# CNT Synthesis from POME by Pyrolysis using Tubular Furnace

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# CNT Synthesis from POME by Pyrolysis using Tubular Furnace

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**Abstract.** The utilization of the palm oil waste, such as Palm Oil Mill Effluent (POME), is desirable to reduce environmental problems and increase its value as a source of biomass. POME can be processed to make Carbon Nanotube (CNT), a cylindrical carbon allotrope composed of graphene sheets. CNT, since its nanosized and high electrical conductivity, is well-suited to be used as electrodes in energy storage device such as battery. This study focuses on CNT synthesis from POME by pyrolysis process at 900°C using ferrocene as a catalyst in flowing nitrogen atmosphere. The synthesis of CNT consists of preparation of raw material (POME), synthesis of resin oil, pyrolysis, and characterization of CNT. The result shows that this process yields 0.28 g CNT (from 15 g POME, using 30 weight-% Ferrocene) whose diameter varies between 26-171 nm, the surface area is 404.62 $m^2g^{-1}$. From the XRD analysis, a C (002) is detected at 2θ of 29.098° with intensity of 3.173 Å, slightly under perfect graphite intensity (3.354 Å). It can be concluded that CNT can be produced from POME using pyrolysis process; an affordable yet applicable way on industrial scale to produce a good quality of CNT.

## 1. Introduction

Indonesia is the largest palm oil producer in the world with capacity of 31.4 million tons per year [1]. As consequence, abundant wastes are generated. Palm oil mill effluent (POME) is the liquid waste which represents 61% of total waste. From each ton of processed palm oil fresh fruit, 0.7 – 1 $m^3$ 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 nitrogen, phosphate, calcium, potassium, carbon and magnesium, so it can be processed biologically to a fertilizer and biogas [3]. However, to process POME to biogas, vast investment, especially huge area is needed. Because of that, in Indonesia, biogas from POME is still not commercially applicable. Nevertheless, POME has a prospect to become the raw material of valuable carbon nanotubes (CNT).

Today, carbon nanotubes (CNT) can be derived from organic liquid such as, turpentine oil, neem oil, and even organic wastes, like Bio-oil PCB and waste cooking oil. POME is a liquid waste which is rich of organic compounds, so it has potential as a carbon source to produce CNT.

CNT is a cylindrical allotrope of carbon with nanometric size. CNTs have high electrical conductivity of $10^7$ $S.cm^{-1}$. Application of CNTs in energy storage such as supercapacitor produce specific capacitances of 12-120 $F.g^{-1}$, energy density of 0.5-40 $Wh.kg^{-1}$and power density of 30-100 $kW.kg^{-1}$ [4]. Combination of graphene and CNT will prevent graphene layer attachment, thus increasing capacitance [5].

## 2. Methods

### *2.1. Materials*

CNT was produced from Palm oil mill effluent (POME) which was collected from 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]. Gas Chromatography-Mass Spectroscopy (GC-MS) analysis of POME used in this research, gives characteristic as shown in Table 1.

**Table 1** Retention data of compounds from POME

| *No* | *Compound* | *Receptor* | Area |
|---|---|---|---|
| *1* | Cyclohexanecarboxylic acid | $C_7H_{12}O_2$ | 58.39 |
| *2* | Hexanoic acid | $C_6H_{12}O_6$ | 14.74 |
| *3* | 1,3,5-Trimethyl-6-oxabicyclo | $C_{10}H_{16}O_2$ | 5.53 |
| *4* | Furanone | $C_6H_{10}O_3$ | 1.40 |

Regulation of Minister of Environment and Forestry No. 5 of 2014 about standard specification of palm oil waste, limit its pH of 6-9, BOD of 100 mg $L^{-1}$ max, COD of 350 mg $L^{-1}$ max etc. While POME used in this research has pH of 3-6, BOD of 15,600 mg $L^{-1}$ and COD of 25,000 mg $L^{-1}$. This means that the POME used in this research does not comply the standard specification. According to its large amount, this waste will potentially damage the environment, so it should be utilized to produce a valuable substance such as CNT.

Formaldehyde water solution used to polymerize POME and ammonium hydroxide as catalyst. Pyrolysis of the resin used ferrocene as catalyst in nitrogen flow. Ferrocene are frequently used as precursors to prepare carbon nanostructures, because they cannot only act as carbon source, but also give rise to small metal clusters as catalyst.

### *2.2. CNT Production*

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

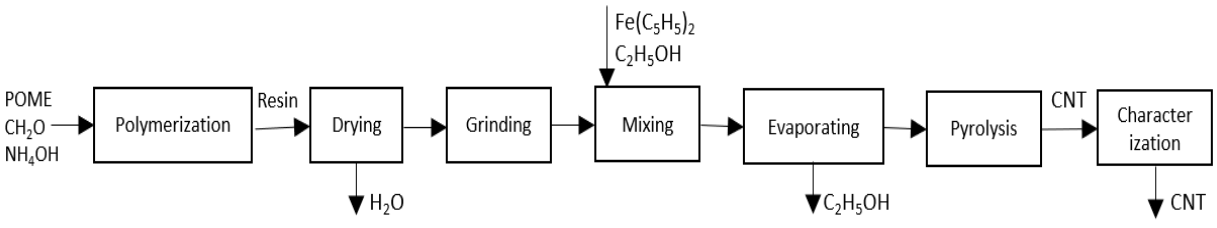



**Figure 1** Process flow diagram of CNT synthesis

### *2.3. Characterization*

The CNT produced by pyrolysis is characterized as follows: the chemical composition is analyzed using FT-IR, its morphology is analyzed using SEM and TEM, its graphitic characteristic is determined using Raman spectroscopy, its crystallinity is determined using XRD, while its surface area is analyzed using Nitrogen adsorption-desorption analysis with BET calculation method.

The electrochemical performance of CNTs was tested by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) methods. Electrochemical measurements were carried out using Gamry V3000 potentiostat – galvanostat, by means of an asymmetrical two-electrode configurations with 6 M KOH solution as electrolyte at room temperature. The negative electrode of the asymmetrical cell was prepared by mixing CNT with polyvinylidene fluoride (PVDF), which is coated on 1 cm2 stainless steel mesh and dried at 80°C for 1 day. The positive electrode was prepared by mixing NiO with PVDF, which is coated on 1 $cm^2$ stainless steel mesh and dried at 80°C for 1 day. Nafion 212 impregnated with the electrolyte, was placed between both electrodes.

## 3. Results and Discussion

The morphology of CNT made from POME using ferrocene as catalyst by pyrolysis at 900ºC, was identified using SEM and TEM. There are 4 samples of CNT produced with different catalyst concentration (0%, 20%, 25% dan 30% wt). The SEM observation results are shown on Figure 2. Figure 2a shows the pyrolysis product formed without ferrocene; it reveals amorphous carbon only. This Figure confirms that carbon nanostructure cannot be formed without catalyst.

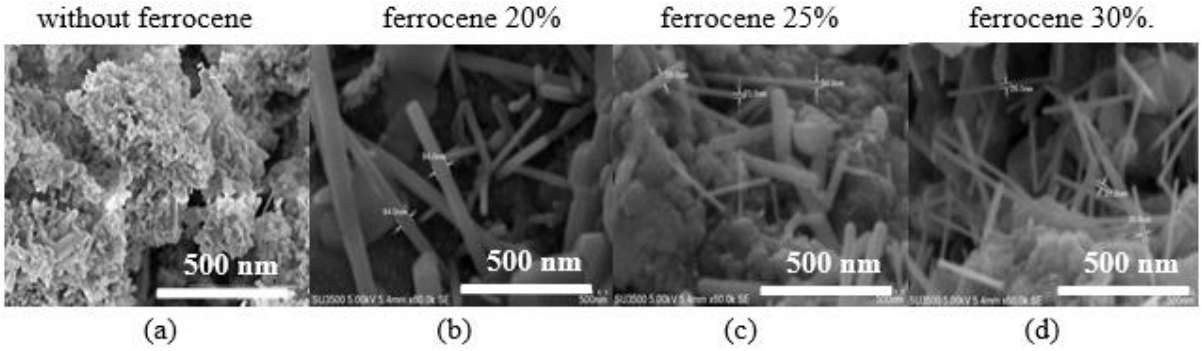



**Figure 2** SEM micrographs of CNT with different catalyst concentration

Figure 2b presents the SEM observation of pyrolysis product using 20%-wt. ferrocene, which indicate the existence of CNT of 84-94 nm diameters. The CNT with smaller diameter will give larger capacitance in supercapacitor [7]. As shown on Figure 2b, 2c and 2d, increasing the mass percent of ferrocene (up to 30%), will increase the amount of CNT obtained. This assumption is supported by Table 2 which presents the alteration of CNT yield due to variation of ferrocene concentration.

**Table 2** Carbon yield of pyrolysis (mass ratio of carbon product and initial POME) as ferrocene concentration changed

| %-wt. ferrocene | 20 | 25 | 30 |
|---|---|---|---|
| %-wt. C in product | 2.02 | 2.17 | 1.87 |

As the mass percent of ferrocene increased, the number of nuclei initiator become larger, and increase the number of carbon nanotubes. 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 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, the shape of the Fe catalyst may be changed, e.g. from nanoparticle to nanorod by cylinder carbon formation around it. If the catalyst is reduced before the decomposition of resin, the size of the Fe catalyst does not increase during the growth of the nanotubes. In this condition, the decomposition of pyrolysis oil-based resin will result in the formation of nanotubes free of metal [8]. TEM micrographs of CNT formed with 30%-wt. ferrocene reveals some single open-end tubes, as shown on Figure 3. Ferrocene concentration more than 30%-wt. didn't significantly change the yield of CNT [9].

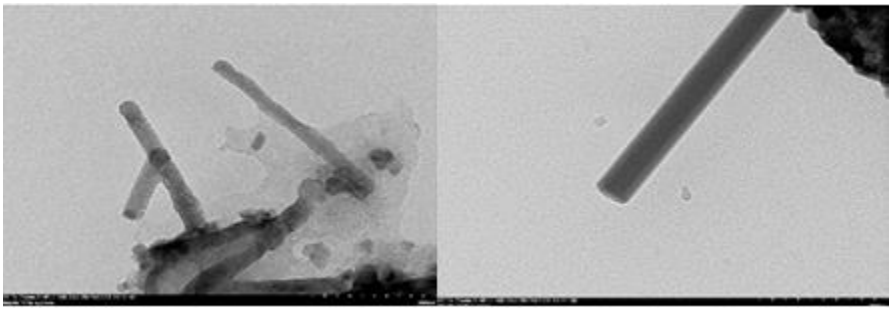
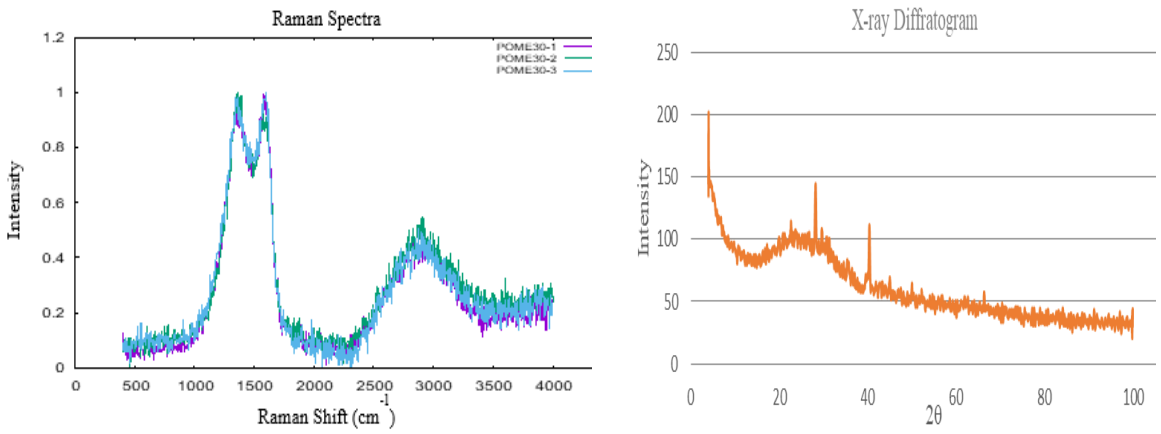


**Figure 3** TEM micrographs of CNT with 30%-wt. ferrocene

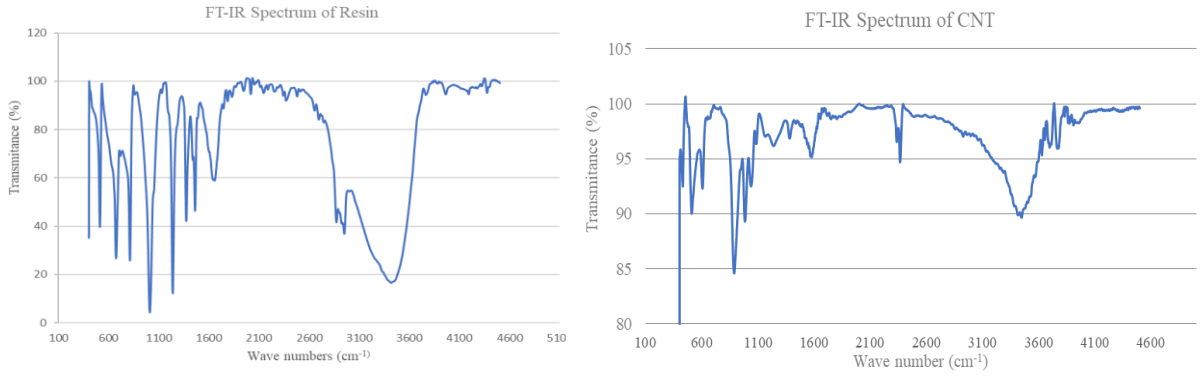
Raman spectroscopy provides information about the structure and the presence of disorder in the sample. Figure 4a shows the representative Raman spectra of a CNT formed with 30%-wt. ferrocene. In the Raman-shift range of 500–2000 $cm^{-1}$, two peaks are observed at 1350 $cm^{-1}$ and 1582 $cm^{-1}$ corresponding to D and G bands, respectively. The G band oriented pyrolytic graphite and suggests the CNT are composed of crystalline graphitic carbon. The higher intensity of the G band peak indicates the 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 (IG/ID) is used to characterize the purity of CNT. Higher IG/ID ratio indicates a higher degree of graphitization [10]. The IG/ID ratio of 1.01 represents graphitization of CNT. This is in agreement with TEM micrographs of CNT which show a hollow form.




(a) (b)

**Figure 4** Raman spectra & X-ray diffractogram of CNT using 30% wt of ferrocene

Figure 4b shows the typical XRD pattern of CNT sample. The peaks at 2θ of 29.098° with intensity of 3.173 Å, slightly lesser a perfect graphite intensity (3.354 Å) are indexed to be the (00.2). The presence of the (00.2) peak in the XRD spectra indicates the concentric cylindrical nature of the CNT, or the multi-walled CNT (MWCNT). The nature of surface groups of resin-oil was studied by FT-IR and the results are shown in Figure 5a. The detectable transmission band at 3413 $cm^{-1}$ represents the stretching vibration of O-H bond in alcoholic or phenolic compounds. The peak at wave numbers 2800-3000 $cm^{-1}$ are assigned to alkane stretching vibration. The peak at wave number 1600 $cm^{-1}$ is assigned to stretching vibration of C-O bond in aldehyde, ketone or carboxylic groups. While the peak at wave number 1300 $cm^{-1}$ is assigned to stretching vibration of C-N bond in amine group probably present from $NH_4OH$ addition.




(a) (b)

**Figure 5** FT-IR spectrum

FT-IR spectrum of CNT is depicted on Figure 5b. The large peak at wave number ~3430 $cm^{-1}$ is assigned to stretching vibration of hydroxylic groups attached on CNT surface [11]. Transmission band at wave number 3728 $cm^{-1}$ can be interpreted as stretching vibration of free hydroxylic groups, while the peak at wave number 3425 $cm^{-1}$ represents the stretching of O-H bond in carboxylic and alcoholic groups. The peak at wave number 2380 $cm^{-1}$ can be interpreted as stretching of C=O bond in carboxylic groups. The broad peak at wave numbers 1442–1736 $cm^{-1}$ can be assigned to CNT, and the peak at wave number 1372 $cm^{-1}$ is interpreted as stretching of N-$CH_3$ bond. These identified bonds indicate the specific framework of CNT [12]. Therefore, it can be concluded that CNT is formed from cyclohexane carboxylic acid in POME.

The surface area and porosity of CNT were determined using nitrogen adsorption-desorption with BET calculation method. The surface area of CNT made from POME is 404.62 $m^2g^{-1}$, while commercial CNT has surface area between 120 and 500 $m^2g^{-1}$ [7]. The cyclic polarization of the asymmetrical cell made of produced CNT gives cyclic voltammograms that can be used to calculate the cell capacitance. The cell capacitance can be calculated based on cyclic voltammogram data, following this equation [4]:

$$C = \frac{\sum |I|.\Delta t}{m.\Delta V} \quad (1)$$

Where C is capacitance (F/g), I is electric current (Amperes), $\Delta$t is time elapsed (second), m is cell mass (grams) and $\Delta$V is voltage difference (Volt). The voltammograms obtained with various scan rate are presented on Figure 6, while the capacitance data are depicted on Table 3.

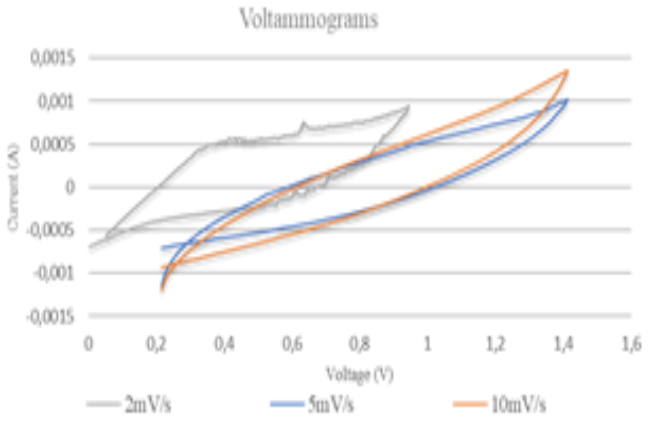
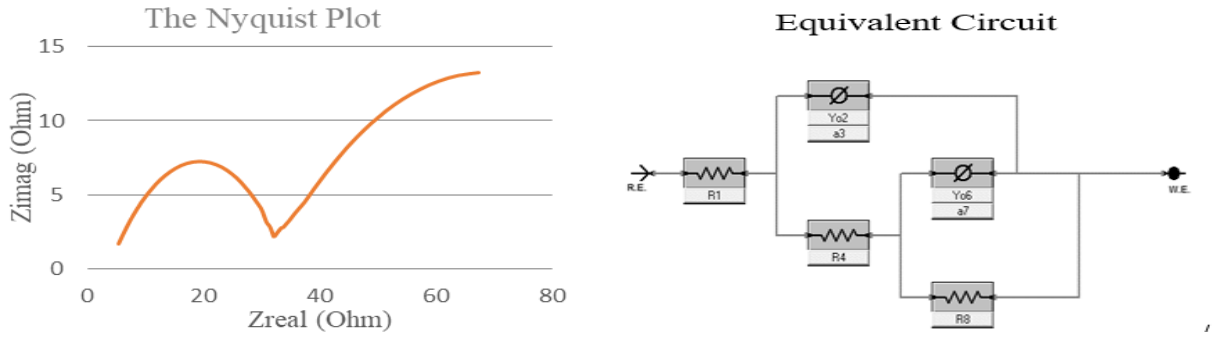



**Figure 6** Voltammograms of asymmetrical cell of CNT with various scan rate

Table 3 Asymmetrical cell capacitances (F/g carbon)

| Scan rate (mV/s) | 2 | 5 | 10 |
|---|---|---|---|
| Cell capacitance (F/g) | 26.09 | 17.04 | 9.87 |

In general, increasing scan rate will reduce the cell capacitance. This phenomenon reveals that at higher scan rate, ionic diffusion in pores become faster and induces more ionic collisions. Too large number of ionic collisions will produce an irregular electrical double layer which has a lower capacitance [13-16] The application of Electrochemical Impedance Spectroscopy on asymmetrical cell of CNT provides the Nyquist curve which represents the relation between real and imaginary impedances, as depicted on Figure 7a. The Nyquist plot gives the information of the cell components' resistance as well as its capacitance that allow designating the cell configuration. Such cell configuration is presented as an equivalent electric circuit on Figure 7b.




(a) (b)

**Figure 7** The Nyquist plot of asymmetrical cell made of CNT and its equivalent circuit

This Nyquist plot shows a large resistance of charge transfer as well as of mass transfer, while the equivalent circuit displays a normal equivalent circuit of an asymmetrical cell, despite its resistances and capacitances values. These phenomena reveal that CNT can be used as the electrode of an electrochemical device, but should be well-ordered to obtain very low resistances and high capacitances.

## 4. Conclusion

CNT can be produced from POME using pyrolysis process at 900°C in flowing nitrogen atmosphere, using Ferrocene as catalyst. All morphology and physical examinations results confirm the CNT formation. The CNT yield increases with the concentration of ferrocene. The capacitance of CNT cell is still low and its resistance is still high due to the cell construction which is not well-organized.

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