Thus three precursors which are being used for large-scale production of carbon fibers are PAN, rayon, and pitches [13].

Other precursors are generally used where mechanical properties are not important. Regular textile grade PAN contains 15% co-monomers. However, the amount of co-monomers in PAN used for carbon fibers should be lower than 8% [13]. Commercially available PAN precursors differ appreciably in several of their characteristics, such as molecular weight and its distribution, crystallinity, diameter, molecular orientation, and impurities level [12]. These characteristics can
considerably vary the mechanical properties and other properties of the final carbon fibers.

Many companies prefer to manufacture their own precursors using modified procedures, such as incorporation of certain additives to catalyze the cyclization reaction [57], resin coatings to suppress cyclization exothermicity [58], and post-spinning stretching in superheated steam and nitrogen to improve the structure [59,60]. The spinning and drawing of precursor fibers also play an important role. Modulus and strength of the final carbon fibers have been found to be directly related to stretch-ratio of the precursor [61,62]. However, the properties of carbon fibers deteriorated when the draw-ratio was very high. This was attributed to the creation of defects due to over stretching. It has been strongly emphasized that all factors in processing that are bound to induce defects on the fiber surface (e.g. over stretching, the presence of dust etc.) should be avoided at all costs because they strongly influence fiber properties [13]. Based on the fact that carbon fiber properties depend upon precursor properties, efforts have been made to improve the properties of other precursor fibers also [56].

1.3.2 Processing of Carbon Fibers

Carbon fibers are built by long carbon-carbon molecular chains yielding very stiff fibers. The trends have driven development of carbon fibers in two direction; high-strength (HS) fibers with very high tensile strength and a fairly high strain to failure (1-1.5%) and high modulus (HM) fiber with very high stiffness. The main drawback is the high cost and all carbon composites are relatively brittle. The polyacrylonitrile, pitch based fibers are stabilized in air (a few hours at 250°C) to
prevent melting during subsequent higher temperature treatment. The fibers obtained after this treatment are heated slowly in an inert atmosphere to 1000-1500°C. Slow heating allows the high degree of order present in the fiber to be maintained. The rate of temperature increase should be low so as not to destroy the molecular order present in fibers. The initial stretching treatment of PAN improves the axial alignment of the polymer molecules. During the oxidation treatment the fibers are maintained under tension to keep the alignment of PAN while it transforms into rigid ladder polymer. In the absence of this tensile stress in this step, there will occur a relaxation and the ladder polymer structure will become disoriented. After the stabilization treatment, the resulting ladder type structure has high glass transition temperature so that there is no need to stretch the fiber during the next stage, namely carbonization. There still are present considerable quantities of nitrogen and hydrogen. These are eliminated as gaseous waste products during carbonization that is heating to 1000-1500°C. The carbon atoms remaining after this treatment are in the form of a network of extended hexagonal ribbons. Although these strips tend to align parallel to the fiber axis, the degree of order of one ribbon with respect to another is relatively low. This can be improved by further heat treatment at still higher temperatures (upto 3000°C). This is called the graphitization treatment. The mechanical properties of the resultant carbon fiber may vary over a large range depending mainly on the temperature of the final heat treatment. Hot stretching above 2000°C results in plastic deformation of fibers leading to an improvement in properties.
1.3.3 Types of Carbon Fibers

1.3.3.1 Carbon Fibers from Rayon

Cellulose is a natural polymer and is frequently found in a fibrous form. Cotton fiber, which is cellulosic, was one of the first ones to be carbonized. It has the desirable property of decomposing before melting. It is inappropriate, however, for high-modulus carbon fiber manufacture because it has a rather low degree of orientation along the fiber axis, although it is highly crystalline. It is also not available as a tow of continuous filaments and is quite expensive. These difficulties have been overcome in the case of Rayon fiber, which is made from wood pulp, a cheap source. The cellulose is extracted from wood pulp and continuous filament tows are produced by wet spinning process. Rayon is a thermosetting polymer. The process used for the conversion of rayon into carbon fiber involves the three stages: stabilization in a reactive atmosphere (air or oxygen, <400°C), carbonization (<1500°C), and graphitization (>2500°C). Various reactions occur during the first stage, causing extensive decomposition and evolution of H₂O, CO, CO₂ and tar. The stabilization is carried out in a reactive atmosphere to inhibit tar formation and improve yield. Chain fragmentation or depolymerization occurs in this stage. Because of this depolymerization, stabilizing under tension, as done in the case of PAN precursor, does not work in this case. The carbonization treatment involves heating to about 1000°C in nitrogen. Graphitization is carried out at 2800°C but under stress. This orienting stress at high temperature results in plastic deformation via multiple slip system operation and diffusion. Figure 1.6 shows the process schematically for the preparation of rayon-based carbon fibers. The processing disadvantage was a high weight loss, or low conversion yield to carbon fiber. Typically only 25% of the initial fiber mass remains after carbonization, which
means that carbon fiber made from these materials, are comparatively more expensive than carbon fibers made from other materials.

1.3.3.2 Phenolic Based Carbon Fibers

Phenolic-based carbon fibers prepared using phenol formaldehyde thermosetting resin. PF resin melt spinning at 40-50°C higher than the softening point, stabilized with solution route using HCl-Formaldehyde solution below the melting point of the fibers and carbonization under inert atmosphere. These types of fibers are mainly used for the general purpose application, like insulating materials, as precursor for activated carbon, decorative materials and medical applications. The carbonization of stabilized fibers was carried out at 800°C in inert atmosphere. 

Figure 1.7 shows the schematic diagram of preparation of phenolic-based carbon fibers. During carbonization, evolution of gas molecules like hydrogen and oxygen and non-carbon element removed from the fiber structure, which ultimately reduced the fiber dimension and increase the percentage of carbon atoms. The phenolic based carbon fibers gives yield around 50%, which is low as compared to pitch precursor based carbon fibers.
Figure 1.6 Schematic diagram for preparation of Rayon based carbon fiber preparation
Figure 1.7 Schematic diagram for preparation of Phenolic based carbon fiber
1.3.3.3 Carbon Fibers from Polyacrylonitrile

Polyacrylonitrile (PAN) precursors are the basis for the majority of carbon fibers commercially available today. They provide a carbon fiber conversion yield from 50 to 55%. These precursors can be thermally rearranged before thermal decomposition, which allows them to be oxidized and stabilized before the carbon fiber conversion process, while maintaining the same filamentary configuration. The chemical composition of PAN precursors defines the thermal characteristics that the material displays throughout the oxidation/stabilization portion of the conversion process. These thermal characteristics influence the processing sequences that are used to convert PAN precursors to carbon fiber. Carbon fiber based on a PAN precursor generally has a higher tensile strength than a fiber based on any other precursor. This is due to a lack of surface defects, which act as stress concentrators and, hence, reduce tensile strength. Figure 1.8 shows the Schematic diagram for preparation of PAN based carbon fibers.

1.3.3.4 Carbon Fibers from Pitch

1.3.3.4. (A) Carbon Fibers from Isotropic Pitch

There are various sources of pitch but the three commonly used sources are polyvinyl chloride (PVC), petroleum asphalt, and coal tar. Pitch-based carbon fibers have become attractive because of the cheap raw material and high yield of carbon fibers [53,54,108]. The same sequence of oxidation, carbonization, and graphitization is required for making carbon fibers out of pitch precursors. Figure 1.9 show the flow chart for the preparation of isotropic pitch based carbon fibers. Orientation in this case is obtained by spinning. An isotropic but aromatic pitch is subjected to melt spinning
at very high strain rates and quenched to give a highly oriented fiber. This thermoplastic fiber is then oxidized to form cross-linked structure that makes the fiber nonmelting. This is followed by carbonization and graphitization.

1.3.3.4. (B) Carbon Fibers from Mesophase Pitch

Commercial pitches are mixtures of various organic compounds with an average molecular weight between 400 and 600. Prolonged heating above 350°C results in the formation of a highly oriented, optically anisotropic liquid crystalline phase called mesophase. When observed under polarized light, anisotropic mesophase dispersed in an isotropic pitch appears as micro spheres floating in pitch. Figure 1.10 shows the flow chart for the preparation of mesophase pitch based carbon fibers. The liquid crystalline mesophase pitch can be melt spun into a precursor for carbon fiber. The melt spinning process involves shear and elongation in the fiber axis direction and thus a high degree of preferred orientation is achieved. This orientation can be further developed during conversion to carbon fiber. The pitch molecules (aromatic of low molecular weight) are stripped of hydrogen and the aromatic molecules coalesce to form larger bi-dimensional molecules. Very high value of Young's modulus can be obtained. It should be appreciated that one must have the pitch in a state amenable to spinning in order to produce the precursor fiber. This precursor fiber is made infusible by stabilization in air to allow carbonization without melting. Thus, the pitches obtained from petroleum asphalt and coal tar need pretreatments. The molecular weight controls the viscosity of the melt pitch and the melting range. Thus, it also controls the temperature and the spinning speed. Because the pitches are
polydispersoid systems, their molecular weights can be adjusted by solvent extraction or distillation.
**Figure 1.8** Schematic diagram for preparation of PAN based carbon fiber

1. **Polyacrylonitrile Co-polymers**
   - Wet spinning
     - Coagulating solution bath, precipitation
2. **Polyacrylonitrile fibers**
3. **Stabilization**
   - Air or Oxygen, 250°C
4. **PAN-ox fibers**
   - Black in Colour
5. **Carbonization**
   - Nitrogen of Argon, 1000°C
6. **Graphitization**
   - Argon or Helium, 2800°C
Figure 1.9 Schematic diagram for preparation of Isotropic pitch based carbon fiber
Figure 1.10 Schematic diagram for preparation of Mesophase Pitch based carbon fiber

Petroleum or Coal-tar Pitch

Mesophase Pitch

Melt spinning

Stabilization

Carbonization

Graphitization

Heat-treated at 350-420°C in nitrogen atmosphere

Melt-spinning at 40-50°C higher

Air or Oxygen, <300°C

Nitrogen or Argon, 1000°C

Argon or Helium, 2800°C
1.3.4 Structure of Isotropic and Mesophase Pitch Based Carbon Fibers

The layer plane structure in pitch based carbon fibers is highly graphitic, Optical microscopy and scanning electron microscopy have been extensively used to study their microstructure. A variety of microstructure can be produced merely by modifying the spinning conditions. Most of the pitch based carbon fibers exhibit either the radial, random, flat-layer or radial-folded structures. Generally PAN based carbon fibers exhibit the random or the flat layer structures. Recently D.D.Edie et.al. [23-25,63,64,111] reported the line origin structure in ribbon shaped carbon fibers which gives very good thermal conductivity compare to the conventional round shaped carbon fibers. The cross-sectional structure of carbon fibers also plays an important role in determining mechanical properties of carbon fibers. Transverse structure of the final carbon fibers depends very much upon the type of spinning process used, temperature of spinning, the shape of spinneret. However, the structure is independent of heat treatment temperature [65]. PAN based carbon fibers have higher tensile and compressive strength than pitch based carbon fibers, because PAN based fibers have particle-like structure and smaller crystals as compared to sheet-like structure and larger crystals in pitch based fibers [5].
Figure 1.11 Microstructure of pitch based carbon fibers
1.3.5 Mechanical Properties of Carbon Fibers

1.3.5.1 PAN-Based Carbon Fibers

Table 1.1 Properties of commercially available PAN based carbon fibers

<table>
<thead>
<tr>
<th>Types of Fibers</th>
<th>Tensile Modulus Gpa</th>
<th>Tensile strength Gpa</th>
<th>Electrical resistivity, 10⁻³ Ω cm</th>
<th>Density gm/cc</th>
</tr>
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<tbody>
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<td>T-300</td>
<td>235</td>
<td>3.2</td>
<td>1.8</td>
<td>1.76</td>
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<tr>
<td>AS-4</td>
<td>235</td>
<td>3.6</td>
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<tr>
<td>IM-8</td>
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<tr>
<td>T-50</td>
<td>390</td>
<td>2.4</td>
<td>0.95</td>
<td>1.81</td>
</tr>
<tr>
<td>M40J</td>
<td>390</td>
<td>4.4</td>
<td>--</td>
<td>1.77</td>
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<tr>
<td>GY-7</td>
<td>520</td>
<td>1.8</td>
<td>--</td>
<td>1.96</td>
</tr>
<tr>
<td>M60J</td>
<td>585</td>
<td>3.8</td>
<td>--</td>
<td>1.94</td>
</tr>
</tbody>
</table>
### 1.3.5.2 Pitch Based Carbon Fibers

**Table 1.2** Properties of commercially available Pitch based carbon fibers

<table>
<thead>
<tr>
<th>Types of Fibers</th>
<th>Tensile Modulus Gpa</th>
<th>Tensile strength Gpa</th>
<th>Density gm/cc</th>
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<tbody>
<tr>
<td>BP-Amoco</td>
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<tr>
<td>P-25</td>
<td>160</td>
<td>1.4</td>
<td>1.90</td>
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<tr>
<td>P-55S</td>
<td>380</td>
<td>1.9</td>
<td>2.0</td>
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<tr>
<td>P-75S</td>
<td>520</td>
<td>2.1</td>
<td>2.0</td>
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<tr>
<td>P-100</td>
<td>760</td>
<td>2.4</td>
<td>2.16</td>
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<tr>
<td>P-120</td>
<td>830</td>
<td>2.4</td>
<td>2.17</td>
</tr>
<tr>
<td>K-800x</td>
<td>930</td>
<td>2.9</td>
<td>2.18</td>
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<td>K-1100</td>
<td>930</td>
<td>3.1</td>
<td>2.20</td>
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<td>Mitsubishi</td>
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<td>Kosei</td>
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<td>K-133</td>
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<td>K-135</td>
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<td>2.6</td>
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<td>K-139</td>
<td>740</td>
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<td>Nippon Graphite</td>
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<td>YS-50A</td>
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<td>Isotropic Pitch</td>
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<tr>
<td>Kureha</td>
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<tr>
<td>T101F</td>
<td>33.0</td>
<td>0.80</td>
<td>1.81</td>
</tr>
<tr>
<td>T20F</td>
<td>33.0</td>
<td>0.70</td>
<td>1.57</td>
</tr>
</tbody>
</table>

Department of Materials Science
The property of carbon depends mainly on the precursor, processing, and heat treatment given to the fibers. Table 1.1 and 1.2 shows the typical mechanical properties of PAN based and Pitch based carbon fibers as available commercially. It shows difference in the mechanical properties due to the difference in the structure of carbon fibers.

1.3.6 Application of Carbon Fibers

As explained above, sports goods provided the first bulk outlet for carbon fibers. Where they are used almost exclusively for their high specific stiffness. In golf club shafts they provided extra torsional stiffness, as with squash and tennis rackets, where they appear to provide the players with a larger ‘sweet’ spot on the racket face. In fishing rods they give the fisherman extra reach. They have found applications in skis and ski poles. They have been used to stiffen kyaks and rowing sculls. In bicycles they can achieve workable stiffness for less mass. In racing car bodies, the stiffness and fracture characteristics have been used to provide added safety for the racing driver in the event of crashing, and most racing cars now use carbon fibers. In all these applications the high materials costs have been small compared with the finance spent on pursuing the particular sports.

Aircraft have always been one of the main potential markets for carbon fibers, where high specific properties have always been at a premium. In fixed-wing aircraft the first applications were mainly in stiffness-critical components, such as air brakes, ailerons, rudder and other air-control surfaces, which are relatively lightly loaded. Then they were used in strength-critical components such as tail fins and tail planes, and more
recently in highly stressed wing structures. Military aircraft found the first applications, but carbon fibers have been used increasingly in civil aircraft, where the structures are much larger, because of the saving in fuel, which has become a larger part of the running costs. The first large civil parts to be certified and in production were the engine cowlings. When the wings and tail parts are made of composites, this represents some 25% of the structural mass. To achieve the projected 40-50% usage, much of the fuselage will be made of composite.

In helicopters carbon fibers find some application in stiffening the GRP main rotor blades, and in the tail rotors, but fuselage applications offer a larger market. Carbon fibers are also being used to stiffen advanced composite propellers, which are hybrid structures. They are used to develop engine fan blades, because their properties are ideal for the aerodynamic loads and because many blades can be cast from one mould, which is ideal in the development phase. Unfortunately, their inability to cope with certain bird-strike requirements, which has earned carbon fibers some undeserved notoriety, means that they have not yet been used in service in this application. Carbon fibers find application in space structures because of their high specific properties, but also because of their stability. The near zero coefficient of thermal expansion and high stiffness make high modulus carbon fibers ideal for maintaining antennae dimensions under the extreme thermal gradients in space. This stability to thermal fluctuations is also very useful for precision metrology. The automotive industry has long been courted by the carbon fiber manufacturers because of the large numbers of vehicles, but so far the industry has been driven mainly by economic considerations. Carbon fibers have been used in leaf springs and in transmission shafts on light trucks: certain carbon fiber transmission shafts gave such
superior dynamic performances that a central bearing could be eliminated, resulting in a 80% mass saving. Thermoplastic matrices, with their potentially shorter processing times, may make composites more attractive in the future. In warships, the superstructure has long been mass critical and aluminium alloys have been used. Composite superstructures are being investigated. Another marine application is in submersible craft and diving torsos, where added stiffness is useful. Oil drilling rigs sometimes have teething ropes so long that the mass of the ropes impose a significant load on themselves, and ropes containing carbon fibers are being considered.

Another obvious application is for windmills, where large stiff structures are required for the sails, some designs being as much as 100 m in diameter. Flywheels offer an interesting application: the maximum energy per unit mass that can be stored by a given material is equal to half the specific strength, so carbon fibers are ideal. Low inertia is important in reciprocating machinery such as in spinning, winding and weaving, and there is a knock-on effect in the lower masses and energies in the control mechanisms. A bonus is in the fracture behavior, because when a carbon fiber part fails, it breaks into light fragments and does not do so much damage to the rest of the machinery as metal parts do. Carbon fibers have been used for medical applications. Their high specific properties and their excellent moulding characteristics have been useful for various supports and artificial limbs. Carbon fibers are inert in the body and have thus found uses as implants. It was also discovered that in some internal applications the surface characteristics of the fiber encouraged the regeneration of tendon tissue [9,10,12,13].
1.3.7 Scope of Present Work

The potential of pitch based carbon fiber is both for high performance applications as well as for general purpose applications like in building construction or environment, water purification etc. Latter application demand cheaper way of producing these fibers. The maximum efforts in pitch based carbon fibers go in their stabilization. Therefore finding alternative methods for stabilization is very important aspect of carbon fiber technology. There is not much work done in this direction therefore the prime aim of this research work was to study stabilization behavior of the pitches and the fibers produced from them using chemical methods.