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Biogas: A Natural and renewable Source for Carbon Nanotubes

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Abstract- Biogas produced from animal waste available from a domestic biogas plant has been used as a precursor gas to explore the presence of carbon related nanomaterials. Soot deposited on a stainless steel substrate by the Non Catalytic Open Flame Synthesis process was analyzed. Multiwalled Carbon nanotubes having diameter range 7 to 20 nm and length of 125 nm have been characterized using Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Raman Spectroscopy and X Ray Diffraction (XRD). Thermo Gravimetric Analysis (TGA) showed the purity of synthesized MWCNTs as nearly similar to commercial grade CNTs.

Index Terms- Biogas, Carbon Nanotubes, Flame Synthesis

1. INTRODUCTION

The large scale production and wide application of CNTs makes the selection of raw materials for their synthesis important. The influencing factors which should be considered when selecting a carbon source are the yield and quality of the CNTs produced. Hydrocarbons are the most frequently used carbon sources for the production of CNTs by different methods such as Arc Discharge, Laser Vaporization, Chemical Vapor Deposition and Flame Synthesis [1-4].

Gaseous hydrocarbon fuels such as Methane [5], Ethylene [6] and Acetylene [7] have been used for the synthesis of nanostructures because of their tendency to produce less amorphous carbon during combustion. Among all of the gaseous hydrocarbons, Methane is the most widely used and studied pure fuel even though it is quite expensive [9-12]. It is suitable for the generation of high quality Single and Multiwalled nanotubes (SWNTs and MWNTs) provided that appropriate catalysts and optimal technological regimes are implemented. Higher saturated hydrocarbons such as Liquefied Petroleum Gas (LPG) were successfully used for the production of multiwalled CNTs [13–15].

Aromatic hydrocarbons Benzene [8], Toluene [16] and Xylene [17] were also studied as potential carbon sources for CNTs production however they do not seem to offer substantial advantages over alkanes and alkenes and thus, were not widely used. Oxygen-containing organic compound such as ethanol was successfully used for the synthesis of CNTs [18-19] and it was found to be most suitable for obtaining SWNTs and DWNTs and less acceptable for MWNTs synthesis. Other non conventional liquid fuels, such as Turpentine oil [20], Mustard oil [21] and Eucalyptus oil [22] have been found suitable for the synthesis of CNTs. Some research groups have also reported synthesis of CNTs using solid fuels, prominent among them being commercial Paraffin wax candle [23] with simple wick method, Coal[24],Polythene waste [25] etc.

Commercial applications of CNTs have been rather slow to develop primarily because of the high production costs. The high price is due to the fact that CNT could be produced so far only on a laboratory scale, through different gas-phase processes using costly fuels and equipment and requires a complex cleaning and separating procedures. Comparatively cheaper fuel and less sophisticated equipment is needed to produce carbon nanotubes on bulk scale so as to reduce the cost of the material. Biogas is a renewable energy source which can be produced from regionally available raw materials and recycled waste and is environmentally friendly. Biogas is produced by fermentation of biodegradable materials such as manure, sewage, municipal waste, green waste, plant material, and crops and it comprises primarily of Methane (CH_4) , carbon dioxide(CO_2) traces of H_2S and fractions of H_2O vapors. Biogas was used as precursor for the synthesis of Carbon Nano Particles (CNP) in a CVD process [26]. From the available literature it seems that there is little work done on the flame synthesis of CNTs using this cheap fuel. The present work is a step in direction towards synthesizing CNTs through flame route using Biogas.

2. EXPERIMENTAL PROCEDURE

A simple experimental setup as shown in fig.1 consisting of a co-flow burner, substrate plate, traverse mechanism, acrylic sheet, Oxygen cylinder, rotameters, flow valves, hose pipes, thermocouple and thermocouple readout and a biogas tank (fix dome type) was used to carry out synthesis process. The traversing mechanism was used to adjust the horizontal and vertical movement of the Stainless Steel substrate plate (Grade 316 L and of size 203 × 203 × 3 mm) where soot was collected after the completion of experiment. A transparent acrylic sheet of 6 mm thickness enclosed the setup so that flame could be protected from the effect of surroundings, minimizing the flame disturbance and to allow the optical vision to the flame. The burner consisted of simple tube – in – tube configuration. Three concentric tubes of length 200 mm and diameters 10 mm, 50 mm and 62 mm respectively were arranged coaxially. Two rotameters have been used to measure the volume flow rate of Biogas as well as Oxygen both having range 0 – 25 liters per minute (lpm). Calibrated J Type thermocouple (temperature range 0-650°C) was attached on the substrate plate to sense the surface temperature on which the soot has to be deposited. Supply of Biogas was taken from a small domestic plant where animal waste was the main raw material. Substrate plate for the present study was kept at 45mm from the burner exit (HAB). Fuel flow rate was fixed at 1 lpm and an Oxygen flow rate was varied from1lpm to 2 lpm. with a residence time of 15 minutes as shown in the table1. Soot thus collected was scratched from the substrate and weighed. The collected sample was characterized without any purification.

3. RESULTS AND DISCUSSION

Biogas used as the precursor in the present work was taken from a domestic biogas plant. Gas chromatography was carried out to find the composition of the biogas used and calculation were done for methane and carbon dioxide percentage. Main constituent in the biogas was found to be Methane with 77% by volume and Carbon Dioxide with 23% by volume. SEM images were taken using a JEOL JSM - 6610LV microscope in conventional and high resolution mode. Operating at an accelerating voltage of (0.3 to 30 kV), magnification can be in the range of x5 to 300,000. SEM image of the CNTs synthesized from Biogas is shown in fig.2.This gives information about surface morphology of the sample and confirms the presence of CNTs in the sample.The surface morphology of the CNTs deposited seems to be uniform in nature. TEM images were taken using a Transmission Electron Microscope, Hitachi (H-7500) microscope in high resolution mode. It was operated at 40-120 kV with magnification at 3, 00,000x. Fig.3 shows the TEM micrograph of the carbon nanotube sample collected. It is seen that multiwalled CNTs in the range of outer diameter from 7 to 20 nm and inner diameter from 1.5 to 7 nm. were synthesized. Length of CNTs was approximately in the range of 125nm. The CNTs were made of parallel graphene planes oriented along the tube axis with amorphous carbon structure attaching onto their outer surfaces as no purification was carried out.

Fig. 4 shows the XRD spectra of the synthesized sample. The strong and sharp reflection peak at 27.78° shows that the CNTs are crystalline in nature. The peak (002) arises due to interlayer stacking of graphene sheets. . The presence of this peak in the XRD pattern of CNTs indicates the concentric cylindrical nature of graphene sheets nested together and the multiwalled structure of CNTs. The characteristic 0.32 nm inner layer spacing which provides evidence that highly ordered were CNTs present in sample. The average diameter of the CNTs present was calculated to be 16.20nm.

Using Scherrer Equation the diameter of nanotubes can be calculated

$$D = \frac{0.9\,\lambda}{(B \cos\theta)}$$

In the present sample, value of d = 3.208 Å and 2θ = 27.78°, θ 1.54 Å= .154nm, B (FWHM) = 0.502° = 0.00876 radian,

D is diameter of nanostructure = 16.20 nm

The grown CNTs were characterized by Renishaw invia Raman Microscope 51454 with He-Ar laser (514nm) with 50% laser strength. The ratio between the D band and G band is a indicator of the quality of CNTs in a sample. The Raman spectrum of CNTs synthesized by using biogas is shown in Fig. 5. The sharp peak at 1599.05 cm^{-1} the G band and the peak at 1339.34 cm^{-1} the D band. In this case the RBM was observed as a small peak which indicated very less quantity of SWCNTs as compare of MWCNTs confirming the results obtained from TEM analysis. The intensities corresponding to G and D bands were 826.025 counts and 730.229 counts respectively. In this case the value of I_D/I_G was calculated as 0.88. This intensity ratio indicated higher

orders of the CNTs are present in sample. Fig. 6 shows the weight loss curve for the CNTs synthesized. TGA measures the decrease in sample mass as a function of annealing temperature. Because CNTs generally have

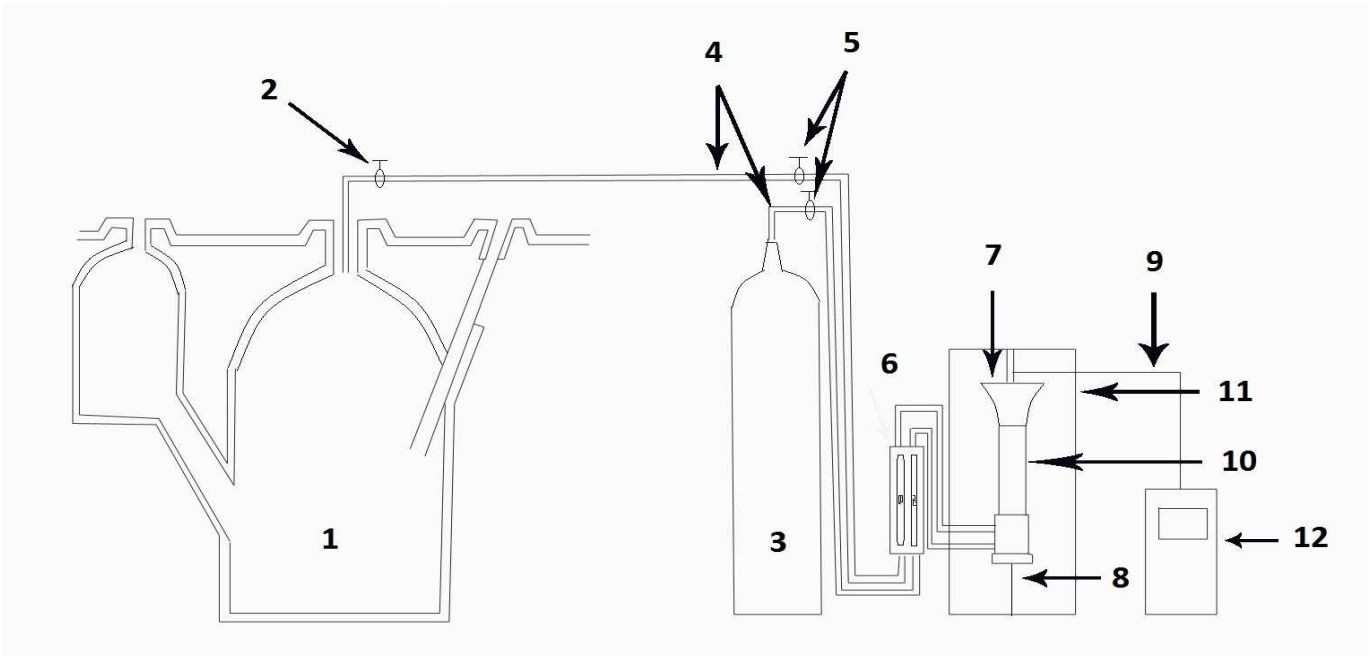

Fig.1: Schematic diagram of the experimental set up

1.Fixed dome type Biogas plant 2.Regulator 3.Oxygen cylinder 4.Hose pipes 5.Flow control valves 6.Rotameters 7.Substrate 8.Traverse mechanism 9.Thermocouple wire 10.Co-flow burner 11.Enclosure 12.Thermocouple readout

Table1. Parameters for bulk production of CNTs using Biogas

S. No.	Oxygen flow rate (lpm)	Biogas flow rate(lpm)	HAB(mm)	Weight of soot (gm / min.)	Residence Time (min.)	Total soot collected (gm)	Temperature range (°C)
1	1	1	45	0.00833	15	3	410
2	2	1	45	0.00867	15	3.15	420

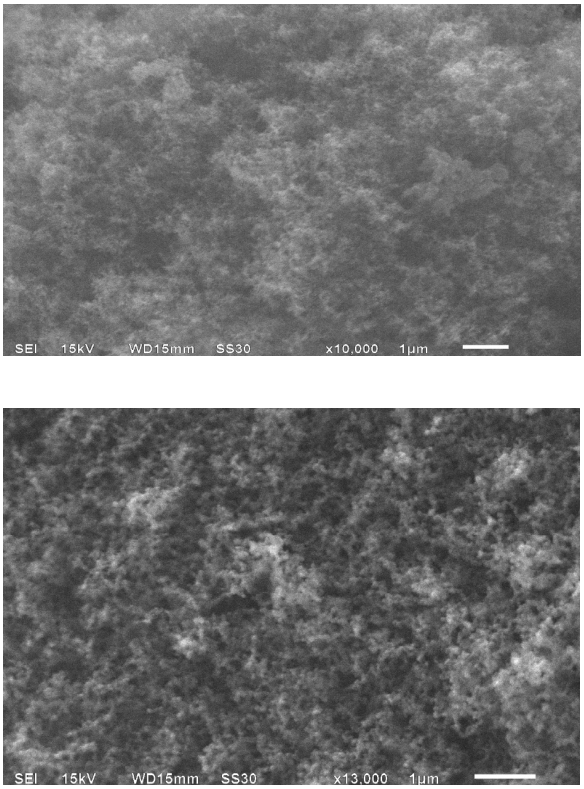

Fig. 2. SEM image of CNTs synthesized using biogas

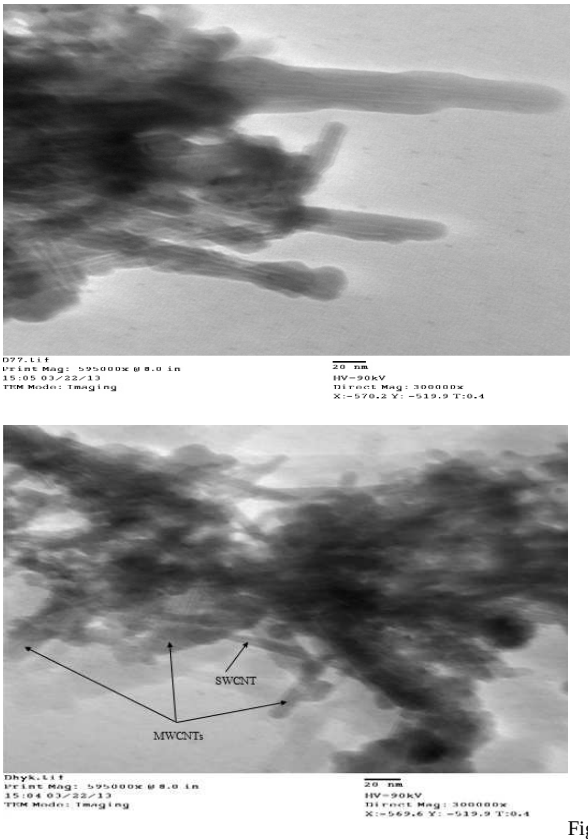

Fig. 3.TEM images of CNTs synthesized using biogas

higher decomposition temperatures than adsorbed molecules and amorphous carbon, TGA data can be used to estimate CNT purity and the presence and concentration of organic molecules attached to CNT sidewalls. The oxidation peak temperature of the synthesized sample was observed at 540 °C, which is an indicative of the overall quality of the nanotube material. The oxidation and thermal degradation of sample was observed from the graph at this temperature and the derivative weight was found to be 95 %.

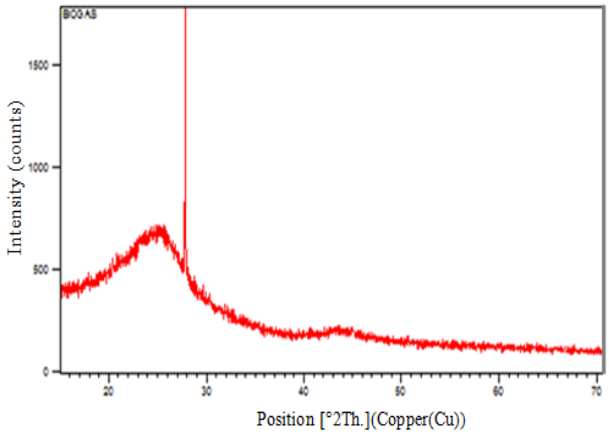

Fig. 4 XRD pattern of CNTs synthesized using biogas

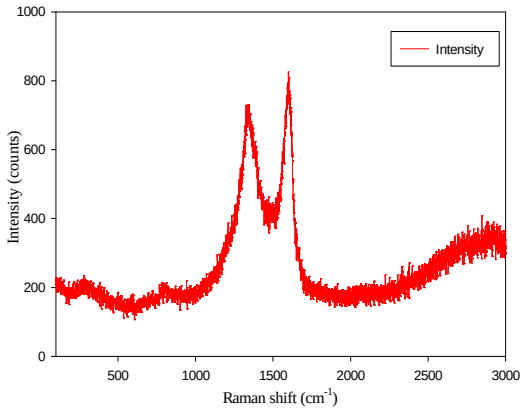

Fig. 5 Raman spectra of CNTs synthesized by using biogas

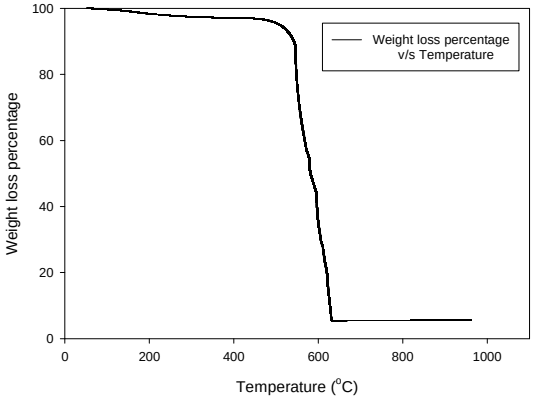

Fig. 6. Thermo gravimetric analysis of CNTs showing weight loss.

4. CONCLUSIONS

The present work demonstrates that carbon nanotubes were synthesized in diffusion flames at atmospheric pressure without the introduction of a catalyst using Biogas as carbon source. The well aligned MWCNTs in diameter range of 7-25nm and lengths upto 125nm were present in the soot sample which was confirmed by the small RBM peak in Raman Spectroscopy. The diversity in diameters and lengths of formed nanotubes is attributed to the strong variation of flame properties along the flame axis including temperature and hydrocarbon radicals. Characterization of unpurified sample reveals that the MWCNTs grown have comparable quality as CNTs grown with other methods and using different fuels as reported by different research groups. The purity of synthesized CNTs has been found to be 90-95% with the help of Thermo gravimetric analysis which is much closer to commercially available CNTs. This research opens the possibility that CNTs can be grown in simple oxy-fuel flames using Biogas as precursor gas.

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REFRENCES

[1] Ebbesen, T W & Ajayan, P M. (1992). Large-scale synthesis of carbon nanotubes, *Nature*, 35, 220-222.

[2] Guo, T, Nikolaev P, Thess A. (1995). Colbert D T & Smalley R E Catalytic growth of single-walled nanotubes by laser vaporization, *Chem. Phys. Lett.*, 243-49.

[3] Andrews R, Jacques D, Rao A M, Derbyshire F, Qian, D, Fan X, Dickey E C & Chen J. (1999). Large-Scale Synthesis of Aligned Carbon Nanotubes, *Chem.Phys. Lett.* 303-467.

[4] Vander Wal R L, Ticich T M, & Curtis V E. (2000). Diffusion flame synthesis of single-walled carbon nanotubes, *Chem. Phys. Lett.* ,323:217.

[5] Yuan L, Saito K, Pan C, Williams F A, Gordon A S. (2001). Nanotubes from Methane Flames, *Chemical Physics Letters* 340, 237-241.

[6] Lee G W, Jurng J & Hwang J. (2004). Formation of Ni-catalyzed multiwalled carbon nanotubes and nanofibers on a substrate using an ethylene inverse diffusion flame, *Combustion and Flame* 139, 167–175.

[7] Height M J, Howard J B & Jefferson W. (2005). Flame synthesis of single-walled carbon nanotubes. *Tester Proceedings of the Combustion Institute* 30, 2537–2543.

[8] Duan H M & McKinnon J T. (1994), Nanoclusters Produced in Flames. *The Journal of Physical Chemistry* 98.

[9] Liming Y, Tianxiang L and Saito K. (2002). Synthesis of Multiwalled Carbon Nanotubes using Methane/Air Diffusion Flames. *Proceedings of the Combustion Institute* 29, 1087–1092.

[10] Merchan-Merchan W, Saveliev, A, Kennedy L A & Fridman A. (2002). Formation of carbon nanotubes in counter-flow, oxy-methane diffusion flames without catalysts, *Chemical Physics Letters* 354, 20–24.

[11]Yuan L, Li T & Saito K. (2003). Growth mechanism of carbon nanotubes in methane diffusion flames, *Carbon* 41,1889–1896.

[12] Merchan-Merchan W, Saveliev A V & .Kennedy L A. (2004). High-rate flame synthesis of vertically aligned carbon nanotubes using electric field control, *Carbon* 42, 599–608.

[13]Qian W & Yu H. (2002). Synthesis of carbon nanotubes from liquefied petroleum gas containing sulfur, *Carbon* 40, 2968–2970.

[14]Qiang Z, Huang J, Wei F, Xu G, Wang Y, Qian W & Wang D. (2007). Large scale production of carbon nanotube arrays on the sphere surface from liquefied petroleum gas at low cost, *Chinese Science Bulletin* 21, 2896-2902.

[15]Ndungu P & Nechaev A. (2008). Carbon nanomaterials synthesized using liquid petroleum gas: Analysis toward applications in hydrogen storage and production, *Int. J. of Hydrogen Energy* 33, 3102–3106.

[16]Yuanzhu M, Yingliang L, Dingsheng Y, Jingxian Z &Yong X. (2005). Synthesis of carbon nanotubes via toluene-thermal

Reduction process at moderate temperature, *Journal of Material Science* 40, 3635-3638.

[17]Clarence S Y, Sunny E I, Geoffrey S S, Emmanuel I U, Graham B, George M & John D C. (2011). Continuous synthesis of multiwalled carbon nanotubes from xylene using the swirled floating catalyst chemical vapor deposition technique, *Journal of Materials Research* 26, 640-644.

[18]Pan C, & Xu X. (2002). Synthesis of carbon nanotubes from ethanol flame, *Material Science Letters* 21, 1207–1209.

[19]Pan C & Bao Q. (2002). Well-aligned carbon nanotubes from ethanol flame. *Material Science Letters* 21, 1927–1927.

[20]Ghosh P, Soga T, Afre RA & Jimbo T. (2008). Simplified synthesis of single-walled carbon nanotubes from a botanical hydrocarbon: Turpentine oil, *Journal of Alloys and Compounds* 462, 289-293.

[21]Dubey P, Muthukumaran D, Dash S, Mukhopadhyay R & Sarkar S. (2005). Synthesis and characterization of water-soluble carbon nanotubes from mustard soot, *PRAMANA Indian Academy of Sciences* 65.

[22]Ghosh P, Afre R A, Soga T & Jimbo T. (2007). A simple method of producing single-walled carbon nanotubes from a natural precursor: Eucalyptus oil, *Materials Letters* 61, 3768-3770.

[23]Li Y & Hsieh C. (2007). Synthesis of carbon nanotubes by combustion of a paraffin wax candle, *Micro & Nano Letters*, 2-3.

[24]Jieshan Q Z W, Zongbin Z & Tonghua W. (2007). Synthesis of double-walled carbon nanotubes from coal in hydrogen-free atmosphere, *Fuel* 86, 1–2, 282–286.

[25]Zhuo C, Hall B, Levendis Y & Richter H. (2011). A Novel Technology for Green (er) Manufacturing of CNTs via Recycling of Waste Plastics, *MRS Proceedings* 04, 1317 (05):06.

[26]Vamathevan K, Gunasekera M & de Alwis A. (2012). The Development of a Process to Synthesize Carbon Nanotubes from Biogas, *Annual Transactions of IESL*, 33-37.