

# Synthesis of Nanocarbon from Polyethylene Plastic Using Stainless Steel Catalyst via Oxidative Heat Treatment Preparation Method

Praswasti PDK Wulan<sup>1a\*</sup>, Kevin Danar Cendana<sup>2b</sup>

<sup>a</sup> "Chemical Engineering, Faculty of Engineering Universitas Indonesia, Depok 16424, Indonesia

<sup>b</sup> "Chemical Engineering, Faculty of Engineering Universitas Indonesia, Depok 16424, Indonesia

Received: December 7, 2015/ Accepted: March 3, 2016

## Abstract

Nanocarbon technology has been growing in recent times due to the excellent electrical, thermal and mechanical properties of nanocarbon. However, nanocarbon has not yet been commercially produced on a large scale because of the expensive production processes. As an alternative, plastic can be used as the carbon source not only because it is affordable but also because it is a waste stream which amount is abundant in the world, including in Indonesia. For the catalyst, Stainless Steel can also be an alternative also because it is cheaper compared to pure nickel and copper. Preparation of the catalyst also plays an important role in the nanocarbon synthesis process. One of the effective preparation methods is oxidative heat treatment at a temperature of 800°C. The advantages of this method are the fairly short time required and the fact that no other material input is required. This preparation method is proved by the increasing amount of nanocarbons that are attached on catalyst up to 2.2% yield with one minute duration heat treatment. The result of XRD shows that carbon nanotubes (CNT) are present on the nanocarbon, synthesised at 800°C and with pyrolysis temperature 450°C, in every heat treatment duration variation. The most optimal heat treatment duration is 10 minutes where

it shows the carbon is evenly spread and has the highest carbon concentration from SEM-EDX characterisation.

**Keywords:** Nanocarbon; Oxidative Heat Treatment; Polyethylene; Stainles Steel.

## 1. Introduction

In recent years, nanotechnology has been becoming more popular. This is due largely to its potential applications, which can stretch to various aspects, such as electronics, materials, biology, chemistry, etc. One of the emerging nanomaterials is nanocarbon, which is attractive because it has excellent electrical, thermal and mechanical properties (Kumar, 2010, Mu'minin, 2010).

Up to now, nanocarbon has not yet been massively and commercially produced because of the expensive production process. This process requires carbon sources from hydrocarbons and nickel or copper-based catalyst precursors. Such catalysts come at a relatively high price. Consequently, to reduce expensive production costs requires cheaper carbon sources and catalysts. One potential carbon source is waste plastic.

Plastic waste material is very abundant in the world, including in Indonesia. In 2013, plastic consumption in Indonesia reach 1.9 million tons and this is predicted to continue to grow. (Wulan, 2015a). One of the highest plastic materials usages is Polyethylene (PE) at around 60% of the world's plastic waste (EPA, 2008, Forum Indonesia Hijau, 2013). The use of plastic as a carbon source can not only resolve both of these problems (cost and waste), but can also produce nanocarbon of a good quality. (Zhuo, 2009, Chung, 2004).

The use of expensive catalysts is proposed to be replaced with Stainless Steel 304 (SS 304). The price of SS 304 is clearly cheaper when compared with nickel and copper, and in addition SS 304 can also function not only as a catalyst but also as a substrate, so additional substrate is not necessary (Alves, 2012, Legend, 2012). SS 304 includes types of non-magnetic stainless steel that contain in the range of 18-20% chrome, and nickel in the range of 8-12% with additional elements in order to achieve the desired properties. Selection of a good catalyst must also accompanied by good catalyst preparation. Catalyst

<sup>1</sup> Corresponding Author

Tel.: +6221-7863516/+6221-78885335; Fax.: +6221-7863515;

E-mail: [wulan@che.ui.ac.id](mailto:wulan@che.ui.ac.id), [praswasti.pdk.wulan@gmail.com](mailto:praswasti.pdk.wulan@gmail.com)\*

preparation plays an important role in the quality and quantity of nanocarbon produced.

Nanocarbon growth research has been carried out in the Department of Chemical Engineering, Universitas Indonesia, for a number of years. The use of SS as a catalyst has also been examined since 2007. Catalyst preparation methods of sol gel-dip coating and sol gel-spray coating have been utilised. Both of these preparation methods have problems, such as catalyst that falls out of the SS substrate after calcination and catalysts that are not evenly distributed across the surface of the substrate (clumping occurs so that the emptiness factor becomes high). One way to overcome this is the oxidative heat treatment preparation method (Zhuo, 2013).

Oxidative heat treatment is a process heating or cooling metal at a certain time interval. The oxidation process occurs due to the presence of air when iron or other metal is heated. The purpose of this treatment is to destroy slippery coating layers on stainless steel so that nanocarbon can grow more easily. The advantages of this method are that the time required is quite short and no other material is required. This preparation method has been shown to be capable of producing Carbon Nanotubes (CNT) using SS catalyst (Zhuo, 2013).

Therefore, the purpose of this current research is to finding the optimal pyrolysis temperature for PE plastics in order to obtain nanocarbon from polyethylene using SS 304 catalyst via the oxidative heat treatment preparation method. Additionally, this research will increase the economic value of waste PE plastic and assist in addressing environmental problems associated with this waste.

## 2. Research Methodology

### 2.1. Stainless Steel Oxidative Heat Treatment

The stainless steel which was used in this research was SS 304 mesh. Selection of SS 304 was based on its price - which is the most inexpensive when compared to other types of Stainless Steel. SS 304 was used as the catalyst and also as the substrate in the process of synthesis of nanocarbon. The SS 304 mesh was cut into 300x100 mm and then rolled into cylindrical form.

The catalyst was then cleaned using acetone by rubbing the surface of the catalyst. Heat treatment was done by heating the catalyst inside a furnace in the presence of air at a temperature of 800°C for 1, 5, 10 and 20 minutes, then quickly removing it from the heated area to air for quenching. The purpose of this preparation method is to coarsen the catalyst substrate surface so that nanocarbon can grow more easily and attach to the catalyst substrate.

### 2.2. Pyrolysis of Polyethylene (PE)

Pyrolysis of polyethylene plastic was conducted in a reactor with the purpose of finding the optimal pyrolysis temperature and identifying the most abundant gases in from the pyrolysis reaction. Pyrolysis was conducted at an

initial temperature of 250°C and increased by 100°C until it reached 750°C. Gas samples were taken every 10 minutes at every temperature level and were analysed by injection into a Gas Chromatography - Thermal Conductivity Detector (GC-TCD) Shimadzu GC-8A with PORAPAK-Q column.

### 2.3. Synthesis of Nanocarbon

Nanocarbon was synthesized with a double- furnace system and two reactors. The first reactor serves as a pyrolysis reactor and the second reactor serves as a synthesis reactor set at 800°C. Carbon sources obtained from pyrolysis of polyethylene plastic (around 10 gram) which is inserted in the first reactor then purged with inert Argon gas at a flow rate of 100 ml/minute and Oxygen gas as co-feed at a flow rate of 33.3 ml/minute (33.3% of inert gas flow rate). Oxygen is used as co-feed because it will react with carbon produced from the pyrolysis process, thus the expected resultant gas should contain CO. CO gas plays an important role in the growth of nanocarbon. Because CO is the primary growth agent, its maximized concentration was targeted and the establishment of a stable flame at the venturi was verified. Combustion effluent is expected to be much cleaner (Zhuo, 2009). The catalyst which has been prepared is inserted in the center of the second reactor, and the subsequent reaction was undertaken for 1 hour. The arrangement of the equipment can be seen in Figure 1.

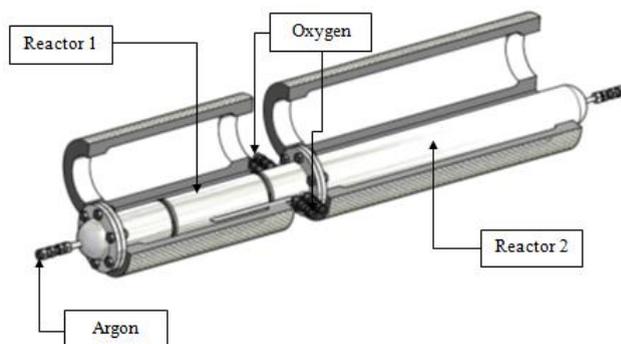


Figure 1 Arrangement of Equipment

### 2.4. Nanocarbon Characterization

Nanocarbon characterization was performed using 4 testing apparatus: Scanning Electron Microscope with Energy Dispersive X-ray (SEM-EDX) Hitachi S-3400, Powder X-ray diffraction (XRD) patterns with a Phillips analytical X-Ray model number BV-2500, Transmission Electron Microscope (TEM) JEOL JEM1400 and Fourier Transform Infra Red (FT-IR) Spectrometer 1000, Perkin Elmer.

## 3. Results and Discussion

### 3.1. Polyethylene Pyrolysis Temperature

As can be seen in Table 1, the highest content of alkanes are produced at a temperature of 450°C, specifically in the form

of butane gas (C<sub>4</sub>H<sub>10</sub>). Propane and butane are more important gases in the formation of nanocarbon when compared with methane, and because of that, the presence of butane is used as a parameter in the determination of the optimum temperature. Butane and propane with high reactivity will give yields of CNTs much higher than methane as it provides higher carbon concentrations. The concentration of carbon is the number of moles of carbon in the overall volume of gas that goes into the reactor (Kimura, 2013). The next parameter is the duration needed for pyrolysis to produce the best gas composition at a temperature of 450°C. Gas samples were taken at minutes 10, 20, 30 and 40 then injected into a gas chromatograph to determine the gas composition.

The results, as shown in Table 2, indicate that pyrolysis gas at minute 10 produced the highest composition of butane (6.71%), so it can be determined that the optimal pyrolysis duration is 10min.

**Table 1** Gas Composition from Pyrolysis of Polyethylene Plastic on Temperature Variation 250°C – 750°C

Gas Component	% Composition					
	250° C	350° C	450° C	550° C	650° C	750° C
CH <sub>4</sub>	97.27	97.12	88.66	89.65	94.45	93.20
C <sub>2</sub> H <sub>6</sub>	0.00	0.09	1.57	0.31	0.13	0.14
C <sub>3</sub> H <sub>8</sub>	0.00	0.00	1.99	1.40	0.68	0.94
C <sub>4</sub> H <sub>10</sub>	0.00	0.00	1.07	0.00	0.00	0.00
Other Gas	2.73	2.79	6.71	8.64	4.75	5.72

**Table 2** Gas Composition from Pyrolysis of Polyethylene Plastic at Temperature 450°C with 10-40 Minutes Heating Duration Variation

Gas Component	Name	% Composition			
		Minute 10	Minute 20	Minute 30	Minute 40
CH <sub>4</sub>	Methane	56.32	92.52	95.84	95.56
C <sub>2</sub> H <sub>6</sub>	Ethane	1.32	0.93	0.33	0.36
C <sub>3</sub> H <sub>8</sub>	Propane	2.10	1.19	0.41	0.41
C <sub>4</sub> H <sub>10</sub>	Butane	3.12	0.65	0.00	0.00
Other Gas	-	37.14	4.72	3.42	3.66

### 3.2. Synthesis of Nanocarbon using Stainless Steel Catalyst without Heat Treatment

To see the effectiveness of the heat treatment method, at the initial stage synthesis of nanocarbon was undertaken using SS 304 mesh catalyst without applying the heat treatment preparation method. Catalyst was cleaned with acetone by polishing using a toothbrush.

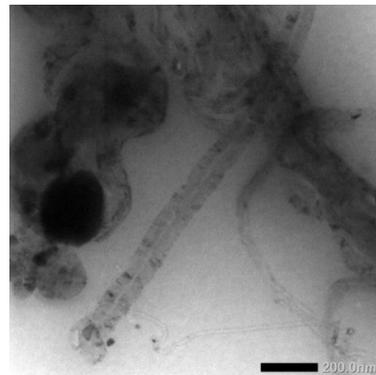
From the initial stage of this research, nanocarbon yield was 38.7% or in other words 3.87 grams of nanocarbon was produced from 10 grams feedstock. This result is larger than compared with using a plate cylinder catalyst. The biggest yield that was produced from the plate cylinder catalyst was 30% (Chairat, 2015). FT-IR and TEM characterization were then performed on the sample obtained.

The results of FT-IR characterization can be found in Appendix A, the largest peak can be seen at a wavelength of about 2600cm<sup>-1</sup>. Another prominent peak is in the area around 2300 cm<sup>-1</sup> wavelength.

Based on Sastrohamidjojo, 2001, it can be seen that the existing bond at a wavelength of about 2600 cm<sup>-1</sup> is O-H that has a wavelength range 2500-2700 cm<sup>-1</sup>. This O-H bond could appear as a result of oxygen that is injected as co-feed and reacts with hydrogen contained in the hydrocarbon gas from pyrolysis.

For the peak at a wavelength of about 2300 cm<sup>-1</sup>, this peak approaches the alkyne bond that appears at range 2100-2260 cm<sup>-1</sup> (Mopoung, 2011, Siregar, 2015). The presence of vibration at a wavelength of 2311.04 cm<sup>-1</sup> indicates the presence of the alkyne (C≡C). So, it can be concluded that the peak contained at a wavelength of about 2300 cm<sup>-1</sup> is CNT.

The results of FT-IR were further reinforced with the results of TEM characterization, in which it can be seen that there is CNT formation beginning to be visible at a magnification of 200nm. The CNT obtained is a relatively perfect CNT because there are no partitions on the inside (tube form).



**Figure 2** The Result of TEM Nanocarbon Characterization without Heat Treatment

However, one problem that occurs is that very few nanocarbons are attached to the catalyst substrate SS 304. In the other words, the 38.7% yield obtained is nanocarbon located under the reactor, not on the catalyst substrate. This problem is the same that occurs when using a catalyst plate cylinder. Therefore the preparation method needed to be adjusted to overcome this problem.

### 3.3. Synthesis of Nanocarbon using Stainless Steel Catalyst with Heat Treatment Duration Variation

To increase the amount of nanocarbon that attached on the catalyst substrate surface, catalyst preparation with heat treatment preparation method was undertaken.

It can be seen in Figure 3, that SS 304 which has been heat-prepared is darker and not shiny. The shiny layer on stainless steel is a Cr<sub>2</sub>O<sub>3</sub> layer which becomes a barrier to corrosion, this layer is a differentiator between stainless steel and plain carbon steels. The Cr<sub>2</sub>O<sub>3</sub> layer is slick and shiny. Loss of the shiny layer will coarsen the surface of the stainless steel and is indicated by the darker color than before preparation (Zhuo, 2013).

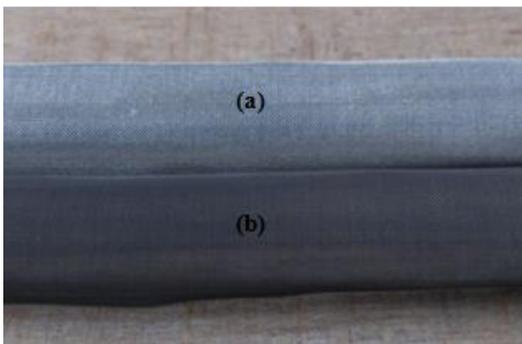


Figure 3 Comparison of SS 304 Before (a) and After (b) Heat Treatment Preparation

Table 3 Nanocarbon Produced with Heat Treatment Duration Variation

Heat Treatment Duration	Carbon on catalyst surface (gram)	Carbon on Under Reactor (gram)	Total (gram)	Yield (%)
1 minute	0.22	2.04	2.26	22.6
5 minutes	0.05	3.58	3.63	36.3
10 minutes	0.08	2.35	2.43	24.3
20 minutes	0.05	2.00	2.05	20.5

If we examine the nanocarbon that attached to the catalyst in every heat treatment duration variant in Table 3, the largest mass of nanocarbon was found after 1 minute heat treatment, at 0.22 grams of a total 2.26 grams carbon

produced. This proves that the heat treatment preparation method performed can increase the fraction of nanocarbon attached on the catalyst surface.

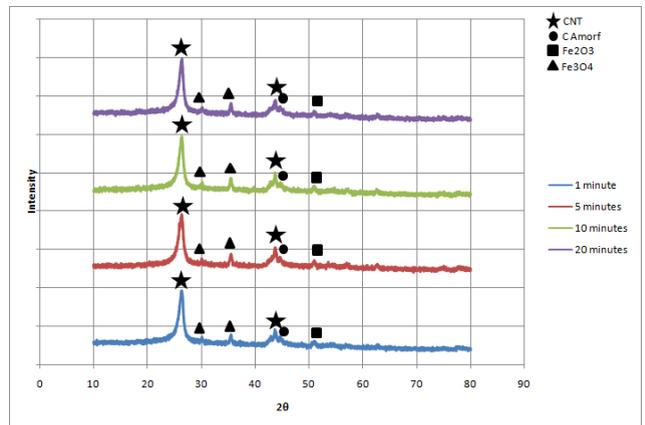


Figure 4 The Result of XRD Nanocarbon Characterization

It can be seen from the results of XRD, that the graphs have a very similar peak pattern for all heat treatment duration variants. CNT has been found at 2θ values of 26; 28,5; 43 and 54.5 (Mopoung, 2011; Wulan, 2015b). The largest peak in the XRD is at 2θ of 26. It can therefore be concluded that there are CNT on the nanocarbon produced through heat treatment preparation method. CNT also formed at 2θ of 43 with considerable intensity. Apart from CNT, there are also other compounds on nanocarbon produced such as amorphous carbon, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. The presence of amorphous carbons indicate that the pyrolysis process has not been completed so that carbon is still amorphous (Mopoung, 2011, Mishra, 2012). Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> are impurities that cause decreased concentrations of CNT. These compounds can be formed because Fe (metal) dissociates from SS 304 and reacts with oxygen from the pyrolysis or co-feed gas (O<sub>2</sub>).

Because the XRD characterization results generated were almost similar, in terms of both peak pattern and intensity, it could not be determined which duration of heat treatment is best for catalyst substrate SS 304. So this required another characterization method, which in this case was SEM characterization. SEM characterization was performed with mapping SEM with the purpose to see the most evenly distributed spread of carbon to determine the most effective heat treatment duration.

As can be seen from the result of mapping SEM in Appendix B, the most evenly distributed spread of carbon (red color) was found for 10 minutes heat treatment duration. This result was also supported with the result of EDX and TEM characterization, in which EDX results show the largest carbon percentage found on 10 minutes heat treatment, equal to 92% (Appendix C), while TEM results show CNT on the nanocarbon sample produced. So it can be concluded that the most effective heat treatment duration is 10 minutes.

## 4. Discussions and Conclusions

From this research, several things can be concluded:

1. Optimal temperature for pyrolysis of polyethylene is 450°C for 10 minutes, which produces the greatest formation of butane.
2. The heat treatment preparation performed was proven to increase the amount of nanocarbon attached to catalyst with largest yield of 2.2% at 1 minute heat treatment duration.
3. The result of TEM characterization shows that nanocarbon synthesised using mesh catalyst substrate without preparation method produced CNT which began to be visible at a magnification of 500nm. CNT production here was better than cylinder plate catalyst.
4. The result of XRD shows there is CNT on every heat treatment duration variation nanocarbon which is marked by a large intensity peak at  $2\theta = 26$
5. The result of SEM-EDX shows the most effective heat treatment duration is 10 minutes which indicated the most equitable spread of carbon and the highest carbon intensity when compared with the others (92%).

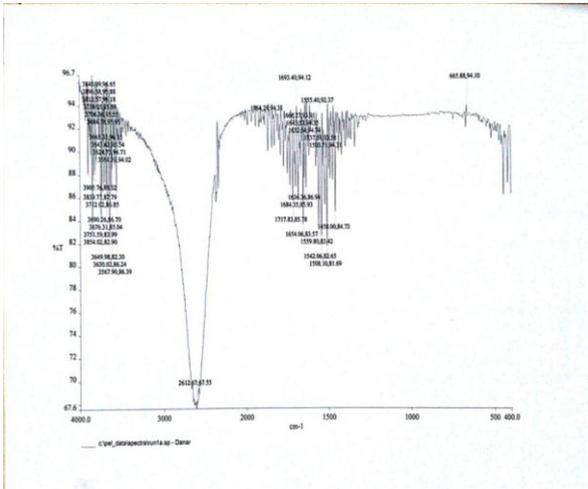
## Acknowledgements

The authors thank PUSLABFOR POLRI for use of mapping SEM, Department of Chemistry FMIPA UGM for use of TEM and UIN for use of XRD. Support from Department of Chemical Engineering Universitas Indonesia is acknowledged.

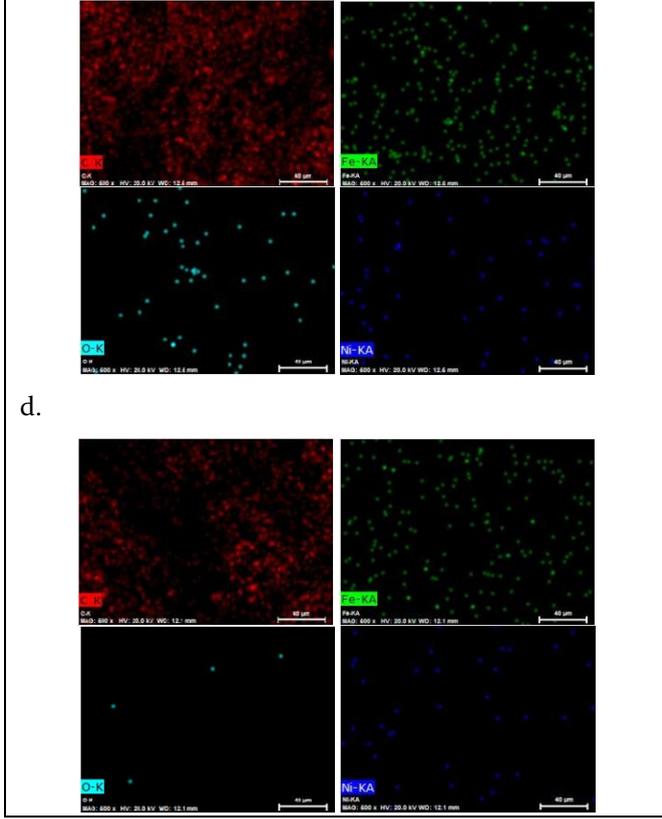
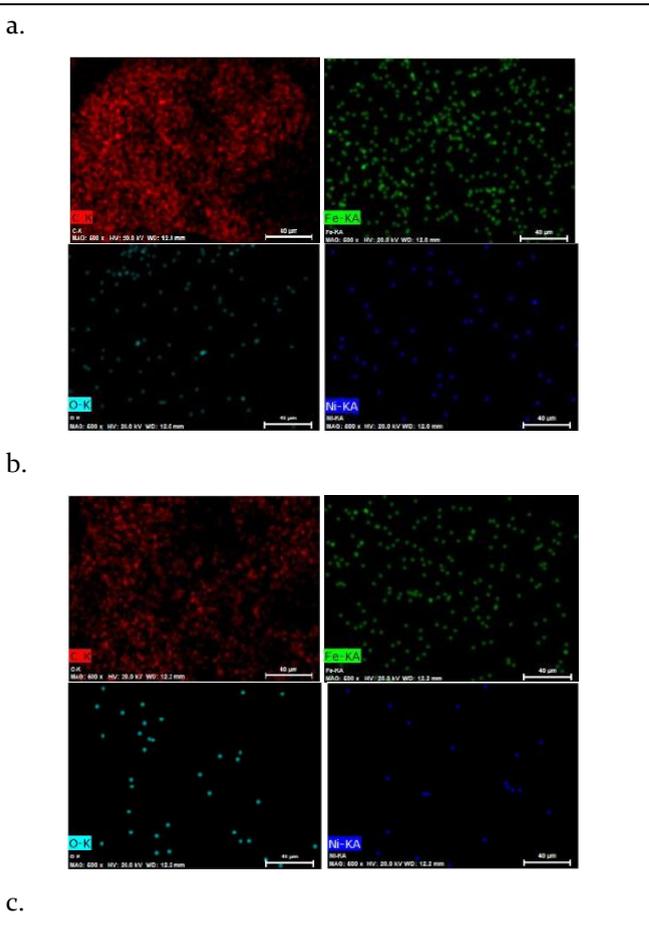
## References

- [1]. Ademiluyi T., Adebayo T.A., 2007. *Fuel Gases from Pyrolysis of Waste Polyethylene Sachets*. J. Appl. Sci. Environ. Manage, Vol. 11 (2) 21-26.
- [2]. Alves, Joner Oliveira. Et al. 2012. *Use of Stainless Steel AISI 304 for Catalytic Synthesis of Carbon Nanomaterials from Solid Wastes*. J. Mater. Res. Technol. 1(3):128-133
- [3]. Baddour, Carole E. et al. 2008. *A simple thermal CVD method for carbon nanotube synthesis on stainless steel 304 without the addition of an external catalyst*. Quebec: Department of Chemical Engineering, McGill University
- [4]. C. Zhuo, B. Hall, H. Richter, Y. Levendis. 2010. *Synthesis of Carbon Nanotubes by Sequential Pyrolysis and Combustion of Polyethylene*. Carbon 48, 4024-4034.
- [5]. Chairat, Ilham. 2015, Uji Kinerja Reaktor *Flame Synthesis* Untuk Produksi Nanokarbon Dari Limbah Kantong Plastik Polietilen (PE), Skripsi, Departemen Teknik Kimia Universitas Indonesia
- [6]. Corrales, T. 2001. *Photooxidative and thermal degradation of polyethylenes: interrelationship by chemiluminescence, thermal gravimetric analysis and FTIR data*. Journal of Photochemistry and Photobiology A: Chemistry 147 (2002) 213-224. Madrid, Spain.
- [7]. E.F Kukovitskii, L.A. Chernozatonskii, S.G. L'vov, N.N. Mel'nik. 1996. *Carbon Nanotubes of Polyethylene*. Chemical Physics Letters 266, 323-328.
- [8]. EPA. *Municipal Solid Waste: 2007 Facts and Figures*. 2008 [cited 2015 April 3]; November 2008: [Available from: <http://www.epa.gov/waste/nonhaz/municipal/pubs/mswo7-rpt.pdf>].
- [9]. Forum Hijau Indoneisa. (2013). *Jumlah Sampah Plastik di Indonesia*. Jakarta: Kementrian Lingkungan Hidup.
- [10]. Kimura H, Goto J, Yasuda S, Sakurai S, Yamura M, Futaba DN, et al. Unexpectedly High Yield Carbon Nanotube Synthesis from Low-Activity Carbon Feedstocks at High Concentrations. ACS Nano. (2013);7:3150-7.
- [11]. Legend, Plumbing, Industrial, Commercial, Hydrnics, 304 & 316 Stainless Steel Fittings & Nipples, SSF-0712, July 1, 2012
- [12]. M. Kumar, Y. Ando. 2010. *Chemical Vapor Deposition of Carbon Nanotubes : A Review on Growth Mechanism and Mass Production*. Journal of Nanoscience and Nanotechnology, Vol. 10, 3739-3758.
- [13]. Mu'minin, Amiril. 2010. *Carbon Nanotube*. Bandung: Departemen Teknik Kimia, Institut Teknologi Bandung.
- [14]. Mishraa, Neeraj Gobind Das, Alberto Ansaldo, Alessandro Genovese, Mario Malerba, Mauro Povia, Davide Ricci, Enzo Di Fabrizio, Ermanno Di Zitti, Madhuri Sharon, Maheshwar Sharon. 2012. *Pyrolysis of Waste Polypropylene for the Synthesis of Carbon Nanotubes*. Journal of Analytical and Applied Pyrolysis 94, 91-98.
- [15]. S, Mopoung. 2011. *Occurrence of carbon nanotube from banana peel activated carbon mixed with mineral oil*. International Journal of the Physical Sciences Vol. 6(7), pp. 1789-1792. Chemistry Department, Faculty of Science, Naresuan University, Phitsanulok, 65000, Thailand.
- [16]. Sastrohamidjojo, Hardjono. 2001. *Spektroskopi*. Edisi kedua, Yogyakarta: UGM-Press.
- [17]. Siregar, Masdania Zurairah. 2015. *Preparation and Characterization Carbon Nanotubes - Chitosan Nanocomposite by Using Oil Palm Shell and Horseshoe Crab Shell*. International Journal of Advanced Research in Chemical Science (IJARCS) Volume 2, Issue 1, PP 6-13.
- [18]. Wulan, Praswasti PDK dan Roselina Simbolon, *Sintesis Carbon Nanotube Dari Limbah Botol Plastik Air Mineral (Polietilen Tereftalat) Dengan Katalis Nikel Menggunakan Metode Pirolisis*, Seminar Nasional Teknik Kimia Teknologi Oleo & Petrokimia Indonesia (SNTK-TOPI), Pekanbaru, Riau, 27 November 2013.
- [19]. Wulan, Praswasti PDK, Taufiq Abdurrahim, Achmad Farizzi . *Sintesis Carbon Nanotube Dari Limbah Plastik Polietilen Tereftalat (PET) Dengan Metode Pirolisis*, Prosiding Seminar Nasional Teknik Kimia Indonesia 2015, Yogyakarta, 12-13 Oktober 2015a
- [20]. Wulan, Praswasti PDK, Widodo Wahyu Purwanto , Mahmud Sudibandriyo, Ajeng Nurcahyani, 2015, *Synthesis Of Aligned Carbon Nanotube (ACNT) Through Catalytic Decomposition Of Methane By Water-Assisted Chemical Vapor Deposition (WA-CVD)*, International Journal of Technology Volume 6 No 7 pp 1119-1127.
- [21]. Y.H. Chung, S. Jou. 2004. *Carbon Nanotubes from Catalytic Pyrolysis of Polypropylene*. Materials Chemistry and Physics 92, 256-259.
- [22]. Zhuo, Chuanwei. 2009. *Synthesis of Carbon Nanotubes from Waste Polyethylene Plastics*. Mechanical Engineering Master's Theses. Paper 31. Northeastern University.
- [23]. Zhuo, Chuanwei. Et.al. 2013. *Oxidative heat treatment of 316L stainless steel for effective catalytic growth of carbon nanotubes*. Applied Surface Science 313, 227-235

**Appendix A. The Result of FT-IR Nanocarbon Characterization without Heat Treatment**



**Appendix B. The Result of Mapping SEM Nanocarbon Characterization with Heat Treatment for a) 1 minute; b) 5 minutes; c) 10 minutes dan d) 20 minutes**



**Appendix C. The Result of EDX Nanocarbon Characterization with 10 minutes Heat Treatment Duration**

