Full factorial design approach to carbon nanotubes synthesis by CVD method in argon environment

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ABSTRACT

Whereas meeting product quantity and quality are prime intent in process optimization of materials manufacturing, the application of the more reliable full factorial experiment has not been well-explored in optimization studies of Carbon nanotubes (CNTs) synthesis. In this study, statistical full factorial design of experiment was explored in the parametric studies of CNTs synthesis via acetylene-chemical vapour deposition (CVD). Bimetallic (Fe-Co) catalyst supported on CaCO3 was employed for the synthesis of CNTs. The dependence of CNTs yield on the growth time (45/60 min), growth temperature (700/750 °C), acetylene flow rate (150/190 ml/min), and argon flow rate (230/290 ml/min) was investigated in the 24 factorial design of experiment. The growth temperature and acetylene flow rate were found to have the most significant effects on the yield of CNTs, and a maximum yield of 170% was obtained at growth conditions of 60 min, 700 °C, 190 ml/min acetylene flow rate, and 230 ml/min argon flow rate. Since acetylene undergoes polymerization or dissolution during non-catalyzed thermal decomposition, the significant effects of temperature and acetylene flow rate as illustrated by the factorial analysis suggests that the selective ability of the Fe-Co/CaCO3 catalyst towards CNTs growth in the thermal decomposition of acetylene in CVD was mainly thermodynamics-controlled. Characterization of CNTs samples synthesized at different conditions shows that highest-yield conditions do not guarantee best quality properties.

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1. Introduction

Extensive research on the synthesis, characterization and applications of carbon nanotubes (CNTs) have been conducted in the past twenty years (Shah and Tali, 2016). Different methods of producing CNTs include arc discharge, laser ablation, electrolysis, sono-chemical (or hydrothermal) and various forms of chemical vapour deposition (CVD) methods (Prasek et al., 2011). But, the thermal CVD process has been widely used because it is simple, inexpensive and...
easily scalable for commercial production (Prasek et al., 2011; Yardimci et al., 2015). It also allows comparatively higher yield and purity of CNTs to be obtained than in other methods (Kumar and Ando, 2010). In the CVD technique, appropriate choice of carbon source, carrier gas, growth temperature, growth time and properties of the catalyst are essential for the controlled growth of CNTs (Yardimci et al., 2015).

Common transition metals employed as catalyst for carbon nanotubes synthesis include Fe, Co, Ni, and their combinations, deposited on different support materials such as SiO2, MgO and Al2O3 (Kumar and Ando, 2010; Tsoufis et al., 2007). Previous studies have shown that Fe–Co bimetallic catalyst supported on CaCO3 is more efficient than other types of metal-support formulations (Cheng et al., 2006; Couteau et al., 2003; Kathyayini et al., 2004; Magrez et al., 2005; Mhlanga and Coville, 2008; Mhlanga et al., 2009; Afolabi et al., 2011; Motchelaho et al., 2011; Chiwaye et al., 2014). Calcium carbonate gives near 100% selectivity, and it can be easily removed from the final CNTs product by simple acid purification (Mhlanga and Coville, 2008). However, the exact roles of growth parameters in CNTs synthesis are still conflicting. Several parameters could influence the synthesis process of CNTs growth, making the application of standard statistical design of experiment (DOE) a necessary approach to guarantee global optimum during optimization of synthesis variables (Porro et al., 2007). Though, several research studies were performed on the effect of various CVD parameters on CNT growth (Tsoufis et al., 2007; Cheng et al., 2006; Mhlanga and Coville, 2008; Mhlanga et al., 2009; Afolabi et al., 2011; Motchelaho et al., 2011; Porro et al., 2007), statistical DOEs were not explored, and most studies were dedicated to investigating either the yield of CNTs or its quality properties. Only few studies have successfully optimized the synthesis of CNTs (Seresh et al., 2009; Santangelo et al., 2012; Silva et al., 2015), the properties of CNTs (Ting et al., 2006), and different applications of CNTs (Cheung et al., 2002; Wang et al., 2012) using the method of Taguchi design of experiment. The Taguchi is a fractional experiment where there is potential to miss important interactions. Fractional experiments disallow analysis of interactions and the interactions are confounded with other effects, which makes it difficult to differentiate between two factors. The full factorial design is an exhaustive approach that makes it impossible for any interactions to be missed as all factor interactions are accounted for. Thus, the full factorial experiment gives a more practical and reliable result than fractional factorial experiments such as the Taguchi.

In fact, reducing the production cost of CNTs growth in large-scale requires quantitative and qualitative optimization studies of CVD parametric effects on CNTs growth, a concept which has not been fully developed. The present work is an optimization study of synthesis parameters involved in carbon nanotubes growth over the bimetallic (Fe–Co) catalyst supported on CaCO3. In this study, rather than fractional factorial experiments, statistical approach of DOE employed in CNTs synthesis was developed by full factorial design to control the yield and quality properties of the CNTs. The article is focused on the determination of the optimum growth conditions of CNTs. Properties of the CNTs were also investigated to determine how the preparation parameters affect the CNTs quality properties.

2. Materials and methods

2.1. Materials

Chemicals used in this study include calcium trioxocarbonate (IV), cobalt (II) trioxonitrate (V) hexahydrate, and iron (III) trioxonitrate (V) nonahydrate which were obtained from Sigma Aldrich. All the chemicals used are of analytical grade with percentage purity in the range of 98–99.99%. Liquid nitrogen, acetylene, argon and nitrogen gases were purchased from British Oxygen Company/Brin’s Oxygen Company (BOC Gases Nigeria Plc, Lagos).

2.2. Methodology

The CVD reactor model XD-1200NT used in this study was manufactured by BioVac Inc. It consists of a quartz tube (52 mm internal diameter, 4 mm thickness and 1010 mm length), placed in a furnace that has heating capacity up to about 1200 °C. Gas cylinders for the carbon source (acetylene) and the carrier gas (Argon) were connected to the inlet of the reactor where flow meters were available for control of gas flows. The control system of the CVD allows for an appropriate temperature program in maintaining consistent and appropriate heating rate, reaction temperature, and cooling rate. The exhaust gases through an exhaust pump at the reactor outlet were collected by bubbling in water. The Ohaus Scout Pro SP202US digital scale used has 200 g weighing capacity with precision of 0.01 g.

2.2.1. Synthesis of Fe–Co/CaCO3 catalyst

The bimetallic catalyst, Fe–Co on CaCO3 support was prepared as described in the literature by wet impregnation method (Afolabi et al., 2011). Precisely 3.62 g and 2.47 g of Fe(NO3)3·9H2O and Co(NO3)2·6H2O respectively were weighed and dissolved in 50 cm3 of distilled water. This was followed by the addition of 10 g of CaCO3 under continuous stirring for 1 h. The resulting slurry was then allowed to dry at room temperature after which it was dried at 120 °C for 12 h, cooled to room temperature, ground and finally screened through a 150 μm sieve. The final powder was then calcined at 400 °C for 16 h.

2.2.2. Synthesis of carbon nanotubes

Carbon nanotubes were synthesized by the decomposition of acetylene in a CVD reactor. A known weight (0.5 g) of the Fe–Co catalyst on CaCO3 support was placed in the ceramic boat, which was inserted in the horizontal quartz tube of the CVD furnace and heating was done at 1000 °C at a flow rate of 30 ml/min to purge the system of air. Once the set temperature was attained (700 °C), the argon flow was adjusted to the required flow rate (230 ml/min) and acetylene was introduced at its required flow rate (150 ml/min). The process was allowed to proceed until the reaction time (45 min) was reached after which the flow of acetylene was stopped. The furnace was allowed to cool to room temperature under continuous flow of argon. The ceramic boat was then removed and weighed to determine the quantity of CNTs produced. Percentage of CNTs yield was determined using the relationship provided by Taleshi (2012) as presented in Equation (1);

\[
\text{CNTs yield} = \frac{(T_{\text{mass}} - C_{\text{mass}})}{C_{\text{mass}}} \times 100
\]
where \( T_{\text{mass}} \) is the total mass of the final catalyst and carbon products after CVD reaction process and \( C_{\text{mass}} \) is the initial mass of Fe–Co/CaCO₃ catalyst.

During CNTs production by CVD experimental procedure, four CVD reaction parameters were varied; reaction time, growth temperature, flow rate of argon (carrier gas), and flow rate of acetylene (carbon source). Levels of factors were chosen following previous studies (Kumar and Ando, 2010; Mhlanga et al., 2009; Motchelaho et al., 2011), and are given in Table 1.

Optimization was carried out using yield of CNTs as the response. Effects of the reaction parameters on the CNTs yield was used to optimize from quantitative point of view, and their effects on CNTs quality or morphology optimizes from qualitative viewpoint. In the former case, Minitab 16 software was used to carry out Analysis of Variance (ANOVA), so that the main and the combined effects of the factors considered are represented in empirical models to show the dependence of CNTs yield on these parameters.

The as-synthesized CNTs were purified by acid treatment to remove Fe, Co, CaO, and CaCO₃ that were introduced into the samples from catalyst used for production; amorphous forms of carbon and other impurities. Every 1 g of as-synthesized CNT sample was washed in 100 ml of 30% H₂SO₄ by continuous stirring for 1 h. The mixture was then washed with distilled water until a pH of 7 was achieved. Water was filtered out to obtain the wet CNT residue which was dried mildly at 120 °C for 12 h.

2.2.3. Characterization of samples

The Fe–Co/CaCO₃ catalyst was analyzed for its crystallinity, thermal stability, morphology, and BET-surface area. As-synthesized and purified CNTs samples were characterized for thermal stability by TGA (TGA 4000 model), crystallinity by XRD (XRD-6000 model), Specific surface area/pore volume by Brunauer-Emmet-Teller (BET) analysis (NOVA 4200e model), chemical composition and purity by FTIR (Frontier FT-IR model) and Raman (Pro Raman-L model), particle size by dynamic light scattering (DLS) technique (Zetasizer Nano-S series), and morphology by TEM (Tecnai G2 F20-Twin) and scanning electron microscopy (SEM)/Energy-dispersive X-ray spectroscopy (EDX).

3. Results and discussion

The synthesized Fe–Co/CaCO₃ catalyst exhibited properties that made it suitable for CNTs growth. The properties of the catalyst and its suitability for CNT growth was investigated using different characterization techniques including XRD, TGA, HRTEM-SEM/EDX and BET which were used to study the catalyst’s crystallinity, thermal behaviour, morphology and surface area respectively. There has been conflicting opinions regarding the phases present in the final Fe–Co/CaCO₃ catalyst material. In this study, the characterization results suggest that the crystalline phase, CoFe₂O₄ was more likely present in the catalyst material. The XRD pattern showed that the solid catalyst is polycrystalline with different crystal sizes resulting in a number of peaks as presented in Fig. 1.

The thermal decomposition of the catalyst conducted in nitrogen environment is shown in the TGA profile presented in Fig. 2. The catalyst thermal decomposition showed four weight loss regimes. The first slope is attributed to loss of unbound water, the next two weight losses are due to conversion of Fe and Co nitrates to form a ternary metal oxide, most likely, CoFe₂O₄. The final weight loss represents the decomposition of CaCO₃ to evolve CO₂ and form CaO.

The SEM micrograph of the catalyst and its corresponding EDX presented in Fig. 3(a) and (b) showed the morphology and qualitative elemental compositions of the sample. The SEM/EDX is evidence that the Fe and Co nanoparticles were well-dispersed in the CaCO₃ matrix, possibly present as cobalt ferrite, CoFe₂O₄.

A high resolution transmission electron microscopy (HRTEM), and the corresponding selected area electron diffraction (SAED) pattern was collected for determination of different phases present in the sample. Fig. 4 shows highly crystalline phases dispersed in the whitish CaCO₃ support matrix. The crystalline phase in the HRTEM further suggests the possible formation of CoFe₂O₄ in the final catalyst.

The wet impregnation method used in catalyst preparation has proved to be effective in dispersing the metal nanoparticles onto the support matrix. This was aided by stirring of the slurry mixture prior to heat treatments. Though, Fig. 4 revealed some zones where metal particles and CaCO₃ support were in isolation from each other, excellently dispersed crystals of the metal particles in the support are illustrated by Fig. 5(a) and (b). The regions of metal particles are the active part or sites of the catalyst on which CNTs would grow, while white bulk regions are the support-dominated regions.

The BET method was used to analyze the specific surface area of the catalyst sample and a value of 3.9 m²/g was obtained. It was observed that the catalyst has surface area similar to that of the CaCO₃ powder used as support. The Fourier transform infrared (FTIR) spectroscopy of the catalyst as presented in Fig. 6 shows the functionalities that were present in the sample.

By comparison with standards, the stretches, bends and sharp bands were used to identify groups that are present. As presented in Fig. 6, three functional groups were identified; the hydroxyl (O–H) from unbound water, carbonate (CO₃²⁻), from the CaCO₃ and the nitrates (NO₃⁻) from Fe(NO₃)³ and Co(NO₃)² salts. Calcium oxide (CaO) was not present because CaCO₃ would not decompose until above the calcination temperature of 400 °C. The Fe–Co/CaCO₃ catalyst possessed good properties that made it suitable for synthesis of Carbon nanotubes.

During CNTs synthesis, the effects of synthesis parameters on the yield of CNTs produced were investigated using a 2⁴ Factorial experimental design which was analyzed in Minitab ANOVA. The summary of the yield results obtained during CNTs synthesis is presented in Table 2.

Results as presented indicate that the highest yield of 170% was obtained at operating temperature of 700 °C, argon flow rate of 230 ml/min, acetylene flow rate of 190 ml/min, and production time of 45 min. In order to study and optimize the effects of operating parameters on CNT production using the CVD method, the 2⁴ factorial Design of Experiment was adopted by varying acetylene flow and argon flow rates, and decomposition time and temperature. Argon flow rate (230 and 290 ml/min), acetylene flow rate (150 and 190 ml/min),

| Table 1 – Levels of factors considered in 2⁴ CNTs production in CVD. |
|---------------------------------|---------|---------|---------|---------|
| Time (min) | Temp (°C) | Ar flow (ml/min) | C₂H₂ flow (ml/min) |
| Upper (+) level | 60 | 750 | 290 | 190 |
| Lower (−) level | 45 | 700 | 230 | 150 |
Fig. 1 – XRD of Fe–Co/CaCO₃ catalyst.

Fig. 2 – TGA curve of the catalyst.

Fig. 3 – Fe–Co/CaCO₃ catalyst’ (a) SEM image and (b) EDX.
Fig. 4 – HRTEM images of the catalyst showing a clear view of light brown Fe\(^{3+}\), dark/black Co\(^{2+}\), and white CaCO\(_3\) bulk.

Fig. 5 – (a) Iron, Cobalt on CaCO\(_3\) matrix (evidence of good dispersal), and (b) active sites having regular arrangement of metal nanoparticles on the support.

Fig. 6 – FTIR of Fe–Co/CaCO\(_3\) catalyst sample.
temperature (700 and 750 °C), and time (45 and 60 min) were varied. Statistical significance of each of the four factors was studied using Minitab ANOVA.

### 3.1. Effect of acetylene flow rate

Though, the ratio of acetylene to argon flow rate was not explicitly considered together in this study, effect of each parameter was studied in the optimization of CNT production by the CVD method. Hence, the flow rate of acetylene was varied between 150 ml/min and 190 ml/min, and its effect on the CNT yield is presented in Fig. 7.

It can be observed that the yield of as-synthesized CNTs increased with increase in acetylene flow rate from 150 to 190 ml/min irrespective of changes in argon flow rates (230/290 ml/min), with an exception of growth conditions at (60 min, 750 °C, and 290 ml/min argon flow rate). The positive effect of acetylene on yield is logical and can be supported by the following analysis. When acetylene (C2H2) is employed as carbon source for CNT growth, the carbon deposition \( \left( Y_c \right) \) can be evaluated using Equation (2) of Dung et al. (2008);

\[
Y_c = \frac{(100 \times m_f)}{m_i}
\]  

where \( m_f \) is the weight of purified CNTs and \( m_i \) is the weight of carbon in the \( \text{C}_2\text{H}_2 \) flow, which can be calculated by using Equation (3);

\[
m_i(g) = \left( \frac{\text{Flourate (l/min) \times Time(min)}/22.4(l/mol)}{24(g/mol)} \right)
\]  

The various acetylene flow rates as functions of carbon deposition are shown in Table 3.

By Equation (2) and Table 3, higher acetylene flow rate and its flow for longer time during CNT growth would increase weight of carbon available for deposition hence there is a corresponding increase in the yield of CNTs. However, other contributing factors such as ratio of acetylene to argon flow rate, and increase in reaction temperature may cause exceptions to this justification. The decrease in CNT yield which was observed at 60 min, 750 °C, and 290 ml/min argon flow rate despite having increased the acetylene flow rate from 150 to 190 ml/min could be due to trade-off between influence of acetylene and that of acetylene to argon ratio. Hence, maximum CNTs yield of 170% was obtained at acetylene flow rate of 190 ml/min.

### 3.2. Effect of argon flow rate

In conjunction with acetylene, the flow rate of carrier gas is one of the important CVD variables that can affect the selectivity and morphology of CNTs especially when supported catalyst is involved. In the present study, CNTs were produced in solely argon environment which served as the carrier gas, without \( \text{N}_2 \) or \( \text{H}_2 \). Here, effect of argon flow rate on yield of CNT was investigated. The carrier gas flow rate was varied between 230 ml/min and 290 ml/min and its effect on yield of CNT is shown in Fig. 8.

It can be observed from Fig. 8 that in the first scenario, the yields of CNTs generally increased when the flow rate ratio of acetylene to argon gas was reduced from (1: 1.53) to (1: 1.93). The second scenario behaved contrarily as the yields of CNTs on yield of CNT was investigated. The carrier gas flow rate was varied between 230 ml/min and 290 ml/min and its effect on yield of CNT is shown in Fig. 8.

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### Table 2 – The 2⁴ matrix for CNT factorial design of experiment (DOE).

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (min)</th>
<th>Temp (°C)</th>
<th>Argon flow (ml/min)</th>
<th>Acetylene flow (ml/min)</th>
<th>CNTs yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
<td>700</td>
<td>230</td>
<td>150</td>
<td>102</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>700</td>
<td>290</td>
<td>150</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>750</td>
<td>230</td>
<td>150</td>
<td>142</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>750</td>
<td>290</td>
<td>150</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>700</td>
<td>230</td>
<td>150</td>
<td>112</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>700</td>
<td>290</td>
<td>150</td>
<td>120</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>750</td>
<td>230</td>
<td>150</td>
<td>126</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>750</td>
<td>290</td>
<td>150</td>
<td>134</td>
</tr>
<tr>
<td>9</td>
<td>60</td>
<td>700</td>
<td>230</td>
<td>150</td>
<td>130</td>
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<tr>
<td>10</td>
<td>60</td>
<td>700</td>
<td>290</td>
<td>150</td>
<td>150</td>
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<tr>
<td>11</td>
<td>60</td>
<td>750</td>
<td>230</td>
<td>150</td>
<td>154</td>
</tr>
<tr>
<td>12</td>
<td>60</td>
<td>750</td>
<td>290</td>
<td>150</td>
<td>152</td>
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<td>13</td>
<td>60</td>
<td>700</td>
<td>230</td>
<td>150</td>
<td>134</td>
</tr>
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<td>14</td>
<td>60</td>
<td>700</td>
<td>290</td>
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<td>16</td>
<td>60</td>
<td>750</td>
<td>290</td>
<td>150</td>
<td>152</td>
</tr>
</tbody>
</table>

\[m_i(g) = \left( \frac{\text{Flourate (l/min) \times Time(min)}/22.4(l/mol)}{24(g/mol)} \right)
\]  

Fig. 7 – Effect of acetylene flow rate on CNT yield at argon flow rate of (a) 230 ml/min, and (b) 290 ml/min.
continued growth. Argon can either suppress or enhance the decomposition rate of acetylene but the dilution of acetylene by more argon gas has been reported to favour this balance (Yap et al., 2004). The effect of argon in the present study agrees with the work of Yap et al. (2004) who found that the addition of argon carrier gas reduced the number of C2H2 molecules that reacted on the surface of the Fe catalyst used by diluting the acetylene, resulting in increased carbon deposition. Consequently, the optimum acetylene to argon flow rate was found at 190:230 ml/min (or 1:1.21).

3.3. Effect of temperature

Growth temperature is another CVD parameter that can affect yield, purity, growth rate and morphology of CNTs. Synthesis temperature could affect the crystallinity of CNTs, and the selectivity of the catalysts. For instance, at temperatures below 650 °C carbon spheres are produced in CVD reaction. Thus, in order to improve selectivity to MWCNTs, appropriate choice of temperature is vital in reducing amorphous carbon and some other forms of carbon that may be formed as side reactions. It has also been reported that high temperatures tend to produce nanotubes of poor quality (Mhlanga, 2009). Acetylene is known to undergo polymerization or dissolution around 780 °C during thermal decomposition (Bone and Coward, 1908). In the present study, growth temperatures between 700 and 750 °C were employed in producing CNTs, and effect of these on the yield is presented in Fig. 9.

It can be observed from the yield-temperature charts (Fig. 9) that temperature showed significant influence on the yield of CNTs. Growth temperature of 700 °C has shown to be more favourable than temperature of 750 °C as lower yields were obtained at the high temperature compared to yields at the lower temperature. MWCNTs have low energy of formation hence their growth is favoured by the low temperature CVD process. In CVD, growth temperature significantly increases yield of CNTs within specific temperature range, above which further temperature will continually reduce the yield of CNTs. In this present study, the yields of CNTs reduced at 750 °C due to the unstable nature of acetylene at the higher temperature, resulting in deposition of large amounts of carbonaceous compounds (evident in the SEM image of Fig. 18(b) – Section 3.9) instead of the nanotubes.

3.4. Effect of growth time

The main effect of reaction time in CVD process is on the CNTs morphology. Carbon nanotubes are possibly produced within few minutes from the commencement of CVD reaction provided other reaction parameters are correct. However, it is thought that shorter reaction times favour smaller diameter CNTs while longer growth duration favours the growth of short, thick and fibrous MWCNTs due to continued carbon deposit on the formed CNTs. Another opinion is that an exponential expansion of nanocrystalline carbon sheath over time causes the diameter to increase. Thus, the diameter of CNTs produced with Fe–Co/CaCO3 catalyst system can be best controlled by the catalyst particle size and growth duration. While the inner diameter may remain unchanged with variation in reaction times, shorter reaction times yield higher quality CNTs with higher aspect ratios compared to longer times (Mhlanga, 2009). In this present study, effect of growth time (45–60 min) on the yield of CNTs was investigated. Fig. 10 shows the yield-time charts.

Results as presented in Fig. 10 showed that the effect of synthesis time on the yield of CNTs does not follow a specific trend. Varying time from 45 to 60 min tends to somewhat increase the yield at lower growth temperature of 700 °C and partly caused reduction in yields at higher growth temperature of 750 °C. This suggests that either of the growth temperature conditions is dominated by different kinetic regimes. The observation is also consistent with reports that have identified morphology and diameter-control as the main effect that variation in synthesis time could cause (Mhlanga, 2009; Kaatz et al., 2006; Kara et al., 2011).

3.5. Empirical model equation

The responses obtained in Table 2 of 2st experimental factorial design was used in carrying out a factorial design analysis

<table>
<thead>
<tr>
<th>S/N</th>
<th>Acetylene flow (ml/min)</th>
<th>Reaction time (min)</th>
<th>C available for deposition (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>45</td>
<td>7.232</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>60</td>
<td>9.643</td>
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<td>45</td>
<td>9.161</td>
</tr>
<tr>
<td>4</td>
<td>190</td>
<td>60</td>
<td>12.214</td>
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</tbody>
</table>

Table 3 – Theoretical justification of acetylene flow rate on CNT yield.
which involved an analysis of variance (ANOVA) to generate empirical models for main and combined effects on CNTs yields. The factorial design of experiment and its analysis was carried out in Minitab statistical analysis software. The overall evaluation of the statistical factorial analysis is that the growth temperature and acetylene flow rate are significant having p-values of 0.000 (100% confidence level) and 0.043 (95.7%) respectively. Growth time and argon flow rate were shown to be statistically insignificant at \( \alpha = 0.05 \). The Minitab-generated plot of effects showing the significant and non-significant factors at \( \alpha = 0.05 \) is presented in Fig. 11.

The estimated coefficients generated from factorial analysis were used to obtain the regression model in coded variables as follows;

\[
\text{Yield} = 0.9506 + 0.0044B - 0.0281C + 0.0481D \\
- 0.0094AB + 0.0156AC - 0.0131AD - 0.0169BC \\
- 0.0406BD - 0.0331CD
\]  

where \( A = \text{time (min)} \), \( B = \text{temperature (°C)} \), \( C = \text{argon flow rate (ml/min)} \), and \( D = \text{acetylene flow rate (ml/min)} \). It can be generally deduced from the estimated effects of this empirical model that time and acetylene increased the yield hence these have positive effects on MWCNTs yield. Whereas temperature and argon flow rate reduced the yield, that is, these have negative effects. The model was re-analyzed using only the two factors (temperature and acetylene flow) that are statistically significant at \( p < 0.05 \) to generate a linear model which relates MWCNTs yield to temperature and acetylene flow. The R-square and the adjusted R-square are very close (difference less than 4%) and temperature was the most statistically significant. The ANOVA result is presented in Table 4.

P-value of acetylene flow rate improved to 0.043 because the model has been reduced to factors with significant effects. The reduced empirical model equation that predicts the dependence of yield on significant CVD synthesis parameters as obtained from Minitab ANOVA in coded variables is given as in Equation (5);

\[
\text{Yield} = 0.9506 + 0.0044B - 0.2131D
\]  

Numerical optimization of Equation (5) for the yield otherwise called response optimization attained a global solution of 162.375% maximum predicted yield at growth conditions of 45 min time, 700 °C temperature, 190 ml/min acetylene flow rate, and 230 ml/min argon flow rate; having desirability of 0.947774. This corresponds to growth parameters of experimental run 2. Further, in order to investigate the nature of relationship between the CVD parameters and yield of nanotubes, surface plots of all four variables were generated in Minitab as function of CNT yield using their two-way interaction effects (Fig. 12).

The surface plots presented in Fig. 12(a,d,e,f,g,j,k,l) are evidence that many of the interaction effects behaved non-linearly and so, were unable to be handled by Minitab ANOVA which is a linear model analysis of variance. A high level optimization of CVD-parameters for CNTs growth would
therefore require three levels (low, mid and high) rather than the two levels considered in the full factorial experimental design, in order to establish the significance or otherwise of the non-linear factors that were ignored by Minitab ANOVA. Presented in Table 5 is a comparative analysis between the CNTs yield obtained in the present study with that reported by previous authors in acetylene CVD and other gas mixtures.

It can be observed in Table 5 that CNT yields higher than that obtained in this work were reported by previous authors due to nature of catalyst employed (Yardimci et al., 2015; Cheng et al., 2006), type of carrier gas and its flow ratio to the flow of precursor (Cheng et al., 2006; Kathyayini et al., 2004; Mhlanga and Coville, 2008; Mhlanga et al., 2009; Motchelaho et al., 2011), or increased quantity of catalyst used (Motchelaho et al., 2011). The table also shows that CVD reactor-related factors such as the reactor geometry and position of the catalyst could affect CNTs yield due to variation in temperature profile within the different systems used by the authors (Mhlanga and Coville, 2008; Mhlanga et al., 2009; Motchelaho et al., 2011). Nonetheless, it is difficult to compare between the present study and the ‘large-scale production’ of Couteau et al. (2003) because of wide variation in process parameters considered. Generally, the use of argon as carrier gas in the present study could be largely responsible for its yield disparity from results of previous studies.

Purified and as-synthesized CNTs were characterized by various techniques. The CNTs produced in this study using Fe–Co/CaCO₃ catalyst were analyzed for their morphology, thermal behaviour, crystallinity, particle size, and surface properties. Irrespective of the method used to make CNTs, the CNTs are always produced with a number of impurities whose type and amount depend on the technique used. Most of the CNTs synthesis methods produce powders which contain only a small fraction of CNTs and also other carbonaceous particles such as nanocrystalline graphite, amorphous carbon, fullerenes and different metals (typically Fe, Co, Mo or Ni) that were introduced as catalysts during the synthesis. These impurities interfere with most of the desired properties of CNTs and cause a serious impediment in detailed characterization and applications. Therefore, one of the most fundamental challenges in CNT research is the development of efficient and simple purification methods. Most common purification methods are based on acid treatment of synthesized CNTs. There are many suggested methods for CNTs purification but no purification method that fulfils all the requirements for technical processing is currently available (Motchelaho et al., 2011). The nature of the impurities depends on the synthesis method, reaction time, type of catalyst, catalyst support and carbon source employed. In this study, the as-synthesized CNTs were purified using 100 ml of 30% H₂SO₄ per 1 g of CNT sample. In order to evaluate the purity of the CNTs produced, the SEM/EDS images of purified and as-synthesized samples were collected and are presented in Fig. 13(a)–(d) for easy comparison.

The EDS as presented in Fig. 13 revealed that CaO, CaCO₃, and amorphous carbon in the un-purified CNTs were effectively removed by the H₂SO₄ purification process. But Fe and Co metallic components were not completely removed. As-synthesized nanotubes have purity of about 81 wt % C, while the purified samples are about 90 wt % C. As shown in the SEM micrograph, globular particles found at the ends of the as-synthesized CNTs are the Fe and Co catalyst, being partially removed in the purified material. In the H₂SO₄ acid treatment to remove the residual CaCO₃ and CaO catalyst from as-grown

---

Table 4 – ANOVA on significant factors.

<table>
<thead>
<tr>
<th>Term</th>
<th>DF</th>
<th>Seq SS</th>
<th>Adj S</th>
<th>Adj MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>1</td>
<td>0.72676</td>
<td>0.72676</td>
<td>0.72676</td>
<td>99.16</td>
<td>0.000</td>
</tr>
<tr>
<td>C₂H₂ (ml/min)</td>
<td>1</td>
<td>0.03706</td>
<td>0.03706</td>
<td>0.03706</td>
<td>5.06</td>
<td>0.043</td>
</tr>
<tr>
<td>Error</td>
<td>13</td>
<td>0.09528</td>
<td>0.09528</td>
<td>0.00733</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>15</td>
<td>0.85909</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R-Sq = 88.91% R-Sq (adj) = 87.20%.
Fig. 12 – Bi-factor Yield-control of MWCNTs at low/high settings of two other factors held constant.
CNTs, formation of an insoluble calcium sulphate (CaSO₄) was identified as a disadvantage of H₂SO₄ purification when CaCO₃ is used as catalyst support. But, this was carefully handled in the present study. The insoluble CaSO₄(s) precipitates out of solution and was easily decanted away from top layer together with some light carbonaceous substances. Also, Fig. 13(b) shows that the CNTs are cut after purification and its ends were opened, which is one of the disadvantages of the acid purification methods. The methods often open the ends of CNTs, cut CNTs, and damage the surface structure of the CNTs.

The SEM characterization was used to study the effects of the four CVD parameters on quality of CNTs produced. Therefore, six as-synthesized CNTs were systematically selected as presented in Table 6 such that the effects of individual growth parameters can be conveniently investigated.

![Fig. 13](image_url)  
*Fig. 13 – SEM of (a) as-synthesized CNT, (b) purified CNT; and EDS of (c) as-synthesized CNT showing presence of impurities, 80.8 wt % C, (c) purified CNTs showing 92.29 wt % C.*

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursor and gas mixture, composition in (ml/min) in brackets</th>
<th>Yield (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–Co/CaCO₃ (0.5 g)</td>
<td>Acetylene (190) in Argon (230), at 700 °C for 60 min</td>
<td>170</td>
<td>This work</td>
</tr>
<tr>
<td>Co–Mo/MgO (15 mg)</td>
<td>Methane (50) in Hydrogen (200), at 950 °C for 40 min</td>
<td>1526</td>
<td>Yardimci et al. (2015)</td>
</tr>
<tr>
<td>Fe–Co/nano-CaCO₃ (0.3 g)</td>
<td>Acetylene (100) in Nitrogen (300), at 750 °C for 20 min</td>
<td>283</td>
<td>Cheng et al. (2006)</td>
</tr>
<tr>
<td>Fe–Co/CaCO₃ (50 mg)</td>
<td>Acetylene (30) in Nitrogen (1167)°, at 720 °C for 30 min</td>
<td>30b</td>
<td>Couteau et al. (2003)</td>
</tr>
<tr>
<td>Fe–Co/CaCO₃ (0.5 g)</td>
<td>Acetylene (30) in Nitrogen (300), at 700 °C for 60 min</td>
<td>358</td>
<td>Kathyayini et al. (2004)</td>
</tr>
<tr>
<td>Fe–Co/MgO (0.5 g)</td>
<td>Acetylene (30) in Nitrogen (300), at 700 °C for 60 min</td>
<td>229</td>
<td>Kathyayini et al. (2004)</td>
</tr>
<tr>
<td>Fe–Co/CaCO₃ (0.2 g)</td>
<td>Acetylene (90) in Nitrogen (240), at 700 °C for 60 min</td>
<td>1215</td>
<td>Mhlanga and Coville (2008); Naseri et al. (2010)</td>
</tr>
<tr>
<td>Fe–Co/CaCO₃ (1.0 g)</td>
<td>Acetylene (90) in Nitrogen (240), at 700 °C for 60 min</td>
<td>250c</td>
<td>Motchelaho et al. (2011)</td>
</tr>
</tbody>
</table>

* Converted from (70 l/h).  
° Yield was 100 g/day (continuous-wise mass production).  
°° Converted from experimental yield of 3.5 g reported by the author.
The factorial experimental run 10 which showed the highest yield from the numerical optimization was used as a basis of comparison with five other experimental runs. In terms of growth parameters, experimental run 10 differs from run 2 by synthesis time, run 9 by acetylene flow rate, run 12 by argon flow rate, and run 14 by reaction temperature. Experimental run 7 was also considered for comparison with run 10 because it showed the least yield in the factorial experimental design.

The CNTs were analyzed by Scanning electron microscopy (SEM) in order to study the morphology, alignment, density of tubes, and purity of tube bundles. The SEM results revealed that all CNTs produced in this study exhibited branching tubes. Because either of quantitative or qualitative optimization seeks different goals, comparisons were made between the SEM images of samples of highest yield (run 10) and lowest yield (run 7), both purified and as-synthesized as presented in Fig. 14.

The two CNT samples varied in terms of growth parameters that were studied in this work: time, temperature, acetylene, and argon flow rates. While sample 10 was grown at 700 °C, 60 min, 190 ml/min acetylene flow rate and 230 ml/min argon flow rate; sample 7 was grown at 750 °C, 45 min, 150 ml/min acetylene flow and 290 ml/min argon flow rate. The SEM image of as-synthesized sample 7 in Fig. 14(b) showed that the high reaction temperature of 750 °C used in CNTs-growth reduced its quality as can be seen in its fibrous nature. It also contains some carbonaceous substances which are due to self-pyrolysis of the MWCNTs at the high temperature. The growth of noodles also caused diameter-irregularity along the tubes. Again, it can be observed from Fig. 14(d) that the high temperature has caused MWCNTs of run 7 to possess larger diameters than run 10. The increase in CNTs diameter due to high growth temperature in acetylene CVD is consistent with various literature reports (Bandow et al., 1998; Lee et al., 2001; Kaatz et al., 2006). Nanotubes of run 10 are more aligned as they stand erect especially after purification (Fig. 14(a) and (c)). Further, the SEM results revealed that run 10 MWCNTs were modified by the H_2SO_4 acid treatment where tubes were cut, CNT ends were opened and surface structure of the CNTs were partly damaged. But, the fibrous run 7 MWCNTs are able to withstand alterations from the acid treatment (Fig. 14(d)).

| Table 6 – Selected experimental runs and their growth parameters. |
|------------------|------------------|------------------|------------------|
| Run              | CVD reaction parameters | Morphology (SEM) |
|                 | Temp (°C) | Time (min) | Acetylene (ml/min) | Argon (ml/min) |
| 10 As-synth.     | 700       | 60         | 190               | 230             | Fig. 14(a) |
| 7 As-synth.      | 750       | 45         | 150               | 290             | Fig. 14(b) |
| 2 As-synth.      | 700       | 45         | 190               | 230             | Fig. 14(b) |
| 9 As-synth.      | 700       | 60         | 150               | 230             | Fig. 14(b) |
| 12 As-synth.     | 700       | 60         | 190               | 230             | Fig. 14(b) |
| 14 As-synth.     | 750       | 60         | 190               | 230             | Fig. 14(b) |

Fig. 14 – SEM image of (a) as-synthesized run 10, (b) as-synthesized run 7, (c) purified run 10, and (d) purified run 7 MWCNTs.
Hence, quantitatively and qualitatively, the growth parameters used for run 10 seems to have resulted in better morphology-CNTs compared to run 7. The influence of process parameters on morphology of MWCNTs was also studied using the results of SEM analysis. This was carried out by investigating the qualitative effects of CNTs growth parameters on morphology of the as-synthesized nanotubes. It was done for all four variables according to the selection in Table 6.

3.6. Effect of growth time on morphology

Experimental runs 10 and 2 were used to study the effect of synthesis time on morphology of the MWCNTs produced by CVD. The same growth parameters of 700 °C temperature, 190 ml/min acetylene flow rate, and 230 ml/min argon flow rate was used to grow both MWCNT samples, but at different growth duration. Sample 10 was obtained at 60 min while sample 2 was obtained at 45 min. The SEM results of as-synthesized run 10 and run 2 MWCNTs are compared in Fig. 15.

As revealed by the SEM images, the effect of growth time on MWCNT morphology seems to be on the aspect ratio and the tube density. This agrees with observations made by Kara et al. (2011) who investigated the effect of gas flow rate and synthesis time on CVD-MWCNT-growth using methane, methanol and ammonia gas with nickel catalyst. Their SEM images revealed that the growth time mainly affected CNT length and density. Mhlanga (2009) also reported that shorter reaction times tend to yield higher quality CNTs with higher aspect ratios compared to longer times. But, this is contrary to Chiwaye et al. (2014) & Kaatz et al. (2006) who reported that longer time increases the diameter of nanotubes either due to nanocrystalline carbon sheath that expands exponentially with time or as a result of continued carbon deposit on the formed CNT. However, in the present study, the MWCNTs of experimental run 2 have higher aspect ratio compared to run 10 samples but it contains much amorphous materials that were not burnt off at the lower time. Run 10 samples have higher tube density.

3.7. Effect of acetylene flow rate on morphology

In order to investigate the morphology-dependence of MWCNTs on acetylene flow rate, samples of experimental run 9 were obtained using a lower acetylene flow rate of 150 ml/min which varied it from run 10 that was grown at higher acetylene flow rate of 190 ml/min. Fig. 16 compares the SEM images of both samples.

Fig. 16(b) showed that low acetylene flow rate resulted in deformed tubes and incomplete growth as the gaseous reactant was not accessible to many catalyst particles. Sufficiently long, uniform and denser nanotubes were obtained at higher acetylene flow rate as exhibited by run 10 MWCNT samples (Fig. 16(a)). Except for a bigger abnormal tube observed in run 9 nanotubes sample, run 10 MWCNTs have larger diameters than run 9 tubes due to higher acetylene flow rate. This agrees with the work of Kara et al. (2011) who found that increasing gas flow rate caused increase in the diameter and density of nanotubes.

3.8. Effect of argon flow rate on morphology

Using the same reaction conditions as in experimental run 10, the MWCNTs of run 12 were grown at argon flow rate of 290 ml/min, which distinguished it from run 10 samples that were grown with 230 ml/min argon flow rate. Fig. 17 compares the SEM images of both samples so as to investigate the effect of argon flow rate on MWCNTs morphology.

Argon was responsible for the branching of tubes that are present in the MWCNTs which increased at the higher argon flow rate of 290 ml/min. The MWCNTs possess branching due to the C2H2/argon gas mixture used in their growth. Other types of carrier gases are known to yield different CNTs structures. For instance, the mixture of C2H2/N2/H2 has been reported to form bamboo-like, while C2H2/H2 tends to produce dome-capped nanotubes (Yap et al., 2004). The SEM images in Fig. 17 showed that the increase in flow rate of argon gas from 230 ml/min (run 10) to 290 ml/min (run 12) resulted in MWCNTs with larger diameter. This observation can be explained by the widely-accepted dissociative adsorption mechanism of C2H2 on metal nanoparticles and subsequent vapour-liquid-solid model. Yap et al. (2004) established that a balance between carbon decomposition and its desorption rate favours the growth of high-density, vertically-aligned MWCNTs. In this context, carrier gases can either suppress or enhance the decomposition rate of acetylene but in the case of argon, the dilution of acetylene by more argon gas has been reported to favour this balance. In the absence of argon gas, a

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Fig. 15 — SEM of (a) as-synthesized run 10, and (b) as-synthesized run 2 MWCNTs.
thicker carbon deposit occurs due to excessive adsorption and decomposition of C_{2}H_{2} on the surfaces of metal nanoparticles. The formation of a carbon layer on the surface of catalyst particles can prevent further contact of C_{2}H_{2} molecules with metal catalysts, resulting in termination of CNT growth. In this case, the decomposition rate of C_{2}H_{2} was higher than both the carbon diffusion rate into the metal nanoparticles and the desorption rate of carbon from the nanoparticles. But, in the presence of argon as carrier gas, the addition of the gas dilutes the acetylene in the growth chamber. This reduces the
coverage and number of acetylene molecules on the surface of catalyst metal nanoparticles, hence the rate of carbon diffusion and carbon desorption was balanced for continued growth.

3.9. Effect of temperature on morphology

The effect of temperature on morphology was studied by varying the growth temperature between 700 °C (for run 10) and 750 °C (for run 14) while keeping other parameters
constant. Presented in Fig. 18(a) and (b) are the SEM images of run 10 and run 14 CNTs samples for proper comparison.

It can be observed from Fig. 18 that the temperature of 750 °C was not favourable for the growth of good quality MWCNTs as the products were fibrous, twisted and lack diameter-uniformity along the tubes. Apart from the deformations, tube bundles also exhibited different diameter width some of which are larger than the diameter of run 10 nanotubes sample. The diameter-increase with growth temperature agrees with the observations in previous studies. The cloudy nature of Fig. 18(b) is evidence of carbonaceous materials that are result of self-pyrolysis of the MWCNTs at 750 °C.

Further, transmission electron microscopy (TEM) images of the as-synthesized and purified CNTs were obtained for more precise and accurate morphology and diameter-study of the materials. The clustered TEM images of as-synthesized CNTs produced at different conditions are presented in Fig. 19(a)–(f).

The TEM results as presented showed that the wall structures of CNTs vary, and their diameter distribution are not the same. Encapsulated metal nanoparticles are also observed along the inside diameter of the nanotubes samples (Fig. 19(b)) which were introduced by the metal catalysts used for CNTs growth. Carbon nanotubes grow by either tip or root mechanism thereby encapsulating catalyst metal nanoparticles within the tubes. This suggests how the nano sizes of the metal particles could affect the diameter of the final nanotubes. Thus, the different sizes of metals in the catalyst alloy are responsible for wide diameter distributions of nanotubes. The nanotubes have varying outer diameter and wall structures due to different sizes of catalyst metal nanoparticles, growth conditions, or insufficient growth time to complete a uniform growth of walls throughout the sample. SEM and EDS results previously presented have also shown that the metal particles are not removed from CNTs even after acid purification process. Another important observation is the large cluster of catalyst particles found in Fig. 19(f) which is an agglomerate of metal and mainly CaCO3 support material. The as-synthesized CNTs contained significant amount of the residual catalyst, impurities, and amorphous forms of carbon. While the catalyst support material can be removed by acid treatment, it was difficult to remove the metal particles by the acid purification method. The location of the metals inside the tubes also poses a challenge to the CNTs purification process.

The TEM image presented in Fig. 20(a) confirms how concentric tubes of hexagonal graphite are arranged to form MWCNTs. In addition, Fig. 20(b–d) show that the numbers of walls vary in the CNTs samples depending on their growth conditions. While some of the CNTs samples exhibit regular wall structures (Fig. 20(d)), some other samples have deformations due to influence of growth conditions (Fig. 20(a–c)).

The TEM images of purified MWCNTs samples 10 and 7 were studied for their diameter distribution as shown in Fig. 21(a) and (b). Diameter distribution is one of the primary factors that determine the possible area of applications of nanomaterials. For instance, sizes of nanoparticles required for drug delivery nanostructures in cancer/tumor treatments are to be essentially greater than the intercellular gap of the healthy tissue but smaller than the pores found within the tumor vasculature (Patel et al., 2012). Small-diameter MWCNTs with a narrow diameter distribution have are also known to be more suitable for industrial mechanical reinforcement and polymer-composite applications. In the present study, CNTs sample 10 which showed the highest yield
were produced at growth temperature of 700 °C while sample 7 nanotubes with the least yield were produced at 750 °C. The TEM and SEM images earlier presented have shown that sample 7 MWCNTs have larger average diameter compared to sample 10 nanotubes because of differences in their growth temperature.

Results as presented revealed that the diameter distributions of the two samples differ. Temperature conditions of 700 °C used in producing sample 10 MWCNTs favoured the growth of smaller diameter CNTs compared to growth temperature of 750 °C applied in producing sample 7 nanotubes. The result also implies that the diameter distribution can be controlled by CVD growth parameters.

The TEM/EDS of CNTs as obtained from TEM analysis and its corresponding elemental analysis which was taken from SEM/EDS data were compared as presented in Fig. 22(a)–(h) for purified CNTs samples 10 and 7, and as-synthesized samples 10, 7, 2, 9, 12, and 14. While the TEM/EDS gives qualitative

**Fig. 20** – TEM image evidence of multiple walls, (a) concentric tubes from tip (as-synthesized run 12), (b) several walls (as-synthesized run 10), (c) several (as-synthesized run 7), and (d) as-synthesized Run 12 MWCNTs.

**Fig. 21** – Diameter-size distribution of purified MWCNTs (a) run 10, and (b) run 7.
Fig. 22 – TEM/EDS elemental compositions of MWCNTs (a) purified 10, (b) as-synthesized 10, (c) purified 7, (d) as-synthesized 7, (e) as-synthesized 2, (f) as-synthesized 9, (g) as-synthesized 12, and (h) as-synthesized 14.
information on the elements present in the CNTs samples, the SEM/EDS microanalysis corroborates the TEM/EDS graph by giving the exact amount of each element that is present.

Results as presented in Fig. 22 showed that C, O, S, Ca, Fe, Co, and Cu were present in the MWCNTs in varying amounts. Purified sample 10 (Fig. 22(a)) and sample 7 (Fig. 22(c)) contained mainly C, and small amounts of Fe, Co, and S. The presence of Sulphur in purified CNTs sample is attributed to the H₂SO₄ acid used in purification. Iron and cobalt are found in all purified and as-synthesized CNTs because metal catalysts cannot be removed by acid treatment. The as-synthesized MWCNTs contain metal catalysts (Fe and Co), Ca, O, and mainly, C. The compositions of the as-synthesized samples suggest the possible presence of CaCO₃, CaO, and oxides of Fe and Co metals. However, it is important to note that the carbon contents in the purified and as-synthesized CNTs are sufficiently high, ranging from 84 to 97.77%.

The TEM images of nanotubes from selected area of the clustered MWCNTs samples are presented in Fig. 23(a)-(f). The TEM results of as-synthesized CNTs further confirm the elemental compositions shown by the EDS result of Fig. 22, especially as it reveals the presence of encapsulated metals in all samples.

It can be seen from the TEM image presented in Fig. 23(a) that the CNTs produced at 700 °C has smaller average diameter of about 25 nm compared to CNTs sample of Fig. 23(b) that has average diameter of 40 nm because of increase in growth temperature from 700 °C to 750 °C. A comparison between (a) and (c) shows that both have similar diameter of 25 nm, an indication that the difference in growth time from 45 to 60 min had no significant effect on diameter of CNTs. Because sample 9 nanotubes were grown with lower acetylene flow rate of 150 ml/min than the 190 ml/min used in producing sample 10, lower-diameter MWCNTs of about 20 nm as shown in 23(d), containing amorphous substances were obtained. By comparing Fig. 23(a) with 23(e), an adequate supply of acetylene, and the increase in argon flow rate from 230 ml/min to 290 ml/min favoured increase in average diameter of MWCNTs from 25 nm to 30 nm. Sample 14 MWCNTs have the largest diameters of about 60 nm because of combined influence of increase in growth temperature, synthesis time and acetylene flow rate. Corresponding selected area electron diffraction (SAED) patterns were also collected from the TEM analysis to study the phases present in the samples. The SAED patterns are presented in Fig. 24(a)-(f).

The SAED patterns of all samples confirmed the graphitic nature of MWCNTs especially the innermost ring which is due to the usual strongest reflection plane (002) of graphite. As illustrated in Fig. 24(b), the occurrence of the sharp rings at reciprocal lattice spacing (1/d) of 2.9, 4.8, 5.7 and 8.5 nm⁻¹ are in good agreement with those reported for graphite. As observed in (b), rings in all other samples are at similar distances from the zero. Corrias et al. (2007) also collected SAED pattern of MWCNTs and observed sharp rings attributable to the MWCNT at reciprocal lattice spacing of 3.1, 5.0, 6.0 and 8.5 nm⁻¹. Again, it can be observed from the SAED that the CVD reaction parameters affect the crystallinity of MWCNTs. Among all samples considered, run 10 which represented the highest yield is the least crystalline as it showed diffuse rings in its SAED pattern, which is typical of amorphous substances. The sharp rings obtained in the remaining samples are evidence of polynanocrystalline material, where each

Fig. 23 – TEM images of as-synthesized MWCNTs (a) run 10, (b) run 7, (c) run 2, (d) run 9, (e) run 12, and (f) run 14.
ring represents diffraction from crystals of similar size. The single bright spots are reflections from certain individual crystals.

X-Ray diffraction technique was used to investigate the crystallinity of the purified and as-synthesized MWCNTs. The XRD pattern of the as-synthesized MWCNTs is shown in Fig. 25. The XRD reveals the characteristic pattern of graphitized carbon and the (002) graphitic line observed around $2\theta$ of $26^\circ$ for all samples corresponds to an inter-planer spacing of about 0.343 nm which is usually attributed to graphite. This pattern also indicates a high degree of crystallinity which suggests a low content of amorphous carbon and impurities from the catalyst which are usually metal particles.

In Fig. 25, graphite walls of CNTs are identified by peak ‘C’; and residual iron carbide by peak ‘Fe3C’. Other peaks attributable to the graphitic planes of carbon have occurred at $2\theta$ of 42.5° and 44°. In order to use the X-ray diffraction technique for investigating phases that are present before and after acid purification, XRD patterns of purified MWCNTs that showed the highest and the lowest yield were collected and are shown in Figs. 26 and 27 respectively.

Further, the X-ray diffraction pattern of purified CNT samples of run 7 and 10 as shown in Figs. 26 and 27 revealed that only the characteristic graphitic peaks at $2\theta$ values of 26°, 42.5° and 44° were left behind after purification. The minor peak at 65° may be small impurities remaining in the
purified materials. It was also confirmed that CaO and CaCO₃ were removed during the purification process. However iron carbide (Fe₃C) could not be removed by acid washing since it is encapsulated inside the tube and is shielded from the acid during purification. The XRD results of the purified MWCNTs can be considered reliable considering their consistencies as presented for purified CNT samples 7 and 10 in Fig. 28.

An extended data analysis was carried out on the XRD patterns. Particle sizes of MWCNTs produced were calculated using XRD peak broadening by measuring the FWHM and applying the Debye-Scherrer equation. For this purpose, a MATLAB code was developed and the nanotubes particle size results are presented in Fig. 29(a)–(h).

The XRD-crystallite size of MWCNTs is a rough estimate of the nanotubes diameter for the area sampled. Similar to observations made in SEM and TEM results of the CNTs, the XRD crystallite sizes have also shown that the growth parameters employed in the CVD reactor played significant roles in determining the nanotubes size. It is important to note that the CNT sample 9 which showed the least average diameter in
TEM analysis of the samples has also exhibited the least crystallite size of 14.30 nm. CNTs sample of run 14 showed the largest average diameter of 60 nm in TEM analysis and biggest crystallite size of 21.56 nm. The growth mechanism of CNTs showed that the final step involves a gradual formation of graphitic carbon network which could also determine the extent of crystallization and crystal growth of the hexagonal structure. Growth conditions are responsible for final structure of the nanotubes.

The thermal behaviour of the purified MWCNT sample 10 which showed the highest experimental yield was carried out using TGA. Carbon nanotubes have characteristics TGA curve depending on gas environment, which is either nitrogen or air. The TGA was done at heating rate of 10°C/min up to temperature of 900°C under nitrogen environment. The % weight loss against temperature for the MWCNT is presented in Fig. 30.

The TGA curve showed that there is a gradual initiation of transition up to 155°C before a continuous decomposition afterwards. This gradual onset is due to nanotubes being contaminated with amorphous carbon and other types of carbonaceous impurities that oxidize at temperatures lower than that of nanotubes. Apart from this, the thermal degradation is single-step decomposition up to 900°C. The purified MWCNTs start to degrade around 200°C under nitrogen atmosphere. The maximum rate of weight loss occurred at 588.75°C and was the maximum. The DTG also indicated another decomposition temperature around 750°C. Thermal degradation kinetics of the nanotube produced in this study was carried out by fitting TGA data in Kissinger equation. The activation energy (Ea) value can be calculated using Equation (6) from the Kissinger method;

\[
\ln \frac{\beta}{T_{\text{max}}^2} = \frac{-E_a}{R} \frac{1}{T_{\text{max}}} + \ln nAR(1-a_m)^{n-1}
\]

where A is the pre-exponential factor, E_a is the apparent activation energy of the degradation reaction, R is the universal gas constant, and \( \beta \) is the heating rate. To determine activation energy by Kissinger method, the activation energy was calculated from the \( T_{\text{max}} \), the temperature at which the maximum degradation occurs for different heating rates by assuming that \( a_m \) or weight loss percentage at \( T_{\text{max}} \) is constant.

Thus, the activation energy was computed from the linear dependence of the \( \ln (\beta/T_{\text{max}}^2) \) versus \( 1/T_{\text{max}} \) plot for various heating rates and following the relationship of \( E_a = -R \times \text{slope} \). The \( E_a \) of the material was then obtained as 54 kJ/mol which represents the thermal stability of the MWCNT, but the value is lower than that obtained by Li et al. (2006). The discrepancy could be attributed to the different gas environment used. Thermal degradation studies were conducted by Li et al. (2006) in air while nitrogen was used in the present study.

Specific surface area (m²/g) of the selected samples is presented in Table 7, showing all MWCNT samples to have high surface areas. The high surface area is as a result of their nanoscale sizes. An interesting observation in the BET-surface area results is the higher surface areas exhibited by MWCNTs sample 12. Earlier SEM and TEM morphology results showed that alteration in growth time (for run 2) and argon flow rate (for run 12) revealed no significant diameter changes in the carbon nanotubes produced. Many literature have reported that the influences of these two parameters are mainly on the aspect ratio of MWCNTs.

In addition, the BET surface area result was used to estimate MWCNTs particle size. Using the literature density value of 2.1 g/cm³, the particle diameter of 10.47 nm for the purified highest-yield MWCNT evaluated by Equation (7) agrees well with the 10.7 nm obtained from analysis of XRD peak broadening.

\[
D_{\text{BET}} = \frac{6000}{(272.979 \times \frac{4}{3}) \times 2.1 \times 10^6} = \frac{6}{(272.979 \times 2.1 \times 10^6)} = 10.47 \text{ nm}
\]

(7)

For the sake of comparison, BET-total surface area, \( S_t \) (m²) was used as basis for which the monolayer capacity was calculated. It relates the BET-specific surface area (m²/g) to the total surface area (m²) and sample weight (g). Monolayer volume or capacity is the number of molecules covering the
surface of a layer that has the thickness of one molecule. The monolayer capacities of the MWCNTs obtained are presented in Table 8.

Table 8 showed that the purification process improved the surface area of the CNTs produced due to the removal of large particle-sized impurities. Sample 14 has the smallest surface area in the list. The SEM analysis of this sample earlier presented showed diameter-irregularities along the tubes, and the particle size from XRD peak broadening was largest for this sample (21.56 nm), hence establishing the poor surface area observed here. Though, it has the largest diameter among all samples, it is most likely that its tubes are the shortest. Peigney et al. (2001) also established that the surface area of MWCNTs decreases with increasing walls and nanotube diameters. However, the trend of the surface areas presented in Table 8 do not strictly obey the observation made by Peigney and co-workers (Peigney et al., 2001) because it was difficult to identify the actual sizes of MWCNT in the XRD size analysis of unpurified samples; the average sizes are affected by contribution from sizes of impurities present in varying quantities in the samples. Another reason for the discrepancy between surface area-particle size correlation in the present study and
the reported trend is that the MWCNTs exhibit different length. This explains why run 14 sample that has the least surface area but larger particle size (or diameter) is expected to have shorter length than others.

Particle size of the MWCNTs was determined by dynamic light scattering (DLS) technique. The particle size result together with the diameter of 18 nm measured from the TEM image for the purified sample 10 MWCNT as shown in Fig. 32 was used to obtain the length and aspect ratio of the nanotube sample.

Also, a correlation chart for length, diameter, and aspect ratio was developed based on Z-average diameter determined by DLS, independent of information from other characterization techniques such as TEM, SEM and XRD. Using the Z-average \( D_h \) of the sample as given by DLS, the literature values of aspect ratio of MWCNT was used to correlate length and diameter of this single CNT sample. Z-average (or hydrodynamic diameter) of the sample represents neither the length nor the diameter of the nanotube (Horiba Scientific Ltd, 2015). Equation (8) was used for the estimation of length and diameter based on these aspect ratios.

\[
D_h = \frac{L}{\ln(h_d) + 0.32}
\]

The values of aspect ratio \( L/d \), along with Z-average from DLS were substituted to obtain the corresponding lengths and diameters of run 10 MWCNT produced in the present study. This analysis gave a correlation between the aspect ratio, length and diameter for this MWCNT sample, as shown in the chart of Fig. 33.
An important application of the chart in Fig. 33 is that a reliable estimate of the length and aspect ratio of the CNTs can be made if diameter is provided from other analysis such as TEM and XRD. For the MWCNT sample under consideration, an average diameter of 18 nm was obtained from the TEM analysis (Fig. 32). This value suggests an aspect ratio (L/d) of about 600 and length of 10.7 μm, using the correlation chart (Fig. 33). The aspect ratio of 600 is low, which is evidence that the purified sample 10 nanotubes were either cut during the acid purification process or the longer growth duration of 60 min has yielded nanotubes with lower aspect ratio. Aspect ratios are important factors that determine the applicability of CNTs in various areas. It is expected that CNTs with various lengths can be used in a variety of fields, such as electronic, biological, and composite materials. Hence, the aspect ratios of purified and as-synthesized highest-yield and lowest-yield CNTs samples 10 and 7 were obtained from their DLS and TEM diameter results, and results are presented in Table 9.

Results as presented in Table 9 reveal that length and aspect ratios of CNTs are reduced after acid purification treatment. The difference in aspect ratios of samples grown at different CVD conditions also indicates that length and aspect ratios are growth parameters-dependent. The acid treatment which tends to cut CNTs during purification is one good method that could be used to control the lengths and aspect ratios of the nanotubes. The BET surface areas of acid-treated MWCNTs are usually higher than that of the pristine MWCNTs due to decrease in the MWCNT length, open-endedness, and the removal of metallic catalysts and amorphous carbon during the acid treatment. Acid treatment leads to structural alterations, particularly the length of the MWCNTs, thereby allowing the control of MWCNT aspect ratios. Using the results of quantitative and qualitative characterization of MWCNTs produced by the various combinations of CVD growth parameters that have been presented, a summary showing the distribution of MWCNTs properties as functions of the growth variables is presented in Table 10.

### 4. Conclusion

The approach of full factorial design of experiment has not been well explored in the optimization of process parameters in carbon nanotubes synthesis. The widely used fractional experiments are characterized by the potential to miss important interactions and the interactions are confounded with other effects, making it difficult to differentiate between two factors. The full factorial design accounts for all factor interactions. This present study investigated the combined influences of key process parameters on the yield and quality properties of CNTs using the statistical approach of Full factorial design of experiment, and findings from the study are summarized as follows;

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run 10 purified</th>
<th>Run 10 raw</th>
<th>Run 7 purified</th>
<th>Run 7 raw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave. diam. (nm)</td>
<td>20</td>
<td>25</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>Length (μm)</td>
<td>10.7</td>
<td>11.5</td>
<td>13.4</td>
<td>14.9</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>600</td>
<td>490</td>
<td>450</td>
<td>420</td>
</tr>
</tbody>
</table>

---

**Table 9 – Aspect ratios of CNTs samples produced.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run 10 purified</th>
<th>Run 10 raw</th>
<th>Run 7 purified</th>
<th>Run 7 raw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave. diam. (nm)</td>
<td>20</td>
<td>25</td>
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<td>Aspect ratio</td>
<td>600</td>
<td>490</td>
<td>450</td>
<td>420</td>
</tr>
</tbody>
</table>

---

**Table 10 – Quantitative and qualitative effects of CVD parameters on MWCNT growth using the quantitative optimal Fe–Co/CaCO₃ catalyst.**

<table>
<thead>
<tr>
<th>MWCNT</th>
<th>Yield (%)</th>
<th>XRD crystal. size (nm)</th>
<th>BET-surf. area, m²/g</th>
<th>Dia. (TEM), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 10</td>
<td>170</td>
<td>20.35</td>
<td>270.06</td>
<td>25</td>
</tr>
<tr>
<td>Run 7</td>
<td>24</td>
<td>19.65</td>
<td>290.13</td>
<td>40</td>
</tr>
<tr>
<td>Run 2</td>
<td>156</td>
<td>16.78</td>
<td>530.44</td>
<td>25</td>
</tr>
<tr>
<td>Run 9</td>
<td>112</td>
<td>14.30</td>
<td>285.05</td>
<td>20</td>
</tr>
<tr>
<td>Run 12</td>
<td>134</td>
<td>17.53</td>
<td>540.20</td>
<td>30</td>
</tr>
<tr>
<td>Run 14</td>
<td>50</td>
<td>21.56</td>
<td>380.44</td>
<td>60</td>
</tr>
</tbody>
</table>

* As-synthesized MWCNT samples were used.

---

**Fig. 33 – Correlation chart between the aspect ratio, length and diameter of the highest yield MWCNT sample.**
1) Multi-walled carbon nanotubes with optimum yield of 170% at experimental conditions of 60 min, 700 °C, 190 ml/min acetylene flow rate, and 230 ml/min argon flow rate was successfully produced using the synthesized Fe–Co/ CaCO₃ catalyst.

2) Reaction temperature and the flow rate of acetylene were found to have the most significant effects on the yield of CNTs.

3) During CNTs growth, the four parameters: temperature, time, argon flow rate and acetylene flow rate, were found to have effect on morphology of the MWCNTs. Temperature and acetylene flow rate mainly affected diameter while growth time and argon flow rate primarily affected aspect ratios.

4) Sulphuric acid purification of the as-synthesized CNTs proved effective, but its use in the CaCO₃-supported catalyst required the simple decantation of CaSO₄ precipitates that were formed in the reaction of residual CaCO₃ and CaO with H₂SO₄.

5) Characterization of CNTs samples synthesized at different conditions showed that highest-yield conditions do not guarantee best quality properties.

Funding

This work was supported by the Tertiary Education Trust Fund (TETFund), Nigeria [grant number TETF/DESS/NRF/FUTM-2016/STI/VOL 1].

Acknowledgements

We express our sincere thanks to the Centre for Genetic Engineering and Biotechnology (CGEB) (STEP-B centre of excellence) of Federal University of Technology Minna, Nigeria for providing support through the use of research facilities.

References


