# Formation Of Carbon Material On Nickel Catalyst During Reaction With The Vapour Produced From The Pyrolysis Of Sewage Sludge

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*Abstract* — It is a research on the formation of carbon material on nickel catalyst during reaction with the vapour produced from the pyrolysis of sewage sludge. The method used for carbon nanotube (CNT) production is the catalytic chemical vapour deposition (CCVD) method. In this research, the nickel catalyst act as the catalyst for carbon nanotube (CNT) production. The catalyst preparation also plays an important role in carbon nanotube growth rate. The nickel catalyst undergoes the incipient wetness impregnation (IWI) since the method is more faster, inexpensive, and the final property and configuration can be control in advance. The nickel catalyst were characterized by using FTIR and TGA.

***Keywords— carbon material, catalytic chemical vapour deposition, incipient wetness impregnation,***

## 1. INTRODUCTION

Pyrolysis is a thermal process where organic materials such as biomass and oil are decomposed and lighter materials such as gas, vapor, liquid products, and char are produced.[1] The sludge was composed of difference solid particles suspended in an impure water sequence. In sewage sludge, the solid particle consist of the complex mixture of organic such as proteins, carbohydrates and others. Other than that, it also consist of inorganic matters, living and dead microorganisms. The sewage sludge consist of different components. Each of them came from origin that have their own definitive and rare production conditions indicate that the sewage sludge's properties are highly flexible. There are many factors that effect the characteristics of sewage sludge such as the wastewater characteristic, treatment system uses in wastewater treatment plant (WWTP) and others.[2]

There were restraint in the pyrolysis and combustion process which were materials that was used in the waste treatment due to production of organic compounds. The product's description and quantity was acknowledge as a part of advancement of the pyrolysis devices. The product formed from the pyrolysis. In the incinerator, there will be the possibility of danger toxic of the pyrolytic compounds formed. It was due to the low value of oxygen ratio. Based on other authors, temperature used in the pyrolysis of sewage sludge was between 400-700°C to obtained the fuel produced from the waste. [3]

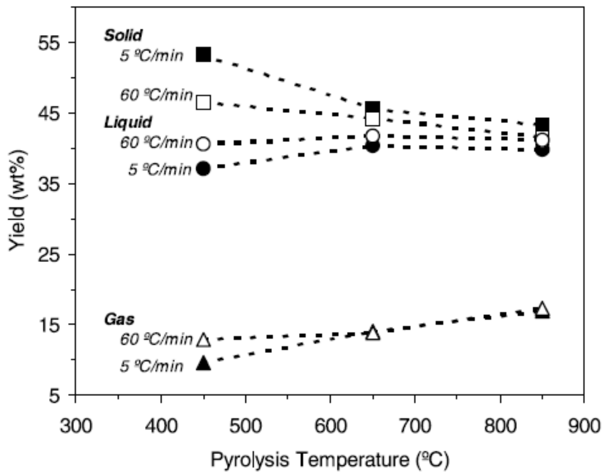


Figure 1.1 : Diversity of the yields of solid, liquid and gas products depending on the pyrolysis temperature and heating rate. [4]

Based on the figure above, the products of pyrolysis which in solid, liquid and gas form rely upon the pyrolysis operating condition such as temperature and heating rate. According to others author, regarding the experiment involving identical category of waste, the solid fraction will decline while the gas fraction will increment due to temperature rise. During temperature rise from 450°C to 650°C, the liquid fraction hardly increment. The liquid fraction will maintained almost stable when temperature was above 650°C. The heating rate will take place or have impact when at 450°C or below end temperature. As a conclusion, when fixed at temperature of 450°C, the more of heating rate will resulting in more effective of pyrolysis. There will be more yield in the liquid and gas while lessening in solid residue.[4]

Carbon nanotubes (CNTs) are nanostructures that is derived from rolled graphene planes and have unique chemical and physical properties. CNTs usually exist as single (SWNTs), and multi-walled (MWNTs) structures. The CNTs are valuable and can be used in the field of drug delivery, blood cancer, breast cancer, brain cancer, liver cancer, cervical cancer, gene therapy, immune therapy, biomedical imaging, biosensors and tissue engineering. [5]

There are several advantages of carbon nanotube that was listed by Pandey and Dahiya, which were biocompatible, non-biodegradable and non-immunogenic nature. It also is highly elastic nature and have the possibility of intracellular delivery. Other than that, it may exhibit minimum cytotoxicity, 96% of CNT excreted by urine and remaining 4% by faeces. CNT also have ultra-light weight and do not break down during processing. It has an open end on both sides that cause the inner surface attainable and consequential incorporation of species within nanotubes is notably simple. The nanotubes have longer inner volume corresponding to the diameter of nanotubes for entrapment. The CNTs are capable to enter cells by voluntary mechanism due to its tubular and nano needle shape. Lastly, It has distinct inner and outer surface, which can be differentially modified for chemical biochemical functionalization.[5]

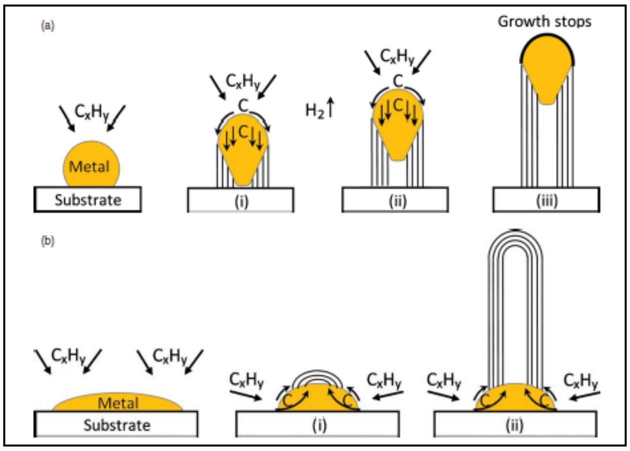


Figure 1.1 : Tip-growth model and base-growth model of CNT's growth mechanisms. [6]

By refering to the figure above, the catalytic growth of CNT can display two different mechanisms. Firstly, based on diagram (a), the mechanism is called tip growth where the particles are lifted off the substrate and they are found at the tip of the CNTs. Based on diagram (b), the mechanism is called the base growth with the catalyst particle staying on the substrate surface during the growth. The vertically oriented carbon nanotubes (VA-CNTs) appeal to much interest for their small diameter and potential length which was long and density are often grown in the base growth mode. [7]

Catalytic chemical vapour deposition (CCVD) was expressed as a simple and budgetary technique for synthesizing carbon nanotubes (CNT) at low temperature which is 300°C –1200 °C and ambient pressure. CCVD can utilize a variety of carbon sources in any state whether solid, liquid, or gas. Other than that, it permits the use of various substrates. Lastly, the CCVD method also allows the growth of carbon nanotube in a variety of forms, such as powder and films.[8]

There was a consistent increment in the sewage sludge formation that was disposed by urban and industrial wastewate. In sewage sludge, majority of the pollutants which is heavy metals reappeared after were removed in the decontamination system. So, the sewage sludge in the contaminants come to be really concentrated. To solve the problem, the common ways to get rid of sewage sludge were by the agricultural use of sewage sludge, land filling and incineration. The common ways still does not totally disposed of the danger of contamination.[4]

Carbon nanotubes have been well synthesized by using the catalytic chemical vapor deposition (CCVD) technique. It also involving the typical purifying hydrotreating catalysts containing nickel-molybdenum(Ni–Mo) and cobalt-molybdenum(Co–Mo) supported on $Al_2O_3$ catalysts at 700°C in a reactor using natural gas as a carbon source.[9]. Xiang et al. conducted studies on preparationof catalyst and the parameters of chemical vapor deposition (CVD) analogous to the synthesis of single-walled carbon nanotubes (SWNTs) by alcohol catalytic CVD.[10]. Shah and Tali conducted studies on the material aspects carbon sources, catalysts and substrates with regard to CCVD synthesis of carbon nanotubes are reviewed in light of latest developments and understandings in the field. [11].

There are many studies on the CNT production by several methods such as laser ablation, CCVD and arc discharge. By using biogas created from the process of pyrolysis of sewage sludge, through the CCVD process to produce CNT. Furthermore, the pyrolysis of sewage sludge can act as a way to manage or treat the sewage sludge. Hence, reducing the amount of sewage sludge produced. Besides that, the products formed from the pyrolysis can be used as the carbon source and then producing the carbon nanotube which were useful to the society.

In aspect of catalyst preparation, there were several methods. One of the methods was the incipient wetness impregnation(IWI) or also known as dry impregnation. The impregnation method consists in first dissolving a catalyst precursor and then contacting a support with this solution. In this method,the whole precursor deposits onto or into the substrate. The solvent is then evaporated and the catalyst was dried. In a case of organic supports and molecules, incubation takes place,but the method is the same.[12] The method's advantages were faster,low cost and properties of final product can be controlled. Other than that, the method can conveniently prepare a layer of active matter on the catalyst's surface. Since the method was faster meaning that the time used to prepare the catalyst can be shorter, low cost required and others, it is resulting in better method than the others.[13]

## 2. METHODOLOGY

### *2.1 Materials*

The catalyst preparation involves the nickel(II) nitrate hexahydrate with 99.999% trace metals basis (Sigma-Aldrich), ethanol(made in Germany) and aluminium oxide (Sigma-Aldrich). The catalytic chemical vapor deposition(CCVD) method involves the pyrolysis of sewage sludge from Jasin Central Sewage Treatment Plant and nitrogen gas as carrier.

### *2.2 Catalyst preparation*

The nickel catalyst was prepared by using incipient wetness impregnation (IWI) method. Firstly, the 3g of nickel(II) nitrate hexahydrate ($Ni(NO_3)_26H_2O$) was dissolved in 18ml of ethanol or distilled water. Then, the aluminium oxide ($Al_2O_3$) was added to the mixture until the mixture form slurry. The mixture then dried into oven at 50°C for 24hours. The obtain mixture then calcined at 1000°C in the furnace for 2 hours.

### *2.3 CCVD synthesis*

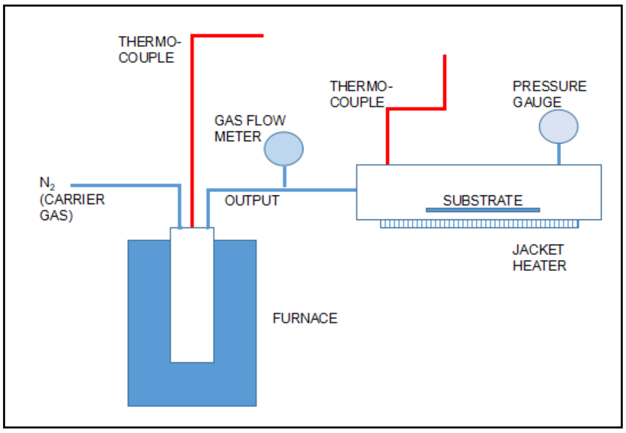


Figure 2.3 : The experimental set-up of catalytic chemical vapor deposition (CCVD) method.

The Figure 2.3 shows that the catalytic chemical vapour deposition (CCVD) method was run by using Jasin sewage sludge of approximately 0.3 g with catalyst of approximately 0.1g. It it based on the ratio of sewage sludge to catalyst which is 3:1. There are two reactor involved which are for pyrolysis and catalyst. Reactor 1 indicate pyrolysis of sewage sludge while the Reactor 2 indicate the catalytic chemical vapour deposition (CCVD) of nickel catalyst. Set point for Reactor 1 is 600°C while set point for Reactor 2 is 800°C.[14] The catalyst used were the nickel with ethanol and nickel with distilled water in the catalyst preparation. The thermocouple was attached to the reactors to record the temperature of every 10 minutes. The experiment was conducted for 30 minutes. The nitrogen gas of 0.8 LPM was supply during the experiment. The nitrogen gas act as carrier gas to the pyrolysis of sewage sludge.

### *2.4 Characterization of the catalyst*

#### *2.4.1 Thermogravimetric Analysis (TGA)*

The thermo-gravimetric analysis (TGA) functions to characterize the carbon nanotube were measuring the metal catalysts in CNT and the concentration of organic species that was attached to CNT. There were also limitation in using TGA which were it does not provide an unambiguous separation between the content of single-walled CNT and carbonaceous impurities. It also required a large amount of sample which was more than 10mg and the data interpretation is usually subjective. [15] The thermogravimetric analysis were carried out by using TGA/SDTA851$^e$ with starting temperature at 25ºC and end temperature at 1000ºC under air flow of 50mLmin$^{-1}$ and heating rate at 20ºC/min.

#### *2.4.2 Fourier Transform Infrared (FTIR) Spectroscopy*

FTIR spectra of the hydrogel were recorded by using FTIR (Perkin-Elmer Spectrum One). Small amount of catalyst is used to analyse with using FTIR to detect functional groups exists in the sample. The spectra were recorded at CPU32 from 4000 to 800cm$^{-1}$ with 4 scan to detect the spectra contained in the gels.

## 3. RESULTS AND DISCUSSION

### *3.1 CCVD Synthesis*

During the incipient wetness impregnation method, there are two sample of catalyst which were nickel with distilled water and nickel with ethanol. There are two reactor involved which are for pyrolysis and catalyst. Reactor 1 indicate pyrolysis of sewage sludge while the Reactor 2 indicate the catalytic chemical vapour deposition (CCVD) of nickel catalyst.Temperatures recorded during the CCVD experiment are as follows.

| Sample | Time (min) | Temperature of Reactor 1 (°C) | Temperature of Reactor 2 (°C) |
|---|---|---|---|
| Nickel with distilled water | 0 | 31.1 | 34.9 |
| | 10 | 457 | 449 |
| | 20 | 689 | 768 |
| | 30 | 691 | 767 |
| Nickel with ethanol | 0 | 30.7 | 35.8 |
| | 10 | 454 | 467 |
| | 20 | 670 | 766 |
| | 30 | 671 | 766 |

Table 3.1 : Temperatures of reactors

Based on Table 3.1, the heating rate of each reactors can be determine by calculating the average heating rate (°C/min). From the nickel with distilled water, the heating rate of Reactor 1 is 22°C/min which is lower than heating rate for Reactor 2 at 24.4°C/min. Next, the heating rate of nickel with ethanol were calculated for both reactors. The heating rate for Reactor 1 is 21.34°C/min which is lower than Reactor 2 at 24.34°C/min. Both samples exhibit the lower heating rate for Reactor 1 which is the pyrolysis for sewage sludge. Nevertheless, the heating rate have little impact on sludge pyrolysis reaction activation energy and correlative to reaction rate.[16]

### *3.2 Thermogravimetric Analysis (TGA)*

The TGA analysis was done in order to study the thermal stability and purity of as-grown CNTs by using the nickel catalysts. TGA also can prove whether CNTs have a higher oxidation temperature than amorphous carbon by determination of the nature and/or the content of different carbonaceous species in the catalyst.[17] There were common ways to estimate the quantity of the deposited carbon during the reaction with the vapour from pyrolysis of sewage sludge by CCVD is the direct weight of the catalyst before and after the reaction but this method is vulnerable to high experimental errors. The TGA analysis allows for a more accurate result of the deposited carbon.[9] Based on research by Pinjari et al., all catalysts shows three mass changing steps which were vaporization of physically adsorbed moisture, surface oxidation of metallic nickel and degradation of graphitized carbon. Due to the vaporization of physically adsorbed moisture by the solid particles, initial mass loss occurred between 20°C to 100°C.[18]

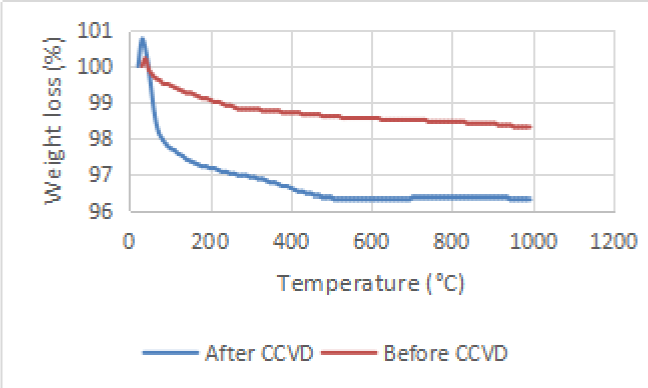


Figure 3.2.1 : TGA of nickel with distilled water

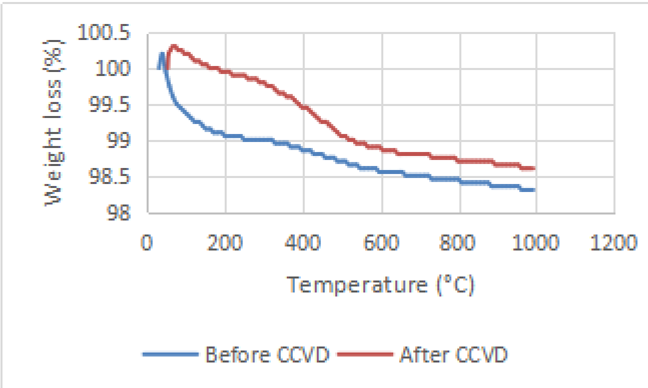


Figure 3.2.2 : TGA of nickel with ethanol

Figure 3.2.1 and Figure 3.2.2 shows the TGA curves of nickel catalyst with distilled water and nickel catalyst with ethanol, respectively. Each graph comparing the catalyst before CCVD and after CCVD synthesis. Based on the both nickel catalyst after CCVD, they showed an initial weight loss tendency which may be attributed to the loss of physically adsorbed water by the catalyst. In the subsequent heating process, all sample except for nickel catalyst with ethanol after CCVD go through a identical weight loss tendency with heating which is a single step weight loss pattern indicates the absence of other carbonaceous products.[19] The nickel catalyst with ethanol after CCVD exhibit two-step weight loss process . Based on research by Awadallah et al., the weight loss occurs because of the combustion of carbon begins at temperatures of equal or higher than 300°C depending on the nature of the carbon species.[9]

### *3.3 Fourier Transform Infrared (FTIR) Spectroscopy*

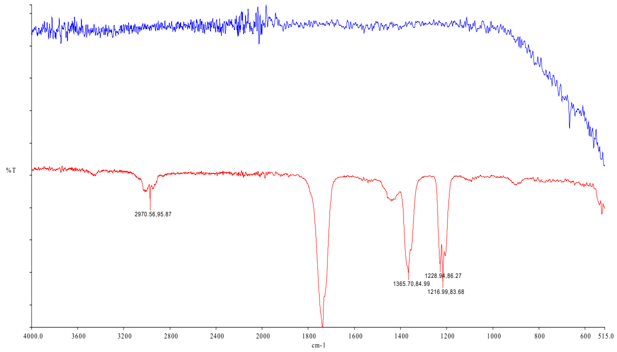

Figure 3.3.1 : FTIR spectra of nickel catalyst with distilled water.

Based on Figure 3.3.1, it shows FTIR spectra of nickel catalyst with distilled water. The blue line indicate the nickel catalyst before CCVD process while red line indicate the nickel catalyst after CCVD process. Nickel catalyst before CCVD shows that no functional group since there is no peak occurred.There were four peaks in the catalyst after CCVD process which are 2971cm-1, 1366cm-1,1217cm-1 and 1229cm-1. Based on research by Yahyazadeh and Khoshandam, the peak observed at about 1618 cm–1 is attributed to the C-C stretch band of the CNTs while the C-C vibration was similar to internal defects, and the O-H vibration at 3414 cm1 was correlate with amorphous carbon due to the tendency of amorphous carbon against atmospheric air . A signal at 1384 cm1 is ascribed to stretching in the plane =C-H bond or stretching mode –OH. [20]

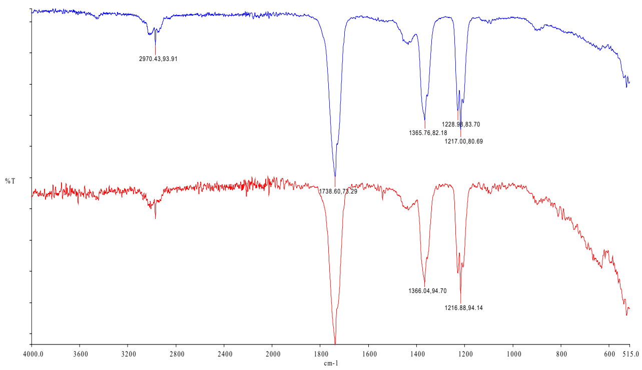

Figure 3.3.2 : FTIR spectra of nickel catalyst with ethanol

Based on Figure 3.3.2, it shows the FTIR spectra of nickel catalyst with ethanol. The blue line indicate the nickel catalyst before CCVD process while red line indicate the nickel catalyst after CCVD proces. Both line shows that it have the functional groups. The peaks obtained for nickel catalyst after CCVD process is 1366cm-1 and 1216cm-1 while the peaks obtained for nickel catalyst before CCVD process is 2970cm-1, 1366cm-1, 1229cm-1, and1217cm-1.

## 4. Conclusion

The heating rate have little impact on sludge pyrolysis reaction activation energy and correlative to reaction rate. Based on the both nickel catalyst after CCVD, they showed an initial weight loss tendency which may be attributed to the loss of physically adsorbed water by the catalyst. In the subsequent heating process, all sample except for nickel catalyst with ethanol after CCVD go through a identical weight loss tendency with heating which is a single step weight loss pattern indicates the absence of other carbonaceous products. Nickel catalyst with distilled water before CCVD shows that no functional group since there is no peak occurred.There were four peaks in the catalyst after CCVD process which are 2971cm-1, 1366cm-1, 1217cm-1 and 1229cm-1. The peaks obtained for nickel catalyst with ethanol after CCVD process is 1366cm-1 and 1216cm-1 while the peaks obtained for nickel catalyst before CCVD process is 2970cm-1, 1366cm-1, 1229cm-1, and 1217cm-1. In my opinion, the synthesis parameter needed to be research in depth to produce the carbon nanotube.

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