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Chapter

Carbon Nanotube from Unconventional Precursor-Optimization of Synthesis Parameters

Karthikeyan Srinivasan,
Angulakshmi Sathyamoorthi Venkatasamy
and Mageswari Subramanian

Abstract

Carbon is a versatile element of distinctive properties and has been described as the key element of living substance. Carbon nanostructures have attracted lots of interest, due their prominent properties. Spray pyrolysis method is adopted for synthesis of carbon nanotubes (CNTs). Contrast to any petroleum product, there is no fear of its ultimate shortage as it is a renewable source and can be obtained easily by cultivating as much quantity as required. Synthesize well crystalline multiwalled carbon nanotubes (MWNTs) from unconventional precursor of methyl ester of *Helianthus annuus* oil by optimize the parameters such as reaction temperature, catalyst composition and feed rate of carbon precursor in order to obtain good yield with desirable morphology.

Keywords: carbon nanotube, spray pyrolysis, optimization

1. Introduction

Carbon nanotube (CNTs) can be considered to be a potential candidate of the forthcoming century due to its extraordinary properties [1–5]. In the year 1985, an important breakthrough in carbon research was realized by the work of Kroto et al. [6], which resulted in the discovery of a large family of all carbon molecules, called 'fullerenes'. Discovery of CNTs is attributed to Iijima [7] as the first scientist who was looking for new carbon structures, in the deposit formed on graphite cathode surfaces during the electric-arc evaporation (or discharge) that is commonly employed to produce fullerene soot. The most important methods of synthesis of CNTs are electric arc discharge, laser evaporation and chemical vapor deposition methods (CVD) [8, 9]. Arc-discharge method is the easiest and most common method of producing CNTs. Ando has carried out the arc-discharge evaporation of pure graphite rods in various kinds of ambient gases (He, Ar and CH_4) since CNTs were first discovered [10]. Laser technique is not economically advantageous because the process involves high purity graphite rods, high power lasers and low yield of CNTs. The CVD is another popular method for producing CNTs in which

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hydrocarbon vapor is thermally decomposed in the presence of a catalyst [11]. Several researchers describe the method for synthesizing CNTs in large scale from petroleum-based precursors such as benzene, xylene and hexane. In current, CNTs synthesized from unconventional precursors such as *camphor*, *eucalyptus* oil, *Pine* oil, *Citrus limonum* oil and *Brassica juncea* oil [12–16]. The main objective is to explore whether pyrolysis of natural carbon precursor of methyl ester of *Helianthus annuus* oil over Fe, Co and Mo catalysts supported on silica can be usefully employed for synthesis of good quality carbon nanotubes at low temperature conditions using spray pyrolysis method. Response surface methodology-based Box-Behnken design was employed in order to optimize the process parameters for synthesis of MWNTs.

2. Experimental methods

The spray pyrolysis method is similar to CVD method and the only difference with CVD is the vaporization and pyrolysis of carbon source occurs simultaneously in spray pyrolysis whereas these processes occur independently in two steps in CVD method. The Fe-Co-Mo catalysts supported on silica (0.5 g) was placed in the quartz boat and then inserted into the center of a quartz tube placed in the electrical heating furnace. The carrier gas nitrogen was flushed out before switch on the reaction furnace to remove air and create nitrogen atmosphere. The temperature was raised from room temperature up to the desired CNTs growing temperature. Subsequently, the carbon precursor methyl ester of *Helianthus annuus* oil was introduced into the quartz tube through spray nozzle at the rate of 20 mL/h. The deposition time lasted for 60 min at the chosen temperature. Nitrogen flow was maintained until the furnace was cooled to room temperature. The product collected was then weighed and stored in air tight container for further characterizations.

3. Results and discussion

The morphology of MWNTs synthesized at 550, 650 and 750°C using methyl ester of *Helianthus annuus* oil as a precursor is studied. The MWNTs grown at 550°C are mostly tangled with diameter in the range of 22–48 nm as shown in scanning electron microscope (SEM) image in **Figure 1a**. A nice growth of web like structure of MWNTs with diameter of 20–45 nm is observed at 650°C (**Figure 1b**). The SEM image of MWNTs synthesized at 750°C is shown in **Figure 1c**. The MWNTs with diameter of 75–100 nm is observed at 750°C (**Figure 1c**). The results are in good agreement with Li et al. [17].

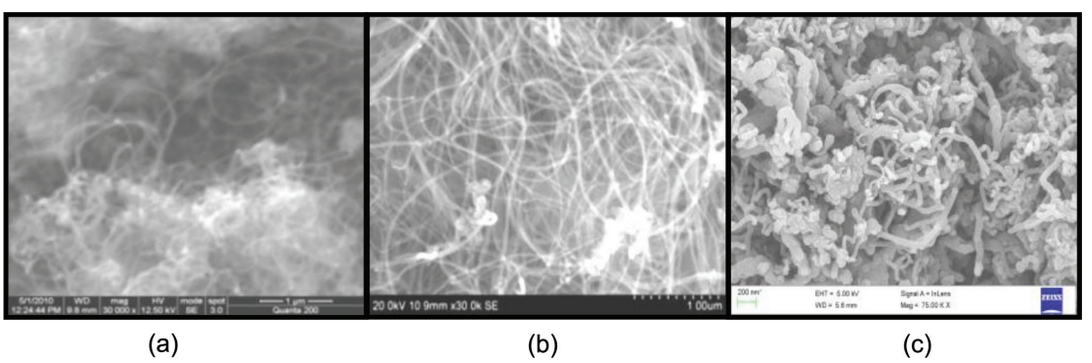


Figure 1.
(a–c) SEM images of MWNTS grown at 550, 650 and 750°C.

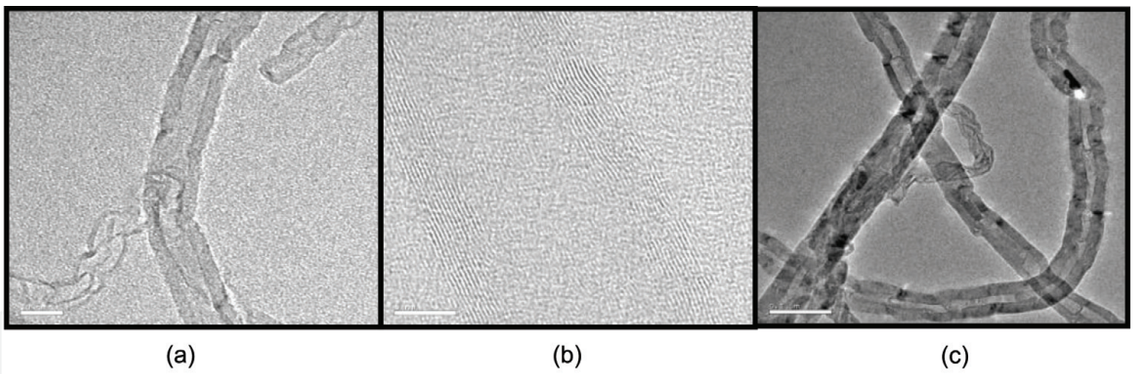


Figure 2.
(a–c) HRTEM images of MWNTS grown at 550, 650 and 750°C.

High resolution transmission electron microscope (HRTEM) recorded for the MWNTs synthesized at 550°C is shown in **Figure 2a**. HRTEM analysis shows a rope like tubular structure of MWNTs grown on the surface of chosen catalyst clusters. The HRTEM image (**Figure 2b**) clearly shows well-graphitized layers of MWNTs with inner and outer diameter in the range of 8–13 and 16–24 nm respectively, grown from catalytic decomposition of methyl ester of *Helianthus annuus* oil at 650° C. The selectivity towards MWNTs formation is observed in the best optimized condition of the present study at 650°C. The carbon deposit obtained at 750°C is found to be consisting of MWNTs of diameter 65–75 nm (**Figure 2c**).

The crystalline nature of the sample synthesized is studied using Raman spectrum and it is depicted in **Figure 3a**. In this study, the D and G peaks are observed at about 1370 and 1563 cm^{-1} for the samples synthesized at 550°C. The intensity ratio value of the G and D band, i.e., I_G/I_D value 0.71 provides important information relative to the purity and structural quality of the nanotubes that the MWNTs are made up of defective layers. D and G peaks are observed at about 1335 and 1545 cm^{-1} for the samples prepared at 650°C as shown in **Figure 3b**. The I_G/I_D ratio calculated from the peak area is 1.8. A further increase in temperature from 650 to 750° C results in a rapid drop in the I_G/I_D ratio to one (**Figure 3c**). Among the chosen experimental temperatures, the highest I_G/I_D ratio is observed for 650°C. This indicates the highest quality and purity of samples formed at 650°C. The absence of peaks below 300 cm^{-1} in Raman spectrum of the carbon deposits obtained in this study reveals the absence of single walled carbon nanotubes (SWNTs) [18]. The catalytic vapor deposition of methyl ester of *Helianthus annuus* oil over Fe catalyst supported on silica at 650°C results in a considerable quality of carbon nanotubes deposit (**Figure 4a**). However, as-grown CNTs are diameter in the range of 60–90 nm with poor structure and contains abundant amount of amorphous carbon. In **Figure 4b** MWNTs grown is in the range of diameter of 28–70 nm using Fe-Co catalyst.

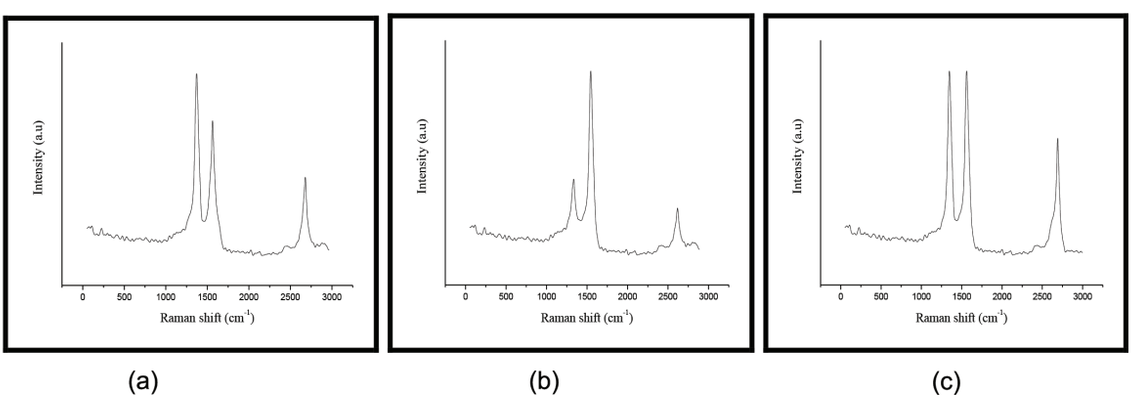


Figure 3.
(a–c) Raman spectrum of MWNTS grown at 550, 650 and 750°C.

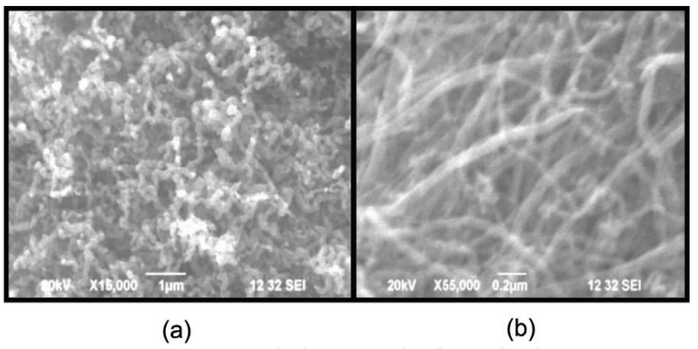


Figure 4.
(a and b) SEM images of MWNTS grown using Fe, Fe-Co catalyst supported on silica.

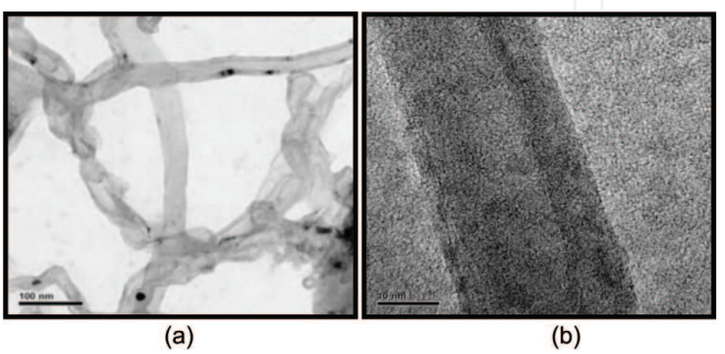


Figure 5.
(a and b) HRTEM images of MWNTS grown using Fe, Fe-Co catalyst supported on silica.

The HRTEM image (**Figure 5a**) of MWNTs synthesized over Fe catalyst supported on silica shows the poor crystallization of walls and a layer of amorphous carbon on outer surface of the tube. The outer diameter of MWNTs are around 40–60 nm respectively. The tubular structure of CNTs (**Figure 5b**) grown over Fe-Co catalysts supported on silica are MWNTs with thick in size and covered with layer of amorphous carbon. The inner and the outer diameter of the MWNTs are 15 and 20–30 nm, respectively.

The Raman spectrum recorded for the MWNTs obtained over Fe catalysts supported on silica where shown in **Figure 6a**. The spectrum shows G-band at 1554 cm^{-1} and a peak at 1339 cm^{-1} corresponds to D-band. The I_G/I_D value of 0.65

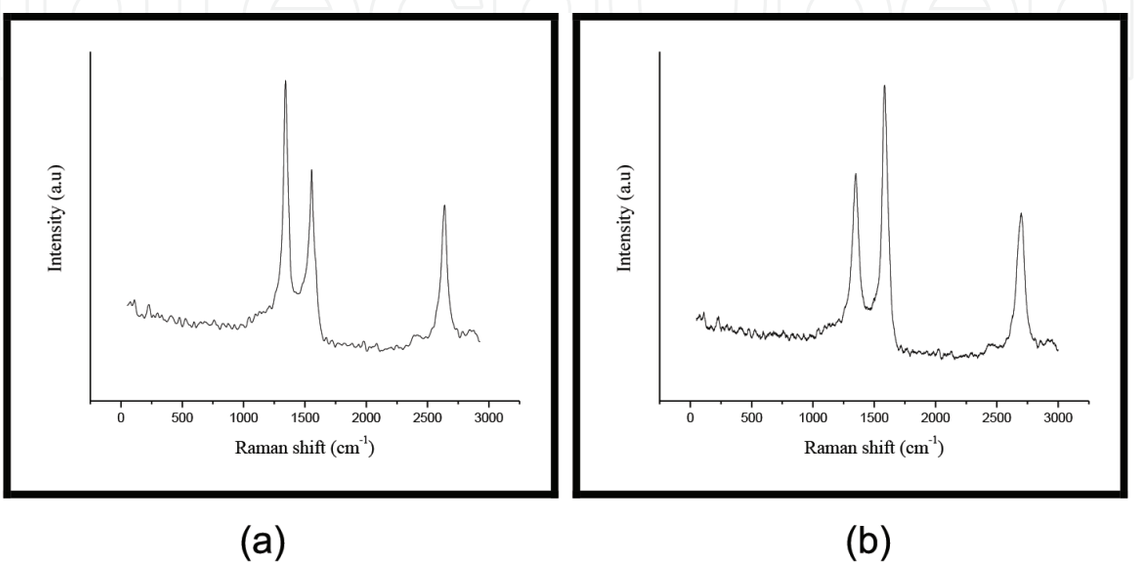


Figure 6.
(a and b) Raman spectrum of MWNTS grown using Fe, Fe-Co catalyst supported on silica.

evidences the imperfection in graphitization of MWNTs layers. Using Fe-Co catalyst spectrum show G-band at 1584 cm^{-1} and a peak at 1349 cm^{-1} corresponds to D-band. The value of I_G/I_D for the MWNTs grown on Fe-Co catalysts supported on silica is 1.1.

SEM image of MWNTs formed at the flow rate of 10 mL/h are of 50–80 nm in diameter with spaghetti like structure (**Figure 7a**). The increase in precursor flow rate to 30 mL per hour has resulted MWNTs are thick in size with diameter in the range of 40–70 nm as shown in **Figure 7b**. This may be due to higher rate of decomposition of precursor [19].

Methyl ester of *Helianthus annuus* oil at a flow rate of 10 mL/h produced MWNTs of poor quality in graphitization is evident from HRTEM image shown in **Figure 8a**. **Figure 8b** shows the defective structure of MWNTs synthesized using precursor flow rate of 30 mL/h. The tube diameter is relatively thicker in the range of 40–60 nm with amorphous carbon at the outer wall of the tube [20]. The G-band is observed at 1576 cm^{-1} and D-band is observed at 1351 cm^{-1} for the precursor flow rate of 10 mL is shown in **Figure 9a**. The I_G/I_D ratio calculated is 1.1. This indicated that the MWNTs formed are of moderate graphitization. In the flow rate



Figure 7.
(a and b) SEM images of MWNTS grown at the flow rate of 10 and 30 mL.

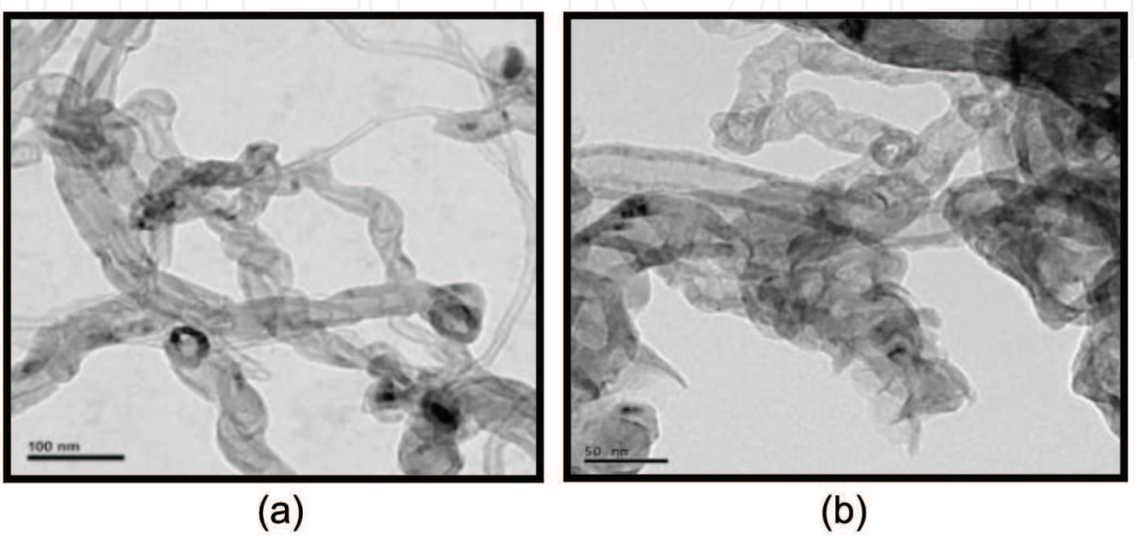


Figure 8.
(a and b) HRTEM images of MWNTS grown at the flow rate of 10 and 30 mL.

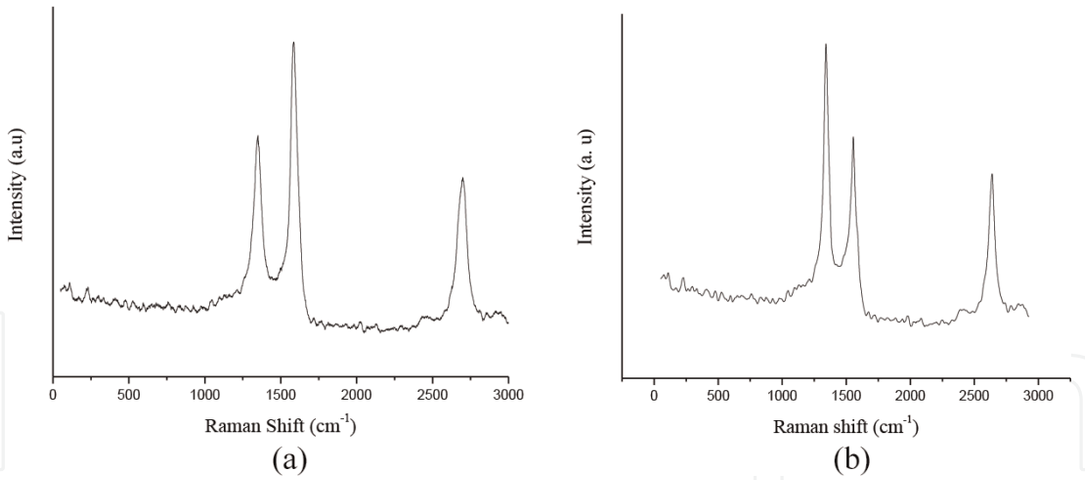


Figure 9.
(a and b) Raman spectrum of MWNTS grown at the flow rate of 10 and 30 mL.

of 30 mL/h appearance of D and G peaks at 1341 and 1554 cm^{-1}, respectively, with I_G/I_D value of 0.65 indicates the formation of MWNTs with defective graphitic layers (**Figure 9b**).

4. Box-Behnken design and data analysis for the yield percentage of MWNTs

Reaction temperature (°C), composition of catalyst (g) and feed rate of precursor (mL) were considered as independent process variables, and their individual and interactive effects on the yield percentage (as a response) of MWNTs were investigated using the Box-Behnken design approach. Syntheses of MWNTs experiments are conducted according to the design matrix and the corresponding results are tabulated in **Table 1**. The quadratic equation for predicting the optimum point was obtained according to the Box-Behnken design and input variables and then the empirical relationship between the response and the independent variables in the coded units for the yield percentage of MWNTs from the chosen precursor methyl

Run	Factor 1	Factor 2	Factor 3	Response 1
	A: reaction temperature (°C)	B: catalyst composition (g)	C: feed rate of precursor (mL)	Yield (%)
1	550	0.5	10	15
2	650	0.75	30	60
3	750	0.75	20	55
4	550	0.5	30	35
5	650	0.5	20	78
6	650	0.75	10	40
7	650	0.5	20	75
8	650	0.5	20	76
9	750	0.5	10	42
10	650	0.5	20	72

Run	Factor 1	Factor 2	Factor 3	Response 1
	A: reaction temperature (°C)	B: catalyst composition (g)	C: feed rate of precursor (mL)	Yield (%)
11	650	0.5	20	71
12	550	0.75	20	20
13	550	0.25	20	10
14	750	0.25	20	50
15	650	0.25	10	37
16	650	0.25	30	50
17	750	0.5	30	45

Table 1.
Box-Behnken design matrix and corresponding response for methyl ester of Helianthus annuus oil.

ester of *Helianthus annuus* oil were presented on the basis of the experimental results as follows:

$$Y = 74.4 + 14A + 3.5B + 7C - 1.25AB - 4.25AC + 1.75BC - 26.575A2 - 14.075B2 - 13.575C2 \quad (1)$$

5. Analysis of variance (ANOVA)

The statistical significance of the quadratic model was evaluated by the ANOVA. The ANOVA results for the quadratic equation summarized in **Table 2** for the yield percentage of MWNTs from the chosen precursor of methyl ester of *Helianthus annuus* oil.

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F
Model	7195.064706	9	799.4516	24.68532	<0.0001
A—temperature	1568	1	1568	48.41641	0.0002
B—catalyst composition	98	1	98	3.026026	0.1255
C—feed rate of carbon precursor	392	1	392	12.1041	0.0103
AB	6.25	1	6.25	0.192986	0.6737
AC	72.25	1	72.25	2.230922	0.1789
BC	12.25	1	12.25	0.378253	0.5580
A^2	2973.602632	1	2973.603	91.81834	<0.0001
B^2	834.1289474	1	834.1289	25.75608	0.0014
C^2	775.9184211	1	775.9184	23.95866	0.0018
Residual	226.7	7	32.38571		
Lack of fit	193.5	3	64.5	7.771084	0.0382
Pure error	33.2	4	8.3		
Cor total	7421.764706	16			

Table 2.
ANOVA for RSM parameters fitted to a polynomial equation for methyl ester of Helianthus annuus oil.

ANOVA indicates that the actual relationship between the response and significant variables represented by the above quadratic equations are accurate. The significance of the coefficient term is determined by the values of F and p and the larger the F-value and smaller the value of p, the more significant is the co-efficient term. The p is lower than 0.05, suggesting the model to be statistically significant. For the present synthesis process, the ANOVA results indicated the Model F value was 24.68 for methyl ester of *Helianthus annuus* oil, suggesting only 0.01% chance of a "Model F value" so large could occur due to noise and most of the variation in the response could be explained by the regression equation and the model was significant.

6. Three dimensional response surface plots

To study the interaction between all three variables, three dimensional surfaces and two dimensional contours were plotted by keeping one variable constant at central level and the other two varying within the experimental ranges.

In **Figure 10**, the response surface and contour plots were developed for methyl ester of *Helianthus annuus* oil as a function of temperature and catalyst composition while feed rate of precursor was kept constant as 20 mL. In this experiment, **Figure 10** indicates that the response is sensitive to the reaction temperature. The yield percentage of MWNTs increases with increase in temperature and attains peak at optimum temperature (650°C) for methyl ester of *Helianthus annuus* oil. Low yield obtained at 550 and 750°C is possibly due to the fact that the catalyst could not be activated and high rate of pyrolysis followed by encapsulation of catalyst respectively. High yield obtained at 650°C in this study is attributed to almost equal rate of pyrolysis of precursor and CNTs growth. The highest yield obtained at high temperature (750°C) was probably due to condition may be attributed to thermal energy of precursor vapors which favors high rate of cracking on the catalyst [21].

The response surface and contour plots were developed for methyl ester of *Helianthus annuus* oil using the variables temperature and feed rate of carbon precursor by keeping catalyst composition (0.5 g) as constant. As can be understood from **Figure 11** increase of precursor feed rate from 10 to 20 mL increases the yield percentage of MWNTs. Further increase of flow rate to 30 mL leads to reduction in the yield of MWNTs.

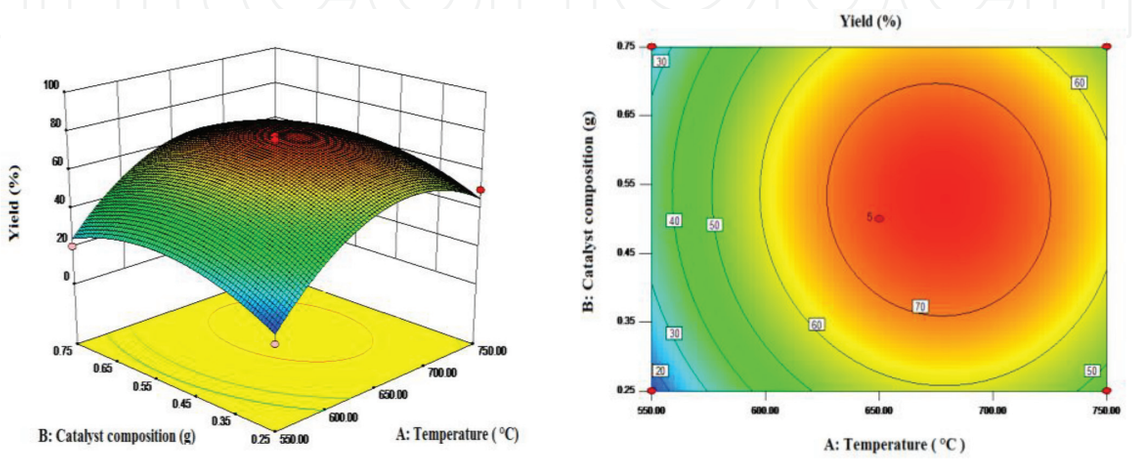


Figure 10.
Response surface and contour plots for the yield of MWNTs as the function of temperature and catalyst composition.

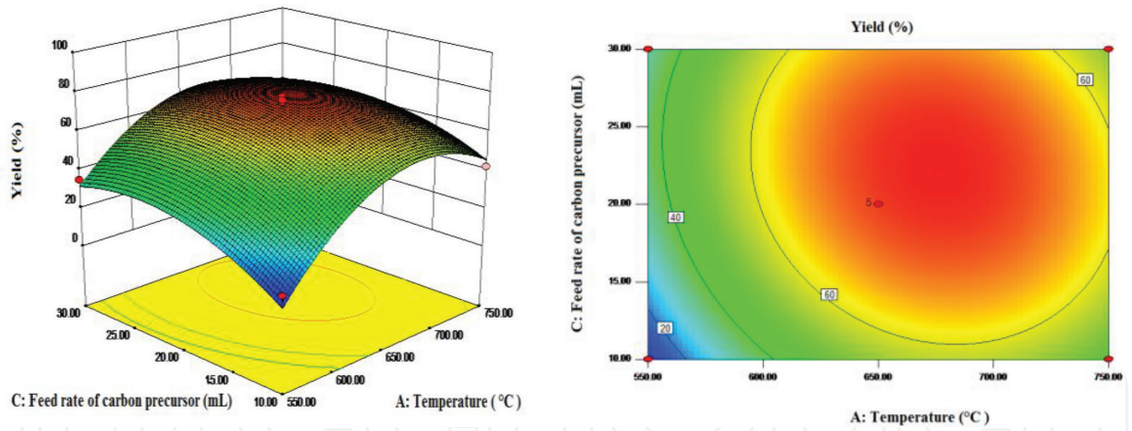


Figure 11.
Response surface and contour plots for the yield of MWNTs as the function of temperature and feed rate of precursor.

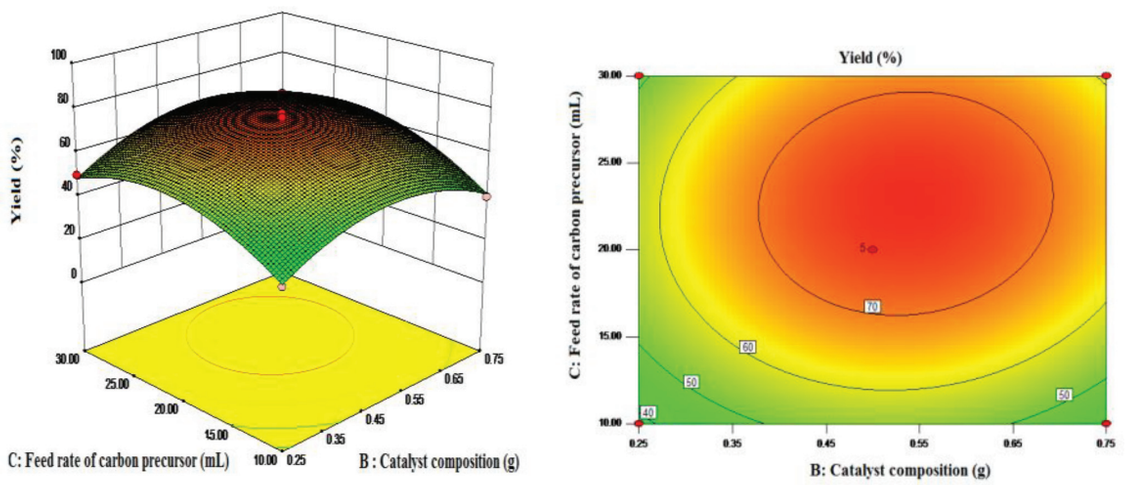


Figure 12.
Response surface and contour plots for the yield of MWNTs as the function of catalyst composition and feed rate of precursor.

The interactive effect of the feed rate of carbon precursor and catalyst composition on the percentage of yield of MWNTs at constant temperature of 650°C is illustrated in **Figure 12**. Piedigrosso et al. reported that amount of nanotubes formed over silica supported Co catalyst depends on content of Co [22]. A strong relationship between the catalyst and yield of MWNTs deposit was observed in this study. It is seen from **Figure 12** that the yield percentage of MWNTs increases with increasing catalyst composition attains maximum and starts decreases. Increase in yield at optimum condition may be due to synergistic advantages of high catalytic decomposition, effectiveness in growing CNTs and promotional character of Fe, Co and Mo respectively.

7. Optimization of process variables

The numerical optimization was used to optimize the yield percentage of MWNTs from methyl ester of *Helianthus annuus* oil, and optimum values are presented in **Table 3**. A desirability value of 1.0 was obtained after optimizing the process parameters. The experimental values of yield percentage of MWNTs grown from methyl ester of *Helianthus annuus* oil under the optimal conditions closely

Variables	Optimum values
Reaction temperature (°C)	674.29
Catalyst composition (g)	0.53
Feed rate of precursor (mL)	22.28
Yield percentage (predicted)	77.11
Yield percentage (actual)	78

Table 3.
Obtained optimum values of the process variables and responses.

agree with the predicted values (**Table 3**) obtained from the model and validate the findings of response surface optimization.

8. Conclusion

The present work reveals the natural precursor of methyl ester of *Helianthus annuus* oil as carbon precursor for synthesis of carbon nanotubes. Utilization of Fe, Co and Mo catalysts supported on silica for synthesis of well-graphitized carbon nanotubes with high yield at low temperature conditions using spray pyrolysis method is successfully reported. Optimization studies by applying Response Surface Methodology, a Box-Behnken design for optimizing the process parameters such as reaction temperature, catalyst composition and feed rate of precursor clearly indicated the efficiency of yield percentage of MWNTs.

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