Variations of Furnace Affecting the Catalytic Chemical Vapour Synthesis of Carbaon Nanotubes - A Review

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Abstract: *Carbon nanotubes are the finest example of the crystallized form of carbon. They are basically the rolls of graphite sheet which are electrically and thermally more conductive, mechanically more stronger and biologically and chemically more active. The purpose of CNTs production could be different. It could be application based or research based and sometimes could be commercial based. These purposes could be best served with catalytic chemical vapor deposition technique assembled with suitable reactor. Recent advancement in direction of CNTs production have shown the experimentation with the apparatus which are designed to follow the most popular technique of CCVD. Variation in designs of reactors serves different needs which could be controlling the product morphology, optimizing the productivity or scaling up the process. This letter discusses a general overview on the suitability of apparatus for conducting CCVD and the focus will be on the most popular and basic designs of the reactors for the production of CNTs.*

Keywords: Carbon nanotubes, Chemical vapour deposition, Floating catalyst, Fixed Bed Catalyst.

1. Introduction

Carbon nanotubes ("CNTs") shows impressive physical properties. They are roughly eighty times stronger, six times stiffer (i.e., Young's Modulus), and exhibit one-sixth of the density of high carbon steel[1-2]. Carbon nanotubes have a diameter usually of the order of 0.5 nanometers to 100 nanometers and are having a length of up to about 1 centimeter. The elongated nanotubes have carbon hexagons arrangement in a concentric manner and both ends of the tubes are normally capped with a pentagon-containing fullerene like structures. Carbon nanotubes shows a single wall or multiwall structure. They can be a metal or semiconductor depending on the diameter of the nanotubes and the helicity of the arrangement of rings in the walls of rolled graphene[3-5]. Dissimilar carbon nanotubes can be joined together to allow the formation of molecular wires which leads to interesting electrical, magnetic, thermal, optical and mechanical properties.[6-8].These unusual properties have mark the potential applications of carbon nanotubes in field of material science and nanotechnology. Carbon nanotubes is the new material proposed for electron field emitters in panel displays, logic devices, memories, single molecular transistors and other nanoelectronic devices such as scanning probe microscope tips. CNTs also find applications in gas and electrochemical energy storage. They act as catalyst and are proteins/DNA supporter and are excellent energy absorbing materials[9-15].

Carbon nanotubes are synthesized by diverse methods such as arc discharge, laser ablation and CCVD. However, CCVD has been widely followed, as it is more promising for bulk production of CNTs, and hence more suitable for commercialization. The purpose and development of CCVD for production of CNTs by the scientific community are based on the following facts: lower reaction temperature, higher purity, better alignement and higher yield of the products, which directly cuts the cost of the production and supports the large-scale production[18]. Remarkable efforts have been made to study the key parameters affecting the CNTs production and morphology in CCVD process. In CCVD method CNTs are processed in a reaction furnace where gaseous carbon feedstock is flushed in the presence of catalyst. There are mainly two processing system configurations proposed for CCVD of CNTs. First and the most popular is horizontal configuration and second is vertical configuration.

2. Key Parameters

1) Catalyst
Catalysts plays an important role in the CCVD synthesis of CNTs. By improving the characteristics of catalyst will automatically enhance the CNTs quality and the process yield. Materials having the capability of decomposing hydrocarbon and hence lead to the formation of CNTs are employed as catalyst in CCVD processes[19-21]. Transition metals as nanoparticles are found to be the most effective catalysts. The ability of transition metals to support CNT growth are related to these factors: (a) decomposition of volatile carbon compounds by catalytic activity , (b) ability to form metastable carbides, and (c) carbon diffusion through and over the metallic particles[22-25]. The careful selection of the catalyst and support significantly improves the process yield. Chemical or physical Interactions between support and catalyst nanoparticles are important for the catalytic properties of the nanoparticles. Weak interactions leads to tip-growth mode whereas strong interactions yield to base-growth[23]. A Strong metal–support interactions improves the dispersion, controls the narrow size distribution, and reduce sintering as well as agglomeration of active metal particles. Growing CNTs on different supports with same catalyst shows that substrates with larger surface areas, such as alumina and silica, will support CNT nucleation and growth[26-30]. The carbon source atoms diffuses readily on a high surface area to the catalyst particles. It is known that transition metals like Iron

(Fe), cobalt (Co), and nickel (Ni) can act as nanoparticles to produce CNTs and the diameter of nanotubes is directly related to the catalyst particle size. Large particles as compared to fine and well-dispersed particles are found to be inactive for CNTs formation. Optimization of the catalyst particles and their dispersion on support decides the number of active points for hydrocarbon decomposition[31-32]. The scientific and technological challenges related with catalyst system is to find the synthesis methods that can fulfill the requirements in terms of their composition and structure.

2) Temperature

Every stage of CNT growth is thermally activated and a characteristic threshold temperature required for each step[22]. The starting temperature of CCVD for CNT synthesis have been reported higher than 500 ∘C .Earlier, it was believed that a very high temperature (e.g.,1000–2000 ∘C) is favorable for the formation of SWCNTs over MWCNTs[33] ,but with the new CVD methods, especially FBCVD, it becomes possible to lower growth temperature of SWCNT[34-36]. CNTs morphology is found to be dependent on the temperature. Muataz et al. analysed the role of reaction temperature in CNTs synthesis by examining the floating catalyst method, by using benzene and ferrocene as carbon feedstock and catalyst, respectively[37]. It was found out that MWCNTs synthesis occurs at temperatures higher than 500∘C and maximum numbers of walls with lesser impurity is obtained at 850∘C. At higher reaction temperature non-tubular carbon like nanofibers are obtained. A correlation between the average diameter and the length of CNTs and temperature was observed. Therefore it was proposed that temperature is a dominating factor for CNT diameter control. Similar conclusions have been reported by other researchers [38-41]. Increasing the reaction temperature increases the metal particle size during the CVD growth of CNTs and the nanotube diameter. But there are some inconsistencies about the exact effect of the temperature on CNTs growth mechanism. It was observed that raising the temperature has increased the length as well as the crystallinity of the nanotubes. Son et al.[42] observed that the CNT diameters produced from methane in a fluidized bed reactor decreases with the increase of reaction temperature .The effect of temperature was evident on the growth rate, purity and the crystallinity of CNTs in all the above mentioned studies.

3) Carrier Gas

In CNT synthesis process, for reducing the formation of amorphous carbon and to decrease the contact time between carbon feedstock and catalysts, the carbon feedstock has to be diluted with the help of a carrier gas[22,66]. Carrier gas also keeps the chamber free of oxygen to avoid carbon oxidation. The carrier gas should be nonreactive. Argon, hydrogen and nitrogen are mostly used as carrier gases because they can easily form an inert atmosphere. Other gases like helium[67] or NH3[66] are also used. Carrier gases are found to affect the growth, structure and properties of CNTs. Qingwen et al.[68] investigated the effect of carrier gas on the CVD process. When argon was used, MWNTs are produced and when hydrogen was used, some SWNTs were formed. In presence of NH3 bamboo-like structures with larger diameters are obtained using ferrocene as catalyst and acetylene as a carbon source as compared to CNTs obtained in nitrogen[69]. Nature of gaseous environment has a direct influence on the strength of the metal–support interaction.

4) Time and Space Velocity

In the CCVD process, there is time limit beyond which nucleation becomes difficult and leads to deactivation of the catalytic nanoparticles. Different optimum time are proposed for CCVD with respect to processing parameters and type of catalyst as well as carbon source[39,65,68-70]. For CNT nucleation, accumulated carbon atoms have to reach a critical concentration inside the catalyst particles, which depends on the deposition rate. Kouravelou and Sotirchos[71] proved that the rate of deposition depends on carbon precursor nature , the catalyst composition and on temperature. It has been reported that CNTs shows different morphologies for different reaction times. Lamouroux[72]   observed that short reaction time is good for SWCNT growth. Kim et al.[73] reported that CNTs diameter is decided by duration time of tubes in the heating zone of reactor. Roman and Somenath[74] reported about the mean diameter of MWCNTs that increases with the CVD durations, probably due to sintering and agglomeration of particles. CNTs length can also be controlled by the length of the deposition time. Qian et al.[70] reported CNTs sampled at different periods have different thermal stability.

As the residence time increases, the concentrations of active radicals and intermediates in the gas phase increases and they start to recombine and active radicals consume the available carbon that would have otherwise formed CNTs. The space velocity is the volume flow rate relative to the catalyst mass and is an important parameter for many comparative measurements in catalytic process [75,76]. The space velocity in fluidized bed reactors is relatively high as compared to fixed bed; therefore synthesis of desired CNTs like single or doublewall is highly favored[77,78]. High space velocity can be obtained by using high gas flow rate. A disadvantage of high flow rates is that it cools down the bed zone and hence effect the deposition quality [79]. Also, high gas velocity influences the stablility of fluidization of catalyst and produces CNTs of low bulk density [77,80].

5) Horizontal Furnace

The horizontal furnace is the well known configuration for the production of carbon nanotubes. In general in its simplest form, it requires a heated quartz tube in which reactant gases are flowed over the substrate/catalyst that sits in a removable ceramic boat/holder which is placed in the centre of the quartz tube as shown in Fig 1. The horizontal furnace has an advantage that there is no(or small) temperature gradient in the heating zone[31,81-83]. In many cases, the length of nanotubes are controlled simply by the length of the deposition time. The typical horizontal system, can be used in the floating and fixed-bed catalyst technique.

3. Floating Catayst Technique

Floating catalyst technique[18,81,84-89] is followed by the introduction of mixture of catalyst and reactants in gas phase to the reactor that is maintained at an elevated growth temperature where the CCVD reaction is going to take place as shown in Fig 2. In the reactor the gas phase catalyst simply transforms into nano-sized solid phase active catalyst particles. The major difficulty of this method is in preventing the coalescence of particles. At first the solid nano-catalysts have to adhere to the reactor surfaces and only then they get the sufficient residence time to grow CNTs. If the nanocatalysts are unable to adhere to the reactor walls at sufficiently high temperatures then they are simply swept away with the unused reactants and unreacted gas phase catalysts and carrier gases thus thereby reducing the efficiency of process.

Ravindra et al.[90]. reported the synthesis of aligned carbon nanotubes (CNTs) by floating catalyst method using ferrocene as catalyst precursor and acetylene as carbon precursor.The reaction was carried out at 850°C in double stage horizontal chemical vapor deposition (CVD) apparatus. The obtained aligned CNTs were purified by air oxidation and acid treatment method. This process not only produces aligned CNTs but also avoids the step of preparation of metal catalyst. The advantage of this method is its simplicity and use of cheap precursors to produce high purity aligned CNTs. The apparatus as shown in Fig. 4 consists of two stage horizontal furnace fitted with quartz tube. Argon gas was used as carrier gas. Ferrocene was taken in a quartz boat, placed inside the first heating furnace. Ferrocene was vaporised at 230°C and carried by argon flow (600sccm) to the second heating furnace where the temperature has reached to 850°C. Acetylene gas flow (15 sccm) was allowed to reside in the reactor for 10 min. A black film was deposited onto the walls of quartz tube, which was collected after the reactor is cooled down to room temperature. The advantage above method is that there was no need for the catalyst preparation step and it was a continuous process.

Xianfeng Zhang et al.[91] synthesized vertically aligned and highly dense carbon nanotube (CNT) arrays on quartz substrates by catalytic decomposition of a ferrocene–xylene mixture at 850°C in a quartz tube horizontal reactor. Ferrocene- xylene solution was fed continuously into a two-stage tubular horizontal quartz reactor by a flux pump. Ferrocene acts as a producer for Fe catalyst particles and xylene was selected as carbon source. The temperatures at preheating stage were maintained at 300°C and at decomposition stage of the reactor at 850°C. After the reactor was cooled to room temperature in Argon ambient, the nanotube films were easily peeled off from the quartz substrates. It was suggested that CNTs are formed by tip growth mechanism. As CNTs grows, the Fe catalyst particles detach itself from quartz substrate, and rise at the tips of the growing nanotubes and are encircled by carbon layers, and kept in the cavities of CNTs. CNTs does not stop growing even with the stop of Fe catalyst particles. With the continuous feeding of Fe catalyst and carbon source, CNTs grow into a length of few millimeter. This might be due to the higher temperature at preheating stage, the higher feed rate of solution ,and the continuous feeding method of solution by a flux pump and an injector. The higher temperature is favorable for the decomposition of ferrocene to Fe catalyst particles and the higher feed rate provides abundant Fe catalyst particles and carbon source in continuous manner and leads to growth of aligned and long CNTs.

4. Fixed Bed Catalyst Technique

Alternatively, in the fixed-bed process, the solid phase catalyst is put in holders which are placed inside the reactor and the gas phase reactant is flowed over when sufficient growth temperature is attained as shown in Fig.3. The efficiency of growth of CNTs by this process is also limited due to inhomogeneous gas–solid contact. In a horizontal fixed-bed reactor, catalyst particles becomes less effective and less reactive as more number of nanotubes grows up they will cover the surface and hence limit the diffusion of the carbon source gas through the catalyst particles.

Direct growth of carbon nanotubes on silicon substrate can be potentially exploitated in the semiconductor industry. This is investigated by the chemical vapor deposition of CNTs on Si substrates from ethylene precursor using iron as a catalyst[92]. Clean Si substrates with a native oxide layer was dipped in a 2-propanol suspension of Fe(NO3)3·9H2O for few seconds and then heated in a horizontal tube furnace under argon until the growth temperature was reached. Then Hydrogen was introduced for 15 min (pre growth time) after which ethylene was allowed to flow for a further 6 min(growth time) and after that the furnace was allowed to cool down under argon flow. It was observed that CNTs are produced in a temperature range between 830°C and 980°C and CNT yield first increases with temperature as it reach to 900°C indicates a minimum energy required to activate the catalyst particles and then declines which show a loss of catalyst either due to subsurface diffusion of iron nanoparticles or due to evaporation of iron particles at elevated temperature

Maoshuai He [93] reported a well-designed Fe-Ti-O solid solution catalyst for SWNT growth. The Fe-Ti-O catalyst was prepared by depositing Ti layer onto premade Fe nanoparticles with high-temperature air calcinations , which are supported by porous Si3N4 grid. The Si3N4 supported Fe-Ti-O catalyst was then loaded into a horizontal CVD reactor with a quartz tube. The reactor was heated to 800°C in the presence of helium flow. After stablization, the helium was replaced by carbon feedstock in form of CO for SWNT growth. The reactor was then cooled to room temperature. The results identifies Fe-Ti-O catalyst get reduced to the form the TiOx-supported small Fe nanoparticles for SWNT growth. The strong metal-support interactions provided by partial reduction of TiOx enhances the wettability of Fe nanoparticle and leads to the preferential growth of large-chiral-angled SWNTs. This work provides the base for selective chiral angle growth of SWNT.

5. Vertical Furnace

The vertical furnace configuration provides the continuous production of carbon nanotubes and carbon nanofibers[81,94-97]. The carbon source and catalyst mixture is injected from the top end of the furnace and carbon filaments are formed during the flight and are collected at the bottom end. The vertical furnace is advantageous in the sense that it is employed for the mass production of carbon nanotubes and nanofibers and the high purity of obtained product eliminates the need for purification or removal from the substrate. The vertical furnace configuration have been commercialized to produce multiwall nanotubes in amounts of tons per year. This geometry of reactor can be used with two methods namely floating reactant method and fluidized-bed method as shown in Fig. 5 and 6 respectively.

A. Floating Reactant Method

To meet the huge demand for carbon nanotube in the market, a continuous growth process of carbon nanotube production has been developed, since the horizontal method described above was a non-continuous method, and was not suitable for industry-scale production. Endo developed the continuous method called the floating reactant method[98]. This method includes a vertical furnace, in which the metal catalyst, carbon source, and gases are fed from the top end of the furnace. The catalyst particals float and fall inside the furnace and leads to growth of carbon nanotubes which are collected at the bottom end of the furnace. The method is applicable for the volume production of carbon nanotubes, and the quality of the product was highly pure as well. The production system using vertical reactor is now widely used in a Japanese company and they are producing carbon nanotubes which are available in the market.

Carbon single-walled nanotubes (SWCNTs) are known to have unique mechanical, thermal and electric properties. SWCNTs therefore have a high potential to be used various applications and for that it is important to realize their large-scale production. The best approach proposed was the continual injection of a pre-prepared colloidal solution of the metal catalyst particles into a modified vertical floating reactor [99]. In the case of SWCNTs, the catalyst particles diameter plays a crucial role of in the synthesis. It is required to have adequate diameter, with narrow distribution, of the catalyst particles and to avoid the conditions of their agglomeration. This requisite restricts the organometallics concentration and synthesis parameters, which limits the synthesis rate and yield. The continuous synthesis of SWCNTs has been reported with a high production yield up to 6 g/h (after purification),using above mentioned approach. The advantage of this method is the use of an injector that introduces the pre-synthesized catalyst, consisting of metal particles having diameters that are suitable for the growth of SWCNTs and prevent agglomeration during synthesis and achieves high efficiency of the synthesis. By using a powder support, the formation of undesired carbon forms has been avoided.

Ranadeep Bhowmicka [100] analysed parametric details of the production of single-wall carbon nanotubes (SWCNTs) by the floating catalyst method in a vertical furnace using an alcohol precursor. Alcohol precursors has been used instead of traditional hydrocarbon sources as they resulted in a better yield of the SWCNT because of the role played by decomposed OH radicals. The reaction of OH radical with solid carbon leads to the reduction in the formation of soot and thereby restricts the production of amorphous carbon in the SWCNT product[101]. Zhu et al.[102], was the first to one to report the synthesis of long arrays of single-walled carbon nanotubes with a floating catalyst method in a vertical furnace. n-Hexane with ferrocene and thiophene was introduced into the reactor after heating the reactor to the pyrolysis temperature. SWCNTs formed in abundance during this continuous process. In this work ethanol and ferrocene is used as the carbon and catalyst precursor, respectively, H_2 as the carrier gas and thiophene as a yield promoter[103]. Gaseous mixture get pyrolysed in the first zone or the bottom of the furnace with nucleation and growth of the SWCNTs in the other zones. As the SWCNT are light in weight they align themselves along the direction of gas flow and form bundles by adhering to other tubes by the Van der Waals forces. This formation of well-aligned SWCNT bundles is characteristic of the floating catalyst method [104]. It was found that increasing the residence time and with higher concentrations of metal catalyst in the precursor solution (i.e. ferrocene in ethanol) the diameter of the tubes produced increases. With the increase of growth temperature both larger and small diameter SWCNTs were formed, in contrast to previous reports of increasing diameter with temperature. Varying the size distribution of the SWCNTs by controlling these parameters can meet the needs of specific applications.

Mass production of carbon nanotubes in different forms has been developed and studied widely using various methods. The floating catalyst CVD method was known to be employed by various research groups for the mass production of carbon nanotubes[105]. Lee et al.[106] fabricated the vapor phase growth of aligned carbon nanotubes by heating the flowing mixtures of acetylene and iron pentacarbonyl in a horizontal quartz tube reactor. Satish Kumar et al.[84] synthesized singlewalled carbon nanotubes from acetylene with organometallic mixtures in a two-stage furnace. Nikolaev et al.[107] studied the gas-phase synthesis of singlewalled carbon nanotubes from carbon monoxide with iron pentacarbonyl in a horizontal quartz tube reactor under a high-pressure and elevated-temperature. Zhu et al.[108] employed mixtures of n-hexane or benzene with ferrocene and thiophene in a vertical furnace for the production of double-walled carbon nanotubes. Ci et al.[109] investigated the fabrication of carbon nanofibers through a floating catalyst method using mixtures of benzene, thiophene and ferrocene in a vertical furnace. All the above experimental studies clearly leads to the possibility of mass production for CNTs and parameters of fabrication, such as composition of mixtures, pressure, and temperature, were found to significantly influence the yield and quality of carbon nanotubes[110]. But the yield of carbon nanotubes obtained from all the above methods was limited

(from milligrams to a few grams). Therefore, more reliable and economic techniques were developed where multiwalled carbon nanotubes (MWNTs) were synthesized using a chemical vapor deposition floating catalyst method in a vertical reactor. Methane as the carbon source (in comparison with acetylene, benzene, and thiophene) and nitrogen as the carrier gas (in place of hydrogen) were used in this method. A vertical reactor was employed to carry out the continuous fabrication process in the absence of any substrate, which is beneficial to the mass production of MWNTs. In addition, preparation variables such as the compositions of mixture gases for the CVD reaction, operational temperature, and pressure were systematically studied to find an optimal condition for the growth of MWNTs.

B. Fluidized Bed Reactor

The fluidized bed CVD (FBCVD) consists of a vertical furnace in which supported-catalyst particles are placed in centre of furnace and are suspended by an upward flow of gas. Fluidization is a process of transformation of solid particles which are suspended in a gas into a fluid like state. FBCVD process uses the advantages of both the floating and fixed-bed catalyst systems[111]. It provides great heat and mass transfer like in the floating catalyst system and the catalyst nanoparticles adhere to a support surface and are large in size and massive enough that to be not swept away along with the reactant gas or carrier gas stream. This system provides a large contact area between the reactants and catalyst particles, and leads to a highly effective chemical reactions and better heat transfer. The CNT formation rate is known to be directly associated with the availability of the active catalyst sites so FBCVD is more efficient for production of large quantities of CNTs as compared to the other types of CCVD. Fluidized bed reactors are widely used for different industrial purposes, such as fluid catalytic cracking, fluidized bed combustion, or fluidized bed bio-filter[79]. Fluidized bed reactors provides excellent gas–solid contact and controls the highly exothermal reactions. Now a days, fluidized bed reactors with supported nano-metal catalysts are very much effective for mass production of CNTs[77,79,112-124]. It consists of a vertical reactor enclosed by an electrical furnace .In the mass production of CNTs, FBCVD technique as compared to fixed beds and floating catalyst technology is highly robust, flexible and highly productive[125-127]. Also, the FBCVD can be easily scaled-up and operated continuously which makes this technique cost-effective for large-scale production of CNTs.

The fluidization process provides a high space velocity that facilitate an efficient gas–solid contact, and therefore high mass and heat transfer. In result a high process yield, product homogeneity and purity are attained. FBCVD is a flexible process in terms of operating conditions. The operation parameters like gas mixture and temperature can be finely tuned according to the desired product. Availablity of space for growing CNTs and the residence time and hence the activity of catalyst can be controlled which favors the selective mass production of CNTs[125,126]. Xu and Zhu[128] emphasizes the superiority of these kinds of

reactors for mass production of CNTs by developing fluidized bed metal–organic chemical vapor deposition (MOCVD) as a one-step preparation of highly dispersed metal-supported catalysts. This method has some advantageous over the conventional methods since it eliminates the drying and the subsequent calcinations operations. Prepared supported-catalyst particles activities were analysed for CNTs synthesis through FBCVD using acetylene and it was observed that the deposited metals were highly dispersed on the surface of the support particles. FBCVD is proved to be a versatile method to fulfill the priority of this method for large-scale production.

Parameters which influence the FBCVD, include intrinsic properties of particles, reactor geometry, fluidizing velocity. The intrinsic properties of particles, e.g., particle density, particles size as well as their size distribution and surface characteristics directly affect the fluidization. Nanoparticles can be easily fluidized due to the formation of light agglomerates. Fluidization quality is described by applied gas flow velocity to the minimum fluidization velocity ratio (U/Umf). Minimum fluidization velocity is the superficial fluid velocity at which the upward drag force exerted by the fluid is equal to the apparent weight of the particles in the bed. Minimum fluidization velocity depends on particle size and particle density and fluid properties as well. The value of Umf is usually determined experimentally by measuring the pressure drop as a function of gas velocity. It also may be predicted by some empirical or semi-empirical correlations. Venegonia et al.[112]in their parametric study for CNTs growth by FBCVD measured the Umf of SiO2 particles to grow MWCNTs. Carbon yield tends to increase when the (U/Umf) ratio decreases, because of the increase in residence time of the gaseous precursors into the bed. Alternatively, Son et al.[116] reported that at gas flow rates of 2Umf, the heat and mass transfer are relatively low leading to lower carbon yield. Microscopic observation showed that obtained product of FBCVD are a 3D network structure formed from large amounts of CNTs rather than a liner structure of individual CNT. Wang et al.[129] observed CNTs in tangled and loose agglomerates with wide size distribution. During the process larger agglomerates and agglomerate morphology of nanotubes provides good fluidization and results into high-quality CNTs production on large-scale at low cost.

6. Conclusion

The major challenge is the mass production of CNTs which is critical for their future applications. Significant advancement during the last few years predicts the development of new CVD methods for commercialization. Various process parameters can be altered according to the desired characteristics of CNT product. Whether it is the density of the product , alignment of the tubes, their yield, type, chirality, diameter, length, distribution, purity or cost cutting of the process everything can be achieved by using the right type of reactor. A fundamental key to further control the effective parameter of the selective reactor for the desired CNT is the understanding of different mechanisms of CNTs formation, which helps in determining their structure and characteristics.

However, every method discussed has certain ambiguities and further research will improve the yield, purity and selectivity of CNTs growth. It has been highly suggested that further investigations, both theoretical and experimental, are required to investigate the effective parameters involved in different processes. This will improves the design and operation of horizontal and vertical reactors and facilitates the production of CNTs which is best desirable.

References

[1] Dresselhaus M and Dai H: Carbon Nanotube Special Issue, Materials Research Society, Warrendale, PA.2004, 29

[2] Golberg D, Costa PM, Mitome M and Bando Y: Nano Research. 2008, 1:166-175.

[3] H.W. Zhu, C. L. Xu, D. H. Wu, B. Q. Wei, R. Vajtai, P. M. Ajayan, Science 2002, 296, 884.

[4] Iijima, Nature 1991, 354, 56

[5] S. Iijima, T. Ichihashi, Nature 1993, 363, 603

[6] A. Hirsch, *Fullerenes and Related Structures: Topics in Current Chemistry*, Springer, New York, NY, USA, 1998.

[7] R. H. Baughman, A. A. Zakhidov, andW. A. De Heer, "Carbon nanotubes—The route toward applications," *Science*, vol. 297, no. 5582, pp. 787–792, 2002.

[8] A. Jorio, G. Dresselhaus, and M. S. Dresselhaus, *Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications*, Springer, Berlin, Germany, 2008.

[9] Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature* **354**: 56-58

[10] Jeong, H. J., Jeong, H. D., Kim, H.Y., Kim, J. S., Jeong, S. Y., Han, J. T., Bang, D. S. and Lee, G. W. (2011). All- Carbon nanotube - based flexible field -emission devices : from cathode to anode. *Adv. Funct. Mater.* DOI: 10. 1002/ adfm. 201001469

[11] Mao, X., Wu, Y., Xu, L., Cao, X., Cui, X. and Zhu, L. (2011). Electrochemical biosensors based on redox carbon nanotubes prepared by noncovalent functionalization with 1,10- phenanthroline - 5,6 - dione. *Analyst* **136**: 293-298.

[12] Kauffman, D. R. and Star, A. (2010). Graphene *versus* carbon nanotubes for chemical sensor and fuel cell applications. *Analyst.* **135**:2790-2797.

[13] Titus, E., Singh, M. K., Cabral, G., Paserin, V., Babu, P. R., Blau, W. J., Ventura, J., Araujo, J. P. and Gracio, J. (2009). Fabrication of vertically aligned carbon nanotubes for spintronic device applications. *J. Mater. Chem.* **19**: 7216-7221

[14] Milne, W. I. and Teoa, K. B. K. (2006). Aligned carbon nanotubes/fibers for applications in vacuum microwave amplifiers. *J. Vac. Sci. Technol.* B. **24**: 344-348.

[15] Dillon, A. C., Jones, K. M., Bekkedahl, T. A., Kiang, C. H., Bethune, D. S. and Heben, M. J. (1997). Storage of hydrogen in single- walled carbon nanotubes. *Nature*. **386**:377- 379.

[16] Titus, E., Singh, M. K., Cabral, G., Paserin, V., Babu, P. R., Blau, W. J., Ventura, J., Araujo, J. P. and Gracio, J. (2009). Fabrication of vertically aligned carbon nanotubes for spintronic device applications. *J. Mater. Chem.* **19**: 7216-7221

[17] Milne, W. I. and Teoa, K. B. K. (2006). Aligned carbon nanotubes/fibers for applications in vacuum microwave amplifiers. *J. Vac. Sci. Technol.* B. **24**: 344-348.

[18] Endo M, Takeuchi K, Kobori K, Takahashi K, Kroto HW, Sarkar A. Pyrolytic carbon nanotubes from vapor-grown carbon fibers. Carbon 1995;33(7):873–81.

[19] Y. Yao, L.K.L. Falk, R.E. Morjan, O.A. Nerushev, E.E.B. Campbell, Synthesis of carbon nanotube films by thermal CVD in presence of supported catalyst particle, J. Mater. Sci. 15 (2004) 583–594.

[20] A.Kukovecz, Z.Konya, N.Nagaraju, I. Willems,A. Tamasi,A. Fonseca, J.B.Nagy, I. Kiricsi, Catalytic synthesis of carbon nanotubes over Co, Fe and Ni containing conventional and sol–gel silica–alumina, Phys. Chem. Chem. Phys. 2 (2000) 3071–3076.

[21] K.Y. Tran, B. Heinrichs, J.F. Colomer, J.P. Pirard, S. Lambert, Carbon nanotubes synthesis by the ethylene chemical catalytic vapor deposition (CCVD) process on Fe, Co, and Fe–Co/Al2O3 sol–gel catalysts, Appl. Catal. A: Gen. 318 (2007) 63–69.

[22] K.B.K. Teo, C. Singh, M. Chhowalla, W.I. Milne, Catalytic Synthesis of Carbon Nanotubes and Nanofibers, Encyclopedia of Nanoscience and Nanotechnology, vol. X, American Scientific Publisher, 2003, pp. 1–22.

[23] S.B. Sinnott, R. Andrews, D. Qian, A.M. Rao, Z. Mao, E.C. Dickey, F. Derbyshire, Model of carbon nanotube growth through chemical vapor deposition, Chem. Phys. Lett. 315 (1999) 25–30.

[24] G. Ortega-Cervantez, G. Rueda-Morales, J. Ortiz-Lopez, Catalytic CVD production of carbon nanotubes using ethanol, Microelectron. J. 36 (2005) 495–498.

[25] L. Zheng, X. Liao, Y.T. Zhu, Parametric study of carbon nanotube growth via cobalt-catalyzed ethanol decomposition, Mater. Lett. 60 (2006) 1968–1972.

[26] S.S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H.J. Dai, Self-oriented regular arrays of carbon nanotubes and their field emission properties, Science 283 (1999) 512–514.

[27] X.Z. Liao, A. Serquis, Q.X. Jia, D.E. Peterson, Y.T. Zhu, H.F. Xu, Effect of catalyst composition on carbon nanotube growth, Appl. Phys. Lett. 82 (2003) 2694.

[28] A. Serquis, X.Z. Liao, J.Y. Huang, Q.X. Jia, D.E. Peterson, Y.T. Zhu, Co–Mo catalyzed growth of multi-wall carbon nanotubes from CO decomposition, Carbon 41 (2003) 2635.

[29] M. Su, B. Zheng, J. Liu, A scalable CVD method for the synthesis of singlewalled carbon nanotubes with high catalyst productivity, Chem. Phys. Lett. 322 (2000) 321–326.

[30] H. Dai, M.S. Dresselhaus, G. Dresselhaus, P. Avouris (Eds.), Nanotube Growth and Characterization, Carbon Nanotubes, Springer-Verlag, Berlin/Heidelberg, 2001.

[31] H. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Singlewall nanotubes produced

by metal-catalyzed disproportionation of carbon monoxide, Chem. Phys. Lett. 260 (1996) 471–475.

[32] Y.Y.Wei, G. Eres, V.I. Merkulov, D.H. Lowndes, Effect of catalyst film thickness on carbon nanotube growth by selective area chemical vapor deposition, Appl. Phys. Lett. 78 (2001) 1394.

[33] P.M. Ajayan, Nanotubes from carbon, Chem. Rev. 99 (1999) 1787–17799.

[34] K. Mizuno, K. Hata, T. Saito, S. Ohshima, M. Yumura, S. Iijima, Selective matching of catalyst element and carbon source in single-walled carbon nanotube synthesis on silicon substrates, J. Phys. Chem. B 109 (2005) 2632–2637.

[35] E. Mora, T. Tokune, A.R. Harutyunyan, Continuous production of single-walled carbon nanotubes using a supported floating catalyst, Carbon 45 (2007) 971–977.

[36] Sh.Maruyama, R.Kojima,Y. Miyauchi, Sh. Chiashi, M.Kohno, Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol, Chem. Phys. Lett. 360 (2002) 229–234.

[37] A.A. Muataz, A. Fakhru'l-Razi, C. Guan, E. Mahdi, A. Rinaldi, Effect of reaction temperature on the production of carbon nanotubes, NANO: Brief Rep. Rev. 1 (2006) 251–257.

[38] Y. Yao, L.K.L. Falk, R.E. Morjan, O.A. Nerushev, E.E.B. Campbell, Synthesis of carbon nanotube films by thermal CVD in presence of supported catalyst particle, J. Mater. Sci. 15 (2004) 583–594.

[39] R. Andrews, D. Jacques, D. Qian, T. Rantell, Multiwall carbon nanotubes: synthesis and application, Acc. Chem. Res. 35 (2002) 1008–1017.

[40] J.E. Herrera, L. Balzano, A. Borgna, W.E. Alvarez, D.E. Resasco, Relationship between the structure/composition of Co–Mo catalysts and their ability to produce single-walled carbon nanotubes by CO disproportionation, J. Catal. 204 (2001) 129–145.

[41] G.Y. Xiong, Y. Suda, D. ZWang, J.Y. Huang, Z.F. Ren, Effect of temperature, pressure, and gas ratio of methane to hydrogen on the synthesis of double-walled carbon nanotubes by chemical vapor deposition, Nanotechnology 16 (2005) 532–535.

[42] S.Y. Son, Y. Lee, S.Won, D.H. Lee, High-quality multiwalled carbon nanotubes from catalytic decomposition of carboneous materials in gas–solid fluidized beds, Ind. Eng. Chem. Res. 47 (2008) 2166–2175.

[43] P. Piedigrosso, Z. Konya, J.F. Colomer, A. Fonseca, G. Van Tendeloo, J.B. Nagy, Production of differently shaped multi-wall carbon nanotubes using various cobalt supported catalysts, Phys. Chem. Chem. Phys. 2 (2000) 163–170.

[44] T. Yamadai, T. Namai, K. Hata, D.N. Futaba, K. Mizuno, J. Fan, M. Yudasaka, M. Yumura, S. Ijima, Size-selective growth of double-walled carbon nanotube forests from engineered iron catalysts, Nat. Nanotechnol. 1 (2006) 131–136.

[45] L. Qingwen, Y. Hao, Z. Jin, L. Zhongfan, Effect of hydrocarbons precursors on the formation of carbon nanotubes in chemical vapor deposition, Carbon 42 (2004) 829–835.

[46] W. Mi, J.Y. Lin, Q. Mao, Y. Li, B. Zhang, A study on the effects of carrier gases on the structure and morphology of carbon nanotubes prepared by pyrolysis of ferrocene and C2H2 mixture, J. Nat. Gas Chem. 14 (2005) 151– 155D.

[47] L. Zheng, X. Liao, Y.T. Zhu, Parametric study of carbon nanotube growth via cobalt-catalyzed ethanol decomposition, Mater. Lett. 60 (2006) 1968–1972.

[48] F.R. Garcıa-Garcıa, M. Perez-Cabero, D.M. Nevskaia, I. Rodrıguez-Ramos, A. Guerrero-Ruiz, Improving the synthesis of high purity carbon nanotubes in a catalytic fluidized bed reactor and theircomparative test for hydrogen adsorption capacity, Catal. Today 133–135 (2008) 815–821.

[49] W. Qian, T. Liu, F.Wei, Z.Wang, G. Luo, H. Yu, Z. Li, The evaluation of the gross defects of carbon nanotubes in a continuous CVD process, Carbon 41 (2003) 2613–2617.

[50] K.B. Kouravelou, S.V. Sotirchos, Dynamic study of carbon nanotubes production by chemical vapor deposition of alcohol, Rev. Adv. Mater. Sci. 10 (2005) 243–248

[51] E. Lamouroux, Ph. Serp, Y. Kihn, Ph. Kalck, Identification of key parameters for the selective growth of single or doublewall carbon nanotubes on FeMo/Al2O3 CVD catalysts, Appl. Catal. A: Gen. 323 (2007) 162–173.

[52] Y.A. Kim, T. Hayashi, M. Endo, Y. Kaburagi, T. Tsukada, J. Shan, K. Osato, S. Tsuruoka, Synthesis and structural characterization of thin multi-walled carbon nanotubes with a partially facetted cross section by a floating reactant method, Carbon 43 (2005) 2243–2250.

[53] B. Roman, M. Somenath, Mechanism of carbon nanotube growth by CVD, Chem. Phys. Lett. 424 (2006) 126–132.

[54] B. Louis, G. Gulino, R. Vieira, J. Amadou, T. Dintzer, S. Galvagno, G. Centi, M.J. Ledoux, C. Pham-Huu, High yield synthesis of multi-walled carbon nanotubes by catalytic decomposition of ethane over iron supported on alumina catalyst, Catal. Today 102/103 (2005) 23–28.

[55] J. Hagen, Industrial Catalysis: A Practical Approach, 2nd ed., Wiley-VCH Verlag GmbH & Co., KGaA,Weinheim, Germany, 2006.

[56] Y. Liu,W. Qian, Q. Zhang, G. Ning, G. Luo, Y.Wang, D.Wang, F.Wei, Synthesis of high-quality, double-walled carbon nanotubes in a fluidized bed reactor, Chem. Eng. Technol. 32 (2009) 73–79

[57] D.E. Resasco,W.E. Alvarez, F. Pompeo, L. Balzano, J.E. Herrera, B. Kitiyanan, A. Borgna, A scalable process for production of single-walled carbon nanotubes (SWNTs) by catalytic disproportionation of CO on a solid catalyst, J. Nanopart. Res. 4 (2002) 131–136.

[58] C. Vahlas, B. Caussat, Ph. Serp, G.N. Angelopoulos, Principles and applications of CVD powder technology, Mater. Sci. Eng. R 53 (2006) 1–72.

[59] E. Mora, T. Tokune, A.R. Harutyunyan, Continuous production of single-walled carbon nanotubes using a supported floating catalyst, Carbon 45 (2007) 971–977.

[60] M.Endo, Chemtech 18, 568(1988)

[61] N.M.Rodriguez, J.Mater.Res.8, 3233(1993)

[62] M.Joseyacaman, M.Mikiyoshida, L.Rendon and J.G.Santiesteban, Appl.Phys.Lett.62, 657(1993).

[63] B.C.Satish Kumar, A.Govindaraj, and C.N.Rao, Chem.Phys.Lett.307,158(1999).

[64] R.Sen, A.Govindaraj, and C.N.Rao,Chem.Phys.Lett.267,276(1997).

[65] Y.Y.Yang, S.M.Huang, H.Z.He, A.W.H.Mau, and L.M.Dai, J.Am.Chem.Soc.121,10832(1999).

[66] D.C.Li, L.M.Dai, S.M.Huang, A.W.H.Mau, and Z.L.Wang, Chem.Phys.Lett.316,349(2000).

[67] C.Singh, M.S.P. Dhaffer, and A.H.Windle, Carbon 41,363(2003).

[68] R.Andrews, D.Jacques, A.M.Rao, F.Derbyshire, D.Qian, X.Fan, E.C.Dickey, and J.Chen, Chem.Phys.,Lerr 303,467(1999).

[69] Ravindra R and B.R.Bhat,Metals,Materials andMinerals,Vol.21, No.2 pp.95-99(2011).

[70] Xianfeng Zhang , Anyuan Cao, Bingqing Wei, Yanhui Li , Jinquan Wei ,Cailu Xu , Dehai Wu Chemical Physics Letters 362 (2002) 285–290.

[71] Amit K. Chakraborty, J. Jacobs, C. Anderson, and C. J. Robertsand Michael R. C. Hunt, Applied Phys. 100, 084321 (2006)

[72] Maoshuai He , Lili Zhang , Hua Jiang , He Yang , Fr_ed_eric Fossard , Hongzhi Cui , Zhipei Sun , Jakob B. Wagner , Esko I. Kauppinen , Annick Loiseau , Carbon 107(2016)865-867.

[73] H.G.Tennent, J.J.Barber, and R.Hoch, Hyperion Catalysis, Cambridge, MA,1996.

[74] T.Kato, K.Kusakabe, and S.Morooka, J.Mater.Sci.Lett 11,674(1992).

[75] H.W.Zhu, C.L.Xu, D.H.Wu, B.Q.Wei, R.Vajtai, and P.M.Ajayan, Science 296,884(2002)

[76] S.Ohshima, H.Ago, H.Inoue, and M.Yumura, New Diam. Front. Carbon Technol. 11,437(2001).

[77] Morinobu Endo, Takuya Hayashi, Yoong Ahm Kim and Hiroyuki Muramatsu, Applied Physics Vol. 45, No. 6A, 2006, pp. 4883–4892.

[78] Elena Mora, Toshio Tokune, Avetik R. Harutyunyan, Carbon 45 (2007) 971–977.

[79] Ranadeep Bhowmicka, Bruce M. Clemensa, Brett A. Crudenb, Carbon 46(2008)907–922.

[80] Maruyama S, Kojima R, Miyauchi Y, Chiashi S, Kohno M. Low temperature synthesis of high-purity SWCNT from alcohol.Chem Phys Lett 2002;360:223–9.

[81] Zhu HW, Xu CL, Wu DH, Wei BQ, Vajtai R, Ajayan PM. Direct synthesis of long single-walled carbon nanotube strands.Science 2002;296:884–6.

[82] Li Y, Kinloch IA, Windle AH. Direct spinning of carbonnanotube fibers from chemical vapor deposition synthesis.Science 2004;304:276–8.

[83] Cheng HM, Li F, Sun X, Brown SDM, Pimenta MA, Marucci A, Chem Phys Lett 1998;289:602–10.

[84] Lin CC, Huang CM, Kuo CS, Li YY, Hu CC, Chen CC.Continuous productions of carbon nanotubes with methane,nitrogen and Fe(CO)5 using a CVD vertical reactor. J Chinese Inst Chem Engrs 2004;35:595–601.

[85] Lee CJ, Lyu SC, Kim HW, Park CY, Yang CW. Large-scale production of aligned carbon nanotubes by the vapor phase growth method. Chem Phys Lett 2002;359:109–14.

[86] Nikolaev P, Bronikowski MJ, Bradley RK, Rohmund F, Colbert DT, Smith KA, et al. Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. Chem Phys Lett 1999;313:91–7.

[87] Zhu H, Xu C, Wei B, Wu D. A new method for synthesizing double-walled carbon nanotubes. Carbon 2002;40:2023–5.

[88] Ci L, Li Y, Wei B, Liang J, Xu C, Wu D. Preparation of carbon nanofibers by the floating catalyst method. Carbon 2000;38:1933–7.

[89] Baker RTK. Catalytic growth of carbon filaments. Carbon 1989;27:315–23.

[90] Firoozeh Danafara, A. Fakhru'l-Razi , Mohd Amran Mohd Salleha, Dayang Radiah Awang Biaka. Chemical Engineering 155 (2009) 37–48.

[91] Ph. Venegonia, R. Serp, R. Feurer, Y. Kihn, Parametric study for the growth of carbon nanotubes by catalytic chemical vapor deposition in a fluidized bed reactor, Carbon 40 (2002) 1799–1807.

[92] V.N. Parmon, G.G. Kuvshinov, V.A. Sadykov, V.A. Sobyanin, New catalysts and catalytic process to produce hydrogen and syngas from natural gas and other light hydrocarbons, Stud. Surf. Sci. Catal. 119 (1998) 677–684.

[93] M. Perez-Cabero, I. Rodriguez-Ramos, A. Guerrero-Ruiz, Characterization of carbon nanotubes and carbon nanofibers prepared by catalytic decomposition of acetylene in a fluidized bed reactor, J. Catal. 215 (2003) 305–316.

[94] A. Morancais, B. Caussat, Y. Kihn, Ph. Kalck, D. Plee, P. Gaillard, D. Bernard, Ph. Serp, A parametric study of the large scale production of multi-walled carbonnanotubes by fluidized bed catalytic chemical vapor deposition, Carbon 45 (2007) 624–635.

[95] S.Y. Son, D.H. Lee, S.D. Kim, S.W. Sung, Effect of inert particles on the synthesis of carbon nanotubes in a gas–solid fluidized bed reactor, J. Ind. Eng. Chem. 13 (2) (2007) 257–264.

[96] F.Wei, Q. Zhang,W. Qian, H. Yu, Y.Wang, G. Luo, G. Xu, D.Wang, The mass production of carbon nanotubes using a nano-agglomerate fluidized bed reactor: a multiscale space–time analysis, Powder Technol. 183 (2008) 10–20.

[97] Ch.H. See, A.T. Harris, A comparison of carbon nanotube synthesis in fixed and fluidised bed reactors, Chem. Eng. J. 144 (2008) 267–269.

[98] S.Y. Son Dong, H. Lee, S.D. Kim, S.W. Sung, Y.S. Park, J.H. Han, Synthesis of multi-walled carbon nanotube in a gas–solid fluidized bed, Korean J. Chem. Eng. 23 (2006) 838–841.

[99] H. Yu, Q.F. Zhang, G.S. Gu, Y. Wang, G.H. Luo, F. Wei, Hydrodynamics and gas mixing in a carbon nanotube agglomerate fluidized bed, AIChE J. 52 (12) (2006) 4110–4123.

[100] Ch.H. See, O.M. Dunens, K.J. MacKenzie, A.T. Harris, Process parameter interaction effects during carbon nanotube synthesis in fluidized beds, Ind. Eng. Chem. Res. 47 (2008) 7686–7692

[101] R. Philippe, Ph. Serp, Ph. Kalck, Y. Kihn, S. Borde're, D. Plee, P. Gaillard, D. Bernard, B. Caussat, Kinetic study of carbon nanotubes synthesis by fluidized bed chemical vapor deposition, AIChE J. 55 (2009) 450–464.

[102] R. Philippe, Ph. Serp, Ph. Kalck, Y. Kihn, S. Borde're, D. Plee, P. Gaillard, D. Bernard, B. Caussat, Kinetic study of carbon nanotubes synthesis by fluidized bed chemical vapor deposition, AIChE J. 55 (2009) 465–474.

[103] X.B. Liu, H. Sun, Y. Chen, R. Lau, Y. Yang, Preparation of large particle MCM- 41 and investigation on its fluidization behavior and application in singlewalled carbon nanotube production in a fluidized-bed reactor, Chem. Eng. J. 142 (2008) 331–336.

[104] W.Z. Qian,W. Fei,W. Zhanwen, L. Tang, Y. Hao, L. Guohua, X. Lan, Production of carbon nanotubes in a packed bed and a fluidized bed, AICHE J. 49 (3) (2003) 619–625.

[105] C.T. Hsieh, Y.T. Lin,W.Y. Chen, J.L.Wei, Parameter setting on growth of carbon nanotubes over transition metal/alumina catalysts in a fluidized bed reactor, Powder Technol. 192 (1) (2009) 16–22.

[106] N. Shah, Sh. Ma, Y.Wang, G.P. Huffman, Semi-continuous hydrogen production from catalytic methane decomposition using a fluidized-bed reactor, Int. J. Hydrogen Energy 32 (2007) 3315–3319.

[107] C.B.Xu, J. Zhu, One-steppreparation of highly dispersed metal-supported catalysts by fluidized-bed MOCVD for carbon nanotube synthesis,Nanotechnology 15 (2004) 1671–168.

[108] Y. Wang, F. Wei, G. Luo, H. Yu, G. Gu, The large-scale production of carbon nanotubes in a nano-agglomerate fluidized-bed reactor, Chem. Phys. Lett. 364 (2002) 568–572.
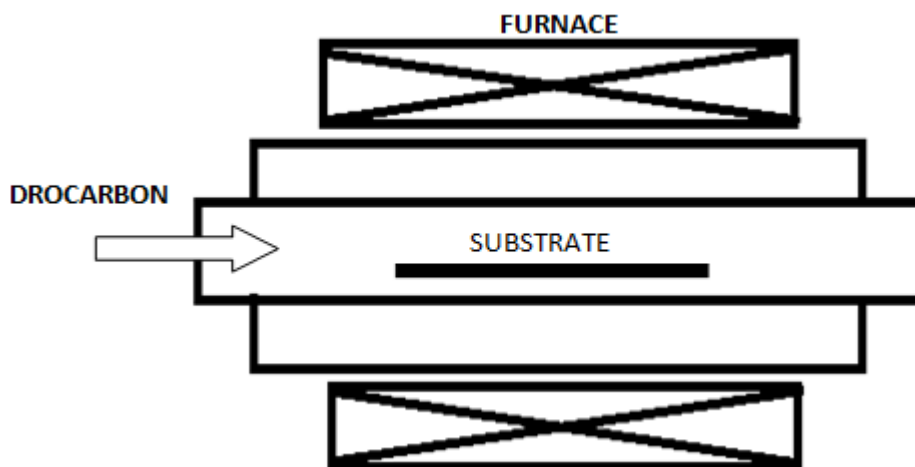
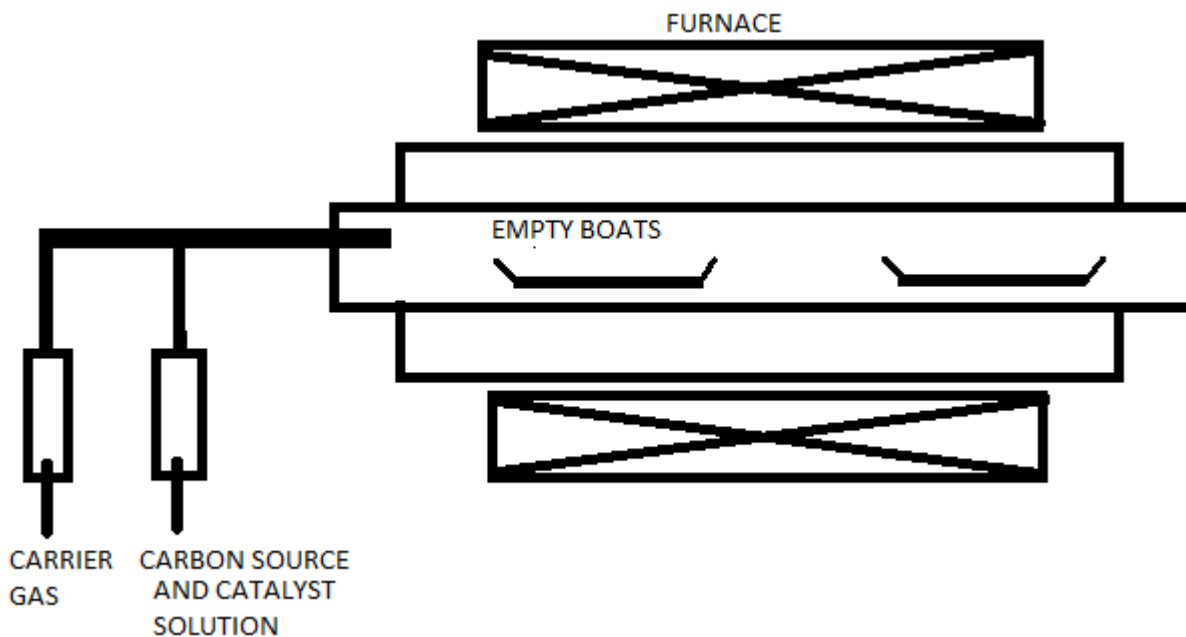**Figure 1:** Schematic of horizontal furnace.

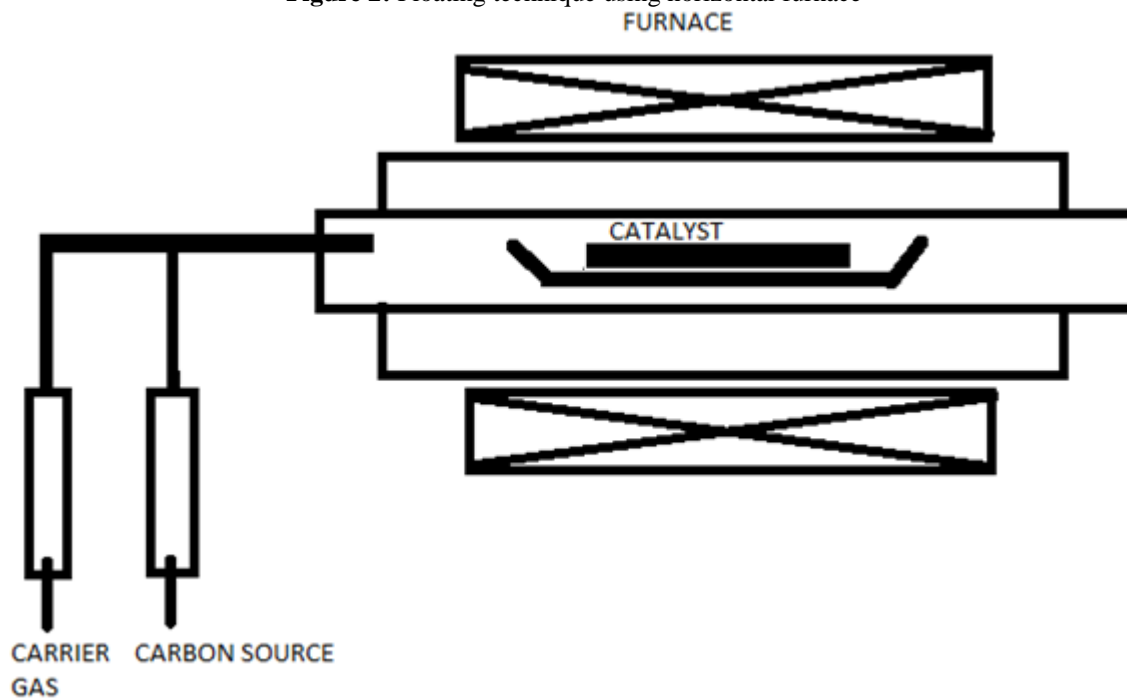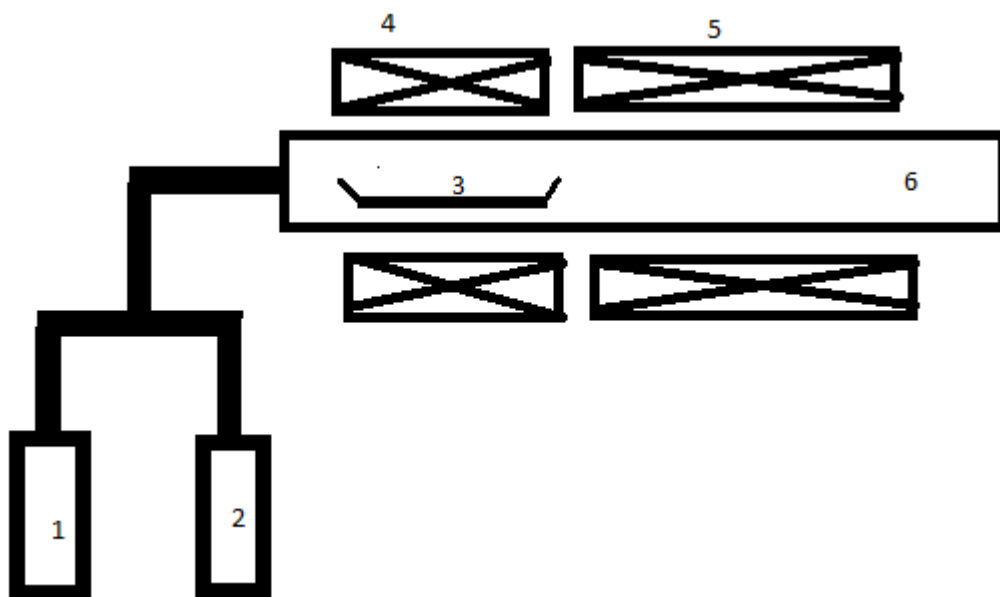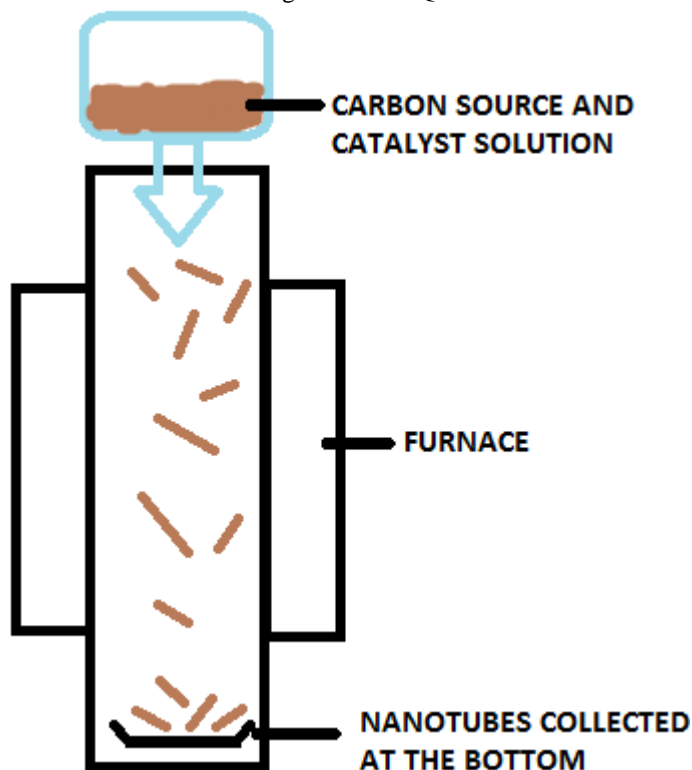**Figure 2:** Floating technique using horizontal furnace

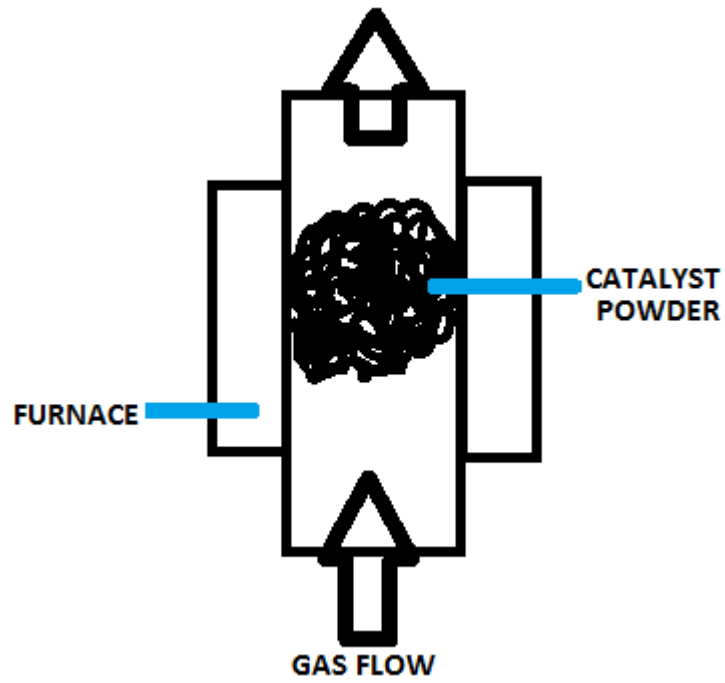**Figure 3:** Fixed-bed technique using horizontal furnace

Figure 4: Two stage horizontal furnace ; 1. Carrier gas cylinder. 2.Hydrocarbon gas cylinder. 3. Quartz boat. 4. First heating furnace. 5. Second heating furnace. 6.Quartz tube.

Figure 5: Vertical furnace using floating catalyst method

Figure 6: Vertical furnace using fluidized bed method