Carbon nanotubes synthesis in fluidized bed reactor equipped with a cyclone

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Abstract. This work aimed to observe the performance of a fluidized bed reactor which was equipped with a cyclone in the synthesis of carbon nanotubes (CNT) by chemical vapor deposition. Liquefied petroleum gas with a constant volumetric flow rate of $1940 \text{ cm}^3/\text{minutes}$ was fed to the reactor as a carbon source, while a combination of metal components of Fe-Co-Mo supported on MgO was used as catalyst. The CNT synthesis was carried out at a reaction temperature which was maintained at around $800 – 850 \degree C$ for 1 hour. The CNT yield was decreased sharply when the catalyst feed was increased. The carbon efficiency is directly proportional to the mass of catalyst fed. It was found from the experiment that the mass of as-grown CNT increased in proportion to the increase of the catalyst mass fed. A sharp increase of the mass percentage of carbon nanotubes entrainment happened when the catalyst feed was raised from 3 to 7 grams. Agglomerates of carbon nanotubes have been formed. The agglomerates composed of mutually entangled carbon nanotubes which have an outer diameter range $8 – 14 \text{ nm}$ and an inner diameter range $4 – 10 \text{ nm}$, which confirmed that the multi-walled carbon nanotubes were formed in this synthesis. It was found that the mesopores dominate the pore structure of the CNT product and contribute more than 90 % of the total pore volume.

1. Introduction

In the development of nanotechnology, carbon nanotubes (CNT) lately have become a particular concern of researchers and industrial communities. CNT have led to the development of intensive research in the field of science and technology due to their superior physical and chemical properties such as superior mechanical strength, excellent electron conductivity and other superior surface properties [1,2]. Based on the way how the energy source is introduced, three methods of synthesizing carbon nanotubes which have been widely developed are arc discharge, laser ablation and chemical vapor deposition (CVD) [3].

Among the three methods of synthesis, the CVD method is the most easily adapted for large-scale production in industrial applications since it requires lower reaction temperatures to produce at a low cost and provide high carbon nanotubes yield [4,5]. In the synthesis of carbon nanotubes by CVD method, the growth mechanism involves the decomposition of carbon source compounds into carbon atom [6].

In the presence of a catalyst, such carbon atom then deposited to form a structure of carbon nanotubes. The structure of the carbon nanotubes includes the wall number, diameter, length, orientation, and alignment, can be controlled by setting the reaction parameters during the growth of the carbon nanotubes [7]. Various carbon sources such as $\text{CH}_4$, $\text{CO}$, $\text{H}_2/\text{CO}$, $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, and $\text{C}_6\text{H}_6$ have been widely used for the synthesis of carbon nanotubes by CVD method [8,9].
To date, fluidized bed reactor is considered as the most superior reactor type for large-scale production of carbon nanotubes due to the availability of sufficient space to stimulate the rapid growth of the carbon nanotubes, superior in facilitating excellent heat and mass transfer, easy to scale-up and suitable for continuous production [10,11]. Moreover, fluidized bed reactor provides a high space velocity which would trigger the achievement of a high carbon nanotubes yield [12]. Lately, the development of the synthesis of carbon nanotubes by CVD method using a fluidized bed reactor has focused on mass production [13]. Therefore, the capacity of a fluidized bed reactor during the synthesis of carbon nanotubes becomes a very important parameter.

In this work, we present the performance of a fluidized bed reactor which is equipped with a cyclone in synthesizing carbon nanotubes by CVD method. In this study it has been shown that with the use of cyclone the reactor is capable of synthesizing CNT with a high enough capacity which reach 23.39 g as-grown CNT per batch. The main observed parameters is the carbon nanotubes yield and the reactor capacity. The reactor capacity is represented by the mass of as-grown carbon nanotubes which are produced in a single batch operation. The carbon efficiency and some physical characteristic include the orientation, the morphology and the bulk density of the carbon nanotubes product are also investigated.

2. Experimental

2.1. Catalyst preparation

The combination of the transition metals Fe, Co and Mo which were supported on MgO was used as a catalyst in this work. Fe and Co act as the active components, while the role of the Mo component is as a promoter and to prevent rapid deactivation of the catalyst [14-17]. The catalyst was prepared using a wet impregnation method [8]. Ferric (III) nitrate nonahydrate (Fe(NO$_3$)$_3$.9H$_2$O), cobalt (II) nitrate (Co(NO$_3$)$_{2}$.6H$_2$O), ammonium heptamolybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O) and magnesium oxide (MgO) were used as metal precursors. The catalyst was prepared to achieve a weight percent composition of Fe:Co:Mo:MgO (4:4:2:90).

2.2. The reactor

The fluidized bed reactor arrangement was schematically presented in figure 1. The reactor was made of a quartz tube 95 cm in height, 2.60 cm inner diameter and 0.20 cm thick. A tubular electric furnace which capable to supply 1.2 kW heat covered the reactor. The furnace was equipped with a temperature controller and able to raise the temperature of the furnace up to 900 °C. A K-type (chromel-alumel) thermocouple was embedded between the inner surface of the furnace and the outer surface of the reactor tube and serves to detect the furnace temperature.

A cyclone, which was made of stainless steel SS 304 having a diameter of about 7.8 cm and volume of about 1000 cm$^3$, was mounted on the top of the reactor. It is connected to the reactor exit gas line. The cyclone serves to separate the fine carbon nanotubes particles which were carried by the flowing gas out of the reactor. A thin plate, which is made of quartz porous material with a pore size of 400 mesh, was fitted at a distance 54 cm above the bottom of the reactor tube. It serves as a gas distributor and to retain the catalyst/product carbon nanotubes. The area under the quartz plate is a preheating zone, while the area above the quartz plate is a reaction zone. A certain amount of quartz wool was placed on a quartz plate that serves to avoid blockage of the quartz plate pores due to the growth of the carbon nanotubes.

2.3 Experimental procedure

The experiments were performed in a constant volumetric rate of feed gas mixture. The total feed gas flow rate was 1940 cm$^3$/minutes which consist of 77% vol argon, 13 % vol liquefied petroleum gas (LPG) and 10 % vol hydrogen. The furnace temperature was maintained at 900 °C. While the amount of calcined catalyst fed was varied at 3, 5, 7 and 9 grams.
After reduced catalyst was fed to the reactor, reduction stage was started by flowing the hydrogen at a flow rate of 500 cm$^3$/minutes. The catalyst reduction process was held for 5 hours at furnace temperature 750 °C. Then the furnace temperature was raised to 900 °C. After the furnace temperature reach 900 °C, the synthesis of carbon nanotubes was started by introducing the feed gas mixture to the reactor while maintaining the furnace temperature at 900 °C. The synthesis reaction is terminated by stopping the flow of LPG gas. The furnace was then switched off and the reactor was cooled by flowing argon gas. As grown carbon nanotubes were removed from the reactor as well as from the cyclone and were stored for analysis.

![Diagram of fluidized bed reactor arrangement]

**Figure 1.** The schematic of fluidized bed reactor arrangement

### 2.4 Characterization techniques
The orientation of the CNT product was analyzed using scanning electron microscope - JSM-6510A/JSM-6510LA (Analytical/Analytical low vacuum SEM). While transmission electron microscope, TEM JEOL JEM 1400, were used to observe its diameter and morphology. The BET surface area and pore characteristic of the CNT were analyzed using Surface Area Analyser, Quanta chrome Nova 2000 Series - NovaWin - Instruments version 11.03.

### 3. Results and discussions

#### 3.1 The CNT yield and the carbon efficiency
In this work, the CNT yield is defined as the mass of carbon nanotubes produced per unit mass of catalyst fed. The profile of the CNT yield at various of catalyst mass fed was presented in figure 2. It
can be seen that a sharp decrease in the CNT yield occurs when the catalyst feed was increased, that is from 3.61 g CNT/g catalyst at 3 grams catalyst feeding to 1.88 g CNT/g catalyst at 7 grams catalyst feeding. The availability of space for the growth of carbon nanotubes become a significant contributing factor in increasing the growth rate of the carbon nanotubes. The more the amount of catalyst fed will result in the less ratio of the available space for the carbon nanotubes growth to the mass of the catalyst. Thus it can be understood as the amount of catalyst feed is raised, then the CNT yield decreased. It should be noted that decreasing the CNT yield is associated with lowering the quality of CNT in regard to increasing the level of impurities content derived from the residual catalyst. Further addition of catalyst feed to 9 grams resulted in a slighter decrease in CNT yield to 1.60 g CNT/g catalyst. At high catalyst feeding ratio of the available space for the carbon nanotubes growth to the mass of the catalyst will be very low resulted in denser growing carbon nanotubes particles. This dense particle will create more intense collisions between particles and inhibit the occurrence of particles entrainment. Consequently, there will be more particles of carbon nanotubes have enough time to grow then avoid a sharp drop in CNT yield.

The carbon nanotubes yield resulting from this work is comparable to the yields obtained by Zhang et al. [18] which is 3.8 g CNT/g catalyst and relatively greater than the yield achieved by some other researchers, i.e. Baddour et al. [19]: 0.96 g CNT/g catalyst, Huang et al. [20]: 1.48 g CNT/g catalyst, Danafar et al. [21]: 0.6-0.8 g CNT/g catalyst, Zhao, et al. [22]: 0.22 g CNT/g catalyst, and Hsieh et al. [23]: 0.7-3.0 g CNT/g catalyst. Figure 3 also expose the carbon efficiency in accordance with the amount of catalyst fed. The carbon efficiency is defined as the percentage of the amount of carbon available in the feed gas which is converted into carbon nanotubes. The liquefied petroleum gas which was used in this work has a chemical composition as follow: 1.7 %mol C₂H₆, 71.7 %mol C₃H₈, 11.4 %mol i-C₄H₁₀ and 15.2 %mol C₆H₁₀. From these data, the available carbon which was supplied to the reactor will be 23.51 g carbon/hour. Base on these amount of the available carbon and the amount of CNT produced at the end of synthesis, the carbon efficiency was calculated.

In general, the carbon efficiency is directly proportional to the mass of catalyst fed. This can be explained that the more the mass of catalyst in the reactor, the contact time between the gas feed and the catalyst will be longer so that the conversion of hydrocarbons into carbon nanotubes will be

![Figure 2. The CNT yield and carbon efficiency in various catalyst feed](image-url)
higher. In this work, the highest carbon efficiency was 66.8% which was achieved when the mass of catalyst feed was 9 grams. From an economic viewpoint, a higher carbon efficiency is preferred because it reflects more efficient carbon source utilization. The carbon efficiency resulting in this work are comparable to those obtained in fluidized bed reactor studied by some other researchers, among others Morancais et al. [24] obtained carbon efficiency 48 - 75 % using Fe/Al₂O₃ catalyst at 450 -750 °C, while Venegonia et al. [25] got carbon efficiency 15-50 % applying Fe-SiO₂ catalyst at 750 -1350 °C.

3.2 The reactor performance and the CNT entrainment

Reactor capacity indicates how much the ability of the reactor for producing carbon nanotubes in one batch operation. The capacity of the reactor is a very important parameter for commercial-scale production applications since it will determine the economic level of the reactor operation. In this work, reactor capacity was expressed as mass of as-grown carbon nanotubes that can be produced in a single batch synthesis process. In this case, a mass of as-grown carbon nanotubes is a mass of carbon nanotubes obtained from the reactor at the end of the synthesis reaction, it includes the mass of the catalyst. Mass of as-grown CNT produced at various of catalyst mass feeding was presented in figure 3. It was shown that mass of as-grown CNT increase in proportion to the increase of the catalyst mass fed. It also can be seen that the reactor is capable of producing as much 23.4 grams as-grown in one batch synthesis when catalyst feed is 9 grams. It should be noted that the capacity of the produced as-grown carbon nanotubes was also counted the as-grown nanotubes products which were carried by exit gas stream (called as carbon nanotubes entrainment) and were separated by the cyclone.

![Graph of as-grown CNT production](image)

**Figure 3.** Mass of as-grown the CNT produced in various catalyst feed and the percentage which were carried by the flow of gas exit the reactor

Observations which was conducted during the experiment found that the entrainment of partly carbon nanotubes in the gas stream only occurs especially in a short time interval just after the synthesis reaction begins. It shows that the carbon nanotubes are in the early growth phase and are at the top section of the fluidized bed, such particles still have a small size so that it easily carried by the flow of gas.

The percentage of as-grown carbon nanotube entrainment which were separated in the cyclone was also shown in the figure. It can be seen in the figure that a sharp increase of the mass percentage of
carbon nanotubes entrainment happened when the catalyst feed was raised from 3 to 7 grams. The lowest percentage of carbon nanotubes entrainment is 8.5 % mass when catalyst feed is 3 grams, and its highest value reaches 20.3 % mass which happens at 7 grams catalyst feeding. It indicates that the addition of an amount of the catalyst feed to a certain extent causes increasing the formation of carbon nanotubes with smaller particle size. The smaller the particle size of carbon nanotubes will be the greater the potential to be carried by the flow of gas. The experimental results also showed that further addition of catalyst feed from 7 to 9 grams decreased the percentage of carbon nanotubes entrainment. Adding a further amount of the catalyst feed will shorten the distance between the fluidized particles in the reactor chamber leading to the greater chance of collisions among the growing carbon nanotubes particles. The particles collision will become the barrier for the small particles of carbon nanotubes to be carried by the flow of gas out of the reactor.

3.3 The CNT orientation and morphology
The orientation of CNT product can be observed from SEM image with a magnification of 5,000 times which was presented in figure 4. From that figure, it can be observed that the agglomerates of carbon nanotubes have been formed in synthesis with the fluidized bed reactor. From the image can also be observed that each CNT agglomerate was composed of several smaller size sub-agglomerate. The orientation of carbon nanotubes is mutually entangled with each other to form a sub-agglomerate. Furthermore, during their growth carbon nanotubes in a single sub-agglomerate form a network with other sub-agglomerates then some sub-agglomerates are integrated into a bigger agglomerate.

It also can be seen that the size of an agglomerate was ranging from about 2 – 5 µm. The formation of a stable agglomerate size is certainly influenced by the interaction of the gas-solid during the occurrence of the fluidization phenomenon during the synthesis of carbon nanotubes.Clearer visualization of the orientation of the carbon nanotubes products was shown by SEM image with a magnification of 50,000 times which was presented in figure 5. From the image, it was seen more clearly that long carbon nanotubes were linked to one another to form a woven carbon nanotubes. The woven carbon nanotubes had lead to the formation of a stable agglomerate.

Figure 4. SEM image of the CNT at 5,000 times magnification produced with the catalyst feed 3g

Figure 5. SEM image of the CNT product at 50,000 times magnification produced with the catalyst feed 3g

To investigate the morphology of the carbon nanotubes, TEM image capture was carried out and the results were displayed in figure 6 for synthesis with catalyst feeding 3 and 7 grams as representative
samples. By making manual measurements using a ruler on the basis on scaling shown in the images, it was found that the carbon nanotubes have an outer diameter range 8 – 14 nm and an inner diameter range 4 – 10 nm. It was confirmed that multi-walled carbon nanotubes have been formed in this synthesis. In the image was also found that a rest of catalyst particle stand at the end of carbon nanotubes. This indicated that the growth of carbon nanotubes follow the tip-growth mechanism.

![Figure 6. TEM image of the CNT produced with the catalyst feed: (a) 3g and (b) 7g](image)

The morphology of the carbon nanotubes, resulting from the synthesis with catalyst feeding 3 and 7 grams, which were entrained by the flowing gas and collected in the cyclone were also investigated by taking its TEM image and the images were presented in figure 7. The diameter of the carbon nanotubes was measured using similar previous method applied in the determination of the diameter of carbon nanotubes which were collected from the reactor. The measurement results showed that carbon nanotubes which were carried by the gas stream have an outer diameter in the range 8 – 22 nm and inner diameters in the range 6 – 14 nm.

![Figure 7. TEM images of the CNT carried by gas and separated in the cyclone with the catalyst feed: (a) 3g and (b) 7g](image)
3.4 The surface area and pore volume of the CNT

Surface area and pore volume distribution were determined from the isotherm adsorption-desorption of N$_2$. The analysis was conducted to both CNT product which were collected in the reactor and which were carried by the gas stream and collected in the cyclone. The BET surface area was presented in figure 8, while the total pore volume was shown in figure 9. In the determination of the total pore volume, it was assumed that the pores were to be filled with liquid N$_2$. It was determined from the amount of nitrogen vapor adsorbed at a relative pressure $P/P_0 \approx 1$, where $P_0$ is the N$_2$ saturation pressure. From both figure can be seen that CNT which were collected in the reactor have BET surface area in the range 115 - 148 m$^2$/g and it was higher than BET surface area of the CNT carried by gas and separated in the cyclone which is in the range 71 - 79 m$^2$/g. The same thing happened to the total pore volume. The CNT which were collected in the reactor have a total pore volume in the range of 0.768 – 1.531 cm$^3$/g and it was higher than the total pore volume of the CNT carried by gas and separated in the cyclone which is in the range of 0.513 - 0.612 cm$^3$/g.

The micropores (pore size < 2nm) volume distribution of the CNT product collected in the reactor, which was determined using the Horvath-Kawazoe (HK) slit model, was expressed as cumulative micropores volume and presented in figure 10. It was shown that micropores with a pore size range 0.3 – 0.5 nm dominate the micro porosity. It can be seen from the figure that experiments which were conducted by varying the mass of the catalyst resulted in CNT with micropores volume in the range 0.0468 – 0.0598 cm$^3$/g. The Barret, Joyner and Halenda (BJH) method was used to determine the mesopores volume distribution of the CNT product collected in the reactor. Mesopores are pores with pore size range 2 – 50 nm. The result expressed as the cumulative BJH pore volume and presented in figure 11.

![Figure 8. BET surface area of the CNT](image)

![Figure 9. Total pore volume of the CNT](image)

Even though the determination using BJH method include measurements on a limited range of macropores, but the cumulative pores volume curves tend to be flat in the macropores sizes range (pore size > 50 nm). It means that the determined pore size was dominated by the mesopores. At the level of the catalyst mass varied, the mesopores volume in the CNT product is in the range 0.7361 – 1.4933 cm$^3$/g. It means that the mesopores contribute more than 90 % of the total pore volume in the CNT product.
Figure 10. Cumulative micropore volume of the CNT collected in the reactor at all mass catalyst varied

Figure 11. Cumulative BJH pore volume of the CNT collected in the reactor at all mass catalyst varied

4. Conclusions
The mass of as-grown CNT increase in proportion to the increase of the catalyst mass fed. A sharp increase of the mass percentage of carbon nanotubes entrainment happened when the catalyst feed was raised from 3 to 7 grams which indicate that the addition of an amount of the catalyst feed to a certain extent causes increasing the formation of carbon nanotubes with smaller particle size. The availability of space within the reactor for the growth of carbon nanotubes was considered become the factor that affecting the CNT yield. In general, the carbon efficiency is directly proportional to the mass of catalyst fed. Agglomerates of carbon nanotubes have been formed in synthesis using the fluidized bed reactor. The agglomerates composed of mutually entangled carbon nanotubes which have an outer diameter range 8 – 14 nm and an inner diameter range 4 – 10 nm, which confirmed that the multi-walled carbon nanotubes were formed in this synthesis. High mass catalyst feeding resulted in more dense fluidized catalyst particles and generate a more compact carbon nanotubes agglomerate. It was found that the mesopores dominate the pore structure of the CNT product.

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