Extraction of valuables from coal tar pitch

Thesis on

"Extraction of valuables from coal tar pitch"

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Pitour Murmu

Abstract

A simple and low cost effective way to synthesize carbon nano molecules (CNMs) from coal tar pitch has been demonstrated. The CNMs were synthesized from coal tar pitch (CTP) by using nano CaCO3 as template combined with KOH activation strategy at temperatures ranging from 850-950 ^{0} C. Characterization of the CNMs were done by Scanning electron microscopy (SEM), X- ray diffraction (XRD) and UV-VIS spectroscopy. The images of SEM showed porous and hollow structure with much similarity to activated carbons. The results of XRD showed the change from crystalline to amorphous with the increase in temperature and from the UV-VIS spectroscopy band gaps of the obtained CNMs were calculated. Also the various characteristics of coal tar pitch were examined and analysed in this work.

Contents

1. Introduction

Coal-tar pitches (CTP) are products of coal conversion, which are shiny, highly viscous and are generally dark brown or black in colour and have been used since long time ago. However, their usage as a profitable industrial material started at the end of the 19^{th} and beginning of the 20^{th} centuries, when CTP started to be used in different areas related to the technologies of carbon production (e.g., carbon anodes). The occurrence of mass emergence of CTPs into the market was probably due to the substitution of traditional and obsolete beehive coke ovens by coke-making facilities, such as those developed by Koppers at the beginning of the 20^{th} century. These facilities produced coke of better quality, while at the same time all the by-products generated during the coking process of coal could be recovered and subsequently transformed. This incident led to the industrial birth of coal-tar pitch.

Because of their affinity and binding capacities to other carbon products like petroleum coke, CTPs promptly found application in the production of carbon items for the aluminium industry. This gave a great urge to the production of CTP with CTP production constantly increasing during the 20^{th} century. Nowadays, CTPs are not only an inimitable binder in the aluminium industry but also have widened their sectors of application to other industrial areas, such as graphite electrodes for electric arc furnaces, refractory briquettes, etc.

However, the stringent regulations concerning the emissions of pollutants to the atmosphere and the sharp decline in coal tar supply as a result of the closing down of various coke ovens have made it necessary to find an alternative binder that is more environment friendly and that can fill the gap left by the progressive coal tar deficit. Some of the strategies pursued to address these problems are for example the development of hybrid pitches based on blends of CTP and petroleum pitch in different proportions or the development of pitches based on coal-tar fractions, i.e., anthracene oil-based pitches. Both solutions seem to be encouraging from the point of view of alternative more environment friendly feed stocks.

It is evident from above that the production of CTPs is dependent on their industrial consumption in the applications and usage in various fields. However, it must be kept in mind that CTP is an excellent source of polycyclic aromatic compounds (PACs) that can be easily polymerized or condensed giving rise to graphitic materials. For this reason, CTPs have also found application in other speciality fields where highly structural, mechanical, electrical and thermal properties are required. Carbon fibers, polygranular graphites, needle coke, carbon-carbon composites are some of the areas in which CTPs are used, especially for scientific purposes.

Preparation of Coal Tar Pitch

The industrial production of CTPs consists of the fractional distillation of the coal tar at temperatures close to 400^0C. By this procedure, the coal tar yields a series of liquid fractions suitable for different industrial applications and a residue which is solid at room temperature, called coal-tar pitch.

Two different types of CTPs are usually produced: binder and impregnating grade. The main difference between these two pitches resides in the quinoline insoluble content (much lower in the impregnating CTPs) and in the softening point (approx. 110^0C for binder and 90^0C for impregnating grade). The heaviest coal tar distillation fraction, which distills nearly between $270\text{-}400^0$C is anthracene oil. This fraction is composed of 3 to 5 ring aromatic PACs that has eluded all attempts at polymerization by conventional thermal treatments at atmospheric pressure. Its conversion into a pitch requires the use of specialized forms of treatment that allow the polymerization of low-molecular weight PACs to take place.

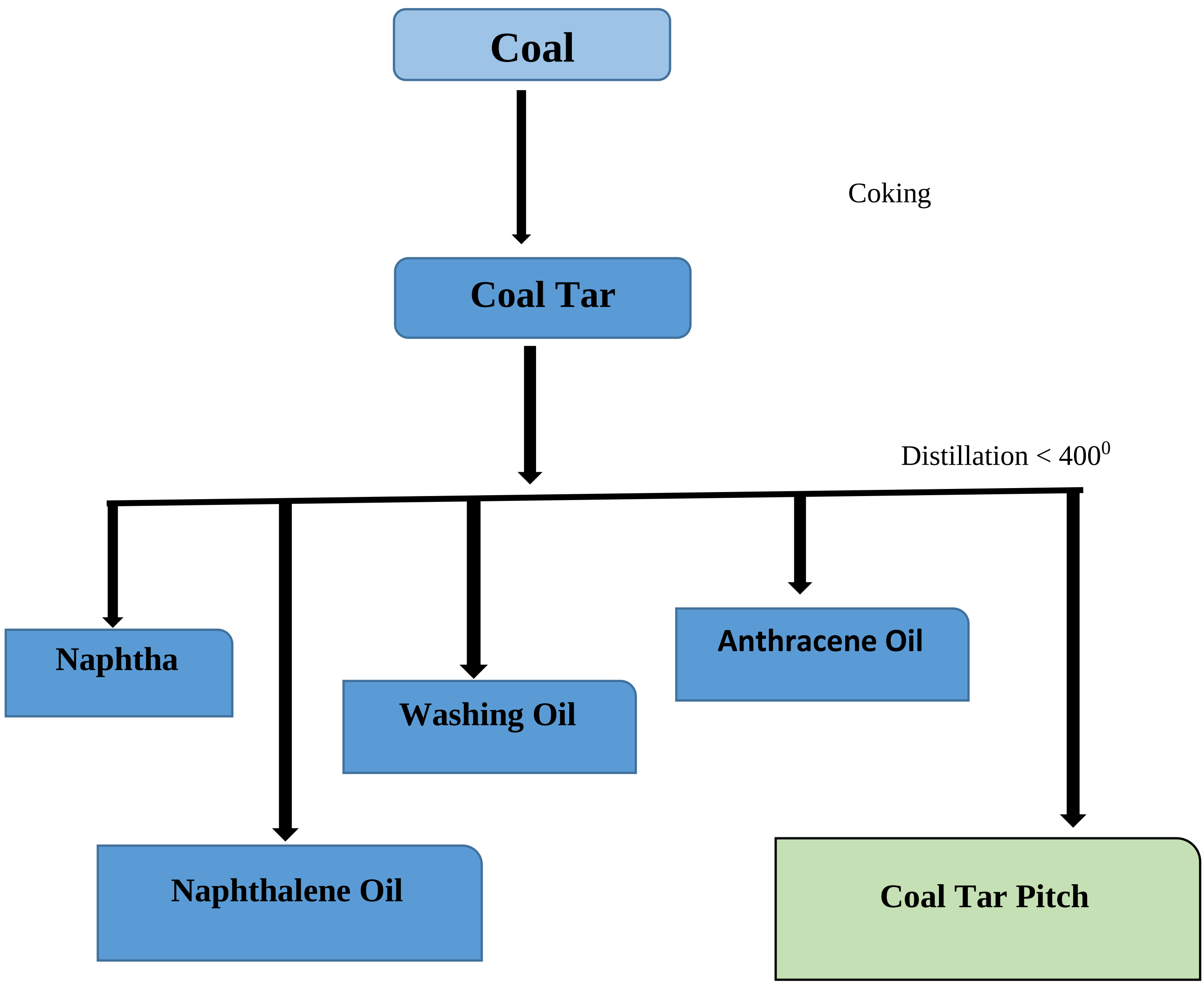


Fig.1 Schematic representation of products obtained from coal

This type of pitches are produced with the specific aim of fulfilling the requirements for binder and impregnation agents, mainly for carbon anodes and graphite electrodes. For this reason, their use in other fields, such as precursors for advanced carbon materials, usually requires a pre-treatment of the commercial pitches in order to adapt their composition and characteristics for their further utilization. For example, thermal treatment in an inert atmosphere and air-blowing are procedures commonly used to reduce the emission of volatiles during pitch processing and also to increase pitch carbon value, without altering most of the fundamental characteristics of the pitches (e.g., wetting capacity, fluidity etc.). Basically, thermal treatment can be considered as an interrupted carbonization (350-450^{0}C) that involves distillation, polymerization and even the formation of mesophase. The result is pitches that are able to produce carbons with a lower porosity, higher density and pre-graphitic order. All these improvements make thermally treated pitches excellent precursors for matrices of different types of composites, carbon fibers, self-sintering graphites etc. On the other hand, air-blowing has similar effects to thermal treatment but at a lower temperatures (< 350^{0}C). This is because oxygen promotes the formation of free radicals that favor polymerization reactions. In this case, polymerization occurs via the formation of planar macro molecules and the formation of cross-linked structures. The latter restricts mesophase development during air-blowing.

Carbon Materials From Coal Tar Pitch

The versatility for processing CTPs in order to enhance certain properties gives rise to materials with different structures and different properties. Thus fluidity and a higher softening point are really desirable parameters for the preparation of carbon fiber. Fluidity permits the spinning of the fiber, while a high softening point prevents the spun pitch from deforming during stabilization and subsequent carbonization/graphitization. On the other hand, the attraction between the matrix precursor and the fibers (wetting capacity) and plasticity are the most relevant parameters for the preparation of C/C composites and self-sintering graphites respectively. In this regard, air-blowing and thermal treatment are promising procedures for enhancing these properties.

From the arguments presented above it is clear that treated pitches have a great potential as precursors for obtaining carbon materials. Moreover, the coexistence of two phases in thermally treated pitches (isotropic fraction and mesophase) offer new possibilities for obtaining two additional precursors: the isotropic phase, mainly consisting of polymerized pitch, and the mesophase with an already established pre-graphitic order.

Carbon Fibers

Carbon fibers display excellent structural, mechanical, electrical and thermal properties. For these reasons, they are widely used in structural and functional applications.

Pitch-based carbon fibers are usually grouped into two categories: (i) general purpose carbon fibers (GPCF) and (ii) high-performance carbon fibers (HPCF). Despite their different origins, both type of fibers are prepared following a similar sequence of steps: (i) spinning to generate the green fiber, (ii) stabilization to make the fiber in-fusible and (iii) carbonization to consolidate the structure of the carbon fiber. In the case of the HPCF, the processing also includes a graphitization step for achieving a higher graphitic order.

Coal-tar pitches have proved to be excellent precursors for both types of fibers. This is because CTPs have an aromatic composition that makes spinning and stabilization a process easily controllable. However, the use of CTPs in the preparation of fibers is obstructed by the problem of the solid

particles (primary quinoline insolubles) which must be eliminated before processing in order to avoid the deformation of the fiber. For this reason, filtration or solvent extraction must be performed before processing. CTPs can be used to produce general purpose carbon fibers with a tensile strength of over 400 MPa and a modulus of almost 40 GPa. Anthracene oil-based pitches emerge as an alternative to CTPs in this application because of the total absence of solid particles that makes the tedious and time-consuming step of primary QI removal unnecessary.

Synthetic Graphites

Synthetic graphites are attractive materials whose applications can be easily found in modern advanced technologies where a high chemical, mechanical, electrical and thermal performance is required (e.g.,nuclear reactor walls, electrodes for electric discharge machines, etc.). Such beneficial combination of properties are a consequence of the unusual structure of these graphites which consists of very fine anisotropic local units (microcrystallites) that confer an isotropic behaviour on the whole material.

Carbonaceous mesophase is an excellent precursor for obtaining polygranular synthetic graphites because mesophase is a self-sintering thermoplastic material, which is able to generate very pure, highly dense material by thermal treatment in an inert atmosphere without the need for an external binder. This eliminates the tedious mixing and repetitive impregnation or carbonization steps involved in the traditional granular carbon technology used for preparing synthetic graphites.

The mechanism of mesophase growth in CTPs favours the formation of discrete microspheres. This is because at the initial stages of mesophase formation, QI particles tend to surround the mesophase making it more difficult to coalesce. The result is a mesophase, which is rich in microspheres and plastic enough to be moulded by pressing. Moreover, when the mesophase is excessively plastic, the mesophase plasticity can be gradually reduced by means of oxidative stabilization. After moulding and controlled carbonization/graphitization, CTP-based mesophase is able to produce graphites with a flexural strength of 80-100 MPa. Values above 100 MPa have been reached using anthracene oil–based mesophase as carbon precursor.

Carbon fiber reinforced carbon composites

Carbon fibers are superb structural materials because of their excellent mechanical properties.However, their use in structural applications requires the presence of a second component (matrix), which confers stiffness and structural consistency on the material. The combination of fibers and matrix results in a composite in which the most positive characteristics of each individual component are linked. There are many types of composites. However, those made of carbon fibers and a carbonaceous matrix are especially interesting (carbon fiber reinforced carbon composites, C/C) because they preserve, and even improve, their mechanical properties with increasing temperature.

This makes C/C ideal materials for use in extreme high-performance applications (e.g., aircraft brakes, components of aerospace shuttles, walls of nuclear reactors).

The preparation of these composites involves the liquid impregnation of the fibers with pitch and the subsequent moulding/curing of the prepared by pressing and carbonization up to ~ 1000 ℃. The presence of QI in the composites exerts a great influence on both their mechanical strength and the mechanism of failure. CTPs with a high QI content (especially binder CTPs ~ 10 wt.% of QI) give rise to matrices in which mosaics is the predominant optical texture. These mosaics contribute to improving mechanical strength (400-500

MPa), but at the same time, give rise to a strong fiber/matrix adhesion that tends to fail via a catastrophic-like failure mechanism.

The properties of pitch based C/C composites can be improved substantially by densification. This procedure involves filling the open porosity of the composite by applying several cycles of impregnation/carbonization until the desired density and hence mechanical strength is achieved. An alternative to reducing the over long impregnation/carbonization cycles is to use high carbon yield pitches.

CTP, and more specifically CTP-based mesophase, is also shown to be a superb infiltration agent for the impregnation/densification of carbon fiber performs. The high carbon yield, a highly suitable viscosity, low exudation capacity, and exceptional conductivity make CTP-based mesophase an ideal precursor for pitch infiltration in composites destined for frictional applications and other specialty utilities where high thermal conductivity is required (e.g., nuclear reactor walls).

Other carbon materials

Recent studies have proved the potential of CTP-based materials in other fields and for novel applications that are still being under research, such as anodic material for Li-ion batteries, graphite foams or graphitizable materials for supercapacitors.

Secondary Li-ion batteries are one of the most promising batteries because of their light weight, high working performance and environmentally-friendly composition. The anodic material of these batteries is composed of carbon. By using both isotropic pitch and mesophase it is possible to obtain carbons with a high capacity and good recycling behaviour.

Graphite foams are attractive materials that exhibit high thermal conductivity, very low density, high permeability and excellent thermal stability. Graphite foams can be obtained from a variety of precursors, one of which is CTP-based mesophase. The traditional preparation of these materials requires the use of thermal cycles under pressure in the presence of a blowing agent and a subsequent pressure drop. The result is a material with a reticulated structure that has applications in several fields, such as that of heat exchangers, radiators or structural insulators.

Other types of material of great interest in carbon technology include those graphitizable materials that are able to generate porosity. CTP-based mesophase or CTP-based coke are unique precursors for obtaining activated carbons with a high electric conductivity. These materials are usually prepared by chemical activation (e.g. KOH), resulting in the formation of uniform micro and mesopores. Recent studies have shown that these carbons are superb materials for electrodes in supercapacitors. This is because CTP-based mesophase and CTP-based coke are able to generate high surface areas and can be easily prepared in the form required (e.g., powder, fibers, etc.). Moreover, graphitizable carbons offer many advantages over other materials, such as a better conductivity, a higher density or a higher yield during processing.

2. <u>Aims & Objectives of the project</u>

Aim of the project

- Production of valuables from coal tar pitch and find its application by a simple and economic process.

Objectives of the project

i) Chemical analysis of the given coal tar pitch sample.

- ➢ Chemical composition by CHN Analyzer.
- ➢ Softening point and Quinoline solubility determination.
- ➢ Identification of functional groups: FTIR

ii) Synthesis of valuable product from CTP

iii) Study of the operating parameters of the process.

iv) Characterization of obtained product

- ➢ Identification of crystallinity, structural characterization: XRD , SEM
- ➢ Spectrophotometric characterization: UV-VIS Spectroscopy: Determination of band gap.

3. Literature Review

Introduction

This chapter provides some information on the literatures surveyed and reviewed to perform the present investigation. Here an attempt has been made to identify some effects of temperature and addition of chemicals which may have significant effect on production and characterization of the synthesized material.

Journal Name	Author/s	Description
Synthesis of porous graphene-like carbon materials for high performance super-capacitors from petroleum pitch using nano-CaCo3 as a template. [New Carbon Materials,2018,33 (4):316-323]	Ming-jie Liu,Feng Wei,Xue-mei Yang,Shi-an Dong,Ying-jie Li,Xiao-jun He	Using nano-CaCo3 as template coupled with KOH activation porous graphene-like carbon materials (PGCMs) were synthesized from petroleum pitch.Short pores in PGCMs improve their electronic conductivity and shorten ion transfer distance.
Catalytic graphene formation in coal tar pitch- derived carbon structure in the presence of SiO2	Maciej Gubernata, Aneta Fraczek- Szczyptaa, Janusz Tomalab,	In this paper a simple and effective way of graphene generation from coal tar pitch using SiO_2

nanoparticles. [Ceramics International 44 (2018) 3085–3091]	Stanislaw Blazewicz	nanoparticles is provided and its characterization is done using XRD,TEM and Raman Spectroscopy.
ZnO template strategy for the synthesis of 3D interconnected Graphene nanocapsules from coal tar pitch as supercapacitor electrode materials. [Journal of Power Sources 340 (2017) 183-191]	Xiaojun He, Xiaojing Li, Hao Ma, Jiufeng Han , Hao Zhang ,Chang Yu ,Nan Xiao , Jieshan Qiu	Graphene nanocapsule is produced using Nano-ZnO template and their electrical properties are studied to be used as Supercapacitor electrode materials.
Meltblown Solvated Mesophase Pitch-Based Carbon Fibers: Fiber Evolution and Characteristics. [Journal of carbon research C 2017,3,26]	Zhongren Yue , Chang Liu and Ahmad Vakili	Production of carbon fibers along with thermal analysis in mesophase pitch development and study of microstructure of the obtained carbon fiber is done.
Preparation of fluffy graphene nanosheets from coal-tar pitch with nano-Al_2O_3 as filler. [Journal of Analytical and	Kang Wang, Xialan Zhang, Xinqi Zhang, Qilang Lin, Xiangdong Huang	This paper provides study of Graphene nanosheets production from Coal-tar pitch using nano Al_2O_3 and various effects of

Applied Pyrolysis 117 (2016) 354–356]		carbonization for its preparation.Characterization of the obtained product is also done.
Interconnected mesoporous carbon sheet for supercapacitors from low-cost resources. [Materials Letters 158 (2015) 237–240]	XiaotingWang, HaoMab, HebaoZhan, MoxinYu, Xiao jun He, Yong Wang	This paper gives an insight on procedure of synthesis of porous carbon materials sheet for supercapacitor and its characterization of electrical properties.
Value-added Synthesis of Graphene: Recycling Industrial Carbon Waste into Electrodes for High-Performance Electronic Devices. [Scientific Reports 5:16710 (2015)]	Hong-Kyu Seo, Tae-Sik Kim, Chibeom Park, Wentao Xu, Kangkyun Baek, Sang-Hoon Bae, Jong-Hyun Ahn, Kimoon Kim, Hee Cheul Choi & Tae-Woo Lee	The growth of CTP-derived graphene and its Characterization with demonstration of practical applications of graphene films.
Facile preparation of graphene nanosheets by pyrolysis of coal-tar pitch with the presence	Hao Xu, Qilang Lin, Tianhong Zhou, Tingting Chen, Shuping	Preparation of graphene nanosheets has been provided by thermal

of aluminum. [Journal of Analytical and Applied Pyrolysis 110 (2014) 481–485]	Lin, Shaohai Dong	treatment of coal tar pitch in the presence of aluminium.detailed analysis of the effect of pyrolysis is given.Structural characterization is done.
In situ fabrication of carbon nanotube/ mesocarbon microbead composites from coal tar pitch. [Materials Letters 62 (2008) 3585–3587]	Zhi Wang , Bin Wu, Qianming Gong , Huaihe Song, Ji Liang	Preparation of carbon nanotubes or mesocarbon microbeads from coal tar pitch has been discussed along with the structural examination and its characterization.
Mesophase development during thermal treatment of pitches. [Journal of Optoelectronics and Advanced Materials Vol. 10, No. 4, April 2008, p. 896 - 899]	A. Bara, A M. Bondar,D. Patroi, R Vasilescu-Mirea,S.Hodorogea, C. Banciu	This paper provides an insight into the development of mesophase during thermal treatment and the analytical methods and characterization of the obtained mesophase pitch.

Conclusion of literature review

After extensive literature study it has been observed that there are various methods of production of valuables from coal tar pitch which mainly depends on the processing temperature and the type of catalysts used in the process. Process bottlenecks and advantages of extraction of products are presented below.

Process bottlenecks

- ❖ High temperature process: More energy is required during operation.
- ❖ Full chemical characterization is not feasible.
- ❖ Different heating rate has different effect on carbonization.
- ❖ Taking into consideration the energy consumed and materials needed, the process becomes expensive.
- ❖ Pyrolysis of coal tar pitch results in emission of volatiles into the atmosphere, which is harmful for the environment.

Advantages of extraction of products from coal tar pitch

- ➢ The raw material(CTP) used for the process is easily available and is cheap.
- ➢ The products obtained have generally good chemical, mechanical, electrical and thermal properties.
- ➢ Since the products are obtained from residue (CTP) which is considered waste, the process is of economic value.

Research Gap

- Formation of carbon matrix for catalyst preparation to provide greater surface area.
- Full chemical characterization of coal tar pitch.

4. Experimental Methodology

❖ Sample Preparation

The sample coal tar pitch(CTP) obtained from Himadri Speciality Chemical Ltd. was first finely ground in a mortar and pestle and then the pulverized sample was passed through a 150 mesh. Then the material which passed through was stored in a suitable container.

❖ Characterization of sample

1. Softening point determination: The procedure of determining softening point was carried out as followed in standard "Ring & Ball Test" method.

2. Quinoline solubility: 1 gram of sample was taken and dissolved in 25 ml of quinoline in a beaker .Then the solution was placed in a water bath at a temperature of 80 $\pm 5^0$C for 30 minutes. The resultant solution was filtered in a Gooch Crucible and the retentate was measured in weight.

3. Chemical composition analysis: The powdered sample was analysed by 2400 series II CHNS/O Analyser-Perkin Elmer.

4. Functional group determination: Fourier transformed infrared spectroscopy (FTIR)

- **Sample preparation:** The powder sample and KBr must be ground in a mortar and pestle to reduce particle size to less than 5 nm in diameter. Then pellet formation of the sample is done under high pressure and tested by FTIR instrument.

- **Operation and methodology:** The sample absorbance of the infrared light's energy at various wave lengths is measured to determine the material's molecular composition and structure. The frequency range is measured as wave number over the range of 4000 cm-1 to 400 cm-1. Percentage transmittance vs wave number is plotted and analyzed the peak. Analysis is shown in the next section.

- **Operating instrument:** Perkin Elmer Spectrum-2 is used for FTIR analysis of different synthesized photocatalyst.

❖ Preparation of Carbon nano molecule (CNM) from Coal Tar Pitch

Materials required:

i) Coal Tar Pitch (CTP)

ii) KOH (Potassium Hydroxide)

iii) $CaCO_3$ (Calcium Carbonate)

Synthesis Procedure:

6 gram of KOH was first finely ground in a mortar and pestle. Then CaCO3 powder was added into it and mixed homogeneously. Then 4 gram of CTP powder prepared earlier was added into this and again a homogeneous mixture is made. This mixture was then put in a furnace and heated at a temperature of 850^0C for nearly 2 hours. After heating the resultant mixture was washed in 2M HCL and then dried in a hot air oven at a temperature of 100^0 C for 12 hours. The material thus obtained was designated as Carbon nano molecule (CNM)-(t), "t" being the temperature at which it was heated. So the above mentioned material obtained was designated CNM-850. Similarly we get CNM-900.We apply similar procedure to obtain CNM-950,the only difference being the amount of CTP added which for this case was taken as 6 gram.

Samples	Temperature (^{0}C)	Qty. Of KOH & $CaCO_3$ (gram)	Qty. Of CTP (gram)
CNM-850	850	6	4
CNM-900	900	6	4
CNM-950	950	6	6

Table 1. Different samples and their respective parameters

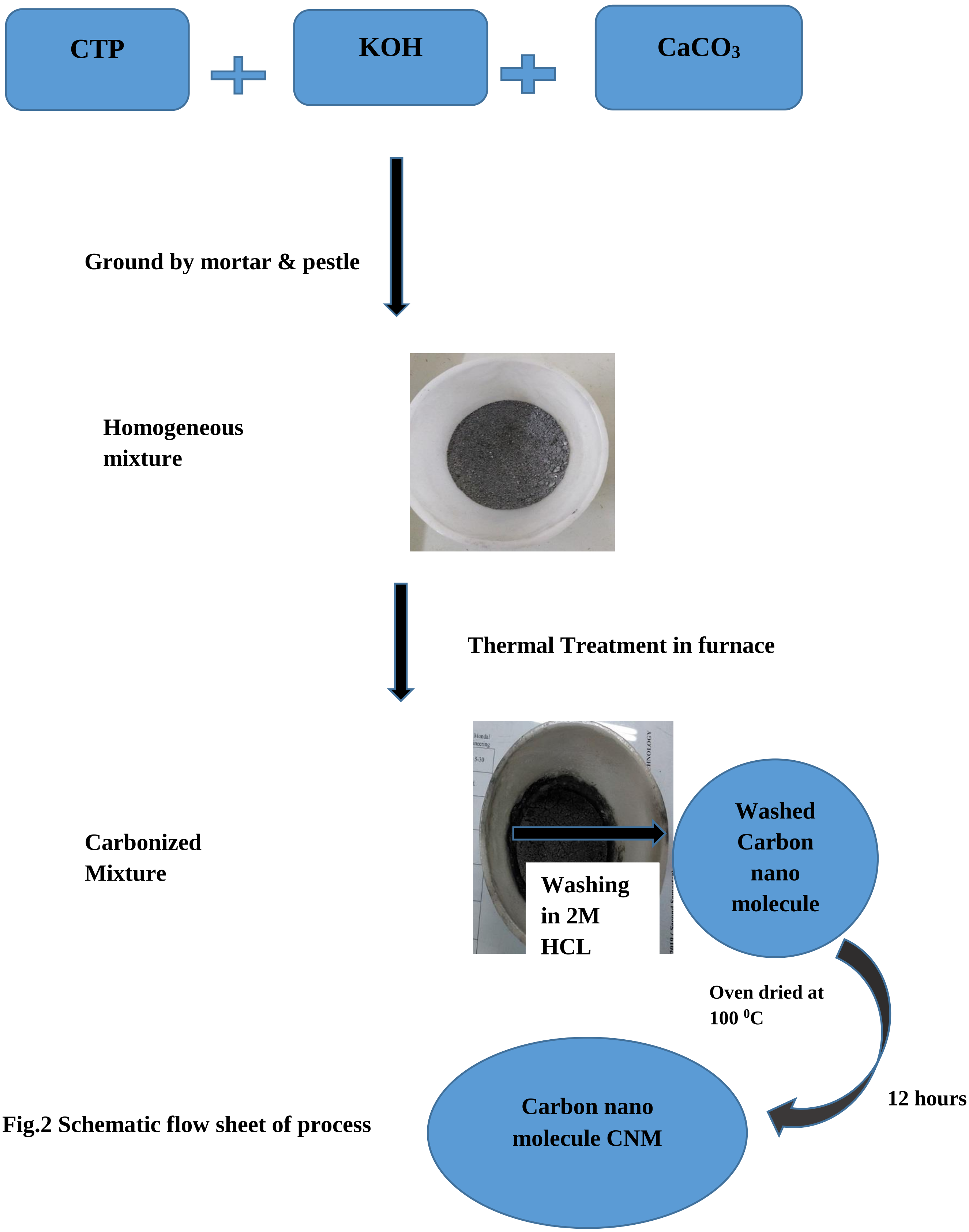


Fig.2 Schematic flow sheet of process

Characterization of Synthesized Carbon nano molecule (CNM)

The three samples were characterized by SEM (Scanning Electron Microscopy) for structural determination, XRD (X-Ray Diffraction) for crystallinity, and UV-VIS spectroscopy for band gap calculation.

Structural characterization: scanning electron microscopy (SEM)

Sample preparation: Specimens are coated with a thin layer of 20 nm to 30 nm of conductive material of gold.

Operation and methodology: SEM uses an electron instead of a beam of light, which is directed towards the specimen under examination. An electron gun is located top of the device, shoots out a beam of highly concentrated electrons (15 kV) and photograph is formed. Photograph of the sample is shown in the next chapter.

Operating instrument: Hitachi S-3400 Scanning electron microscopy has been used to analyze the structural characterization of different synthesized catalysts.

Crystallinity of samples: X-ray diffraction (XRD)

Sample preparation: Powder XRD is carried using a pinch of sample.

Operation and methodology: X-ray falls on the sample and reflected x-ray is detected by X-ray detector. Governing principle for XRD is Bragg's law ($n\lambda=2d\sin\theta$). Different peaks are obtained at various 2θ angles with various intensities. Then intensity vs 2θ is plotted and peaks are analyzed using JCPDS library and literature review for crystal plane. Analysis of XRD is shown in the next chapter.

Operation instruments: Rigaku, Ultima III Difractometer is used for XRD analysis. **Band gap calculation: UV-VIS spectroscopy**

Sample preparation: Pinch of powder sample is dispersed into water by ultra-sonication for 15 min. and taken into quartz cuvette for the UV-VIS spectroscopy.

Operation and methodology: UV-VIS spectroscopy follows Lambert's Beer law. Two cells are used for this analysis one is reference cell (water) and another is sample cell (aqueous solution of catalyst). Monochromatic beam of light is passed through the sample and reference cell both and gives the absorbance vs wavelength plot.

Band gap calculation: For optical band gap can be measure by empirical relation known as Tauc formula: $\alpha h\nu=A(h\nu-E_g)^n$

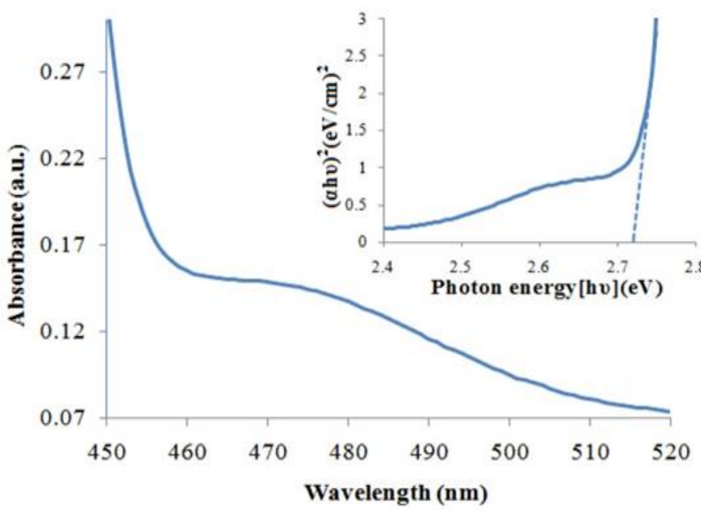


Fig.3 Tauc plot

Where, hν= Photon energy

α= Absorption co-efficient

A= Constant

n= Constant depending upon the transition

Here, A=1 and =1/2 so, the formula can be written as $(\alpha h\nu)^2 = (h\nu - E_g)$

$h\nu = hc/\lambda = 1240/\lambda$

A graph is plotted between $(\alpha h\nu)^2$ as an ordinate and $h\nu$ as abscissa. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis (Tauc plot) helps in obtaining the value of band gap.

Operational instrument: Perkin elmer 365 UV-VIS spectroscopy is used for this analysis.

5. Result and Discussion

Characterization of Coal Tar Pitch(CTP)

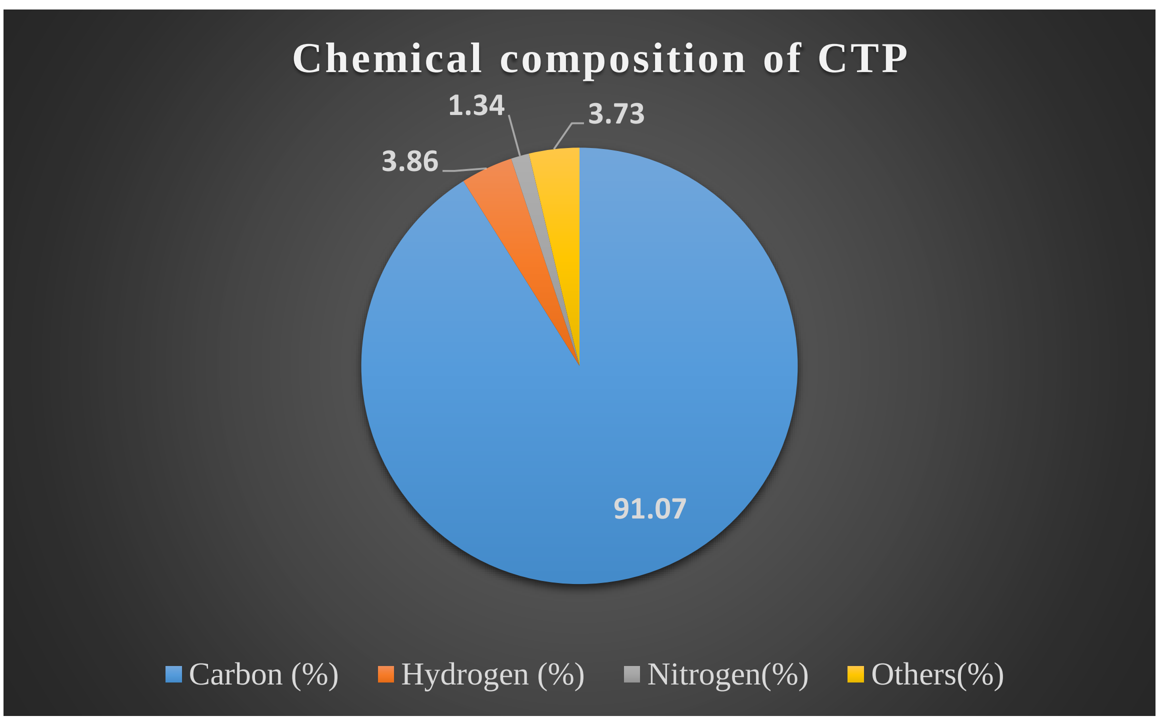
The various characteristics of coal tar pitch (CTP) are presented below.

i) **Softening Point-** Following the Ring & Ball test ,the softening point of CTP came to be 100^0C.

ii) **Quinoline Insolubles (QI):** The result of the solubility test was recorded and the Quinoline insolubles was found to be 15% by weight.

iii) **Chemical Composition:** The result of C,H,N Analysis tested in 2400 series II CHNS/O Analyser-Perkin Elmer is tabulated below.

Carbon (%)	Hydrogen (%)	Nitrogen(%)	Others(%)
91.07	3.86	1.34	3.73



iv) **Functional group determination: Fourier Transformed Infrared Spectroscopy (FTIR)**

From the FTIR spectra shown below, it can be seen that at 1055 cm^{-1} there is a slight broad peak due to the presence of C-H bending (aromatic).Again sharp peaks can be observed at 1532 cm^{-1} due to CH_3,1664 cm^{-1} due to C=O stretching,2856 cm^{-1} for C-H stretching (aliphatic),2927 cm^{-1} due to C-H stretching (aromatic) and a broad absorption results at 3460 cm^{-1} due to O-H stretching vibration.

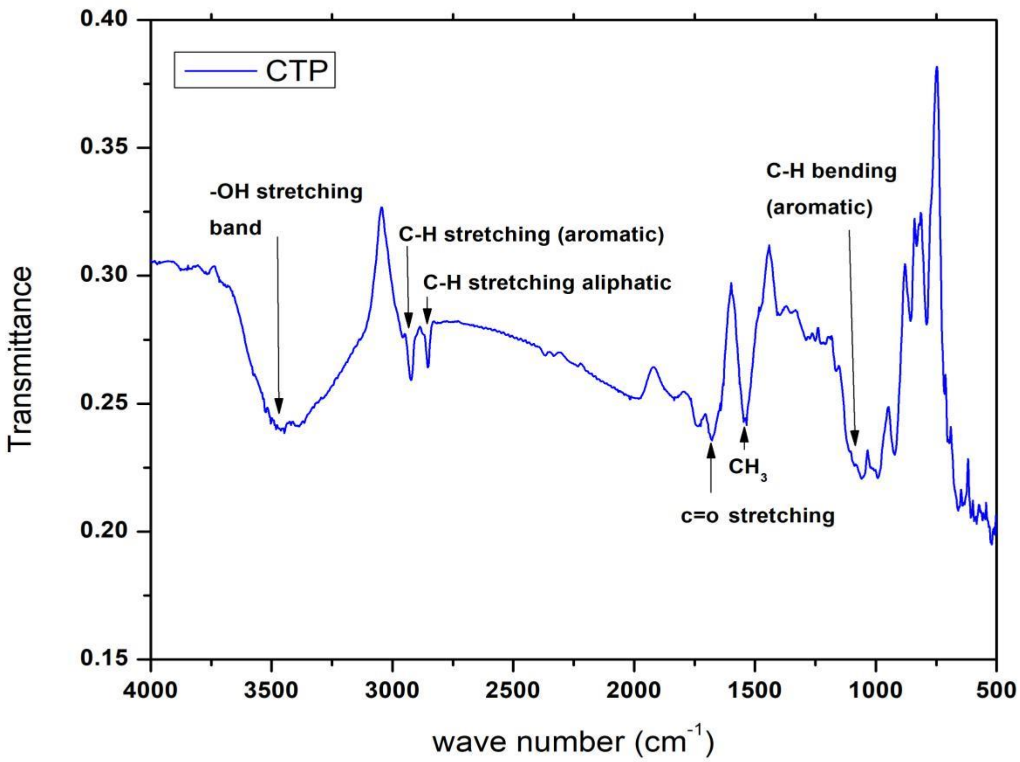


Fig.4 FTIR image of CTP

Characterization of carbon nano molecule (CNM)

In this three different characterization were performed for the obtained carbon nano molecules (CNM). They are SEM, XRD and UV-VIS spectroscopy. The results generated were studied and are provided below.

- **Morphological Characterization: Scanning Electron Microscopy(SEM)**

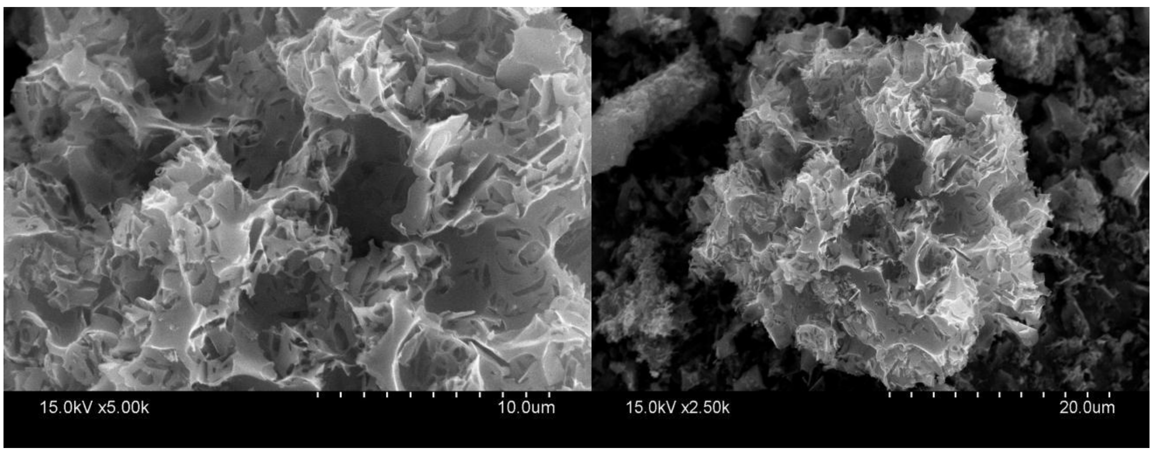


Fig.5 SEM images of CNM-950

SEM images of CNM-950 at a scale of 10 and 20 µm was obtained using using Hitachi S-3400 at an accelerating voltage of 15.0 kV.It shows a porous cauliflower like structure as that of activated carbons.

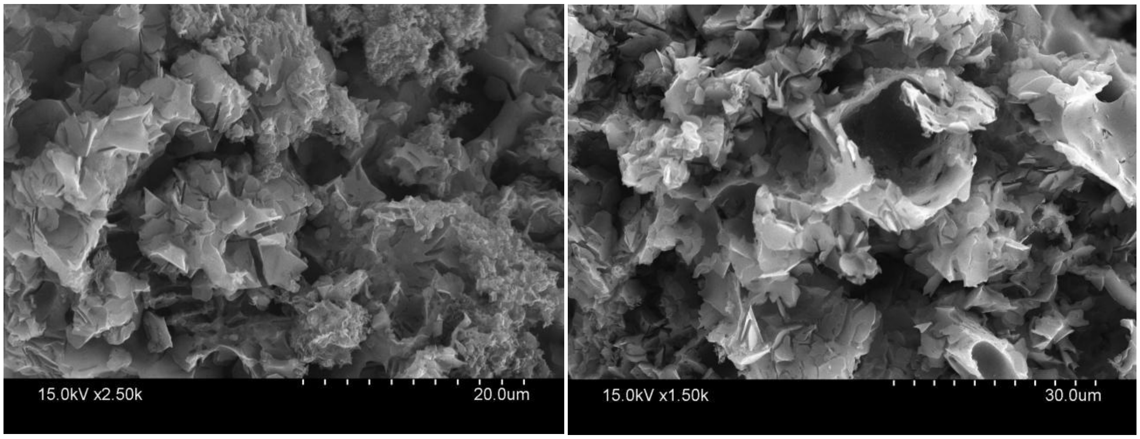


Fig.6 SEM images of CNM-900

From the above image it can be seen that it also shows some porous flakes but of less porosity as compared to CNM-950.

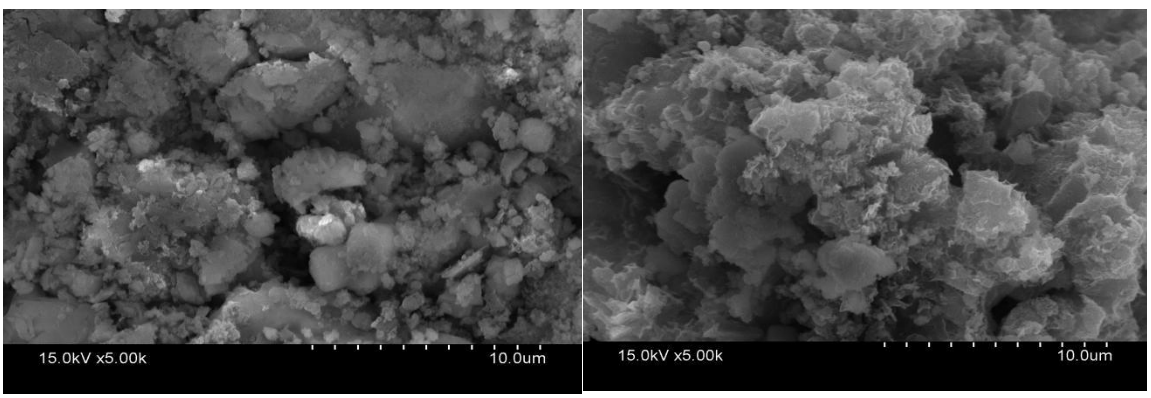


Fig.7 SEM images of CNM-850

The above image shows that as compared to the porous nature of CNM-950, in CNM-850 there is much less porosity and just in the starting phase of developed flake layers as seen in CNM-900 and CNM-950.From this it can be inferred that temperature plays a crucial role in layer formation and porosity development.

- **Characterization for crystallinity: X-ray diffraction (XRD)**

In the obtained XRD pattern shown in the figure below, three diffraction peaks can be seen at the planes (100), (111) and (200) respectively which corresponds to simple cubic lattice of CNM. With the increase in temperature the crystallinity of CNMs changes from crystalline to amorphous.

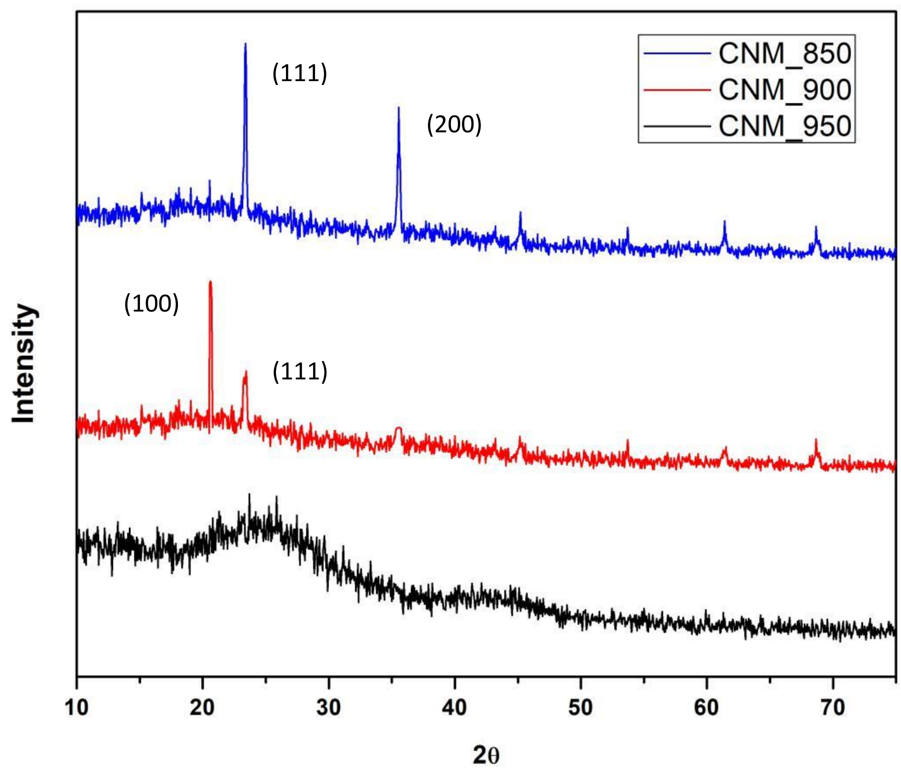


Fig.8 XRD pattern of CNMs

- **Spectrophotometric characterization: UV-VIS spectroscopy: Band gap calculation**

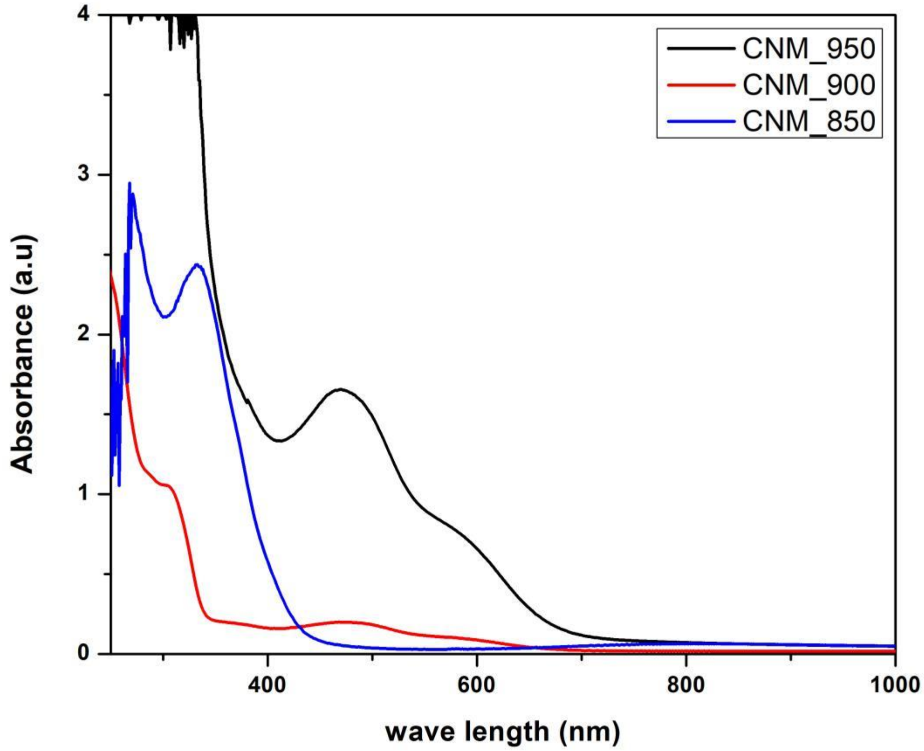
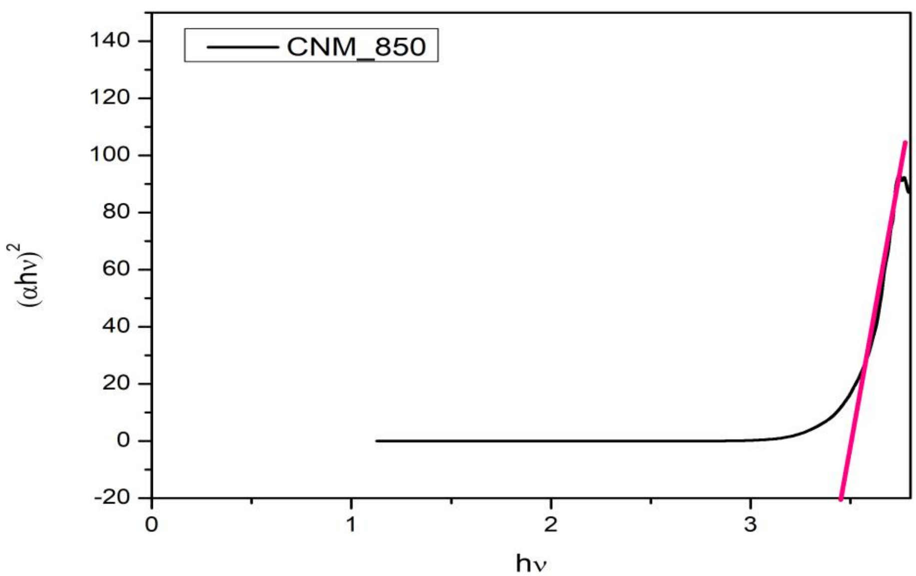
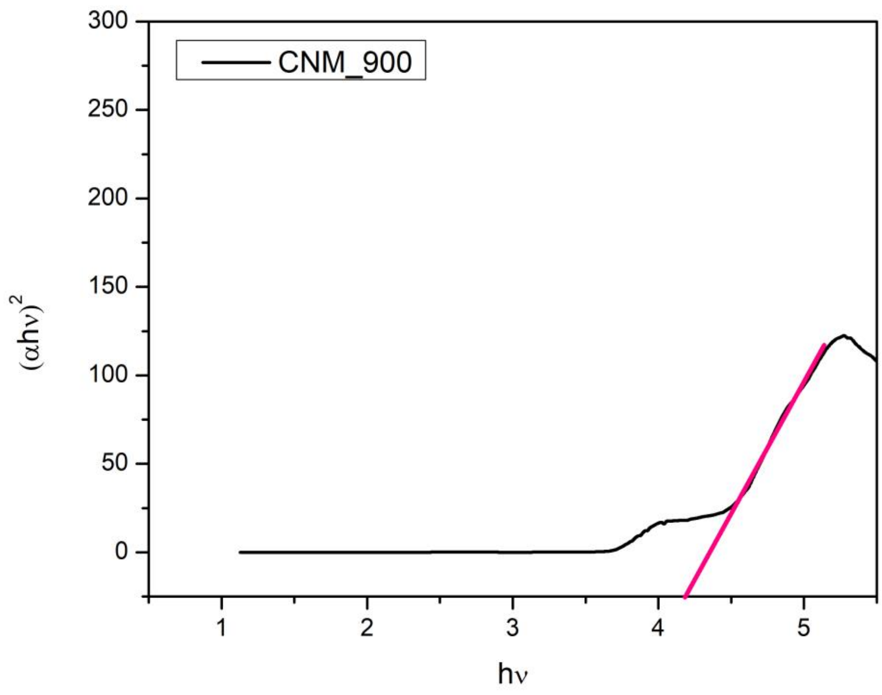


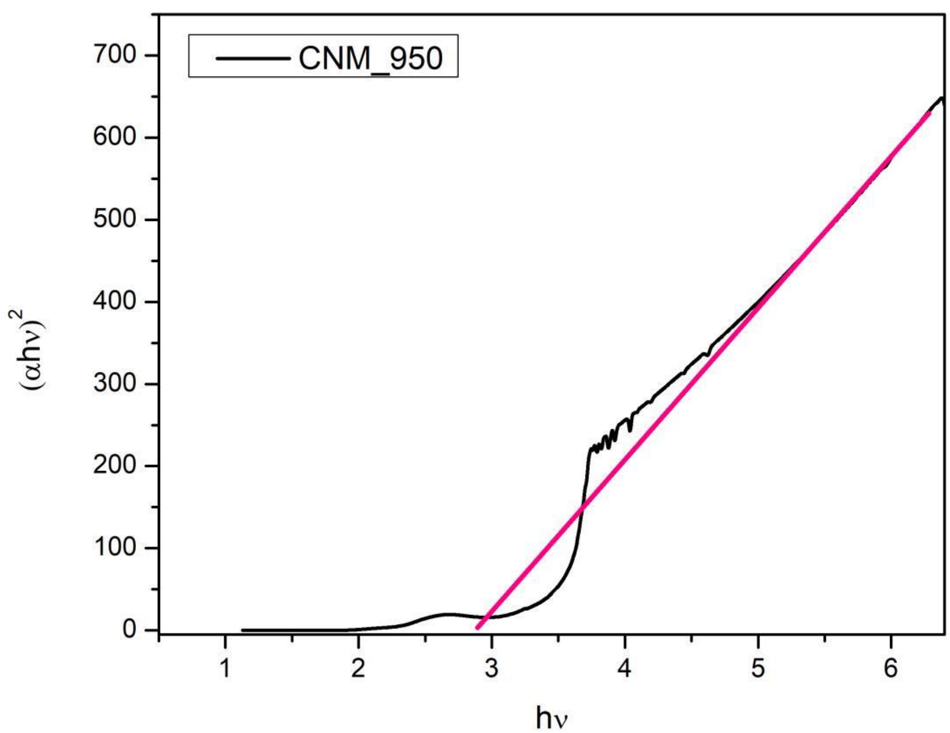
Fig.9 UV-VIS spectroscopy of CNMs

From the UV-VIS it is observed that peak obtained at 500 nm,380 nm and 310 nm for CNM-950 , CNM-900 and CNM-850 respectively. Therefore it can be inferred that CNM-950 and CNM-850 absorbs spectrum of visible light but CNM-900 absorbs spectrum of UV light.

Band gap Calculation:







Sample	Band gap (eV)
CNM 850	3.4
CNM 900	4.2
CNM 950	2.9

6. Conclusion

Carbon nano molecules (CNMs) have been synthesized from coal tar pitch by using nano-$CaCO_3$ as template along with KOH activation. The synthesized CNMs were produced by varying the temperature and composition of the used materials i.e CTP, $CaCO_3$ & KOH and further characterized by Scanning electron microscopy (SEM),X-ray diffraction (XRD) and UV-VIS spectroscopy.The SEM images showed that the CNMs have a porous structure having similarity with activated carbons and as the temperature is increased from 850^0C to 950^0C the morphology of the CNMs changed significantly with showing more porosity at higher temperature. The XRD results showed that the CNMs changed the crystallinity from crystalline to amorphous with increasing temperature. From the UV-VIS spectroscopy results it was found that the CNMs absorbed light in visible and ultraviolet (UV) spectrum and have a band gap in the range of 2.9 - 4.2 eV. Furthermore the various characteristics of coal tar pitch were also found and have softening point at 100^0C and QI content of 15 % by weight. Overall this work gives a novel method for the preparation of low cost carbon nano molecules from coal tar pitch.

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