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Synthesis of Highly Dispersed Single Walled Carbon Nanotubes from Furnace Oil and Light Diesel Oil by Modified Chemical Vapour Deposition Method

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ABSTRACT : The carbon nanotubes have been synthesized from heavy petroleum fractions like furnace Oil (F.O.) and Light diesel Oil (LDO) and characterized by Scanning Electron Microscopy, Transmission Electron Microscopy. Modified chemical vapour deposition method is one of the cheapest method for the synthesis of carbon nanotubes. In this present investigation an indigenously designed reactor has been fabricated for the Production and collection of soot from the raw material. The soot collected is then purified by sohxlet extraction method. The purified CNTs is the then oxidized with dilute nitric acid. The oxidation has been confirmed by -CO stretching frequency at ~1725cm^{-1} by the FTIR spectroscopy. The above synthesized CNTs have been made dispersed in different solvents. Its dispersed stability has been tested at different temperature and results shows that it is highly disperses in acetone and distilled water as compared to ethanol and methanol and stable even up to 60°C. Result shows SWCNTs having ~70nm in case of F.O and ~ 90nm in case of L.D.O.

Keywords: Carbon Nanotubes, scanning electron microscopy, Transmission electron microscopy

I. INTRODUCTION

Single walled carbon nanotubes (SWCNTs) were first synthesized in 1993 by Iijima *et.al.* [1] and Bethune *et.al.* [2] using the sublimation of graphite by electric arc discharge in the presence of metal catalyst. SWCNTs have attracted a great deal of attention due to their unique physical, chemical and mechanical properties [3-4]. They are expected to be useful in many different applications areas of this material such as field emission displays, superconductors, batteries, hydrogen storage, nanotechnology tools, chemical sensors, electronic devices and polymeric composites [5-7] and nanoelectronics [8-10] to fuel-cell technology [11] and material science [12]. The extreme mechanical and transport properties of CNTs have inspired scientists and engineers a wide range of potential applications [13] Despite the outstanding properties of individual CNTs their insolubility hinders the transfer of those properties into the bulk [14]. Covalent functionalization represents an efficient way to render the CNTs soluble either in aqueous or Organic phase, by attracting differen5t functional groups directly to the CNTs [15]. literature screening shows that nitric acid is extensively used to oxidize CNTs. Nitric acid treatment produces mainly carboxylic groups [16-18], which contributes to the solubilization of nanotubes [19-20]. Although there are several method of production of CNTs like Arc discharge method, Laser Ablation method and Chemical vapour deposition method and these methods required sophisticated equipment for their operation. Unfortunately however, till date only purified petroleum products such as methane, ethylene, and acetylene are in practice use as raw materials for synthesis of CNTs. In view of the foreseen crisis of fossil fuels in near future, it is the time's prime demand to explore regenerative materials for CNT synthesis. In this investigation, we are successful to produce CNTs from heavy petroleum fraction with the help of an indigenously Design reactor. These heavy petroleum fractions are used for burning purpose in the furnaces or boilers only and they are secondary products of petroleum industry having higher molecular masses of hydrocarbon chains.

II. EXPERIMENTAL

A. Materials

The heavy petroleum fractions (F.O. and L.D.O) as raw material for the synthesis of CNTs were collected from IOC terminal, Suchi pind, GT Road Jalandhar. The terminal gets its oil supply from Panipat refinery (7th refinery of Indian oil. It receives crude oil from Vadinar and Mundra Ports in Gujarat coast. The refinery is designed for processing both indigenous & imported crude oil) around 270 Km away through pipelines. The average composition and properties of the two raw material chosen as starting material for nanotubes synthesis are in Table No.1. Both contains hydrocarbon chains of higher molecular masses like F.O. > C40 and L.D.O.>C15. The Analytical Grade E-Merck Chemicals like Nitric Acid, Ammonia, Benzene, Petroleum Ether, Acetone, Acetonitrile, Ethanol, Methanol, were used in the study. Whereas, Borosil make glassware were used in the study. All glassware's were washed with conc. HNO_3 and distilled water before used.

Table 1. Characteristic Properties of F.O and L.D.O

S.No	Characteristic	F.O.	L.D.O.
1.	Acidity, Inorganic	Nil	Nil
2.	Flash poin	66°C	66°C
3.	Kinematics viscosity, cSt, max.	180	2.5 to 15.7
4.	Sediment, percent by mass, max.	0.25	0.10
5.	Sulphur, percent by mass, max.	4.0	1.8
6.	Water content, percent by Volume, max.	1.0	0.25
7.	Density, mg/ml	0.9927	0.8725
8.	Pour Point	–	12°C for winter and 21°C for summer
9.	Copper strip corrosion for 3 h at 100°C	–	–
10.	Cetane number, Min	–	–
11.	Distillation 90 percent volume recovery at °C, Max	–	–
12.	Acidity, total mg of KOH/G, Max	–	–

Equipment : An indigenously designed reactor was fabricated in the institute workshop for the synthesis of carbon nanotube from various raw materials as shown in Fig. 1.

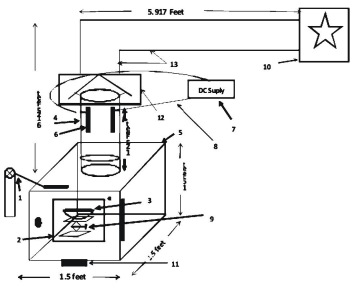

Fig 1. Block diagram of Electrical Precipitator unit

B. Methods

(i) Proximate Analysis

Fixed carbon content in each raw material was determined by Proximate Analysis. Proximate Analysis was carried out in a platinum crucible. One gram of the raw material (Density of F.O. is 0.99 mg/ml and L.D.O. is 0.87 mg/ml) was taken in the Pt-crucible and put it in oven at 110-120°C for 1 hour to find the moisture content in the raw material. After removing the moisture from the raw material, further content was heated at 950°C for 7 minute in muffle furnace to find out the volatile content. The ash content was calculated by taking the crucible at 750°C for half-an-hour in muffle furnace. The carbon/hydrocarbon content was calculated as 100-[Moisture+ Volatile + Ash Content]. The results of proximate analysis for F.O. and L.D.O. are shown in Table 2.

Table 2. Result of Proximate analysis of F.O and L.D.O

S.No.	Material	% Moisture Content (x)	% Volatile Content (y)	% Ash Content (z)	% Organic Content $100 - [x + y + z]$
1.	F.O	1.5	98	0.5	98%
2.	L.D.O	3.8	96	0.2	96%

(ii) Preparation of CNTs

Predetermined quantity of the raw materials F.O. and L.D.O. (about 40ml) was taken in the metallic bowl inside the reactor and heated above the flash point. A small amount of the spark with the help of match stick will start the ignition and door of the reactor was closed to control the supply of the air in the combustion chamber to control the soot production. From the Table 3 It can be concluded that the F.O. is producing maximum soot under controlled condition. Combustion process can be seen through the glass window in the centre of the front window. The soot produced by the combustion of the raw material was collected from specific area of the reactor as shown in Fig. 2*a*, 2*b*, 2*c* below. After collection of the soot from the reactor, the soot was kept in the vials for further analysis.

Table. 3 Yield of soot produced from different materials under different condition

S.No.	Material Taken (ml)	Quantity Taken(ml)	Soot with O_2 Supply (mg)	Soot without O_2 Supply (mg)	After Purification (mg)
1	Furnace Oil	40	0.717	0.729	0.660
2	Light Diesel Oil	40	0.361	0.422	0.369

Fig 2. Soot collected from Electrode (2*a*), Detachable Chimney (2*b*) and Canopy (2*c*) of the electrical precipitator unit

(iii) Purification of Carbon Nanotubes

The above synthesized CNTs were purified by Sohxlet extraction method with the help of different solvents like Pet-ether, Acetonitrile, benzene, and acetone. Soot was put into thimble made from Whatman filter paper No. 42 and put into Sohxlet apparatus. The Sohxlet was run about 24 hour. After the solution in the Sohxlet portion become colourless.Thimble was taken out and dried in the oven at 110°C for 5 minute.

(iv) Solubility of CNTs

Weighed amount of 1.5 gram of purified CNTs was taken in round bottom flask. About 200ml of dilute Nitric acid in 1:5 ratio (One part of acid in Five parts of distilled water) was taken in the Round bottom flask and stirred for five minute and refluxed for 24 hours. The presence of brown fumes in the round bottom flask indicates the progress of the reaction and the termination of reaction can be seen from the disappearance of the brown fumes which are due to the liberation of NO_2 gas indicating the completion of oxidation with the attachment of -COOH group on the surface of CNTs. Next step is the digestion of the above oxidized solution on the water bath by adding distilled water so as to remove the excess of acid till the pH become neutral. Finally, about 0.75g of modified CNTs was obtained, showing the approximately 50% oxidation occurred. The addition of polar groups (-COOH,-OH in case of nitration) on the surface of CNTs was Characterized by IR-technique.

III. RESULTS AND DISCUSSION

A. SEM observations

Carbon nanotubes synthesized from F.O. and L.D.O was made water soluble before characterization by Scanning Electron microscopy Technique (Model LEO 435 VP, 120kv). In this technique the sample was made soluble in volatile solvent (Ethanol) and sonicated in Ultra-Sonic bath for 5 minute for uniform dispersion of the solution. After sonication, sample was fed on Aluminum stub with the help of micropipette and fed into sputtering device for gold plating which makes the sample conducting in nature Fig. 3 (*a*) Shows the SEM images of CNTs synthesize from F.O. having diameter ~66nm & length ~1.14u (Magnification of x 33000) and Fig. 3 (*b*) another image of CNTs taken from different portion of the sample Shows the SEM images different dimensions of CNTs synthesized from F.O. having diameter of ~71nm and length of ~ 482nm (Magnification of x 50000) and Fig. 3(*c*) Shows the SEM images of CNTs synthesized from L.D.O. having length of ~120-150nm and length in micrometers (Magnification of × 40000).

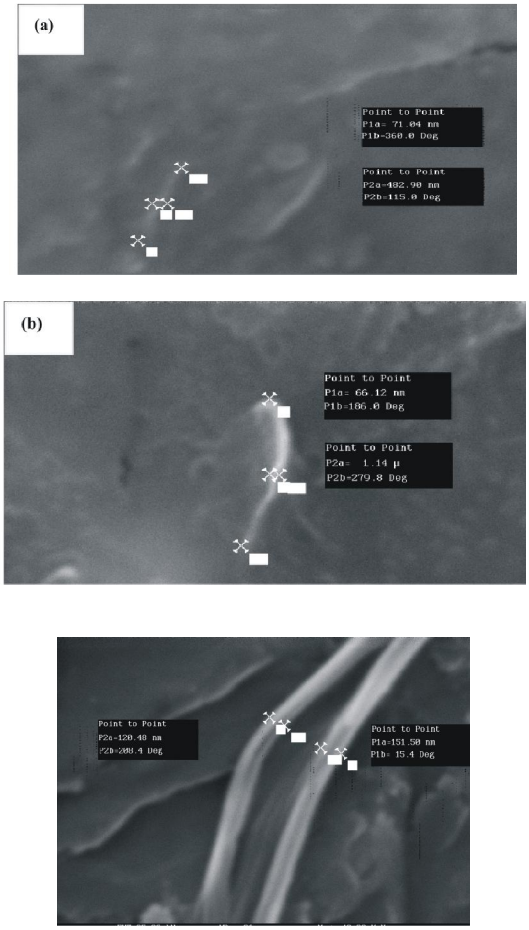

Fig. 3 SEM images of CNTs synthesize from F.O and L.D.O.

B. TEM Observations

The above synthesized CNTs has been characterized by Transmission Electron Microscopy Technique (H7540, 120Kv) to know the internal structure of the CNTs.In this technique the sample was made soluble in volatile solvent

(Ethanol) and sonicated in Ultra-Sonic bath for 5 minute for uniform dispersion of the solution. After sonication, the sample solution was pipette out with micropipette and drop on the TEM grid. Evaporate the solvent; the dried sample was inserted into TEM equipment for further analysis. Fig. 4 (*a*) shows the TEM images of SWCNTs synthesized from L.D.O having outer diameter of ~20nm & inner diameter of ~1-2.5nm (Magnification of × 40000). Fig. 4 (*b*) shows the TEM images of Bundles of SWCNTs synthesized from F.O. having outer diameter of ~15-20 nm and inner diameter of ~ 5-10 nm with length of ~50-80 nm with Nanoparticles of ~50nm diameter (Magnification of × 20000). Fig. 4 (*c*) shows the TEM images of SWCNTs synthesized from F.O. (Magnification × 60000). Fig. 4 (*d*) shows the TEM images of straight and bent structure of SWCNTs synthesized from F.O. having OD ~5-7nm and ID ~2-3 nm and nanorods type Structure (Magnification of × 40000).

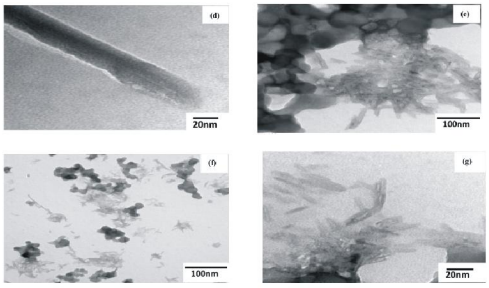

Fig. 4. TEM images of CNTs synthesize from F.O and L.D.O.

C. IR Observations

In order to introduce the solubility in Purified CNTs, nitration of CNTs synthesized from various raw materials was carried out. The attachment of -COOH Group was conformed from the FTIR spectrum (Nicolet, Avatar 320). The dried sample of nitrated-CNTs was taken and pellet was formed with KBr. The FTIR Characteristic of unmodified CNTs shows the absence of peak due to -COOH group at 1700-1725 cm^{-1} as shown in Fig. 5 and FTIR characteristic of modified (nitrated) CNTs shown the presence of peak of -COOH group due to nitration of CNTs in the 1700-1725cm^{-1} as shown in Table 4, 5 as below.

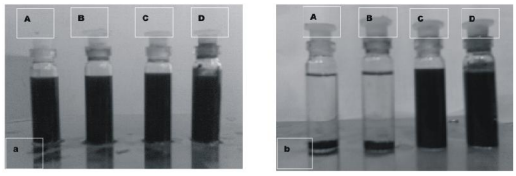

Fig. 5. Dispersion pattern of CNTs in different solvents at 0 Hours Dispersion pattern of CNTs in different solvents after 56 Hours.

Table 4. Absorption spectrum of unmodified CNTs and Nitrated CNTs

Sample	Absorption band due to CO frequency of COOH group	Absorption band due to OH frequency
CNTs	—	—
Nitrated CNTs	1720-1725 cm^{-1}	~ 3400 cm^{-1}

D. Dispersion of CNTs

In general, there have been two different approaches employed to disperse CNTs [21]. Physical methods such as ultrasonication and milling can separate the CNTs from each other. However, this method can damage or disrupt the CNTs. Chemical methods involved covalent and non covalent functionalization have been studied to improve the wettability of the CNTs and to reduce their agglomeration in liquid phase [22-26]. In this investigation 0.5 mg of the Soxhlet purified CNTs was mixed with 10 ml of different solvents like ethanol (*a*), methanol (*b*), acetone (*c*), DI water (*d*) and sonicated for 5 min for uniform dispersion by Ultrasonic cleaner (LOBA life, model 3.5 L 100 H/spl) and stand for 56 hours. From above, the stability of dispersed CNTs in Acetone and DI water will be more as compared to Ethanol, Methanol. The stability of dispersed solution of CNTs in acetone, DI water was tested by keeping the solution at constant different temperature for 5 hours as shown in Table 5 below.

Table 5. Thermal stability of Dispersed solution of CNTs in acetone and DI water.

Sample	40°C	50°C	60°C
Acetone + CNTs	Stable	Stable	Stable
DI water + CNTs	Stable	Stable	Stable

1. O2 Cylinder with flow meter
2. Glass window
3. Combustion chamber
4. Detachable chimney
5. Metallic box
6. Copper electrodes

Sample	40°C	50°C	60°C
Acetone + CNTs	Stable	Stable	Stable
DI water + CNTs	Stable	Stable	Stable

7. DC supply
8. Wires
9. Screw Jack
10. Exhaust with blower
11. Screw Jack for metallic box
12. Connector
13. Fixed chimney with blower

IV. CONCLUSION

Production of Carbon Nanotubes by Modified Chemical Vapour Deposition Method using Electrical precipitator was achieved successfully. Beside Carbon Nanotubes other nanostructures like carbon nanorods, Nano-particles were also observed. Size of Single- walled carbon nanotube obtained from this method was from a minimum of ~4nm to a maximum of 20nm in dimensions. The above method can be used for the mass production of Carbon nanotube from carbon rich wastes using electrical precipitator and help in the reduction of environmental pollutions.

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