OPTIMISING CARBON NANOTUBE CONTINUOUS PRODUCTION IN A SWIRLED FLOATING CATALYST CHEMICAL VAPOUR DEPOSITION REACTOR

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ABSTRACT

Effects of various factors affecting the rate of Carbon Nanotubes (CNTs) produced in a Swirled Floating Catalyst Chemical Vapour Deposition (SFCCVD) reactor were investigated. This study was performed in a vertical silica tube plug flow reactor developed by Iyuke at this University. Transmission Electron Microscopy (TEM) images revealed that both Single–Walled and Multi–Walled Carbon Nanotubes were produced continuously by this method. Experimental results also showed that pyrolysis/reaction temperature, acetylene flow rate, hydrogen flow rate and ratio of acetylene to hydrogen flow rate affect the rate of production of carbon nanotubes. Maximum production rate of 0.31g/min was obtained at operating conditions of acetylene flow rate of 370ml/min, hydrogen flow rate of 180ml/min and pyrolysis temperature of 1000°C. It is worth mentioning that to the best of our knowledge such CNTs production rate and technique have not been reported in the open literature

1.   INTRODUCTION

An enormous interest has been directed towards the synthesis, characterisation and application of carbon nanotubes (CNTs) since their discovery by Iijima in 1991 (Iijima, 1991). This is due to their unique and extraordinary mechanical and electronic properties which make them versatile in many applications such as batteries (Che et al, 1999); flat panel display (Wilder et al, 1998); composites (Shaffer, 2004); chemical sensor (Kong et al, 2000); transistor and catalyst support in fuel cell (Li et al, 2004; Chan et al, 2004; Matsumoto et al, 2004 and Rajesh et al, 2002). This has necessitated their commercial production to meet this increasing demand. Among many other production methods, Catalytic Chemical Vapour Deposition (CCVD) has been identified as the best method for mass synthesis of these materials (Couteau et al, 2003; Kathayini et al, 2004 and Goddard et al, 2003).

Various catalysts and carbon sources have been employed in CCVD production of CNTs (Iyuke and Danna, 2005; Mitri and Sotirchos, 2005; Unalan and Chhowalla, 2005; Kuwana and Saito, 2005 and Wang et al, 2002). This work reports the synthesis of CNTs from acetylene source and using ferrocene as the catalyst (Fe) source. The effects of change in reaction temperature and the flow rates of the carrier and carbon source gases on the production rate of CNTs are also studied. This CNTs production technique is continued in this laboratory into mass production of CNTs for synthesis of great performance Membrane Electrode Assembly (MEA) for Proton Exchange Membrane (PEM) fuel cell application.

2.   EXPERIMENTAL

The apparatus used for the CNTs production is the one developed by Iyuke (2005), presented schematically in Figure 1. It consists of a vertical silica plug flow reactor [1] immersed in a furnace [2] with a sensitive temperature regulator. A system of rotameters, pressure controllers and valves controls the flow of hydrogen, nitrogen, argon

and acetylene gases into the reactor. The upper end of the reactor is connected to a condenser [3] which leads to two delivery cyclones [4 &5] where the CNTs produced are collected. The ferrocene catalyst used was poured into a silica vaporiser [6] placed on a heater with a sensitive temperature regulator. This catalyst vaporiser is connected to the swirled mixer [7] which in turn leads into an inlet leading into the reactor.
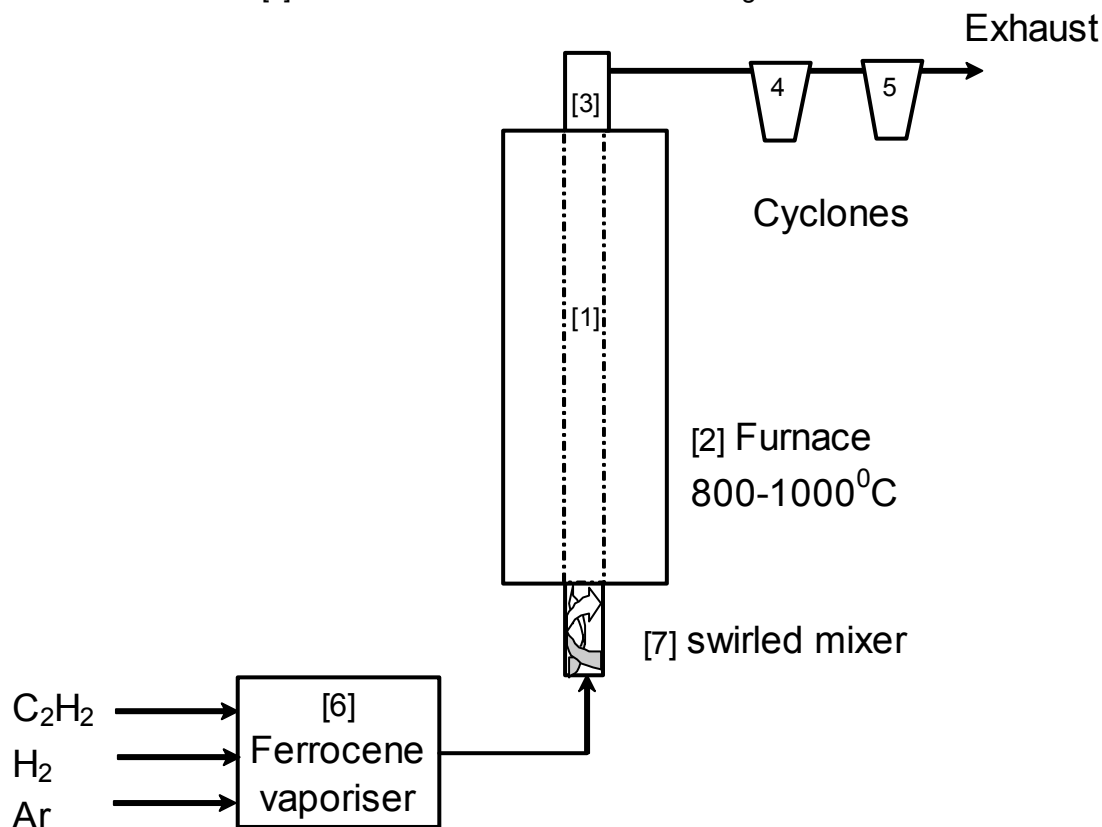
Exhaust

Cyclones

[2] Furnace
800-1000^{0}C

[7] swirled mixer

C$_2$H$_2$
H$_2$
Ar

[6] Ferrocene vaporiser

Figure 1: *Schematics of swirled floating catalyst chemical vapour deposition reactor (Iyuke 2005)*

Nitrogen was first turned on to purge the system of any impurity. The reactor and ferrocene heater were switched on while the nitrogen was running. At reactor temperature of about 300°C, nitrogen was turned off to prevent it from reacting with oxygen. Argon was then turned on at prescribed flow rate to continue purging and act as a carrier gas. At reactor temperature of 900°C, 950°C and 1000°C and catalyst heater at 150°C, 5 grams of ferrocene was charged into the heater at intervals while hydrogen and acetylene gases were turned on at specified flow rates. The system was allowed to run for 10 minutes after which the ferrocene had been exhausted. The smoky products or carbon vapour evolved from the reactor was cooled at the condenser and collected in the cyclones. The wall of the reactor was also scrapped clean of CNTs.

3.   RESULTS AND DISCUSSION

CNTs were synthesized at different pyrolysis/reaction temperatures, flow rates of acetylene and hydrogen. Acetylene was used as carbon source and CNTs produced were collected at different points of the equipment namely: Cyclone [4], Cyclone [5] and Reactor. Figures 2-3 show the TEM micrographs of CNTs produced. The images reveal that the products in cyclone [4] is a mixture of Single-Walled Carbon Nanotubes (SWNTs) and Multi-Walled Carbon Nanotubes (MWNTs) as shown in Figures 2 a and b respectively while the samples from cyclone [5] and reactor only confirm the presence of MWNTs as observed in Figures 3 a and b. However, the CNTs collected at all the points are free of iron particles and contain less amorphous carbon as revealed in

Figures 2-3. This could be attributed to the nature of catalyst used and the starting pyrolysis temperature as explained by Lewis and Smith (1984) cited by Kuwana and Saito (2005).
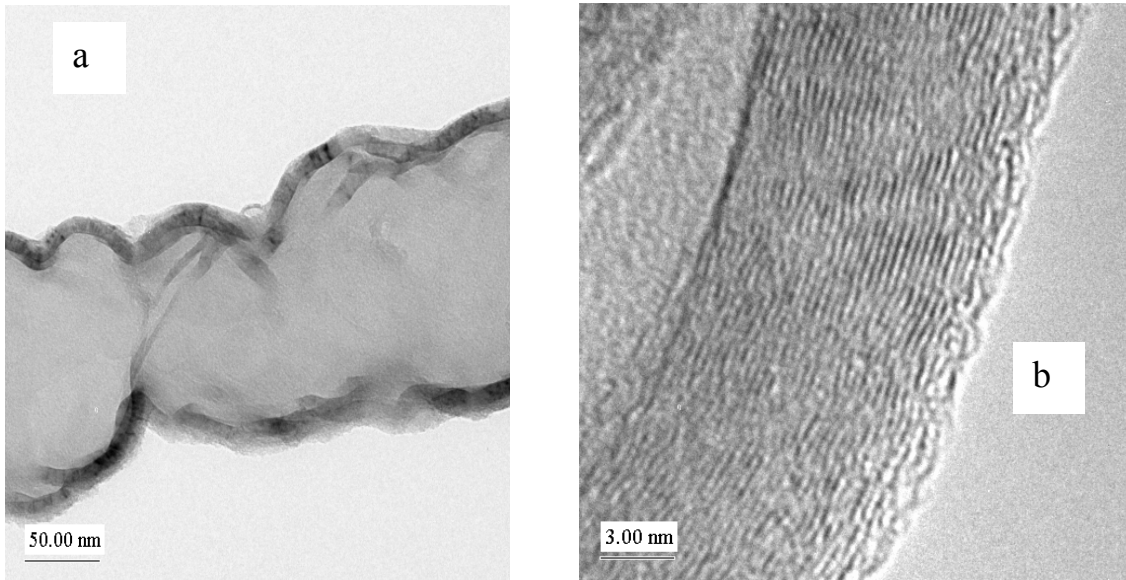

Figure 2: *TEM images (a) SWCTs in cyclone [4], (b) MWCTs in cyclone [4]*
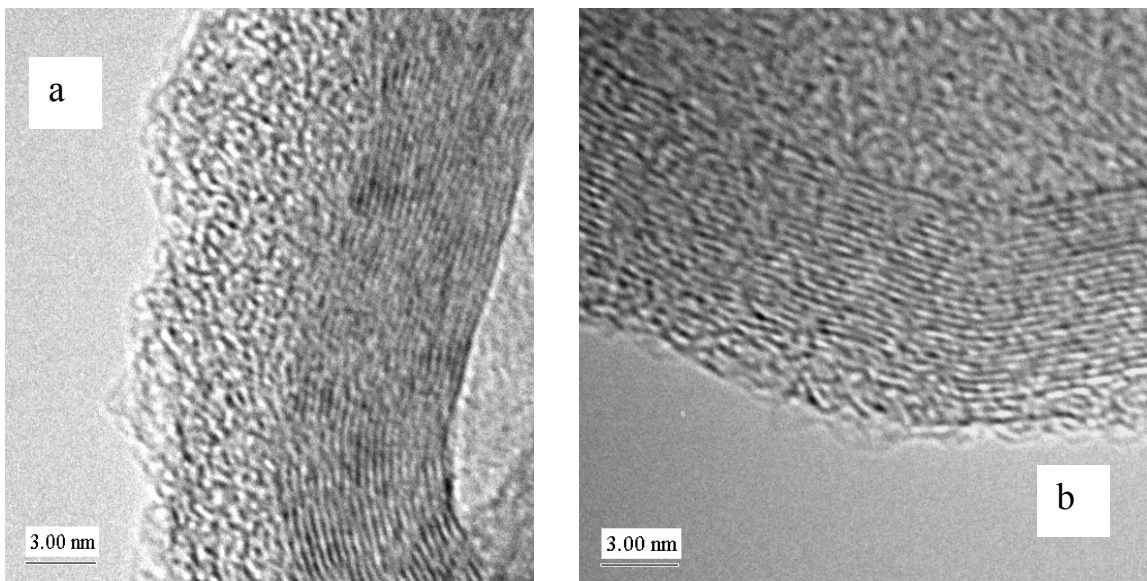

Figure 3: *TEM images (a) MWCTs in cyclone [5], (b) MWCTs on reactor [1] wall*

Figure 4 shows the effect of acetylene flow rate on production rate of CNTs at various temperatures. It is observed from the Figure that the CNTs production rates increase with increase in acetylene flow rate at temperatures 900°C and 950°C while a slight decrease in CNTs production rate was observed at acetylene flow

rate of 370ml/min at 1000°C. The Figure also reveals that the maximum CNTs production rate was obtained at the acetylene flow rate of 370ml/mi and temperature of 1000°C when hydrogen flow rate was 118ml/min. This is in contrast to the report of Liu et al, (2002) when no CNTs were found at such a temperature though these authors used $Fe(CO)_5$ as catalyst and pentane carbon source. The figure also indicates that the higher the flow rate of carbon source the more the CNTs quantity produced at a given time. This also disagrees with the findings of Unalan and Chhowalla (2005) where CNTs production rate was not enhanced at higher flow rate of ethanol carbon source due to introduction of more oxygen. These discrepancies could be attributed to the different types of reactors used by these authors as compared to this work. Liu et al, (2005) and Unalan and Chhowalla (2005) used horizontal semi-continuous reactor for CNTs synthesis while a vertical swirled floating catalyst continuous reactor was used in this work.

The effect of different flow rates of acetylene: hydrogen ratio on production rate of CNTs at different temperature range of 900-1000°C is shown in Figure 5. The Figure shows that the rate of production initially increases with increase in C_2H_2/H_2 ratio at all the temperatures. Different CNTs production rate peaks were observed for different C_2H_2/H_2 at different temperatures. However, the highest CNTs production rate was observed at 1000°C and this corresponds to C_2H_2/H_2 of 5 the flow ratio of while the minimum CNTs production rate was obtained at flow ratio C_2H_2/H_2 of 1 at 950°C and 1000°C. This reveals the influence of hydrogen in the production of CNTs. Hydrogen is not only required to create velocity profile in the reactor but also takes part in the pyrolysis of acetylene. According to Kuwana et al, (2005), the three stages of reaction during pyrolysis of acetylene to give CNTs confirm the major role of hydrogen as shown in the equations below:

$$C_2H_2 \rightarrow 2C + H_2 \qquad\qquad\qquad\qquad\qquad\qquad\text{(i)}$$
$$C_2H_2 + 3H_2 \rightarrow 2CH_4 \qquad\qquad\qquad\qquad\qquad\text{(ii)}$$
$$2CH_4 \rightarrow 2C + 4H_2 \qquad\qquad\qquad\qquad\qquad\text{(iii)}$$

The overall reaction is therefore:

$$2C_2H_2 \xrightarrow{\;Fe(C_{10}H_{10})\;} 4C + 2H_2 \qquad\qquad\qquad\qquad\text{(iv)}$$

It could be observed from equation (iii) that the methane produced in equation (ii) decomposed at reactor temperature to produce CNTs and hydrogen. The above also confirms the important role of the ratio of carbon source to hydrogen for good and high quality production of CNTs. The inset is a high quality, long and pure CNT obtained at C_2H_2/H_2 ratio equal to 5 and CNT production rate of 0.32 g/min.

From the experimental results shown in Figure 6, at various hydrogen flow rate, constant acetylene flow rate and temperature range of 900-1000°C. It is observed from the Figure that the highest production rate of CNTs was obtained at hydrogen flow rate of 181 ml/min for 900 and 1000°C, while the maximum rate was obtained at hydrogen flow rate of 118 ml/min when the pyrolysis temperature is 950°C. At higher flow rate of hydrogen, the rate of CNTs produced decrease, this could be attributed to low residence time of the reactant in the reactor because hydrogen will create high velocity profile and thereby push off the acetylene away at a faster rate from the reaction zone of the reactor.

The effect of temperature on CNTs production rate at various ratios of acetylene and hydrogen is presented in Figure 7. The results show that at flow ratio of 1.492, 2.102 and 2.61 the rate of CNTs produced increased linearly with temperature, while at flow ratio of 2.044, the rate of CNTs produced decreased as the pyrolysis temperature changes from 900 – 950°C and increases again at pyrolysis temperature above 950°C. When the flow ratio of acetylene and hydrogen is 1.534 and 3.136, the rate of CNTs increases between temperatures range of 900 – 950°C and decreases above 950°C. This is an inverse of the results obtained when the flow ratio is 2.044 at same temperature range of 900 – 950°C.
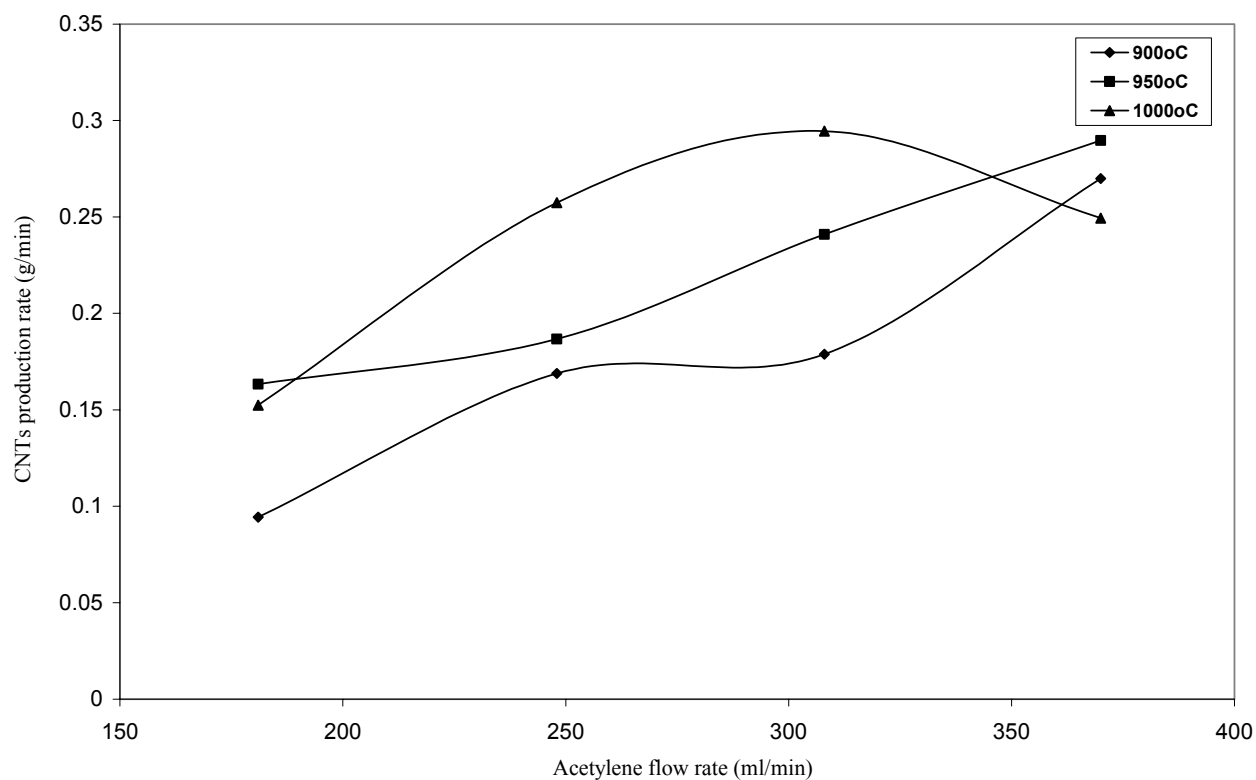
Figure 4:Effect of acetylene flow rate on CNTs production rate
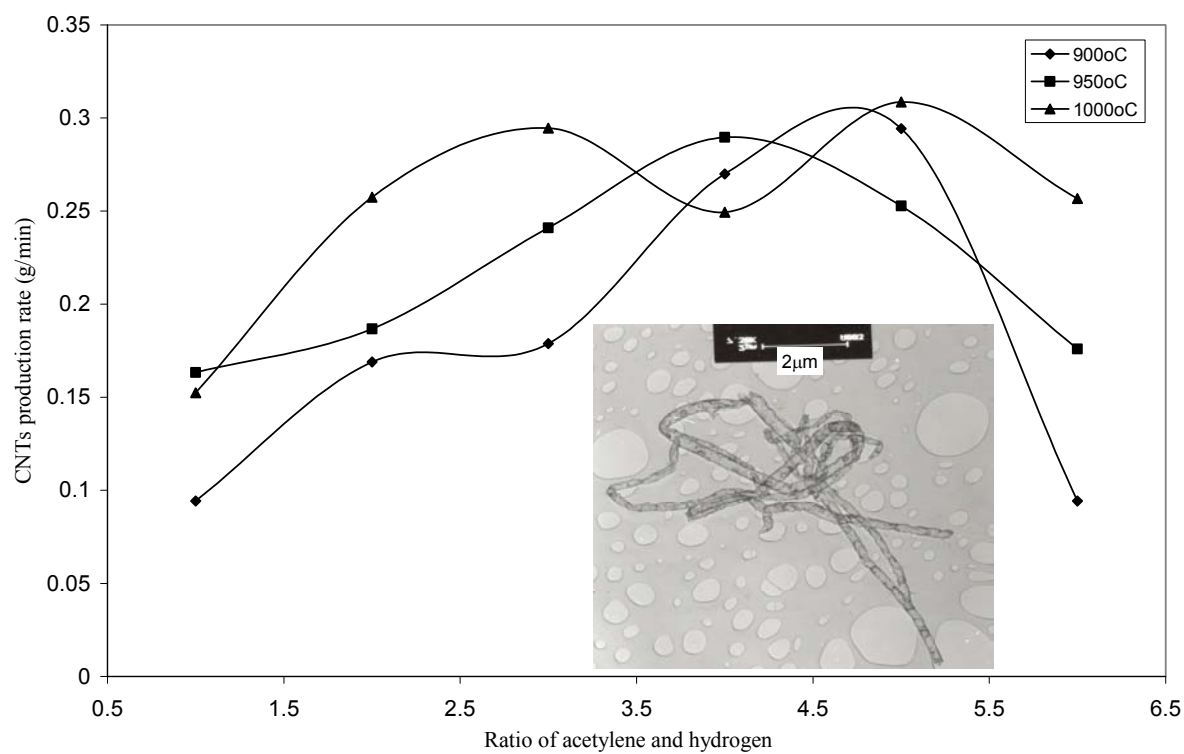

Figure 5: Effect of ratio of acetylene and hydrogen at various temperature on CNTs production rate [inset is CNT]
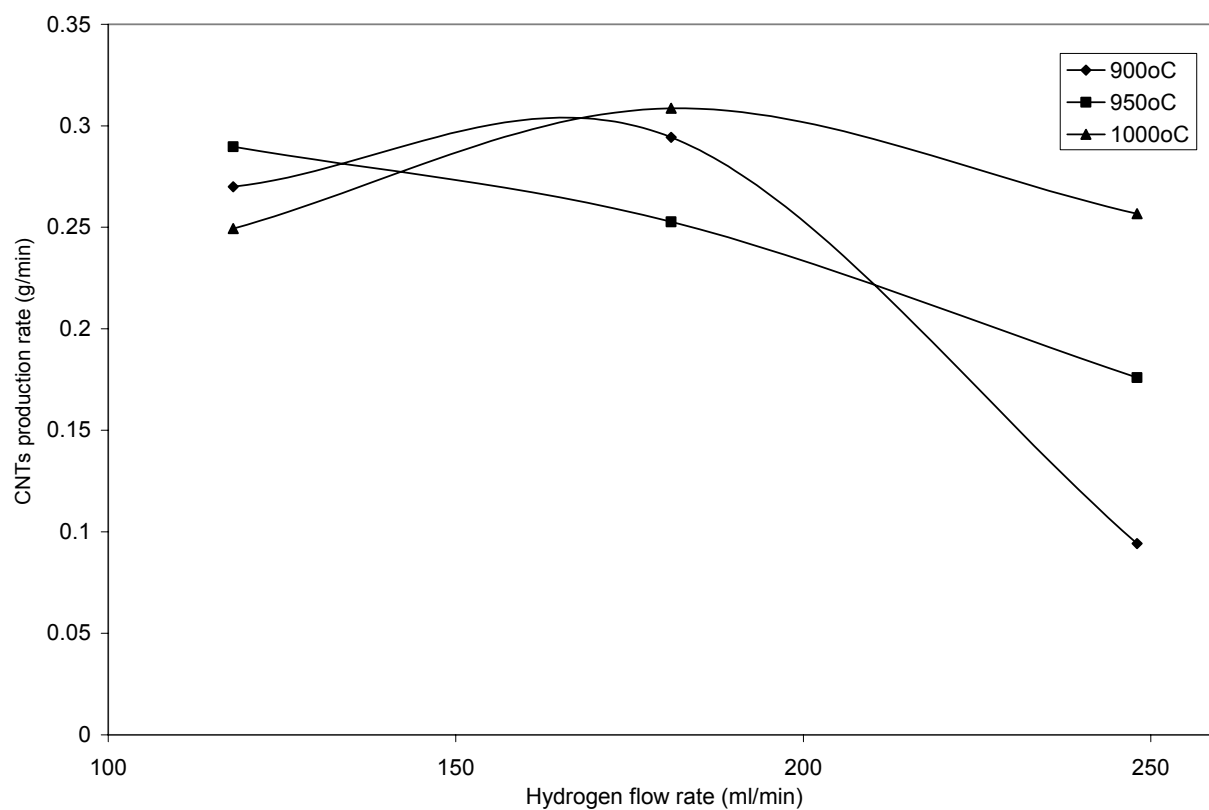
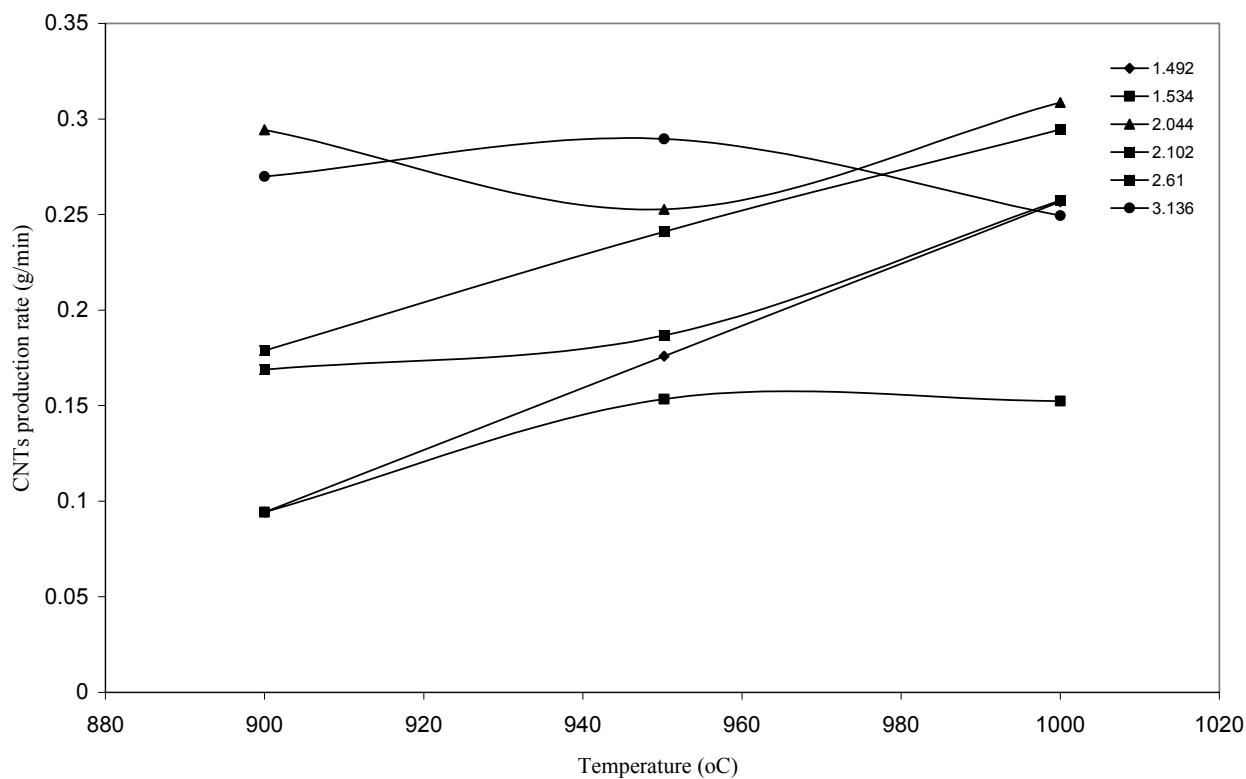Figure 6: Effect of hydrogen flow rate on CNTs production rate.

Figure 7: Effect of temperature on CNTs production rate at various ratios of acetylene and hydrogen

4. CONCLUSION

The studies conducted on the operating parameters on production rate of CNTs from acetylene using ferrocene as catalyst show that reactor temperature, acetylene (carbon source) flow rate and ratio of acetylene to hydrogen flow rate and hydrogen flow rate affect the production rate of CNTs and hence the final yield of the products. TEM images also reveal that the products synthesized by SFCCVD method are a mixture of Single-Walled Carbon Nanotubes and Multi-Walled Carbon Nanotubes. The maximum production rate of 0.31g/min was obtained at operating conditions of acetylene flow rate of 370ml/min, hydrogen flow rate of 180ml/min and pyrolysis/eaction temperature of 1000°C. The CNTs production rate observed in this technique would enhance the global efforts to produce CNTs in mass and in turn produce MEA for better performance and cheaper PEM fuel cell.

REFERENCES

Chan, K. Y., Ding, J., Ren, J. W., Cheng, S. A. and Tsang, K. Y. "Supported Mixed Metal Nanoparticles as Electrocatalysts in Low Temperature Fuel Cells", *Journal of Material Chemistry.* Vol. 14 pp 505-516, 2004.

Che, G., Lakshimi, b. B., Martin, C. R., and fisher, E. R, "metal-Nanocluster-Filled Carbon Nanotubes: Catalytic Properties and Possible Applications in Electrochemical Energy Storage and Production", *Langmuir,* Vol. 15 pp 750-758, 1999.

Conteau E, Hernadi K, Seo K, Seo J.W, Thien – Nga L, Miko Cs, Gaal R and Forro L., "CVD Synthesis of High Purity Carbon Nanotubes using $CaCO_3$ Catalyst Support for Large Scale Production", *Journal of Chemical Physics Letter*, Vol. 378. pp 9 – 17, 2003.

Goddard III, W. A., Brenner, D. W., Lyshevsk, S. E. and Iafrate, G. J., Handbook of Nanoscience, Engineering and Technology. CRC Press, USA p 18, 2003.

Iijima, S., "Helical Microtubules of Graphite Carbon", *Nature.* Vol. 354, No 6348 pp 56-58, 1991.

Iyuke, S.E., "Swirled Fluidised Bed Chemical Vapour Deposition Reactor", University of the Witwatersrand, Johannesburg. SA Patent Appl. No: 2005 03438, 2005

Iyuke, S. E. and Danna, A. B. M., "Morphological Study of Carbon Nanotubes Synthesized by FCCVD". *Journal of Microporous and Mesoporous Materials.* Vol. 84 pp 338-342, 2005.

Kathyayini H, Nagaraju N, Fonseca, A and Nagy J.B., "Catalytic Activity of Fe, Co and Fe/Co Supported on Ca and Mg oxides, Hydroxide in the Synthesis of Carbon Nanotubes". *Journal of Molecular Catalysis*. Vol. 223. pp 129 – 136, 2004.

Kuwana, K., Endo, H., Saito, K., Qian, D, Andrews, R. and Grulke, E. A., "Catalytic Deactivation of Carbon Nanotubes", *Journal of carbon*, Vol. 43, pp 252 – 260, 2005.

Li, W., Liang, C., Qiu, J. L. H., Zhou, W., Sun, G., and Xin, Q., "Multi-walled Carbon Nanotubes Supported Pt-Fe Cathodic Catalyst for Direct Methanol Fuel Cell", *Journal of Reaction Catalyst Letters,* Vol. 82 pp 235-240, 2004.

Liu, X., Huang, B. and Coville, N. J., "The $Fe(CO)_5$ Catalyzed Pyrolysis of Pentane: Carbon Nanotubes and Carbon Nanoball Formation", Carbon. Vol. 40 pp 2791-2799, 2002.

Matsumoto, T., Komatsu, T., Nakano, H., Arai, K., Nagashima, Y., Yoo, E., Yamazaki, T., Kijima, M., Shimizu, H., Takasawa, Y. and Nakamura, J., "Efficient Usage of Highly Dispersed Pt on Carbon Nanotubes for Electrode Catalysts of Polymer Electrolyte Fuel Cells", *Journal of Catalyst Today.* Vol. 90. pp 277-281, 2004.

Mitri, S. P. and Sotrirchos, S. V., "Production of Carbon Nanotubes using CVD- Study of the Operating Parameters", *Journal of Review Advanced Materials Science.* Vol. 10 pp 314-319, 2005.

Rajesh, B., Karthik, V., Karthikeyan, S., Thampi, R. K., Bonard, J. M. and Viswanathan, B., "Pt-WO3 Supported on Carbon Nanotubes as Possible Anodes for Direct Methanol Fuel Cells", *Journal of Fuel*. Vol. 81 pp 2177-2190, 2002.

Shaffer, M., "Prospects for Nanotubes and Nanofibre Composites", *Journal of Composites Science and Technology*. Vol. 64 pp 2281-2282, 2004.

Unalan, H. E. and Chhowalla, M., "Investigation of Single-Walled Carbon Nanotube Growth Parameters Using Alcohol Catalytic Chemical Vapour Deposition", *Journal of Nanotechnology.* Vol. 16 pp 2153-2163, 2005.

Wang, Y; Wei, F; Gu, G. and Yu, H., "Agglomerated Carbon Nanotubes and its Mass Production in a Fluidized-Bed Reactor", *Journal of Physica B*. Vol. 323 pp 327-329, 2002.

Wilder, J. W. G., Venema, L. C., Riszler, A. G., Smalley, R. E., and Dekker, C., "Electronic Structure of Atomically Resolved Carbon Nanotubes" *Nature*, Vol. 391 pp 59-62, 1998.