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OPTIMIZATION OF REACTION CONDITION FOR PRODUCTION OF CARBON NANOTUBES USING CONTINUOUS ROTARY REACTOR SYSTEM

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ABSTRACT

Carbon nanotubes (CNTs) is discovered in decades ago, however the commercial applications of CNTs have not been fully realized yet. The reasons lie in two interrelated aspects: the difficulty in mass production of CNTs and hence the high production cost. Previously, a horizontal rotary reactor was successfully developed for the continuous and large-scale production of CNTs *via* catalytic chemical vapor deposition of methane. In this study, the independent process parameters, i.e. reaction temperature, methane partial pressure, catalyst feed rate and catalyst residence time, were investigated using response surface methodology approach, which focused on investigation of the effects of process parameters on the carbon content, and were optimized simultaneously using numerical optimization method based on the experimental results obtained. The optimum operating condition obtained was a reaction temperature of 833 °C, reaction time of 165 minutes, methane partial pressure of 0.54 atm and catalyst amount of 260 mg/min. The carbon deposits synthesized under optimum reaction condition had high carbon content of 95.40 wt%, equivalent to carbon yield of 2073.9%. The carbon deposits were solely CNTs with diameter distribution of 10.18±1.02 nm and ID/IG ratio of 1.262. The carbon deposition rate of approximately 323 gCNTs/hr based on the catalyst feeding rate of 260 g/min was achieved.

Keywords: Carbon nanotubes; Catalytic chemical vapor deposition; Continuous production; Rotary reactor system

INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991[1], CNTs have attracted muchattention from the research community credited to their superior electronic,

mechanical and chemical properties. These properties of CNTs render them to have various potential applications which include hydrogen storage [2], catalyst support [3], selective adsorption agents[4], composite materials [5], and field emission devices [6]. However, the applied researches of CNTs in various applications have not been fully realized yet. The reasons lie in two aspects: the difficulty in mass production of CNTs and hence the high production cost. The imbalance in market demand-supply chain that causes the selling price of CNTs remains high and this slows down the growth of CNT applied products in the market. The common strategies for synthesizing CNTs can be categorized into the following groups: arc- discharge [7], laser ablation [8], and catalytic chemical vapor deposition (CCVD) methods [9]. Arc- discharge and laser ablation methods require high temperatures, i.e., above 1000 °C, to synthesize CNTs, both processes enable the production of high quality CNTs. Up to now, CCVD is known to be the promising way for large-scale and cost effective production of CNTs as compared to aforementioned processes. CCVD can be conducted in either batch or continuous mode. In our previous report, a continuous processing method, namely horizontally oriented rotary reactor system, was successfully developed for mass production of CNTs [10]. However, further improvement of process through optimizing the reaction conditions is required to increase the production capacity and also enhance the quality of the CNTs synthesized.

EXPERIMENTAL

CNTs were synthesized via CCVD over bimetallic Co-Mo/MgO catalyst which had been tested earlier to be effective in the batch-wise synthesis [11,12]. Meanwhile, methane was used as the carbon precursor for the synthesis of CNTs. The bimetallic 10Co-20Mo/70MgO catalyst was prepared by sol-gel method. The calculated amount of catalyst precursors: $Co(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were first dissolved in distilled water. Then, citric acid was added to the homogenous mixture as a foaming agent to create catalyst with porous structure. The homogenous mixture was stirred and heated at 90 °C for an hour and the resulted high viscous sol was then baked overnight at 120 °C. The foamy catalyst was grinded into fine powder and calcined in air at 700 °C for 2 hours.

In this study, four process parameters of the horizontally oriented rotary reactor system (Figure 1), namely reaction temperature (A), catalyst residence time (B), methane partial pressure (C) and catalyst feed rate (D), were investigated using central composite design (CCD) of response surface methodology (RSM) approach. These parameters were selected because they were reported to have significant influence either on the carbon yield or the morphology of the synthesized CNTs. The range for each process parameter is summarized in Table 1.

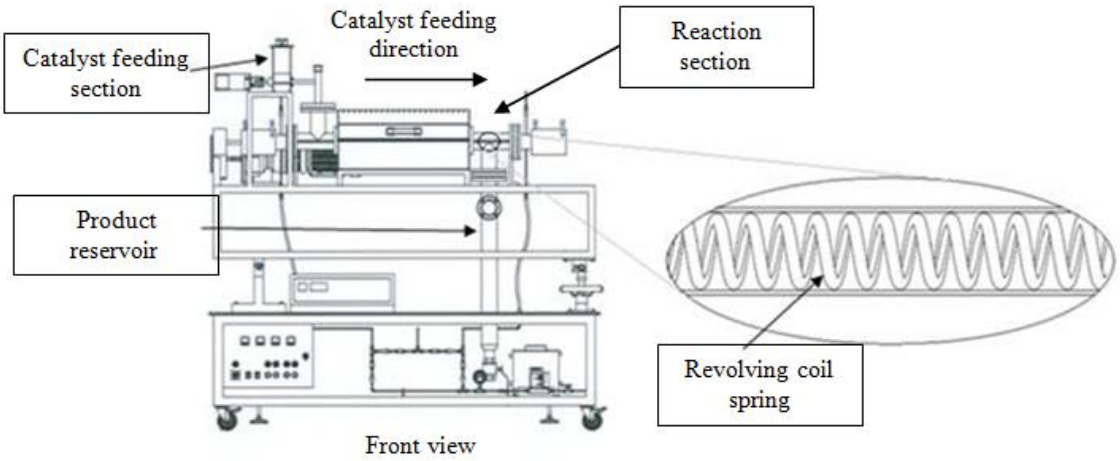

Figure 1: Schematic diagram showing the horizontal oriented rotary reactor system. Inset: the design of the reaction section [10]

Table 1: Process parameters for CCVD process study in horizontal oriented rotary reactor system

Parameter	Name	Unit	Low	High
A	Reaction temperature	[^{O}C]	600	1000
B	Catalyst residence time	[minutes]	60	180
C	Methane partial pressure	[atm]	0.2	1.0
D	Catalyst feed rate	[mg/min]	100	500

The present process study focused on investigation of the effect of process parameters on the carbon content of the as-produced carbon deposits. A total number of 30 runs were conducted for studying the individual influences of each process parameter and the possible interaction effects on carbon content (response Y). The responses from the resulting 30 runs are presented in Table 2. The results were analyzed using ANOVA which was performed by Design Expert Software. The optimum reaction condition for the high yield synthesis of CNTs was simulated using the numerical optimization method (Constrained Nonlimear Optimization Algorithms) programmed in the Design Expert Software (version 6.0.6, State-Ease, Inc,. Minneapolis, MN).

Table 2: Experimental matrix of RSM-CCD for CCVD process study in horizontal oriented rotary reactor

Process Parameter					Response
Run No.	A: Reaction temperature [°C]	B: Catalyst residence time [minutes]	C: Methane partial pressure [atm]	D: Catalyst feed rate [mg/min]	Y Carbon content [wt%]
1	600	120	0.6	300	45.53
2	700	90	0.4	200	73.65
3	800	120	0.6	300	89.53
4	900	150	0.4	200	85.49
5	800	60	0.6	300	80.96
6	800	120	0.6	500	87.59
7	800	120	0.6	300	90.18
8	900	150	0.4	400	84.32
9	900	150	0.8	400	85.87
10	900	150	0.8	200	87.48
11	700	90	0.8	200	78.99
12	700	150	0.4	200	87.66
13	800	180	0.6	300	95.13
14	900	90	0.8	400	79.06
15	800	120	0.2	300	66.75
16	700	150	0.8	200	88.96
17	700	150	0.4	400	84.37
18	800	120	0.6	300	89.38
19	700	90	0.8	400	76.53
20	900	90	0.4	200	78.60
21	800	120	0.6	100	93.84
22	700	90	0.4	400	70.58
23	800	120	0.6	300	89.92
24	700	150	0.8	400	86.55
25	800	120	0.6	300	90.14
26	1000	120	0.6	300	77.05
27	900	90	0.4	400	75.94
28	900	90	0.8	200	82.17
29	800	120	1.0	300	90.81
30	800	120	0.6	300	89.80

The carbon samples were characterized using transmission electron microscope (TEM) (Philips, model CM12), thermogravimetric analyzer (TGA) (TA Instrument, SDTQ600) and Raman spectroscopy (Renishaw, inVia Raman microscope) as to study the morphology, the quality and the purity of the produced CNTs. The yield of carbon produced over the catalyst in the rotary reactor, as defined below, was determined from

TGA. The data of carbon yield can be easily obtained from the thermogravimetric analysis of the as-synthesized CNTs through thermal oxidation. The wt% loss by carbon oxidation and wt% of residue after oxidation corresponds to the carbon content and the catalyst content, respectively.

$$\text{Carbon yield} = \frac{\%\ \text{weight loss by carbon oxidation}}{\%\ \text{of residue after oxidation}} \text{x} 100\%$$

RESULTS AND DISCUSSION

Numerous models including mean, linear, two factor interaction (2FI), quadratic and cubic were fitted by DoE to the carbon content (response Y) and the result is presented in Table 3. From the analysis, one can note that the models of linear, quadratic and cubic were significant model as the probability index, "Prob> F" values calculated were below 0.05. The "Prob> F" value represents the probability of error that is involved in accepting the observed results[13]. Further examination of the coefficient of determination (R^2) indicates that the linear model had an unacceptable R^2 value, *i.e.* 0.3510. Thus, the linear model was eliminated from consideration. Meanwhile, the cubic model is aliased because the full CCD matrix does not provide sufficient unique design points to determine all the terms in the cubic model, so this model was not selected although it had the highest R^2 value. The quadratic model was chosen considering: (i) the "Prob> F" value was low, *i.e.* 0.0003 and (ii) the R^2 value of 0.8310 was of an acceptable level.

Table 3: Sequential model sum of squares for response Y

Source	Sum of Squares	Mean Square	F Value	Prob > F	R^2	Recommendation
Mean	205800	205800				
Linear	980.601	245.150	3.3809	0.0242	0.3510	
2FI	36.0800	6.01000	0.0640	0.9987	0.3639	
Quadratic	1305.07	326.270	10.361	0.0003	0.8310	Suggested
Cubic	461.190	57.6501	36.620	< 0.0001	0.9961	Aliased

The experimental results were then thoroughly analyzed by ANOVA. Polynomial regression model was developed using CCD to analyze the relationship exists between the chosen process parameters and carbon content (response Y). The ANOVA for the response Y is summarized in Table 4.

Table 4: ANOVA table of response Y

Source	Sum of Squares	Mean Square	F Value	Prob > F	Significance
Model	2321.7	165.84	5.2700	0.0014	√
A	269.81	269.81	8.5700	0.0104	√
B	432.91	432.91	13.750	0.0021	√
C	230.08	230.08	7.3100	0.0163	√
D	47.800	47.800	1.5200	0.2368	X
A^2	1146.3	1146.4	36.420	< 0.0001	√
B^2	1.2400	1.2400	0.0390	0.8455	X
C^2	175.38	175.38	5.5700	0.0322	√
D^2	5.6800	5.6800	0.1800	0.6770	X
AB	29.130	29.130	0.9300	0.3513	X
AC	0.5400	0.5400	0.0170	0.8972	X
AD	0.1400	0.1400	0.0044	0.9479	X
BC	5.9700	5.9700	0.1900	0.6695	X
BD	0.0950	0.0950	0.0030	0.9570	X
CD	0.2000	0.2000	0.0064	0.9375	X

As a rule of thumb, values of "Prob> F" less than 0.05 indicate a significant model term and smaller the value of "Prob> F", the more significant is the corresponding model term. From Table 4, it was found that the main effects of reaction temperature (A), catalyst residence time (B), and methane partial pressure (C), as well as second-order effect of reaction temperature (A^2) and methane partial pressure (C^2) were significant. Meanwhile, other model terms include the main effects of catalyst feed rate (D), the second-order effect of reaction time (B^2) and catalyst amount (D^2), as well as all the interaction effect between process parameters (AB, AC, AD, BC, BD, and CD) are insignificant.

In the continuous CDM process, the catalyst feed rate (Parameter D) has no significant effect on carbon content, whereas the catalyst amount appeared to be a significant process parameter affecting the carbon content in the batch-wise CDM process. It is possibly due to the narrow range of the catalyst feed rate selected for the continuous process study, *i.e.* 100-500mg/, which caused less significant effect on the carbon content as compared to the other studied process parameters. The insignificant model terms were then eliminated from the analysis to ensure that the selected quadratic model provides a better prediction of simulated response Y at various CDM process conditions.

Table 5: Comparison between experimental and simulated value of response Y

Process Parameter					Carbon Content, Y	
Run	A Reaction temperature (^oC)	B Catalyst residence time (minute)	C Methane partial pressure (atm)	D Catalyst feed rate (mg/min)	Experimental	Simulated
1	700	120	0.5	300	75.29	78.03
2	800	150	0.4	150	91.65	88.66
3	900	120	0.2	250	73.64	70.50

The quadratic model was selected to describe the response surface of carbon content within the selected range of these process parameters. The polynomial regression equation built with actual factors is given in Equation (1) as follow:

In term of actual factors: Carbon content, Y (wt%) =
$-401.75857 + 1.07277A + 0.14157B + 92.25078C - 6.49523x10^{-4}A^2 - 63.97461C^2$ (1)

where A represents the reaction temperature, B represents the catalyst residence time and C represents the methane partial pressure.

In addition to the 30 experimental runs used to develop the quadratic model Equation (1), another 3 experimental runs at random CCVD process conditions were conducted to validate the developed quadratic model for response Y. The experimental and simulated results were summarized in Table 5. A comparison of the experimental results with the model values of carbon content, response Y predicted from the polynomial regression equation above is presented in Figure 2, which denotes a good convergence between the experimental and simulated values of carbon content with a R^2 value of 0.8870.

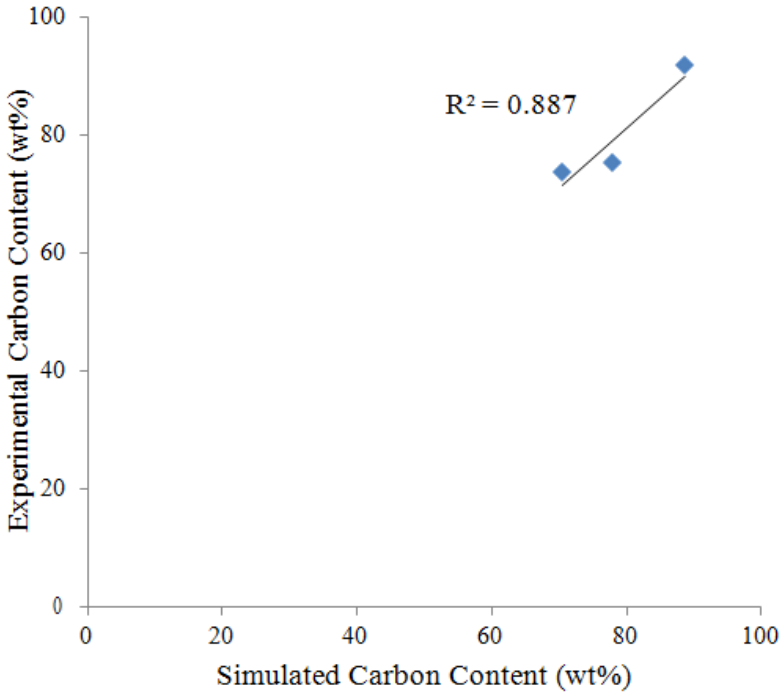

Figure 2: Parity plot of experimental and predicted value of response Y

The independent process parameters and the response which were identified to be important in the synthesis of CNTs *via* CCVD process using continuous rotary reactor system were optimized simultaneously using numerical optimization method (Constrained Nonlinear Optimization Algorithms) in Design Expert Software (version 6.0.6, State-Ease Inc., Minneapolis, MN) based on the experimental results obtained. All the process parameters and the response with respective to the specified high and low limit of experiment region that have to satisfy were defined for the optimum process conditions as listed in Table 6. The ultimate goal for the synthesis of CNTs from catalytic decomposition of methane using continuous rotary reactor system is to maximize the carbon content of carbon deposits obtained at optimum process condition to realize large-scale production of CNTs.

Table 6: The preset goal with the constraints for all the independent process parameters and response in numerical optimization

	Process Parameter	Ultimate Goal	Experimental Region	
			Lower Limit	Upper Limit
Process Parameter	Reaction temperature, A [°C]	In range	700	900
	Catalyst residence time, B [minutes]	In range	90	180
	CH_4 partial pressure, C [atm]	In range	0.4	0.8
	Catalyst feed rate, D [mg/min]	In range	200	400
Response	Carbon content, Y [wt%]	Maximize	90	95.13

The suitable process condition could be selected based on the levels of desirability, which represents the level of satisfaction that the preset criteria for all process parameters and response have been fulfilled. There were several sets of combination predicted as the optimum process condition and ranked according to the desirability order. The optimum process condition for the highest desirability was a reaction temperature of 833 °C, catalyst residence time of 165 minutes, methanepartial pressure of 0.54 atm and catalyst feed rate of 260 mg/min, which gave carbon deposit with the predicted carbon content of 95.40 wt%, equivalent to carbon yield of 2073.9% of carbon deposits. The experiments were carried out at the suggested optimum process condition in order to obtain the experimental carbon content. Table 7 tabulates the experimental results conducted at the suggested optimum process condition along with the calculated absolute error between experimental and simulated carbon contents. The results presented in Table 7 shows that the simulated carbon content of carbon deposits close to the experimental values with the mean absolute error of 0.90. Since the quadratic model developed by DoE has fitted the experimental data with R^2 of 0.8310 for carbon content (response Y), thus the deviation between the experimental and the predicted values is within tolerable and acceptable limit.

Table 7: Reproducibility test under optimum CDM process condition over bimetallic 10Co- 20Mo/70MgO catalyst

Run	Carbon Content [wt%]		Absolute Error
	Experimental	Simulated	
1	95.21	95.20	0.20
2	93.83	95.20	1.65
3	94.60	95.20	0.84
Mean Absolute Error			0.90

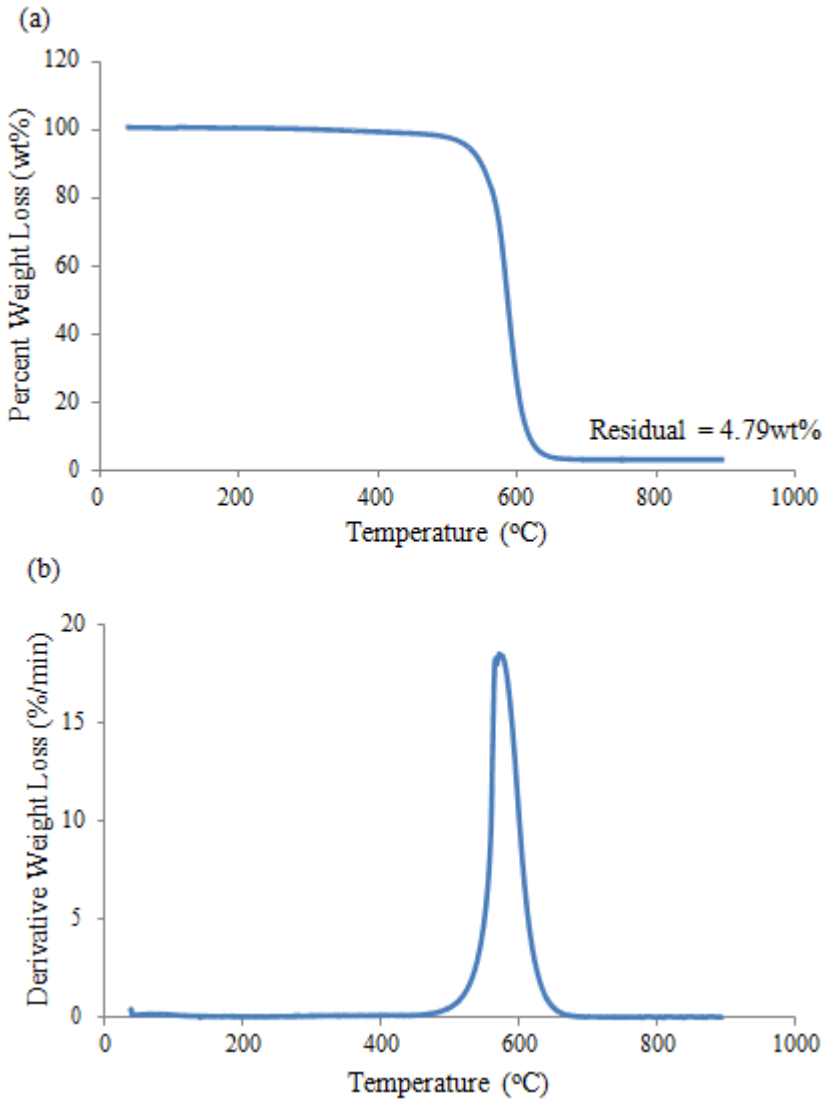

Figure 3: (a) Thermogravimetric curve and (b) Differential thermogravimetric curve of the carbon deposits synthesized at optimum CCVD process condition in rotary reactor system

The morphology and physical properties of carbon deposits synthesized using continuous rotary reactor at suggested optimum CCVD process condition over bimetallic 10Co-20Mo/70MgO catalyst were characterized using TEM, TGA and Raman spectroscopy. TGA was employed to determine the carbon content and carbon yield of the carbon deposit and the analysis result is presented in Figure 3. From the thermogravimetric curve as shown in Figure 3(a), the carbon content was determined to be wt% as reflected by the weight loss in the carbon oxidation. The carbon yield was calculated to be 1987.7%. The carbon deposits were mainly CNTs as there is only one significant carbon oxidation peak starts to rise at *ca.* 500 °C and no other significant peaks were found in the temperature range 300–400 °C, which corresponds to the oxidation of amorphous carbon[14] in differential thermogravimetric curve shown in Figure 3(b). The carbon deposition rate of approximately 310 gCNTs/hr based on the catalyst feeding rate of 260 mg/min was achieved**.**

The TEM images shown in Figure4 confirmed that the carbon deposits consisted of CNTs as clear hollow cores were observed. The diameter distribution of the CNTs synthesized using rotary tubular reactor was calculated to be 10.18±1.02 nm.

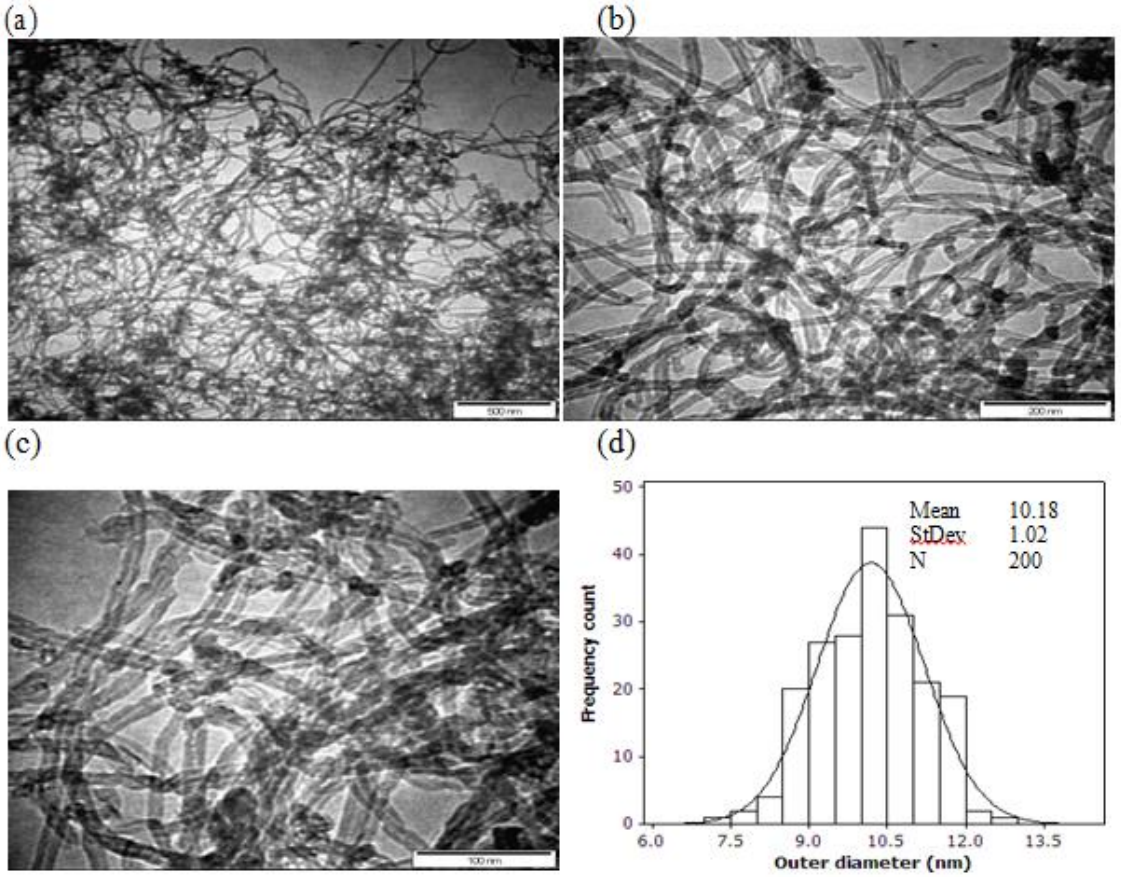

Figure 4: TEM image at (a) 3kV, (b) 10kV, (c) 22kV magnification and (d) diameter distribution of the carbon deposits synthesized at optimum CCVD process condition in rotary reactor system

The carbon deposit was further characterized using Raman spectroscopy to examine the degree of graphitization of the synthesized CNTs and the result was shown in Figure 5. Since no significant peak appears in the RBM region, it can be concluded that MWCNTs are the main products synthesized when the reaction process conducted at the suggested optimum CDM process condition. There were two major bands observed, namely D- and G-bands. The D-band, observed in the range of 1200–1400 cm^{-1}, is activated by disordered graphite, wall disorder, fibers, or nano-clusters in graphite that relate to the level of disordered carbon and defect concentration in CNTs. Meanwhile, the G-band, observed in the range of 1500–1700 cm^{-1}, is associated with the tangential stretching mode that is attributed to the degree of graphitization of CNTs. The ratio of intensity of D- to G-bands (ID=IG ratio) can be regarded as an index for the crystalinity order of CNTs. From Figure 5, the intensity of D-band is slightly higher than the intensity of G-band, giving the ID/IG ratio of 1.262.

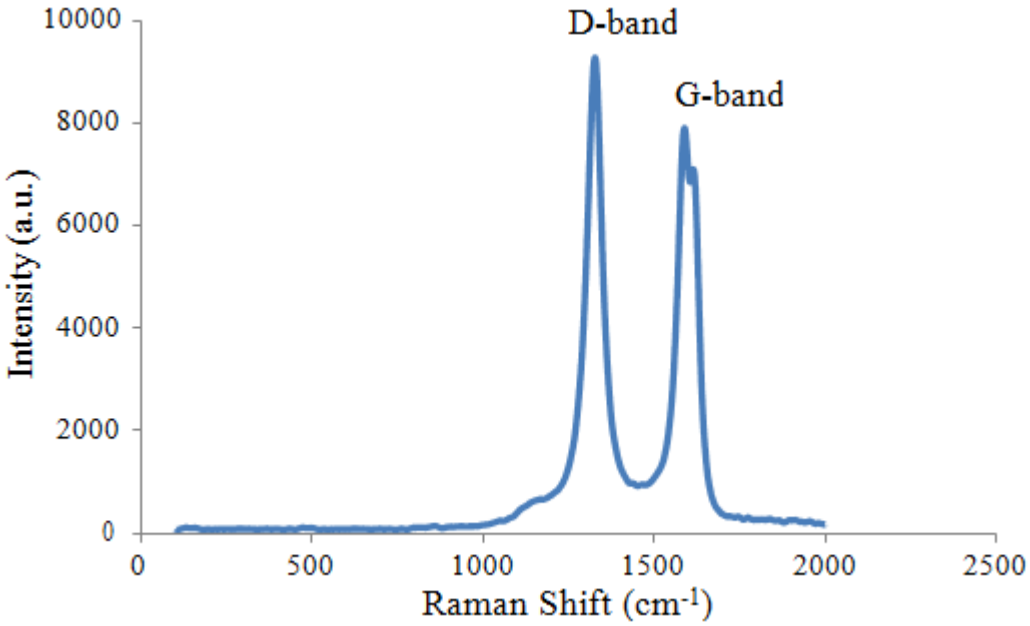

Figure 5: Raman spectrum of the carbon deposits synthesized at optimum CCVD process condition in rotary reactor system

CONCLUSION

From the ANOVA analysis on response Y (carbon content), the main effect of each process parameter, except catalyst feed rate, emerged as the major effects over the carbon content and there was no interaction exists between process parameters which have significant effect on the response of interest over the range of process parameters selected in the present experimental study. The independent process parameters and the response which identified to be important in the synthesis of CNTs from catalytic

decomposition of methane were optimized simultaneously based on the experimental results obtained. The optimum operating condition obtained was a reaction temperature of 833 ℃, reaction time of 165 minutes, methane partial pressure of 0.54 atm and catalyst amount of 260 mg/min. The carbon deposits synthesized under optimum operating condition had high carbon content of 95.21 wt%, equivalent to carbon yield of 1987.7%, and high selectivity towards the synthesis of CNTs rather than other kinds of carbon nanostructures. The carbon deposition rate of approximately 310 g CNTs/hr based on the catalyst feeding rate of 260 g/min was achieved. Under TEM observation, the carbon deposits were solely MWCNTs with quite uniform diameter distribution of 10.18±1.02 nm. From Raman spectroscopy characterization, the intensity of D-band is slightly higher than the intensity of G-band, giving the I_D/I_G ratio of 1.262.

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