

# Experimental Analysis and Power Law Model of Multiwall Carbon Nanotubes Yield on Fe-Co-Ni Ternary Metal Catalyst

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## Abstract—

This article presents the synthesis of multi wall carbon nanotubes (MWCNTs) via chemical vapour deposition (CVD) method. The CVD technique is widely used due to high throughput of CNTs as compared to laser ablation (LA) and arc discharge techniques (ADT). The ternary transition metal catalyst used for CNTs synthesis. The use of ternary metal catalyst provided favorable conditions for high yield and high quality CNTs as against binary of singular metal catalyst. The ternary metal catalyst Fe-Co-Ni with 3%, 5%, 7% and 10% loadings on the CaCO<sub>3</sub> substrate prepared by the wet impregnation method. The active range of temperature for the CNTs synthesis was kept between 600 °C to 750 °C with a temperature step of 50 °C. The acetylene (C<sub>2</sub>H<sub>2</sub>) gas is used as an active carbon source and argon gas as carrier element. The time of deposition kept in all the experimental evaluation is 30 minutes with the mass flow rate of carbon bearing gas at 60 ml/min. The maximum carbon deposits 0.786 gm obtained is with 10% metal catalyst at 700 °C reaction temperature and it decreases thereafter. The experimental results obtained with variable temperature are then modelled with analytical models. The power law model and the third degree polynomial model used to predict the CNTs yield for the variable temperature. The power law model predicts the modelled CNTs mass is well below the 10% error for all the input conditions, whereas the third degree polynomial model deviates considerably from the experimental CNTs deposits. The purity of the carbon deposit is tested with Raman analysis and I<sub>D</sub>/I<sub>G</sub> ratio obtained for as synthesized CNTs is 1.31. The SEM imaging shows bundles of CNTs present after three stage purification.

*Index Terms*— Carbon nanotubes; Catalyst; Synthesis; Scanning electron microscopy.

This paragraph of the first footnote will contain the date on which you submitted your paper for review.

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## I. INTRODUCTION

With the discovery of carbon nanotubes (CNTs) by Iijima in 1991, the CNTs became the focus of study for the worldwide research community. A CNT is a tubular structure with hexagonal rings of carbon atoms in its layer. The diameter of CNT is of the order of nanometer while the length up to a few micrometers [1]. The properties of nano material are far different than the material on micro or macro sizes. The demand of miniaturized product is continuously increasing in every sector of life. CNT has an extraordinary property; very high strength, many times stronger than steel, high electrical conductivity, high thermal conductivity, etc. Due to their excellent properties CNT is used as a reinforcement material for many composites and nano-electronic applications [2]. The potential applications of CNTs include energy storage, energy conversion device, high strength composites, sensors, hydrogen storage, semiconductor device and many more. [3], [4]. The quest to explore the new properties with different material and optimizing the process of CNTs synthesis is continuously ongoing. The various techniques adopted for synthesis of CNTs are chemical vapour deposition, arc discharge, laser ablation, and microwave heating. The chemical vapour deposition most is most popular and efficient method of CNT synthesis due to the less costly apparatus and high yield and very less impurities compared to other methods of CNTs synthesis [5]. The nanotubes developed by CVD technique have more likely to be structurally defective[6]. The yield of CNTs is dependent on a number of factors such as type of catalyst and support material, precursor gases, flow rate and reaction temperature inside the furnace during synthesis[7]. Courea et.al, proposed the synthesis of MWCNTs by CVD using Fe-Co binary catalyst with CaCO<sub>3</sub> support material for mass production of CNT [8]. Ritschel et.al, worked out the CNT synthesis on rhenium catalyst with MgO substrate [9]. Generally it is witnessed during research that at low temperature (600 - 900 °C) CVD yields MWCNTs while high temperature likely to develop SWCNT. The morphology of CNT is dependent on the molecular structure of the precursor. It has been observed that linear hydrocarbon like methane, ethylene, acetylene yield straight hollow CNTs while curled CNTs are formed when hydrocarbon like benzene, xylene are used. The carbon precursor such as acetylene, benzene mostly employed for MWCNT as they stable and active at relatively low temperature are unsuitable

for SWCNTs. For SWCNT high activation energy is required, therefore the very few precursor like methane and carbon monoxide with a fairly high degree of stability can be used. Jiang et.al used the polypropylene as a precursor for the synthesis of MWCNTs [10]. The yield of CNT also depends on the size of metal particles used in catalyst preparation. The catalyst may be used singularly, binary or ternary. Patil et.al, examined that, maximum yield of CNT occurs using binary metal catalyst [11]. Flahaut et.al, investigated the synthesis of SWCNT by binary catalysts using Fe- Ni, Co-Ni and Fe-Co combinations and obtained the SWCNT with 20-50 nm, 10-20 nm and less than 10 nm respectively [10], [12]. Cheng et.al presented a novel floating catalyst approach for large scale SWCNT production by catalytic pyrolysis with a reaction temperature of 1100°C -1200°C with benzene precursor [13].

The present article discusses the effect of reaction temperature on the ternary metal catalyst. The carbon deposition is carried with 600°C to 750°C with a temperature step of 50°C. The three stage purification carried out to clean the carbon deposit. Thereafter quality of CNTs is analyzed with Raman analysis. The surface morphology is observed with the help of SEM imaging. The analytical models are presented and yield of CNTs is predicated and then it validated with experimental results obtained.

## II. EXPERIMENTAL

### *Catalyst preparation:*

Thereafter quality of CNTs is analyzed with Raman analysis. The surface morphology is observed with the help of SEM imaging. The analytical models are presented and yield of CNTs is predicated and then it validated with experimental results obtained.

The mixture as produced was stirred well to form a precipitate catalyst. The catalyst thus formed was first dried in an oven at 120°C for 5 to 6 hours. The catalyst is calcined at various temperatures from 600°C to 750°C in the air for 20 minutes. The as received catalyst is then used for CNT synthesis. The various proportions, 3%, 5%, 7% and 10 % catalysts were produced by the above mentioned method by selecting the mass as per respective molar ratio.

### *CNT synthesis:*

The catalytic chemical vapour deposition method was used CNTs synthesis. The acetylene (C<sub>2</sub>H<sub>2</sub>) was used as a carbon gas while argon (Ar) as an inert gas. The dried catalyst was placed in a quartz boat inside the furnace. A controlled flow of argon at 50 ml/min was maintaining an inert environment throughout the experiment. The catalyst is heated into the furnace at different operating temperature (600 °C to 750 °C) by setting the temperature, time, and supply current on proportional integral derivative (PID) controller. The cracking of acetylene starts around 600°C. Once the reaction temperature attained, C<sub>2</sub>H<sub>2</sub> precursor was supplied at a rate of 60 ml/min for 30 minutes. A decomposition of precursor

liberates hydrogen, undecomposed C<sub>2</sub>H<sub>2</sub> and solid carbon. The gaseous products were then passed through the bubbler before leaving to the environment. The solid carbon was then diffused into the catalyst to produce CNTs by catalytic reaction, whereas some fraction of the solid carbon was accumulated on the tubular reactor wall as an amorphous carbon. The decomposed carbon strikes the surface of the metal particle. The continuous reaction of carbon on metal catalyst starts growing the CNTs on the metal particle. Commonly there are two predominant CNT growth approaches; tip growth and base growth. Depending upon the bond between metal particle and the substrate either of the two is active. The tip growth occurs, when the interactive bond between metal particle and the substrate is weak and the acute angle between them. The base growth occurs when metal-substrate bond is strong which form obtuse angle between them and the growth of the CNT up with catalyst particle imbedded at the bottom [1], [14]. To avoid the oxidation or burn of the CNTs the as deposited carbon deposit was cooled in the argon atmosphere. The deposited CNT with catalyst were the collected from the boat. The carbon yield is calculated as follows [15];

$$\text{Carbon yield} = \frac{\text{Wt. after reaction} - \text{Wt.of catalyst}}{\text{Wt.of catalyst}} \times 100\%$$

The unpurified CNT as received after synthesis contains the amorphous carbon. The unpurified CNTs then soaked in an acid bath (HCl and/or HNO<sub>3</sub>) for 24 hours and ultra sonicated. Well sonicated CNTs then washed with distilled water and then filtered by Whatman filter paper. The purified CNT is then dehydrated in an oven at 110 °C for 2 hours. The figure 1 shows the schematic of the CVD setup used for the CNTs synthesis. Figure 2 (a) shows the actual photograph of catalyst used for the deposition and Figure 2 (b) shows the photograph of the CNTs deposited samples. It is observed that the CNTs deposited on catalyst lead to increase in the volume and thus the catalyst is bulging out of the quartz boat used for deposition. Earlier to deposition the catalyst surface is the flat while after deposition the flower like structure is grown. The enlarged view of the grown deposit is shown in figure 2(c).

### *Scanning electron microscopy (SEM) and Raman Spectroscopy:*

The SEM observations were carried out on JEOL JSM FEG-SEM7600 at IIT Bombay to observe the morphology of CNT produced. The figure the carbon nanotubes synthesized at the 600 °C with 7% seed Fe-Co-Ni catalyst. Figure 3(a), (b) and (c) shows that, the bundles of CNTs average diameter of 50 nm with the range of 24 nm to 100 nm. The length carbon nanotubes range from 1000 nm to few micrometers. It is evident from the image that the significant bundles of carbon nanotubes are observed while the trace of the metal catalyst remain after the purification.

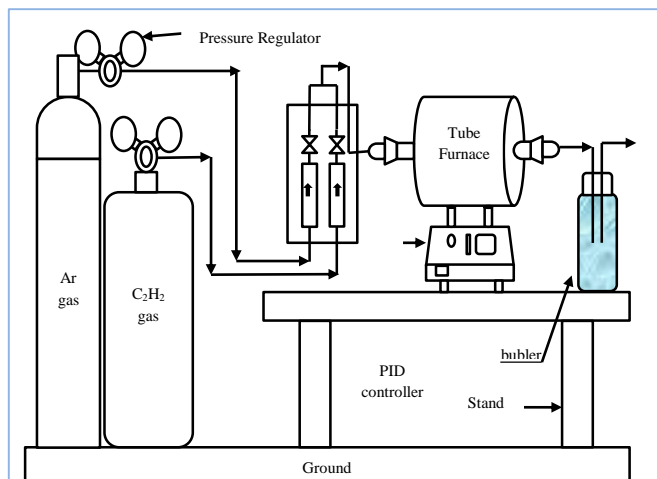


Figure 1. Layout diagram of experimental setup for CNT synthesis by chemical vapour deposition process

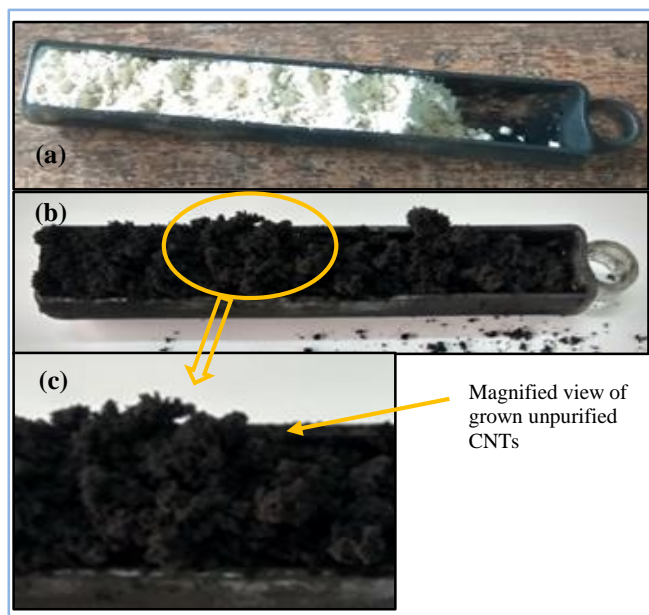


Figure 2. Photographs of catalysts in a quartz boat (a) before synthesis (b) after synthesis by CVD in tube furnace with  $C_2H_2$  carbon precursor and Ar as a carrier gas

The Raman spectroscopy is a used for a qualitative understanding of the CNTs in terms of purity. Raman spectroscopy shows two distinct peaks known as D-band and G-band. The D-band ( $\sim 1350\text{ cm}^{-1}$ ) indicates the defects in the graphitic material while G-Band ( $\sim 1580\text{ cm}^{-1}$ ) represents the graphitic band which represents the purity level. The  $I_D/I_G$  ratio is indicative of the quality of the CNT. Lower  $I_D/I_G$  ratio indicates fewer defect and hence better structural quality. The  $I_D/I_G$  ratio for  $HNO_3$  treated sample obtained as 1.31 while for HCl treated samples as 1.37.

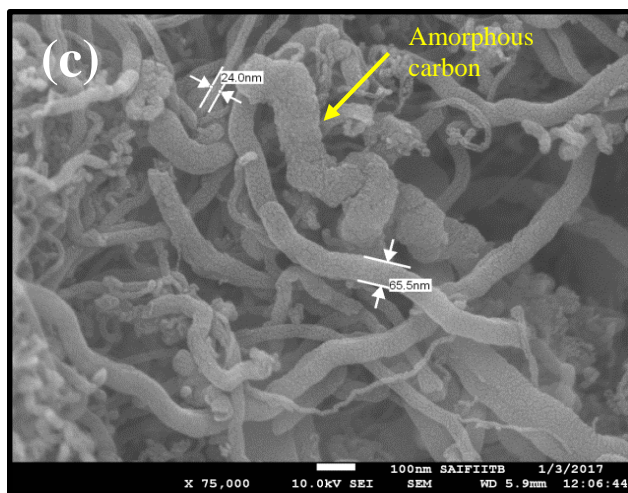
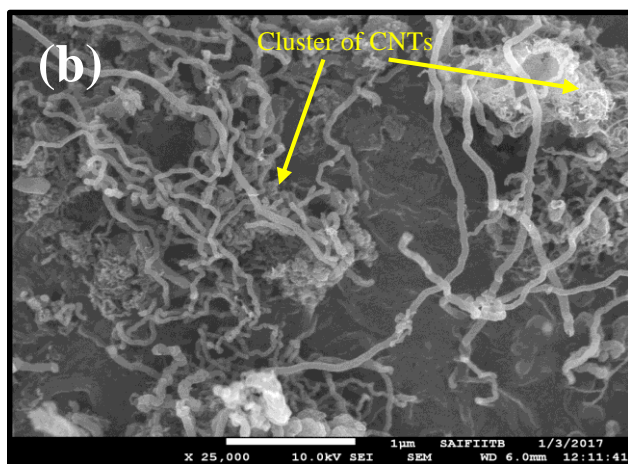


Figure 3. Scanning Electron Microscopy images of MWNTs synthesized by Fe-Co-Ni catalyst at the 7% loading at  $600\text{ }^\circ\text{C}$  (a) - (b) magnification of 25000X (c) magnification of 75000X showing the amorphous carbon layer on the surface of carbon nanotubes.

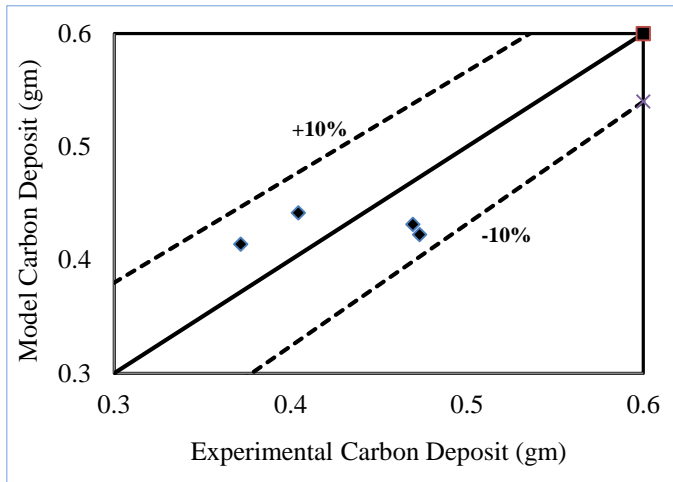


Figure 4. Parity plot for 3% catalyst loading

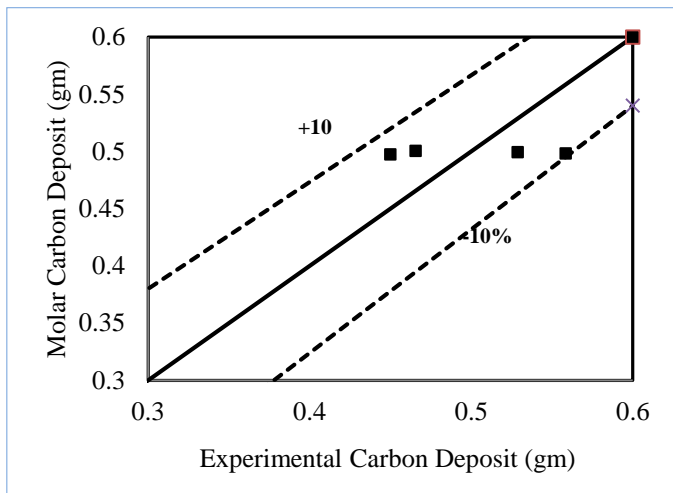


Figure 5. Parity plot for 5% catalyst loading

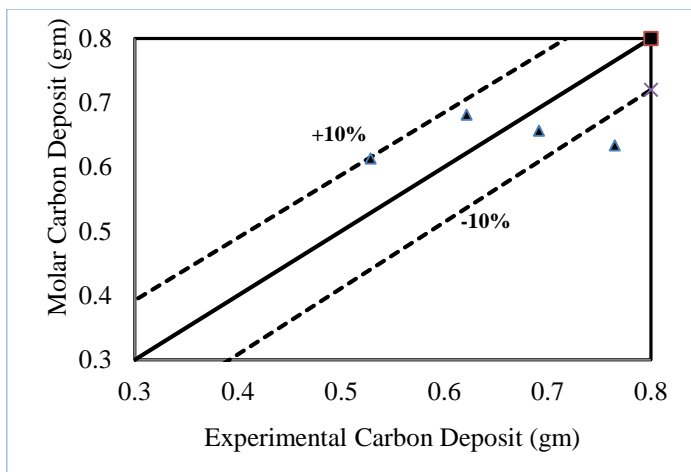


Figure 6. Parity plot for 7% catalyst loading

TABLE I  
CARBON DEPOSIT OBTAINED WITH VARIOUS TERNARY CATALYSTS LOADING FROM 3% TO 10%

T°C	3% Catalyst		5% Catalyst		7% Catalyst		10% Catalyst	
	Exp	Mod	Exp	Mod	Exp	Mod	Exp	Mod
600	0.404	0.442	0.466	0.500	0.622	0.682	0.642	0.717
650	0.469	0.432	0.529	0.499	0.692	0.656	0.766	0.695
700	0.473	0.423	0.559	0.498	0.765	0.634	0.786	0.674
750	0.371	0.414	0.450	0.497	0.529	0.613	0.570	0.656

WHERE; T – TEMPERATURE IN °C

EXP- EXPERIMENTAL VALUE

MOD- MODEL VALUE

TABLE II

THE POWER LAW CONSTANTS OBTAINED FOR THE VARIOUS CATALYST LOADINGS

Constant	3% Catalyst	5% Catalyst	7% Catalyst	10% Catalyst
a	2.817	0.60471	13.962164	9.340221
b	-0.2896	-0.0295778	-0.47207	-0.40126

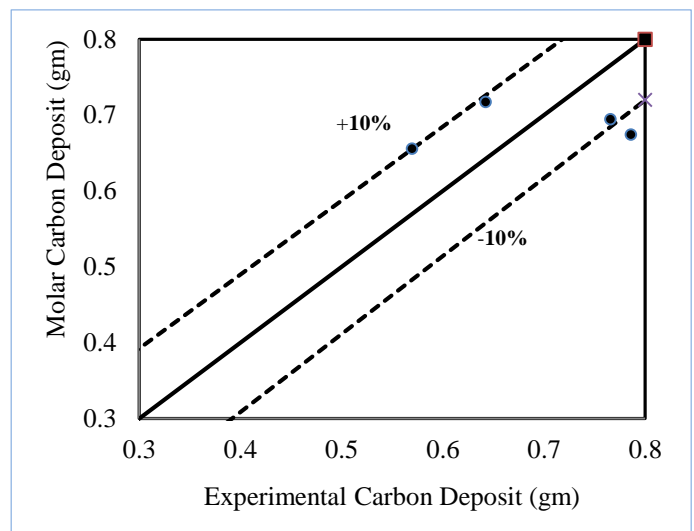


Figure 7. Parity plot for 10% catalyst loading

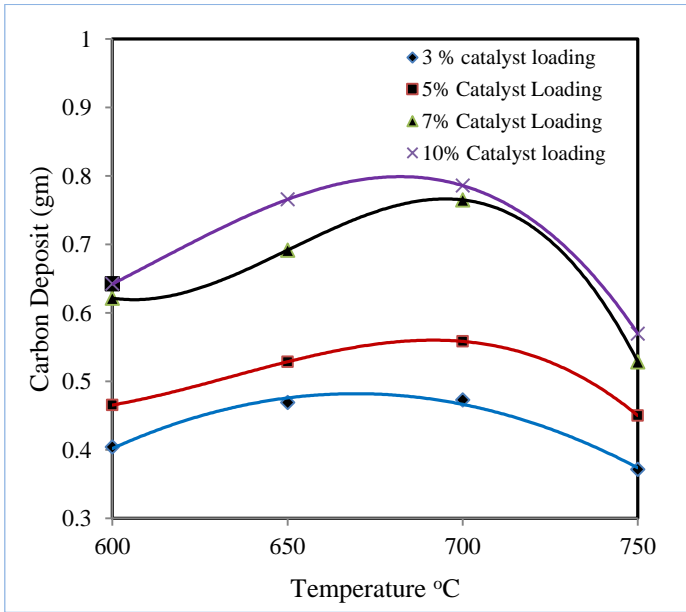


Figure 8. Third order polynomial curve for various catalyst loading

### III. RESULTS AND DISCUSSION

From SEM observations, it is evident that long carbon nanotubes with few microns in size while diameter varies from 24 nm to 100 nm. The carbon nanotubes are agglomerated and the bundles are observed. The SEM image suggests that few impurities also present. Figure 3(c) shows a higher magnification image of a carbon nanotube. It is used to evaluate the diameter and length of carbon nanotubes. The surface morphology of carbon nanotubes is plain and the tubes are entangled with catalyst at the tip or sometime it is entrapped into the tubes. Few branch carbon nanotubes are observed.

The power law model is developed to predict the carbon yield for various temperatures is as follows:

$$Y_{carbon-yield} = aT^b \dots\dots\dots(1)$$

Where;  $Y_{carbon-yield}$  is the model value of the purified CNTs and T is the reaction temperature and 'a' and 'b' are the constants. The experimental CNTs deposit obtained is fitted and the constants are evaluated for the various catalyst loadings. The table-I show the experimental CNTs obtained and the model value of CNTs obtained. Table-II shows the constants for each catalyst loading used for the reaction. The model yield of CNTs and the experimental yield of CNTs is then represented on parity plots. The figure 4, 5, 6 and 7 shows the parity plots for 3%, 5%, 7% and 10% catalyst loading. It is observed that there is good agreement between experimental values and theoretical values of carbon deposits. The most of the results are well within the error band of 10%.

Third order polynomial models developed to predict carbon deposit for various various temperatures at different catalyst loading are as follows:

$$Y_{carbon-yield} = -6E-08T^3 + 0.0001T^2 - 0.0583T + 11.029$$

$$R^2 = 1 \dots\dots\dots(2)$$

$$Y_{carbon-yield} = -1E-07T^3 + 0.0003T^2 - 0.1668T + 35.169$$

$$R^2 = 1 \dots\dots\dots(3)$$

$$Y_{carbon-yield} = -4E-07T^3 + 0.0008T^2 - 0.5284T + 114.2$$

$$R^2 = 1 \dots\dots\dots(4)$$

$$Y_{carbon-yield} = 9E-08T^3 - 0.0002T^2 + 0.195T - 51.421$$

$$R^2 = 1 \dots\dots\dots(5)$$

Where;  $Y_{carbon-yield}$  is the model value of the purified CNTs and T is the reaction temperature

Figure 8 shows the experimental carbon deposit obtained with various catalyst loadings. The third order polynomial curve fitting suggests that the coefficient of regression ( $R^2$ ) for the entire fitted curve is one. However, the model's value deviates significantly as compared to experimental carbon deposit. Thus, it is inappropriate to predict the carbon by the third order polynomial method.

### IV. CONCLUSIONS

In this study, high yield carbon nanotubes synthesized by using ternary catalyst prepared by the wet impregnation method. The synthesis was carried out in a tubular furnace by CVD technique in with variable temperature from 600 °C to 750 °C with different catalyst percentage. The SEM images at different magnification confirms that there are bundles of CNTs produced. It has been also observed that some agglomerated clusters along with some impurities on the CNTs surface. Raman analysis suggests that the better crystalline CNTs obtained after three stage purification process. The maximum yield of carbon deposit obtained at 700 °C for 10% catalyst loading. The carbon deposit obtained with 600°C is 0.642 gm while to that at the 700°C is 0.786 gm and then it reduces to 0.570 gm. It is observed that the carbon deposition for optimum temperature of 700°C at 3 % catalyst loading is 0.473 gm, for 5 % catalyst loading is 0.559 gm, for 7% catalyst loading is 0.765 gm and 10% catalyst loading is 0.786 gm. It is observed that the carbon deposit increases with increasing percentage of catalyst loading. The power law model provides better fits as compared to the third order polynomial with the experimental carbon deposits. It is witnessed that the power law model confirms the most of the experimental results are in less than 10% error band while third order polynomial fit do not yield better results though the coefficient of regression in all cases is one.

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