Identification of Carbon loss in the production of pilot-scale Carbon nanotube using gauze reactor

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Abstract. Carbon loss more than 65% was the major obstacles in the Carbon Nanotube (CNT) production using gauze pilot scale reactor. The results showed that the initial carbon loss calculation is 27.64%. The calculation of carbon loss, then, takes place with various corrections parameters of: product flow rate error measurement, feed flow rate changes, gas product composition by Gas Chromatography Flame Ionization Detector (GC FID), and the carbon particulate by glass fiber filters. Error of product flow rate due to the measurement with bubble soap gives calculation error of carbon loss for about ± 4.14%. Changes in the feed flow rate due to CNT growth in the reactor reduce carbon loss by 4.97%. The detection of secondary hydrocarbon with GC FID during CNT production process reduces carbon loss by 5.14%. Particulates carried by product stream are very few and merely correct the carbon loss about 0.05%. Taking all the factors into account, the amount of carbon loss within this study is (17.21 ± 4.14)%. Assuming that 4.14% of carbon loss is due to the error measurement of product flow rate, the amount of carbon loss is 13.07%. It means that more than 57% of carbon loss within this study is identified.

1. Introduction

The broadening use of Carbon Nanotube (CNT), especially within the purpose of research and commercial leads to the need of producing CNT on a mass scale. CNT is applied as one of the components in nano-technological electronic equipments, sensor, electrodes, semiconductors, fuel cells, within the sector of health, and research. Seeing the big potential for CNT applied in various fields, research and investment continue to be developed to be able to synthesize CNTs worldwide [1]. In Indonesia, the mass production of CNT is considered to be in the development process meaning that within a few years it will become a new promising business opportunity in which the needs of CNT for the purpose of research and industry can be met from the domestic production. Related to the CNT production, the Department of Chemical Engineering of Universitas Indonesia has successfully developed the study as well as the production of CNT on a pilot scale [2], [3], and [4].

CNT is synthesized using a gauze-structured catalyst reactor through decomposition reaction of catalytic methane. Methane is chosen as a reactant due to high ratio of hydrogen/carbon [5]. This reactor system is designed with the capacity of 1kg/day CNT production which is scaled up based on a gauze-structured laboratory-scale catalyst reactor [6]. On a small scale, CNT produced is far from the
target of 1 kg per day; as a matter of fact, the production of CNT is only 240 gram per day [2]. This is due to the instability of feed flow rates of the reactor which is prone to leakage. Reevaluation as well as improvement regarding the pilot-scale reactor has been held [3]. The increase of the CNT production, however, does not show any significance (307 gram/day). CNT production is sometimes restrained due to catalyst factor [7]. Using the same reactor, the replacement of the catalyst with Fe/MgO and Ni/MgO is conducted in order to obtain CNT with better quality and quantity [4]; nevertheless, the production of CNT decreases compared to the one using Ni-Cu-Al as the catalyst. Further evaluation shows that carbon loss during the synthesis of CNT using the system of gauze-structured catalyst reactor is considerably high, more than 65% of the carbon mass is unidentified (Figure 1). This leads to the structured catalyst reactor designed for the production of CNT 1 kg/day is not applicable commercially.

The cause of the high number of carbon loss during the synthesis of CNT remains unknown. An error during the process of collecting data, especially during the process of measuring the feed flow rates is allegedly considered to have caused the carbon loss; notwithstanding, further study regarding that is yet to be conducted. On the other hand, the change on the feed flow rate due to the increase of resistance for the presence of catalyst and the growth of CNT in the reactor need further examination as it affects the calculation of carbon loss. Another possibility is that the release of CNT as particulates during the process of production and handling becomes another issue causing the magnitude of carbon loss [8]. The uncertain conversion of methane into other compounds such as ethane, ethylene, and other hydrocarbons becomes another possible factor. A number of studies report that site-products in the form of volatiles of organic compounds (VOC) and polycyclic aromatic hydrocarbon (PAH) are formed during the synthesis of CNT with ethylene as the feedstock [9]. As for methane with other hydrocarbon concentration as the feedstock, namely ethylene and ethane which are much smaller than H₂ and CH₄; however, this gives an impact towards the mass of carbon converted while the reaction takes place. The unidentified compounds during the synthesis of CNT result in the considerably high number of carbon loss.

Therefore, this study aims at identifying the carbon loss during the synthesis process of CNT using a pilot-scale structured catalyst reactor. Carbon loss is identified by analyzing the error measurement of the product flow rate on the bubble soap and the change of the feed flow rate because of the presence of catalyst and growth of CNT within the reactor, the analysis regarding whether or not carbon particulates exist in the product stream using gravimetric method where carbon particulates are filtered using filters made out of glass fiber, and the analysis of the composition of the reactor output product using DC-FID and GC TCD. The success of this study will become a stepping stone in increasing the production of CNT using gauze-structured catalyst reactor. As the identification of carbon loss during the synthesis of CNT brings to light, it means that the improvement of the reactor in order to achieve the production target of 1 kg/day is able to be conducted. Such process is ready for
the commercial purpose on an industrial scale so that it is able to mass produce CNT in Indonesia so that it meets the domestic needs of CNT for research and industrial purpose.

2. Experimental Method

This research will be conducted in Chemical and Natural Product Engineering Laboratory (CNPE), Department of Chemical Engineering, UI. The first step of the research is analyzing the error measurement of flow rates using bubble soap. Nitrogen gas is flowed using a mass flow controller (SIERRA Smart-trak series) with the flow rate set at 2.5L/min, then conducting a gas sampling to bubble soap. The next step is to measure the actual flow rate of the gas for 9 times using different volumes of bubble soap: 100 ml, 150 ml, and 200 ml, 3 times of sampling on each bubble soap. Further step is to repeat the above steps for the flow rate set at 1 L/min, 2 L/min, and 3 L/min and then analyzing the error during collecting the data of the flow rate using bubble soap.

For CNT production, 18.29 gram of Fe(NO$_3$)$_3$.9H$_2$O, 0.9 gram (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O, 150 gram Mg(NO$_3$)$_2$.6H$_2$O, and 76.29 gram of citric acid is dissolved in 100ml of deionized water; then being sonicated for 40 minutes and being stirred for 3 hours until forming into gel. The catalyst is calcined for an hour at 800 °C; then the catalyst powder is grounded and dissolved in isopropanol to be the coat of the wiremesh 304 which is in the form of structured configuration using the method of spray coating. Wiremesh 304 is type 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 [10]. The catalyst substrate is loaded in to a quartz tube equipped with a digital atmospheric furnace. The series of the research is available in Figure 2. Glass fiber filter (Pall Corp. A/E type with the diameter of 4.7 cm), which has been weighed, is installed in-line within the circuit in order to filter carbon particular carried within the gas flow.

![Figure 2. Schematic reactor equipment.](image.png)

Prior to the synthesis of CNT, calibration is conducted between gas chromatography with Thermal conductivity detector (GC TCD), gas chromatography with Flame ionization detector (GC FID) and massflow controller. GC calibration is performed in order to determine the retention time and response factor (RF) of each gas which is going to be identified, while the flow meter calibration aims to adjust the listed values of the flow rates in the flow meter with the actual gas flow rate measured by bubble soap. Leakage check is performed by draining nitrogen gas to the circuit.

The catalyst, then, is heated up to 850 °C. Once the heated catalyst meets the temperature, H$_2$ gas with the flow rate of 240 L/h is discharged for 10 minutes in order to reduce the oxides of the catalyst. The reaction begins to take place by canalizing methane gas (purity level 99.9%) into the reactor. Methane flow rate set in the mass flow controller is 2,414 L/min. During the reaction process, the product flow rate is measured using bubble soap, while the output gas composition is analyzed using GC TCD (8A type Shimadzu), Porapak Q column packing with Argon gas carrier to determine the
composition of CH₄, H₂, CO, and CO₂. While, in order to find out the presence and the composition of secondary hydrocarbon, GC FID (Shimadzu 2014), Porapak N column packing with Helium gas carrier are used. After the process of reaction, the result of CNT is weighed using a digital scale. Glass fiber filters are also weighed and analyzed using SEM EDX (Scanning Electron Microscopy Energy Dispersive X-Ray) in order to find out regarding particulate compositions. The calibration of feed rate (methane) is conducted for three times in order to comprehend the effect of catalyst and CNT growth in the reactor towards the feed flow rate. The first one is conducted when the reactor is empty, the second one is done when the catalyst is loaded into the reactor, and the last one is conducted after the reaction process in which CNT will have grown within the reactor. The calibration is held using methane gas set at the same set point with the mass flow controller (2,414 L/min) and under the same condition (P = 1 atm, T = 27 °C).

3. Result and Discussion

3.1 Initial Calculation of Mass Balance and Carbon Loss
Several studies have been conducted as shown in Figure 1. The result showed that the average carbon loss reached 68%. This is due to the instability of feed flow rates of the reactor which is prone to leakage. The calculation of the initial mass balance and carbon loss only involves the raw data obtained during the reaction process: input feed rate, product rate measured using bubble soap, and product gas composition identified by only Gas Chromatography Thermal Conductivity Detector (GC TCD) before any correction using identification method undertaken within this study. The input of feed flow rate is 1,266.84 mL/min for the first 7 minutes then constantly set at 2,919.61 mL/min until the reaction process lasts for 70 minutes. The actual CNT mass obtained is 19.6 grams. Based on the experimental data, the input carbon mass rate, the output carbon mass rate, and the theoretical CNT mass formed can be seen in Figure 3.

![Figure 3. The carbon mass rate in and out during the reaction.](image)

\( M_{\text{CNT theoretical}} \) is the same as dark area in Figure 3 which is 27.09 grams. \( M_{\text{CNT actual}} \) obtained from the experiment is 19.6 grams. The initial carbon loss can be evaluated using equation 1.

\[
\% \text{ Carbon loss} = \frac{M_{\text{CNT theoretical}} - M_{\text{CNT actual}}}{M_{\text{CNT theoretical}}} \times 100\%
\] (1)
Based on equation (1) the initial carbon loss is 27.64%. These result showed that the initial carbon loss requires correction using aforementioned correction factors.

3.2 The effect of product flow rate measurement error using bubble soap towards carbon loss

Based on the result of the study, the value of relative error towards flow rate measurement using bubble soap is available in Figure 4.

![Figure 4. Relative measurement error of flow rate.](image)

Errors during the measurement of product flow rate cause further errors in the calculation of carbon loss. From the calculation in Table 1, the error commonly occurs in the calculation of carbon loss since the measurement of product flow rate using bubble soap is 4.14%, so the value of carbon loss is formulated as follows:

\[
\% \text{ Carbon Loss} = \frac{\int_{0}^{t} \left( Q_{\text{product}} y_c - \frac{F_M R_c}{k_f R_T} \right) - M_{\text{CNT actual}}}{\int_{0}^{t} \left( Q_{\text{product}} y_c - \frac{F_M R_c}{k_f R_T} \right)} \times 100\%
\]

From equation (2) the amount of carbon loss is \(27.64 \pm 4.14\)%

| Time (minute) | \(Q_{\text{product}}\) (mL/min) | relative error | absolut error (mL/min) | error Carbon loss |
|---------------|-----------------|----------------|------------------------|-----------------|
| 0.00          | 0.000           | 0.00%          | 0.00                   | 0.00            |
| 5.48          | 2.188           | 1.78%          | 38.94                  | 3.56%           |
| 9.42          | 3.856           | 2.52%          | 97.03                  | 4.50%           |
| 15.46         | 3.102           | 2.16%          | 66.89                  | 4.71%           |
| 20.42         | 3.084           | 2.15%          | 66.26                  | 4.30%           |
| 24.00         | 3.044           | 2.13%          | 64.83                  | 4.28%           |
| 28.00         | 3.017           | 2.12%          | 63.92                  | 4.25%           |
| 36.00         | 2.798           | 2.02%          | 56.62                  | 4.14%           |
| 46.00         | 2.839           | 2.04%          | 57.94                  | 4.06%           |
| 55.00         | 2.855           | 2.05%          | 58.47                  | 4.09%           |
| 60.00         | 2.602           | 1.94%          | 50.54                  | 3.99%           |
| 65.00         | 2.704           | 1.98%          | 53.64                  | 3.93%           |
| 70.00         | 2.602           | 1.94%          | 50.54                  | 3.93%           |
It can be seen from Table 1, the calculation is merely based on errors caused during the measurement of product flow rate. The error occurred during the process of weighing the actual mass of CNT and the measurement of product gas composition can be removed since the value is smaller compared to the error during the measurement of product rate.

### 3.3 The effect of feed flow rate changes due to CNT growth in the reactor towards carbon loss

In order to determine the effect of catalyst and CNT growth towards the change of feed flow rate. Feed flow rate calibration was done when the reactor is empty and reactor load with catalyst substrate. Changes occurred in the feed flow rate affect the amount of carbon loss. The result of the feed flow rate calibration is shown in Figure 5. Catalyst substrate inside the reactor will affect carbon loss value that can be calculated using equation 3.

\[
\% \text{ Carbon Loss} = \frac{\int_{t_0}^{t} \left[\frac{Q_{\text{CH}_4 \text{ feed}} \cdot P \cdot \text{MR}}{RT} - W_{\text{cout}}\right] dt - M_{\text{CNT actual}}}{\int_{t_0}^{t} \left[\frac{Q_{\text{CH}_4 \text{ feed}} \cdot P \cdot \text{MR}}{RT} - W_{\text{cout}}\right] dt} \times 100\% \quad (3)
\]

Figure 5 shows that the addition of catalyst substrate within the reactor results in the decrease of the feed flow rate to 1,144.5 mL/min or 28.16% compared to the flow rate in the empty reactor. The decrease of flow rate is caused by the resistance of wire mesh that leads to the rising of feed gas pressure. The increasing pressure of the feed gas then leads to a greater mass of the gas that the gas flow rate turns smaller. The result of calibration after synthesis shows a decrease in the feed flow rate of 118 mL/min. The decrease of the flow rate is caused by the resistance due to CNT growth in the catalyst substrate. The large amount of the resistance as a result of CNT aligns to the growing mass of CNT. The existence of CNT, will increase the resistance that leads to the decreasing of feed flow rate to 4.04%.

Within this research, if the feed flow rate used is the calibration with empty reactor, the theoretical mass of CNT is 63.51 gram, while the actual mass of CNT is only 19.60 gram meaning that the accumulation of the carbon loss is 69.14%. This result is in line with the previous studies which have average carbon loss of 68%. The result of carbon balance calculation after correction of feed flow rate reduce the initial carbon loss from 27.64% to 22.66% or decrease by 4.97% without any correction.
Accordingly, calibration using empty reactor is not applicable for this study. Therefore, it is required to calculate the initial mass balance and carbon loss using the feed flow rate after correction within catalyst inside the reactor.

3.4 Analysis of the reactor output gas with GC FID and its effect towards carbon loss calculation

From the experimental results, in the first few minutes, it is only hydrogen and methane gas detected by GC TCD in which the hydrogen concentration is much greater than methane. In 28th minute, CO and CO$_2$ emerge with high concentration: 36.43% for CO and 46.22% for CO$_2$. The presence of these two gases during the reaction process is caused by the imperfect catalyst reduction. The reaction is as follows [11]:

$$\begin{align*}
6\text{CH}_4 + 6\text{Fe}_2\text{O}_3 & \rightarrow 12\text{Fe} + 3\text{C}_{\text{(solid)}} + 3\text{CO}_2 + 12\text{H}_2\text{O} \\
6\text{CH}_4 + 5\text{Fe}_2\text{O}_3 & \rightarrow 10\text{Fe} + 3\text{C}_{\text{(solid)}} + 3\text{CO} + 12\text{H}_2\text{O}
\end{align*}$$

Moreover, at the 28th minute, hydrogen loss becomes considerably high compared to other times. This is due to the fact that H$_2$O is not detected by both GC TCD and GC FID. The following from top to bottom shows peaks appearing in the minute of 5.48, 36, and 70 when product gas characterization with GC FID:

![Figure 6. GC FID Chromatograph of gas product (a)6 minute, (b)36 minute, and (c) 70 minute.](image)

The result of characterization with GC FID in Figure 6, shows that during the process of methane decomposition, secondary hydrocarbon which is not detected by GC TCD is formed. Hydrocarbons detected by GC FID are CH$_4$, C$_2$H$_2$, C$_3$H$_4$, C$_4$H$_6$, and C$_4$H$_{10}$. In the first few minutes, there is no C$_4$H$_{10}$. Only after the 20th minute, C$_4$H$_{10}$ begins to form in which its concentration keeps increasing. The formation of such secondary hydrocarbon is due to the reaction process of coupling (merging) on the surface of the catalyst [11]:

$$\begin{align*}
2\text{CH}_4 & \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2 \\
2\text{CH}_4 & \rightarrow \text{C}_2\text{H}_2 + 3\text{H}_2 \\
2\text{CH}_4 & \rightarrow \text{C}_4\text{H}_6 + 4\text{H}_2 \\
2\text{CH}_4 & \rightarrow \text{C}_4\text{H}_{10} + 5\text{H}_2
\end{align*}$$
The concentration of secondary hydrocarbon continues to increase as the time of reaction process continues. However, the number of secondary hydrocarbon formed is not very high. The average concentration is 1.44%; the highest concentration of secondary hydrocarbon is during the 28th minute which is 15.93%. It is the moment when CO and CO\(_2\) are formed. The detection of secondary hydrocarbon with GC FID affects the composition of product gas and reduces the value of carbon loss. The relation between carbon loss and the product gas composition is expressed by equation 2. Based on the calculation the identification of secondary hydrocarbon on GC FID reduces the number of carbon loss by 5.4% compared to the one merely using GC TCD. It means that 5.41% of carbon loss is the result of methane conversion into a secondary hydrocarbon which was not detected using merely GC TCD. Carbon loss which was initially 27.64% now becomes 22.23%.

3.5 Analysis of particulates in the output of the reactor and its effect on carbon loss

The result of the study shows that the addition of filter mass after the 70-minute reaction process is 0.0127 gram. Based on FESEM result in Figure 7 (a) and (b), there is a black bundle on the filter after being characterized using EDX in Figure 7 (c) and (d). The filtered substance using fiber filter is carbon. It is also supported by comparing the initial composition of the filter with the composition after the filter is used for the reaction process. Initially, the carbon composition on the filter was 9.35% and after the reaction process, the carbon composition rises to 51.64%. It means that there is carbon particulates in the gas stream which is very little compared to those found in the catalyst substrate.

![Figure 7. SEM EDX of filter (a) & (c) before CNT production; (b) & (d) after production.](image)

In this study, particulates carried by the product stream do not provide any significant changes towards carbon loss identification. Based on equation 4 the carbon loss during the reaction process after the particulates analysis is 27.59%. This means that 0.05% of carbon loss is the result of carbon carried by product gas as particulates.
3.6 Carbon mass balance and total carbon loss

If all the factors mentioned in the previous subchapters are considered, the carbon loss equation is shown by the equation 5.

\[
\text{% Carbon loss} = \frac{M_{\text{CNT theoretical}} - M_{\text{CNT actual}} - M_{\text{particulate}}}{M_{\text{CNT theoretical}}} \times 100\% \tag{4}
\]

Accordingly, the calculations of mass balance and carbon loss within this subchapter have taken all the factors of carbon analysis. The calculations are performed using a calibrated feed flow rate with the presence of catalyst, adding the correction of the feed flow rate due to CNT growth, correction of gas composition based on gas product analysis of GC TCD and FID, and particulates. Generally, the conversion of carbon mass during the reaction process can be seen in Figure 8.

![Figure 8. Carbon feed converted into other products.](image)

Based on the discussion in 3.2, the number of error in the calculation of carbon loss is 4.14%. Hence, from the entire analysis of all factors causing the high amount of carbon loss during the pilot-scale CNT production, the following value is obtained: Carbon loss = (17.21 ± 4.14) %. Based on the calculation above, if 4.14% of carbon loss is due to the error measurement of product flow rate using bubble soap, then the amount of carbon loss is 13.07%. Such amount is smaller than the amount of carbon loss before any correction by the studied factors which is 27.64%. The amount is much smaller compared with carbon loss during empty reactor calibration which is 69.14%. The comparison and variation of carbon loss identification techniques results is available in Figure 9.
Figure 9 shows that the use of the feed rate during reactor calibration containing catalyst gives the most significant impact in carbon loss identification. This is due to the difference in calibrated feed rate without and with catalyst is 28% which means that the theoretical mass of CNT is comparatively larger than it should be. Furthermore, the use of GC FID and feed flow rate correction due to CNT growth also has considerable influence. With the presence of GC FID, methane conversion to C$_2$ and C$_4$ is detected although the concentration is rather small. However, since the carbon in the compounds has more than one mole coefficient ratio (2 for C$_2$ and 4 for C$_4$), it means that the 0.01 mol loss of gas will become proportional to the 0.02 mol loss of carbon at C$_2$ and 0.04 mol loss of carbon at C$_4$ so that the carbon mass loss becomes high. Within the study, carbon loss of ± 13.07% is left unidentified. The possibility is that the formation of other compounds such as poly aromatic hydrocarbon (PAH) or other in situ compounds during CNT production with CVD (chemical vapor deposition) process contributes to the occurrence of carbon loss. Such compound is commonly identified as GC-MS, yet it is not used within the study.

4. Conclusion
By this study, we have successfully identified carbon loss during the synthesis process of CNT using a pilot-scale structured catalyst reactor. The result of initial carbon loss is 27.64%. The value of initial carbon loss decrease from 27.64% to 22.66% by using correction of feed flow rate. Error of product flow rate due to the measurement with bubble soap gives calculation error of carbon loss for about 4.14%. It is also can be identified that the detection of secondary hydrocarbon with GC FID during CNT production process reduces carbon loss by 5.14%. Particulates carried by product stream are very few and merely correct the carbon loss about 0.05%. Taking all the factors into account, the amount of carbon loss within this study is 13.07%. The success of this study will become a stepping stone in increasing the production of CNT using gauze-structured catalyst reactor. As the identification of carbon loss during the synthesis of CNT brings to light, it means that the improvement of the reactor in order to achieve the production target.

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