FORMATION OF CARBON MATERIAL ON COBALT CATALYST DURING REACTION WITH VAPOUR PRODUCED FROM THE PYROLYSIS OF SEWAGE SLUDGE

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Abstract— The production of sewage sludge has become one of the main concerns in every developing country, and several techniques to control this waste production has been developed such as pyrolysis method. To fully utilized the process, it is stated the pyrolysis of sewage sludge can bring benefits to the industries and it is theoretically can produce carbon material such as carbon nanotubes (CNTs) from sewage sludge by using catalytic chemical vapour deposition (CCVD) method. In this work, the effect of cobalt (Co) catalyst on the growth of CNTs was systematically studied. The synthesis was done by contacting the vapour produced at 600°C from the pyrolysis process of sewage sludge on cobalt catalyst using CCVD process at temperature 800°C for 30 minutes synthesis time. The carbon material formed on cobalt catalyst was analyzed by using Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The experimental results revealed that CNTs production produced based on FTIR analysis at a peak of 1737 cm⁻¹ and the formation of N-stretching at 1250 and 1372 cm⁻¹ of C-N and N-CH₃, respectively. The C-H bend is presence at 640 cm⁻¹ in the analysis, assigned as Alkyne C-H bend. Meanwhile, the TGA measurements was carried out under air gas flow, show the dominant weight loss is recorded at the temperature range of 400-600°C corresponding to the removal of impurities in carbon material also due to the decompositions of nanotubes.

Keywords— pyrolysis sewage sludge, cobalt (Co) catalyst, incipient wetness impregnation (IWI), carbon nanotubes (CNTs), catalytic chemical vapour deposition (CCVD)

I. INTRODUCTION

Rapid urbanization in developing a new country brings pros and cons in term of socio-economy, civilization, industries, and etcetera. Along with this development, without proper practice, the rapid growth on the production of sewage sludge from wastewater treatment cannot be control. As mentioned, improper techniques in managing sewage sludge have become environmental concerned [1]. Therefore, several techniques have been developed in handling the problem and one of the techniques used is the pyrolysis method. Pyrolysis has the potential option in reducing large volume, eliminating pathogen compound, and the valuable end products such as bio-oil, biochar, and syngas [2]. It was hypothetically stated from the pyrolysis of sewage sludge will bring the benefits aspects in certain factors. Pyrolysis will produce the vapour from the sewage sludge and lead into the carbon formation on the Cobalt catalyst. The aim of this study, it is to produce a Carbon Nanotubes (CNTs) along the process. CNTs production have extensive research from the time it was first discovered by Sumio Iijima in the early 1990s [3]. CNTs can be divided into 2 main types which Single-Walled Carbon Nanotubes (SWCNTs) and Multi-Walled Carbon Nanotubes (SWCNTs). Having different morphology for each CNTs gives benefits in terms of properties in electronic, chemical, mechanical and electromechanical aspects which had been pointed out in other studies for the potential applications of CNTs [4]. CNTs is one of carbon formed during the process of catalytic chemical vapour deposition (CCVD), although several processes can be conducted in examining the CNTs formation such as laser ablation and arc discharge [5].

The formation of CNTs under CCVD process also dependent on types of catalyst used. Commonly, the catalysts which fall under a group of transition metal is mandatory to choose in the production of CNTs [6]. Most catalysts used is cobalt, iron, and nickel during the process [4]. These three catalysts are the most frequently used catalyst in CNTs growth. Sivakumar at. al., (2011) has conducted a study in synthesizing the MWCNTs via methane CVD using Fe and Ni as a catalyst with support of low-cost activated carbon [7]. A different study conducted the synthesized CNTs on Co catalyst supported on MgO by using waste plastic, isopropanol and ethanol as carbon source was reported and high degree formation of CNTs can be formed in waste plastic dependent on several parameters [8]. Moreover, in a recent study conducted, the synthesized high-yield super-bundle SWCNTs by using Fe-Mo/MgO catalyst in water assisted CVD [9]. Since the different uses of catalyst give different production of CNTs in the process, therefore the studies regarding carbon formation under transition metal of catalyst are conducted. In this study, the main catalyst selected for the process is cobalt catalyst in synthesizing the CNTs.

It is also mentioned that the type of carbon source plays an important role in synthesizing CNTs. The CNTs can be synthesis from the organic compound as conducted in several studies such as the production of CNT from xylene which liquid hydrocarbon [10]. Meanwhile, under different studies, toluene and benzene which also types of liquid used to synthesise CNTs [11][12]. Kim et. al., (2007) conducted a study on ethylene in CNTs productions [4]. In addition to these, greener approached is investigated under different studies. The usage of palm oil in producing CNTs also had been conducted. Besides, a study of CNTs growth on green bio-hydrocarbons palm oil precursors conducted, were based on the results, it is possible to

conduct the growth of CNTs in palm oil bio-hydrocarbons based [6]. As stated by Kamalarakan et. al., (2003), the main parameters in the CNTs production is dependent on the atmosphere, catalyst, carbon source and growth temperature [13]. Therefore, this study is conducted based on the green approached by taking the sewage sludge as the carbon source with uses of Co catalyst and growth temperature of 800°C for the carbon material production.

II. METHODOLOGY

A. Catalyst preparation

Cobalt catalyst was obtained by incipient wetness impregnation (IWI) method from Cobalt II Nitrate Hexahydrate (Co(NO₃)₂.6H₂O) with support of alumina, Al₂O₃. 2 grams of Co(NO₃)₂.6H₂O was added with 3mL of ethanol (C₂H₅OH) and stirred until the solution were perfectly mixed. 3 grams of alumina support then added to the solution until the texture becomes slurry and left for one hour before it is dried in the oven at 50°C for 24 hours. The calcination of the catalyst was conducted at 1000°C for 2 hours in the furnace before the CCVD process takes place. The same experiment was replicated using distilled water for replacing the ethanol.

B. Catalytic Chemical Vapour Deposition (CCVD) process

The synthesis of carbon formation on the catalyst was carried out by using sewage sludge sample from Jasin wastewater treatment plant. To conduct the experiment, 0.3g of sewage sludge sample was placed inside the first furnace with a setpoint temperature of 600°C and nitrogen gas flow at 0.8 LPM to conduct the pyrolysis process. Therefore, the catalyst was put inside the hollow cylindrical in the second furnace with a setpoint temperature of 800°C. The vapour products from the pyrolysis is connected to the second furnace to allow the contact of vapour with the Co catalyst. The experiment was conducted for 30 minutes and the temperature for each furnace is recorded for every 10 minutes. Fig 1 shows the experimental set up for the CCVD process.



Fig 1: Experimental setup of the CCVD process

C. Catalyst characterization

1. Thermal Gravimetric Analysis (TGA)

The TGA was carried out on Mettler-Toledo (TGA/DSC1/HT) thermal analyzer under air flow at the heating rate of 20° /min to obtain information on the decomposition and the burning properties of carbon nanotubes and impurities present in the catalyst. The temperature of the sample varied from 25° C to 1000° C.

2. Fourier Transform Infrared (FTIR)

The FTIR spectrometer was recorded on Perkin Elmer Spectrum One FT-IR Spectrometer. FTIR studies were carried out in a range of 515 - 4000 cm⁻¹ in the absorbance mode. In each of the analysis, 0.02 g of catalyst sample was investigated. The FTIR results with the support of TGA results give a reasonably good picture of the formation of carbon material and attachment of CNTs in the catalyst.

III. RESULTS AND DISCUSSION

A. Catalytic Chemical Vapour Deposition (CCVD) Process

The CCVD process is done by taking the catalyst prepared from the ethanol and distilled water solution for the carbon formation in this study. The catalyst derived from ethanol is labeled as Sample A and Sample C. Meanwhile for the distilled water-based catalyst is labeled as Sample B and Sample D. These four samples were run under the same synthesis time and every change in temperature are recorded in 10 minutes intervals. Referring to Table 1, Furnace 1 indicate the pyrolysis takes place in the process and Furnace 2 indicate the CCVD process.

Table 1: Experimental result of the CCVD process for furnace 1 and furnace

Sample	Time	Furnace 1	Furnace 2
	(mins)	Temperature (°C)	
Sample A (EtOH)	0	30.5	29.3
	10	263	345
	20	649	733
	30	678	776
Sample B (Distilled Water)	0	30.5	36.1
	10	367	457
	20	670	760
	30	672	767
Sample C (EtOH)	0	30.9	35.3
	10	365	459
	20	648	767
	30	649	769
Sample D (Distilled Water)	0	30.2	30.6
	10	277	423
	20	662	766
	30	680	771

Based on Table 1 above, the changes in temperature happened in both furnace as the process take place. The first furnace was initially set at 600°C for the pyrolysis is exceeding the number as the highest temperature recorded is at 680°C, however, this temperature is not exceeding the CCVD process temperature at the second furnace. Meanwhile, the set point temperature is at 800°C is set for the second furnace, with the highest temperature recorded is 776°C in Sample A. By observing the temperature changes in both furnaces, the average heating rate is done as the heating rate of Furnace 1 is 22.3°C/min and Furnace 2 with 25.7°C/min. Due to the set point temperature for Furnace 1 is set a bit lower than Furnace 2, it is explained the average heating rate for Furnace 1 is lower than Furnace 2. However, other studies mentioned the heating rate has a little impact on sludge pyrolysis reaction activation energy and in proportion to reaction rate [14]. The formulas in calculating average heating rate is given in equation below.

$$T_{S} = \frac{T_{F}(^{\circ}\text{C})}{t \text{ (min)}}$$
$$T_{avg} = \sum_{S=1}^{n} \frac{T_{S}}{4}$$

Where; T_s = Heating rate of sample, (°C/min)

 T_F = Final temperature of the sample, (°C)

t = Time duration, (mins)

Meanwhile, Table 2 shows the results of the weight changes in each sample after conducting the CCVD process.

Table 2: Weight of sample after CCVD process

Catalyst	Weight before CCVD (g)	Weight after CCVD (g)	Changes (g)
Sample A	0.1	0.07	0.03
Sample B	0.1	0.09	0.01
Sample C	0.1	0.08	0.02
Sample D	0.1	0.09	0.01

Based on Table 2, sample A, B, C and D showing a change in term of weight before and after the CCVD process. The actual weight before CCVD is 0.1g, but each sample shows a significant loss in weight after the process. Sample A with loss of 0.03g in weight, Sample B and D with 0.01g weight loss changes and Sample C with 0.02g weight loss. The changes in the sample due to the removal of water which related to TGA analysis. However, it is also possible to include human intervention while handling the sample. Since the cylindrical hollow used in the second furnace is quite small and might cause the loss of the catalyst sample when it is inserted into the hollow.

B. Fourier Transform Infrared Spectroscopy (FTIR)

Based on the FTIR results, the samples from the CCVD experiment is tested for each ethanol and distilled water derived catalysts. Before and after CCVD is investigate based on the functional group formed in each of the samples. Fig 2 shows the FTIR analysis on catalyst based on ethanol solution.



Fig. 2: FTIR curve for Co catalyst-based ethanol before the CCVD process

Based on Fig 2, there is no functional group formed in Co catalyst-based ethanol before the CCVD process as the catalyst is in pure form since there is no reaction process in the catalyst after the calcination of the catalyst prepared. Meanwhile, the Co catalyst produced based on distilled water show a peak on the analysis which due to the impurities and noises in the sample. Fig 3 shows the peak results from the FTIR analysis.



Fig 3: Peak analysis of Co catalyst-based distilled water before the CCVD process

However, both of the derived catalyst which ethanol and distilled water solution are taken for investigation in this study. Based on the experiment conducted, Fig 4 shows the FTIR analysis of Co catalyst after the CCVD process in a range of 515–4000 cm⁻¹. Each sample shows the constant and dominant peak at 640, 1250, 1372 and 1737 cm⁻¹ which corresponds to C-H, C-N, N-CH₃, and CNT, respectively. The presence of consistent peak of C-N and N-CH₃ at 1250 cm⁻¹ and 1372 cm⁻¹ in the sample show the stretching vibrations studied by Choi et. al., where the presence of intercalated N atoms between the graphite layer at the inner part of nanotubes walls [15]. Besides, the presence of a functional group at the peak of

1737 cm⁻¹ shows the CNT formation at this feature which attributed to MWCNTs vibrational mode as conducted in other studies [16]. The C-H bend also present at 640 cm⁻¹ in the analysis. The typical group frequency, wavenumber (cm⁻¹) for C-H bend ranges from 610-680 with assigned as Alkyne C-H bend [17].



Fig 4: Peak results on sample Co catalyst after the CCVD process

C. Thermogravimetric Analysis (TGA)

TGA analysis was carried out under air flow gas at the heating rate of 20°/min to obtain the information on decomposition and burning properties of CNTs and impurities in it. The temperature of the sample varies in this analysis with the starting temperature start at 25°C to 1000°C and the flow of air gas at 50 L/min. Since the temperature for each sample show a variation in TGA analysis the graph is plotted based on each sample as shown in Fig 5.





Fig 5: TGA curve after CCVD process (a) Sample A (b) Sample B (c Sample C and (d) Sample D

Based on Fig 5, the analysis showing the weight gradient is constantly decreases with the increase of temperature. The weight loss in the TGA analysis was due to the combustion of carbon atoms in the samples by air. The curves reveal a small weight loss due to water removal around 50°C and compared to other studied conducted which the removal of water happened at 80°C [18]. However, the dominant weight loss steps recorded in the analysis are at a temperature range 400-600°C for sample C and D in the TGA curve due to the removal of impurities in carbon material also due to the decomposition of nanotubes [19]. According to Toussi et. al., (2011), the residual weight at high temperature was due to metal oxides from the catalyst [20]. As shown in Fig 5, the residual weight in mg present in the catalyst at high temperature in TGA analysis. Different studies also reported that the oxidation temperature was around 330°C for amorphous carbon, 500-600°C for SWCNTs and 700°C for MWCNTs, respectively [21][22]. Since the weight gradient in the analysis is constantly decrease, it is hard to determine the formation of amorphous carbon without conducting qualitative tests on each sample.

IV. CONCLUSION

In this study, we analyzed the pyrolysis of sewage sludge on the production of carbon formed. It is hypothetical can produce the CNTs and based on the experiment conducted, the FTIR analysis shows the clear formation of C-N and N-CH3 stretching at a strong peak of 1250 and 1372 cm⁻¹ respectively. This is proved by studies conducted where the presence of intercalated N atoms between the graphite layer at the inner part of nanotubes walls. CNTs attribution also appeared at 1737 cm⁻¹ in the process of this study. The C-H bend is present at 640 cm⁻¹ in the analysis with assigned as Alkyne C-H bend. Meanwhile, TGA has been used to study the weight loss of CNTs as a function of temperature. It is found the dominant weight loss due to the decomposition of nanotubes occurs at 400 -600°C temperature range based on the previous studies conducted. The formation of amorphous carbon in the catalyst is hard to determine without conducting qualitative tests on each sample. However, this study proved there is a formation of carbon material and CNTs on the cobalt catalyst during the reaction of vapour produced from the pyrolysis of sewage sludge as the carbon sources.

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