Buletin Teknik Elektro dan Informatika
(Bulletin of Electrical Engineering and Informatics)
Vol.1, No.4, December 2012, pp. 305~312
ISSN: 2089-3191

Optimization of Flame Synthesis of CNT Structures using Statistical Design of Experiments (SDOE)

Rabinder Singh*, Akash Deep*, Jyoti Bharj, Nishtha Arya***
Department of Mechanical Engineering*
Department of Applied Physics**
Dr. B. R. Ambedkar National Institute of Technology, Jalandhar-144011, INDIA.
Tel: +91-181-2690301 Ext - 3110; Fax: +91-181- 2690324,
e-mail: bharjrs@nitj.ac.in

Abstract

A statistical designed experimental approach was followed to investigate the various diffusion flame conditions for the synthesis of carbon nanotube structures utilizing domestic Liquefied petroleum gas (IS – 4576) as the fuel carbon source. LPG flow rate, Oxygen flow rate, Height above burner (HAB) and Exposure time have been identified to generate different flame conditions based on varying One factor at a time (OFAT) approach. Two–level 'full factorial' design model in "Minitab12" software has been used for design of experiments. The 16 samples of soot with different flame conditions were collected on the surface of stainless steel plate. The output parameters i.e. weight of soot and substrate surface temperature were analysed by Analysis of variance (ANOVA) to ensure that the experimentation is following the physics of the diffusion flame. Transmission electron microscope (TEM) images showed the growth of well aligned single walled carbon nanotube structures with high aspect ratio as 220nm – 650nm diameter and 534nm – 1803nm length. In the present study the parametric range for producing the single walled carbon–nanotube structures through LPG diffusion flame have been found for optimization.

Keywords: Flame synthesis, carbon nanotube, design of experiment

1. Introduction

Formation of fibrous carbon in diffusion flames was first observed by Saito et al. while conducting soot characterization studies[1, 2]. The growth was observed at a certain height above the burner corresponding to colour change from brown to black. Later, Yuan et al. completed detailed characterization studies with ethylene– air co – flow and N_2 diluted ethylene– air diffusion flames to produce carbon nanotubes [3, 4, 5 and 6]. Vander Waal et al. reported similar results with premixed flame synthesis especially with an uncoated stainless steel mesh [7, 8, 9and 10]. Vander Wal et al. also utilized diffusion flame to produce SWCNTs at atmospheric pressure [11]. Later on more experiments were performed using counter flow diffusion flames for synthesis of MWNTs due to their 1-D geometry and convenience in positioning the catalyst substrate in the flame [12, 13,14, 15, 16, 17, 18and 19]. Merchan et al. recorded the formation of CNTs in a methane oxygen counter diffusion flame without any catalysts [16]. Currently, oxy-flames are being pursued for CNT synthesis due to the high temperature and radical concentration obtained at the flame location [17]. Encouraged by the potential of flame synthesis process Bharj et al. used domestic LPG as fuel and a gas welding torch to produce aligned SWCNTs. A stainless steel plate of thickness 2.5 mm has been used as substrate to collect the soot produced after the combustion of LPG. CNTs of length 325 nm to 616 nm corresponding to 2 mm diameter of nozzle at 140 mm standoff distance, substrate surface temperature of 625 K and flow rate of 1.8 LPM were obtained [20].

From the preceding investigations, it becomes evident that the combustion and flame synthesis method appears to meet the demands of Materials Science and Engineering in tailor making carbon nano structures with desired composition, structure and property. This fact can be better understood in relation to the success of the flame synthesis of paraffin candle wick method for the growth of CNTs [21]. Flames are scalable and are capable of commercially being used for the production of solid carbon forms such as carbon black and printing ink. Appropriately tailored flame conditions may provide an ideal environment for growth of CNTs on

Received August 12, 2012; Revised October 15, 2012; Accepted October 29, 2012

a large commercial scale. Thus this method has the potential and inherent advantages to become scalable commercial manufacturing technique of synthesis of desired quality of CNTs.

The traditional experimental strategy for optimization of any synthesis process is the OFAT approach. In this approach, one of the parameter remains constant and all others are varied turn by turn. The response of the system is studied as a function of the changing variables. The major shortcoming of this approach is the number of experiments grows very fast with the number of variables and levels of variation of each variable, thus, the complete optimization of real systems becomes unfeasible. The reason for this is that OFAT assumes that the effects of variables are completely independent, whereas the response of a real system to change in any single parameter appears often as the gross effect of several parameter alterations. Statistical design of experiments (DOE) is the science of obtaining the largest possible amount of information about a system with smallest number of experiments [22].

In the present study, we intend to prove that the DOE approach can be utilized successfully for the rapid optimization of flame synthesis of carbon nanotube growth. This study has been envisaged for the investigation of soot generated through domestic hydrocarbon fuel such as LPG (IS – 4576) by a simple continuous diffusion flame on a co–flow burner under open environmental conditions. ANOVA is used to analyse the interaction of various parameters to the response (Weight of soot and Substrate surface temperature) by making the interaction plots in Minitab 12. The formation of CNTs was confirmed by TEM. The goal of the optimization is to achieve the best parametric conditions of flame synthesis for growth of CNTs for specific carbon deposit quantity.

2. Experiment

2.1 Experimental setup

The experimental tests were carried out in a combustion test rig to study the correlation between flame conditions and the yield of CNTs. The schematic diagram of experimental setup is shown in Figure 1. The experimental setup consisted of the co-flow burner, substrate plate, traverse mechanism, acrylic sheet, gas cylinders (oxygen & LPG), rota meters, valves, hose pipes, thermocouple and thermocouple readout. The combustion takes place inside a transparent enclosed frame so that the flame is protected from the effect of surroundings and to allow the optical vision to the flame. The upper part of the frame is open to allow the exhaust gases to escape from inside the frame. The burner consists of simple tube – in – tube configuration. Two concentric tubes are arranged of diameters 10 mm and 50 mm respectively of length 200 mm. The traverse mechanism for the movement of the substrate is placed at the upper side of the frame. The base plate of traverse mechanism slides over the channels so as to move the assembly left & right. The substrate is a stainless steel plate of size 203×203 mm Grade 316 L. Gas supply system is designed to store and supply the fuel and oxidizer to the combustion chamber. LPG (IS – 4576) is used as fuel and pure oxygen (99.9% pure) is used as oxidizer. LPG cylinder is having maximum storage capacity 44 litres at 2 MPa pressure and oxygen cylinder can store 20 kg oxygen by weight at 700 MPa pressure. Two rota meters are used to measure the volume flow rate of the LPG as well as Oxygen both having range 0 – 25 litres per minute (lpm). A thermocouple wire (Al – Cr, K – Type) is attached on the substrate plate to sense its surface temperature on which the soot has to be deposited. The numerical value of temperature is displayed on a calibrated K – Type thermocouple readout between the range of 0 – 1200 ℃ with maximum linearity error ± 1.

2.2 Design of experiments (DOE)

When analysing a process, experiments are often used to evaluate in which process inputs have a significant impact on the process output, and what the target level of those inputs should be to achieve a desired result (output). Designed Experiments are powerful tools to achieve cost savings by minimizing process variation and reducing rework. In the present study, there are four parameters of the experimentation i.e. LPG flow rate, Oxygen flow rate, HAB and Exposure time. There can be many numbers off levels of variation of each parameter for the experimentation. For example: if we take 3 levels of each parameter the maximum possible number of experiments to be performed are 81. In actual practice each and every possible combination of different levels of these parameters is difficult to investigate and evaluate.

‘Minitab 12’ offers four types of designed experiments: factorial, response surface, mixture, and Taguchi (robust). The requirement of the present experimentation is to optimize the variation each and every parameter for the growth of CNTs with the minimum number of experiments without repetition. Efficient optimization requires the early identification of key process parameters. This can be achieved by assuming that all parameters generate a predominantly linear response which is measured by setting each parameter to a ‘‘low’’ and a ‘‘high’’ value. Such a ‘‘full factorial’’ design is usually unfeasible for real-life systems since 2^k runs are required for k parameters. So, 2 – level ‘full factorial’ design model is used with 4 factors. Minitab automatically generates the run order of all possible combinations. The minimum and maximum level of numerical values of each parameter is decided on basis of initial trials performed before the actual experimentation. In the initial trials the minimum values are decided at which the soot start depositing on the substrate and the maximum value is decided when the soot particles tends to burn out. Minitab automatically generates the run order of all possible combinations. Total 16 combinations flame parameters generated by the Minitab. The experiments can now be performed according to the generated run orders and obtain the desired Response (output).

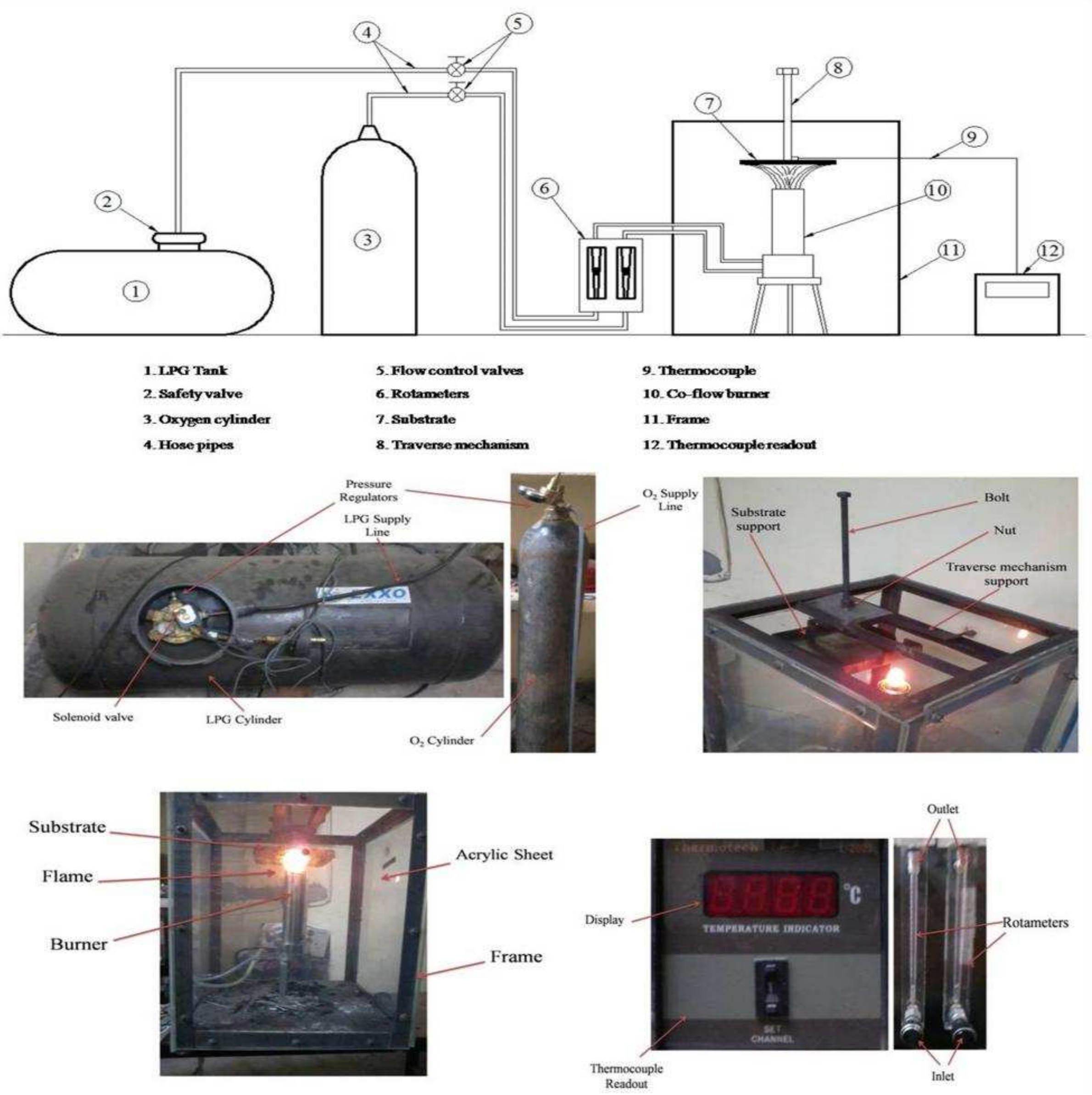


Figure 1. Schematic diagram of experimental setup

2.3 Sample preparation

Experiments were being performed as per the run orders, generated by Minitab, taking the respective parametric combinations of flame parameters. Normal Diffusion Flame (NDF) was created by the ignition of domestic LPG on the burner. Flame was enriched with pure oxygen to stabilize the flame as well as to change the flame conditions. Soot gets deposited on the substrate at various conditions of the flame.

2.4 Sample purification and filtration

Cross–flow micro filtration technique has been used to remove the impurities from the carbon material collected at the substrate .The samples were prepared by dispersion of the carbon material in ethanol using ultra sonication for 30 minutes. The collected soot was weighed both before and after filtration and it was found that net yield of purified soot varied between 81 to 89%. It was further observed that the purified soot powder was completely dissolved in distilled water.

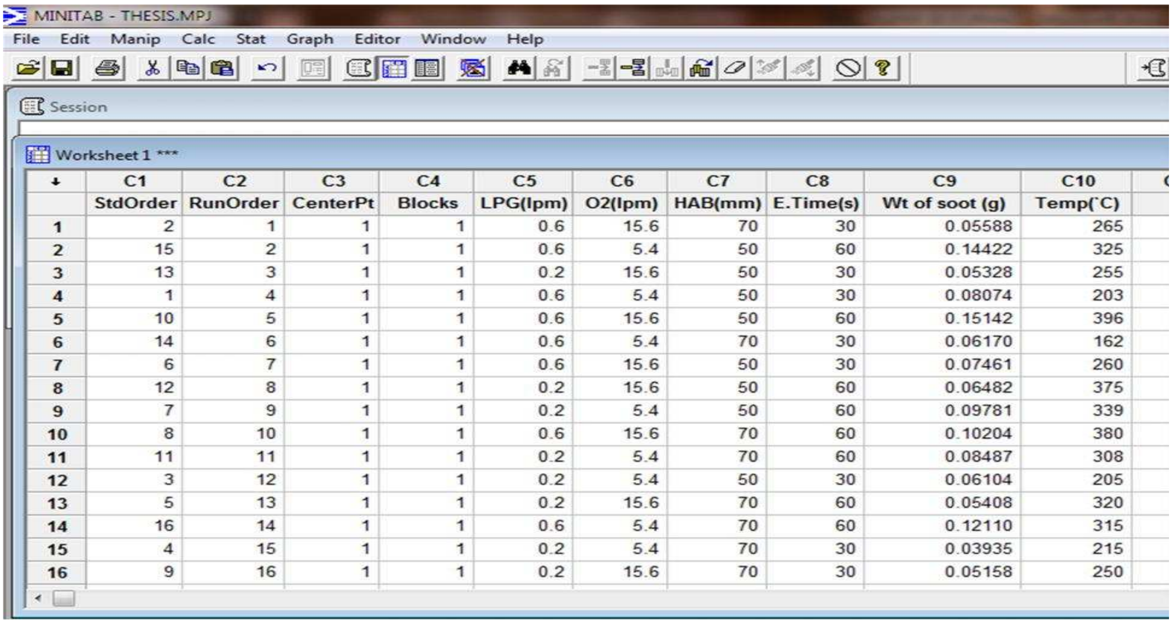
2.5 Sample characterization

The drops of dispersed material were dried and placed on copper carbon coated grid after negative staining for TEM analysis. TEM micrographs were recorded on high resolution "Philips CM-10" electron microscope instrument for the analysis of the deposited carbon material under "Sophisticated Analytical Instrumentation Facility (SAIF)" at Department of Anatomy, All India Institute of Medical Sciences (AIIMS), New Delhi.

3. Results and discussion

The numerical values of each response, obtained during the experimentation, were again put in the corresponding row in Minitab worksheet for the further analysis which is shown in Figure 2. Analysis of variance (ANOVA) is used to analyse the interaction of various parameters to the response (i.e. Weight of soot and Substrate surface temperature) by making the interaction plots in Minitab. Minitab automatically generates the interaction plots for both the responses by performing statistical analysis.

Figure 3. and Figure 4. shows the interaction plots for Weight of Soot and Substrate Surface Temperature respectively. Since we were interested in tuning the system towards high SWCNT yield, it requires the screening of unimportant variables from interaction point of view. From the interaction plots, it was observed that the oxygen flow rate and exposure time can be taken as



↓	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	StdOrder	RunOrder	CenterPt	Blocks	LPG(lpm)	O2(lpm)	HAB(mm)	E.Time(s)	Wt of soot (g)	Temp(˚C)
1	2	1	1	1	0.6	15.6	70	30	0.05588	265
2	15	2	1	1	0.6	5.4	50	60	0.14422	325
3	13	3	1	1	0.2	15.6	50	30	0.05328	255
4	1	4	1	1	0.6	5.4	50	30	0.08074	203
5	10	5	1	1	0.6	15.6	50	60	0.15142	396
6	14	6	1	1	0.6	5.4	70	30	0.06170	162
7	6	7	1	1	0.6	15.6	50	30	0.07461	260
8	12	8	1	1	0.2	15.6	50	60	0.06482	375
9	7	9	1	1	0.2	5.4	50	60	0.09781	339
10	8	10	1	1	0.6	15.6	70	60	0.10204	380
11	11	11	1	1	0.2	5.4	70	60	0.08487	308
12	3	12	1	1	0.2	5.4	50	30	0.06104	205
13	5	13	1	1	0.2	15.6	70	60	0.05408	320
14	16	14	1	1	0.6	5.4	70	60	0.12110	315
15	4	15	1	1	0.2	5.4	70	30	0.03935	215
16	9	16	1	1	0.2	15.6	70	30	0.05158	250

Figure 2. Worksheet of operating parameters and response variables

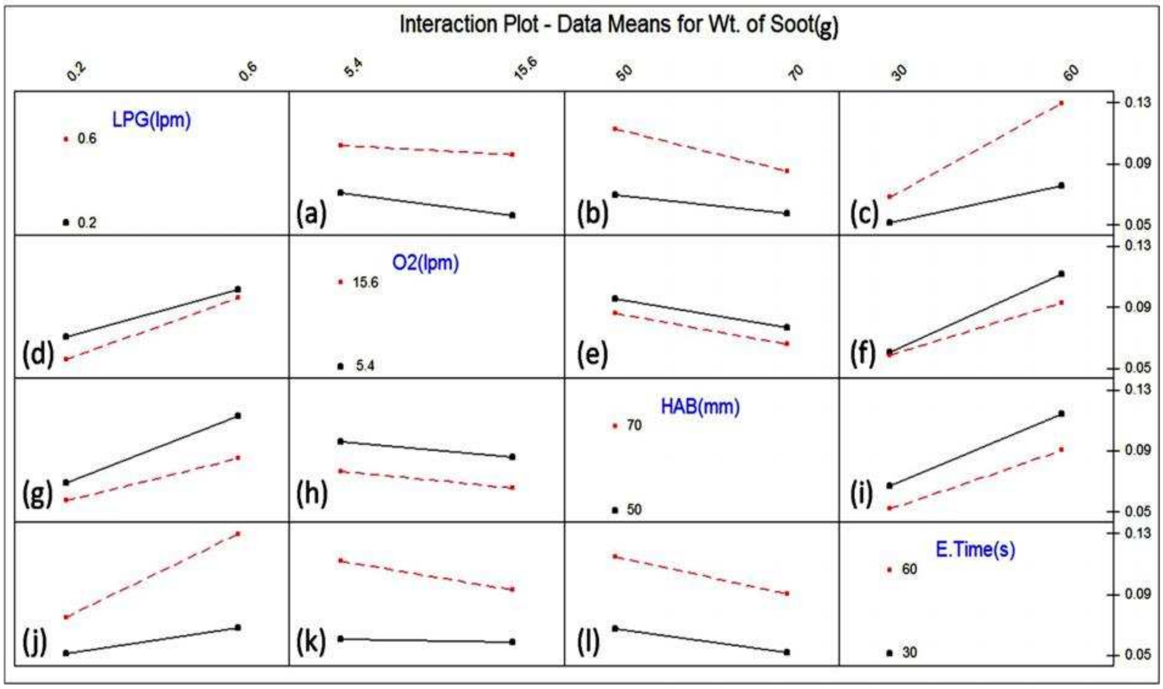


Figure 3. Interaction plot – Data means for Weight of Soot (g).

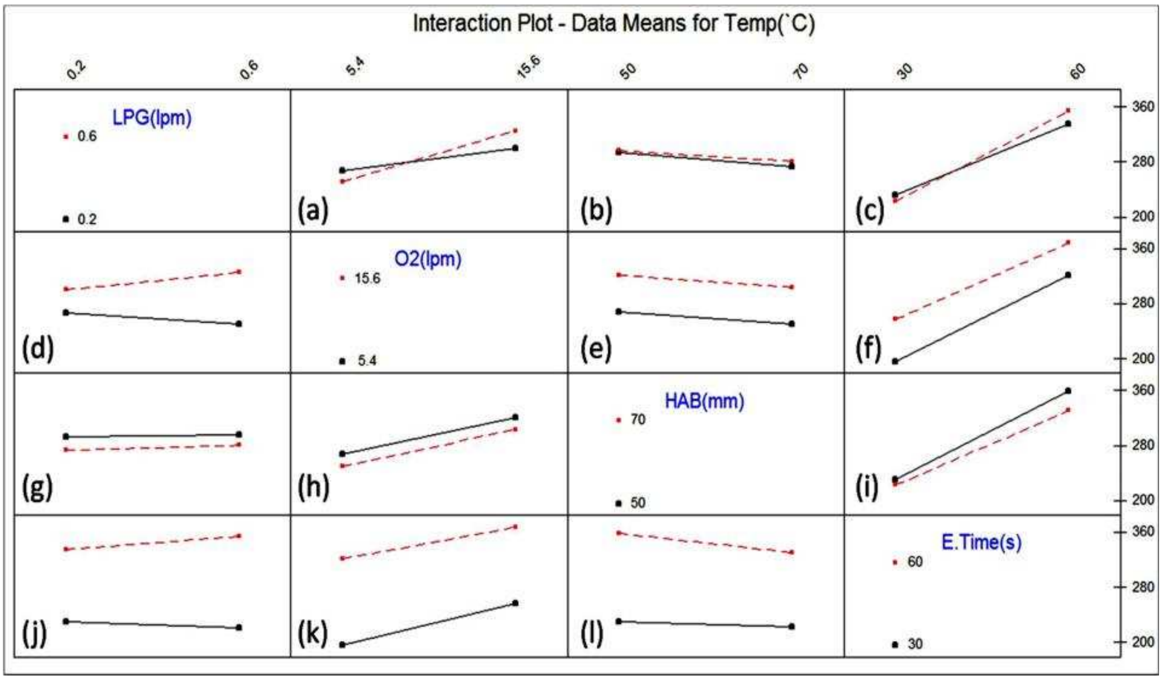
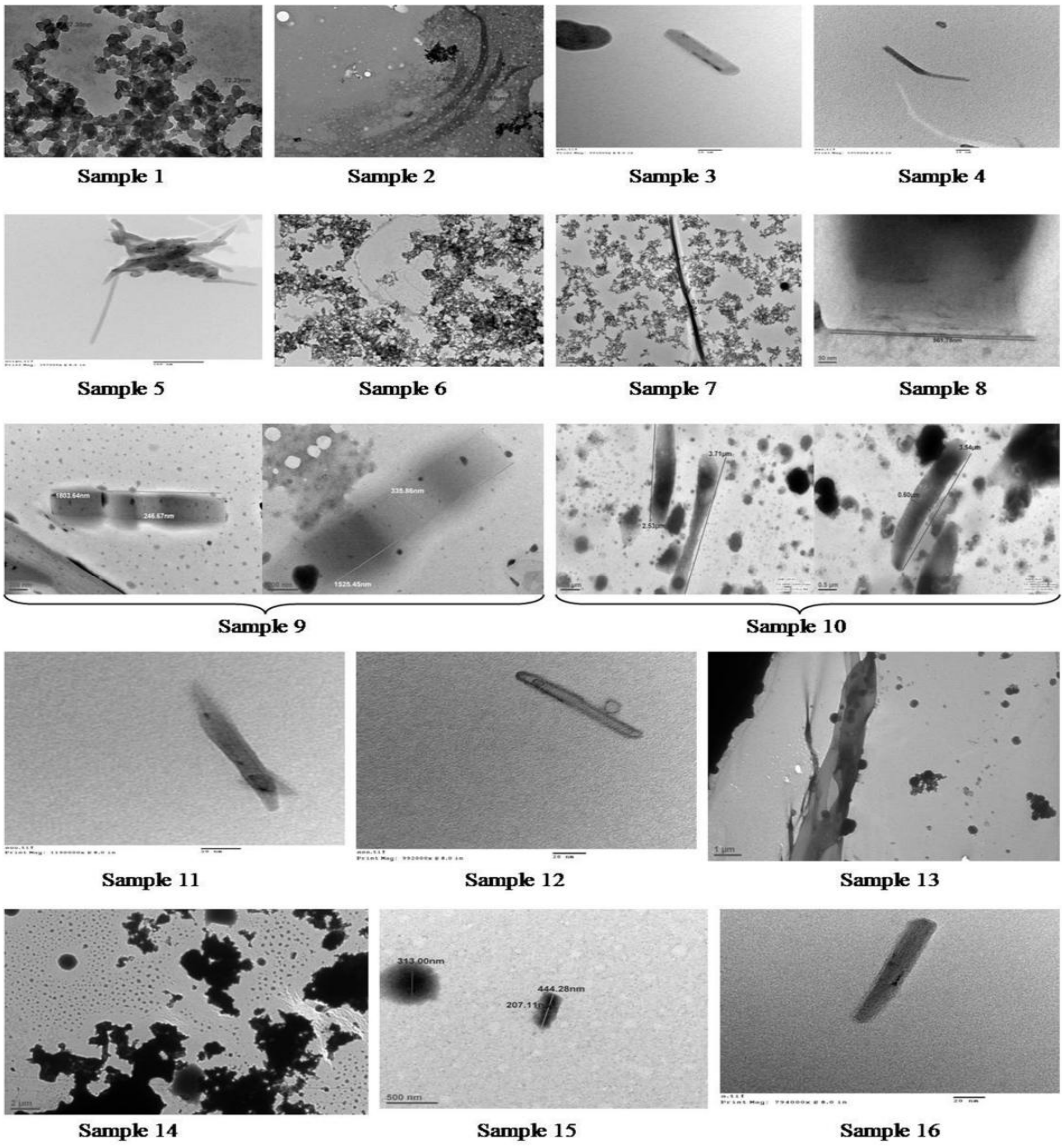


Figure 4. Interaction plot – Data means for Substrate Surface Temperature.

3.1. Effect of flow dynamics

It was observed that the flow rates of LPG and oxygen significantly influence the formation and characteristics of carbon nanostructures synthesized in different flame environments. When LPG flow rate of 0.2 lpm is made with oxygen flow rate of 5.4 lpm, a well-mannered growth of nanostructures was observed.



Sample 1 Sample 2 Sample 3 Sample 4

Sample 5 Sample 6 Sample 7 Sample 8

Sample 9 Sample 10

Sample 11 Sample 12 Sample 13

Sample 14 Sample 15 Sample 16

Figure 5. TEM images carbon nanostructures

The TEM images of the samples which include these particular proportions of flow rates of LPG and oxygen appeared with more clarity. The clarity of images indicates to the purity of the nanostructures. On the other hand when the same LPG flow rate was combined with the oxygen flow rate of 15.6 lpm very thin nanostructures were observed. So it can be assumed from the physics of flame that when the oxygen flow rate was more, the gas phase temperature in the flame is more due to which the size of the nanoparticles become small before the growth takes place and the grown nanostructures also very small in size as compared to others.

Similarly when the LPG flow rate of 0.6 lpm is made oxygen flow rate of 5.4 lpm the concentration of carbon is more as compared to LPG flow rate 0.2 lpm with same oxygen flow rate. The growth of nanostructures was observed in some samples and some of the samples come out with soot particles or under grown carbon particles. TEM images of samples of these particular proportions of LPG and oxygen flow rate indicates thick and dense nanostructures. Therefore it can be assumed that the samples may either contain burnt particles which could have been separated during the filtration or thick soot particles. On the other hand when the same LPG flow rate is made with oxygen flow rate 15.6 lpm, the relative flow rate almost becomes same as with LPG flow rate 0.2 lpm and oxygen flow rate 5.4 lpm. TEM images of these samples, indicates that the nanostructures are under grown.

3.2. Effect of sampling technique

Effective sampling was decided during the initial trials before the actual experimentation. According to visual observation the maximum visible flame length was approximately 75 to 90 mm. Substrate has to be placed within the luminous zone which starts somewhere above the burner and below the tip of the flame. The minimum exposure time was decided when the layers of soot starts depositing and the maximum exposure time was decided at which the soot deposited starts burning.

It was noticed that when the substrate was placed above the flame for 30 seconds, either there was no growth of nanostructures or there are under grown nanostructures and when the substrate was placed above the flame for 60 seconds, most of the samples have shown sufficient growth of nanostructures. In case of the samples taken at 70 mm HAB, most of samples showing growth of nanostructures are either not aligned or their growth is non-uniform. It was also noticed that the samples taken at HAB = 70 mm and for 30 seconds exposure time has not shown the growth of the nanostructures. The half of the samples taken at HAB = 70 mm and for exposure time 60 seconds have shown under grown carbon particles and half of the samples shown some growth but they are more dense and distorted or not aligned. The nanostructures of all the samples taken at HAB = 50 mm for 30 seconds exposure time are under grown but with 60 seconds exposure time, the sufficient growth of nanostructures was noticed.

3.3. Effect of substrate temperature

The experimental results showed that the substrate temperature also plays an important role in growth of CNTs. During the flame synthesis, the substrate temperature cannot be kept constant. Therefore the final temperature is recorded at the end of the set exposure time. The growth of CNTs has been observed when substrate surface temperature reached above 300 ℃. The effect of various experimental parameters on growth of CNTs is summarized in Table 1.

Table 1. Optimized parametric matrix for carbon nanostructures

Parameters	Parametric Range		Characterization of CNT structures
	LPG Flow rate	Oxygen Flow rate	
Flow dynamics (lpm)	0.2	5.4	Well aligned large sized CNTs, diameter 220 – 650 nm
		15.6	Well aligned small sized CNTs, diameter 2 – 5 nm
	0.6	5.4	Dense chains of carbon nanoparticles
		15.6	Thick cylindrical carbon nanostructures
HAB (mm)	50		Well aligned CNTs
	70		Irregular and curved CNTs
Exposure time (seconds)	30		Initiation of CNT formation
	60		Well aligned CNTs, diameter 220 – 650 nm
Substrate Temperature (℃)	162- 215		No growth
	250 – 285		Nanoparticles, diameter 20 – 73 nm
	308 – 320		Irregular and curved CNTs
	325 – 396		Well aligned CNTs, diameter 220 – 650 nm

4. Conclusion

We reported the successful application of statistical design approach of experiment for optimization of flame synthesis of carbon structures. This experimental study represents the effects of various flame parameters and resulting substrate surface temperature on the formation of carbon nanotubes and nanostructures. TEM micrographs confirm the presence of CNTs in the collected samples.

1. .It was found that there is a specific requirement of LPG and oxygen concentration for the growth of CNTs. The growth of CNTs was observed with two combinations of LPG, Oxygen flow rates i.e. 0.2 lpm, 5.4 lpm and 0.6 lpm, 15.6 lpm respectively.
2. The samples with the combination of LPG, Oxygen flow rate 0.6 lpm, 5.4 lpm were showing thick and dense carbon particles. This is due to high carbon concentration during the combustion. Whereas the samples with combination of LPG, Oxygen flow rate 0.2 lpm, 15.6 lpm were showing very thin carbon particles or small sized CNTs (~2nm diameter) were

observed. Therefore the size of nanostructures (in diameter) is strongly influenced by LPG, Oxygen concentration during the combustion. Therefore, more fuel concentration during the combustion gives dense and thick carbon particles whereas more oxygen concentration gives small size carbon particles.

3. The substrate surface temperature is also the important parameter which influences the growth of CNTs. It was observed that there were well grown and aligned CNTs when the substrate surface temperature is within the range of 325 – 396 ℃.

Acknowledgement

The authors are grateful to the management of Dr. B.R. Ambedkar National Institute of Technology, Jalandhar for giving necessary financial support to carry out this work.

References

[1] Saito, K., Gordon, A. S., Williams, F. A., & Stickle, W. F. A study of the early history of soot formation in various hydrocarbon diffusion flames. Combustion Science and Technology pp. 103-119, (1991).

[2] Saito, K., Williams, F. A., & Gordon, A. S. Structure of laminar co-flow methane air diffusion flames. Journal of Heat Transfer-Transactions of the ASME pp. 640-648 (1986).

[3] Yuan, Liming, Tianxiang Li and Kozo Saito. Growth mechanism of carbon nanotubes in methane diffusion flames. (2003).

[4] Yuan, Liming, Koso Saito, Chunxu Pan, F. A. Williams and A. S. Gordon. Nanotubes from methane flames. Chemical Physics Letters 340: pp. 237-241. (2001).

[5] Yuan L, Saito K, Pan C, Williams FA, Gordon AS. Nanotubes from methane flames. 340:pp. 237-41 (2001).

[6] Yuan, L. M., Saito, K., Hu, W. C., & Chen, Z.. Ethylene flame synthesis of well-aligned multi-walled carbon nanotubes. Chemical Physics Letters. pp. 23-28(2001).

[7] Vander Wal., Randall L. “Flame synthesis of substrate-supported metal-catalyzed carbon nanotubes.” Chemical Physics Letters 324: pp. 217-223 (2000).

[8] Vander Wal., Randall L. Flame synthesis of Ni-catalyzed nanofibers. Carbon 40:pp. 2101-2107 (2002).

[9] Vander Wal., Randall L. Fe-Catalyzed Single-Walled Carbon Nanotube Synthesis within a Flame Environment. Combustion and Flame.pp. 130: 37-47(2002).

[10] Vander Wal., Randall L. and Aaron J. Tomasek. Soot nanostructure: dependence upon synthesis conditions. Combustion and Flame 136: pp. 29-40 (2004).

[11] Vander Wal R.L, Ticich T.M, Curtis V.E. Diffusion flame synthesis of single-walled carbon nanotubes. Chem. PhysLett; 323 (3-4): pp. 217-23(2000).

[12] Hou, S.-S., Chung, D.-H., & Lin, T.H. High-yield synthesis of carbon nano-onions in counterflow diffusion flames. Carbon. Pp.938-947(2009).

[13] Li, T. X., Zhang, H. G., Wang, F. J., Chen, Z., & Saito, K. Synthesis of carbon nanotubes on Ni-alloy and Si-substrates using counterflow methane–air diffusion flames. Proceedings of the Combustion Institute, 1849-1856 (2007).

[14] Merchan-Merchan, W., Saveliev, A., & Kennedy, L. A. Carbon nanostructures in opposed-flow methane oxy-flames. Combustion Science and Technology. pp. 2217-2236 (2003).

[15] Merchan-Merchan, W., Saveliev, A., & Kennedy, L. A. High-rate flame synthesis of vertically aligned carbon nanotubes using electric field control. Carbon pp. 599-608 (2004).

[16] Merchan-Merchan, W., Saveliev, A., Kennedy, L. A. &Fridman A. Formation of carbon nanotubes in counter-flow, oxy-methane diffusion flames without catalysts. Chemical Physics Letters pp. 20-24 (2002).

[17] Merchan-Merchan, W., Saveliev, A. V., & Nguyen, V. Opposed flow oxy-flame synthesis of carbon and oxide nanostructures on molybdenum probes. Proceedings of the Combustion Institute, 1879-1886 (2009).

[18] Saveliev, A. Metal catalyzed synthesis of carbon nanostructures in an opposed flow methane oxygen flame. Combustion and Flame pp. 27-33 (2003).

[19] Xu, F. S., Zhao, H., & Tse, S. D. Carbon nanotube synthesis on catalytic metal alloys in methane/air counterflow diffusion flames. Proceedings of the Combustion Institute. pp. 31, 1839-1847 (2007).

[20] Jyoti bharj, sarabjitsingh, Subhash chander, Rabinder Singh. Flame synthesis of carbon nanotubes using domestic LPG. AIP conf. Poc. 1324,doi: 10.1063/1.3526241.

[21] Li YY and Hsieh CC. Synthesis of carbon nanotubes by combustion of a paraffin wax candle. Micro & Nano Letters 2-3 (2007).