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Optimization Parameters of Multi Walled Carbon Nanotubes' Diameter Using Taguchi Design of Experimental Approach

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Abstract: In this study, the effect of operating parameters in improving the diameter of multi-walled carbon nanotubes using Taguchi Experimental Design was presented. Wet impregnation method was employed for the bimetallic (Fe-Ni) on kaolinite clay catalyst development and the MWCNTs were synthesized via catalytic vapour deposition technique. The catalyst was then characterized to determine its suitability for the synthesis of MWCNTs using Scanning Electron Microscopy (SEM), Energy Dispersion X-Ray (EDX), X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) for the surface morphology, elemental analysis, crystallinity and surface functional group respectively. The results of the SEM and the EDX show that the ferrites are well dispersed on the kaolinite support while the XRD and the FTIR depict high level of catalyst crystallinity and efficient ferrite ($NiFe_2O_3$) compound for MWCNTs nucleation process. The well characterized catalyst was used for the Taguchi optimization process in a CVD reactor. The effect of reaction temperature, reaction time and acetylene flow rate were determined on the diameter of the MWCNTs produced. The pristine diameter formations of the MWCNTs produced were observed to vary between 23.6 – 57.6 nm. A L9 Orthogonal Array signal to Noise ratio and analysis of variance (ANOVA) are applied to study performance characteristics of the parameters. Reaction temperature was found to be significant factor with percentage contribution of 82.60%. Hence, wet impregnation method proved efficient for the production of catalyst in the synthesis of diameter controllable MWCNTs using Catalytic Vapour Deposition techniques.

Keywords: Multi-walled Carbon Nanotubes (MWCNTs), Catalytic Chemical Vapour Deposition (CCVD), Taguchi Design of Experiment (TDE), Fe-Ni/Kaolinite Clay Catalyst, MWCNTs Diameter

1. Introduction

The demand for carbon nanotubes (CNTs) is increasing due to their various commercial applications and the increasing annual number of CNT related journal publications and issued patents. Due to their extraordinary mechanical, electrical and optical properties, CNTs have stimulated extensive research since their discovery by Sumio Iijima in the early 1990s [1]. CNTs can be described as nanoscale rolled up one atom-thick sheets of graphite called graphene that are closed at each by half of a fullerene molecule and are of two types, structures comprising only one cylinder are termed Single Walled Carbon Nanotubes (SWCNTs) and this was first observed by Iijima and Ichihashi in 1993 [2], whereas structures containing two or more concentric graphene cylinders are characterized as Multi-Walled Carbon Nanotubes (MWCNTs) [1]. These classification can also be made pending the diameter range of the CNTs. The diameter range of SWCNTs is small (0.4-3 nm) than that of MWCNTs whose vary from two to >100 nm and usually grow perpendicular to the substrate.

It is to be kept in mind that for above mentioned characteristics, CNTs possess a high surface area per unit weight, good mechanical properties, and high electrical conductivity at metallic state and high thermal

conductivity/stability [3] which makes their applications possible in electromagnetic and microwave absorbing coatings, fibres, radiation sources and nano-meter-sized semiconductor device, thermal interface materials, X-ray tubes, sensor, energy storage and energy conversion devices, membranes for water purification and gas separation among others [3].

Till date, catalytic chemical vapour deposition (CCVD) is one of the best techniques to obtain large quantities of high purity and cost effective CNTs [4-8]. Although there are other techniques which are being used for synthesis of CNT like arc discharge [5] and laser ablation [6, 7] but CCVD appears to be the most versatile and promising technique both in terms of bulk production and direct device integration. Studies show that modifying the parameters of the CCVD processes control the physical characteristics of the resulting CNTs [9]. Also, Atike *et al.* [10] and Romero *et al.* [11] conducted an experiment to explore factors, such as reaction temperature, reaction time and flow rate of the carbon source, which alter the structure of the CNTs produced in CCVD equipment.

Most of the studies were conducted with the objectives of increasing CNTs yield and improving catalyst performance and stability while only a few have focused on improving the quality of the CNTs produced [12, 13]. More specifically, only a few studies still investigated the effects of reaction temperature, reaction time and acetylene flow rate on the diameter of CNTs during production [14, 15]. In view of this background, these present studies seek to address the effects of reaction condition determine the parameters that would affect diameter of a MWCNTs using Taguchi experimental design for industrial and commercial application.

2. Materials and Methods

2.1. Materials

The kaolinite clay used in this study was source from Kankara, Kastina State, Nigeria and used without any treatment or modifications. All the chemicals were supplied by Sigma Aldrich: $Fe(NO_3)_3.9H_2O$, and $Ni(NO_3)_2.6H_2O$, used were of analytical grade with percentage purity of 99.99%. Analytical grade carbon source (C_2H_2) and carrier gas (Ar) with 99.99% purity were purchased from British Oxygen Company/Brin's Oxygen Company (BOC Gases Nigeria Plc, Lagos).

2.2. Methods

2.2.1. Catalyst Preparation and Characterization

The catalyst was prepared with $Fe(NO_3)_3.9H_2O$ and $Ni(NO_3)_2.6H_2O$ solutions with Fe-Ni ratio of 1:1 to make a 0.25 M solution. The resulting solution was then impregnated onto the 8 g powdery kaolinite clay which serves as a support. The mixture was allowed to age for 1 hour on a magnetic stirrer at 2000 rpm. The resulting slurry was pre-calcinated at 130°C for a period of 10 hours. This impregnated precursor was cooled to room temperature, ground and finally screened with 150 µm sieve and later calcined at 500°C for 16 hours in a static air furnace. The resulting catalyst was subjected to HRSEM-EDX Analysis for the visual determination of surface characteristics and metal particle dispersion, XRD Analysis for the bulk crystal structure, and FTIR Analysis for general chemical and molecular structure.

2.2.2. Operating Conditions for MWCNTs Production

MWCNTs synthesis was done in a tubular quartz tube reactor placed horizontally in a furnace set inside an electric variable temperature nichrome wire furnace at atmospheric pressure, loaded with 1.0 g of the prepared catalyst. The furnace was heated at 10°C/min while argon (Ar) was allowed to flow at a flow rate of 30 mL/min to create an inert environment, removal of contaminants and prevent sample oxidation during the experiment. Once the desired temperature was reached, the Ar flow rate was adjusted to 230 mL/min. The carbon source (C_2H_2) was thereafter introduced and the reaction was allowed to proceed for a specified period of time. Subsequently, the flow of acetylene was stopped and the furnace was allowed to cool down to room temperature under a continuous flow of argon at flow rate of 30 mL/min after the reaction time was attained. The operating parameters were set according to the Taguchi Design of Experiments (TDE) orthogonal matrix, with the parameters enumerated in Table 1. The resulting prepared CNTs were subjected to XRD analysis for the determination of their average diameters of each corresponding runs and HRSEM analysis for the visual morphology of the prepared CNTs.

Table 1. *Taguchi design of experiment factor level listing.*

Level	Reaction temperature (°C)	Reaction time (minutes)	C_2H_2 flow rate (mL/min)
1	750	45	150
2	800	60	180
3	850	75	210

3. Results and Discussion

3.1. Catalyst Characterization

The dispersion of the Fe and Ni particles on kaolinite clay is shown in Figure 1. The loading of the catalyst is denoted with a circle covering up of the surface of the support. The random arrangement of the metal loading is an indication of high porosity, which resulted in more active sites for the catalysis reaction to take place. Figure 2 shows that the prepared catalyst contained C, O, Al, Si, Ti, Fe and Ni at different proportion. The Al, Si, and Ti stemmed from the kaolinite clay support, Fe and Ni comes from their respective metal salts, while the C originated from the holey carbon grid in the cause of the analysis. This result also revealed that the catalyst contained Fe-Ni in an approximately 1:1 ratio which agreed with the chosen stoichiometry for the catalyst preparation.

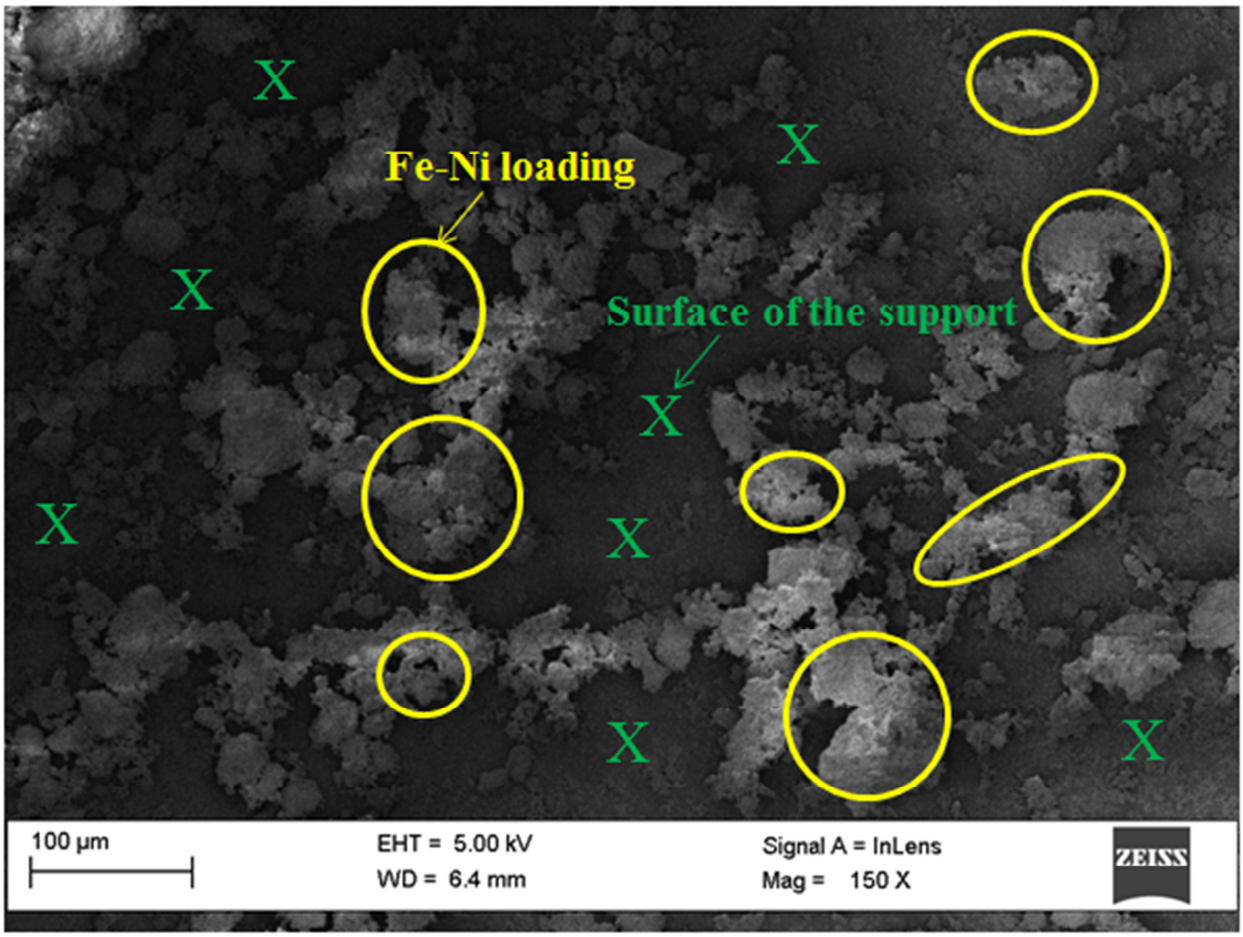

Figure 1. *HRSEM Micrograph of Fe-Ni/kaolinite clay catalyst.*

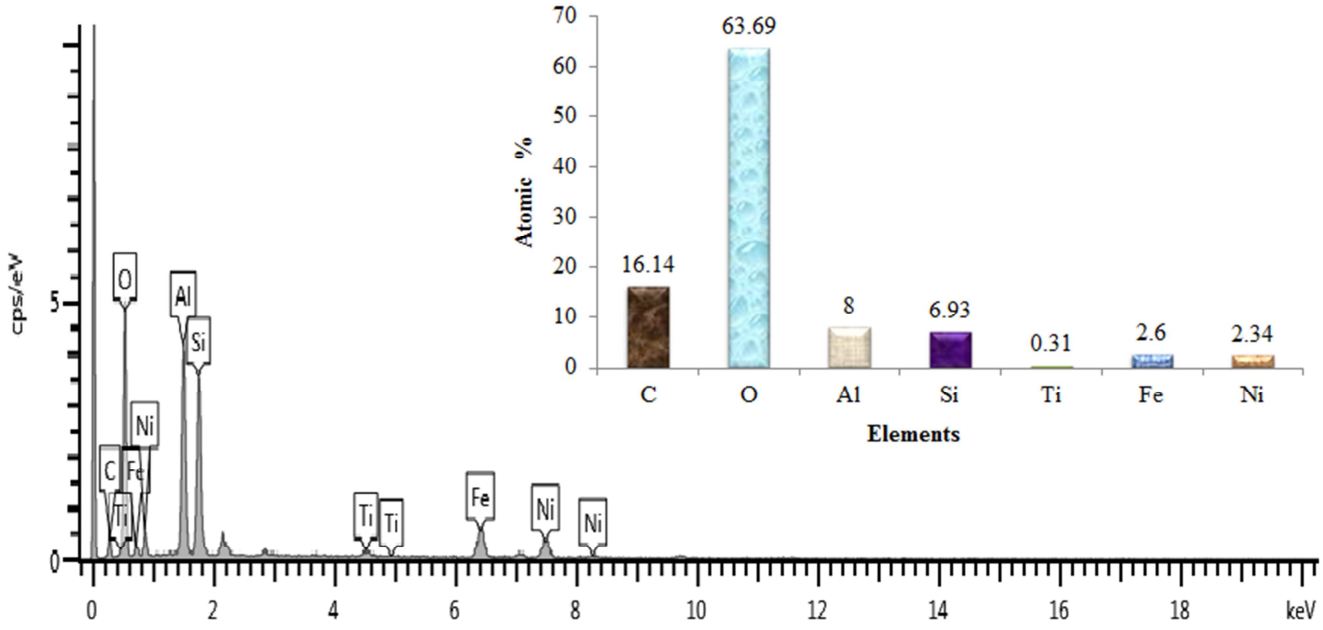

Figure 2. *EDX Micrograph of Fe-Ni/kaolinite clay catalyst.*

XRD Analysis result shown in Figure 3 confirmed the presence of kaolin and Fe-Ni composites. The 2θ value at 33.15° and 35.71° represent characteristics peak of crystalline Fe-Ni composite with crystal plane (111). While the 2θ value at 25.32, 30.24, 43.42, 57.57, 62.98 and 75.20° correspond to the kaolinite mineral phase.

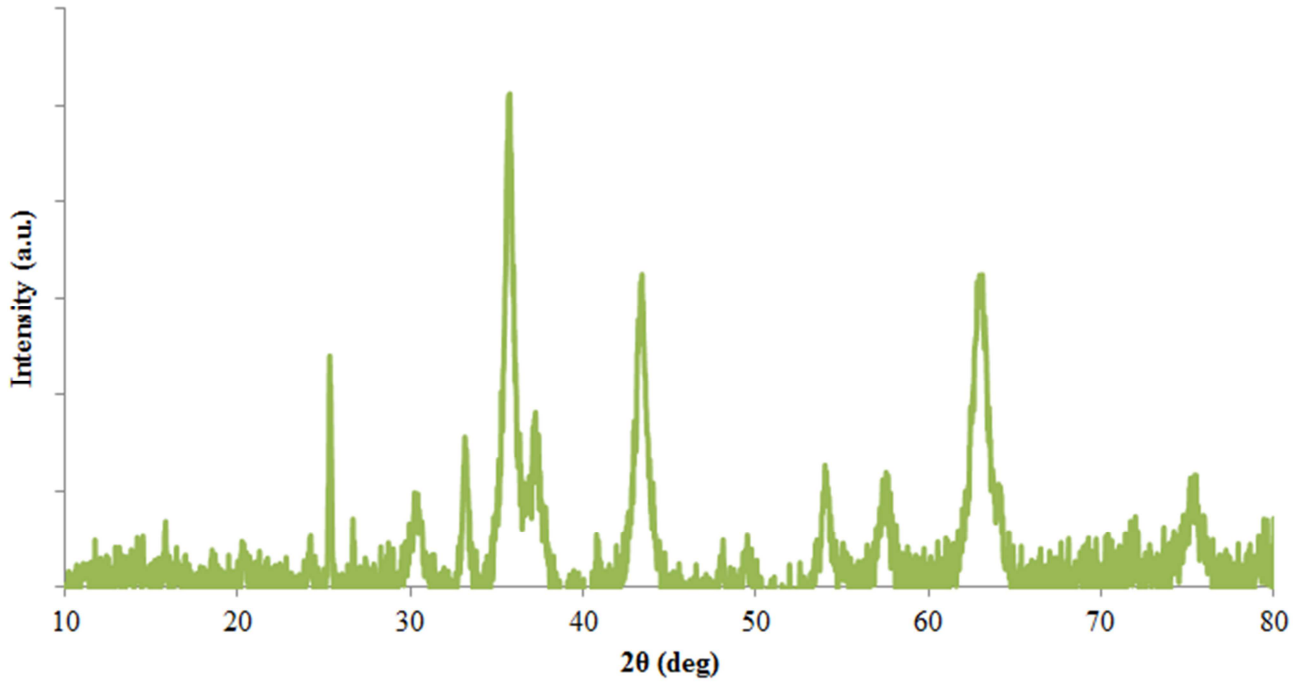

Figure 3. *XRD Micrograph of Fe-Ni/clay catalyst.*

FTIR Analysis also confirmed the presence of kaolinite materials such as O-Al-O, Si-O-Al, and Si-O-Si at absorption band 733 cm^{-1}, 943 cm^{-1} and 1067 cm^{-1} respectively as presented in Figure 4. The two absorption bands assigned to the octahedral (Ni-O) and tetrahedral site (Fe-O) at 430 cm^{-1} and 566 cm^{-1} respectively also revealed the presence of Fe-Ni composites in form of spinel ferrites ($NiFe_2O_4$) favourable to the production of MWCNTs.

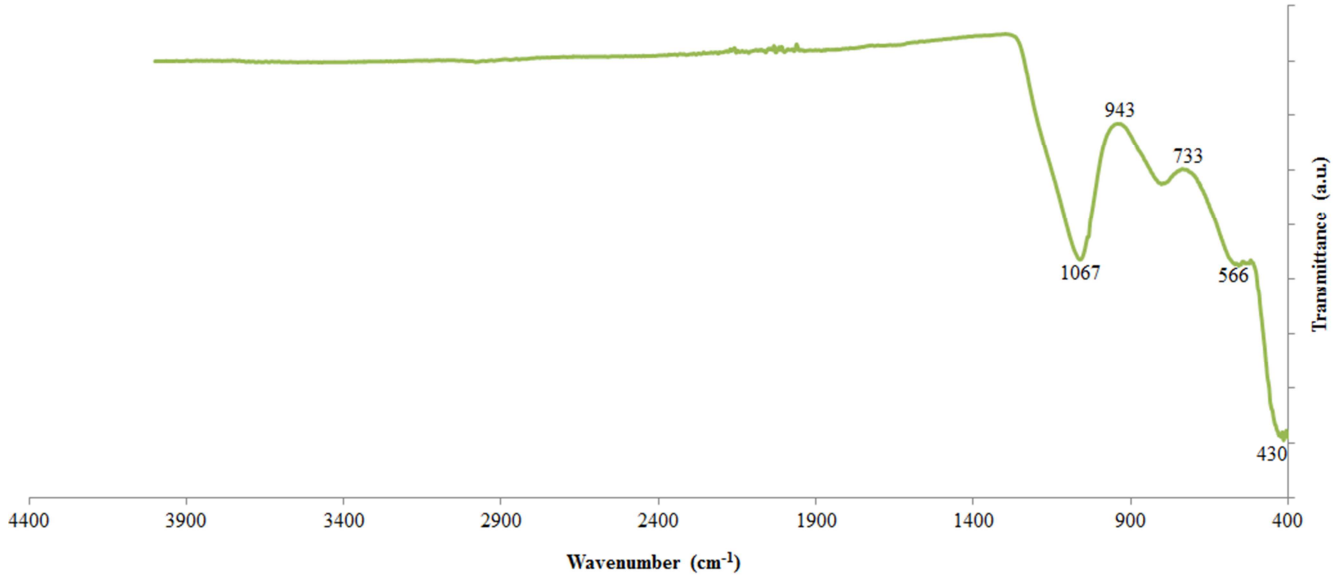

Figure 4. *FTIR Micrograph of Fe-Ni/clay catalyst.*

3.2. Characterisation and Optimization of MWCNTs Production

The optimization was based on the minimum average MWCNT diameter from the XRD results in Figure 5(a) using *Debye-Scherrer formula* presented in Equation (1) [16].

$$D = \frac{0.9\,\lambda}{\beta\,\mathrm{Cos}\theta} \quad (1)$$

Where λ is wave length of X-Ray (0.1541 nm), β is FWHM (full width at half maximum), θ is the diffraction angle and D is the average diameter of the MWCNTs. The XRD patterns as shown in Figure 5(a) show major peaks around 2θ = 26° and 44°, which were denoted with "C" representing the characteristic planes of a typical graphitized carbon of MWCNTs for all the runs. Also, the HRSEM micrograph in Figure 5(b) shows clear, neat, whitish and well oriented MWCNTs for all the runs at different experimental conditions.

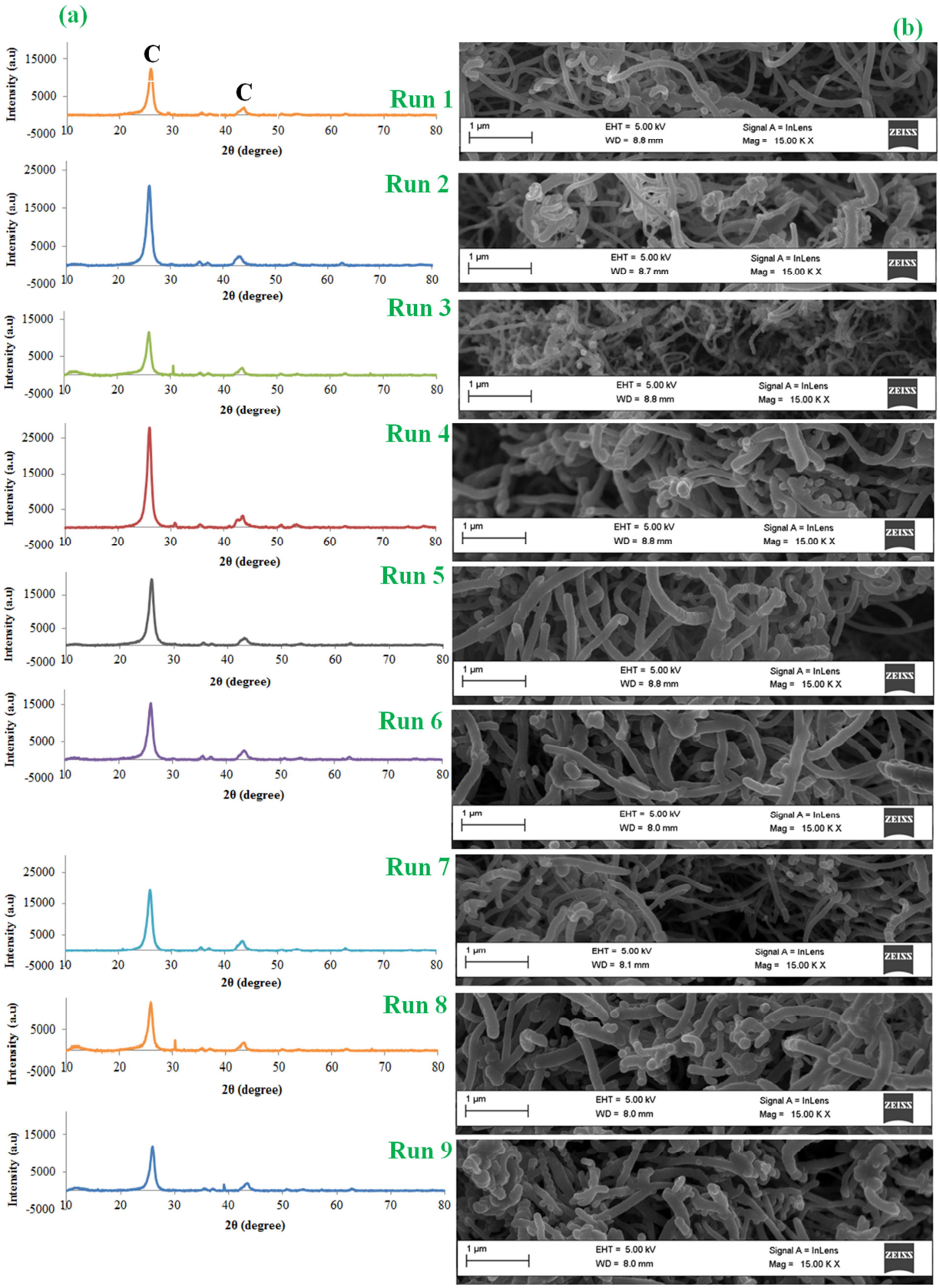

Figure 5. *(a) XRD pattern (b) HRSEM micrograph of MWCNTs at different runs conditions.*

Incorporating the TDE parameter values set in Table 1, the MWCNT average diameter data from the XRD results corresponding to the TDE orthogonal matrix are shown in Table 2.

Table 2. *Summary of MWCNT average diameter from XRD results using Debye-Scherrer formula.*

Runs	Reaction temperature (°C)	Reaction time (minutes)	C_2H_2 flow rate (mL/min)	MWCNTs Diameter (nm)
1	750	45	150	45.6
2	750	60	180	38.8
3	750	75	210	23.6
4	800	45	180	34.1
5	800	60	210	51.3
6	800	75	150	46.8
7	850	45	210	25.5
8	850	60	150	40.4
9	850	75	180	57.6

Table 2 shows the diameters of the tubes formed satisfies the diameter range for multi-walled carbon nanotubes (2 to 100 nm) and hence only show that the tubes formed are mostly multi-walled nanotubes. The minimum average diameter occurs at Run 3, with corresponding parameters at: 750°C reaction temperature; 75 mins reaction time; and 210 mL/min acetylene flow rate. The observed values of MWCNTs diameter for each runs in Table 2 were analysed using MINITAB software.

Table 3. *Response for Signal to Noise Ratios (Larger is better).*

Level	Reaction temperature	Reaction time	Acetylene flow rate
1	30.88	30.59	32.83
2	32.80	32.62	32.63
3	31.53	32.01	29.76
Delta	1.91	2.03	3.07
Rank	3	2	1

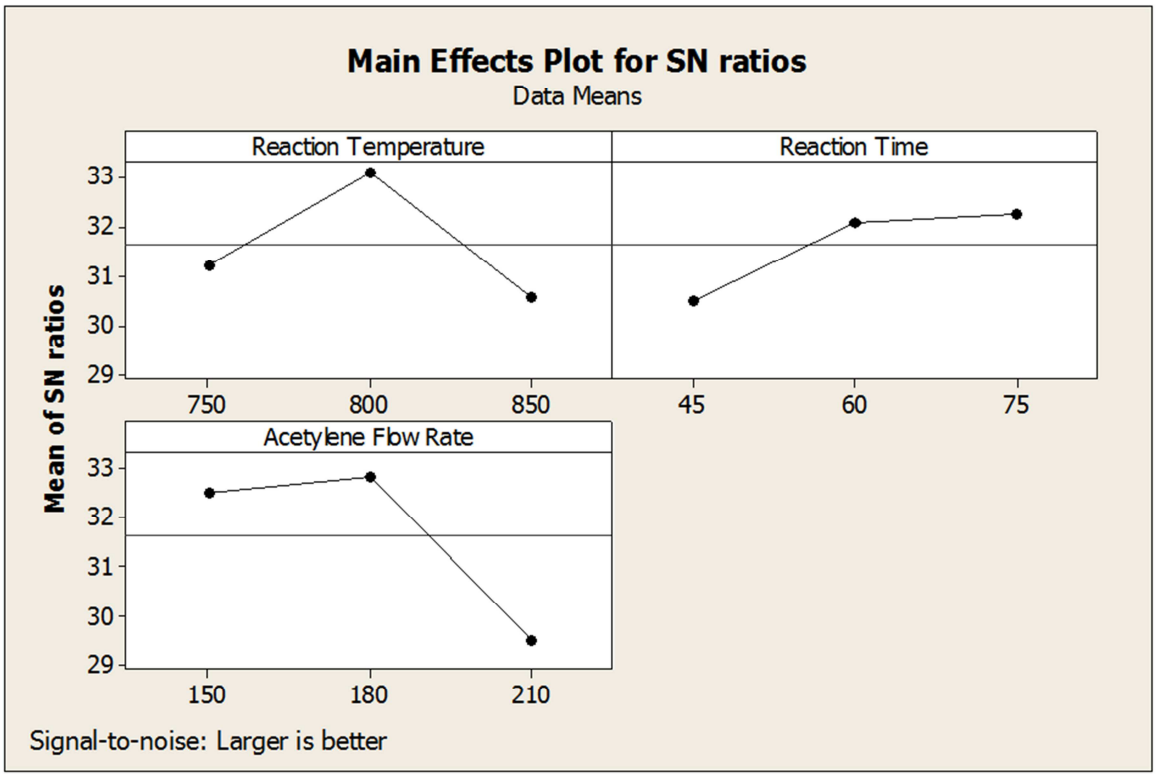

Figure 6. *Main effect plot of S/N ratio for MWCNTs diameter.*

Table 4. *Analysis of variance for S/N Ratio.*

Source	DF	Seq SS	Adj SS	Adj MS	F-ratio	P (% contribution)
Reaction temperature	2	5.687	5.687	2.844	0.21	0.826
Reaction time	2	6.517	6.517	3.259	0.24	0.805
Acetylene flow rate	2	17.686	17.686	8.843	0.66	0.604
Residual Error	2	26.971	26.971	13.486		
Total	8	56.862				

As response parameter, diameter of the MWCNTs of the samples is given in Table 2. The relative percentage contribution (P) and F-ratio of each factor obtained by the ANOVA method are given in Table 4. It can be concluded from Tables 3 and 4, based on F-value, that the significance of factors prevails in the following order of importance: reaction temperature, reaction time and acetylene flow rate. The most significant factor is reaction temperature with percentage contribution to MWCNTs diameter of 82.60%. The next significant factor is reaction time which contributed 80.50%, and third significant factor is the acetylene flow rate with percentage contribution of 60.40%.

Also, the effects of individual parameters at different levels on the diameter of the MWCNTs are shown in Figure 6. The results revealed that, effect is increasing with increase in reaction temperature up to 800°C beyond that it is

decreasing. So the optimum reaction temperature is level 2 (800°C) while the minimum reaction temperature is level 3 (850°C). While for the reaction time, its effect is increasing with increase in reaction time. So the optimum reaction time is level 3 (75 mins) and its minimum is level 1 (45 mins). Finally, the effect of acetylene flow rate was observed to be similar to that of the reaction temperature with optimum acetylene flow rate at level 2 (180 mL/min) and minimum acetylene flow rate at level 3 (210 mL/min).

Table 5. *Response for Means.*

Level	Reaction temperature	Reaction time	Acetylene flow rate
1	36.33	35.03	43.97
2	44.20	43.08	43.75
3	40.20	43.50	32.90
Delta	7.87	8.05	11.07
Rank	3	2	1

4. Conclusions

In this study, optimization of process parameters for the production of MWCNTs over Fe-Ni/kaolinite clay in a catalytic chemical vapour deposition reactor was investigated. The effects of process parameters such as the reaction temperature, reaction time and the acetylene flow rate on the average diameter of MWCNTs were identified. The optimization was performed in terms of the diameter of the MWCNTs formed from the XRD results. The Catalyst characterization confirmed the presence of kaolin clay minerals and Fe-Ni composite catalyst components in form of ternary oxide ($NiFe_2O_4$) which is necessary in the production of MWCNTs. The XRD results allowed the determination of the MWCNTs diameter using *Debye-Scherrer formula.* The smallest average diameter of the MWCNT was 23.6 nm produced under 750°C reaction temperature, 75 mins reaction time and 210 mL/min acetylene flow rate. Whereas, the largest average diameter was obtained to be 57.7 nm under 850°C reaction temperature, 75 mins reaction time and 180 mL/min acetylene flow rate. This work demonstrates the method of using Taguchi methods for the optimizing the MWCNTs diameter parameters for response characteristics.

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