Upscaled synthesis of carbon nanotube from palm oil mill effluent using pyrolysis for supercapacitor application

P Widiatmoko, N F Nugraha, H Devianto, I Nurdin, and T Prakoso

Department of Chemical Engineering, Bandung Institute of Technology, 40132, Bandung, Indonesia

E-mail: pramujo@che.itb.ac.id

Abstract. The utilization of Palm Oil Mill Effluent (POME) is advantageous to reduce environmental problems and increase its value as a source of carbon. Carbon nanotube (CNT) was synthesized by pyrolysis of POME and ferrocene mixture at 900°C under a flowing nitrogen atmosphere. CNT is nanosized and has high electrical conductivity; it is compatible as electrodes for energy storage devices such as supercapacitor. The study investigated the process for the upscaled formation of CNT from POME. The synthesis consists of POME polymerization, pyrolysis, and CNT characterization. Additionally, before pyrolysis, the CNT collecting system was applied in tube furnaces. The result showed that this process produced 1.2 g of CNT, a diameter of 47-100 nm, and a surface area of 635.5 m².g⁻¹. XRD analysis, 2θ of 26.58° indicated structure of graphite C (002), Raman spectra resulted ratio I_G/I_D of 1.16 indicated higher graphite than disorder. CNT was characterized and applied as electrode material for supercapacitor which exhibits a specific capacitance of 13.98 F.g⁻¹.

1. Introduction

Indonesia is the largest palm oil producer in the world with a capacity of 37.8 million tons per year [1]. As a consequence, abundant wastes are generated. Palm oil mill effluent (POME) is the liquid waste that represents 62% of total waste. From each ton of processed palm oil fresh fruit, 20 m³ POME is produced [2]. Palm oil mill has been regarded as a profit-making industry for the past decades. Besides revenue from the palm oil production itself, the abundance of biomass could generate high economic return to the palm oil mill by converting it to value-added products [2]. POME contains rich organic compounds, so it has potential as a carbon source to produce carbon nanotubes (CNT). Several carbon precursors such as methane, acetylene, benzene have been used as a carbon feedstock to synthesize CNTs [3–5]. These carbon precursors are related to fossil fuels and there may be a crisis for these precursors soon. There are few reports on the synthesis of CNTs from natural precursors, e.g. turpentine oil, neem oil, and even organic wastes, like Bio-oil PCB and waste cooking oil [6–8]. The advantage of using natural precursors as a carbon feedstock for synthesizing CNTs is that they are inexpensive and have no chance of shortage soon.

Many processes have been reported for their synthesizes, such as arc discharge, laser ablation, chemical vapor deposition (CVD), and Pyrolysis [9–12]. CVD is the most promising method for synthesis CNT but expensive. We have been using pyrolysis due to simple and inexpensive method [13]. One of them, this method vaporizes carbon precursor at lower temperatures and pyrolyzes at
higher temperatures in one step furnace while in CVD takes two steps. The pyrolysis method has attracted attention due to the possibility of producing carbon nanotubes on a commercial scale [14].

CNT is a cylindrical allotrope of carbon with nanometric size. CNTs have a high electrical conductivity of $10^7$ S.cm$^{-1}$. Application of CNTs in energy storage, such as supercapacitor, produces specific capacitances of 12-120 F.g$^{-1}$. KPEE-ITB Laboratory succeeded in producing CNT from POME by pyrolysis. However, the yield of CNT is still low, and the capacitance of supercapacitor does not meet commercial standards [15]. The study will investigate how to increase the production of CNT by adding three times the amount of raw materials and utilization of the CNT collecting system made by stainless steel mesh at the end of the tube furnace.

2. Methods

2.1. Materials

CNT was produced from Palm oil mill effluent (POME) which was collected from the palm oil mill of PT. Perkebunan Nusantara VIII in Bogor. The POME can also be described as wastewater rich in organic carbon with a colloidal suspension of 95 - 96% water, 0.6 - 0.7% oil, and 4 - 5% total solids, including 2 - 4% suspended solids [6]. Formaldehyde water solution (Merck, purity~37%) used to polymerize POME and ammonium hydroxide (Merck, purity~28%) as catalyst. Pyrolysis of the resin used ferrocene (purity~98%) as a catalyst in nitrogen flow. Ferrocene is frequently used as a precursor to prepare carbon nanostructures because it cannot only act as a carbon source but also give rise to small metal clusters as catalysts.

2.2. CNT Production

Figure 1 represented the process flow diagram of CNT synthesis. POME has to be polymerized with a 37% formaldehyde solution with a weight ratio of 5:6.5, and ammonium hydroxide as catalyst at 95°C for 4 hours. The resin formed is heated at 60°C for 2 hours and at 120°C for 12 hours. After that, the resin was ground to fine powder, mixed with 20-30%-w ferrocene, and homogenized with ethanol at 50°C until the mixture is uniform and all ethanol is evaporated. Afterward, the mixture is loaded in a ceramic crucible and placed in the tube furnace.

![Figure 1. Process flow diagram of CNT synthesis.](image)

Figure 2 represented the utilization of the CNT collecting system made by stainless steel mesh at the end of the tube furnace. The pyrolysis process consists of 2 steps; the first step is conducted at 200°C during 1 hour with heating rate of 5°C/min in natural atmosphere, and the second is run at 900°C for 1 hour with a heating rate of 3°C/min in flowing nitrogen atmosphere.
2.3. Characterization

The surface morphology of CNT was investigated by using scanning electron microscopy (SEM) (Hitachi SU3500, Japan) and using a transmission electron microscope (TEM) (Hitachi H9500, Japan). The Crystal structure of CNT was obtained from a powder X-ray diffraction pattern by using a Bruker D8 advanced diffractometer with monochromatized Cu K radiation. Nitrogen sorption isotherm of the sample was measured using a NOVA 3200e, Quantachrome Instruments, USA. Surface areas are obtained from the nitrogen sorption isotherm using multipoint Brunauer-Emmett-Teller (BET). A Raman spectrum of the CNT was measured by Raman spectrometry (Renishaw, model no. H 45517) using an argon ion laser (λ=532 nm).

The electrochemical performances of CNTs were studied by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) methods. Electrochemical measurements were carried out using Gamry V3000 potentiostat–galvanostat, utilizing a symmetrical electrode configurations with 6 M KOH solution as electrolyte at room temperature. Electrode of the symmetrical cell was prepared by mixing CNT with polyvinylidene fluoride (PVDF), which is coated on 1 cm² of stainless steel mesh and dried at 80°C for 1 day. Nafion 212 impregnated with the electrolyte, was placed between both electrodes. The specific capacitances of supercapacitors were computed from CV curves by using the following equation (1) [16].

\[
C_{sp} = \frac{2}{m|V_2 - V_1|} \int_{t=0}^{t(V_2)} i(V)dt
\]

(1)

Where ‘\(C_{sp}\)’ is the specific capacitance (F.g⁻¹), ‘m’ is the mass of the active electrode (g), ‘V’ is the cell voltage (V) and integral of \(i(V)dt\) is the area under the CV curve. Specific capacitances are also computed from the GCD by using the following equation (2) [17].

\[
C_{sp} = \frac{2I}{(|\Delta V/\Delta t|)m}
\]

(2)

Where ‘I’ is the current (A), ‘\(\Delta V\)’ is the discharge voltage difference between \(\Delta t\) period, and ‘m’ is the mass of the active electrode (g).

3. Result and Discussion

Increasing of raw material amount and utilization of a stainless steel mesh-based collecting system increased the yield of CNT from 0.46% to 0.96% (the maximum fix carbon yield was 2.94%). The
The growing mechanism of CNT during the synthesis can be proposed as follows: nanometer iron produced from ferrocene decomposition accumulates carbon on its surface with the formation of the Fe–C solid solution. After a very short period of time, the Fe–C solid solution reached a supersaturated point and carbon atom started to nucleate and grow in a nanotube shape during the slow growth [8]. The CNT that moved from the ceramic boat was caused by the influence of the growth mechanism of nanocarbon at 900°C. When the catalyst is mixed directly with the raw material, CNT growth in the gas phase and is carried by inert gas so that the product covers the inner wall of the tube furnace [9].

The morphology of CNT was identified using SEM and TEM. There are 4 samples of CNT, which are commercial CNT (CNT CO), CNT before scale up (CNT BS), CNT after scale-up at ceramic crucible (CNT CC) and CNT after scale-up at stainless steel mesh (CNT SS). The SEM observation results are shown in Figure 3.

![SEM micrographs of (a) CNT CO, (b) CNT BS, (c) CNT CC, and (d) CNT SS.](image)

The SEM images showed that all of CNT were cylindrical. Figure 3a indicated the CNT with a diameter between 5 and 10 nm. CNT with a smaller diameter will give larger capacitance in supercapacitor [6]. CNT BS has a diameter between 30 and 72 nm. Increasing three times amount of raw materials produced CNT with smaller distance diameter of 47-59 nm for CNT CC and 80-100 nm for CNT SS. Transmission electron microscope (TEM) is widely accepted that the carbon nanotube diameter can be determined by directly measuring the distance between two dark lines associated with carbon nanotubes in a TEM image. Representative TEM overviews of the samples investigated are shown in Figure 4. From a qualitative point of view, these samples mostly consist of multiwalled nanotubes with a hollow inside.

![TEM micrographs of (a) CNT CO, (b) CNT BS, and (c) CNT CC.](image)
In particular, the samples labeled CNT CO, BS and CC indicated similar diameter results with SEM. It presents the smaller diameter for CNT CO with the larger capacitance in the supercapacitor. On the contrary in Table 1, CNT before and after scale-up have a similar diameter. CNT has an external diameter of 8.9-57 nm, and multiwalled nanotubes (MWCNT) have an external diameter of 5-100 nm [18]. The large specific surface area includes a relatively small contribution from the surface area of the particles and a major contribution from the pores inside the particles [19].

The internal diameter of CNT or pore of CNT can increase the active surface area for the electrical double layer between electrodes and electrolytes in the supercapacitor [20]. All samples have a diameter of 2-50 nm, which is the size range of the mesopore regime. When the pore size is in the mesopore regime, counter-ions enter mesoporous carbon materials and approach the pore wall to form an electric double-layer capacitor (EDLC) [15]. The pore size under the mesopore will have an impact on the low value of the specific capacitance of the supercapacitor [19].

Table 1. Diameter measurement results from TEM micrographs.

| Sample   | Average Diameter (nm) |
|----------|-----------------------|
|          | Internal | External |
| CNT CO (a) | 4.8      | 8.9      |
| CNT BS (b) | 25       | 43       |
| CNT CC (c) | 26       | 57       |

Raman spectroscopy is an important tool for studying CNT samples, which provides information about the structure and the presence of disorder in the sample. Figure 5 shows the representative Raman spectra of CNT CO, CNT BS, CNT CC, and CNT SS. In the Raman-shift range of 500-2000 cm corresponding to D and G bands, respectively. The G band-oriented pyrolytic graphite and suggests the CNT is composed of crystalline graphitic carbon. The higher intensity of the G band peak indicates a higher degree of graphitization/crystallinity. The D band-oriented disorder in the sp2-hybridized carbon and indicates lattice distortions in the curved tube ends. The intensity ratio of G and D peaks ($I_G/I_D$) is used to characterize the purity of CNT. Higher $I_G/I_D$ ratio indicates a higher degree of graphitization [6].

![Figure 5. Raman spectra of (a) CNT CO, (b) CNT CC, (c) CNT SS, and (d) CNT BS.](image_url)
Figure 5 shows crystalline CNTs more dominant than disorder carbon. It can be seen from all CNT samples which have a higher G-band than the D-band. Commercial CNT has the highest ratio of 1.58 while the CNT results of this study have a ratio of 1.01 to 1.14. Although 1.01 to 1.14 is not the best value, it is much higher and encouraging than many recent reports of CNTs by similar thermal decomposition ($I_G/I_D = 0.85–1.3$) [21]. Raman’s analysis shows CNT CC has a higher $I_G/I_D$ ratio than CNT SS. CNT CC is formed with more stable temperature conditions (the location is located right in the heating area) while CNT CC is formed at a lower temperature because it moves away from the heat source of the tube furnace [22].

Figure 6 shows the typical XRD pattern of the CNT sample. The peaks at 20 of 29.098° with intensity of 3.173 Å, slightly lesser a perfect graphite intensity (3.354 Å) are indexed to be the (002) [8]. The peak on the widened XRD spectrum shows the amorphous carbon structure generated by the destruction process of the initial graphite structure during the pyrolysis process. The resulting carbon structure is an intermediate structure between graphite and amorphous structures called turbostratic structures or random layered lattice structures [23].

![Figure 6. X-ray diffractogram of CNT CC and CNT CO.](image)

Before and after the scale-up, the results of XRD showed the same thing, that the CNT POME had a peak of impurities such as cementite at 33.80° and 36.58°. The impurity is formed due to POME resin decomposition and ferrocene catalyst decomposition. Fe from catalyst decomposition and carbon from resin decomposition react to iron carbide or Fe$_2$C (cementite) [24].

Analysis of nitrogen absorbed on the surface of the CNT was measured by the method of Brunauer Emmet Teller (BET) to determine the surface area. The surface area of a CNT comes from the surface area of the outer tube (first layer) and inner tube (n-layer). The BET results in Table 2, CNT CC have the highest surface area while CNT SS approaches commercial CNT. The higher the surface area, the less CNT layers are formed. CNT with the SWNT type has a surface area of more than 1200 m$^2$g$^{-1}$ [18].

**Table 2.** Surface area measurement results from BET method.

| Sample  | Specific surface area (m$^2$g$^{-1}$) |
|---------|-------------------------------------|
| CNT CO  | 644.62                              |
| CNT CC  | 669.10                              |
| CNT SS  | 522.68                              |

CNT which produced is aimed for supercapacitor. Therefore, the electrochemical performances of CNT were studied by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) methods. CV study of supercapacitor with CNT electrode was performed in the potential window between -0.4 to 0.4 V with a scan rate from 2 to 10 mV.s$^{-1}$. Figure 7a shows the CV curves of supercapacitors with various scan rates. non-ideal CV
curves (not quasi-rectangular) were obtained at all scan rates. The deviation of the rectangular shape in the CV curve ensures the presence of both non-Faradaic reaction / electrical double layer (EDL) and faradaic reaction (pseudo-capacitance) in charge storage.

In the case of supercapacitor with CNT electrode, the pseudo-capacitance associated with redox reactions of surface functional groups is always coupled with the non-Faradaic double-layer capacitance. The specific capacitance will be influenced by functional groups or rather the oxygenated functional groups. Oxygenated functional groups absorbed on the surface of a porous electrode could be oxidized or reduced with the electrode potential as shows on reaction [25].

\[
\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^- \quad (3)
\]

The area under the curves increases with the decrease of scan rates, which is mainly due to a higher scan rate, ionic diffusion in pores become faster and induces more ionic collisions. Too large numbers of ionic collisions will produce an irregular electrical double layer, which has a lower capacitance [26-28]. Table 3 shows that the supercapacitor with the CNT electrode offers the highest specific capacitance at a scan rate of 2 mV.s\(^{-1}\).

![Graphs and Equations]

\textbf{Figure 7.} (a) CV curves of supercapacitor with different scan rates, (b) CV curves of supercapacitor with different electrodes, (c) GCD curves of supercapacitor with different electrodes, (d) Nyquist plots of supercapacitor with different electrodes, and (e) equivalent circuit model.
Figure 7b show the CV curves of supercapacitor with various CNT electrode and Table 3 show the specific capacitance. Specific capacitance supercapacitors with electrodes from CNT POME was still low than commercial CNT. Commercial CNT have the highest specific capacitance (23.32 F.g$^{-1}$) due to the higher crystallinity of commercial CNT (Raman spectroscopy results), have smaller pore diameters and have more CNT thereby increasing the formation of electrical double layers (TEM results) [18].

### Table 3. Specific capacitance as a function of scan rate with different electrodes.

| Sample         | Specific capacitance at scan rate variation (mV.s$^{-1}$) |
|----------------|----------------------------------------------------------|
|                | 2             | 4             | 6             | 8             | 10            |
| CNT CO / (F.g$^{-1}$) | 23.32         | 12.63         | 9.52          | 7.96          | 6.36          |
| CNT CC / (F.g$^{-1}$)    | 14.42         | 8.41          | 5.75          | 4.29          | 3.43          |

The GCD curves for the different electrodes recorded at a current density of 1 mA.cm$^{-2}$ are shown in Figure 7c. As seen in this figure, all the cells show a similar symmetrical triangular curve with a nearly linear variation of voltage as a function of time during charge and discharge. This type of curve is typical for carbon-based supercapacitors [17]. However, despite having a similar shape, the curves for the CNT CC didn’t return to the initial potential value.

Oxygenated functional groups have initiated faradaic or pseudo-capacitance reactions and affected the GCD curve. These reactions still leave a charge when the discharge time has run out [25]. As seen in Figure 7c, the GCD curve of CNT CO has a GCD curve with lower potential compared to CNT CC. As seen in equation 2, Voltage is inversely proportional to the specific capacitance produced so that the ideal GCD curve is a curve with a low voltage [29]. Based on the calculation of specific capacitance of the CV and GCD curves, both have relatively the same results, and CNT CO is still unable to compete with CNT CC.

### Table 4. Specific capacitance with different electrode from CV curves and GCD curve.

| Sample     | Specific capacitance (F.g$^{-1}$) at 2 mV.s$^{-1}$ |
|------------|-----------------------------------------------------|
|            | (CV)       | (GCD)       |
| CNT CO     | 22.46      | 23.32       |
| CNT CC     | 12.14      | 14.42       |

Electrochemical Impedance Spectroscopy (EIS) is a non-destructive process to gather the kinetic information of the electrode. The EIS measurements were performed in the frequency range between 100.000 – 0.001 Hz. The obtained data are plotted in the form of the Nyquist plot shown in Figure 7d. This plot reveals three different frequency-dependent regions, which provide extensive information regarding the electrode materials. At the high-frequency region, the starting point of the curve (electrolyte resistance, Ru) followed by a semi-circular loop is present in both curves. The value of Ru does no effect on imaginary Z and follows Ohmic law. Increasing the initial value of $Z_{real}$ induced an increase in the Ohmic resistance generated [16].

The Nyquist curves for all samples have the same starting point, so that the electrode variation has no effect on electrolyte resistance. The diameter of the semicircle represents the charge transfer resistance (R1). Decreasing the diameter of semicircle induced decreases the charge transfer resistance [16]. GCD curve in constant current represented CNT CC when the initial discharge has a higher potential than CNT CO. The greater the resistance, the greater the voltage required (V=IR). The higher potential, the smaller capacitance or charge stored in the double layer electrical phenomenon (C=Q/V). The Nyquist curve was analyzed by fitting based on equivalent circuit modeling which can be seen in Figure 7e and the results of the resistance values in Table 5.
Table 5. Resistance values of supercapacitor with different electrodes.

| Parameter | CNT CO | CNT CC | Unit  |
|-----------|--------|--------|-------|
| Ru        | 5.2430 | 9.9140 | Ohm   |
| CPE1      | 0.0538 | 0.0128 | F     |
| α         | 0.4595 | 0.2088 |       |
| R1        | 106.5000 | 130.2000 | Ohm |
| CPE2      | 0.0004 | 0.0004 | F     |
| α8        | 0.8852 | 0.7722 |       |
| R2        | 238.1000 | 256.8000 | Ohm |

The Ru value between the electrodes is at the same level. The formation of an electrical double layer on the surface of CNT CO is formed more as indicated by the value of α approaching 1. The closer to the value of 1, increase the formation of an electrical double layer [17]. R1 represents the amount of charge transfer resistance in the electrical double layer. CPE1 is comparable in value to double-layer electrical capacitance. Decreasing R1 and increasing CPE1 induced better supercapacitor performance [30].

4. Conclusions
CNT has been successfully prepared on upscaled with the utilization of a stainless steel mesh-based collecting system. It was found that the present technique gives a higher yield of CNT from 0.46% to 0.96% (the maximum fix carbon yield was 2.94%). CNT has relatively similar characteristics to CNT before scale-up, CNT was characterized and applied as electrode material for supercapacitor, which exhibits a specific capacitance of 13.98 F.g⁻¹. However, the capacitance of supercapacitor does not meet commercial standards due to still has considerable resistance between electrodes and electrolytes in the EIS analysis.

5. Acknowledgment
This work is supported by Badan Pengelola Dana Perkebunan Kelapa Sawit during the fiscal year 2018.

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