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Recycling of an Effluent Soot from Kademia Diesel-Power Plant as a Carbon Source for the Synthesis and Characterization of NanoCarbon

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ABSTRACT

Soot obtained as an effluent from Kademia diesel-power station was recycled and utilized as feedstock for preparation of nano carbon particles. The porosity, surface area analysis featured by BET N_2 adsorption, proximate analysis, Fourier Tranform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) were employed for the structural and morphological characterization of the halocarbon formed.

Ultimate analysis of the fuel oil samples indicate that the H/C ratio of nanospheres is less 0.085 which is an indication of crystallization in the nanomaterial formed.

The results obtained from BET analysis had specific surface area increases to 50 m^2/g, comparing with 28 m^2/g of that the raw soot. SEM results shows a variations in size and shape of nanocarbon particles formed. The FTIR spectrum of soot shows characteristic signals in the range of 400-4000 cm^{-1} where corresponding to SO_4^{2-} (600 cm^{-1}), NO_3^- (850 cm^{-1}), CO_3^{2-} (900 cm^{-1}), SiO_4^{4-} (1050 cm^{-1}), C–OH aromatics (1250 cm^{-1}), NO_3^- (1300 cm^{-1}), CO_3^{2-} (1650 and 1720 cm^{-1}), C=CH alkenes (2930 cm^{-1}), and C – OH alcohols (3400 and 3550 cm^{-1}). XRD investigation indicates the presence of large amount of amorphous material in association with nanocarbon at moderately high intensity broad peak; $2\theta=23.5140^o$, where at the low intensity; $2\theta=48.6389^o$ indicate of the low quality of nanomaterial presented in the soot.

Keywords: Diesel Soot, NanoCarbon, Characterization, XRD, SEM, FTIR

استرجاع الدقائق الكربونية المتطايرة من محركات الديزل في محطة كهرباء ديزلات الكاظمية لتحضير وتقييم خواص كربون بدرجة النانو

الخلاصة

تم اعادة تدوير السخام المتخلف من نفايات الغاز العادم لمحطة كهرباء ديزلات الكاظمية واستخدامها كمادة اولية لتحضير دقائق نانوكربون . لقد تم تقييم دقائق النانوكربون التركيبية بطرق تحليلية عديدة مثل المسامية, المساحة السطحية, التحليل التقريبي للعناصر,طيف الاشعة تحت الحمراء, حيود الاشعة السينية, والمجهر الالكتروني.

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لقد بين التحليل النهائي لعناصر زيت الوقود انخفاض نسبة هيدروجين/كربون للكريات النانوية الى اقل من 0.085 مما يدل على تبلورها بشكل مواد نانوية. كما ان النتائج المستحصلة من تحليل BET تشير الى زيادة في المساحة السطحية النوعية الى 50 m^2/g مقارنة مع 28 m^2/g للسخام الخام. نتائج SEM تظهر الاختلافات في حجم وشكل جسيمات النانوكربون المتكونة. ان تحليل الطيف FTIR بينت اشارات مميزة في حدود 400-4000 cm^{-1} حيث 850) NO_3^- (cm^{-1}), 600) SO_4^{2-} (cm^{-1}) CO_3^{2-} (900 cm^{-1}), SiO_4^{4-} (1050 cm^{-1}), C–OH aromatics (1250 cm^{-1}), NO_3^- (1300 cm^{-1}), CO_3^{2-} (1650 and 1720 cm^{-1}), C=CH alkenes (2930 cm^{-1}), and C – OH alcohols (3400 and 3550 cm^{-1}). تحليل XRD يدل على وجود كمية كبيرة من المواد الغير متبلورة بالاشتراك مع جسيمات النانوكربون عند شدة مجال مرتفع $2\theta=23.5140^o$ بينما عند الشدة المنخفظة $2\theta=48.6389^o$ تشير الى تدني نوعية المواد النانوية الموجودة في السخام.

INTRODUCTION

Nanocarbon technologies since their discovery in 1991 [1] offers the enormous possibilities to reduce waste products and undesirable effluents. The nono-products i.e. single-walled CNTs., multi-walled CNTs, fullerenes, graphene, carbon nano fiber and nanodiamonds; for their greater efficiency are plying a major role in many applications. [2,3]. According to the market research report [4], the production capacity for all nanocarbon products was 4,065 tons in 2010, and is expected to exceed 12,300 tons in 2015. The actual production was less than 25% of the capacity in 2010 and about 50% of the capacity in 2015. Total production cost is estimated at about $435 million in 2010 and is expected reach a value of $1.3 billion in 2015. However, the problem of high production cost is highly desirable to synthesize a well purified CNT at relatively simple, low cost and scalable technique.

Diesel-power engines during an incomplete combustion for high fuel to air ratios are assumed to be a larger pollution producer of carbonaceous soot particles in the nanoscale [5] and their particles contain some of a minor materials of volatile organic component, lubricating oil and inorganic compounds such as ash and sulfur compounds [6]. The soot formation due to pyrolysis and oxidation mechanism; formation of the benzene and subsequently polycyclic aromatic hydrocarbons (PAH), inception of the first particles, growth of soot particles due to reactions with gas phase species, particle coalescence, agglomeration and oxidation [7].

The soot chain structure composed up to 4000 of smaller spherical particles. These primary particles are agglomerated in clusters and can contain between 10^5 to 10^6 carbon atoms [8, 9] most of agglomerate soot particles can vary from 10 to 1000 nm and surface area reach to 200 m^2/g. Nanoparticles constituting the agglomerate are more or less spherical with a diameter typically from 10 to 80 nm but most of them are between 15-30 nm [10].

In the present work, effluent soot from Kademia diesel-power plant is recycled and used as carbon source for nonmaterial.

EXPERIMENTAL DETALES

Engine Description and Proximate and Ultimate Analysis of Fuel oils

Kademia-Diesel-power plants are used as case study. The station working with a Hyundai 4-stroke type H25/33, direct injection single acting and trunk piston type with turbocharger and inter-cooler. Diesels are equipped with synchronous generators

with power ratings of 240 kW. The general layout of a Hyundai diesel engine power plant [11] is shown in Figure (1). Technical specifications are given in Table (1). Typical exhaust composition in volume ratio are given in Table (2).

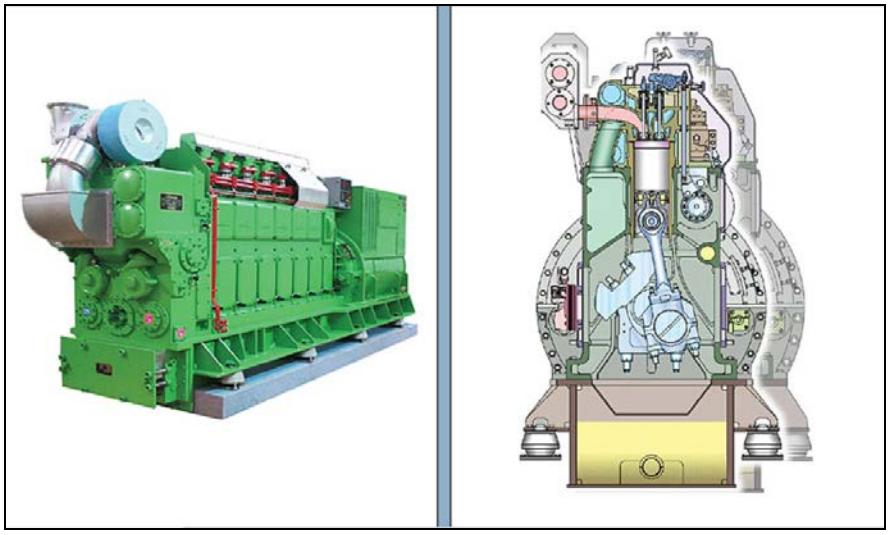

Figure (1) The General Layout Of A Hyundai Diesel Engine.

Table (1) Diesel Engine Characteristics.

Model	**Hyundai H25/33S**
Type	4-stroke, single acting and trunk piston type with turbocharger and inter-cooler
Cylinder Configuration	In-line
Rated Speed	720 rpm
Power Per Cylinder	240 kw
Mean Piston Speed	7.9 m/s
Mean Effective Pressure	24.7 bar
Combustion System	direct injection
Compression Ratio	17:1
Cylinder Firing Order	1-4-2-6-3-5

Table (2) Typical Exhaust Composition in Volume Ratio at Full Load.

Component	**Concentration**
N_2	Approx. 75%
O_2	Approx. 13%
CO_2	Approx. 5%
H_2O	Approx. 6%
Ar	Approx. 1%
Soot, Ash, NOx, CO, HC, etc	Residue

The performance of the diesel engine with light fuel oil LFO and heavy fuel oil HFO were supplied from local refineries. The specifications are listed in Table (3).

Table (3) Specifications of Fuel oils.

Lab. Inspection Data	HFO	LFO
SP. Gravity@15.6 ^{o}C	0.9425	0.8313
API Gr. @15.6 ^{o}C	18.6	38.7
Flash point ^{o}C	100	66
Pour point ^{o}C	+21	-12
Vis Cst@50 ^{o}C	138.5	2.8
Carbon Residue wt%	7.5	0.09
Total sediment	Traces	Nil
Water vol%	Nil	Trace
Sulfur wt%	3.7	0.87
Ash Content wt%	0.014	0.009
Vanadium ppm	45.1	Nil
Asphaltenes wt%	1.7	-----
Sodium ppm	35.34	96.56
Al ppm	63.58	39.57
Ca ppm	1800	
Zn ppm	10.11	
P ppm	27.82	
Nickel ppm	Nil	20.9

The proximate analysis was carried out to determine the fixed carbon content for LFO and HFO. The water content, volatile matter and Ash content for supplied fuels were performed according to ASTM D 3173-87, ASTM D3175-11, and ASTM D3175-11 respectively. The CHNO analysis was calculated from ultimate values.

Sample Preparation

Soot samples were recycled from the effluent of Kademia diesel-power station. Soxhelt extraction was used for 48 hr with acetone. The purification step was performed to remove any trapped oil and soluble impurities. The soot samples were subjected to appropriate analytical methods for characterization. The extracted oil was recycled as diesel-like fuel.

Surface Area and Pore Volume Analysis

The specific surface area and pore volume of the soot particles were analyzed by BET N_2 method using Micomeritics ASAP 2020 analyzer. The standard isotherm was used to calculate the surface area [12].

X-Ray Diffraction (XRD)

Measurements were performed using a shimadzu X-ray diffract meter with CuKα radiation (λ=1.54060 A). A Scintillation counter detector was used to collect scattered X-ray. The angle 2θ was ranged from 20-50° with a step-size of 0.02° and a preset time of 0.10 s. The XRD spectrum of each sample was also recorded. [13].

Scanning Electron Microscope (SEM)

The morphology and particle size of the soot was examined with using VEGA TESCAN scanning electron microscope (SEM). Micrographs were taken at 16 kV with a working distance in the range of 6.541-6.591 mm.

Ftir Spectrophotometer

FTIR Spectroscopy was used in this study to obtain qualitative bond and functional group information such as SO_4^{2-}, NO_3^-, SiO_4^{2-}, and NH_4^+, and organic functional groups like aliphatic carbons, carbonyls, and organic nitrates. FTIR spectra of the CNT from diesel soot were recorded on Shimadzu FTIR-8400S model working with the requirements of EMC Directive 2004/108/EC and low voltage Directive 2006/95/EC. The spectra were recorded in the range 400-4000 cm^{-1} with resolution of 4 cm^{-1} and applying 10 repetitive scans to obtain a good signal-to-noise ratio.

RESULTS AND DISCSSION

Proximate and Ultimate Analysis

Ultimate analysis of the LFO-HFO samples are presented in Table (4). Elemental (C, H, N, O contents) are calculated as (85.06%-85.27%), (9.05%-7.31%), (3.88%-3.99%), and (2.01%-3.43%) respectively. The H/C ratio range varies within the limit of 0.1058-0.0857 which confirms an ordered structure for the CNS. The H/C ratio of nanospheres in the sample of soot is less 0.085 and this low value is an indication of crystallization in the nonmaterial formed.

Table (4) Typical Ultimate Analyses.

Parameter		**LFO (%)**	**HFO (%)**
Moisture (M)		0.1	0.4
Volatile matter (VM)		95	98
Ash (A)		0.009	0.014
Carbon (C)		85.06	85.27
Hydrogen (H)		9.05	7.31
Nitrogen (N)		3.88	3.99
Oxygen(O)		2.01	3.43
HC ratio (H/C)		0.1058	0.0857
Relationship Between Ultimate Analysis and Proximate Analysis [14]			
%C	=	$97.116-0.425(VM)-1.110\ (M)+0.00315(VM)^2$	
%H	=	$4.192+0.029(VM)-0.593(M)+0.013(VM)(M)$	
%N	=	$2.965-0.032(VM)-0.175(M)+0.017(M)^2+0.00044(VM)^2$	
%O	=	100 - %C - %H - %N	
HC ratio	=	H/C	

BET Analysis

The calculated surface area was 50 m^2/gm, total pore volume of 0.052196 ml/gm and average pore size of particles 2 nm. BET analysis shows that the specific surface area of the CNS increases to 50 m^2/g, comparing with that of the raw soot, 28 m^2/g, it increased by twice. The pore size distribution shows that the improved specific surface area is caused mainly by the pores volumes.

SEM Microscopy

The SEM results are presented in Figures (2-5). These Figures indicate that most soot particles obtained to be irregular clusters and non-uniform in the nanostructure. The fine particles appeared to be soot agglomerated, turning into larger and significantly greater than the actual particle size. [15] .The results show that the

primary particles have a variations in size and shape [16]. Differences in soot particle sizes for the combustion of fuel oil are possible, since the combustion products might be different under different combustion conditions and with different types of fuel oil.

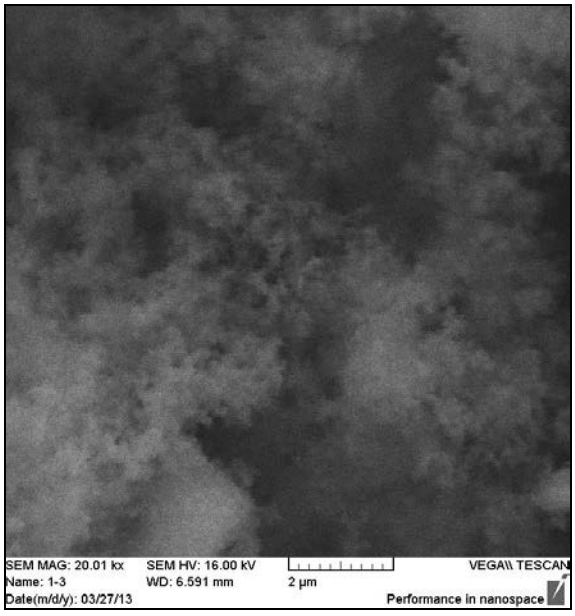

Figure (2) Scanning Electron Micrograph of Diesel Soot (2 µm).

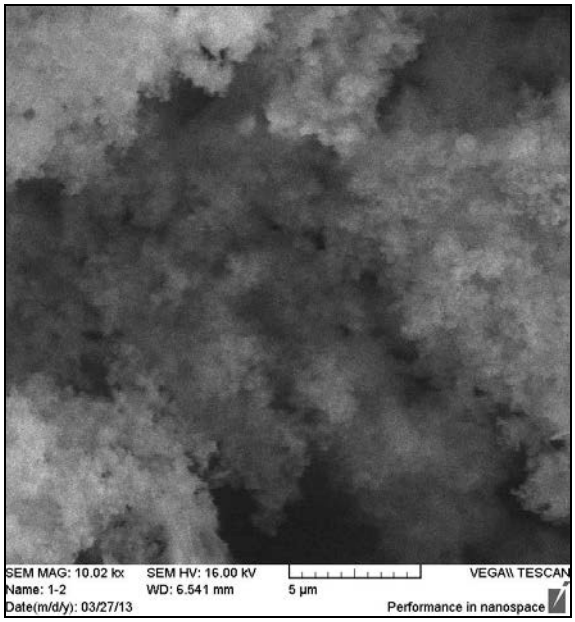

Figure (3) Scanning Electron Micrograph of Diesel Soot (5 µm).

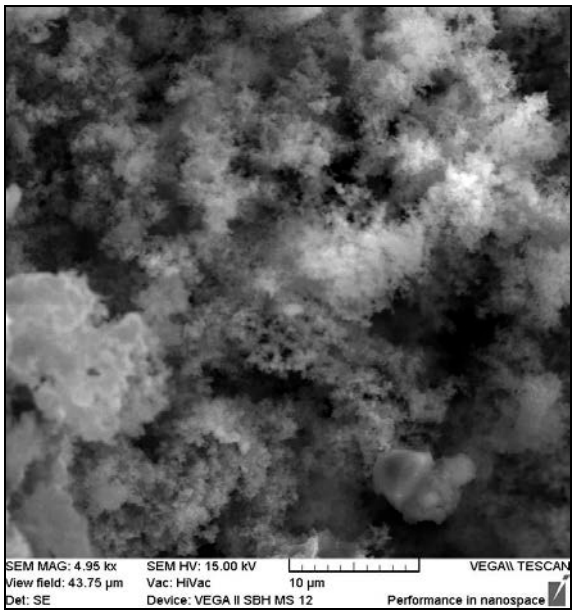

Figure (4) Scanning Electron Micrograph of Diesel Soot (10 µm).

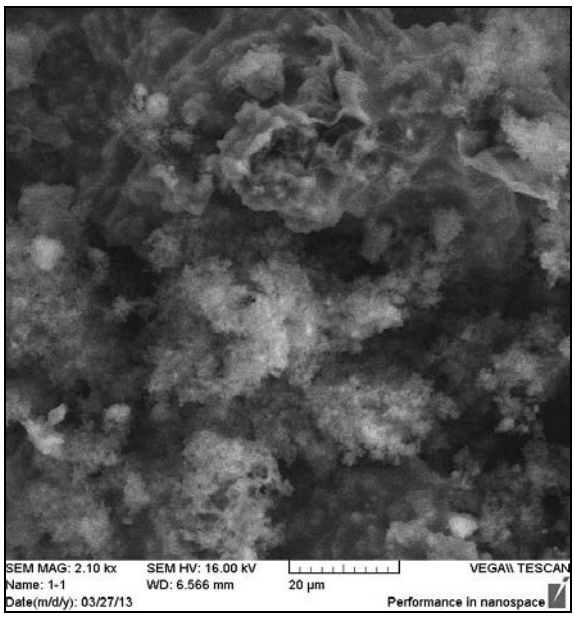

Figure (5) Scanning Electron Micrograph of Diesel Soot (20 µm).

FTIR Spectrum

The FTIR spectrum of soot is shown in Figure (6). Table (5) present a list of the peaks identified in this study. The peaks marked are assigned as follows: SO_4^{2-} (600 cm^{-1}), NO_3^- (850 cm^{-1}), CO_3^{2-} (900 cm^{-1}), SiO_4^{4-} (1050 cm^{-1}), C–OH aromatics (1250 cm^{-1}), NO_3^- (1300 cm^{-1}), CO_3^{2-} (1650 and 1720 cm^{-1}), C=CH alkenes (2930 cm^{-1}), and C – OH alcohols (3400 and 3550 cm^{-1}). Additional interference from

alkenes and alcohol are presented in the region from 2900 – 3500 cm^{-1}; however, the peaks at 3400 cm^{-1} are found within this region.

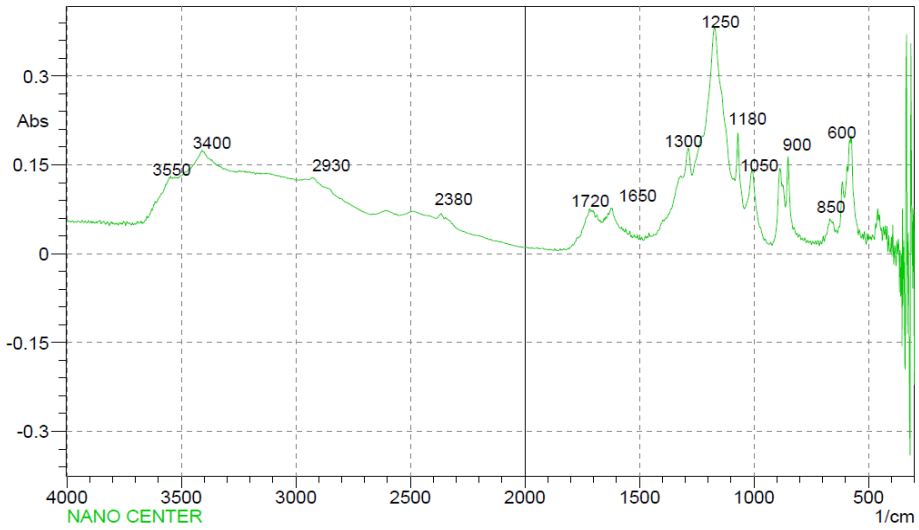

Figure (6) FTIR Spectrum of Soot Obtained.

Table (5) Peaks Used In FTIR Qualitative Study [17].

Quantified (cm^{-1})	Functional Groups	Name
3100-3500	C-OH	Alcohols
3000-3100	C=C-H	Aromatic carbon
2900-3100	C=C-H	Alkene carbon
1452-5, 2800-3000	C-H	Aliphatic carbon
1640-1850	C=O	Carbonyl
1630	$C\text{-}NH^{2}$	Amines
1410-35, 3030-52, 3170-3200	NH_4^{+}	Ammonium
860-80, 1410-90	CO_3^{2}-	Carbonate
815-40, 1350-80	NO_3^{-}	Nitrate
772-812, 1035	SiO_4^{4-}	Silicate
612-5, 1103-35	SO_4^{2-}	Sulfate

XRD Study

Figure (7) represents the average crystallite sizes determined by X-ray profile of purified diesel soot .The sample shows only three strongest Bragg diffraction peaks at $2\theta=23.5140^{o}$,25.5101^{o},and 28.5653^{o} respectively corresponding to the crystallite sizes of the sample. The peak at $2\theta=23.5140^{o}$ is moderately high intensity broad peak which indicates the presence of large amount of amorphous material in association with nanocarbon. The low intensity of the peak at $2\theta=48.6389^{o}$ is an indication of the low quality of nano material presented in the soot.

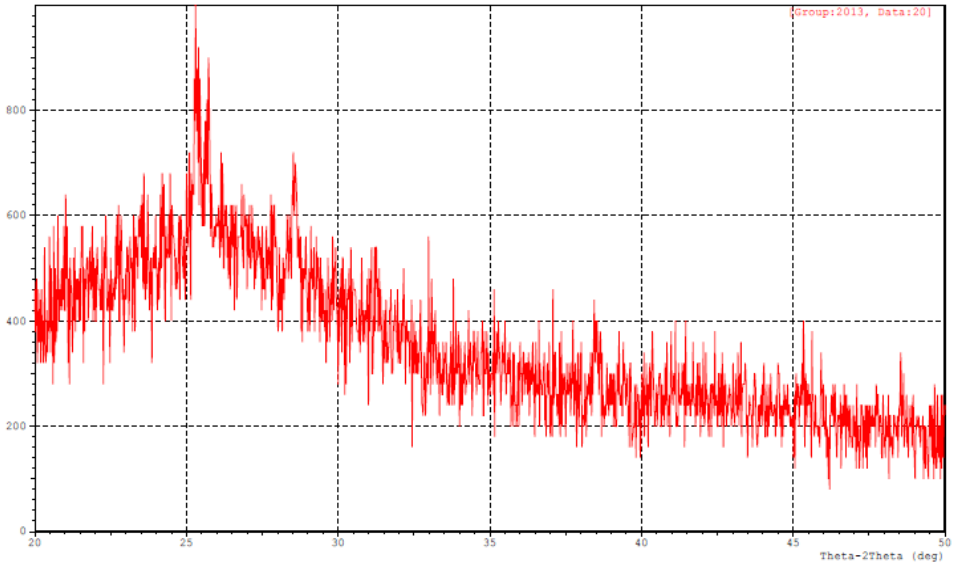

Figure (7) XRD Pattern of Soxhelt Purified Diesel Soot.

CONCLUSIOINS

In the present investigation it was recycled and prepared a nanocarbon from soot produced from Kademia diesel-power station. Diesel soot was characterized in this study with modern analytical equipment to determine the nature of particles. Ultimate analysis of the fuel oil samples show an indication of crystallization in the nanomaterial formed. SEM results shows variations in size and shape of nanocarbon particles formed. The IR spectrum also shows other characteristic signals in the region 400-4000 cm^{-1}, where the most important corresponding to SO_4^{2-}(600 cm^{-1}), NO_3^- (850 cm^{-1}), CO_3^{2-} (900 cm^{-1}), SiO_4^{4-} (1050 cm^{-1}), C–OH aromatics (1250 cm^{-1}), NO_3^- (1300 cm^{-1}), CO_3^{2-} (1650 and 1720 cm^{-1}), C=CH alkenes (2930 cm^{-1}), and C – OH alcohols (3400 and 3550 cm^{-1}) respectively. X-ray diffraction investigation shows the presence of nanocarbon in association with of amorphous nanomaterial presented in the soot.

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REFERENCES

[1].Sumio Iijima, “Helical Microtubules of Graphitic Carbon”, Nature 354, November, 56 - 58 (1991).

[2].Masaki Ozawa and Eiji Ōsawa , “Carbon Blacks as the Source Materials for Carbon Nanotechnology”, Halocarbon Research Institute, Toudai Kashiwa Venture Plaza, 5-4-19 Kashiwa-no-ha, Kashiwa, Chiba 277-0882,Japan, Carbon Nanotechnology’, Dai, L. (Ed.), Chapt. 6, p. 127-151, Elsevier: Dordrecht,(2006).

[3].Ateeq Rahman, Ilias Ali, Saeed M. Al Zahrani And Rabeh H. Eleithy, "Review of The Applications of Nanocarbon Polymer Composites", Nano: Brief Reports And Reviews, Vol. 6, No. 3, 185–203,(2011).

[4].Production and Application of Carbon Nanotubes, Carbon Nanofibers, Fullerenes, Graphene and Nanodiamonds: A Global Technology Survey and Market Analysis, Innovative Research and Products Inc., Feb.1, 2011.

[5].Kittelson, D.B." Engines and Nanoparticles: A Review". J. Aerosol Sci. 29: 575-588,(1998).

[6].Burtscher, H. "Physical Characterization of Particulate Emissions from Diesel Engines: A Review". Aerosol Science 36: 896-932,(2005).

[7].Siegmanna K., Sattlerb K., Siegmannc H.C., "Clustering at High Temperatures: Carbon Formation in Combustion", Journal of Electron Spectroscopy and Related Phenomena 126, 191–202 (2002).

[8].Vander Wal, R. L., Ticich, T. M., Brock S. A."Can Soot Primary Particle Size Be Determined Using Laser-Induced Incandescence?" Combustion and Flame, 116, 291-296(1999).

[9].Smith, O. "Fundamentals of Soot Formation in Flames with Application to Diesel Engine Particulate Emissions", Progress in Energy and Combustion Science (1981).

[10].Amann, C. A.; Siegla, D. C." Diesel Particulates—What They Are And Why". Aerosol Science and Technology, 1, 73 – 101 (1981).

[11].Hyundai Heavy Industries Co., Ltd, Instruction book, Engine type H25/33, copyright@ 2011.

[12].NIST, Certificate of Analysis, Standard Reference Material 1650a, Diesel Particulate Matter. National institute of standards and technology, Gaithersburg, MD, USA, 7 November 2000.

[13].Chen H.X, Dobbins. R.A., "Crystallogenesis of particles formed in hydrocarbon combustion," Combust. Sci. Technol. 159 109–128,(2000).

[14].de Kock J. W., Franzidis J.P.," The Estimation Of Some Properties Of South African Coals From Proximate Analysis", J. of South African Institute of Mining and Metallurgy, July, pp 421-427,(1973).

[15].Kathryn M. B., George W. M., "Generation and Transport of Smoke Components", Fire Technology, 40, 149–176, (2004).

[16].Lapuertaa M., Martosb F.J., Herrerosa J.M.,"Effect of Engine Operating Conditions on the Size of Primary Particles Composing Diesel Soot Agglomerates", Aerosol Science 38, 455 – 466(2007).

[17].Maria, S.F., Russel, L.M., Turpin, B.J., Porcja, R.J., Campos, T.L., Weber, R.J., and Huebert,B.J. "Source Signatures Of Carbon Monoxide And Organic Functional Groups In Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) Submicron Aerosol Types". Journal of Geophysical Research, Vol. 108, No. D23, 8637(2003).