Journal of Industrial Technology Vol. 20(1), 2011 - ICONT 2009, 25 - 36

OPTIMIZATION OF CARBON NANOTUBES SYNTHESIS VIA METHANE DECOMPOSITION OVER ALUMINA-BASED CATALYST

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ABSTRACT : Carbon nanotubes (CNTs) were synthesized from alumina-based catalyst via decomposition of methane in a horizontal reactor system. By using a statistical design of experiments (DoE), six factors (reaction temperature, reaction duration, metal loading of catalyst, amount of catalyst, flow rate of methane and flow rate of nitrogen) were optimized for the synthesis of carbon nanotubes. The response of the process towards the factors was assessed using two quantitative signifiers, which are the yield of carbonaceous material and the I_D/I_G ratio from Raman spectrum. The parameter space for significant factors that influence the response was first screened using a Resolution III fractional factorial design. A response surface which is defined by the most significant parameters was then incurred from Box-Behnken design and finally optimal conditions were found. The morphology of the as-produced CNTs from the selected samples was observed using a Transmission Electron Microscope (TEM).

KEYWORDS : Carbon Nanotubes, Chemical Vapor Deposition, Raman Spectroscopy, Transmission Electron Microscopy, process optimization

INTRODUCTION

Carbon nanotubes (CNTs) had become a captivating and rapid-developing research field, since the discovery by Sumio Iijima in 1991. The unique structural, mechanical and electronic properties of CNTs draw enormous scientific and technologic interest from scientific community, to study the potentiality of CNTs utilization in fields such as super capacitors, reinforcements in high performance composites, hydrogen storage and the list go on (Paradise *et al.*, 2007). To realize the applications of CNTs in diverse fields, large quantity of CNTs with high uniformity and quality are of necessity. To date, many synthesis methods have been developed including arc-discharge (Iijima, 1991), laser vaporization (Guo *et al.*, 1995), and Chemical Vapor Deposition (CVD) (Amelinckx *et al.*, 1994). Out of these three methods, CVD is the most promising method for the scale up production of CNTs due to the advantages of low cost, high yield and ease of control. The synthesis of CNTs via CVD method involves the thermal decomposition of carbon source, followed by the deposition of carbon on the metal catalytic nanoparticles, and finally the excretion of carbon to form the walls of CNTs. In CVD process, the production of CNTs can be controlled by varying the reaction parameters such as type of catalyst, reaction temperature, and flow rate of feed stock and so on. These tunable parameters affect the type of carbonaceous materials growth, the quality and quantity of the as-produced CNTs.

One of the constrictions in the CVD synthesis of CNTs is the growth process, in which a huge number of process parameters need to be optimized for the accomplishment of adequate quantities of as-produced CNTs. It is widely accepted that tuning the process to optimum performance is often difficult and time consuming. One of the common approaches for process optimization is the OFAT (one factor at a time) method. In this experimental strategy, all variables but one are fixed at predetermined values, and the response of the process as a function of the changing variable is studied. Each variable is examined in this way, and the combination of their optimum values is accepted as the global optimum (Kukovecz *et al.*, 2005). However, there are two major deficiencies of this approach, which include; first is the number of experiments which increase drastically with the number of variables, thus, it is rather impractical and unfeasible to optimize a process, and second, it is very unlikely to find the global optimum. It is because OFAT method is assuming that the effects of variables are independent from each other, whereas in a chemical process, the response of the process is usually affected by the interactions of variables.

In recent years, process optimization with the aid of DoE is rapidly gaining popularity in various field related to nanotechnology. Statistical design of experiment is the science of statistically analyzing the largest possible amount of information with the smallest amount

number of experiments (Goh *et al.*, 2001). Common DoE approaches being used include two-level factorial design (FD), combination of fractional factorial design and Response Surface Methodology (RSM), and Taguchi's method. In this present study, we demonstrated a rapid optimization of CVD growth of CNTs on CoO-MoO/Al_2O_3 with the aid of statistical design of experiments (DoE) software. The DoE approach employed was a combination of fractional factorial design and RSM. The decisive parameters were first determined by a fractional screening design and optimization of the decisive parameters was achieved by using a Box-Behnken design to fit the response surface.

MATERIALS AND METHODS

Preparation of CoO-MoO/Al_2O_3 catalyst

CoO-MoO/Al_2O_3 catalysts were prepared by conventional impregnation method. The composition of the catalyst was varied, as mentioned in the discussion part. The CoO: MoO weight ratio was set at 8:2. In all cases, right amounts of $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (RdH) were dissolved in distilled water and then the solution was impregnated onto Al_2O_3 (Ajax). The impregnated samples were sonicated for 5 min and then dried at 105 °C for 12 h. The dried samples were grounded and calcined in air at 700 °C for 5 h. The prepared catalysts were then used without prior reduction in hydrogen.

Synthesis of CNTs

The synthesis of CNTs was carried out in a horizontal quartz reactor (length and diameter of the reactor are 1050 mm and 65 mm, respectively) at an atmospheric pressure. The catalyst was placed on a quartz boat (the length, width and height of the quartz boat are 103 mm, 20 mm and 12 mm, respectively) located at the middle of the reactor. The synthesis conditions were varied extensively and the parameter of all runs are tabulated in Table 1. Methane (99.995 % purity, Air Products Sdn. Bhd.) and nitrogen (99.999 % purity, Air Products Sdn. Bhd.) played the role as carbon precursor and inert gas, respectively. Methane gas was used as a carbon precursor due to its stability at high temperatures, which avoids self-pyrolysis that may cause the formation of amorphous and graphitic carbon (Dai, 2002). After the reaction, the reactor was cooled down to ambient temperature in nitrogen atmosphere.

Characterization

Thermogravimetric analyzer (TGA) (TA Instrument, SDT Q600) was employed to determine the percentage of carbon deposition by measuring the weight loss of the samples at the range of 300 – 700 °C. The Universal V 4.5A software was used to analyze the TGA curves. The percentage of carbon yield is defined below and can be calculated from the TGA.

$$\text{Carbon yield (\%)} = \frac{\text{Carbon deposited on the catalyst}}{\text{Metal loaded on the catalyst}} \times 100\% \quad (1)$$

Raman spectrums were recorded by Raman Microscope (Renishaw) using a laser excitation of 532 nm in the range of 100 - 3200 cm^{-1}. Selected samples were analyzed using a Transmission Electron Microscope (TEM) system (Philips CM12) to investigate the morphology of the as-produced CNTs. For TEM, samples were dispersed in acetone and then deposited on a Cu grid coated with carbon film.

RESULTS AND DISCUSSION

Initial screening of the process parameters

Based on the literature review, a set of starting parameter was taken for process optimization. Six factors were optimized in our experimental system by relying on DoE: (i) reaction temperature, (ii) reaction duration, (iii) amount of catalyst (iv) metal loading of catalyst, (v) methane and (vi) nitrogen volumetric flow rate. An effective process optimization requires early identification of decisive parameters, which conventionally carried out by assuming that all parameters generated a predominantly linear response which is measured by setting each parameter to a "low" and a "high" value. However, such a full factorial design is usually not feasible and time consuming for real-life systems as 2^k runs are required for k parameters. In this study, a rapid screening of the whole parameter space were performed in 8 runs arranged in a 2^{6-3}_{III} fractional factorial design, instead of a total of 2^6= 64 runs are required for a full factorial design. A 2^{6-3}_{III} fractional factorial design is a two level resolution III design where the main effects are confounded with two-way interactions and consequently, all higher-level interactions are equally confounded. The required runs are shown in Table 1 along with the carbon yield and I_D/I_G ratio. The high and low levels for each parameter were chosen on the basis of run #0.

Table 1. Process variables (reaction temperature, reaction duration, metal loading of catalyst, amount of catalyst, flow rate of methane and flow rate of nitrogen) and system responses (carbon yield and the I_D/I_G ratio) of literature-based starting point (run#0) and the 2^{6-3}_{III} fractional factorial design (run#2-#8)

Run	Reaction temperature (°C)	Reaction duration (hr)	Catalyst weight (g)	Metal loading (%)	CH_4 (ml/min)	N_2 (ml/min)	Carbon yield (%)	I_D/I_G
0	750.00	2.50	0.25	25.00	250.00	250.00	306.5	0.661
1	800.00	1.00	0.40	10.00	400.00	100.00	163.2	0.696
2	700.00	1.00	0.10	40.00	400.00	400.00	139.4	0.914
3	700.00	4.00	0.40	10.00	100.00	400.00	235.9	0.854
4	800.00	4.00	0.10	40.00	100.00	100.00	317.4	0.566
5	700.00	1.00	0.40	40.00	100.00	100.00	186.0	1.223
6	700.00	4.00	0.10	10.00	400.00	100.00	241.8	0.887
7	800.00	1.00	0.10	10.00	100.00	400.00	45.1	0.604
8	800.00	4.00	0.40	40.00	400.00	400.00	311.3	0.449

Figures 1 and 2 present the overview of the effects of variables on carbon yield and I_D/I_G ratio, respectively, which were customary in DoE analysis. In these plots the mean is calculated by averaging the response over all runs for both the high and the low setting of the examined parameters. In Figure 1, we may identify the variables "reaction duration", "metal loading" and "nitrogen flow rate" as important factors, "catalyst amount" and "methane flow rate" as moderately important factors and "reaction temperature" as unimportant factor from the viewpoint of carbon yield maximization. Meanwhile, Figure 2 illustrated that the quality of as-produced is greatly affected by "reaction temperature". "Reaction duration", "methane flow rate", and " nitrogen flow rate" as moderately factors and "metal loading" and "catalyst amount" are less important compared to other factors.

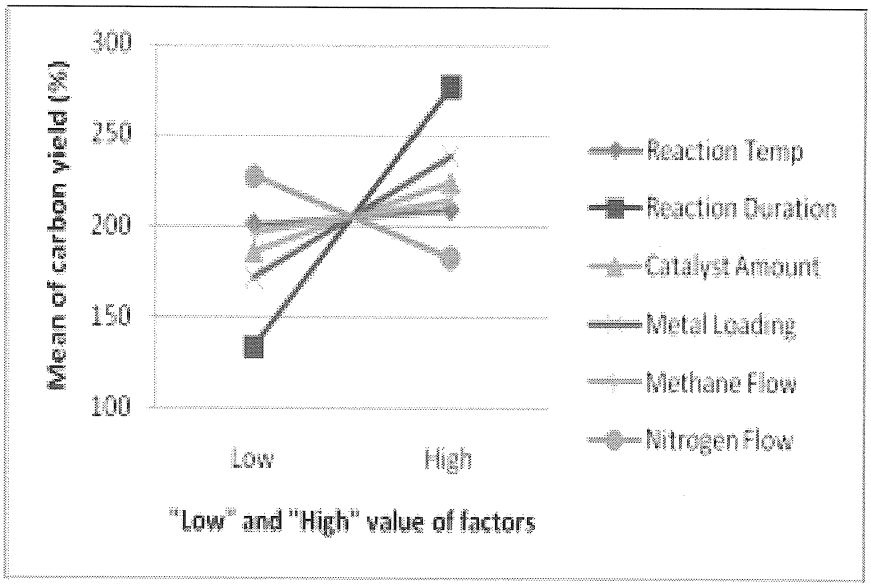

Figure 1. *Carbon yield mean values presented in the main effects plot in order to determine the factors with the largest influence on the carbon yield*

The purpose of the screening was to reduce the number of variables from six down to three. Since the objective of the process optimization is to produce high yield of CNTs with satisfying quality, "reaction duration", "metal loading" and "nitrogen flow rate" were considered as decisive factors from the carbon yield point of view. Meanwhile, "reaction temperature" had great impact on the quality of as-produced CNTs. "Reaction duration" and "reaction temperature" were selected for further detailed optimization since

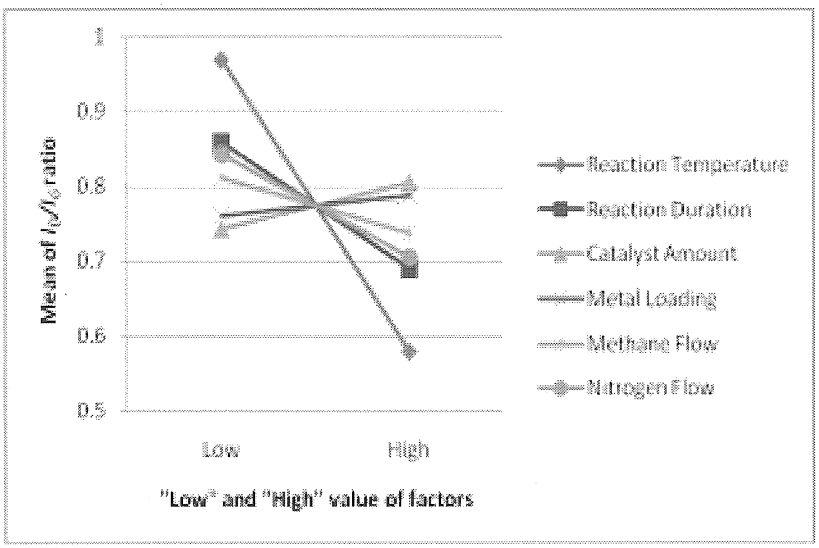

Figure 2. *I_D/I_G ratio mean values presented in the main effects plot in order to determine the factors with the largest influence on the ID/IG ratio.*

these two factors influenced the carbon yield and I_D/I_G ratio the most, leaving "metal loading" and "nitrogen flow rate" to be chosen. As reported previously, the metal loading of catalyst determines the yield and diameter distribution of as-produced CNTs (Chai *et al.*, 2009). Therefore, "metal loading" was selected as the third variable for the process optimization.

Response surface exploration

In order to fit the response of surface defined by the three selected variables ("reaction duration", "metal loading" and "reaction temperature"), more data needs to be collected. A three-level Box-Behnken design with one center point is the least resource-demanding design which is able to identify non-linear relationships for three factors. Box-Behnken design is an independent quadratic design in which parameter combinations are at the center and at the midpoints of edges of the process space (Box G., *et al.*, 1960). Some advantages of Box-Behnken design over other RSM (e.g., central composite designs, three level full factorial design etc.) are (i) it requires minimum number of runs for three factors at three level and (ii) fitted values are as close as possible to observed values, hence minimize residuals or error of prediction (NIST/SEMATECH, 2009). Further optimization of "reaction duration", "metal loading" and "reaction temperature" factors required 13 runs as displayed in Table 2. "Catalyst amount", "methane flow rate" and "nitrogen flow rate" in these experiments were

held at 0.25 g, 250 ml/min and 250 ml/min, respectively. Each run was analyzed for carbon yield (%) and I_D/I_G ratio. The contour plots were then generated by ANOVA for response surface quadratic model as presented in Figure 3

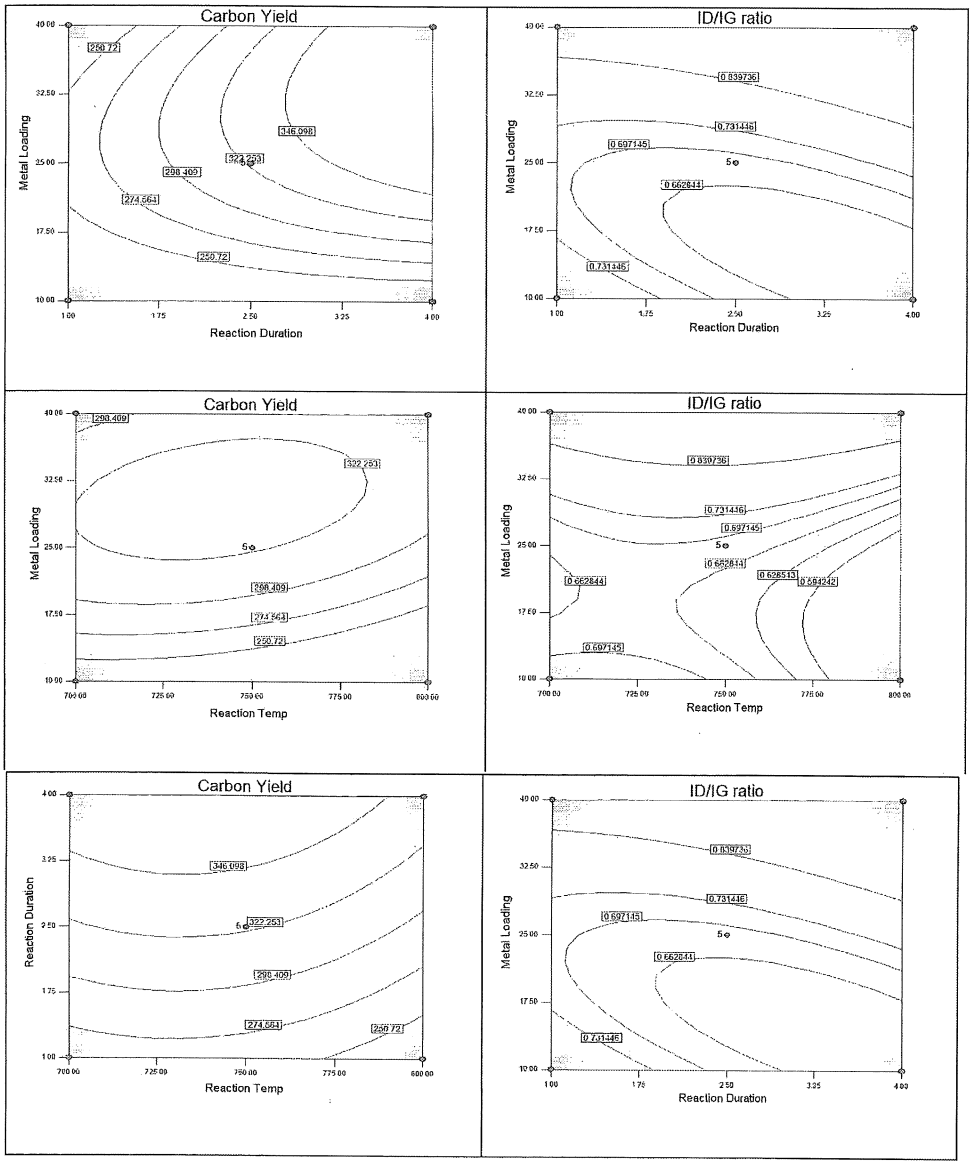

Figure 3. *Contour plots describing the response surface for carbon yield and I_D/I_G ratio as a function of each parameter pair*

The results from Table 2 were fitted using full quadratic response surface equations in Eqs. (2) and (3) for carbon yield and I_D/I_G:

$$\text{Carbon yield, \%} = -14.01a + 53.46b + 49.30c - 18.49a^2 - 9.59b^2 - 63.01c^2 + 1.57ab + 19.75ac - 36.15bc + 324 \quad (2)$$

$$I_D/I_G = -0.053a + 0.025b + 0.16c - 0.068a^2 + 0.047b^2 + 0.16c^2 + 0.001ab + 0.6ac + 0.11bc \quad (3)$$

where a, b and c denote the "reaction temperature", "reaction duration" and "metal loading", respectively. The distribution of the standardized residuals of both fits was found to be normal at 95 % confidence level using an empirical cumulative distribution function test (the Anderson–Darling test).

Table 2. Process variables (reaction temperature, reaction duration, metal loading) and system responses (carbon yield and the I_D/I_G ratio) of the Box-Behnken response surface design (run #9- #21) and the suggested global optimum parameters (run #22)

Run	Reaction temperature (°C)	Reaction duration (hr)	Metal loading (%)	Carbon yield (%)	I_D/I_G
9	750.00	2.50	25.00	324.2	0.693
10	800.00	4.00	25.00	289.4	0.542
11	700.00	2.50	10.00	193.6	0.687
12	750.00	1.00	10.00	170.8	0.772
13	800.00	2.50	10.00	202.3	0.455
14	800.00	2.50	40.00	331.5	0.987
15	750.00	1.00	40.00	206.9	0.769
16	800.00	1.00	25.00	198.0	0.685
17	700.00	2.50	40.00	243.2	0.980
18	750.00	4.00	10.00	224.5	0.788
19	700.00	1.00	25.00	306.1	0.786
20	750.00	4.00	40.00	404.3	1.241
21	700.00	4.00	25.00	390.7	0.639
22	761.77	2.30	26.96	350.0	0.660

A parameter set which is able to maximize carbon yield of minimized I_D/I_G can be obtained analytically from equations (2) and (3). However the objective of this study is to optimize the carbon yield with satisfying quality of as-produced CNTs. In our case the optimum was found at "reaction temperature", "reaction duration" and "metal loading" at 761.77 °C, 2.30 hr and 26.96 %, respectively. The predicted values for the carbon yield and I_D/I_G is 326.07 % and 0.689, respectively. After performing the experiment using these parameters, the values for the carbon yield and I_D/I_G are 349.96 % and 0.653, respectively. The agreement between the predicted and the actual values is acceptable.

The TEM image and Raman spectrum of the sample for Run #22 is illustrated in Figure 4. From the TEM image, one can observed that the carbon deposited are carbon nanotubes. The filamentous carbon are hollow cored. The diameter of the as-produced carbon nanotubes have high uniformity. Two significant peaks at 1350 cm^{-1} and 1595 cm^{-1} represented the D-band and G-band, respectively. The I_D/I_G ratio reveals the degree of ill-organized graphite sheets and it can be used as a measure of the degree of graphitization of the as-produced CNTs. The value of the I_D/I_G ratio is 0.660, suggesting that minor defectiveness were found on the CNTs wall structures.

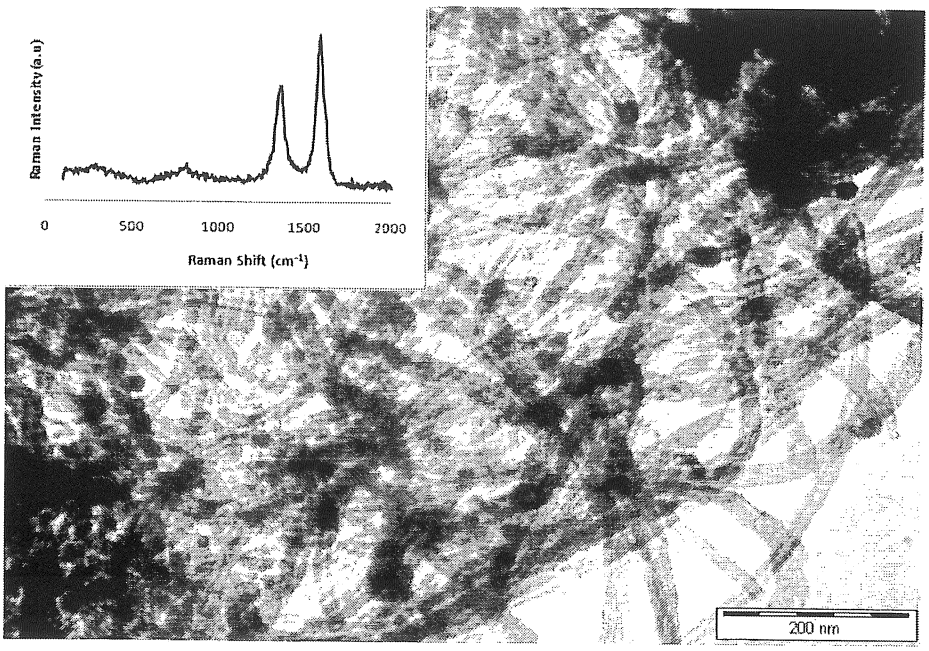

Figure 4. *TEM image and Raman spectrum of the product from the end optimization parameters*

CONCLUSION

A statistical design of expert approach was employed for the process optimization of the CCVD synthesis of CNTs. The six original process variables were rapidly screened by a fractional factorial series in order to identify the three most significant parameters influencing the carbon yield and quality of as-produced CNTs. Further optimization of the three decisive parameters were performed using Box-Behnken design. A total of 23 runs were required to achieve the best performance experimental bench. This effective method can be applied by any laboratory or industry entering the rapidly growing field of nanotechnology.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support provided by the Universiti Sains Malaysia under the Research University Grant Scheme (Project A/C No. 814004), USM-RU-PRGS (Project A/C No. 8032038) and the Malaysian Technology Development Corporation (MTDC) under the Commercialization of Research & Development Fund (CRDF) (MBF065-USM/05).

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