

## Synthesis and Characterization of Diesel, Kerosene and Candle Wax Soot's

Ntaote David Shooto and Ezekiel Dixon Dikio\*

Department of Chemistry, Vaal University of Technology P. O. Box X021, Vanderbijlpark 1900, Republic of South Africa.

\*E-mail: [ezekiield@vut.ac.za](mailto:ezekiield@vut.ac.za).

Received: 4 March 2012 / Accepted: 7 April 2012 / Published: 1 May 2012

---

Diesel, kerosene and candle wax have been used as carbon sources for the production of carbon nanomaterial without a precursor catalyst. Nanomaterials formed in the process were analysed by High resolution transmission electron microscope (HR-TEM), Raman spectroscopy, scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The scanning electron microscopy and transmission electron microscopy analysis of these soot particles confirm our deduction of the soot particles as spherical nanomaterials made up of amorphous and spherically shaped carbon nanospheres with significant configuration to be identified as  $sp^2$  hybridized double walled carbon nanotubes. The size of these soot particles in the nano-range make them dangerous when inhaled.

---

**Keywords:** diesel, kerosene, candle wax, soot, nanospheres

### 1. INTRODUCTION

Diesel fuel which is obtained from crude oil by fractional distillation at a temperature range of 170 – 350°C, is a flammable and volatile product of medium toxicity [1,2]. Diesel oil has a characteristic smell and is free of any suspended materials. It is a complex mixture of individual compounds with carbon numbers between C<sub>9</sub> – C<sub>23</sub>, with most of these compounds members of the paraffinic, naphthenic or aromatic group of hydrocarbons. These three classes of compounds have different chemical and physical properties [2].

Advances in laboratory analytical equipment in the recent past [3], have resulted in the ability to undertake more sophisticated study of a wide range of substances produced from the combustion of hydrocarbons [4].

Many workers had accidentally observed carbon nanomaterials and fibers in deposits inside furnaces dealing with hydrocarbon gases [5]. These products were found growing on graphite rods, quartz tubes, ceramic tubes, fire bricks and other materials of iron, cobalt, nickel or any other material present in the reaction zone [5]. Carbon nanotubes and fibers are being fabricated by the pyrolysis of acetylene [6-8], methane [9], ethanol[10], benzene [11] and carbonization of synthetic polymers, such as polyvinyl alcohol (PVA)[12] among others. Carbon nanospheres (CNS), on the other hand, have a semi-crystalline structure which is a reflection of their unique properties of low density, high porosity, increased surface area and relatively high chemical and thermal stability [13,14]. CNS and carbon nanotubes can be made by a variety of procedures and these include numerous variations of the arc-discharge, laser ablation and chemical vapor deposition processes with inorganic metals and in some instances organometallic complexes are used as catalysts in these methods. The catalysts are generally made from metals or their salts [15].

Hydrocarbons are by far the most widespread precursors among carbon sources employed in the production of carbon nanotubes and carbon nanospheres.

Kerosene which is obtained from the fractional distillation of crude oil constitutes one of the most important fuels used in heating and as a fuel [16]. Kerosene is a complex mixture of aromatic and aliphatic hydrocarbons with carbon numbers predominantly in the  $C_9 - C_{16}$  range [17]. Many workers had accidentally observed carbon nanomaterials and fibers in deposits inside furnaces dealing with hydrocarbon gases [18].

Candle is generally composed of paraffin which is made of heavy straight-chain hydrocarbons obtained from crude petroleum oil [19,20]. Candles have been used since ancient times as a source of light and in various indoor environments [21].

Michael Faraday in 1860 [21,22] described the mechanism of the combustion taking place in a candle flame as a diffusion flame with wax serving as fuel and the wick as transport mode of the fuel by capillary forces. Crude oil based crystalline paraffin waxes are the most important waxes for industrial application. They are solid and crystalline mixtures of hydrocarbons consisting of linear n-alkane and branched *iso*- and *cyclo*-alkanes with carbon lengths ranging from  $C_{16} - C_{30}$  and higher [23-25]. Candle flames present a simple example of a diffusion flame, its burning is still complicated by the nature of its finite cylindrical wick [22].

A health problem related to candle burning is the occurrence and release of metal additives from the wick. Studies of particle emission from a steady burning single paraffin wax candle by Li and Hopke and other researchers, found the size of particles produced to be around 30 nm in diameter [21,26]. Afshari *et al* [27] measured the concentrations of particles emitted from a pure wax candle and a scented candle in a chamber and found the concentrations of particles to be 240 000 particles  $cm^{-3}$  and 69 000 particles  $cm^{-3}$  respectively [21,28]. The particles of matter emitted from candle wax flames, which are hydrocarbons in origin, are soot particles. These soot particles result from competition between soot formation and oxidation. Soot particles smaller than 300 nm are known to have a negative impact on health due to their physico-chemical properties. Studies aimed at providing information on soot characteristics, soot volume fraction and soot morphology have been carried out by several researchers [29-31].

## 2. EXPERIMENTAL

### 2.1 Materials

Diesel and kerosene used in this study was purchased from Shell garage and home use candle wax were purchased from the super market shops in Vanderbijlpark, Republic of South Africa and used without further purification.

### 2.2 Preparation of diesel, kerosene and wax carbonaceous soot

Commercial diesel and kerosene were placed in a simple laboratory lamp with a combustible cylindrical cotton material or wick. The lamps were left for 24 hrs. to enable the cotton material or wick to absorb the diesel or kerosene. The lamp were lighted with a match and allowed to burn. A flat ceramic tile plate was placed above the flame of the lamp to collect soot emitted from the lamp. Candle wax was placed in a simple laboratory fume cupboard. The candle was lighted with a match and allowed to burn. A flat ceramic tile plate was placed above the flame of the candle to collect soot emitted from the candle flame. When an amount of soot approximately equal to 5 - 10 g was collected, the experiment was terminated.

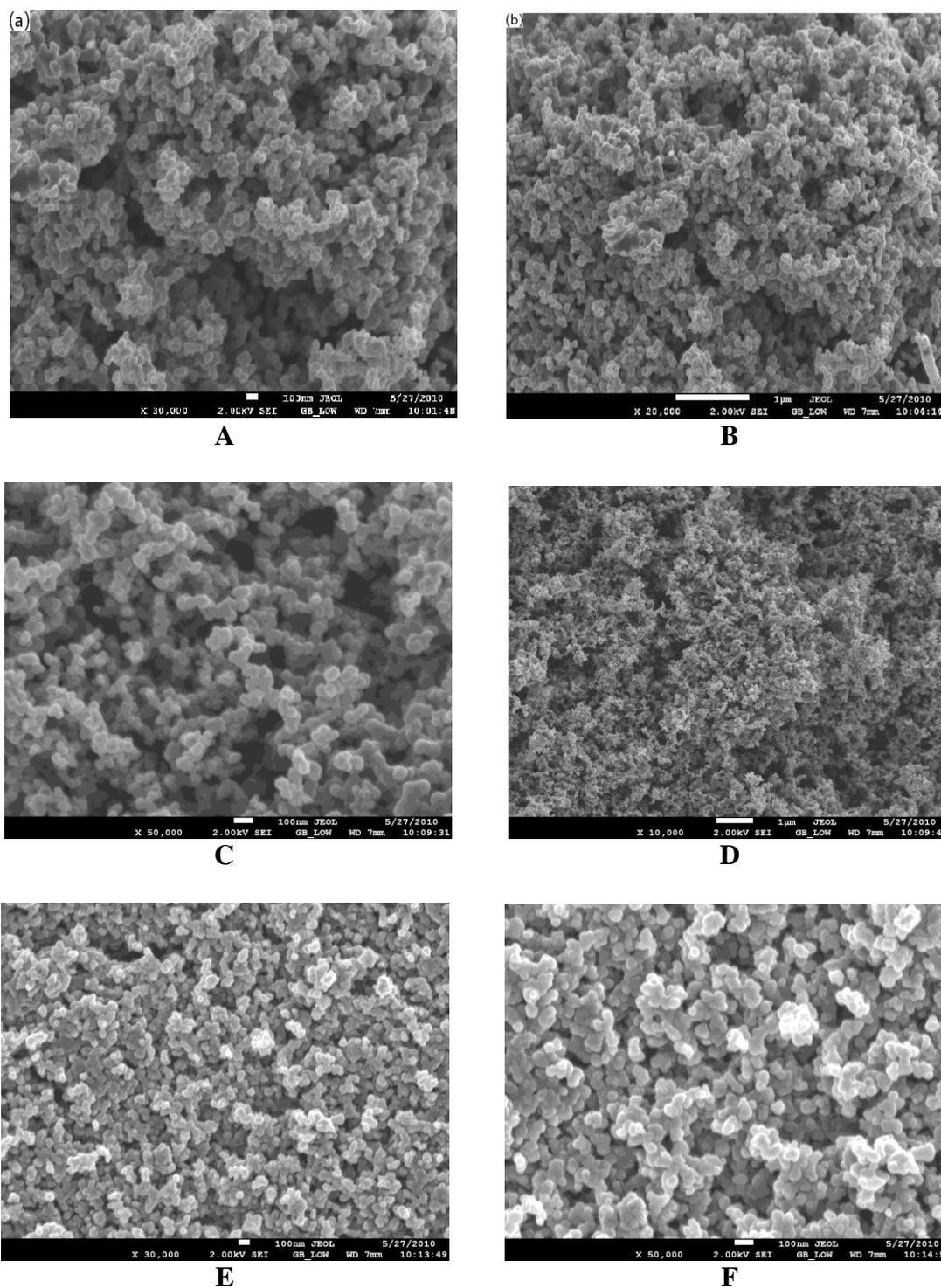
### 2.3 Apparatus and equipment

The morphological features of diesel, kerosene and wax soot were analyzed by Raman spectroscopy, FE-SEM, EDS and XRD. The Raman spectra were obtained by a Raman spectroscope, Jobin-Yvon HR800 UV-VIS-NIR Raman spectrometer equipped with an Olympus BX 40 attachment. The excitation wavelength was 514.5 nm with an energy setting of 1.2 mV from a coherent Innova model 308 argon-ion laser. The Raman spectra were collected by means of back scattering geometry with an acquisition time of 50 seconds. The surface morphology and EDS measurements were recorded with a JEOL 7500F Field Emission scanning electron microscope (FE-SEM). Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 Advanced diffractometer operated at 45 kV and 40 mA with monochromated copper  $K\alpha_1$  radiation of wavelength ( $\lambda = 1.540598$ ) and  $K\alpha_2$  radiation of wavelength ( $\lambda = 1.544426$ ). Scan speed of 1 s/step and a step size of  $0.03^\circ$ .

## 3. RESULTS AND DISCUSSION

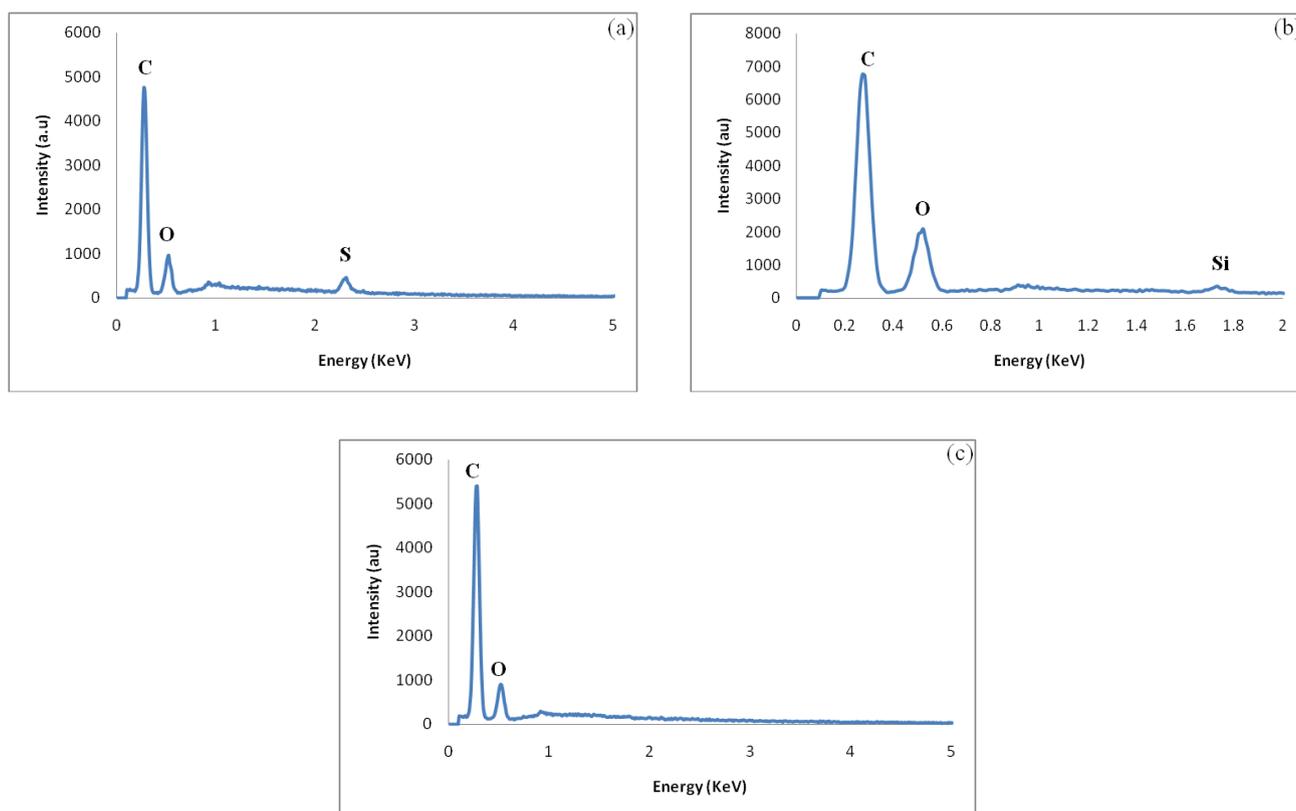
Burning of diesel, kerosene and candle wax to obtain soot is a thermal decomposition process in which the diesel, kerosene and candle wax breaks up to form other substances. The air borne thermolytic particles are extremely small and occur individually. Some particles are seen to form aggregates on the ceramic collector plate. Particles obtained from the atmospheric combustion of diesel, kerosene and wax are a complex mixture of elemental carbon, a variety of hydrocarbons, sulphur and silicon compounds and other species [32].

The FE-SEM micrograph of diesel, kerosene and candle wax thermolytic carbon nanomaterials is presented in figure 1.



**Figure 1.** Field Emission Scanning electron micrograph of carbon nanomaterial obtained from the combustion of (a-b) diesel (c-d) kerosene (e-f) candle wax.

The surface morphology of the carbon deposit obtained is seen to be non-uniform, figure 1 (a-f). There are several grains with what looks like carbon nanotubes formed in figure 1 b in diesel. The diesel, kerosene and candle wax soot particles are extremely small with a majority of the particles about 0.3  $\mu\text{m}$  in diameter. The FE-SEM image of soot particles at 100 nm and 1  $\mu\text{m}$  show particles of carbon which are chain-like agglomerations as shown in figure 1. The SEM of diesel and kerosene look more like amorphous carbon, figure 1 (a to d) compared to the SEM of wax, figure 1 e which have more grains and irregular shaped nanoparticles. These nanoparticles which could not be seen as carbon nanotubes or carbon nanospheres from the FE-SEM micrograph where observed in the Raman spectra.



**Figure 2.** Energy Dispersive Spectroscopy (EDS) of carbon nanomaterial obtained from the combustion of (a) diesel (b) kerosene and (c) candle wax.

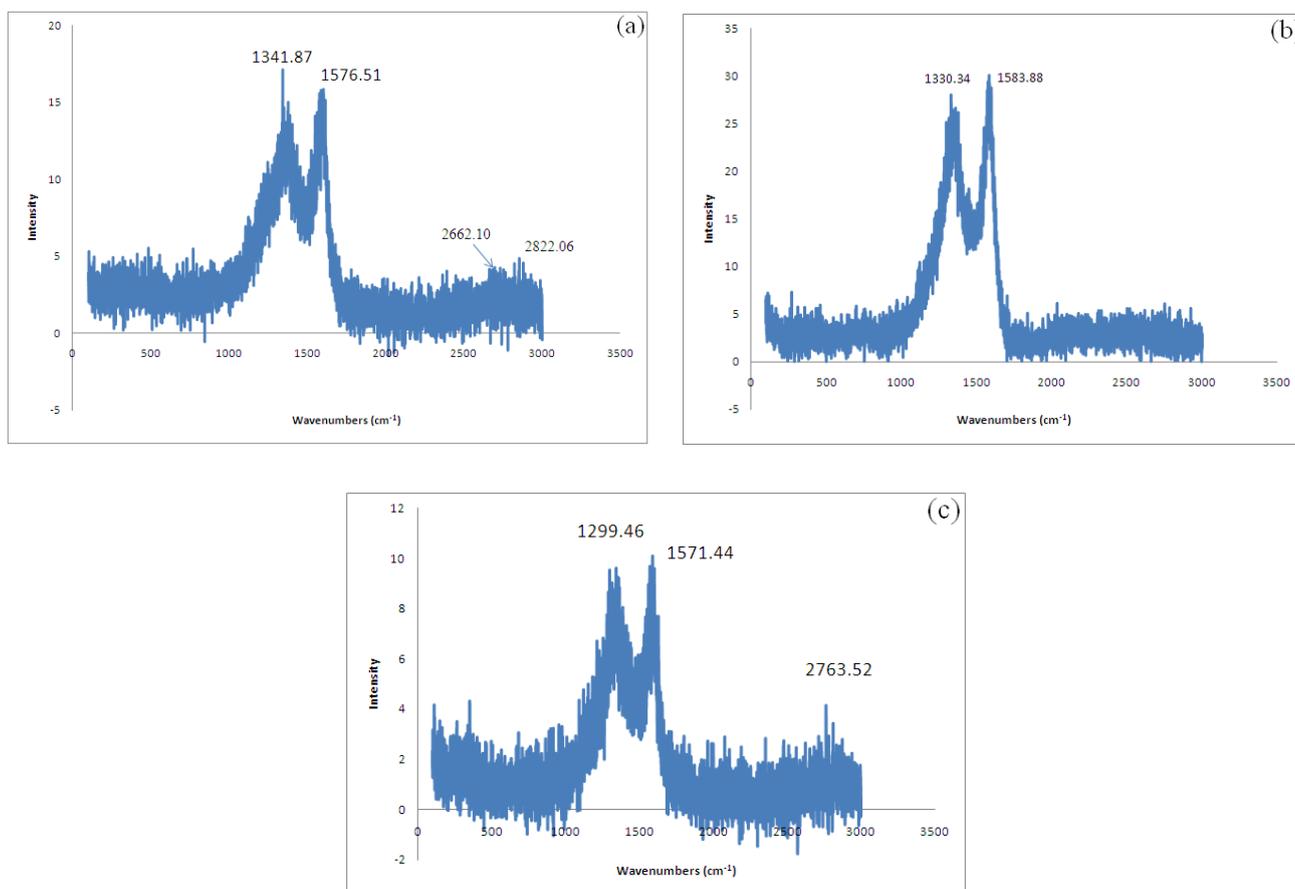
Energy dispersive spectroscopy (EDS) of diesel, kerosene and candle wax soot is presented in figure 2 and table 1. The spectra show the presence of carbon and oxygen as the combustion product of diesel, kerosene and candle wax. The composition of the soot aggregates from the EDS analysis indicates the soot to consist of about 26.77% weight carbon, 72.46% weight of oxygen and 0.77% weight of sulphur in the diesel. The soot consist of about 27.17% weight carbon, 72.63% weight of oxygen and 0.20% weight of silicon in the kerosene and consist of about 27.29% weight carbon and 72.71% weight of oxygen and in the candle wax. The result shows the product of the thermal

decomposition of diesel to be composed mainly of carbon and oxygen with a small percentage of sulphur and silicon as observed.

**Table 1.** Table of percentage weight of element and atom obtained from energy dispersive spectroscopy of diesel, kerosene and wax soot nanomaterial.

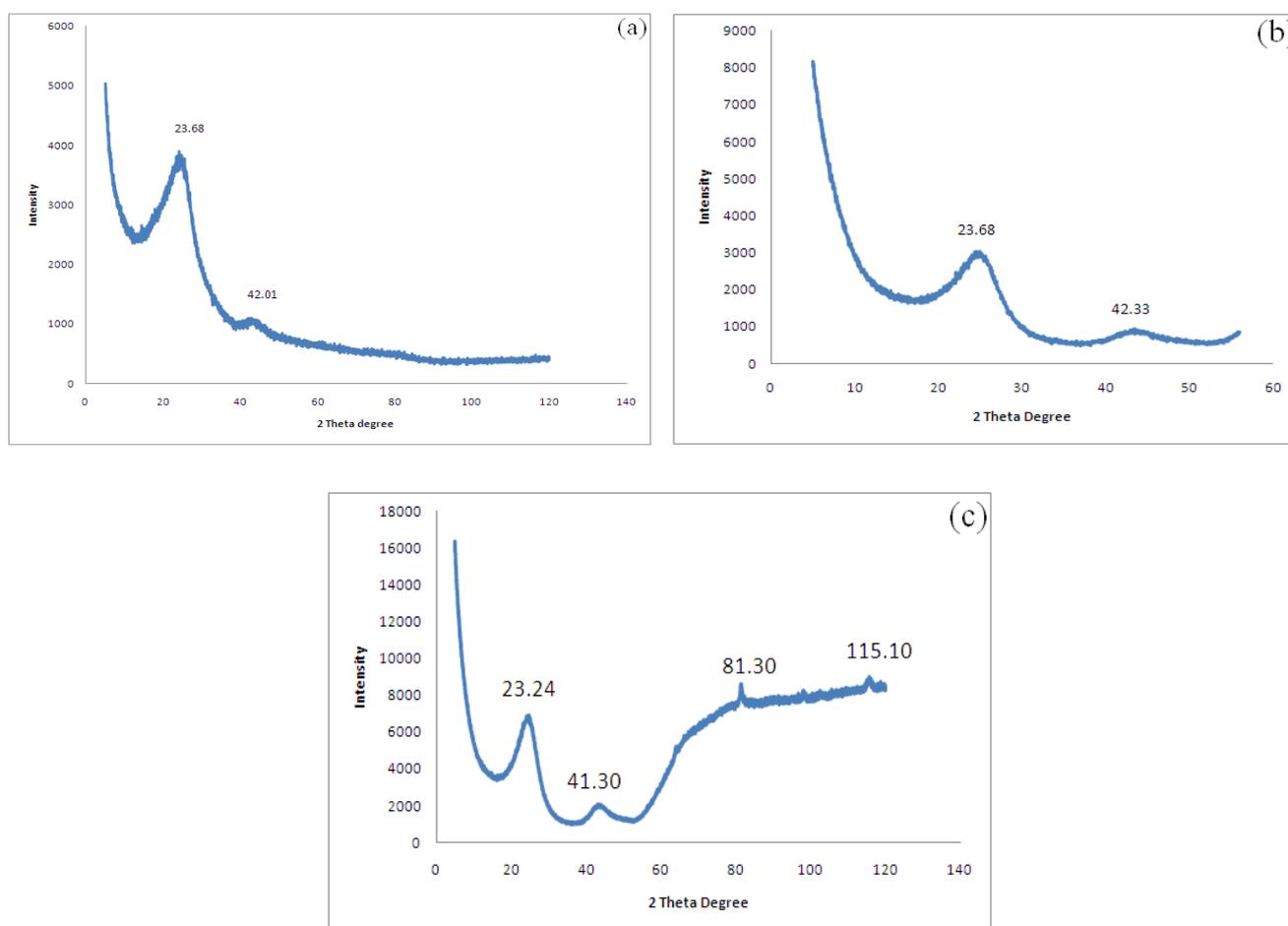
Element	Diesel			Kerosene			Wax		
	Element (% weight)	Atom (%)	Peak Height (au)	Element (% weight)	Atom (%)	Peak Height (au)	Element (% weight)	Atom (%)	Peak height (au)
Carbon (C)	26.77	32.86	4755	27.17	33.23	6765	27.29	33.33	5396
Oxygen (O)	72.46	66.78	821	72.63	66.67	1916	72.71	66.67	817
Silicon (Si)				0.20	0.11	267			
Sulphur (S)	0.77	0.35	344						
Total	100	100		100	100		100.0	100.1	

The Raman spectra of the diesel, kerosene and candle wax soot are presented in figure 3. The Raman spectra show two major bands at (1341.87, 1330.34, 1299.46)  $\text{cm}^{-1}$  and (1576.51, 1583.88, 1571.44)  $\text{cm}^{-1}$  respectively.



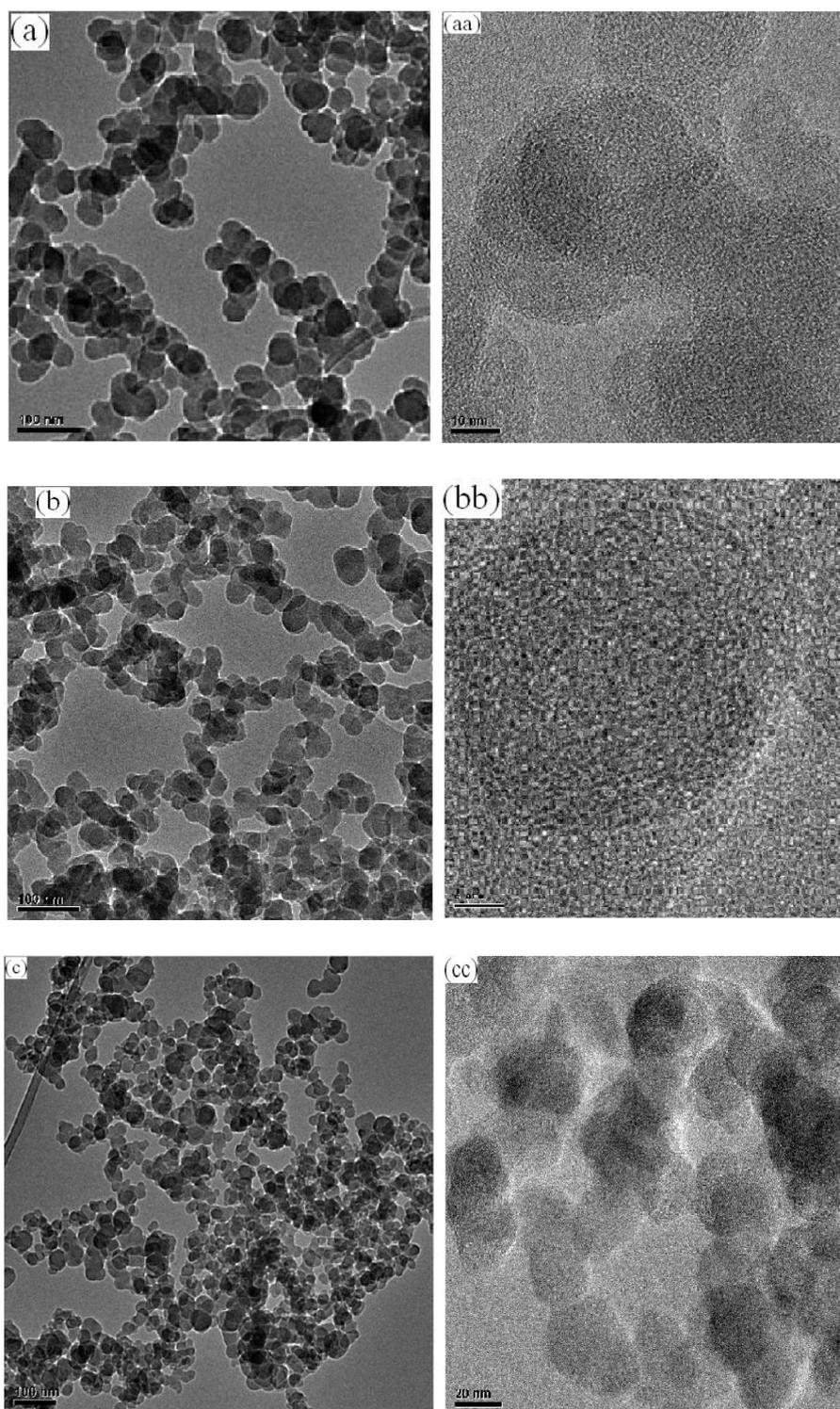
**Figure 3.** Raman spectra of carbon nanomaterial obtained from the combustion of (a) diesel (b) kerosene and (c) candle wax.

These bands are the *D* and *G* bands which indicate the presence of crystalline graphitic carbon in synthesized carbon nanotubes. The *D* band at 1341.87, 1330.34, 1299.46  $\text{cm}^{-1}$  in diesel, kerosene and candle wax has been attributed to the presence of amorphous carbon [10,33,34] and surface defects in carbon nanotubes. The *G* band at 1576.51, 1583.88, 1571.44  $\text{cm}^{-1}$  in diesel, kerosene and candle wax correspond to an  $E_{2g}$  mode of graphite which is related to the vibration of  $sp^2$ -bonded carbon atoms and the presence of ordered carbon nanotubes in a sample. The bands at 1341.87, 1330.34, 1299.46  $\text{cm}^{-1}$  of moderate intensity is associated with vibrations of carbon atoms in disordered graphite. The *D* and *G* bands should produce an overtone which resonates at about 2600  $\text{cm}^{-1}$ . The presence of this resonance peak in the Raman spectra of a CNTs synthesis could be related to the amount of carbon nanotubes produced in the synthesis as well as their purity. The absence of this resonance peak in the soot obtained from diesel, kerosene and candle wax combustion is an indication that the diesel, kerosene and candle wax soot had formed impure as well as few carbon nanotubes in the process. The intensity ratio of these two bands ( $I_D/I_G = 1.100$  in diesel,  $0.934$  in kerosene and  $0.984$  in candle wax) is also considered as a parameter to characterize the quality of CNTs in the samples under investigation.



**Figure 4.** X-Ray Diffraction (XRD) of carbon nanomaterial obtained from the combustion of (a) diesel (b) kerosene and (c) candle wax.

A high intensity ratio would indicate a higher degree of disorder in the CNTs. The intensity of the two peaks are quite high indicating that there exists two dimensional disorder in the carbon nanomaterial produced from this thermolytic process.



**Figure 5.** High Resolution Transmission Electron Microscope (HR-TEM) of carbon nanomaterial obtained from the combustion of (a) and (aa) diesel (b) and (bb) kerosene, (c) and (cc) candle wax

The X-ray diffraction (XRD) patterns for diesel, kerosene and candle wax soot are shown in figure 4. The carbonaceous soot obtained was used directly. The Bragg diffraction peaks at  $2\theta = 23.68^\circ$  and  $42.01^\circ$  in diesel,  $23.68^\circ$  and  $42.33^\circ$  in kerosene,  $23.24^\circ$ ,  $41.30^\circ$ ,  $81.30^\circ$  and  $115.10^\circ$  in candle wax are the only peaks obtained in these X-ray diffraction analysis. These two intense peaks correspond to hexagonal graphite lattice of multi-walled carbon nanotubes [20,21,35]. The peaks at  $2\theta = 23.68^\circ$  is a moderately high intensity broad peak which indicates the presence of large amounts of amorphous material in association with nanotubes. The low intensity of the peak at  $2\theta = 42.01^\circ$ , is an indication of the low quality of carbon nanomaterial present in the soot.

The HR-TEM micrograph of the diesel, kerosene and candle wax soot is presented in figure 5. HR-TEM micrograph of the carbonaceous soot at 100 and 200 nm show nanomaterials obtained from diesel, kerosene and candle wax soot as spherical individual particles. Since no catalyst was used in the production of nanomaterials from these sources, catalyst particle are absent from this HR-TEM micrograph. Morphological details indicating that the nanomaterials obtained from the atmospheric combustion of diesel, kerosene and candle wax as nanospheres, observed in the Raman spectral analysis, is further corroborated in the HR-TEM micrograph [22]. Several nanospheres have agglomerated together in the HR-TEM micrograph, figure 5 (a, b and c). Single nanoparticles of soot indicating the nanospheres to be uniform could also be observed in the micrograph. The HR-TEM micrograph, figure 5 (aa, bb, and cc) reveal lattice fringe images of graphene layers of individual nanospheres. The crystalline presentation of the layers reflects the graphitization of the nanospheres.

#### 4. CONCLUSION

Diesel, kerosene and candle wax soot's were characterized in this study with modern analytical equipment to determine the nature of soot particles. Soot particles were found to form aggregates which were spherical in their morphology. The Raman spectra obtained in this study provide information to confirm these soot's to be double walled nanomaterial as observed from their *D* and *G* bands. The energy dispersive spectroscopic analyses (EDS) of these soot particles show the presence of silicon and sulphur in substantial quantity to enable their positive identification. The scanning electron microscopy and transmission electron microscopy analysis of these soot particles confirm our deduction of the soot particles as spherical nanomaterials made up of amorphous and spherically shaped carbon nanospheres with significant configuration to be identified as  $sp^2$  hybridized double walled carbon nanotubes. The size of these soot particles in the nano-range make them dangerous when inhaled.

#### ACKNOWLEDGEMENTS

This work was supported by a research grant from the Faculty of Applied and Computer Science Research and Publications Committee of Vaal University of Technology, Vanderbijlpark.

#### References

1. D.W.E.A. Santana, M.P. Sepulveda, P.J.S. Barbiera, *J. Fuel*, 86 (2007) 911.
2. M. Al-Ghouti, Y. Al-Degs, F. Mustafa, *J. Fuel*, 89 (2009) 193.

3. W. Jambers, L. De Bock, R. Van Grieken, *J. Anal. Chem.* 355 (1996) 521.
4. R. Kaegi, L. Holzer, *J. Atm. Environ.* 37 (2003) 4353.
5. M. Kumar, P.D. Kichambare, M. Sharon, Y. Ando, X. Zhao, *Mater. Res. Bull.* 34(5) (1999) 791.
6. E.D. Dikio, F.T. Thema, C.W. Dikio, F.M. Mtunzi, *Int. J. Nanotech. Appl.* 4(2) (2010) 117.
7. E.D. Dikio, N. Bixa, *Int. J. Appl. Chem.* 7(1) (2011) 35.
8. J.T. Han, J.H. Woo, H.S. Kim, J.G. Jee, *Bull. Korean Chem. Soc.* 24(12) (2003) 1771.
9. P. Benito, M. Herrero, F.M. Labajos, V. Rives, C. Royo, N. Latorre, A. Monzon, *Chem. Eng. J.* 149 (2009) 455.
10. J. Liu, M. Shao, X. Chen, W. Yu, X. Liu, Y. Qian, *J. Am. Chem. Soc.* 125(27) (2003) 8088.
11. M. Shao, Q. Li, J. Wu, B. Xie, S. Zhang, Y. Q, *Carbon* 40 (2000) 2961.
12. W-J. Jin, H.J. Jeon, J.H. Kim, J.H. Youk, *J. Synth. Met.* 157 (2007) 454 – 459.
13. A. Nieto-Marquez, D. Toledano, P. Sanchez, A. Romero, J.L. Valverde, *J. Catal.* 269 (2010) 242.
14. M. Bystrzejewski, H. Lange, A. Huczko, P. Baranowski, H.W. Hubers, T. Gemming, T. Pichler, B. Buchner, M.H. Rummeli, *J. S. S. Chem.* 181 (2008) 2796.
15. V.O. Nyamori, S.D. Mhlanga and N.J. Coville, *J. Organomet. Chem.* 693 (2008) 2205.
16. M.P. Gomez-Carracedo, J.M. Andrade, M. Calvino, E. Fernandez, D. Prada S. Muniategui, *J. Fuel.* 82 (2003) 1211 – 1218.
17. H. Chung, M-S. Ku, J-S. Lee. *Vib. Spectrosc.* 20 (1999) 155 – 163.
18. D.N. Shooto, E.D. Dikio, *Int. J. Electrochem. Sci.* 6 (2011) 1269 – 1276.
19. S. Zai, H. Zhen, W. Jia-song, *J. Aero. Sci.* 37 (2006) 1484 – 1496.
20. O. Saber, N. Hefny, A.A. Al Jaafari, *J. Fuel. Process. Technol.* 92 (2011) 946 – 951.
21. J. Pagels, A. Wierzbicka, E. Nilsson, C. Isaxon, A. Dahl, A. Gudmundsson, E. Swietlicki, M.J. Bohgard, *J. Aero. Sci.* 40 (2009) 193 – 208.
22. P.B. Sunderland, J.G. Quintiere, G.A. Tabaka, D. Lian, C-W. Chiu, *Proc. Combust. Inst.* 33 (2011) 2489 – 2496.
23. A.K. Kuszlik, G. Meyer, P.A.M. Heezen, M.J. Stepanski, *Chem. Eng. Res. D.* 88, (2010), 1279 – 1283.
24. A.S. Luyt, K. Ishripersadh, *Thermochimica acta.* 333 (1999) 155 – 167.
25. M.T. Zaky, N.H. Mohamed, *J. Taiw. Inst. Chem. Eng.* 41 (2010) 360 – 366.
26. W. Li, P.K. Hopke, *J. Aero. Sci. Technol.* 19 (1993) 305 – 316.
27. A. Afshari, U. Matson, L.E. Ekberg, *J. Indoor Air.* 15 (2005) 141 – 150.
28. E. Gehin, O. Ramalho, S. Kirchner, *J. Atmos. Environ.* 42 (2008) 8341 – 8352.
29. R. Hadeif, K.P. Geigle, W. Meier, M. Aigner, *Int. J. Thermal. Sci.* 49 (2010) 1457 – 1467.
30. T. Hussein, T. Glytsos, J. Ondracek, P. Dohanyosova, V. Zdimal, K. Hameri, M. Lazaridis, J. Smolik, M. Kulmala, *J. Atmos. Environ.* 40 (2006) 4285 – 4307.
31. N. Takaki, H. Sekimoto, *Prog. Nucl. Ene.* 50 (2008) 114 – 118.
32. H. Burtscher, *J. Aero. Sci.* 36 (2005) 896
33. S.K. Srivastava, V.D. Vankar, V. Kumar, *J. Thin Solid Films* 515 (2006) 1552 – 60.
34. A. Eftekhari, P. Jafarkhani, F. Moztaizadeh, *Carbon* 44 (2006) 1343 – 45.
35. E.D. Dikio, *Int. J. Electrochem. Sci.* 6, (2011) 2214 – 2222.