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

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Abstract—**The study describes on catalytic chemical vapor deposition (CCVD) method for production carbon nanotube onto Fe-alumina supported catalyst. Sewage sludge was used as a carbon source. The objective of this study are to investigate the formation of carbon nanotube using iron metal catalyst in CCVD method between reduction and without reduction steps. Besides that, to identified the characterization of Fe-alumina catalyst. The catalyst and their support is prepared by using impregnation method technique. Characterization of iron-alumina catalyst was done by series of analysis before and after the process. Mass of catalyst sample, Thermo-gravimetric analyzer (TGA), and The Fourier transform infrared spectroscopy (FTIR) was used as analyzer the formation of carbon nanotubes (CNTs). The TGA showed that the formation of amorphous carbon occurs at the initially stage and before 300°C. The higher yield of CNTs was produce in experiment 2 with spongy physical appearance carbon material. The FTIR analysis shows the hydroxyl group are present at early stage. Overall the uses of reduction step by allowing the hydrogen gas during reaction occurs increasing the probability of CNTs production.**

Keyword- Carbon Nanotube(CNTs), Catalytic chemical vapor deposition(CCVD), iron catalyst, pyrolysis reaction, sewage sludge

I. INTRODUCTION

Rapid growing of population create a serious challenge to the sustainable development. The other side, rising volume of municipal wastewater produce large number of sewage sludge or the residual by-product of municipal waste water treatment plant (WWTP). Sludge contains many unwanted materials and must be disposed properly. The quantity and nature of sludge depend on the characteristics of the waste water and on the nature and efficiency of the process. It is estimated that sewage sludge is produced at the rate of 0.1-30.8kg per population equivalent annually. [1]. Conventional method of sewage sludge management such as landfilling and agricultural not a best solution because lack of land space and the rising environmental and health concern. In fact, there are something valuable inside the sewage sludge that can be transform into valuable energy via proper technology strategy.

Thermal treatment such as pyrolysis are one of the method for producing valuable gas and liquid from hydrocarbon feedstock. Pyrolysis can be described as the direct thermal decomposition of the organic matrix without oxygen in order to obtain a range of solid, liquid and gas products. [2]. Through the pyrolysis, sewage sludge can produce combustible gas, condensable vapor and char.[3] Among the gas produced, hydrogen gas is most a particular interest among the researcher since, its combustion gives off only water.[4] Thermal treatment of hydrocarbon such as sludge, biomass, waste tire and plastic feedstock offers a more environmentally sound solution to convert the material into something valuable. Production of hydrogen from the sewage sludge become well researched with increasing numbers of studies using pyrolysis technique.

Recently, it has been shown that some of the carbon deposits produced during pyrolysis of sewage sludge are valuable carbon nanotube. Since the discovery of Carbon nanotube (CNT) by Ijima[5], Carbon nanotubes are a valuable form of carbon with an increasingly large number of publications on the subject due to their potential for current and future uses in a wide range of industries including composites, micro electrics and energy applications. There are, various method to produce CNT such as plasma-based arc discharge[6], laser ablation[7], and addition of thermal method that called catalytic chemical vapor deposition (CCVD). Among the technique, CCVD is one of the best method to produce CNTs due it capable to obtain large quantities and high purity materials.[8].

Transition metal e.g., iron, nickel and cobalt catalyst are typically used for hydrogen production because have higher catalytic activity[9] and also cheaper than effective metal catalyst. Catalyst play a key role in the production of CNTs when the metal has been directly exposure to the any source of hydrocarbon such as methane, ethane, trichloroethylene[10] with the proper experiment procedure. In addition, researcher found that decomposition was higher in ion catalyst than other transition metal[11], lead to producing higher hydrogen yield as a result. Beside metal catalyst, supported is an important material to choose in prepared the catalyst sample. Alumina,[12] silica and quarts are among the substrate use in catalyst preparation. In order to obtain the CNTs, there are some method can be used in prepare catalyst nanoparticles such as Sol-gel, coreduction of precursors, impregnation method, ion exchange precipitation and reverse micelle method. Among the method, impregnation technique is most widely used by the researcher due to simple and flexible operation experiment.

Currently, to our best knowledge, little information could be found on the investigation production of CNTs using sewage sludge as source of hydrocarbon. In this paper, two different catalytic process was used on the simultaneous production of CNTs between reduction and without reduction process on catalyst sample. The catalyst and their supported was prepared using impregnation method with fix calcined temperature. This research will undergo pyrolysis reaction where the sewage sludge was used as a raw material to produce carbon source. Then the vapor produce will use to react with iron-alumina catalyst using catalytic chemical vapor deposition method(CCVD) to produce CNTs. Two different synthesis of CNTs experiment setup was used with presence of hydrogen gas and without hydrogen gas.

II. METHODOLOGY

A. Materials

Iron(III) nitrate Nano hydrate, $Fe(NO_3)_3$, Alumina oxide(Al_2O_3), Ethanol (CH_3OH). Nitrogen gas, Hydrogen gas and sewage sludge from Jassin waste water treatment plant (WWTP).

B. Synthesis of catalyst

Iron catalyst were prepared according to Ref.[13] with slight modification by impregnating the metal onto the alumina support, so that 10% metal catalyst will produced. Generally, the impregnation method consists of the first dissolving a catalyst precursor and then contacting a support with the solution. This study used metal nitrate and Alumina support as the main raw material. 3g of iron nitrate was dissolve in 2ml of ethanol, following which the 3g of alumina was added until the mixture turn slurry. After that, the mixture then dry overnight in an oven at 50°C to remove the remaining ethanol deposited on the mixture. This was then calcined at 1000°C for 3hour at a heating rate of 2°C min^{-1} in an air atmosphere. The catalyst were then crushed and sieved to give granular form between 0.05 to 0.18mm.

C. Production of CNTs

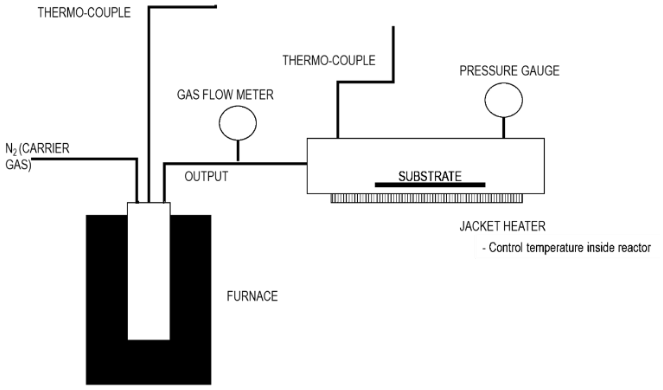

Figure 1: Designated synthesis of CNTs experiment 1

For the first experiment, the system consisted of two different stages of reactor, which are pyrolysis (first reactor) and CCVD (second reactor) part as shown in figure 1. In each experiment 0.30g of the sewage sludge was added inside the first reactor with 5cm in diameter and 155mm of height, where the temperature was heated up to 600°C, with heating rate 50°Cmin^{-1}. The generated gas produces from the first reactor then passed through a tubing to the second reactor, held at 800°C and passed over the 0.1g catalyst where put on the sample boat inside horizontal furnace with diameter 35mm and the length of 350mm. This phenomenon allowing the hydrogen to be produce with carbon deposition on the catalyst. Nitrogen gas was used as the carrier gas with flowrate of 0.8Lmin^{-1}. The total of reaction time is 30min with temperature was reading at every 10min using the thermocouple at the both reactor.

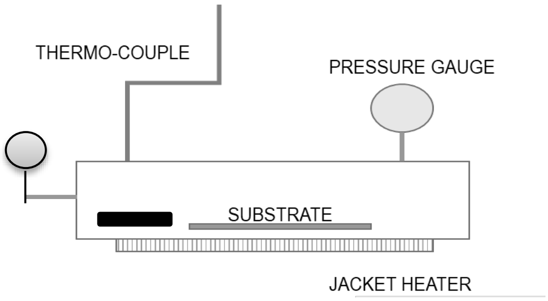

Figure 2:Synthesis of CNTs experiment 2

For the second experiment, only 1 reactor was used along the system. The sample weight was fix and also the operating condition. However, hydrogen and nitrogen gas was supply to the reactor with flowrate of 0.8Lmin^{-1}. In this system a sample and catalyst was put in the same reactor, to minimize the gas from leaving outside and to be expected form a large number of CNTs produced.

D. Characterization of catalyst

The fresh catalyst were then investigated by a series of analysis of technique to characterize the nature of the carbon that was deposited on the surface of the catalyst during the experimental procedure. Thermal analysis was carried out on a Thermo-gravimetric analyzer (TGA) and Differential thermal gravimetric (DTG) were perform according to the previous research parameter[14]. About 5mg of powder was loaded at room temperature into a standard aluminum crucible. The crucible then heated up to 1000°C at a constant rate of 20°Cmin^{-1} in air.

The Fourier transform infrared spectroscopy (FTIR) were analyzer and recorded in transmission mode using Spectrum Two IR Spectrometer to identify the functional group of the catalyst before and after the experiment. The result then compared to the standard list of functional group represented by previous researcher.

III. RESULTS AND DISCUSSION

A. Mass of sample catalyst

Experiment 1	
Weight of sample boat	4.81g
Weight of sewage sludge	0.30g
Weight of sample boat + catalyst (before)	4.92g
Weight of sample boat + catalyst (after)	4.89g

Experiment 2	
Weight of sample boat(catalyst)	4.94g
Weight of sample boat(Sludge)	5.43g
Weight of sample boat + catalyst (before)	5.04g
Weight of sample boat + sludge (before)	5.73g
Weight of sample boat + catalyst (after)	5.39g
Weight of sample boat + sludge(after)	5.18g

From the experiment 1, weight of the sample catalyst before CCVD and pyrolysis process were conducted is 4.92gram. After the experiment was conducted, the mass of the sample slightly decreases to 4.89gram. It was expected that the material of sample boat which are from clay are decreases due to high temperature exposure to the catalyst. Meanwhile in experiment 2, weight of sample boat and catalyst was increases about 0.35g. On the other hand, the weight of sample boat with sludge is decrease from 5.73g to 5.18g.

According to K.A. Shah [15], only 30-40% of sewage sludge will turn into vapor composition after pyrolysis occurs. From the gas produce, it will react to the active catalyst surface and form black particle on the catalyst. For the experiment 1, the teflon tube is using to transfer the gas from reactor 1 to reactor 2. There is a gas which are condensed inside the tube and some of the gas is leak at the feed connection tube. Only 15% of the gas was react to the catalyst in reactor 2. However, in experiment 2, 100% of gas produce are react to the sample catalyst with the present of hydrogen gas as the catalyst activator also to change the Fe(III) species to Ferum oxide.

In experiment 1, the deposition of carbon on catalyst appeared is fine powder indicated the low yield of carbon nanotube. Meanwhile, in sample 2, the physical appearance showed soft and spongy material. This was expected for the formation of carbon material. In general, it was observed that, when the carbon deposit appeared spongy form, the used of catalyst is active for Multiwall Carbon nanotube MWCNTs. There are some parameter that effect the yield of carbon nanotube. The initial observation indicate that support play an important role in catalytic activity of metal particle deposited on it.[16] The major factor influencing the activity was the nature of distribution of metal. The state of distribution of metal are depending on the type of metal-support interaction which in turn depended on the nature of support.

Besides that, method of catalyst preparation also affects the yield of carbon material formation. All the catalyst was reduced before passing the carbon source in CCVD process. The reduction of iron oxide phase to metallic iron was optimum and contribute to the growth of carbon material.[17] Based on previous study, catalyst obtain by the sol gel method shower higher activity in the formation of carbon formation rather than used impregnation method.[13] This was due to the sol-gel method result in the distribution of metal ions in highly homogeneous manner than by impregnation method.[18]

B. Thermo-gravimetric analysis result(TGA)

TGA is one of the method to determine the thermal decomposition or degradation of raw material. Figure 3 and 5 shows the mass loss (TG) and mass derivative loss(DTG) with temperature curve for iron alumina catalyst.

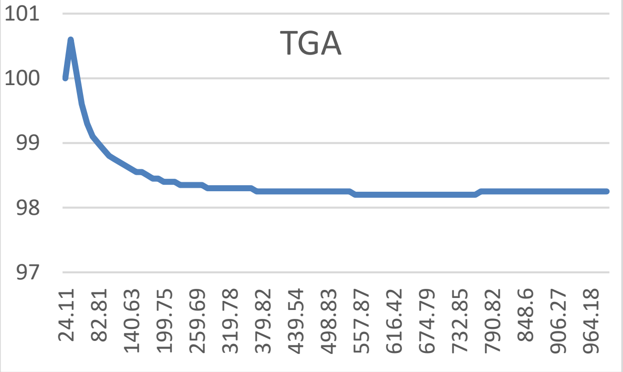

Figure 3: TGA catalyst before CCVD

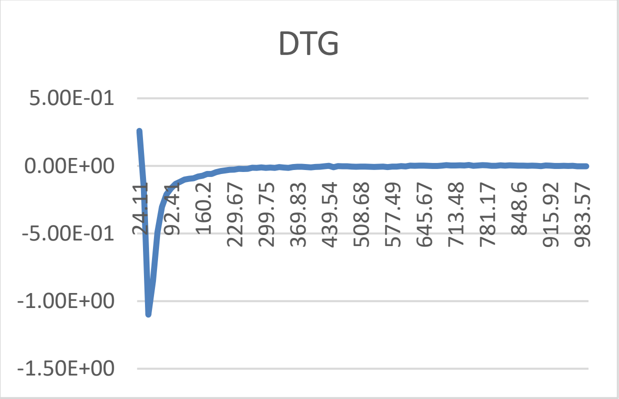

Figure 4:DTG catalyst before CCVD

Thermo-gravimetric analysis results before carbon deposition are presented in Figure 3(TGA) and Figure 4(DTG). This analysis was done after the calcination of catalyst at 1000^{o}C. The curve shows a slight increasing of mass due to exposure to the oxygen before the degradation of catalyst occurs. The degradation is about 3% of weight occurs in the range of 25^{o}C-80^{O}C. This is expected that during calcination process, there are some element that still remain inside the sample.

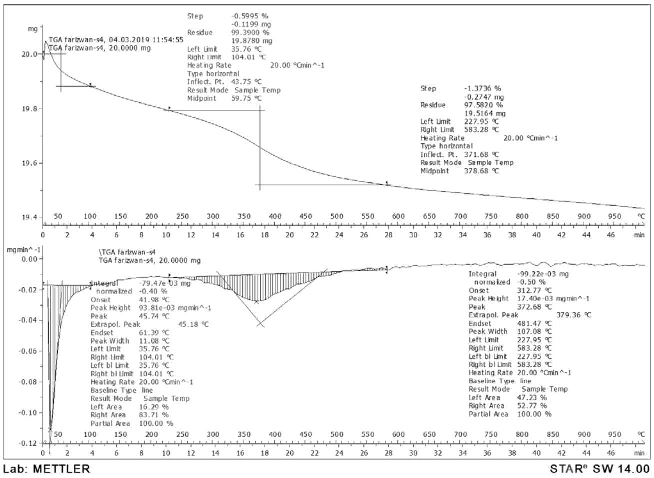

Figure 5:TGA for sample experiment 1 (after)

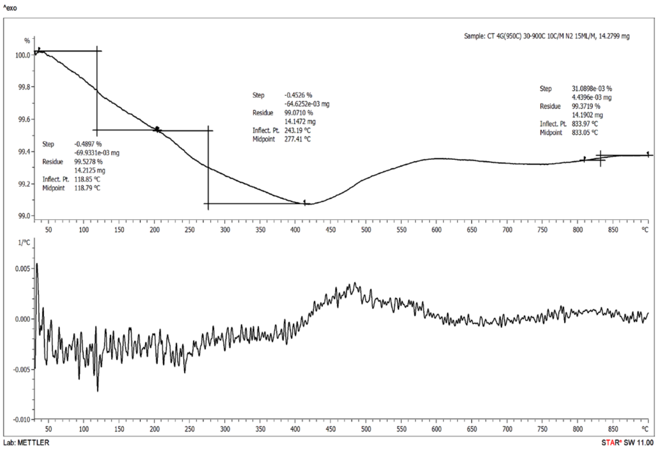

Figure 6: TGA for sample experiment 2 (after)

Figure 5 and 6 refers to the thermo-gravimetric analysis of sample 1 and sample 2 respectively, after the carbon deposition. There is a slight increase of the mass during initial analysis due to incorporation of oxygen to the catalyst. After that, sample 1 shows a weight loss of about 0.2% in the range of 80^{o}C-100^{O}C due to elimination of amorphous carbon. Then, degradation of carbon materials occurs in the range 300^{o}C-500^{O}C with a weight loss of

0.5%. DTG results confirm clearly the elimination of amorphous carbon at early stages of degradation. It can be concluded that sample 1 have a lot of impurities i.e. amorphous carbon.

In experiment 2, the presence of hydrogen gas allowing the formation of carbon materials. Similar with the sample 1, there are two weight loss or degradation of mass along the analysis. A small mass loss between 25ºC-100ºC is attributed to elimination of moisture content and loss of surface hydroxyl groups on the alumina support. According to [19] the absence of mass loss below 400ºC is referring that there is little amorphous carbon presents on the catalyst. The major weight loss about 0.4% can be utilized for estimating the amount of carbon material formation. It can be state that, the is a formation of carbon material in experiment 2.

C. The Fourier transform infrared spectroscopy (FTIR) analysis result.

The iron alumina catalyst also analysis by using FTIR analysis to identified the functional group of the sample.

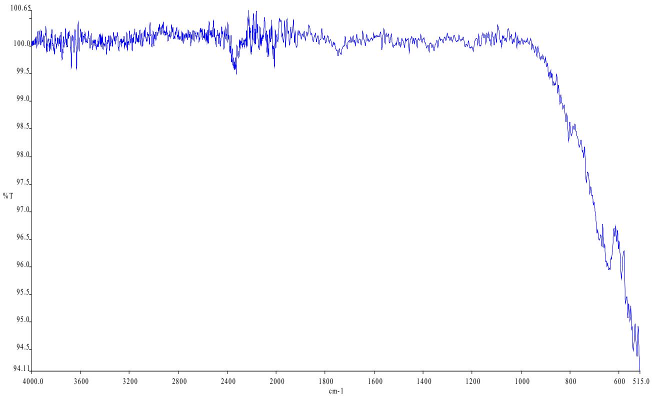

Figure 7: FTIR catalyst before CCVD

Figure 7 shows the analysis result of FTIR before the CCVD was conducted. This analysis was done after calcination process on the furnace at 1000ºC for 3 hours. The FTIR spectrum presents a stable curve along the result. This spectrum shows that, there is no peak or unwanted element contain inside the sample. All the functional group are eliminating cause by the high temperature during calcined. According to [20] ,increasing calcination temperature produced metal particle which were too less growth of carbon material, also producing amorphous carbons, instead deactivate the catalyst.

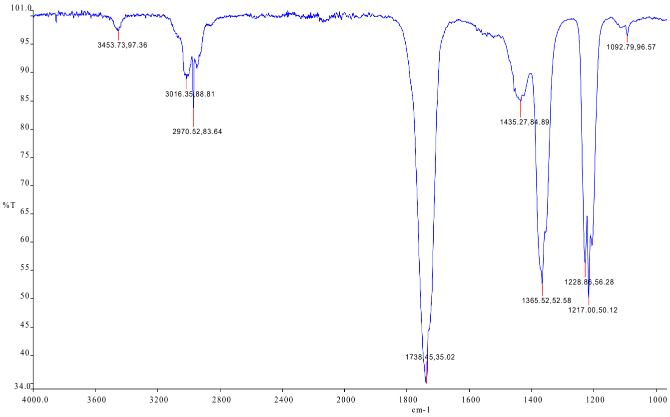

Figure 8:FTIR catalyst for sample experiment 1(after)

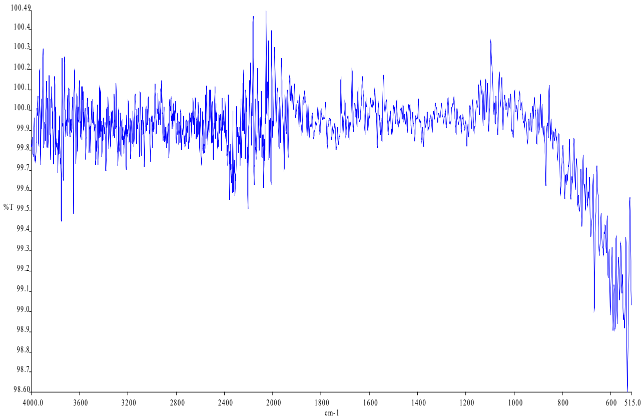

Figure 9: FTIR catalyst for sample experiment 2(after)

The FTIR spectrum of the iron/alumina catalyst was shown as the figure 8, figure 9 for experiment 1 and 2 respectively. For sample in experiment 1, a signal at 3453.73cm^{-1} is associated with vibration of the hydroxyl group. The result then shows double peak at signal 2970 cm^{-1} and 3016 cm^{-1} due to internal defect, and the O-H vibration. [8]Another peak form at a signal 1738.45 cm^{-1} is attributed to the C-C stretch band of the catalyst. A signal at 1217 cm^{-1} is described to the stretching in the plane =C—H bond or stretching mode. Experiment 2, shows very contradict result with experiment 1. The spectrum reading shows noisy peak along the curve. There is causes by present a lot of functional group.

IV. CONCLUSION

Carbon material and hydrogen gas was successfully produced simultaneously on iron catalyst using a sewage sludge. The source of hydrocarbon is coming out from the gas produces from the pyrolysis of sewage sludge. The interaction of catalyst metal and alumina support play a strong part in governing the yield of carbon material. If the interaction is too weak, it allows metal particles too large hence lower yield carbon material production and too strong interaction an intersection hindering production. The work also shows that the reduction step with allowing hydrogen gas, help in activation of surface catalyst and increase probability of interaction between gas and catalyst to produce carbon materials. In term of physical appearance, sample 2 shows sponge material is most related on carbon material present rather than sample 1.

There is a need for changes and adjustment in order to improve the process setting and the analysis accuracy result obtain later. During experiment setup, make sure all the connection was fix properly to prevent the gas release to surrounding. A part from that, increase the surface area of catalyst by rearrange the powder on the sample boat to increase the probability of contacting between gas and catalyst sample. The experiment also need to conduct repeatedly to find out the average result or the best observation. For the analysis of catalyst, it can be conduct some analysis like scanning electro-microscopy (SEM), Thermal electro-microscopy(TEM) and Raman Spectroscopy to figure out the image of carbon material. In order to find the specific surface area and the porosity of the catalyst, the sample can be run using Brunauer-Emmett-Teller (BET) analyzer.

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