J. Environ. Nanotechnol.
Volume 3, No.1 pp. 72-78
ISSN (Print) : 2279-0748
ISSN (Online) : 2319-5541
doi : 10.13074/jent.2013.12.132061

Multivariate Optimization of Carbon Nanotubes Synthesis from Nonconventional Precursor using Box-Behnken Design towards Higher Yield

M. Sathish Kumar[1], K. Manonmani[2], S. Karthikeyan[3*]

[1,2] Department of Mechanical Engineering, Government College of Technology Coimbatore, TN, India.
[3*]Department of Chemistry, Chikkanna Government Arts College, Tirupur, TN, India.

Received: 10.01.2014 Accepted: 10.02.2014

Abstract

Optimization techniques play a significant role in improving the performance and efficiency of a product (or) process. In general these techniques results in maximizing the desired ones and minimizing the non-desired ones. In this context, we identified and optimized the parameters of chemical vapour deposition process to achieve higher yield of carbon nanotubes. We selected the most abundantly available plastic waste, Polystyrene a major source of environment degradation to be the precursor. Polystyrene was thermal degraded in to oil by spray pyrolysis. The extracted PS oil was utilized as resource for producing carbon nanotubes through horizontal fluidized bed reactor. Reaction temperature, catalyst/ support material ratio, and gas flow rate were identified as the paramount parameters that affect the yield. The experimental run orders to optimize the process was obtained by Box Behnken design, a response surface methodology scheme. In total 17 experimental trials were conducted and the respective yield was found. The parametric combination corresponding to higher yield was recognized. The obtained optimum parameters can be readily adapted to any laboratory level CVD synthesis. In this effort Field Emission Scanning Electron Microscope, High-resolution transmission electron microscopy and Raman spectroscopy were adapted to examine the microstructure and morphology respectively.

Keywords: *Box-Behnken design; Carbon nanotubes; CVD; MWNT; Response surface methodology.*

1. INTRODUCTION

Carbon nanotubes are the most of committed novel nanomaterials in the field of nanotechnology. Several research conducted on CNTs clearly states the possibility of property enhancement to a higher level. A numerous literature survey witnesses the improvement in properties and applications. These one-dimensional nano structured materials were produced through several methods like Laser Ablation, Chemical vapour deposition and Arc Discharge method out of which CVD process is widely preferred. Ease of operation low cost and scaling up of production are the advantages of CVD process. Mukul Kumar *et al.* (2010) stated as compared to other processing techniques chemical vapour deposition is superior in the aspect of purity and yield. It also offers best control over growth parameters. The potential research concentrates on the paramount factors cost and quality with quantity. In the way to satisfy this statement, our team carefully selected precursor that keeps the process cost lower and yield to be higher with good quality. Discarded

***S. KarthikeyanTel.: +919442264501**
E-mail: environkarthi@gmail.com

polystyrene does not degrade for hundred years and is reason to select polystyrene as our precursor. The optimization technique we followed was Box-Behnken designs (BBD), a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs. Design Expert V9 software was used for optimization and the results are discussed in detail.

2. EXPERIMENTAL

Synthesis of oil

Pyrolysis and gasification are now recognized as promising routes for the upgrading of solid wastes to more usable and energy dense materials, such as gas fuel and/or fuel oil, or to high value feed stocks for the chemical industry. Moreover, a pyrolysis step is always present in the initial stages of gasification and combustion processes. Polystyrene decomposes at a lower temperature of 240°C. The pyrolysis is done in a tubular furnace and the catalyst used is Zeolite. Final product of the process is polystyrene oil.

Synthesis of nanotubes

The polystyrene oil collected is used for chemical vapour deposition. In this reaction the parameters are set according to the experimental design. The combination of different levels is being set and the reaction is being carried out. Based on the literature survey and our past synthesis experience with various polymer we selected the low and higher value of the parameters which is listed in the table 1. The substrate used in this reaction is silica and the most promising catalyst is ferrocene is used.

The table 2 indicates the box Behnken design and the response value indicate the yield of carbon in percentage. The response value is calculated using the formula

$$Yield = \frac{S_a - S_b}{S_b} x100$$

Where S_a and S_b are the mass of the substrates after and before the reactions respectively. Even though this value includes the percentage of amorphous carbon, SEM analysis images reveals that they are present in negligible quantities compared to Carbon nanotubes. Hence the percentage of yield can be taken as CNT yield.

3. RESULTS & DISCUSSION

The results of this experiment were studied in two aspects. One is the optimization aspect and the other one is the influence of parameters based on the response surface aspect. The software used is reliable since the deviation of the actual value from the predicted value is minimum. The Equation of the quadratic model for predicting the optimal point was derived from the

Table 1. Input parameters and their levels

Name	Units	Level -1	Level 0	Level +1
Reaction temperature	°C	800	900	1000
Catalyst support material Ratio	in %	25	50	75
Gas flow rate	cm^3/min	10	20	30

Table 2. Box Behnken design and the response

Run	A:Reaction temperature	B:Catalyst support material ratio	C:Gas glow rate	Yield
1	0	-1	-1	92
2	-1	-1	0	83
3	1	0	-1	87
4	0	1	-1	92
5	0	0	0	95
6	-1	0	-1	85
7	1	1	0	89
8	1	0	1	90
9	0	-1	1	92
10	0	1	1	91
11	-1	0	1	82
12	-1	1	0	81
13	0	0	0	94
14	0	0	0	93
15	1	-1	0	86
16	0	0	0	95
17	0	0	0	94

Table 3. ANOVA Table

Source	Sum of squares	df	Mean square	F Value	p-value Prob > F
Model	340.6852941	9	37.85392157	74.64153549	0.000004
A-Reaction temperature	55.125	1	55.125	108.6971831	0.000016
B-Catalyst support material ratio	0	1	0	0	1
C-Gas glow rate	0.125	1	0.125	0.246478873	0.634773942
AB	6.25	1	6.25	12.32394366	0.009852121
AC	9	1	9	17.74647887	0.003972624
BC	0.25	1	0.25	0.492957746	0.505279377
A^2	243.2	1	243.2	479.5492958	0.0000001
B^2	14.41052632	1	14.41052632	28.41512231	0.001086755
C^2	1.515789474	1	1.515789474	2.988880652	0.127465661
Residual	3.55	7	0.507142857		
Lack of Fit	0.75	3	0.25	0.357142857	0.788006417
Pure Error	2.8	4	0.7		
Cor Total	344.2352941	16			

Box-Behnken experimental design and input variables. It is given by

$$Y=94.20+2.63A+2E\text{-}16-0.12C+1.25AB+1.50AC-0.25BC-7.60A^2-1.85B^2-0.60C^2$$

Analysis of variances

ANOVA analysis is done to check the effect of factors and their interactions on the response variable. From the ANOVA table 3 the following inference can be made. The Model F-value of 74.64 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, AB, AC, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

In the table 4 "Pred R-Squared" of 0.9524 is in reasonable agreement with the "Adj R-Squared" of 0.9764 i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 24.396 indicates an adequate signal. This model can be used to navigate the design space.

Numerical optimization

Numerical Optimization will optimize any combination of one or more goals. The goals may apply to either factors or responses. The possible goals are: maximize, minimize, target, within range, none (for responses only) and set to an exact value (factors only). In our study we intend to maximize the yield.

A minimum and a maximum level must be provided for each parameter included in the optimization. The table 4 represents the solution for numerical optimization.

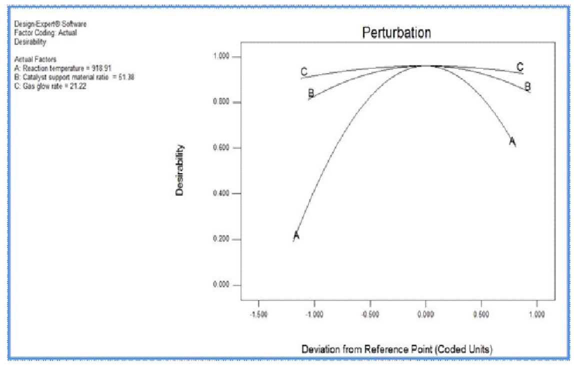

Fig. 1: Perturbation plot

The perturbation plot helps to compare the effect of all the factors at a particular point in the design space. The Fig. 1 indicates the Perturbation plot for the given input parameters and the response.

3D Response surface

To indicate the influence of parameters collectively 3D response surface plots are drawn. In this 3D graphs a steep slope or curvature in a factor shows that the response is sensitive to that factor. A relatively flat line shows insensitivity to change in that particular factor.

In this experiment, the Fig. 3 and indicates that the response is sensitive to the reaction temperature

Table 4. Optimization for higher yield

Number	Reaction temperature	Catalyst Ratio	Gas flow rate	Yield	Desirability	
1	918.91	51.38	21.22	94.44	0.96	Selected

of the synthesis..The yield increases with increase in temperature attains a peak at optimum temperature. The influence of Catalyst is considerable small but aids towards the attainment of yield.

The fig. 3 is the plot of predicted value vs actual value of the response. The experimental yeild almost coincides with predicted value ensuring the confirmation of the model.The fig. 4 indicates the Box cox transformation of the model. The power transforms indicates the best lambda value is -3 and thecurrent model is 1 which shows the nearness of the model towards linearity.

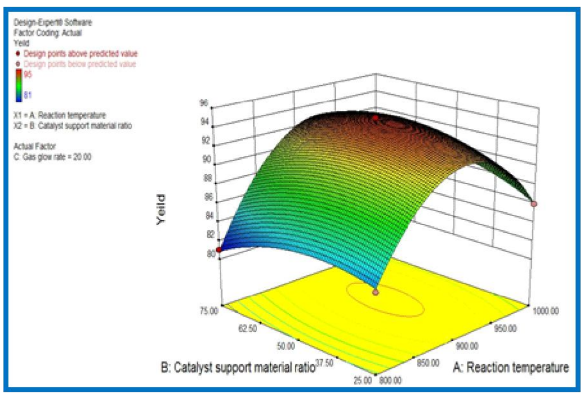

Fig. 2: 3D graph Reaction temperature and catalyst ratio

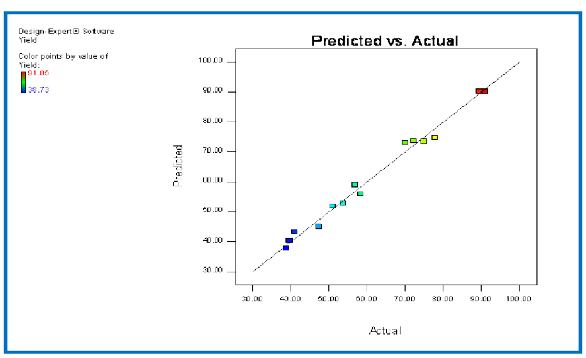

Fig. 3: Predicted Vs Actual plot

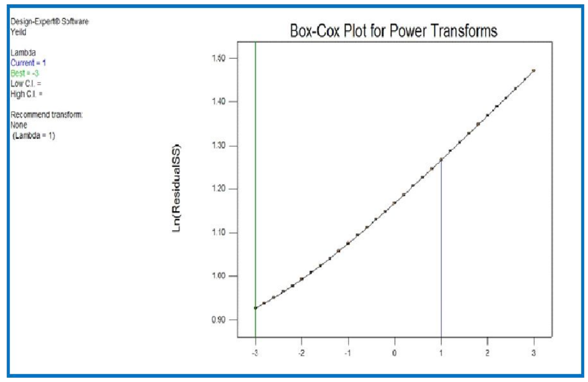

Fig. 4: BOX –COX power transform

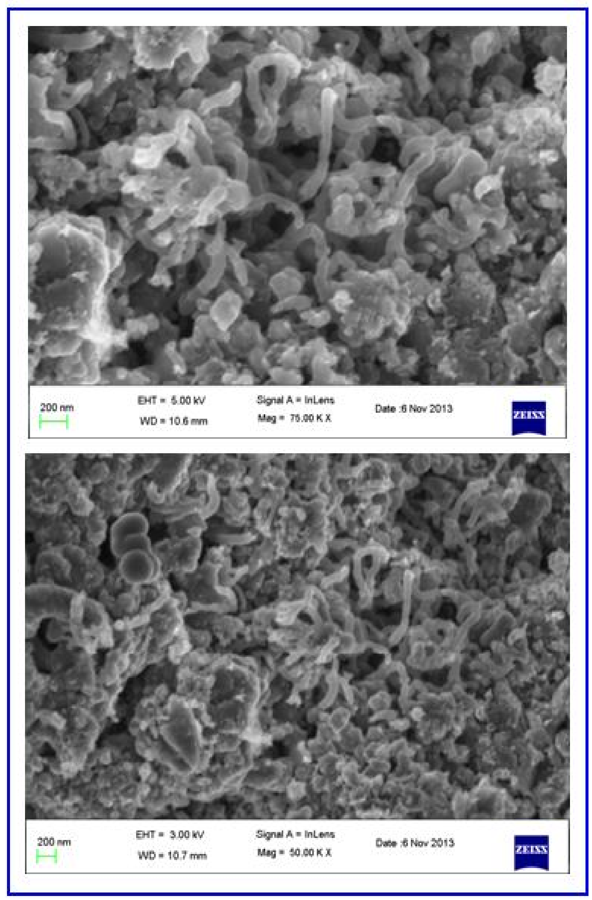

Fig. 5: SEM images

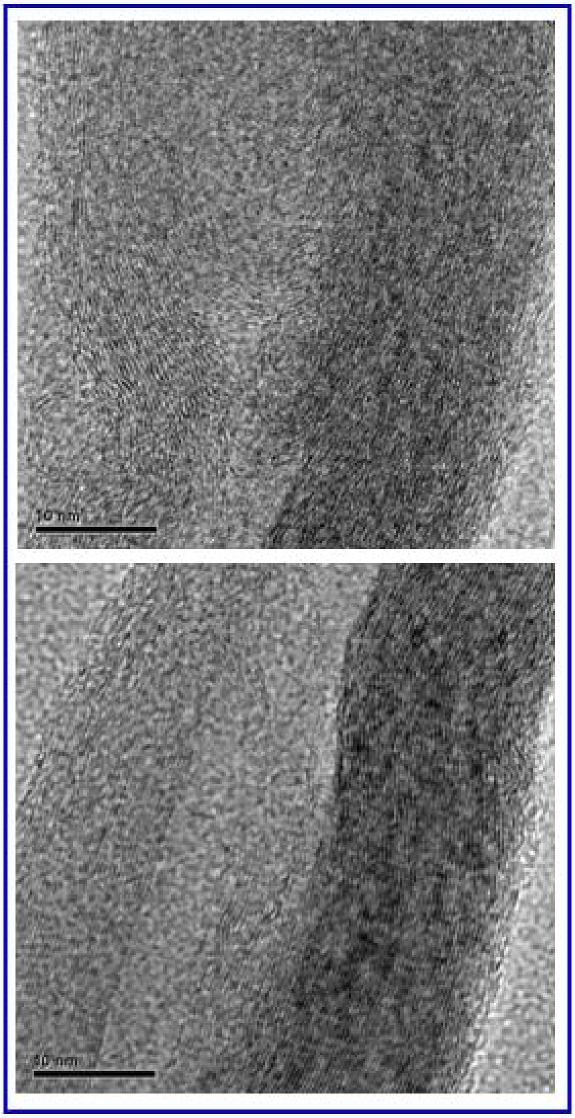

Fig. 6: TEM representation of Carbon Nanotubes

Microstructure and morphology analysis

SEM image with (75x)& (50x) magnification is shown in fig. 5. EHT stands for electron high tension and WD is working distance. In the SEM images the following were observed

- The Diameter of nanotubes is found to be 60 nm.
- Multi walled carbon nanotubes are present.
- There is no presence of vertically aligned carbon nanotubes.
- Amorphous carbon is also present with carbon nanotubes which are not in sizeable quantity.

4. CONCLUSION

The optimization of Carbon nanotube synthesis from non-conventional resources using Box Behnken design has been completed successfully. The summary and findings of this project is as follows The identified waste resources polystyrene, which is a major threat to our green environment, has been selected as the raw material source for synthesizing CNTs which helps in reduction of environmental degradation. Since there is, no combustion or incineration of polystyrene , no hazardous fumes were emitted during the reaction. Thermal cracking takes place in inert atmosphere. Carbon nanotubes can be produced with low cost and high quality. The maximum yield can be achieved through adopting the optimal parameters obtained. The confirmation test results reveal that the optimal parameters can be readily used by any other lab setup to produce CNTs from polystyrene oil.

Reaction temperature is one of the most influencing parameter in synthesizing carbon nanotubes. Silica substrate is the best substrate suitable to grow CNTs through chemical vapour deposition from polystyrene. The SEM images obtained conclude the presence of carbon nanotubes whose diameter is less than 100 nm, which is a novel nano material. Large-scale synthesis is possible with these optimum parameters to achieve maximum yield of carbon nanotubes. The optimum parameters suggested through this experiment are reaction temperature 920 °C , catalyst ratio 1:2 (50%) and the Ar gas volumetric flow rate to be 20 cm^3/min.

REFERENCES

Angulakshmi, V. S., Sivakumar, N. and Karthikeyan, S., Response Surface Methodology for optimizing Process Parameters for Synthesis of Carbon Nanotubes, *J. Environ. Nanotechnol.*, 1(1), 40-45 (2012). http://dx.doi.org/10.13074/jent.2012.10.121019

Faravelli, T., Pinciroli, M., Pisano, F., Bozzano, G.,Dente, M. and Ranzi, E., Thermal degradation of polystyrene, *J. Anal. Appl. Pyrolysis.*, 60, 103–121(2001).

Ferreiraa, S. L. C., Bruns, R. E., Ferreira, H. S., Matos, G. D., David, J. M., Brand, G. C., Da Silva, E. G. P., Portugal, L. A., Dos Reis, P. S., Souza, A. S. and Dos Santos, W. N. L., Box-Behnken design: An alternative for the optimization of analytical methods, 597, 179–186 (2007).

Kukovecz, A., Mehn, D., Nemes-Nagy, E., Szabo, R. and Kiricsi, I., Optimization of CCVD synthesis conditions for single-wall carbon nanotubes by statistical design of experiments (DoE), *Carbon.*, 43, 2842–2849 (2005).http://dx.doi.org/10.1016/j.carbon.2005.06.001

Michael, F. L., De Volder, Sameh, H., Tawfick Ray, H., Baughman, A. and John Hart., Carbon Nanotubes: Present and Future Commercial Applications, *Sci.*, 339, 1(2013).

Mukul Kumar and Yoshinori Ando, Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production, *J. Nanosci. Nanotechnol.,* 10, 3739-3758 (2010).

Setareh Monshi Toussi, Fakhru-Razi, A., Luqman Chuah, A. and Suraya, A. R. , Optimization of Synthesis Condition for Carbon Nanotubes by Catalytic Chemical Vapor Deposition (CCVD), OP Conf. Series: Materials Science and Engineering, 17, 012003 (2011).

Sumio Iijima, Helical Microtubules of graphitic carbon, *Nature.*,354, 7 (1991).

Tai, N. H., Chen, H. M., Chen, Y. J., Hsieh, P. Y., Liang, J. R. and Chou, T. W., Optimization of processing parameters of the chemical vapor deposition process for synthesizing high-quality single-walled carbon nanotube fluff and droving, *Compos. Sci. Technol.*, 72, 1855–1862 (2012).http://dx.doi.org/10.1016/j.compscitech.2012.07.019