Int. J. Electrochem. Sci., 7 **(2012)** 3215 - 3221

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Characterization of Diesel Soot from the Combustion in Engine by X-ray and Spectroscopic techniques

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Received: 26 February 2012 / *Accepted:* 23 March 2012 / *Published:* 1 April 2012

Carbon nanomaterials formed during the combustion of Diesel inside engine is characterized by X-ray diffraction (XRD) and spectroscopic techniques. The soot are collected from the Engine and washed with Acetone. Carbon Nanomaterials produced from diesel soot show the morphology of carbon nanospheres mixed with carbon nanotubes. X-ray diffraction investigation shows the presence of carbon nanotubes in association with amorphous nanomaterial. EDS analysis of Diesel soot indicates that the soot particles to be composed of primarily carbon and oxygen along with hydrogen. NMR spectrum of the soot reveals significant aliphatic component with predominance of methyl and methylene groups on β and γ positions to aromatic rings. There is significant fraction of hydrogen on the γ position at 0.864 ppm, which suggests the existence of large aliphatic chains or saturated rings joined to aromatic rings. The IR spectrum shows characteristic signals in the region 1700-1000 cm^{-1}, where the most important one correspond to C=O stretching of carboxylic acids at 1639 cm^{-1}, C=C stretching of aromatic groups at 1533 cm^{-1}, and aliphatic C-H plane deformation of CH_2/CH_3 groups at 1380 cm^{-1} and 1445 cm^{-1} respectively.

Keywords: Carbon nanospheres, diesel soot, SEM-EDS, XRD, NMR

1. INTRODUCTION

Diesel fuel in general is any liquid fuel used in diesel engines. Petroleum diesel or fossil diesel is produced from the fractional distillation of crude oil between 200 °C and 350 °C and have between 8 and 21 carbon atoms per molecule. The fragments in the diesel soot are suitable precursors for the synthesis of single walled carbon nano tubes (SWCNTs). Studies show that diesel soot contains C_{60}, C_{70} and other fullerenes. Diameter of nanotube synthesized from diesel soot is smaller than those of SWCNTs synthesized from the graphite. The types and quantities of nanoparticles can vary according to operating temperatures and pressures, presence of an open flame, fundamental fuel type and fuel

mixture. As such, the resulting types of nanoparticles from different engine technologies and even different fuels are not necessarily comparable.

Many studies reported the accidental observation of carbon nanomaterials and fibres in deposits inside furnaces dealing with hydrocarbon gases [1-3]. Carbon nanotubes and fibres are also fabricated by pyrolysis of acetylene, methane and carbonisation of synthetic polymers. Hydrocarbons are by far the most widespread precursor among carbon sources used for production of carbon nano structures. Most of these processes are unsuitable for large production of carbon nano materials or nano structures because they are expensive. There is a need to find cheap and simple technique to synthesize carbon nanomaterials. In the present study, soot deposited inside the engine of a commercial diesel vehicle is used as precursor for nanomaterial.

2. EXPERIMENTAL

2.1. Preparation of diesel carbonaceous soot

Soot deposited inside the engine was collected and leached with acetone for removing the oil content and minerals associated with the soot. It is further washed with enormous amount of water and dried in open air at temperature of 80^{o}C for 1hr.The carbon material forms in form of sticky flakes.

2.2. Characterization

The morphological features of nanomaterials were analysed by SEM, EDS, FTIR, XRD and FTNMR. The surface morphology and EDS measurements were obtained by Scanning Electron Microscope (SEM) model JSM 6390 from JEOL Company in Japan. IR spectrum was recorded using Shimadzu FTIR-8400 spectrometer in the region 3500-500 cm^{-1} with a resolution of 4 cm^{-1}. Elemental analysis was carried out using Vario EL III CHNS analyser. NMR measurements done with Bruker Avance III, 400MHz spectrometer with 1H decoupling The XRD measurements were carried out using a Bruker AXS D8 Advance X-ray Diffractometer.

3. RESULTS AND DISCUSSION

Burning of Diesel to obtain soot is a thermal decomposition process in which diesel breaks up to form other substance. The engine borne thermolytic particles are extremely small and occur individually. Some particles are seen to form aggregates. Particles obtained from the combustion of diesel are a complex mixture of elemental carbon, nitrogen, sulphur and hydrogen. The elemental analysis (CHNS-analysis) carried out on the sample reveals presence of carbon-78.37 wt%, nitrogen-0.22wt%, sulphur-2.55 wt% and hydrogen- 7.48wt% respectively.

The SEM micrograph of Diesel thermolytic carbon nanomaterials is presented in Figure.1. The surface morphology of the carbon deposit obtained is seen to be non-uniform. There are several grains

which look like carbon nanospheres. These sphere join together to form chains of spheres. This chain like structure is seen throught the surface. Majority of the particle is about 0.3µm and less. The SEM image of the soot particles at 50 µm and 10 µm show particles of carbon are of chain-like agglomeration (Figure.1 and Figure.2)

Energy dispersive spectrum (EDS) of diesel soot is presented in Figure.3. The spectra show the presence of Carbon and Oxygen as the combustion product diesel along with Sulphur and traces of Calcium and Iron in the studied surface. The soot consists of about 94.97 wt% carbon 0.78 wt% oxygen.

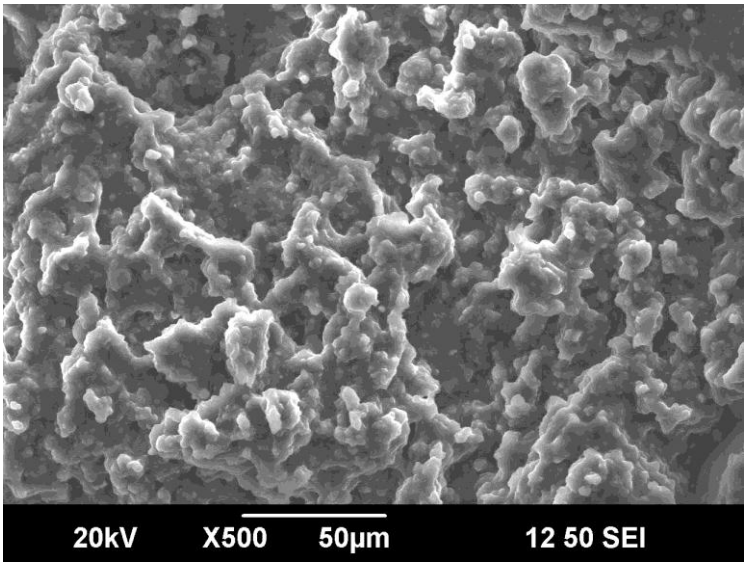

Figure 1. Scanning electron micrograph (SEM) of soot obtained from engine combustion of diesel (50µm)

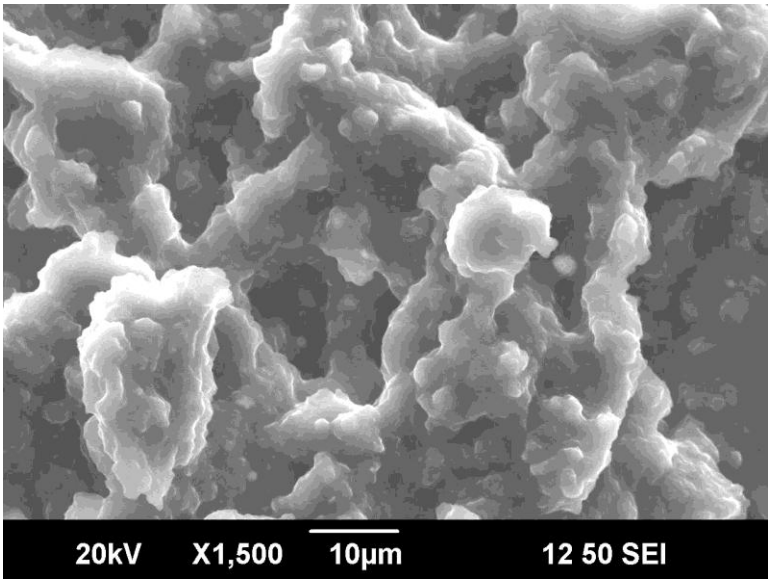

Figure 2. Scanning electron micrograph (SEM) of soot obtained from engine combustion of diesel (10µm)

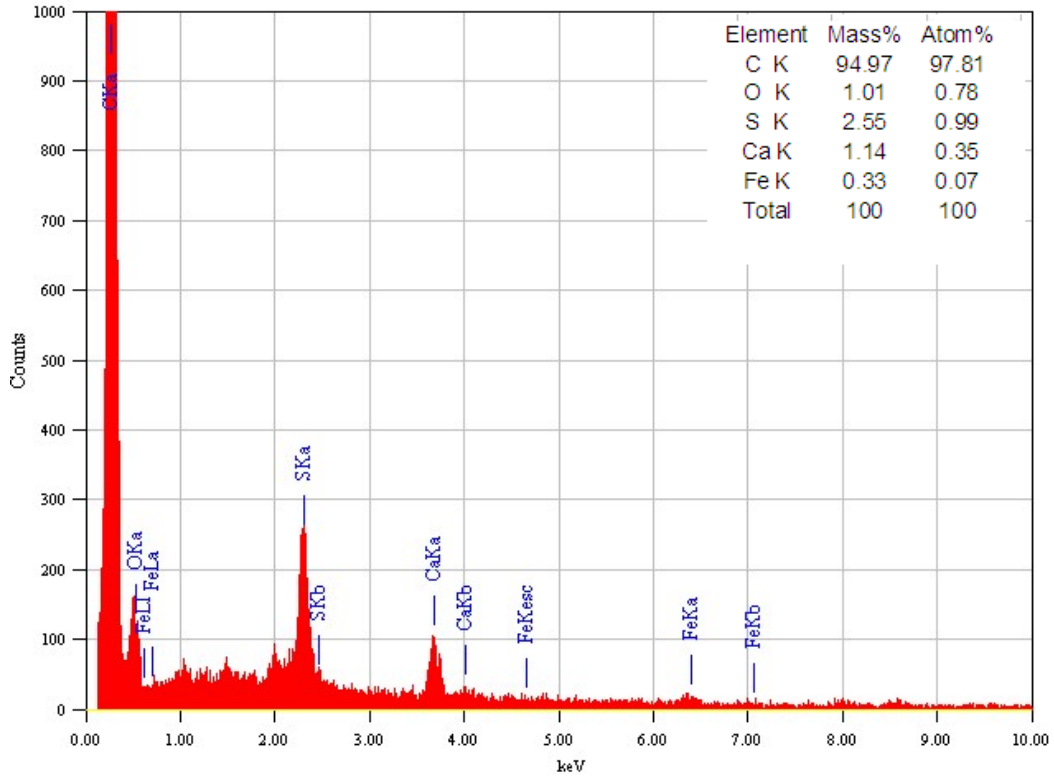

Figure 3. Energy dispersive spectroscope (EDS) spectra of soot obtained from Engine combustion of diesel

The X-ray spectrum (XRD) of diesel soot is presented in Figure.4. The spectrum shows major peaks at 19.32^o and 25.7^o. These bands are the γ and Π bands which indicate the presence of crystalline graphitic carbon in the studied sample. The γ band at ~19^o has been attributed to the presence of amorphous carbon and surface defects in carbon nanotubes [1-10]. This band is associated with aliphatic side chains in the disordered carbon atom. The Π band at ~25^o corresponds to e_{2g} mode of graphite which is related to vibration of sp^2-bonded carbon atoms and the presence of ordered carbon nanotubes in the sample.

The intensity ratio of these two peaks (I_γ/I_Π) is considered as a parameter to characterize the quality of Carbon nanotubes (CNTs) in the sample under investigation. A higher intensity ratio would indicate a higher degree of disorder in the CNTs. The intensity ratio for the two bands observed to be 1.83. This value indicates that comparatively low percentages of CNTs are formed in the Diesel soot.

Many author's reported the presence of peak at ~42.33^o to hexagonal graphite lattice of multi-walled carbon nanotubes [1-2]. Very weak peak at 42.33^o observed in the present study is an indication formation carbon nanomaterial in the soot. The mean crystallite sizes of the particles are determined using Scherrer equation [6-9]. The lateral size of the aromatic lamina (La) formed is found to be 11.7 nm where as stacking height (Lc) is found to be 8.1 nm. The d_{002}-spacing of the lamellae is found to be 3.44 A^o which is near to the value of graphite layer reported in various studies [7-8].

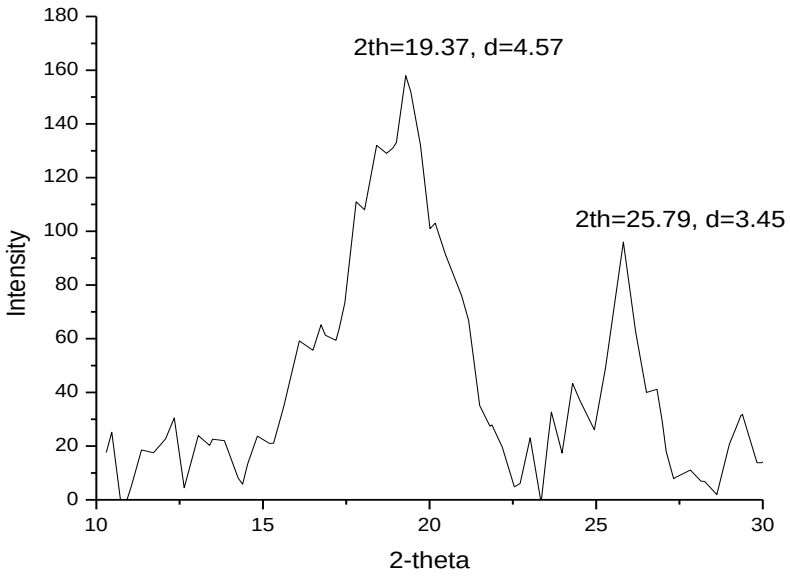

Figure 4. X-ray diffraction spectra of soot obtained from the Engine combustion of diesel

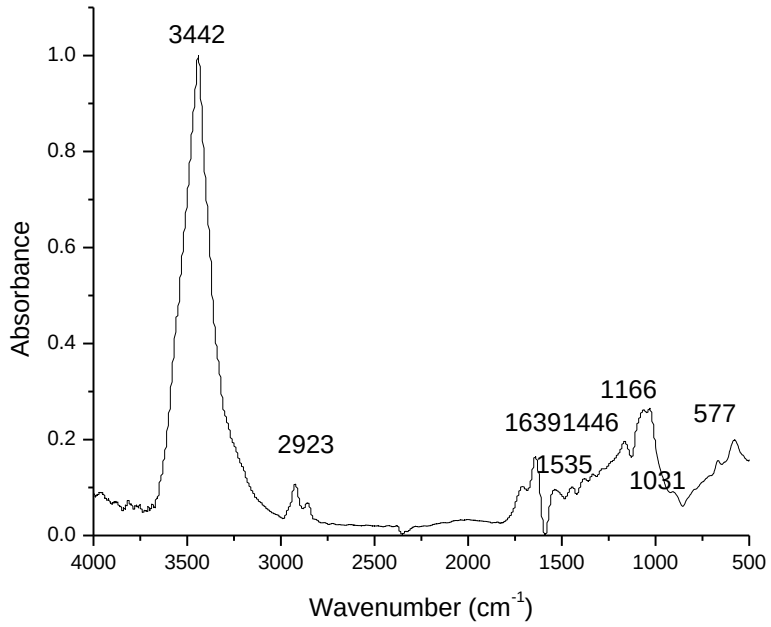

Figure 5. FTIR spectra of soot obtained from the Engine combustion of diesel

The FTIR spectrum of soot is shown in Figure 5. The assignments of these frequencies to their functional groups were carried out by comparison with the assignments reported by various authors [10-11]. The peak at 3459 cm^{-1} is attributed to N-H stretching vibrations. The peaks at 2923 and 2846 cm^{-1} are assigned as CH_2 asymmetric stretching vibration and CH_3 symmetric stretching vibration respectively. The presence of the C-H stretching in aliphatic groups comes mainly from methyl, methylene and methane groups bonded to aromatic rings.

The IR spectrum also shows other characteristic signals in the region 1700-1000 cm^{-1}, where the most important one correspond to C=O stretching of carboxylic acids at at 1639 cm^{-1}, C=C stretching of aromatic or alkene groups that appear at 1533 cm^{-1}, and aliphatic C-H plane deformation of CH_2/CH_3 groups at 1380 cm^{-1} and 1445 cm^{-1} respectively.

There is a broadening in the region 1000-1300 cm^{-1} in the spectrum. This region is a complex section of the IR spectrum, where aromatic C-C and C-H plane deformation structures appear, but the most important structure corresponds to ether C-O-C stretching groups [10-11].

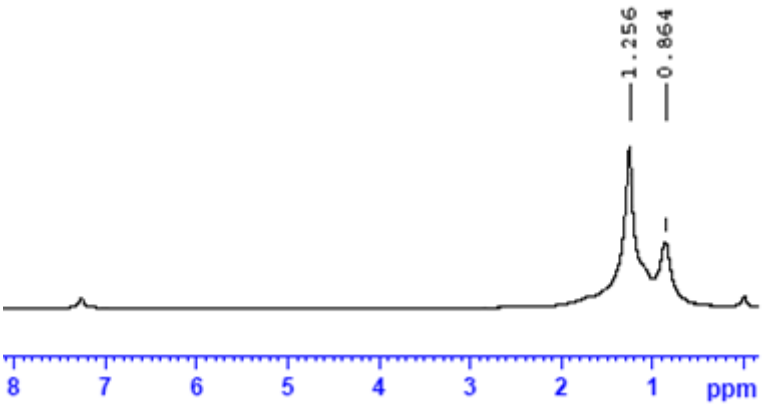

Figure 6. NMR spectra of soot obtained from the Engine combustion of diesel

Figure 6 shows the H-NMR spectrum of Diesel soot. The different hydrogen present in the sample is as follows. The main assigned groups are hydrogen on aromatic rings (Ha, 6.5 -9.0 ppm); hydrogen of CH, CH_2, CH_3 groups on carbon atoms in β position aromatic rings (H_β, 1.0- 2.0 ppm); and methyl hydrogen on carbons γ, δ or higher position to aromatic rings, as well as methyl hydrogen of alkanes, cyclo alkanes and napthenic rings (H_γ, 0.5-1.0 ppm).

The products have significant aliphatic component with predominance of methyl and methylene groups on β and γ positions of aromatic rings [10-13]. It is important to observe that there is a significant fraction of hydrogen on the γ position between at 0.864 ppm, which suggest the existence of large aliphatic chains or saturated rings joined to different types of aromatic rings.

4. CONCLUSION

Carbonaceous soot produced from diesel from engine show the presence of significant amount of carbon nanomaterials. The SEM micrographs provide a clear indication that these nanoparticle are clusters of carbon nanospheres. X-ray diffraction investigation shows the presence of carbon nanotubes in association with amorphous nanomaterial due to the presence of γ and Π bands found in the carbon nanotubes. EDS analysis of Diesel soot indicates that the soot particles to be composed of primarily

carbon and oxygen along with hydrogen. The presence of sulphur is also reported in the EDS analysis. NMR spectrum of the soot reveals significant aliphatic component with predominance of methyl and methylene groups on β and γ positions to aromatic rings. There is significant fraction of hydrogen on the γ position between 0.7 and 0.8 ppm, which suggests the existence of large aliphatic chains or saturated rings joined to aromatic rings. The IR spectrum also shows other characteristic signals in the region 1700-1000 cm^{-1}, where the most important one correspond to C=O stretching of carboxylic acids at 1639 cm^{-1}, C=C stretching of aromatic or alkene groups that appear at 1533 cm^{-1}, and aliphatic C-H plane deformation of CH_2/CH_3 groups at 1380 cm^{-1} and 1445 cm^{-1} respectively.

ACKNOWLEDGMENT
The authors acknowledge the Research centre, Christ University, Bangalore for funding this work.

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