CNT Production through the Catalytic Thermal Decomposition of Methane over Ni-Cu/Al2O3 Catalyst in a Fluidized Bed

Gian Paolo Obligacion Bernardo and Leonila C. Abella

***Abstract*—A study on the optimization of the process parameters and catalyst metal loading was done for the production of CNTs over Ni-Cu/Al_2O_3 in a fluidized bed reactor. The process parameters investigated were the inlet CH_4 concentration and the reaction temperature. Optimization was done in terms of minimizing the diameter of the CNTs formed through the latest Solver function of Excel with integer and binary constraints on respective variables. The determination of the significance of the process and catalyst parameters was through ANOVA, and the behaviour of the response variable as a function of the set parameters was qualified through contour, main effect and interaction plots. Catalyst pre-characterization confirmed the presence of γ-Al_2O_3, NiO and NiCu catalyst components which are necessary in the production of CNTs. Catalyst post-characterization allowed the identification of CNTs and the measurement of their diameters. The smallest average CNT diameter was 48.5 nm produced with 5% CH_4, 30% Ni loading with 12:5 mol: mol Ni: Cu under a 950 ℃ reaction temperature. The initial surface area of the catalyst had no significant effect on the diameter of the CNTs formed. The non-linear model developed illustrated that the CNT diameter was generally inversely proportional with and a strong function of reaction temperature, while it is a weaker function of CH_4 concentration and catalyst metal loading. The model had a PCC of 0.944 and a PCC P-value of 0.000. A minimum CNT diameter of 47.75 nm with the parameters set at 5% CH_4, 10% Ni loading with 12:5 mol: mol Ni: Cu, and 950 ℃ reaction temperature was subsequently predicted by minimizing the model.**

***Index Terms*—Carbon nanotubes, catalysis, methane decomposition, hydrogen storage, CNT diameter model.**

I. Introduction

CNTs have gained attention in the field of research since it has excellent mechanical properties and high electrical and thermal conductivities. Such properties led to the range of its utility from catalyst support, mechanical reinforcement, electrode material in batteries, high-tensile fibers, electronic chips, intracellular manipulation, among others. [1]-[2]. In this research, the highlight among the uses of CNTs falls on its application as a hydrogen-storing medium for fuel cells [3]-[4].

One of the most common methods of producing CNTs is the Catalytic Thermal Decomposition of Methane (CTDM) in a fluidized bed [5] as it is widely accepted due to the simplicity of the reaction, the absence of the emission of harmful gases, and the double-serving-purpose of both producing CNTs and H_2 – two materials which are attractive to cleaner and greener systems. In addition to this, CNTs have been demonstrated to be able to store hydrogen by adsorption depending on the tube diameter of the nanotubes formed [3].

Studies [5]-[6] show that modifying the parameters of the Catalytic Chemical Vapor Deposition (CCVD) processes control the physical characteristics of the resulting CNTs. Also, studies [7]-[9] have been conducted to explore the factors, such as the type of catalysts used, which alter the structure of the CNTs produced.

Several researchers [10]-[12] had identified the viability of Ni-Cu/Al_2O_3 catalysts for the CTDM. The susceptibility of Ni-based catalysts to coking and the acidic nature of Al_2O_3 make these potent catalysts for the production of CNTs through CTDM. Furthermore, Ni has been identified to be the most active metal for the CTDM for the production of H_2 and CNTs, while Cu performs well as a promoter for the process. [13]

Majority of the studies [11], [13], [14]-[16] were conducted with the objectives of increasing H_2 yield and improving catalyst performance and stability while only a few have focused on improving the quality of the carbon produced. More specifically, the carbon produced was often considered to be undesirable as it is cited to be the main cause of catalyst deactivation. Only a few studies [17]-[18] still investigated the effects of those parameters to the production of CNTs desirable for hydrogen storage. There was clear necessity, therefore, to determine the parameters that would be contributory to the production of CNTs that could be capable of storing reasonable amounts of H_2 sufficient for industrial and commercial application in addition to the existing H_2 fuel technologies.

II. Methodology

A. Catalyst Preparation and Characterization

The catalyst solution was prepared with Ni $(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ solutions with 10%, 20%, and 30% Ni loading and a Ni-Cu ratio of 12:5 mol: mol. These were then impregnated onto the powdery Al_2O_3 support following the outline of Cristiani et al. [19]. These impregnated precursors were calcined at 650 ℃ for 4.0 hours in air and then reduced in 50 $^{mL}/_{min}$ 1:9 (vol: vol) H_2: He at 500 ℃ for two hours.

The resulting catalysts were subjected to SEM-EDX Analysis for the ocular determination of surface

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characteristics and metal particle dispersion, XRD Analysis for the bulk crystal structure, and FTIR Analysis for general chemical and molecular structure.

B. Operating Conditions for CNT Production

CNT synthesis was done in a fluidized-bed continuous-flow quartz tube reactor set inside an electric variable temperature nichrome wire furnace at atmospheric pressure, loaded with 0.100g of the prepared catalyst. Total gas flow was set at the minimum fluidization flow rate of 90 $^{mL}/_{min}$, with a 30-minute sampling interval. The operating and catalyst parameters were set according to the Taguchi Design of Experiments (TDE) orthogonal matrix, with the parameters enumerated in Table I.

TABLE I: TAGUCHI DESIGN OF EXPERIMENT FACTOR LEVEL LISTING.

Level	Inlet CH_4 composition	Catalyst Loading	Reaction Temperature
1	5%	10% w/w	750 ℃
2	10%	20% w/w	850 ℃
3	20%	30% w/w	950 ℃

III. RESULTS

A. Catalyst Characterization

The dispersion of the Ni and Cu particles on Al_2O_3 is shown in Fig. 1. Increasing the loading of the catalyst resulted in the covering up of the surface of the support. Porosity increased with catalyst metal loading, which resulted in more active sites for the catalysis reaction to take place.

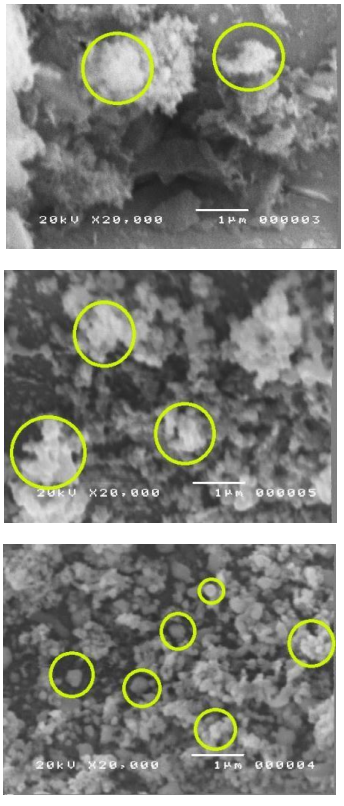

Fig. 1. SEM Micrographs for (a) 10%, (b) 20% and (c) 30% Ni-Cu/Al_2O_3 at 20,000X magnification

XRD Analysis confirmed the presence of γ-Al_2O_3 and Ni-Cu composites. The presence of Ni and unreduced NiO were also detected, while there was no unreduced CuO detected. FTIR Analysis also confirmed the presence of acidic γ-Al_2O_3, Ni-Cu composites, and NiO, favorable to the production of CNTs.

B. Optimization of CNT Production

Optimization was based on the minimum average CNT diameter produced through CTDM. Incorporating the TDE parameter values set in Table I, the CNT diameter data corresponding to the TDE orthogonal matrix are shown in Table II.

TABLE II: SUMMARY OF CNT DIAMETERS THROUGH CTDM

Run	%CH_4	%Ni	T (℃)	CNT Diameter (nm)
1	5	10	750	100.0
2	10	30	850	88.0
3	20	20	950	82.0
4	5	20	850	78.0
5	10	10	950	75.0
6	20	30	750	135.0
7	5	30	950	48.5
8	10	20	750	119.0
9	20	10	850	60.0

It can be seen that the diameters of the tubes formed satisfies the diameter range for multi-walled carbon nanotubes (5 to 150nm), and hence only show that the tubes formed are mostly multi-walled nanotubes. It must be noted that CNFs were also found, but the presence of these did not affect the diameters measured in Table 2 since the CNF diameters were not measured. The minimum average diameter occurs at Run 7, with corresponding parameters at: 5% ($^{vol}/_{vol}$) inlet CH_4 concentration; 30% Ni catalyst loading with 12:5 mol: mol Ni: Cu; and 950 ℃ reaction temperature.

ANOVA of the data in Table 2 reveals that the diameters of CNTs produced is highly dependent only on the reaction temperature (with 87% significance) among the three factors. Probabilities for interaction among the process parameters were also detected. It must be noted, however, that the limitations of the TDE allowed only the detection but disallowed the quantification of such probabilities. The highest probability for interactions was between CH_4 concentration and reaction temperature. This supports thermodynamic theory correlating the characteristics of the gaseous phase and the reaction temperature for the chemical vapor deposition for CNTs.

C. CNT Diameter Non-Linear Model

The trends and curvature profiles of the raw data and the provisions of the TDE imply the use of a general third order non-linear equation with no interacting parameters and with switch variables, Eq. 1.

$$y = s_{F_1} c_{F_1} F^{f_1} + s_{F_2} c_{F_2} F^{f_2} + s_{F_3} c_{F_3} F^{f_3} + s_{L_1} c_{L_1} L^{l_1} + s_{L_2} c_{L_2} L^{l_2} + s_{L_3} c_{L_3} L^{l_3} + s_{T_1} c_{T_1} T^{t_1} + s_{T_2} c_{T_2} T^{t_2} + s_{T_3} c_{T_3} T^{t_3} \quad (1)$$

where F, L and T correspond to the inlet CH_4 concentration, catalyst metal loading, and reaction temperature respectively; f_i is the integer exponent for parameter i; s_i is the binary switch variable for parameter i; c_i is the numerical coefficient of parameter I; and y is the CNT diameter. Iterations using the Solver function of Excel 2010 yielded the following regression equation where the parameter values are {1, 2, 3} as designated in Table I:

$$y = 27.14F^{-1} - 36.46F^{-3} + 13.33L^{2} - 3.64L^{3} + 95.14T^{-1} + 1.74T^{2} \quad (2)$$

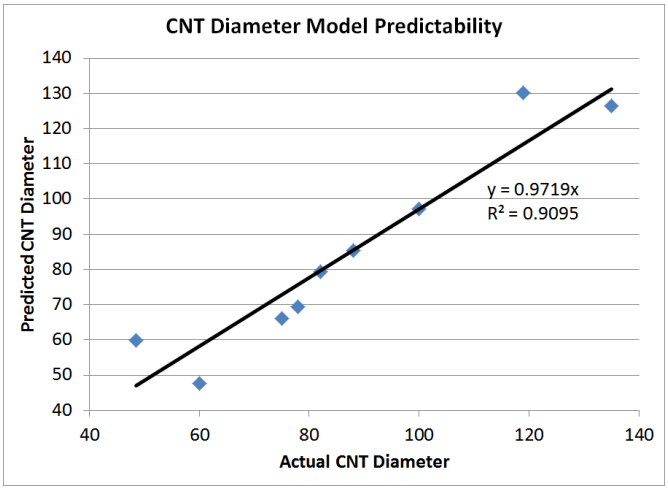

Fig. 2. Simulation for the predictability of the CNT diameter model

Simulation for the predictability of the developed model yielded the data in Fig. 2. The R^2 value is 90.9%; adding interaction terms to the general model could improve the regressions value. The CNT diameters the developed model predicted have a very strong positive correlation with the actual data having a Pearson Correlation Coefficient (PCC) of 0.944 and a PCC P-value of 0.000. These values imply the robustness of the method used in developing the model and the high reliability of the developed model itself.

The characteristics of Equation 2 agree with other studies [12], where the diameter of the CNTs produced was found to be inversely proportional to the reaction temperature. It is clear that the diameter of the CNT is inversely proportional to the inlet CH_4 concentration and reaction temperature, while it is directly proportional to the catalyst metal loading. It can also be seen that, among the parameters, the CNT diameters are mostly dependent on the reaction temperature as indicated by the highest numerical coefficient of 95.14, which is greater than the sum of the coefficients of the other parameters combined.

Minimization of Equation 2 yielded an even smaller CNT diameter at 47.75 nm, with the following set of optimal parameters similar to Run 7, with the difference only being a lower catalyst metal loading: 5% ($^{vol}/_{vol}$) inlet CH_4 concentration; 10% Ni catalyst metal loading with 12:5 mol: mol Ni: Cu; and 950 ℃ reaction temperature. It must be noted that the optimized parameter combination is not present in the TDE run matrix.

IV. Conclusions

A study on the optimization of the process parameters and the loading of the catalyst for the production of CNTs over Ni-Cu/Al_2O_3 in a fluidized bed reactor was investigated. The process parameters were the inlet CH4 concentration and the reaction temperature. Optimization was done in terms of the diameter of the CNTs formed, where a smaller diameter is better since it is conducive to the storage of H_2. Catalyst pre-characterization confirmed the presence of γ-Al_2O_3, NiO and NiCu catalyst components which are necessary in the production of CNTs. Catalyst post-characterization allowed the identification of CNTs and the measurement of the diameter. The smallest average CNT diameter was 48.5 nm produced with 5% CH4, 30% Ni loading with 12:5 mol: mol Ni: Cu, and 950 ℃ reaction temperature.

The fitted general non-interacting-parameter third order non-linear equation model suggests the high-dependence of the CNT diameters on the reaction temperature. Numerical optimization of the fitted model suggests an even lower predicted CNT diameter at 47.75 nm with the parameters set at 5% CH4, 10% Ni loading with 12:5 mol: mol Ni: Cu, and 950 ℃ reaction temperature. The fitted model has a high reliability with a PCC of 0.944 and a PCC P-value of 0.000.

The authors recommend further studies investigating the effect of an interaction among the parameters to develop a model with higher regression reliability values, considering the nature of the growth mechanism of the CNT and the thermodynamic implications accompanying the mechanism.

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