

# The Effect of Reaction Time on the Quality of Hydrogen and Carbon Nanotubes Produced Through Catalytic Decomposition of Methane

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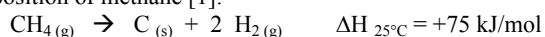
**Abstract:** Carbon nanotubes (CNTs) are tubular carbon molecules with superior mechanical, chemical, optical, and electrical properties. These unique properties make CNTs potentially valuable as hydrogen storage, superconductors, drug delivery and other end-use applications. Catalytic decomposition of methane is a promising method for producing hydrogen and CNTs simultaneously for several reasons: economic, high yield of products, and ease of control. Unfortunately, the presence of a metal catalyst in the CNTs product after reaction causes a negative impact on the quality of CNTs including reducing the electrical resistivity, density, tensile strength and structural properties of the nano tubes which can lead to the reduction of CNTs performance in many applications. Process optimization is needed to produce hydrogen and CNTs with the best quality by varying the reaction time to observe the influence of reaction time on the quality of the CNTs produced through the catalytic decomposition of methane. Production of CNTs was performed in a Gauze reactor at 700°C, 1 atm with methane as a feed was about 315 ml/min. A Stainless steel-wire mesh coated with a Ni-Cu-Al catalyst prepared by the dip-coating method as a spot for carbon deposition. The catalytic performance of the Ni-Cu-Al catalyst and the quality of carbons produced were discussed based on the X-ray diffraction (XRD) results and the Scanning Electron Micrograph (SEM) Image of the used catalysts. The diameter of CNTs produced by a longer reaction time were greater, and it can be concluded that the longer the time reaction, the worse the quality of the CNTs produced. The best of CNTs, which have a smaller diameter was given at 20 minutes reaction time. The crystal diameter of CNTs increased with increasing reaction time ranging from 5.93 nm for 20 minutes reaction to 7.33 nm for 240 minutes reaction.

**Keywords:** Carbon Nanotubes, Hydrogen, Purification, Quality, Reaction time

## 1. Introduction

Large scale production of CNTs has been carried out using arc discharge, laser ablation, and chemical vapour deposition methods [1]. Those processes, however, needed a large amount of energy leading to high costs and are hard to scale up.

Another method used to produce CNTs is catalytic decomposition of methane [1]:



which is a promising method for producing hydrogen and CNTs for several reasons including economics, high yield of product, and ease of control. Metal catalysts, such as Fe, Co, and Ni and metal alloys (e.g., Fe-Co and Fe-Ni), are used in the reaction. Impurities typically present in CNTs are amorphous carbon and the tubular structure possesses  $\text{sp}^3$  hybridization and tube hollow are filled with C atoms that causes encapsulate residual metal catalysts. These defects, present either along the walls of the graphitic tubes or entangled within them, reduce the electrical and structural properties of the nanotubes [2], thus decreasing the carrier density leading to an increase in electrical resistivity [3]. It can be concluded that the presence of impurities in CNTs decreases the quality of the CNTs itself.

CNTs can be applied for hydrogen storage, nanoscale transistors, flat-panel displays, super capacitors, nanoprobe sensors [4], and catalysts [5]. Good quality CNTs are needed to optimize the performance of these applications. The NASA-JSC [6] protocol measures the quality of CNTs according to four different criteria: (i) purity, (ii) thermal stability, (iii) homogeneity, and (iv) dispersability. The purity of CNTs can be inferred from the presence of amorphous carbon in the product.

Increasing CNTs quality can be done by process optimization and post treatment or purification of CNTs products. Research in process optimization to increase the quality of CNTs has been done by varying catalysts, gaseous feeds, temperature, and pressure of reactions. Reaction time also influences CNTs, but it has not been considered since the production of CNTs is

an accumulation process. Therefore, it is essential to know the effect of reaction time on CNTs quality. The effect of reaction time was observed by Wang et al. [7] in the production of aligned CNTs using the chemical vapour deposition method. The deposited carbons were analyzed via SEM Image characterization, it can be concluded that the quality of CNTs with the reaction time of 20 minutes gave better results than longer reaction times.

## 2. Experimental

The experiments of catalytic decomposition of methane were carried out in a gauze reactor heated by an electric furnace. The reactor was 30 cm long with outer diameter 4.5 cm and inner diameter 4.26 cm. All experiments were conducted at atmospheric pressure and at a constant temperature of 700°C. The study was performed by varying the loading catalyst from 0.00034 to 0.00055  $\text{g}\cdot\text{cm}^{-2}$  with a flowrate of 600 mL/min. The catalyst was prepared by the sol-gel method with the molar ratio of Ni:Cu:Al being 2:1:1. The wire mesh was coated with the catalyst using a dip-coating method. The catalyst-coated wire mesh was first dried and then calcined.

The production of CNTs was performed using varying reaction times (20, 30, 40, 50, 60, and 240 minutes). The reaction performance in the gauze reactor was observed during the process using a gas chromatography with a thermal conductivity detector (Shimadzu GC-8A). An activated carbon column was used for  $\text{CH}_4$ ,  $\text{H}_2$ , CO and  $\text{CO}_2$  analysis. The carrier gas used was argon with injection and detector temperatures of 130°C and 100°C, respectively.

Powder X-ray diffraction (XRD) patterns of used samples were acquired in a Phillips analytical X-Ray model number BV-2500. The angle range scanned was 10–100° using a counting step of 0.02° and a counting time per step of 0.8 s. A sample holder with a very low noise level was used, allowing for pattern acquisitions from a small amount of samples with good resolution. The size of carbon crystals was obtained by the Scherrer equation:

$$D_{CNT} = \frac{0.89\lambda}{\beta_d \cos \theta} \times \frac{180^\circ}{\pi}$$

where  $D$  is The size of carbon crystals,  $\lambda$  is the peak length (1.54056 Å),  $\beta_d$  is the corrected half peak width of C. Characterization of CNTs structures and morphologies was carried out using SEM (Hitachi S-3400) coupled to a Si/Li detector for energy dispersive X-ray spectrophotometry analysis.

### 3. Results and Discussion

Six different loadings of catalyst resulting from the dip-coating process were produced, ranging from 0.00034 g/cm<sup>2</sup> to 0.00055 g/cm<sup>2</sup>. The differences 0.00021 g/cm<sup>2</sup> can be considered that the thickness of catalyst layers were similar.

Reactor performance was indicated through methane conversion, purity of hydrogen and carbon yield. Figure 1 showed the difference curves due to the fresh catalyst was used each time reactions. The highest conversion of 88% was reached using 40 minutes reaction time. The lowest conversion was 76%, and the average was 78±5%. Conversion of methane reaches a maximum value at the 5th minute and decreased slowly during the reaction until it reaches a constant value in the 30th minute. This is because the surface of catalyst was covered by the CNTs as the reaction proceeded.

As shown in Figure 2, after reaching its maximum the conversion of methane was relatively stable up to 240 minutes reaction, leading to the conclusion that the catalyst is not deactivated by carbon deposits. The continued activity of the catalyst is also proved by the constant rate of gas product up to 240 minutes reaction.

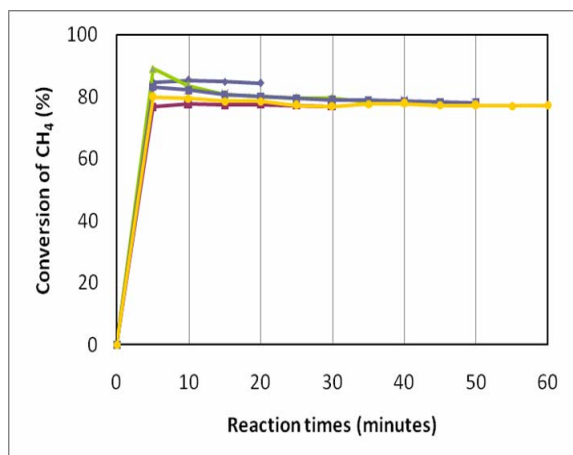


Figure 1. Methane conversion at various reaction times.

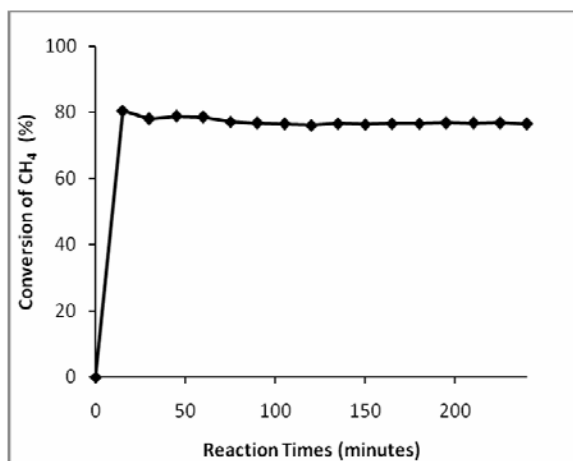


Figure 2. Stability of the catalyst during 240 minutes.

Hydrogen purity is the volume ratio of hydrogen to the total gas in the outlet. This parameter can be used to calculate the amount of hydrogen produced which is proportional to the methane conversion.

As shown in Figure 3, at the beginning of reaction, hydrogen purity was at a maximum since the conversion of methane was also at a maximum. Hydrogen purity decreased with the increase of reaction time so that the production of hydrogen also decreased slowly. Trend of purity of hydrogen is in line with the observations of methane conversion.

Carbon yield is the ratio of carbon mass to the catalyst mass. The quality of CNTs are the function of time that the product mass increased as the reaction time increased (Figure 4 and 5).

Based on SEM characterization (Figure 6), differences in the quality of CNTs occurred at varying reaction times. The

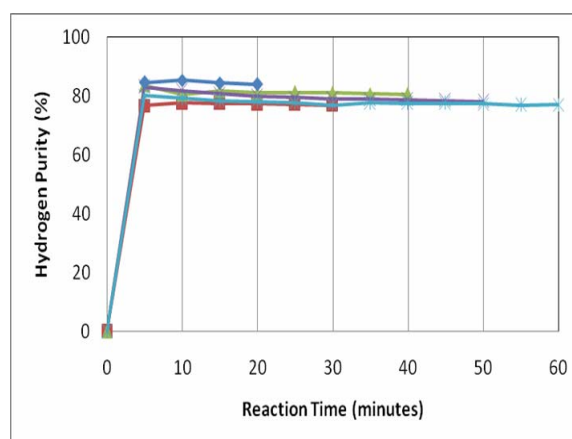


Figure 3. Hydrogen purity at various reaction times.

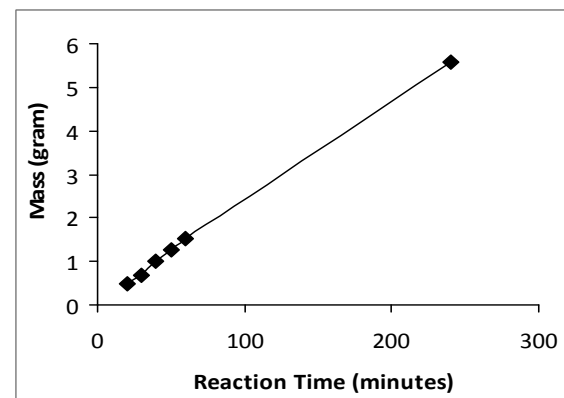


Figure 4. CNTs mass at various reaction times.

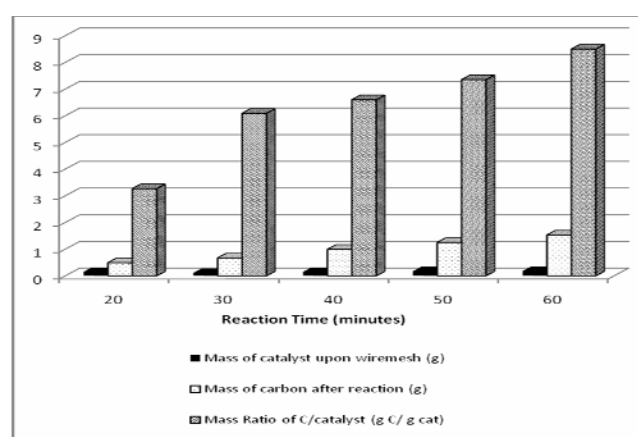


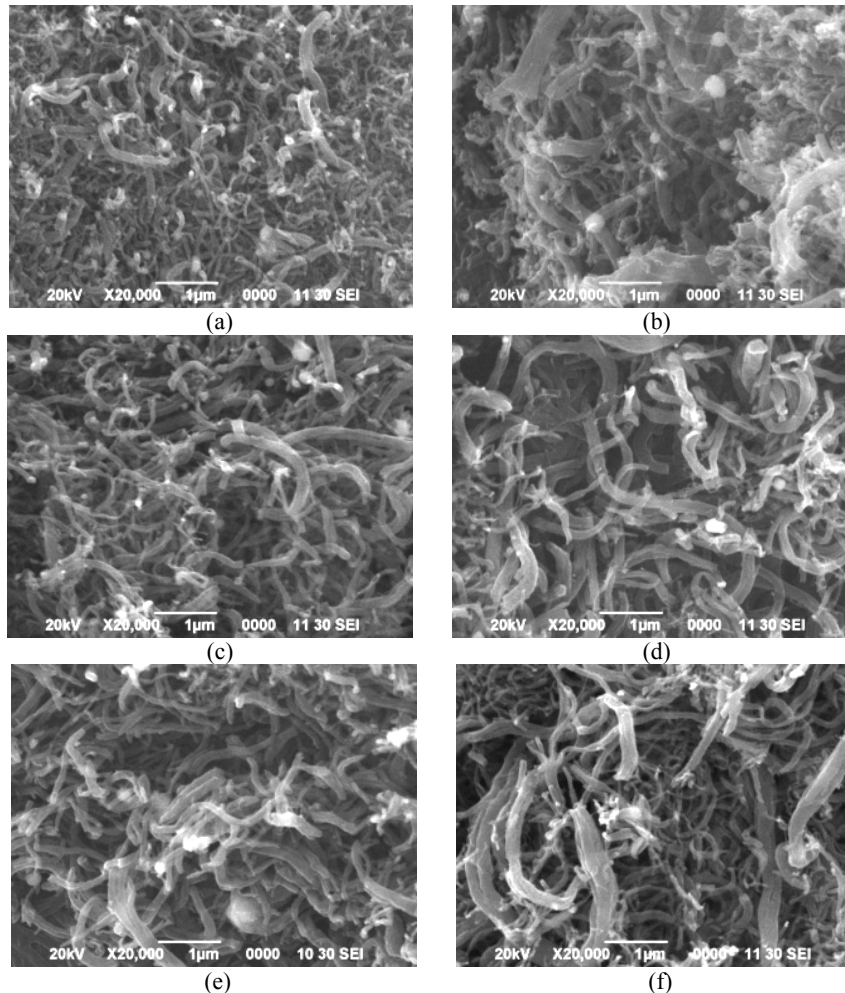
Figure 5. Carbon yield at various reaction times.

CNT had the smallest diameter at 20 minutes reaction time. The diameter of CNTs increased at longer reaction times, thus reducing their quality. Furthermore, the amount of low quality carbons also increased. It can be concluded that the longer the reaction time, the worse the quality of CNTs which happened because the catalyst was covered by carbon deposits.

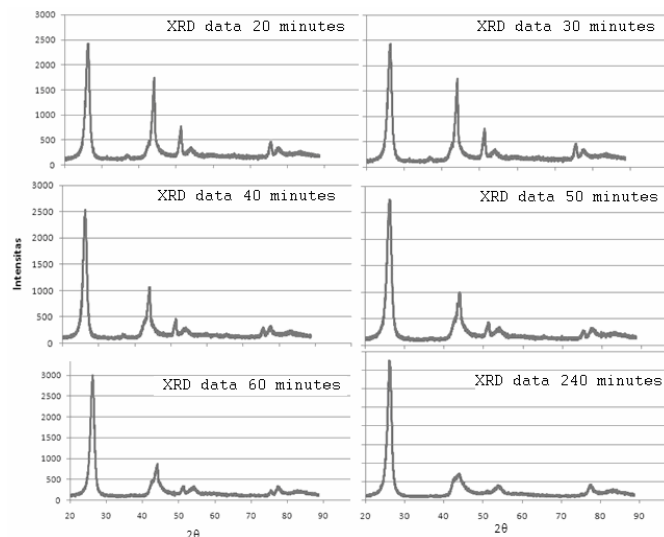
Catalyst Ni-Cu-Al functions as a referrer so that the reaction produces the desired product, namely carbon and hydrogen.

When the reaction takes place over a long time, CNTs grew increasingly far away from the catalyst so that the role of catalyst as a referrer to produce CNTs of good quality is reduced.

Figures 7, which are the results of XRD characterization, shows that the intensities of carbon crystal in  $2\theta$  angle changed as the time reaction increased. Longer reaction time reduced the intensity of carbon crystal, which caused a reduction in the amount of CNTs in the product, especially at  $44.175^\circ$  and  $51.505^\circ$ .



**Figure 6.** SEM images of CNTs at various reaction times; (a) 20 minutes, (b) 30 minutes, (c) 40 minutes, (d) 50 minutes, (e) 60 minutes, and (f) 240 minutes.



**Figure 7.** XRD diffraction for various reaction times.

The result of XRD diffraction for 20 minutes reaction time showed 3 main peaks of carbon crystal intensity. At 40 minutes reaction time the result of XRD diffraction showed that the intensity of carbon peaks were reduced at 44.175°. The difference phenomena occurred at 60 minutes and 240 minutes of reaction time the intensities of carbon peaks at 44.175° and 51.505° became smaller and only one main peak remained at 26.455°. It can be concluded that for the longer reaction time, the intensity of CNTs reduces and the presence of non-crystalline carbon (amorphous carbon) increases.

From the XRD data, the size of carbon crystals can be calculated using the Scherrer equation. The calculation showed that the size of CNTs increased with the increasing of reaction time ranging from 5.93 nm for 20 minutes reaction to 7.33 nm for 240 minutes reaction.

#### 4. Conclusion

The effect of reaction times on CNTs quality was examined. The results show that the quality of CNTs product decreases as the reaction time increases. Based on SEM and XRD characterizations, a reaction time of 20 minutes gave the best quality of CNTs product with the smallest diameter, and least amorphous carbons.

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