SYNTHESIS OF CARBON NANOTUBES FROM NATURAL GAS USING HORIZONTALLY CONTINUOUS ROTARY REACTOR SYSTEM

by

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LIST OF ABBREVIATION

CH_4	Methane
CCVD	Catalytic Chemical Vapour Deposition
CNF	Carbon Nanofibers
CNT	Carbon Nanotubes
Co	Cobalt
DWNT	Double-walled Nanotubes
LPG	Liquefied Petroleum Gas
Mo	Molybdenum
MgO	Magnesium Oxide
MWNT	Multi-walled Nanotubes
N_2	Nitrogen
NG	Natural Gas
SWNT	Single-walled Nanotubes
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis

ABSTRAK

Kajian ini memberi tumpuan kepada sintesis nanotube karbon (CNT) daripada gas asli (NG) menggunakan reaktor putar selanjar. Pemangkin jenis Co-Mo/MgO telah digunakan dalam proses sintesis. Tiga parameter dikaji dalam proses sintesis iaitu suhu tindak balas, nisbah gas asli kepada nitrogen dan masa tindak balas. Ciri-ciri CNT yang terhasil telah dianalisa menggunakan mikroskop transmisi elektron (TEM) dan analisis termogravimetri (TGA). Keputusan menunjukkan bahawa penguraian NG pada suhu 700°C, 800°C dan 900°C bukan sahaja menghasilkan CNT tetapi ia juga menghasilkan nanofiber karbon (CNF). CNT yang dihasilkan mempunyai diameter luar yang lebih kecil (12nm-18nm) berbanding CNF (32nm-44nm). Kaedah gerak balas permukaan (RSM) menunjukkan bahawa hasil karbon dipengaruhi oleh suhu tindak balas dan juga nisbah input NG kepada N_2. Dengan menggunakan RSM, jumlah maksimum karbon sebanyak 547.35% diramalkan dapat dihasilkan dengan system reactor beroperasi pada suhu tindak balas 895°C, masa tindak balas 1.95 jam dan nisbah NG:N_2 pada 0.61.

ABSTRACT

The present research focuses on the synthesis of carbon nanotubes (CNT) from natural gas (NG) using continuous rotary reactor system. The catalyst of Co-Mo/MgO was used during the synthesis process. Three operating parameters were studied namely the reaction temperature, ratio of natural gas to nitrogen (NG:N_2) and the reaction time. CNT produce were characterized using transmission electron microscope (TEM) and thermogravimetric analysis (TGA). The result shows that the decomposition of NG at 700˚C, 800˚C and 900˚C not only produced the desired CNT but also produced carbon nanofibers (CNF). CNT produced had much smaller outer diameter (12nm-18nm) compared to CNF (32nm-44nm). Response surface methodology (RSM) study shows that the percentage of carbon yield is affected by the reaction temperature and the NG to N_2 ratio. Using RSM, the maximum amount of 547.35% of carbon is predicted to produce using the operating reaction temperature of 895°C, reaction time at 1.95hours and NG:N_2 ratio at 0.61.

CHAPTER 1

INTRODUCTION

1.1 Carbon Nanotubes

Carbon nanotubes (CNT) have been recognized as an important material in today's advanced technology development. From its discovery in 1991 by NEC electron microscopist, Sumio Iijima [1], the application of CNT has been widely used in various type of industries namely nanoelectronics, biomedical, electromagnetic, electrochemical, mass storage and others [2]. CNT is favoured in current technology development because of its excellent chemical, physical and electronic properties [3, 4]. Electronic properties of CNT have attracted their use as metallic wires and as semiconducting channels in transistors. CNT also have been found useful in making composites and gas sensors resulting from their tremendous mechanical properties and high surface area.

CNT can be technically defined as a cylinder made up of rolled up sheet of graphene. The structure of CNT can be found as single walled carbon nanotubes (SWNT), double walled carbon nanotubes (DWNT), and multi-walled carbon nanotubes (MWNT). The diameter of CNT typically varies from 0.7nm up to 50nm depending on their shell structure. Tubes with single shell are called SWNT while the one with more than one shell are MWNT. Sometimes, CNT forms with double shell. This type of structure is referred as DWNT. The length of nanotubes can be up to centimeters, giving them an amazing length/diameter ratio.

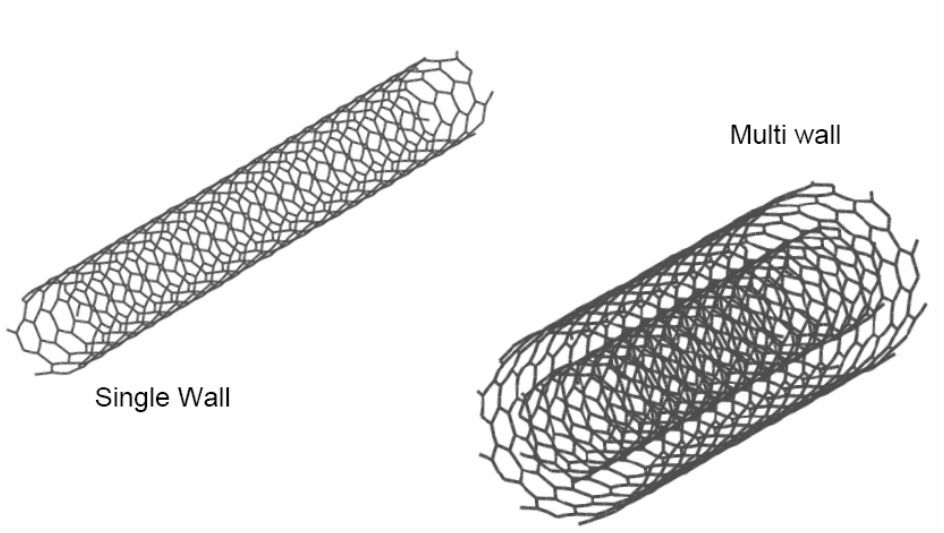

Figure 1.1: Illustration of single wall and multiwall nanotube

Several techniques can be employed in order to synthesize the CNT [5, 6]. It can be prepared by arch-discharge, laser beam evaporation of graphite or catalytic chemical vapour deposition (CCVD) of hydrocarbon. Among those, CCVD has been proven as the most successful technique for large scale production [7, 8]. In addition, CCVD which decompose hydrocarbon through thermal catalytic reaction has been reported as the most economical process and use low energy input [9].

Using CCVD technique, several hydrocarbons gases can be employed as the carbon precursor namely acetylene, ethane, methane, benzene, ethanol, natural gas (NG) and liquefied petroleum gas (LPG). Among them, methane gas is the one which is commonly used in this method. This is because methane is an abundant resource among hydrocarbons and it has been reported that methane is an ideal source for production of highly graphitized CNT due to its kinetic stability at high temperature. CCVD process is highly influenced by the catalyst used as well. Several authors have reported regarding the effect of catalyst in CNT synthesis [10-13].

1.2 Horizontally Oriented Continuous Rotary Reactor System

Horizontally oriented continuous rotary reactor system is a CCVD type of reactor design by Yeoh et al [14]. As the name suggest, this reactor is operated horizontally and it is capable to produce CNT continuously. It utilized the technique of CCVD where catalyst and hydrocarbon gas is fed into the reactor to manufacture the desired CNT.

The word ‘rotary’ in the reactor name shows the mechanism of the reactor to move the catalyst as well as the produced CNT from the feeding area to the reaction section and finally to the product reservoir. The movement is done by the rotary movement of the coil spring built inside the reactor. The rotating coil spring is also function as the controller of the reaction residence time. This is done by adjusting the rotation speed of the coil.

Hence, it gives an extra property to this reactor system as it gives more flexibility to the users to operate the reactor at their own specification. By the development of this reactor, it solved the problem faced by the conventional horizontal and vertical type of reactor which are the residence time problem and to simplify the continuous production of CNT.

1.3 Natural Gas in Malaysia

Malaysia is rich with its natural resources. One of the important resources that have contributed a lot in the nation development is natural gas. Natural gas has been discovered in Malaysia in the year 1983 [15]. Since then, it has played a major role in the increment of energy mix in this country.

Natural gas reserve in Malaysia is the largest in South East Asia and 12th largest in the world. The volume of proven natural gas reserve in 2009 is 87.9 trillion cubic feet and most of the production comes from East Malaysia, especially offshore Sarawak with 42.6 trillion cubic feet [16].There are three LNG processing plants in Malaysia, all located in a massive complex at Bintulu (East Malaysia-Sarawak) and supplied by the offshore natural gas fields at Sarawak. The Bintulu facility is the largest LNG complex in the world, with a total liquefaction capacity of 31 billion meter cubic or 22.7 million metric tons per year [17].

Malaysia is also one of the main producers of natural gas in Asia. The production of natural gas has risen steadily in recent years and reaching 198 million meter cubic per day in 2008 which is an increase of 22% since year 2002 [18]. Malaysia is a significant net exporter of natural gas, primarily in the form of liquefied natural gas (LNG). In 2005, Malaysia exported 21.2 million metric tons of LNG, which accounted for 15% of the total world LNG export. Malaysia was also the world's third largest exporter of liquefied natural gas after Qatar and Indonesia in 2010 [19].

In Malaysia, natural gas has become the main energy contributor since early 20's and currently it still dominated the energy supply in Malaysia. It is expected that natural gas will continue to play a major role in primary energy mix [18]. At the moment, nearly 75% of the energy mix in Malaysia is contributed by natural gas as a source of fuel. Power station sector is the major contribution which account for half of the total natural gas consumption, followed by industrial sector [15]. Natural gas (NG) is supplied by PETRONAS Gas Bhd., Malaysia. The compositions of the gas are as shown in Table 2.1.

Table 1.1: Composition of natural gas [20]

Components		Volume (%)
Name	Molecular Formula	
Methane	CH_4	92.735
Ethane	C_2H_6	4.070
Propane	C_3H_8	0.755
iso-butane	i-C_4H_{10}	0.085
n-butane	n-C_4H_{10}	0.060
Carbon dioxide	CO_2	1.830
Nitrogen	N_2	0.455
Condensate	-	0.010
Hydrogen Sulphide	H_2S	trace

In term of natural gas transmission facilities, Malaysia has one of the most extensive natural gas pipeline networks in Asia. The multi-phased Peninsular Gas Utilization (PGU) project had completed in 1998 and it spans more than 1430km. It has the capacity to transport 2 billion cubic feet per day of natural gas. The goal of the PGU is to expand natural gas transmission infrastructure on Peninsular Malaysia and its initiative has helped to boost domestic natural gas consumption [17].

1.4 Problem Statement

The synthesis of CNT using CVD technique is depending on the catalyst metallic particle formation. CVD method mainly uses gas phase hydrocarbons as a carbon source. The synthesis involves the catalytic decomposition of a carbon containing source on small metallic particle. Even though CNT has been founded more than a decade ago, a cost-effective and high selectivity method for the CNT production has not been established and commercialized.

There are several factors that make CNT expensive. One of them is the type of production system used. Recently, Yeoh et al. [14] has developed a reactor system which enable continuous production of CNT. Using this type of system, the cost to produce CNT is reduced as the system is capable to produce CNT in bulk and it does not require a high usage of labour. It is reported that the production cost of 1g of CNT using this reactor is RM1.74. While using conventional batch system, the cost is RM2.64. These prices are calculated based on methane as the carbon precursor [21].

Another factor that can be considered is the type of carbon precursor used in the system. Purified methane gas is one of the widely used carbon precursor in CNT reaction. The price of purified methane gas per cylinder ($6m^3$) is about RM3000 or RM500/m^3. Meanwhile for natural gas with 90% of its accounts for methane, only cost about RM2.72/m^3. The utilization of natural gas as the feed and the continuous reactor system will definitely give a big impact on the reduction price of CNT production.

Hence, this research is focussing on production of CNT using natural gas as the carbon source via continuous reactor system. Natural gas is chosen due to its abundant availability in Malaysia and because of its cheap price. Moreover, only a few works dealing with natural gas as a carbon source was published until now [8, 22, 23]. Considerable efforts in adjusting the process parameters is done as natural gas contains several different organic compounds and impurities such as N_2, sulphur, CO_2 and H_2O [23]. Bimetallic Co-Mo/MgO catalyst is used in the reaction process as it has been reported to be effective in producing CNT using batch reactor [24].

1.5 Research Objectives

The present research aim at achieving the following objectives:

- To synthesize CNT from natural gas using horizontally oriented continuous rotary reactor system
- To study the process parameters that affects the yield of CNT produce from natural gas

CHAPTER 2

LITERATURE REVIEW

2.1 Synthesis of CNT

Arc-discharge, laser ablation, and catalytic chemical vapour deposition (CCVD) have been the three main methods used for carbon nanotubes synthesis [5, 6]. The first two employ solid state carbon precursors to provide carbon sources needed for nanotubes growth. It also involved carbon vaporization at high temperatures (>1000°C). These methods are well established in producing high-quality and nearly perfect nanotubes structures, despite large amounts of by-products associated with them. However, both techniques suffer from the problem that it is hard to scale up the production of the CNT to industrial scale. The CCVD method currently represents the best hope for large scale production of CNT [25]. CCVD utilizes hydrocarbon gases as carbon sources for carbon atoms and metal catalyst particles as seeds for nanotubes growth.

2.1.1 Arc Discharge

In arc discharge technique, high temperature is needed (>3000°C) to evaporate carbon atoms into a plasma. Reports show that both SWNT and MWNT can be produced [26]. However, it is difficult to control the morphology of the product, such as length, diameter, and number of walls because the mechanisms of CNT production by the arc discharge method are complex. Other than that, this technique generally produced high volume of impure material as well such as carbon whiskers, soot and fullerenes [27].

Arc discharge apparatus consists of two carbon electrodes, the thicker cathode on which the deposit forms is separated from the thinner anode by ~1 mm. During the deposition the anode is consumed. A voltage of 20V - 25V is applied between the electrodes with the operating current around 50A - 120A. The optimal pressure for producing nanotubes is around 500torr of helium. It is reported that fullerenes are efficiently produced at a pressure below 100torr [28, 29].

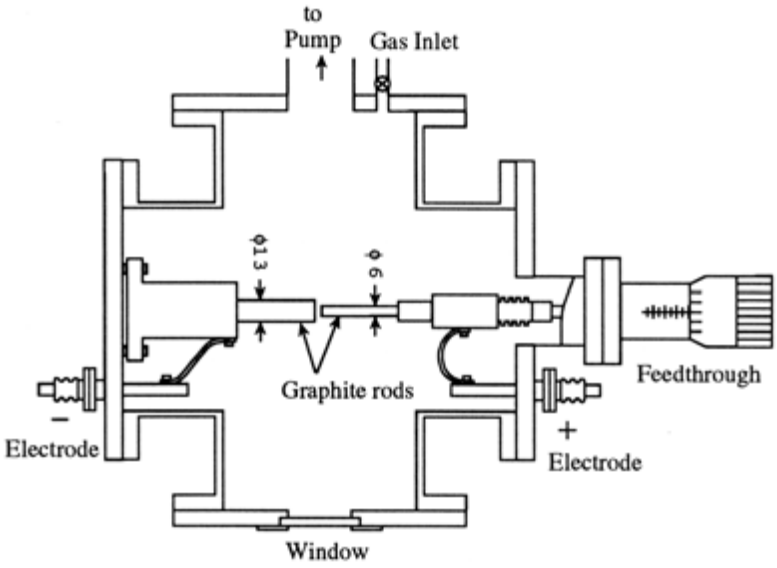

Figure 2.1: Example of arc discharge apparatus [30]

MWNT can be produced without using any catalyst. It is usually found in the inner region of the cathode deposit and they are surrounded by a hard shell consisting of nanoparticles of fullerenes and amorphous carbon. SWNT can be produce with the usage of catalysts such as Co, Ni, Fe, Y and Gd. Mixed catalysts such as Fe/Ni, Co/Ni and Co/Pt are used to grow bundles of SWNT [26].

Wang et al. [31] reported that DWNT which are synthesized continuously using Fe-Mo catalyst has improved the selectivity and purity of the product. Using

TEM, it indicates that the outer and inner diameters of the products are 1.9nm – 4.7nm and 1.2nm – 3.8nm respectively.

Zhao et al [32] on the other hand, study the current and arc pushing force effects on the synthesis of SWNTs by arc discharge. It was investigated by a temperature controlled arc discharging furnace with Co–Ni alloy powder catalyst at 600°C. It is reported that the suitable conditions of the current and arc pushing force of the arcing process was 100 and 80 A respectively.

Another study considers the preparation of DWNT from fullerene waste soot by arc discharge given by Qiu et al [33]. Fullerene waste soot was used as raw material to produce double-walled carbon nanotubes (DWCNTs) by arc discharge in a mixture of Ar and H_2 at 300torr. Generally, the quality of CNT produced using this method is very good as they can have a high degree of graphitisation.

2.1.2 Laser Ablation

Laser ablation utilized a high power laser beams that will vaporise a volume of graphite which is placed in an electrical furnace heated at 1200°C. Argon gas flows at about 500torr will sweeps the CNT from the high temperature zone to the water-cooled copper collector outside the furnace [34].

MWNT is produced when pure graphite is used but if it is composed of 1.2 atom% Co/Ni with equal amounts of Co and Ni added to the graphite then SWNT are synthesised. More than 70% conversion of graphite to SWNT was reported in the condensing vapour of the heated flow tube. The produced material consists of SWNT with a diameter between 10nm - 20nm and up to 100μm in length [34, 35].

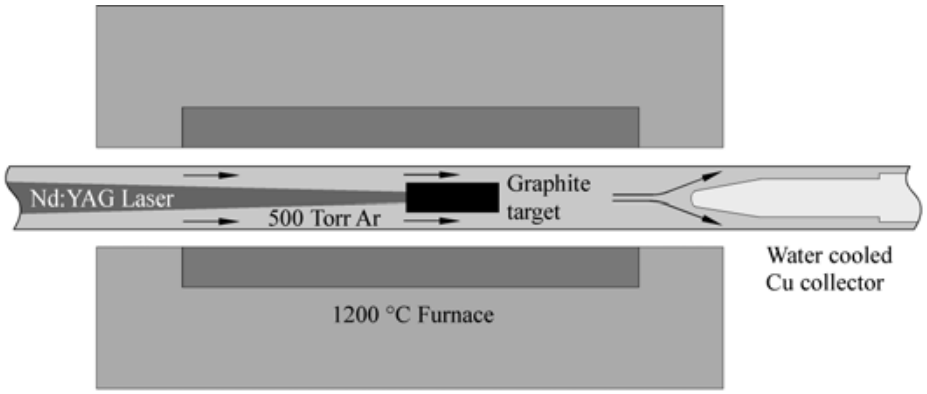

Figure 2.2: Example of laser ablation apparatus [35]

Nikolaev et al. [36] had study the effects of vaporization temperature on the diameter of SWNT. Pulsed laser vaporization preparation of SWNT on Co/Ni and Rh/Pd catalysts was explored, with respect to variations in the production temperature. Lowered production temperature leads to smaller CNT. Preparation of SWNT by pulsed laser vaporization is also reported by Stuerzl et al. [36] The procedure is based on sintering to obtain graphitic targets from common available amorphous carbon powder doped with nickel and cobalt metals. This method provides a high degree of conversion of the initial carbon material into nanotubes.

The effects of catalyst particle size on the purity, yield, and purification efficiency of SWNT produced by pulsed laser vaporization are investigated by Schauerman et al [36]. The purity of SWNT material prepared using Ni and Co nano metal catalyst particles was compared to material preparation using conventional micro metal particles. Result shows that the SWNT material from nano metal catalysts demonstrated a 50% increase in purity.

2.1.3 Catalytic Chemical Vapour Deposition

Catalytic chemical vapour deposition (CCVD) is the most promising synthesis route to produce massive quantities of CNT in an economical way. The formation of carbon filaments from the catalytic decomposition of carbon containing gas over metal surfaces has been known for a long time. However, there was no proof that this method could be used to produce CNT until Yacamàn et al. succeeded [37].

CNT synthesis by CCVD involves heating a catalyst material in a furnace and a hydrocarbon gas flowing through the reactor tube for a phase of time. In general, CNT growth mechanism in the CCVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal. The precipitation of carbon from the metal particle leads to the formation of tubular carbon solids. The catalyst particles serve as seeds to nucleate the growth of nanotubes [38].

CCVD has been reported for preparation of various carbonaceous structures such as carbon nanofibers (CNF), SWNT, MWNT, graphite layers as well as amorphous carbon layers. This method allows selective CNT growth in a variety of forms such as powder and aligned forest of CNT. The produced tubes can adopt various shapes. They can be curved, straight, helix, and planar spiral. The fibers often covered by amorphous carbon and metal nanoparticles are occasionally found at their tips. Even though CCVD's principle is quite simple, the exact growth mechanism of carbon nanotubes remains very complex. This is because many different parameters influence the growth of CNT [39].

The characteristics of the carbon nanotubes produced by CCVD method depend on the operating conditions such as the temperature and the operation pressure, volume and concentration of hydrocarbon, size and the pre-treatment of metallic catalyst, the nature of the catalyst support and the reaction time. The nanotube diameter can be controlled by varying the active particles on the surface of the catalyst. Reaction time on the other hand, affects the length of the tubes. Report proves that up to 60mm long tubes can be produced [40].

2.2 CNT Growth Mechanism

The growth mechanism of nanotubes may be different depending on which method is used. CNT from arc discharge and laser ablation method can be grown without a metal catalyst. While for CCVD technique, metal particles are necessary for CNT growth. The growth mechanism of CNT is complex and not well understood. Several models exist but some of them cannot clearly explain the mechanism. The metal seems to be essential for the growth because they are often found at the tip inside the CNT and also somewhere in the middle of the tube [41].

Baker et al. [42] has made a model of the growth of carbon fibres in 1972. He proposed the mechanism for tip and base growth of carbon filaments. Tip growth involves the decomposition of the carbon containing gas on the front surface of the metal particle producing carbon which then dissolves in the metal. The dissolves carbon then diffuses through the particle forming the filament. Reaction temperature and concentration gradient were proposed to be the main factors of this process. While for base growth, it occurs when there is a strong interaction between metal particles and the support material where the particle remains attach to the surface. An example of tip growth is Ni on SiO_2 while Co or Fe on SiO_2 is more likely to have base growth.

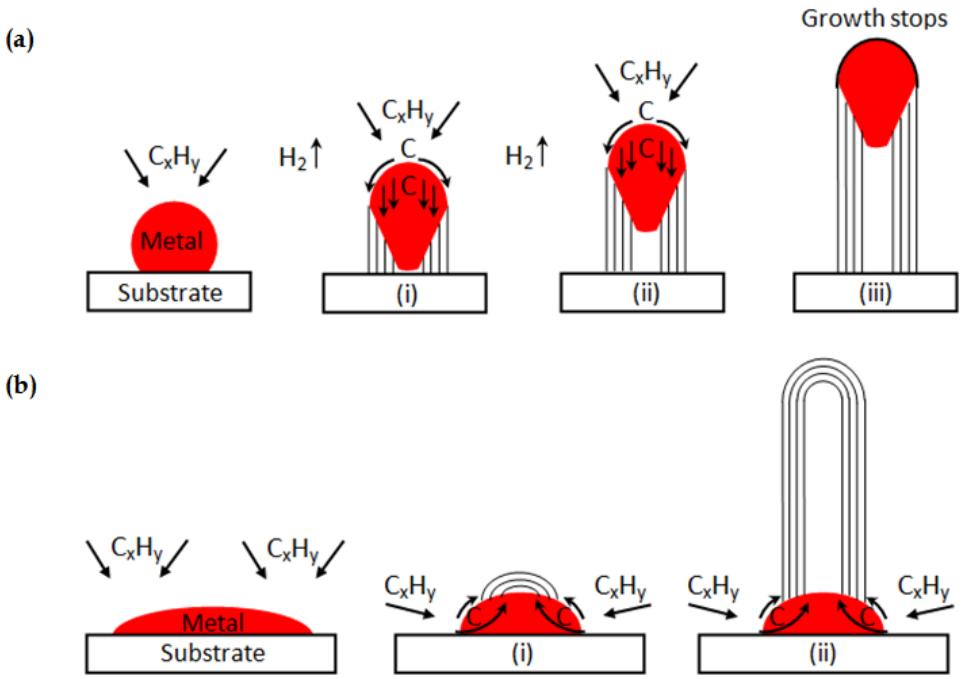

Figure 2.3: (a) Tip growth model (b) Base growth model [43]

Amelinckx et al. [44] has adapted the growth model of Baker et al. to explain the growth of carbon nanotubes. For the synthesis of nanotubes, the metal clusters must present in form of nanosized particles. It had been proposed as well that the metal particle can have two roles.

First of all, it acts as a catalyst for the dissociation of the carbon bearing gas species. Second, carbon diffuses on the surface of the metal cluster or through the metal to form a nanotube. The most active metals to use as the catalyst are Fe, Co and Ni, which are good solvents for carbon.

2.3 Catalyst used in CCVD Technique

Catalyst is an essential part in CCVD method as it serves as a seed for CNT to growth on. Various type of catalysts have been tried to boost the yield and the quality of produced CNT. The effect of different supports has been examined in detail as well. Nanoparticles such as Fe, Co, Mo, Ni, Cu and Au have been tried as catalyst either in pure metallic form (individually) or as alloys (mixture). These nanoparticles transition metal have common advantages of high melting temperatures, high carbon solubility and high carbon diffusion rates. Two factors that define a catalyst particle are its size and composition [45].

There are strong indications of dependence of CNT diameter on the catalyst particles size. Hence, controlling the catalyst diameter can help to govern the diameter of the growth CNT. The method used to apply the catalyst nanoparticles on the growth substrate is an important factor that will affect the morphology of the resulting product [46].

Other than transition metals, it is also has been reported that rare earth oxides can improve the activity and selectivity as potential co-catalysts in several catalytic materials. The selection of the metallic catalyst may affect the growth and morphology of the CNT. The most common metals found to be successful in the growth of CNT are Fe, Co, and Ni. Fe/Mo bimetallic catalyst supported on MgO was found to be the most effective catalyst combination in the synthesis of SWNT and DWNT. MgO support on the other hand is useful in the production of CNT because it can be removed by a simple acidic treatment while other supports require a harsh

hydrofluoric treatment. Almost pure MWNT in large quantities can be produced by the CCVD technique using methane gas on Co-Mo/MgO catalysts or Ni/Mo [39].

Yeoh et al [24] had studied the role of molybdenum in Co-Mo/MgO for large-scale production of CNT. Using methane as the carbon precursor, he observed that the molybdenum (Mo) content in the Co-Mo/MgO has affect the carbon yield, diameter uniformity and quality of CNT produced. It shows that Mo helps the dispersion of active metals on the surface of catalyst support and prevents the agglomeration of active metal particles through the formation of thermally stable Mo species. The optimum composition of Co-Mo/MgO catalysts by means of producing the highest yield of CNT (354.3%) was $Co_5Mo_{20}MgO_{75}$.

2.4 CCVD Carbon Feedstock

Besides catalyst, the other main substance that contributes to the success of CCVD method is the gas phase carbon feedstock or known as the carbon precursor. This is where the carbon that forms the nano-sized tube came from. Several different carbon containing compounds have been used as the precursors which are carbon monoxide (CO), methane (CH_4), ethylene (C_2H_4), acetylene (C_2H_2), benzene (C_6H_6), toluene (C_7H_8), ethanol (C_2H_5OH), methanol (CH_3OH) [45, 47].

In a typical growth situation, carbon precursor is mixed with other gases such as H_2, N_2 or other carbon carriers. This is done to have finer control on the reaction rates inside the CCVD chamber. For example, if the product after dissociation is H_2, then a fine control of premixed hydrogen can be used to check on the dissociation rate of carbon precursor. Carbon precursor gases can themselves produce unwanted nanotubes due to the presence of premixed nanoparticles coming from the contamination in the gas cylinder. These gases are also function as to make an inert environment in the chamber. This is vital to avoid the oxidation of the carbon, where it will keep the chamber free of oxygen. Most extensively used gas to create inert atmosphere are namely nitrogen, helium and argon [48, 49].

Other than purified gases that have been mention earlier, natural gas (NG), liquefied petroleum gas (LPG), coal gas, and gasoline can be utilized as a carbon precursor as well. These gases comprise of several hydrocarbon gas species depending on the type of the product. The advantages of using this type of gases are that they are massively available on the market with relatively cheap price [50].

Several authors have successfully conducted research and publish their work in the area of carbon nanotubes synthesis from natural gas [8, 22, 23]. Lima et al. has synthesized CNT over chromium oxide and iron oxide catalyst and use NG (91.8 CH_4, 5.580 C_2H_6, 0.970 C_3H_8, 0.030 C_4H_{10}, 0.100 C_5H_{12}, 0.800 CO_2 and 1.420 N_2) as the carbon source. The experiment is carried out under H_2/NG and Ar/NG atmospheres in a tubular reactor. It is shown that only the catalyst exposed under H_2/NG produce carbon nanotubes. The CNT produce is MWNT type with the diameter ranging from 5-40nm [23]. According to Dupuis, the diameter of CNT is determined by the diameter of the catalyst metallic particles [51]. In other research, Bonadiman et al. had used Fe–Mo/MgO to synthesize CNT from NG. Both SWNT and MWNT are produce through the process. The efficiency of the SWNT synthesis was reported higher under Ar/NG atmospheres than H_2/NG atmospheres [8].

Lee et al. [20] had also utilized natural gas as the carbon source for CNT synthesis. The experiment had been done using horizontal quartz tube reactor with Co-Mo/Al_2O_3 as the catalyst. The gas which is supplied by PETRONAS Gas is containing of 93% of methane. The result shows that the NG conversion decreased in first 30 minutes (from 46% to 28%) and maintain after 2 hours (25%). Analysis by TGA shows that the carbon yield from the synthesis is about 78.7%.

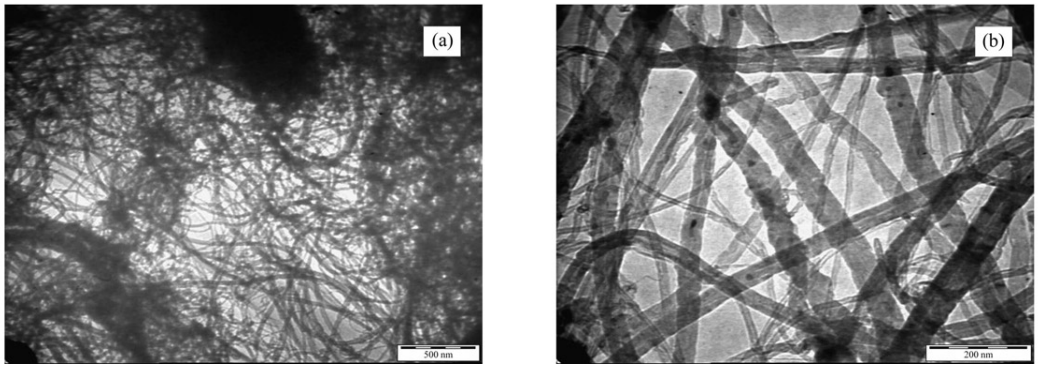

Figure 2.4: Low (a) and high (b) magnification TEM images of filamentous carbons synthesized from natural gas [20]

On the other hand, Zhang et al [52] has done the research on LPG as carbon precursor and has successfully produce CNT arrays in the floating catalyst process. Besides CNT, other form of hydrocarbon has been produced as well namely methane and ethylene. The vertically aligned CNT arrays were reported to have up to 300μm in length for 4 hours growth. The purity of the product can be as high as 97.5%. Diameter of CNT can be minimized to 13nm by controlling the reaction temperature.

2.5 CCVD Reactor System

In this section, the reactor system which utilized CCVD to manufacture CNT is discussed. Usually, the experiment of CNT is conducted in a flow furnace at atmospheric pressure. There are two types of furnace system, the first one is a horizontal configuration, and the second is configured vertically. Horizontal furnace is the most popular type of reactor to be used rather than the vertical arrangement. Here, the catalyst is placed in a quartz or ceramic boat which is put into a quartz tube. The reaction mixture which comprised of the source of carbon precursor and a carrier gas is passed over the catalyst bed at temperatures ranging from 500°C to 1100°C. The system is then cooled down to room temperature. Horizontally oriented reactor is commonly used for batch process. The problem with the batch process is that it is inefficient, labour dependence, expensive and has limited production capacity. The quality of the product might vary from batch to batch as well [39].

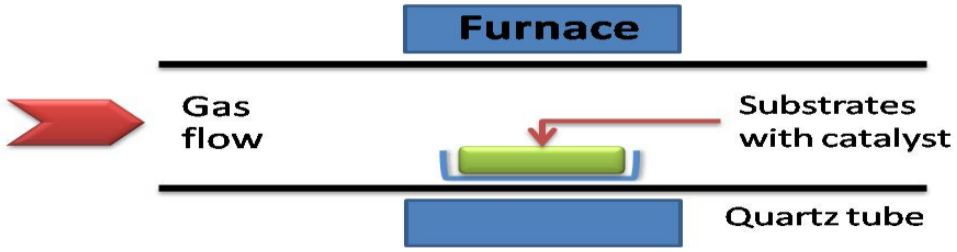

Figure 2.5: Horizontal CCVD reactor system [39]

For the vertical furnace configuration, it usually employed for the continuous mass production of CNT. The catalyst and carbon source is inserted from the top of the furnace and the resultant product grows during floating and it is collected at the base of the chamber. The fluidized bed reactor is a variation of the vertically oriented furnace. Supported catalysts are typically positioned in the center of the furnace and

an upward flow of carbon precursor gases is used. The fluidization process involves the supported catalysts to remain much longer in the furnace than in the vertical floating technique [39].

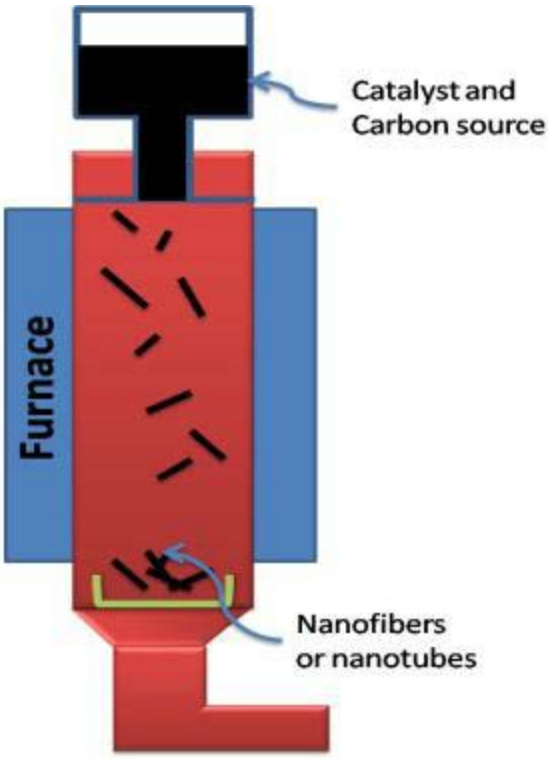

Figure 2.6: Vertical CCVD reactor system [39]

Technically, this process is not a fully continuous system; rather it is a semi-batch system. It is because the catalyst particle is not continuously fed and removes from the system. The varying residence time of catalyst in the reactor is also an issue as it does not confirm that the same batch of catalyst fed into the system will withdraw at the same time.

Yeoh et al. [14] has successfully developed a rotary reactor system (shown in figure 2.7) which enables continuous production of CNT. As what has been described earlier, continuous reactor of CNT is usually built in a vertical orientation. As opposed to that, this reactor is manufactured to be operated in a horizontal orientation with the utilization of revolving coil spring inside the reactor to move the catalyst and the produced CNT.

Using this system, CVD technique is applied where catalyst and carbon source will be fed into the reactor counter current with each other. The residence time of the reaction can be control by adjusting the rotation speed of the coil spring [14].

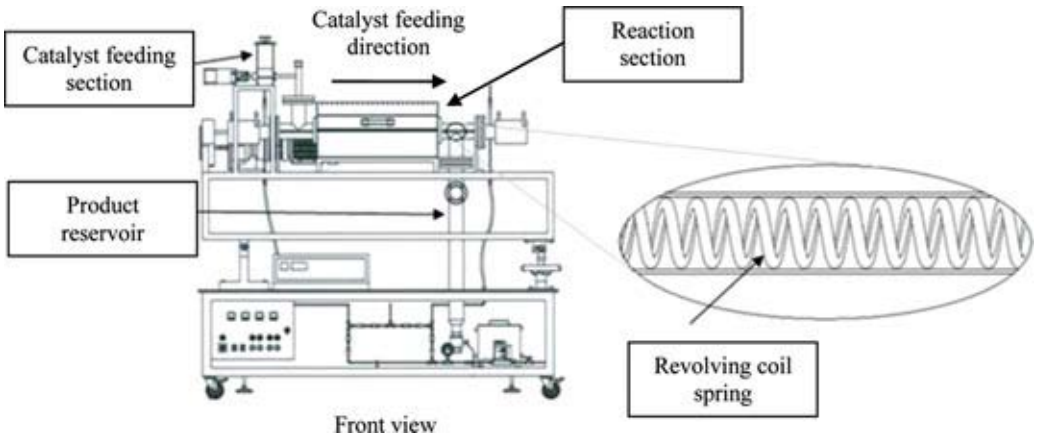

Figure 2.7: Horizontally oriented rotary reactor system by Yeoh et al. [14]

This reactor generally consist of 3 main parts namely catalyst feeding section, reaction section and product reservoir. In the reaction section, a revolving soil spring is built inside enclosed in a hollow tube as well as a split tube furnace. The temperature is controlled by the multi heating zone furnace.