Utilization of camphor as an alternative carbon source for the synthesis of carbon nanotubes using floating catalyst

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Abstract. Due to its extraordinary physical, mechanical and electrical properties, carbon nanotubes (CNT) have continued to develop since it was discovered in 1998. Domestic demand itself has not been fulfilled because the production costs are fairly expensive. Conventional CNT exhibits many toxic effects on invertebrates and also cause genotoxicity in rats and in humans. Camphor-based CNT production is cheap and easy to use for chemical vapor deposition (CVD) because of its volatile and non-toxic properties. This research was conducted with the floating catalyst method using ferrocene (Fe) as a catalyst precursor and camphor as a carbon precursor by varying the number of camphor mass by 1, 3 and 5 grams. The CNT synthesis was performed silica balls and quartz shatter as the substrates, argon as carrier gas with flow rate 100 mL/min, and hydrogen as co-reactant with flow rate 70 mL/min. The operating temperature of the synthesis used was 800°C with a reaction time of 60 minutes. The results showed that camphor decomposed into three compounds which are 40% benzene, 8% toluene, and 52% xylene. The synthesis process with quartz as the substrate produces more carbon deposits than silica balls due to its better heat transfer and the purer silicon dioxide (SiO2) contained in the quartz. CNT has grown to follow a tip growth model with deformations such as the buckling growth model and a continuous growth model was also found. The biggest yield (25 mg/cm²) is obtained at camphor mass of 5 gram with a carbon percentage of 87.1% and average diameter 33 - 44 nm.

1. Introduction

CNT is a material with huge potential to be applied in many fields, such as biosensors, chemical sensors, hydrogen storage, nano-electrics, catalyst support, and the composite as a mechanical reinforcing agent [1]. One important parameter in the process of synthesis of CNT is a carbon source. During this time, most of the carbon source used is fossil fuels such as methane, ethylene, acetylene, LPG, and so forth. In fact, fossil fuels are one source of energy that cannot be renewable. According to The Statistical Review of World Energy released by BP, the natural gas in the world will only exist for up to 55 years. Seeing these facts, the use of renewable carbon source has to be considered. Optimizing the synthesis of CNT which are cheap and easy to produce on an industrial scale is necessary to be done.

Green chemistry is defined as an effort to design chemical processes and products produced with the aim of eliminating the emergence of more dangerous substances. Last version of CNT contains harmful effect on invertebrates and genotoxicity effect in rats and humans. Camphor is easily obtained from re-
newable resources and non-toxic properties, making it the "green" biological source ideal for Nanotube Synthesis.

Camphor (C_{6}H_{10}O) able to produce MWNT at a temperature of 650°C [2, 3]. Besides its low operating temperature, this carbon source is relatively affordable and easily obtained. Camphor is only extracted from lauracea family cinnamon camphor tree latex. This is a white crystalline solid that sublimates at room temperature. Camphor is believed to be capable of producing CNT with high efficiency due to the carbon ring (pentagonal and hexagonal) contained in camphor. Moreover, the abundance of hydrogen in camphor helps reduce metal oxides into metals that served as catalysts, and the oxygen atom will help oxidizing amorphous carbon. The use of camphor as a carbon source in CNT synthesis with the floating catalyst-chemical vapor deposition (FC-CVD) method needs to be done to obtain the recommended factors.

The substrate has an influence on the growth of CNT. SiO$_2$ is one of the most effective and popular types of substrate for CNT growth [4,5]. Chemically, the high carbon activity on the SiO$_2$ substrate carries carbon to not dissolve into the Fe catalyst, making it easily saturated with carbon and depositing carbon atoms on the surface of the substrate which tends to lead to CNT formation [6].

This study uses quartz as reactor shell material for CNT synthesis. Quartz contains one part of silicon and two parts of oxygen or commonly called SiO$_2$. Therefore the aim of this study was to compare silica balls and quartz as substrates with the same synthesis design parameters. Evaluation of the parameter of CNT synthesis are the use of camphor as a carbon source, Fe as a catalyst, argon as an inert gas and hydrogen gas as a co-reactant. The use of hydrogen gas can improve the quality of the CNT produced [7]. The FC-CVD method has never been done on SiO$_2$ ceramic balls and quartz as the substrates. Thus, further research is needed to find out the characteristics of CNT synthesis on SiO$_2$ balls and quartz substrates by using camphor carbon sources and the FC-CVD method.

2. Method
The silica balls manufactured by Jianxu Kelley Chemical Packing. Figure 1 showed a double furnace system to heat up the reactors. There are two kind of reactors, the first reactor is Pyrex reactor that is used to vaporize camphor as the carbon source and ferrocene as the catalyst. The second reactor is quartz-reactor as a CNT synthesis media. Silica balls and quartz are used as the substrate with the prior ultra-sonication process. Camphor and ferrocene are placed in a boat and placed in the middle of the Pyrex reactor, and the substrate is placed in the middle of the quartz reactor as well.

The variation of camphor mass used as a carbon source in the synthesis of CNT processes is 1, 3, and 5 grams with 1% wt of ferrocene as a catalyst. The use of Fe catalyst 1% wt is done because the precursor concentration is too high that is considered to cause the production of carbonaceous products other than CNT. It caused the decomposition that is not catalyzed is promoted [6]. Optimizing the relative concentration of camphor, catalyst and substrate in a double furnace were carried out to achieve a very high CNT growth rate at 800°C.

![Figure 1. Schematic diagram of the experimental set-up](image-url)
Synthesis is done by using argon gas as a carrier gas with a flow rate of 100 mL/min and hydrogen gas as co-reactants with a flow rate of 70 mL/min. Camphor and Fe vaporize simultaneously at 200°C in the sublimation process and pyrolysis process at 800°C in the second furnace. After 60 minutes of reaction, both furnaces is switched off and allowed to cool down naturally. Upon cooling down to room temperature, a deposit of carbon is obtained on the surface of silica balls, and also in the inner wall of the quartz reactor. CNT products are collected from the substrate and also scraped from the inside of the reactor. Gas Chromatography-Flame Ionization Detectors (GC-FID) for analyzing camphor sublimation and camphor decomposition. CNT product was analyzed by Scanning Electron Microscope - Energy Dispersive X-Ray Spectroscopy (SEM-EDX) and Transmission Electron Microscopy (TEM).

3. Results and Discussion

3.1 Camphor sublimation

Table 1 shows that camphor changes from a solid phase to the vapor phase at 200°C. The other word that sublimation occurs at a temperature of 200°C in the sublimation furnace. This is in line with the statement by Kumar in 2010 that camphor does not decompose into simpler compounds under the temperature of 500°C [8]. At a temperature of 500°C, Camphor begins to decompose into benzene and xylene. The amount of xylene also increases with increasing temperature. The camphor at the synthesis temperature of 800°C decomposes into three main compounds namely benzene, toluene, and xylene. This type of cyclic hydrocarbon produces a curved / hunched CNT with tube walls often bridging inside [8].

| Components   | A (%) | B (%) | C (%) |
|--------------|-------|-------|-------|
| Benzene      | 100   | 26.49 | 40.41 |
| Toluene      | 0     | 0     | 7.89  |
| Xylene       | 0     | 73.51 | 51.70 |

The results of camphor decomposition in table 1 are similar to the camphor decomposition by using a vertical pyrex reactor to heat up the camphor up to 800°C to determine the decomposition of camphor vapor after it is entering the synthesis furnace [9]. The output of this sublimation process in the gas phase is then stored in the gas sampler when the furnace’s temperature has reached a temperature of 800°C. The gas is then characterized by GC-FID. From the result of the characterization, it can be concluded that the camphor will be decomposed into Benzene, Toluene and Xylene (BTX) [6]. Xylene dominates camphor decomposition. Xylene is the best carbon source to produce the highest CNT results with little amorphous carbon content [10].

3.2 Comparison of substrate

Figure 2 shows the results of SEM for (a) silica balls (b) quartz at a temperature of 800 °C with Fe catalyst precursors and camphor as carbon precursors. The chemical vapor deposition process of the CNT uses the vapor phase delivery phase of the ferrous metal (Fe) catalyst precursor, observing strong selectivity for growth on silica ball and quartz substrates.

Figure 2.a shows only a few CNT formation that occurs and tends to be agglomerated. On silica balls, the stable particles from iron silicide (FeSi₂) and iron silicate (Fe₂SiO₄) are formed due to chemical reactions between the surface of silicon, oxygen and Fe particles at high temperatures which lead to inhibit the growth of nanotubes [5]. Figure 2.b forms a more uniform CNT. Active iron catalyst particles are formed on the surface of pure silicon oxide which results in the formation of more homogeneous nanotubes of size on the quartz substrate [4,5].
Figure 2. The results of SEM characterization of CNT with (a) silica balls (b) quartz

Figure 3.a and Figure 3.b show the results of SEM mapping for silica balls and quartz substrate respectively. In quartz, the carbon distribution is more evenly distributed compared to silica ball. Figure 3.a there is a fairly even distribution of carbon, but it forms the agglomerate indicated by a red lump in the middle right of the image. This CNT agglomerate shows that carbon clots can increase the size of the CNT diameter and reduce the quality of the CNT produced. The large catalyst particle size can reduce the catalyst density on the surface of the substrate so that this can inhibit the occurrence of van der Waals forces which is the key to CNT growth. This is in line with [11], that catalysts are an important aspect of CNT’s growth. The tight distribution of the catalyst can lead to the occurrence of van der Waals forces between reaction CNT. However, the amount of excess catalyst can cause catalyst agglomeration due to catalyst deposition processes that occur simultaneously [4]. Figure 3.b shows no agglomeration in quartz substrate carbon mapping indicates the surface of the CNT uniform and homogeneous surface. It correspond with Figure 2b.

Figure 3. Carbon mapping SEM at (a) silica balls (b) quartz

Table 2 shows the results of EDX. Detection of Si and Fe compounds proves that the Fe catalyst is spread evenly on the surface of the substrate and Si comes from the ball and quartz substrate used as CNT deposit sites. This means that in quartz, many carbon compounds nucleate to the surface of the catalyst so that a lot of carbon deposits form on the surface of the substrate.

Table 2. EDX results for SiO₂ balls and quartz

| Component | SiO₂ Balls | Quartz |
|------------|------------|--------|
| C (%-wt)   | 64.12      | 76.86  |
| O (%-wt)   | 14.66      | 4.17   |
| Si (%-wt)  | 19.32      | 18.15  |
| Fe (%-wt)  | 1.89       | 0.82   |
At temperatures higher than 500°C, ferrocene decomposes spontaneously together with the chemical reaction of Fe (C₅H₅)₂ → Fe + H₂ + CH₄ + C₅H₆ + ... becomes reactive hydrocarbons and iron clusters act as the core of the catalyst [12]. In this case, ferrocene with its carbon atom works not only as a catalyst but also can act as a carbon source. This reaction is dominated by Fe diffusion through the original silicon oxide layer at high temperatures. This tends to make the deposition process on the silica balls substrate at high temperatures create Fe compounds that are not catalytically active. Complete changes in the chemical properties of Fe particles deposited from the active Fe catalyst into stable compounds such as FeSi₂ and Fe₂SiO₄. These results indicate that the chemical catalyst particles on the substrate are very important for growing carbon nanotubes.

The yield of CNT of quartz is 0.0892 grams and silica balls are 0.0628 grams. Quartz provides better results than silica balls as CNT growth substrate. This is due to two factors, namely the composition of the substrate compound, and the shape of the substrate. The quartz reactor tube has better heat transfer than silica balls. The comparison of heat transfer from quartz and silica balls is determined by equation 2.1.

\[
\frac{T(t) - T_{\infty}}{T_{(i)} - T_{\infty}} = e^{-bt} \tag{1}
\]

where \( T(t) \) is the temperature of such bodies are only a function of time; \( T_{\infty} \) is the medium or ambient temperature; \( T_{(i)} \) is the body temperature of \( i \)-th; \( b \) is proportional to the surface area but inversely proportional to the mass and the specific heat of the body; \( t \) is the time required for the temperature to reach a specified value \( T(t) \). The quartz takes 0.64 times faster than the silica balls to reach the desired temperature. The composition of the substrate compound also affect the results of the synthesis of CNT. Silica balls contain 75% SiO₂ and 17% Al₂O₃, while the quartz glass contains 99% SiO₂. The highest SiO₂ contain will direct the growth of the amount of carbon deposited [11]. Therefore, the quartz substrate will be used in the study of variations in camphor mass.

3.3 Variation of camphor mass

Figure 4 shows the relationship between CNT yield and camphor mass. The increase in camphor mass at a constant argon and H₂ flow rate tends to increase CNT deposition on the surface of the substrate. Synthesis of CNT with camphor mass of 1 gram, unable to make carbon penetrate the catalyst core to nucleate and continue CNT growth. CNT yield of 1 gram is 18.2 mg/cm²; Camphor mass of 3 grams is 21.8 mg/cm² and a 5-gram mass produces a yield of 25.3 mg/cm². This shows the tendency of carbon deposited per unit area to increase as the amount of camphor mass is used.

![Figure 4. Relationship between CNT yield and camphor mass](image-url)
Figure 5. The results of FE-SEM on samples with camphor mass (a) 1 gram (b) 3 gram (c) 5 gram

During the reactor heating process from room temperature to the synthesis temperature of 800 °C, a number of components gradually turn into gas as in table 1 GC-FID results. When the amount of camphor increases, the carbon content, and oxygen in each mixture also increases. Thus, the mixture of iron from ferrocene will be reduced because the process of oxygen decomposition and ferrocene in camphor becomes Fe + CH$_4$ + H$_2$ + C$_5$H$_6$. [6,7]. So, the addition of camphor mass will increase the number of carbon atoms deposited on the substrate.

As shown in figure 5, all samples were able to form CNT. Camphor is a carbon source that has a molecular structure consisting of hexagonal and pentagonal carbon rings so that it has a tendency to form fullerenes and nanotubes [8]. The camphor hexagonal carbon ring is uneven but tilted [14]. So, graphene sheet formation tends to be curved rather than a flat sheet. The presence of a pentagonal carbon ring makes the CNT that is formed not too straight [8].

The particles containing Fe after nanotube growth can be obtained by observing SEM and insert from TEM images of cross sections of the substrate on the lower left side of the image after the nanotube growth process shown in figure 5. Irregularly shaped particles with a diameter of 44 to greater than 80 nm appears on the surface above the oxide area and inside the nanotube cavity. Nanotubes which have the smallest average diameter in figure 5.a, SEM results indicate that iron and carbon are spread over the region of the quartz substrate during the process of FC-CVD. TEM results show that the iron catalyst and quartz substrate can be detected by showing the presence of thin carbon above the layers in the substrate area so that only a small portion of the carbon is detected on the surface of CNT growth. Figure 5b and 5c show that irregularly shaped nanosize particles at the top of the quartz surface are iron gamma active catalysts for the growth of carbon nanotubes in pure SiO$_2$ regions such as quartz [5]. This shows that the higher the mass of camphor on the quartz substrate, the higher carbon activity in the gas phase encourages carbon to dissolve into Fe particles formed on the substrate surface during ferrocene decomposition at high temperatures. So that Fe particles easily become saturated or saturated with carbon atoms, and precipitation of carbon from the surface of Fe particles leads to the formation of tubular carbon solids in sp2 structures [4,5]. Iron particles are chemically stable in the quartz during the full FC-CVD process time. Therefore, gamma Fe catalysts with small dimensions can effectively catalyze the growth of very dense carbon nanotubes in the quartz region. In the lower amount of camphor mass, chemical reactions occur between silicon, Fe, and oxygen, which are present in small concentrations.

Figure 6 shows the relationship between camphor mass and the average diameter of the CNT formed. The type of CNT formed is Multi-Walled Carbon Nanotubes (MWCNT). MWCNT has an outside diameter range of 5-80 nm (US Nanomaterial Research, Inc.). Mass of Camphor of 1, 3 and 5-gram have an average CNT diameter of 44.1 nm; 59.8 nm and 82.8 nm. Increased camphor mass tends to increase the average diameter of the CNT formed. Carbon produced from camphor decomposition (benzene, toluene, and xylene) has a more significant impact on increasing CNT yield. Very clean CNTs that are almost free of ferrocene are produced in high mass camphor as shown in figure 5. This shows that at this temperature catalyst-support interactions are strong enough to grow CNT in the direction of tips growth and gradually increase in mass, ferrocene is more pronounced in
samples [15]. The increase in camphor mass used as a carbon source tends to make the diameter of the CNT formed. This is caused by the more carbon sources used, the more catalysts used due to a fixed catalyst ratio, which is 1% (w/w).

![Figure 6](image.png)

**Figure 6.** Comparison of the mass of camphor is used by an average diameter CNT formed

The particle size of the catalyst is a determinant of the diameter of the CNT [8]. Increased consumption of the amount of catalyst used will lead to the formation of agglomeration of catalyst particles. This also causes the type of CNT that is formed is MWCNT. MWCNT will grow on iron catalyst particles when the particles are still floating in the vapor phase, while MWCNT will grow in groups of catalyst particles that are agglomerated in the solid phase.

4. Conclusion
Quartz substrate has better CNT growth results than silica balls substrate. Quartz requires 0.64 times faster than silica balls to reach the synthesis temperature. Increased camphor mass will increase CNT yield. The yield of CNT for camphor 1, 3 and 5 gram masses is 18.2 mg/cm$^2$, 21.8 mg/cm$^2$ and 25.3 mg/cm$^2$ respectively. The increase in camphor mass made the CNT diameter also increase by 44.1 nm; 59.8 nm and 82.8 nm. Future research will lead to green chemistry as an effort to design chemical processes and products that are produced with the aim of eliminating more dangerous substances. The development of camphor as a renewable resource and non-toxic properties will make it the ideal "green" biological source for Nanotube Synthesis.

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