



Petrographic controls of coal from Ib valley Basin for carbon nano-products formation

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ABSTRACT

The peculiar characters and industrial applications of carbon nanotubes (CNTs) and carbon nanoballs (CNBs) have attracted the interests of technologists, scientists, and policy-makers. Here, authors have synthesized CNTs and CNBs through MCL (molten caustic leaching) method from ten coal samples belonging to Ib valley Basin, Odisha, India. HRTEM (High-Resolution Transmitted Electron Microscopy), FTIR (Fourier Transform Infrared) spectroscopy and XRD (X-ray Diffraction) analyses appraised the presence of carbon nano-particles with varied sizes in the MCL products. The nanoballs are in the range of 52–64 nm and the nanotubes are within the range of 7–15 nm in diameter. The petrographic parameters viz. various macerals and rank, as well as a measure of aliphatic bonds, have a significant impact on the amount of yield, purity, and quality of CNTs/CNBs. Carbon nano-products (CNPs) yield is increased with the fixed carbon content and decreased with volatile matter yield and mineral matter present in coals. Oxygen and hydrogen content in coal have decreased the carbon nano-products yield. Optical microscopic study of coals revealed that the carbon nano-products (CNPs) formation is favored with an increase in vitrinite and liptinite and decrease with inertinite macerals. Inertinite macerals, characterized by high aromaticity with aromatic rings of large size, do not take part (little participation) in reaction with alkalis and in acid treatment. The aliphatic bonds and chains in liptinites and vitrinites help in carbon nano-products synthesis. The proposed empirical equation PEC (petrographic estimate of CNPs) seems to indicate the amount of CNPs yield through the MCL process. The MCL may be a proficient technique for the synthesis of nano-carbons as well as the removal of mineral matter from coals.

1. Introduction

The developments of carbon nanotubes (CNTs) and carbon nanoballs (CNBs) production received growing scientific attention after its first discovery in 1991 (Iijima, 1991). The large-scale synthesis of CNTs and CNBs has been a point of interest due to its unique properties such as extraordinary aspect ratio, high strength, and stiffness, super electrical and thermal conductivity. Owing to its extraordinary properties, it has assorted applications in various fields of computer science, optical science, chemical science, telecom industry, medical industry, electronics, nano-mechanics, biology and catalysis (Baughman, 2002; Dosodia et al., 2009; Harrison and Atala, 2007; Liang and Chen, 2010; Qui et al., 2002; Yu et al., 2003; Zhang et al., 2006). The CNTs will be required on a large/industrial scale in the near future due to their growing

applications day by day. The cost of raw materials, production, purification process and level of yield shall become more important when carbon nanotubes and carbon nanoballs are required in large /industrial scales in the time ahead. In the above views, the very cheap and widely available coal has the potential to remove the inevitable problems. Apart from the cheapness and easy accessibility of coal, the presence of foreign species like Fe₂O₃, FeS₂, Co, Ni, Cu, etc. help in the synthetic process of CNTs. Hence, coal is likely to be a better replacement as solid carbon precursors for the synthesis of CNTs. There are several works regarding making CNTs from different carbon source viz. coal (Pang et al., 1991, 1993; Qiu et al., 2007; Wang et al., 2006; Tian et al., 2004; Yu et al., 2003), graphite (Prasek et al., 2011; Zhang et al., 2000), methane (Hernadi et al., 1996; Kong et al., 1998) bituminous coal (Awasthi et al., 2015), caking coal (Qui et al., 2002), coal and

Abbreviations: CNTs, carbon nanotubes; CNBs, carbon nanoballs; CNPs, carbon nano-products; MCL, molten caustic leaching; PEC, petrographic estimate of CNPs; HRTEM, high resolution transmitted electron microscopy; FTIR, Fourier-transform infrared spectroscopy; XRD, X-ray diffraction

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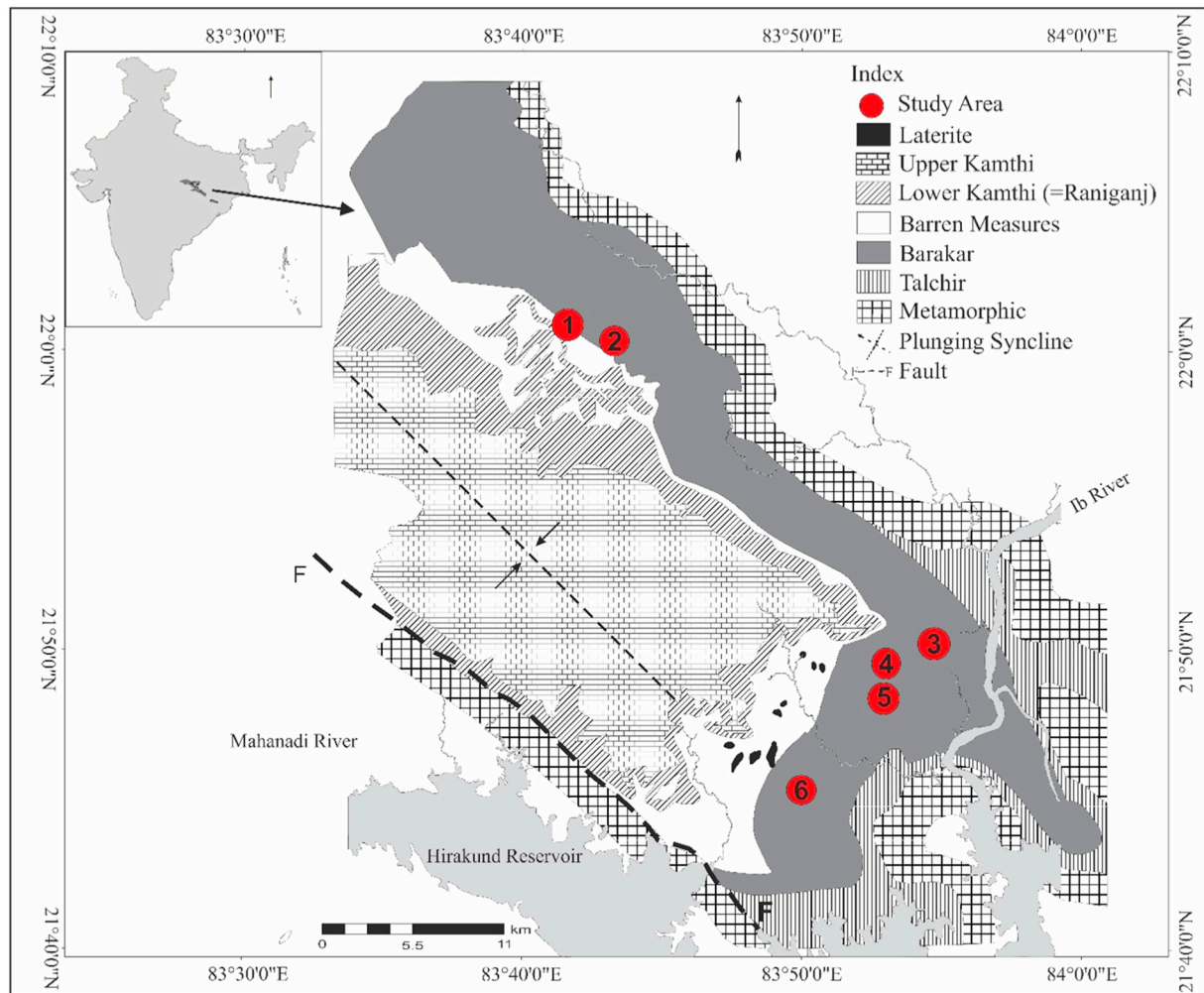


Fig. 1. Geological map of Ib valley Basin (Slightly modified after CMPDIL, 1993).

Explanations: 1 = Basundhara OCP (Sample no. CG-3122, CG-3125, CG-3126); 2 = Kulda OCP (Sample no. CG-3128); 3 = Orient UG (Sample no. CG-3101, CG-3105); 4 = Lajkura OCP (Sample no. CG-3106); 5 = Samleswari OCP (Sample no. CG-3113); 6 = Belpahar OCP (Sample no. CG-3117, CG-3121).

waste plastic (Dosodia et al., 2009) coal and petroleum mixture (Velasco-Santos et al., 2003), carbon monoxide (Dai et al., 1996), kerosene (Pradhan and Sharon, 2002), liquefied petroleum gas (Qian et al., 2002) coal gas (Zeng et al., 2006; Qiu et al., 2004a, 2004b; Qiu et al., 2006), benzene (Cheng et al., 1998; Narkiewicz et al., 2010), acetylene (Li et al., 1996; Tomie et al., 2010), alcohol (Maruyama et al., 2002), and polymers (Kyotani et al., 1996; Terrones et al., 1997).

There are reports of synthesizing carbon nanotubes from coal as a carbon source e.g. the arc discharge method using graphite electrodes (Zhou and Seraphin, 1995), CVD (hot-filament chemical vapour deposition) method (Gan et al., 2000), laser ablation method (Guo et al., 1995), arc plasma method (Wang et al., 2007), catalytic hydrocarbon decomposition (Deepak et al., 2001) and catalytic chemical vapour deposition (Qiu et al., 2004a, 2004b) etc. Moreover, the methods reported for the synthesis of CNTs from coal are expensive and use harsh environments of treatment. There is a simple, mild and susceptible method viz. Molten caustic leaching (MCL) process have been recently proposed by Das et al. (2016) for carbon nanotubes synthesis from low-grade coals. This method might be an alternate technique for nano-carbon synthesis instead following rigorous conventional methods. MCL has the ability to remove foreign particles like mineral matter, sulfur content (organic and pyritic) and trace elements from coal. This effectiveness of MCL enables it for value addition in low and medium grade coal. The macromolecular structure of coal contains inherently different types of weak bonds in it (Baruah and Khare, 2007;

Viswanathan et al., 2009). This method of formation of high-value CNTs/CNBs has motivated our research interest to evaluate the relationship of coal properties with the formation of these carbon nano-products. The role of petrographical parameters of coal on CNTs/CNBs formation in this method is interesting and defines the novelty of our study. An attempt is made to evaluate petrographic parameters with CNPs formation in this work that may facilitate further to enhance the purity and quantity of formation of CNPs. In our work, the MCL method is applied for low to medium rank coal with varying ash yield coal samples collected from Ib valley Basin for synthesizing carbon nanotubes and carbon nanoballs. The use of low-medium grade coal from this coal basin having the third largest coal reserve in India might have a significant impact on the economic activities leading to the conversion of low-rank high ash coals to high-value materials.

2. Geological settings

Ib valley Basin (latitude 21°30'–22°06'N and longitude 83°37'–84°10'E) is an NW-SE part of Mahanadi Master Basin. Ib River, an affluent stream of Mahanadi River after which this Basin was named. This basin is also a continuous part of the Mand-Raigarh Basin, India (Goswami et al., 2006; Tewari et al., 2009; Senapaty and Behera, 2015; Varma et al., 2015). This Basin is formed parallel to the underlying Precambrian rock's structural grain. This basin is bordered by prominent NW-SE lineament at its southern boundary. A North-West plunging

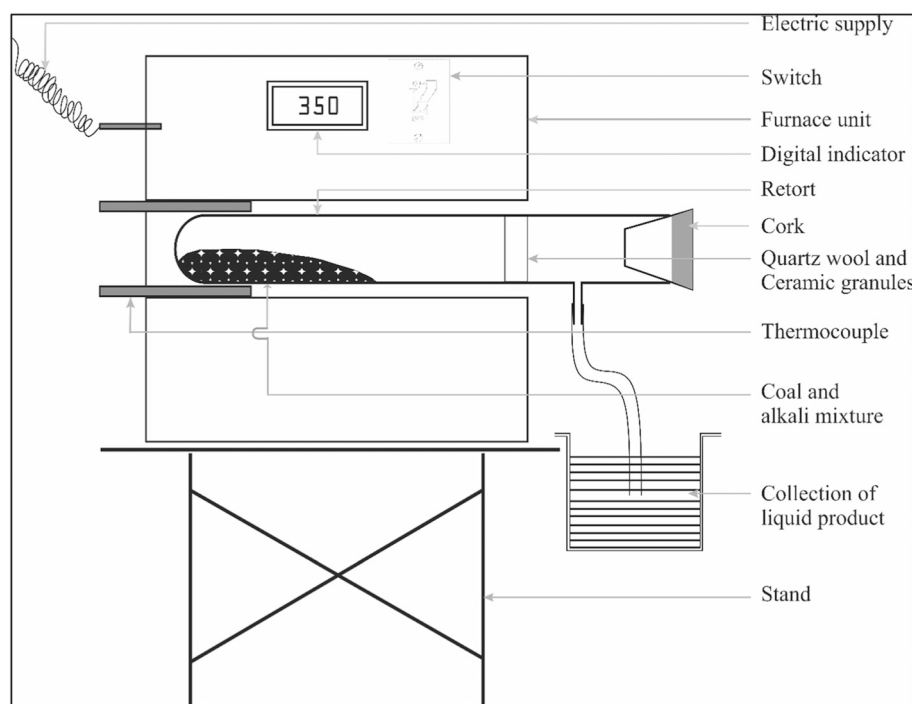


Fig. 2. Diagrammatic sketch of the arrangement of molten caustic leaching method.

syncline has been noticed (Goswami et al., 2006; Tewari et al., 2009). Generally, this Basin contains highly banded low rank, non-coking coals, having a large amount of volatile matter and ash yields (Anandalwar, 1977; Varma et al., 2014). According to the past investigations, the stratigraphic succession starts with Precambrian rocks at the base (Anandalwar, 1960; Ball, 1871; Chaudhury, 1988; GSI, 1997; Mukhopadhyay, 1987; Pal et al., 1992; Raja Rao, 1982;). Gondwana Supergroup consists mainly of the Talchir, Karharabari, Barakar (Cisularian), Barren Measures (Guadalupian), Kamthi Formations. The Kamthi Formations are subdivided into Lower Kamthi (Raniganj; Lopingian) and Upper Kamthi (Olenekian) Formations. The Gondwana Supergroup overlies Precambrian rocks (Singh et al., 2007; Varma et al., 2015). Five coal seams occur in Karharabari and Barakar Formations of this coal basin. Out of these 5 coal seams, three coal seams viz. Ib seam, Lajkura seam, and Rampur seam are commercial. Stratigraphically, Ib seam belongs to Karharabari Formation and the other two are of Barakar Formation (GSI, 1997; Manjrekar et al., 2006). The geological map of Ib valley Basin with the studied areas is shown in Fig. 1.

3. Materials and methods

3.1. Samples collection

Three different seams from Ib-valley coal basin, Odisha were chosen for the collection of 10 (ten) samples. Samples named CG-3101, CG-3105 belong to Lajkura seam and CG-3106, CG-3113, CG-3117, CG-3121, CG-3122, CG-3128 belong to Rampur seam whereas CG-3125, CG-3126 belongs to Ib seam. The chosen samples were crushed and sieved to different sizes ($-1000\mu\text{m}$, $-212\mu\text{m}$, $-74\mu\text{m}$) using standard methods (ASTM, 2010) for various analyses.

3.2. Molten caustic leaching (MCL) process

This process was performed in a quartz reactor, which was placed in a controlled temperature condition. A mixture was obtained by mixing 10-g air dried coal powder ($-212\mu\text{m}$) sample with a ratio 1:1 to NaOH and KOH mixture. The coal powder was thoroughly mixed with the

alkali (partially crushed) and placed in a moisture oven to prevent moisture absorption. Samples were thoroughly weighed and noted. The whole mixture was transferred to a retort and placed in a thermal reactor and heated up to 350°C for 1 h. Quartz wool and ceramic granules were used to seal the empty spaces of the quartz retort. A water pot was placed to collect the liquid tar product. The setup of the experiment is schematically shown in Fig. 2.

3.3. Acid treatment and filtration

The solid char products were collected separately. A mixture was prepared with taking 32% to dilute HCl solution and the solid char products in the ratio of 4:1. An alkali alumino-silicate gel which resulted throughout the MCL process was decomposed by the application of hydrochloric acid. The HCl and the char product mixture were heated to a temperature of 100°C on a hot plate and kept for 15 min. The derived products were filtered out by filter paper and washed with hot distilled water. The washing process was continued until it was free of

Table 1
The carbon nano-products yield (CNPs) and raw samples.

A	B	C	D	E
CG-3101	Barakar Formation	20.70	11.09	53.57
CG-3105	Barakar Formation	20.80	11.23	53.99
CG-3106	Barakar Formation	19.58	06.23	31.82
CG-3113	Barakar Formation	20.25	09.93	49.04
CG-3117	Barakar Formation	20.13	09.32	46.30
CG-3121	Barakar Formation	20.75	10.52	50.70
CG-3122	Barakar Formation	20.13	10.56	52.46
CG-3125	Karharabari Formation	20.93	12.93	61.78
CG-3126	Karharabari Formation	20.15	12.93	64.17
CG-3128	Barakar Formation	20.75	12.13	58.46

Explanations: A = Sample no.; B = Formation; C = wt of the coal and alkali mixture before treatment (grams); D = wt of the final char products after treatment (grams)/ carbon nano-products (CNPs)*; E = carbon nano-products yield (CNPs)* in wt%. * = carbon nano-products yield (CNPs) including carbon nano-chunks, carbon nanoballs, carbon nanotubes with fewer amount of amorphous carbon.

Table 2
Proximate and ultimate analysis of coal samples.

Sample no	W ^a	A ^d	VM ^{daf}	FC ^{daf}	C	C ^{daf}	H ^{daf}	N ^{daf}	O ^{daf}	Rank [*]
CG-3101	11.09	10.37	35.80	59.22	60.52	67.49	4.57	1.18	26.76	Sub-bituminous
CG-3105	9.60	11.27	35.12	60.67	62.51	70.45	4.85	1.12	23.58	Sub-bituminous
CG-3106	7.29	39.80	46.17	47.80	38.35	63.71	5.98	1.00	29.30	Sub-bituminous
CG-3113	10.51	25.59	39.03	54.80	48.60	65.31	4.85	1.29	33.47	Sub-bituminous
CG-3117	9.30	29.08	47.17	46.00	47.61	67.13	5.21	1.28	28.72	Sub-bituminous
CG-3121	9.39	20.06	34.08	61.50	57.06	71.38	5.06	1.09	28.54	Sub-bituminous
CG-3122	6.87	23.15	41.15	54.90	58.25	75.80	4.45	1.09	26.06	Sub-bituminous
CG-3125	5.68	10.27	34.65	63.02	71.08	79.21	4.28	0.98	27.61	Sub-bituminous
CG-3126	4.40	11.60	31.18	67.26	74.19	83.92	3.55	0.93	24.14	Bituminous
CG-3128	4.11	13.04	36.08	62.14	68.32	78.56	3.84	1.15	19.21	Sub-bituminous

Explanations: W = moisture content; A = ash yield; VM = the yield of volatile matter; FC = fixed carbon content; C = carbon content; H = hydrogen; N = nitrogen; O = oxygen; ^a = as analytical state; ^d = on dry basis; ^{daf} = on dry ash free basis. All parameters are in wt% unless indicated *.

chlorine. The final products were collected and weighed. The experiment is repeated for 10 different samples. The results are presented in Table 1.

3.4. Proximate and ultimate analyses of coal samples

The moisture content, ash and volatile matter yields of the samples were determined under proximate analysis applying the standard methods mentioned in ASTM, 2010; ASTM, 2011a, 2011b, 2011c. The ultimate analysis has been done with CHNS (O) Analyser FLASH EA 1112 series at SAIF, IIT-Bombay, India. The results are presented in Table 2.

3.5. Rock Evaluation (RE) pyrolysis

Rock Evaluation (RE) pyrolysis along with TOC analysis is a suitable technique used to measure the quantity, quality, and T_{max} (temperature of maximum pyrolyzate under S2) of organic matter (Espitalié et al., 1987). The samples were grinded and passed through BSS 72 mesh (– 212 µm) and well homogenized to carry out REP and TOC analyses. The pyrolysis process was performed applying Rock-Eval (RE) 6 pyrolyzer. The determined parameters include free thermolabile hydrocarbon released under S1, thermally cracked hydrocarbon under S2, the yield of CO₂ due to the molecular breakdown of kerogen under S3, the temperature that corresponds to the maximum pyrolyzate released as T_{max}. PI (production index), as well as TOC (total organic carbon) contents, were also measured (Table 3) using instructions given by (Espitalié et al., 1987; Lafargue et al., 1998; Peters, 1986; Peters and

Table 3
Rock-Eval pyrolysis of the coal samples.

Sample no.	S1	S2	S3	PI	T _{max} (°C)	TOC	MINC
CG-3101	0.60	59.10	5.32	0.01005	421	57.02	1.05
CG-3105	0.61	112.04	6.31	0.00542	422	68.80	1.33
CG3–3106	1.59	97.23	5.42	0.01609	417	37.70	0.77
CG-3113	0.75	99.02	6.81	0.007517	420	50.62	0.98
CG-3117	0.28	73.06	9.40	0.003818	417	50.37	1.35
CG-3121	0.65	86.61	6.10	0.007449	420	66.14	1.53
CG-3122	1.31	141.99	2.78	0.009142	424	58.33	1.51
CG-3125	2.77	176.16	2.78	0.015481	427	70.58	0.76
CG-3126	3.79	196.15	2.17	0.018956	428	80.87	1.12
CG-3128	1.58	125.66	4.08	0.012417	423	67.60	1.14

Explanations: S1 = amount of thermolabile hydrocarbons (mg HC/g of rock); S2 = amount of thermally cracked hydrocarbon (mg HC/g of rock); S3 = amount of CO₂ yield (mg CO₂/g rock); PI = production index [S1/(S1 + S2)]; T_{max} (°C) = the temperature that corresponds to the maximum pyrolyzate released under S2; TOC = amount of total organic carbon (wt%); MINC = mineral carbon (wt%).

Cassa, 1994).

3.6. Petrographic analysis

The representative coal samples (< 1 mm) were processed for making epoxy impregnated pellets following ISO 7404-2, 2009. The petrographic analysis was executed under both reflected and fluorescent light with “Leica DM 2700P” microscope using 50x objective under oil immersion following ICCP, 1998, 2001, Pickel et al., 2017 (vitrinite, inertinite and liptinite, respectively) at Coal Geology and Organic Petrology Lab., Department of Applied Geology, IIT (ISM), Dhanbad, India. Detailed maceral composition is exhibited in Table 5.

3.7. Fourier Transform Infrared (FTIR) spectroscopic technique

Fourier Transform Infrared (FTIR) spectroscopic technique is an important tool for investigation of the vibrational modes to characterize for purity measurement of carbon nano-materials (Aqel et al., 2012). Here, the FTIR study was performed to characterize various functional groups in the raw coal samples and CNPs. 1 mg of each powdered sample was mixed with 100 mg KBr and pellet was prepared using an evacuated die, applying standard methods (Painter et al., 1981). To reduce the water influence on the spectra the pellets were dried at least for 48 h in a vacuum oven.

3.8. High resolution transmitted electron microscopy (HRTEM)

The MCL products were examined through High Resolution Transmitted Electron Microscopic techniques under Joel JEM-2100 at North-Eastern Hill University (NEHU), Shillong, India to decipher the micro-structural as well as morphological attributes. The MCL products were properly dehydrated in an oven at 100 ± 3 °C and kept in a vacuum desiccator for 15 min. The specifications for analysis under HRTEM were kept at accelerating voltage: 60–200 KV in 50 V steps with the resolution of 1.9 Å to 1.4 Å. To determine the size and structure of the nano-products, the photomicrographs obtained from HRTEM results were further processed and analyzed with the help of “SIMAGIS” and “Image J (v1.47)” program (Burger and Burge, 2006; Burger and Mark, 2008).

3.9. X-ray diffraction analysis (XRD)

An Empyrean X-ray diffractometer at the Department of Earth Sciences, IIT Bombay, India was applied to document X-ray diffractogram of the raw coal samples as well as the obtained MCL products. The powdered samples were taken into an aluminum container with a step-scan mode. The specifications for the XRD method were 0.0130°/step with an angular range of 5 to 69° (2θ) and intensity of 8 s/step. The

source for X-ray radiation was kept as a Copper K α (30 kV, 30 mA). The XRD spectra of both raw and MCL products were studied and compared.

4. Results and discussion

4.1. Molten caustic leaching (MCL) process

The char products were collected separately from the experiment. Huge losses in the amount of yields of char were observed after treating with the acid (HCl). The char product yields and the amount of coal and alkali mixtures taken are displayed in Table 1. The char products were analyzed through High resolution transmitted electron microscopy (HRTEM). The final char products exhibit carbon nano-products (CNPs) viz. carbon nano-chunks, carbon nanoballs, carbon nanotubes along with fewer amount of amorphous carbon. The NaOH and KOH have the tendency to extract SiO₂, Al₂O₃, Ca²⁺, Mg²⁺, SO₄²⁻, etc. from the coal samples (Baruah and Khare, 2007; Das et al., 2016; Gala et al., 1989; Mukherjee, 2003; Mukherjee and Borthakur, 2003). These alkalis dissolve alumina and silica from the clay and other silica- and alumina-bearing minerals present in the coal samples and forms soluble sodium or potassium silicate and aluminates. Later, the treatment of HCl might have removed sodium and potassium alumina-silicates gels, which formed during the MCL process. It has also removed some clay minerals from the coal samples. Similar observations were made by (Baruah and Khare, 2007; Mukherjee and Borthakur, 2001; Mukherjee and Borthakur, 2003). So, the NaOH and KOH mixture might have reduced mineral matter along with the sulfur content from the observed coal samples.

4.1.1. Development of CNPs

Coal contains various weak bonds in its macromolecular structures (matrix). The NaOH and KOH have significant activation properties on carbonaceous matters (Viswanathan et al., 2009; Yoon et al., 2004). During the MCL process, they might have intercalated between the carbonaceous layers and split them into small graphene and fullerene nanofibers. The aliphatic substituents and functional groups in coal get reacted with the alkalis during molten caustic leaching and forms partially ordered and the disordered carbon layers. Followed by the treatment of acid (HCl), the disordered carbon layer might have arranged them into ordered carbon nano-materials with the help of some naturally occurring catalytic mineral species like Fe₂O₃, FeS₂, Co, Cu, Ni, etc. in the coals. Schematic diagram indicating the formation of CNPs and CNBs through MCL process is exhibited in Fig. 3.

4.1.2. Mechanism of amorphous carbon formation

Some amount of amorphous carbon and mineral matter also remain in the MCL products during this process. The condition of the persistence of amorphous carbon is given below in the equation (based on

Gabzdyl and Varma, 1992; Weishauptová and Medek, 1991):

$$\gamma_M > \gamma_{IM} + \gamma_{MIM} \quad (1)$$

where, γ_M = surface tension of amorphous carbon; γ_{IM} = surface tension of isotropic matrix (carbon nano-products) and γ_{MIM} = surface tension of interface.

The surface tension of the amorphous carbon is very high and hence, they attach in the interface during the reaction which doesn't allow them to grow to form carbon nano-products. The viscosity of amorphous carbon units is too high during carbonization. Due to cross-linkage, the shape of these amorphous growth units will not follow the surface tension.

4.2. Results of proximate and ultimate analyses

Table 2 shows the results of proximate and ultimate analyses of collected coal samples. The carbon content (C) exhibits a very good relationship with CNPs yield ($R^2 = 0.93$; Fig. 4A). Similarly, the fixed carbon content (FC^{daf}) with CNPs yield shows a good coefficient of determination ($R^2 = 0.73$; Fig. 4B). Presence of a large amount of carbon content in the raw coals may supply more carbon ions or carbon clusters for development of CNPs. It is noticed that oxygen content is not supportive of the fullerene formation showing a negative relation with CNPs yield ($R^2 = 0.70$; Fig. 4C). Presence of oxygen (O^{daf}) may produce pyrolytic carbons (amorphous carbon), the undesirable product instead of polycyclic carbons and hence reduce the CNPs yield. They may oxidize the small carbon nanofibers and not allowing them to grow up. It creates adverse condition and acts harmful to the fullerene formations. Observations with similar explanations are reported (Geldard et al., 1998; Patney et al., 1999; Thomas et al., 1994). Hydrogen, in addition, exhibits a negative effect on CNPs synthesis ($R^2 = 0.49$; Fig. 4D). Presence of hydrogen may terminate the reactive radicals by instant attachment with them resulting in the production of small ring hydrocarbons instead of ring closure to form fullerenes/extended graphene sheet. Similar views were recorded by Chriswell et al., 1989; Pang et al., 1991; Pang, 1993; Pang et al., 1993; Taylor et al., 1994; Thomas et al., 1994. Ash yield (A^d) in the coal plays a negative role in CNPs formation ($R^2 = 0.82$; Fig. 4E). The mineral matter content (observed under petrographic analysis) has been plotted against CNPs yield and a negative relationship was noticed. It indicates mineral matter present in the coals reduces the CNPs yield ($R^2 = 0.82$; Fig. 4F). This is consistent with the reports regarding mineral matters containing alumina and silica reducing the CNPs yields (Gala et al., 1989; Mukherjee and Borthakur, 2003; Patney et al., 1999; Qui et al., 2002; Yu et al., 2003). It is suggested to remove mineral matters from coal to improve CNPs production. Earlier workers have also put forward similar views in Qui et al., 2002; Yu et al., 2003. In our study alumina and silica-bearing mineral matters were demineralized by MCL process. The MCL process has a tendency of 95% removal of ash forming mineral

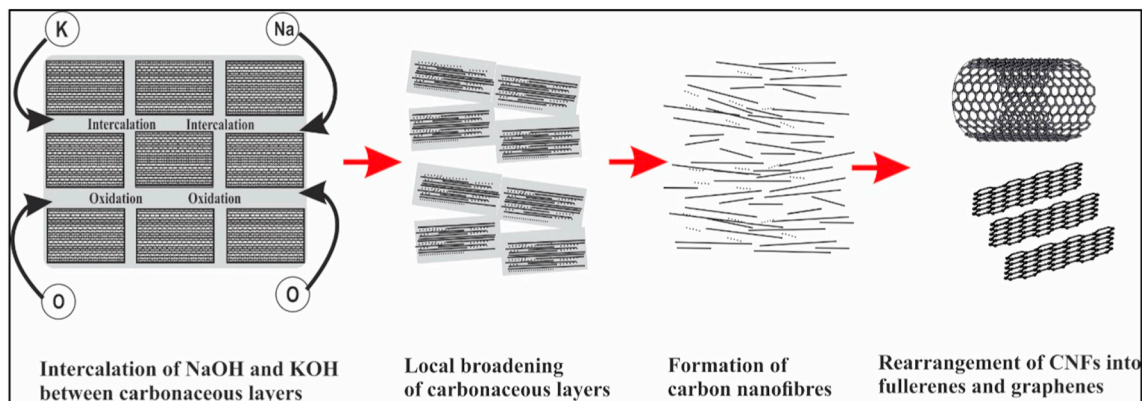


Fig. 3. Sketch illustrating the formation of carbon nano-products through MCL process (based on Yoon et al., 2004).

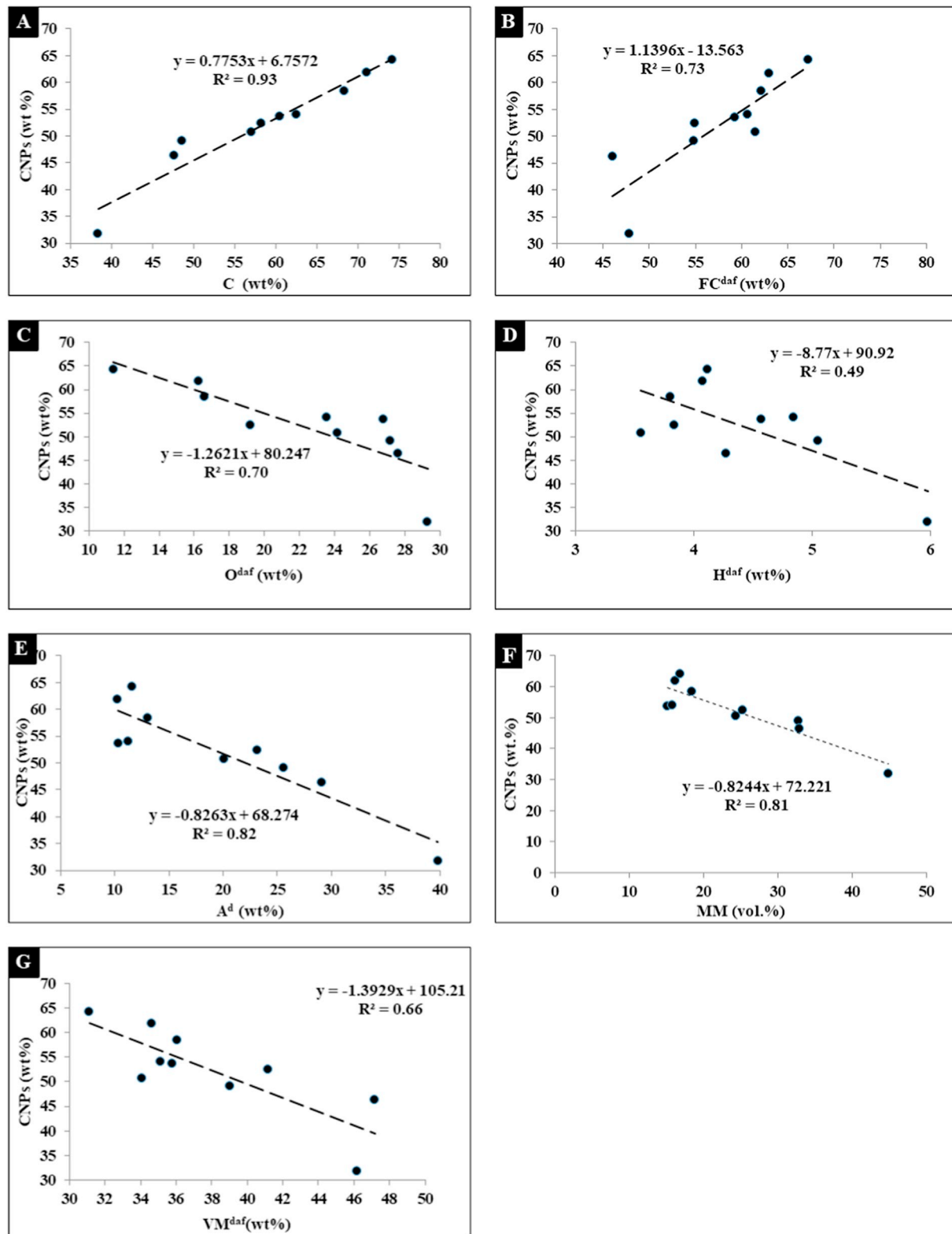


Fig. 4. Relation between various (proximate and ultimate) parameters and carbon nano-products yield viz. A = Relation between carbon content (C wt%) of coal samples and CNPs yield (wt%); B = Relation between fixed carbon content (FC^{daf} wt%) of coal samples and CNPs yield (wt%); C = Relation between oxygen content (O^{daf} wt%) of coal samples and CNPs yield (wt%); D = Relation between hydrogen content (H^{daf} wt%) of coal samples and CNPs yield (wt%); E = Relation between ash yield (A^d wt%) of coal samples and CNPs yield (wt%); F = Relation between mineral matter content (MM vol%) of coal samples under petrographic analysis and CNPs yield (wt%); G = Relation between volatile matter yield (VM^{daf} wt%) of coal samples and CNPs yield (wt%).

Explanations: CNPs = carbon nano-products yield; C = carbon content; FC = fixed carbon content; O = oxygen; H = hydrogen; A = ash yield; MM = mineral matter content; VM = volatile matter yield; ^d = on dry basis; ^{daf} = on dry ash free basis.

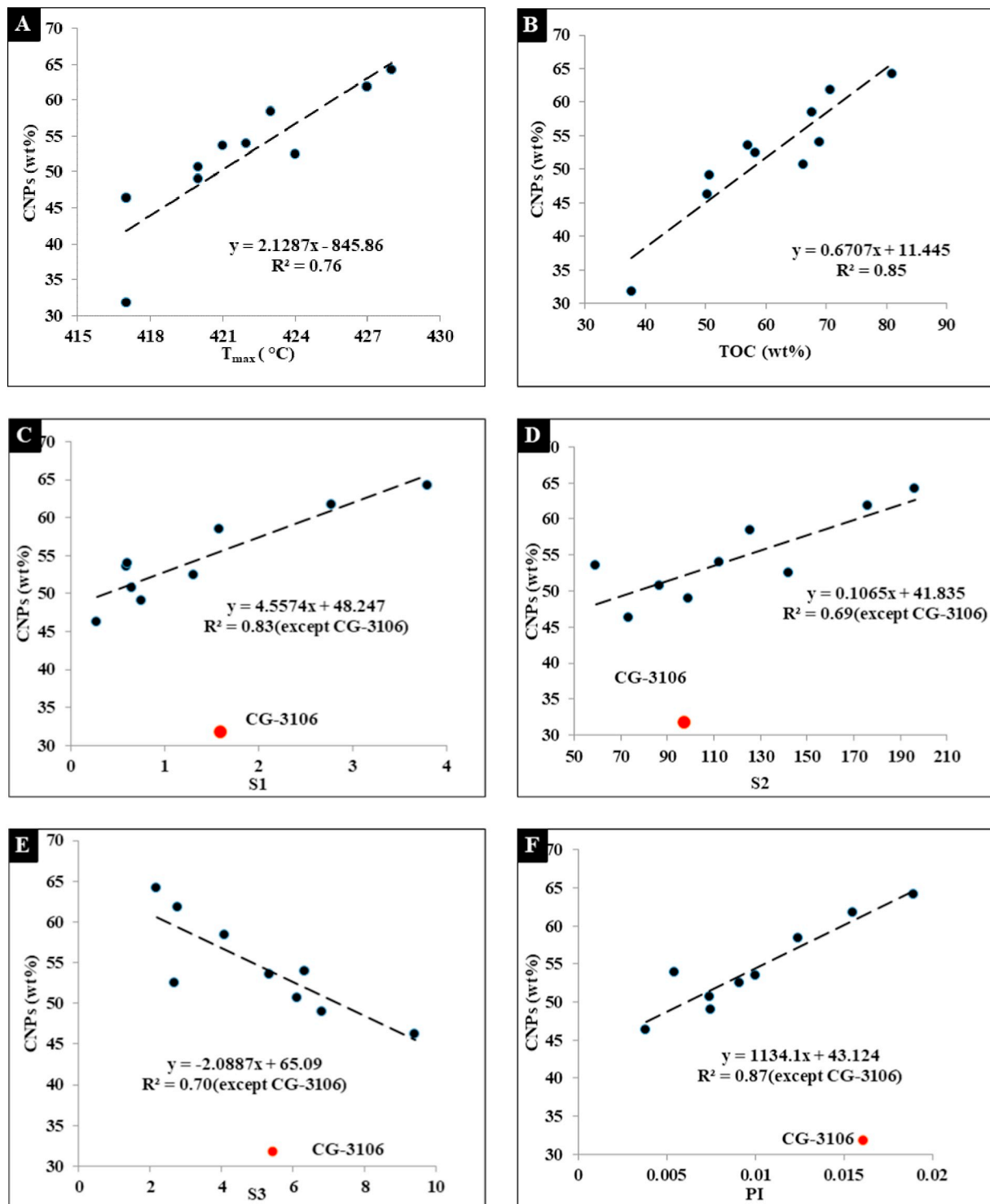


Fig. 5. Relations between various parameters of RE pyrolysis and CNPs yield viz. A = Relation between T_{max} ($^{\circ}\text{C}$) of the coal samples and CNPs yield (wt%); B = Relation between TOC (wt%) of the coal samples and CNPs yield (wt%); C = Relation between S1 of the coal samples and CNPs yield (wt%); D = Relation between S2 of the coal samples and CNPs yield (wt%); E = Relation between S3 of the coal samples and CNPs yield (wt%); F = Relation between PI of the coal samples and CNPs yield (wt%).

Explanations: S1 = amount of free thermolabile hydrocarbons (mg HC/g of rock); S2 = amount of thermally cracked hydrocarbon (mg HC/g of rock); S3 = amount of CO_2 yield (mg CO_2 /g rock); T_{max} = the temperature that corresponds to the maximum pyrolyzate released under S2; TOC = amount of total organic carbon (wt%); PI = production index ($\text{S1}/(\text{S1} + \text{S2})$); MINC = mineral carbon (wt%).

matters (Chriswell et al., 1989; Dosodia et al., 2009). In XRD analysis some amount of hematite and siderites are observed, which may enhance the CNPs yield. The iron group metals might have reacted with carbon to form metal carbides that may become largely active as a

catalyst, with dissociative chemisorption of carbon. Further, the adequate continuous supply of carbon has proceeded the development of carbon nano-products formation. Similar observations regarding iron content in mineral matter favoring CNPs synthesis were reported earlier

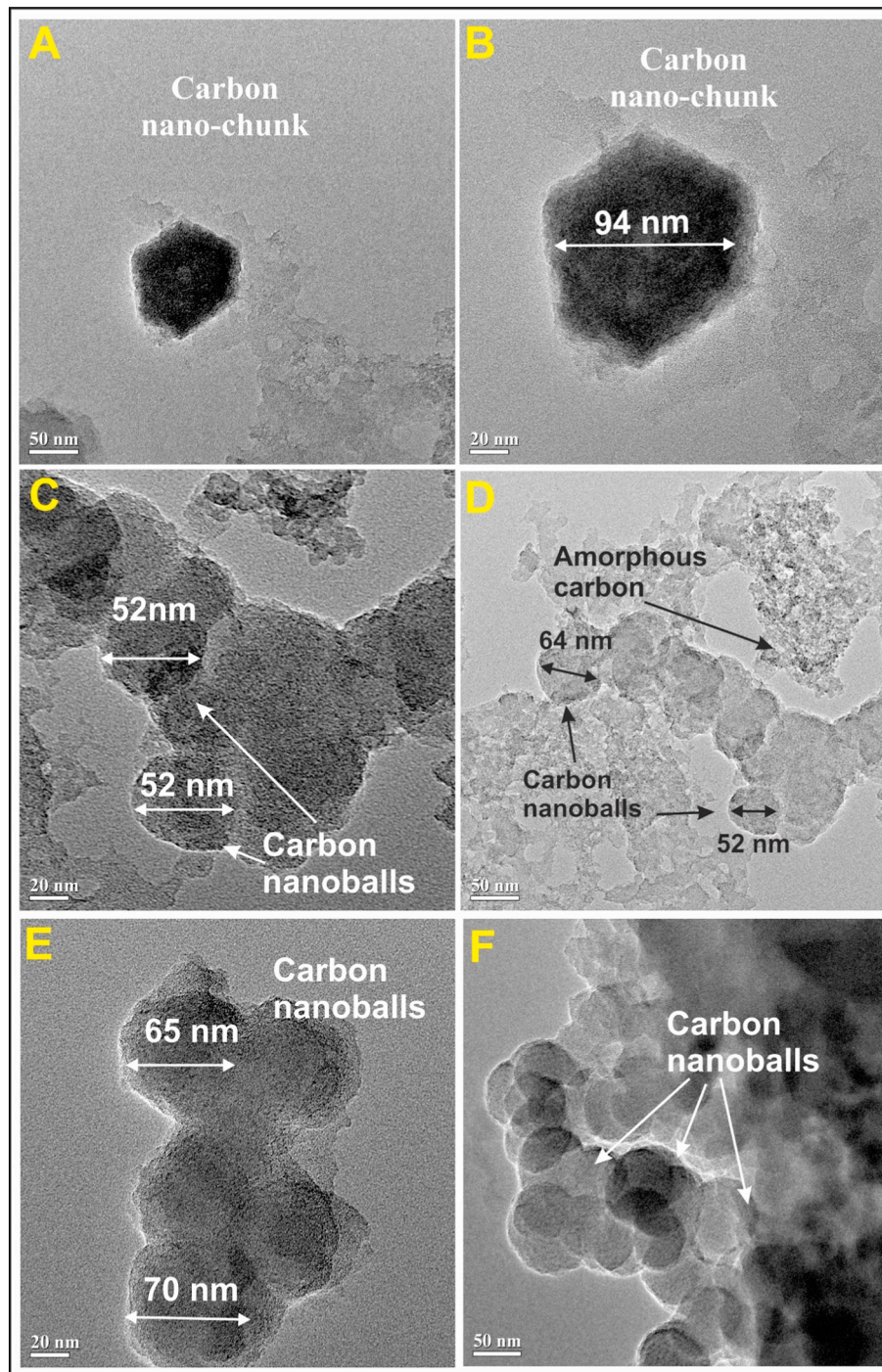


Fig. 6. HRTEM images of carbon nano-products; A&B = carbon nano-chunks, C, D, E& F = carbon nanoballs with various sizes.

in Qui et al., 2002; Yu et al., 2003. Volatile matter content (VM^{daf}) in the coal shows a negative relation to the CNPs formation ($R^2 = 0.66$; Fig. 4G). This might be due to some hydrogen content and some other hetero-atoms, constituting the volatiles, take part in some plasma reactions and reduce the fullerene yield. Similar explanations regarding the volatile matter were reported in Qui et al., 2002; Yu et al., 2003.

4.3. Rock Evaluation (RE) pyrolysis

TOC (organic richness, total organic carbon) and T_{max} determined from Rock Evaluation (RE) pyrolysis might have played a significant role in the CNPs synthesis. The quantity and purity of CNPs synthesis

have been evaluated by the basic parameters of RE pyrolysis. A plot between CNPs yield and T_{max} shows a positive linear correlation ($R^2 = 0.76$; Fig. 5A). T_{max} is the temperature at which maximum amount of pyrolyzate is yielded under S2 curve of RE pyrolysis. The CNPs yield increases with increasing in T_{max} . The CNPs yield with TOC is also showing a good positive correlation ($R^2 = 0.85$; Fig. 5B) indicating that large organic carbon content present in the coal samples facilitates the CNPs synthesis. Therefore, coal with large TOC and high hydrocarbon genetic potential ($GP = S1 + S2$) are needed for the production of CNPs. CNPs yield showing a linear positive correlation with S1 ($R^2 = 0.83$; Fig. 5C). S1, the quantity of free thermolabile hydrocarbons released from the sample, appears to take part in CNPs

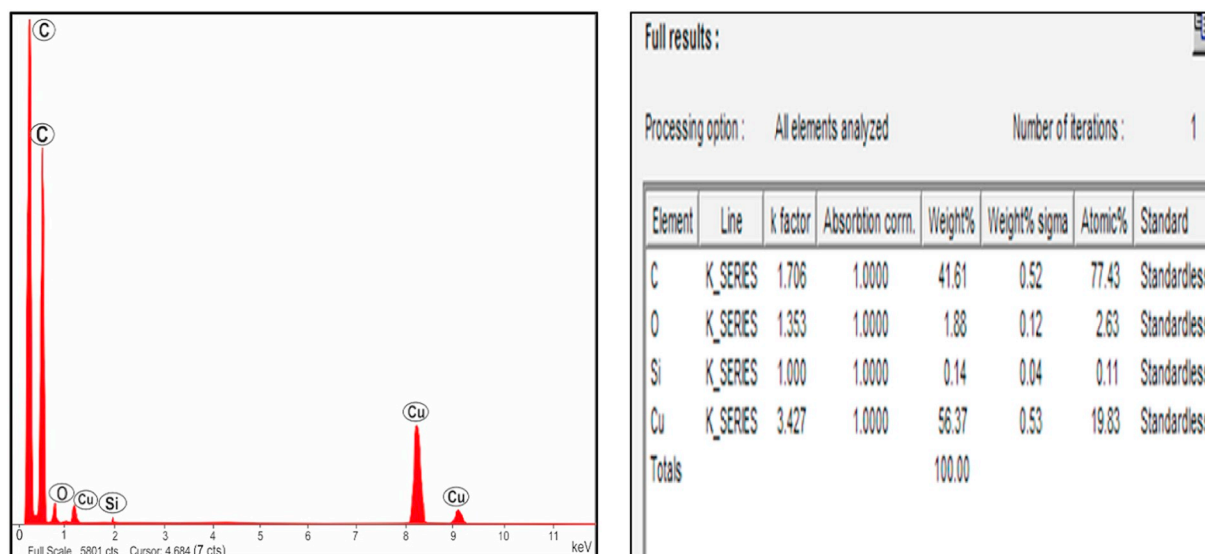


Fig. 7. EDX spectra and measurements of the sample CG-3126 under HRTEM analysis.

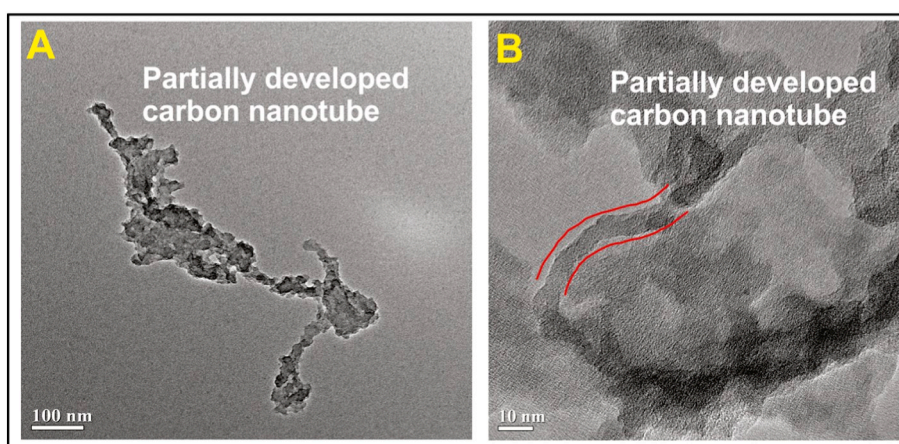


Fig. 8. A & B = HRTEM images of partially developed carbon nanotubes.

formation. It may facilitate the CNPs production by reducing the viscosity of the solution and catalyze the reaction. During the MCL process, NaOH and KOH intercalate between the carbonaceous layers and split them into small carbon nanofibers. The relationship of CNPs yield with S2 ($R^2 = 0.69$; Fig. 5D) exhibits a positive correlation, which may similarly reduce the viscosity and help positively in the formation of CNPs. The S3 under RE pyrolysis indicates the negative influence on the CNPs yield (Fig. 5E). The S3 representing the volume of CO_2 released from the molecular breakdown of carboxyl groups and some other oxygen-containing compounds in kerogen is obtained at 300–390 °C (Peters and Cassa, 1994). The oxygen contents in the compounds might have an unfavorable effect on the CNPs synthesis. Relation to the production index (PI) with CNPs yield showing a positive linear correlation ($R^2 = 0.87$; Fig. 5F). The PI $[S1/(S1 + S2)]$ is a measure of hydrocarbon production level from the organic matter. This may act in a similar way as S1 by reducing the viscosity of the solution. Sample CG-3106 deviates from the trend lines in Fig. 5C, D, E, and F because of a comparatively large amount of ash yield that might have hindered the CNPs synthesis.

4.4. High-resolution transmitted electron microscopy (HRTEM)

A high resolution transmitted electron microscope with energy dispersive X-ray spectrometer (EDX) was employed for characterizing

the MCL products. The different types of carbon nano-structures like nanoballs, nano-chunks, nanotubes, etc. along with some attached amorphous carbon particles in the char products are observed. HRTEM images of carbon nano-chunks or nano-flakes formed in a hexagonal shape by MCL process are shown in Fig. 6A and B. Hexagonal and pentagonal planar flakes combine together in order to accommodate the curvature of the carbon sphere (Pang et al., 1993). Fig. 6C and D represent a partially developed carbon nanoballs (CNBs) structure with a diameter varying from 52 nm to 64 nm. Some amorphous carbon particles are attached to these bunch of carbon nanoballs. Fig. 6E and F can be attributed to the developed carbon nanoballs with a diameter ranging from 61 nm to 70 nm. They are agglomerated as a bunch of nanoballs by Van der Waals forces. Fig. 7 shows the representative EDX measurements of the MCL product of sample CG-3126. Carbon is the leading atomic 77.43 wt% value indicating the presence of CNPs in the sample. Some traces of Cu are appeared due to the copper coating used for the analysis. Some amount of oxygen and silicon also exist may be due to the non-complete dissolution of mineral matters and the presence of some oxides in the sample during the MCL process. A partially developed carbon nanotube can be seen in Fig. 8A and it is in a developing stage. Carbon nanotubes (CNTs) having a thread like structure embedded with some amorphous carbon particles are exhibited in Fig. 8B. Here, the outline is not distinct as it is partially developed. The worm-shaped CNTs with a cylindrical tube-like body structure are

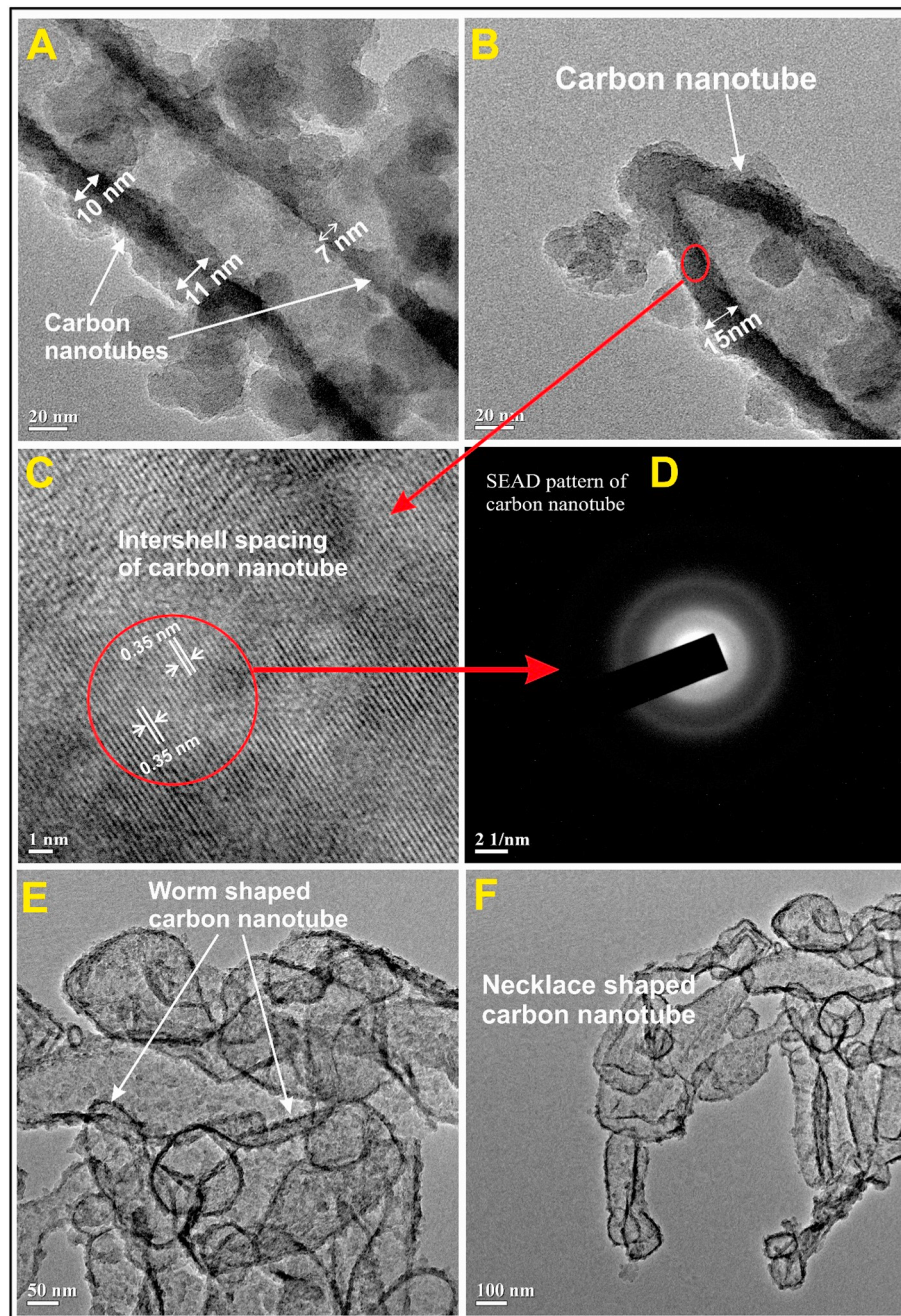


Fig. 9. HRTEM images of carbon nanotubes viz. A & B = cylindrical shaped carbon nanotubes, C = magnified view of the surface with inter-planer spacing, D = Selected area electron diffraction (SAED) pattern of the corresponding image C; E & F = necklace shaped and worm-shaped carbon nanotubes.

depicted in Fig. 9A and it is also attached with amorphous carbons and some nanoballs. The diameter of the CNTs varies from 7 to 11 nm. Fig. 9B also shows a CNT with the diameter of 15 nm. Fig. 9C illustrates the intershell spacing and layering of the carbon nanotube. The measured inter-planar distance of the carbon layers is observed to be 0.35 nm. Selected area electron diffraction pattern (SAED) (Fig. 9D) in the corresponding image (Fig. 9C) records the presence of nano-

particles, which is characterized by a structure of fine rings. The other figures (Fig. 9E and F) display the typical HRTEM microphotographs of carbon nanotubes formed along with some agglomerated amorphous carbons. These carbon nanotubes are showing necklace and worm shapes and appear to be entangled with a wavy morphology. Similar shaped carbon nanotubes were also reported in Kuhlmann et al., 1999; Patney et al., 1999.

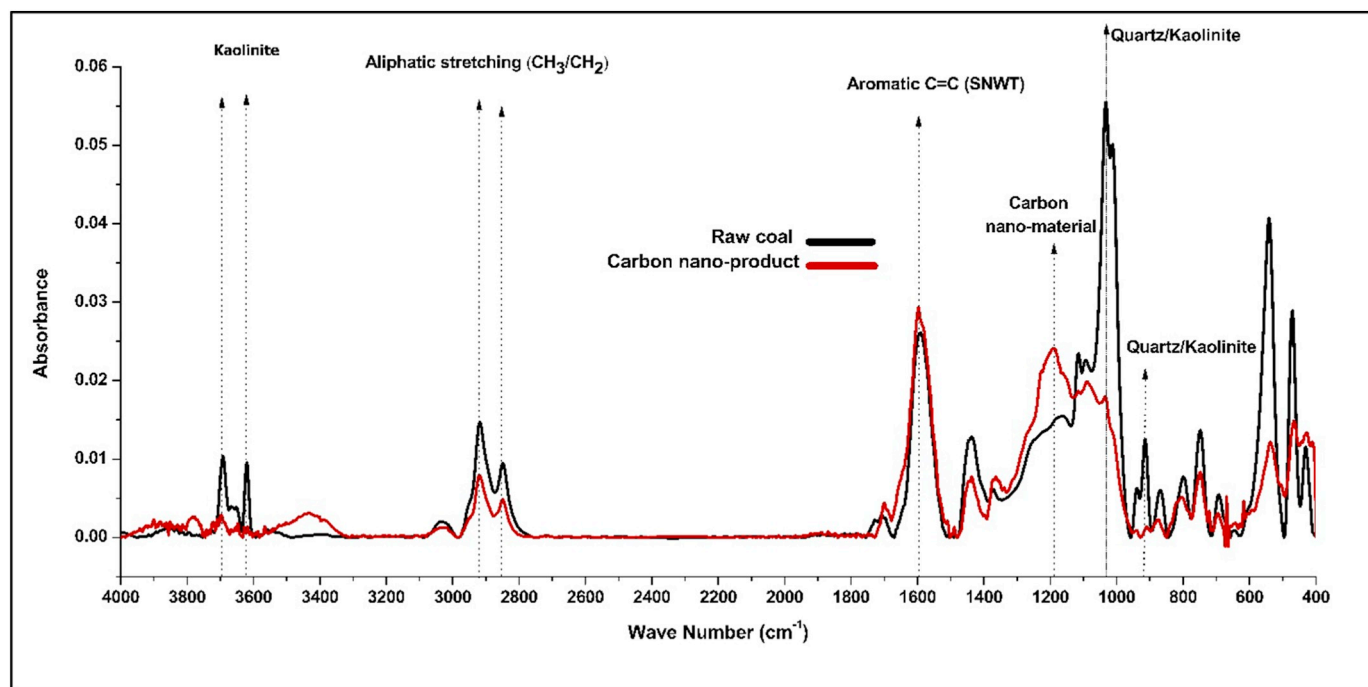


Fig. 10. FTIR spectra of raw sample and carbon nano-product (CNPs).

Table 4

Various semi-quantitative ratios from FTIR analysis.

Sample no.	A-factor	I_{AL}	I_{AR}
CG-3101	0.438	0.150	0.850
CG-3105	0.584	0.399	0.601
CG-3106	0.645	0.412	0.588
CG-3113	0.500	0.098	0.902
CG-3117	0.500	0.094	0.906
CG-3121	0.455	0.255	0.745
CG-3122	0.616	0.510	0.490
CG-3125	0.820	0.523	0.477
CG-3126	0.765	0.710	0.290
CG-3128	0.796	0.475	0.525

Explanations: I_{AL} = Index of aliphaticity, I_{AR} = index of aromaticity.

4.5. Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) of both raw coal samples and obtained MCL products has been studied. Some significant changes in FTIR spectra have been observed in Fig. 10.

4.5.1. Raw samples

The hydroxyl stretching and –OH group of kaolinite are observed in 3694 cm^{-1} and 3620 cm^{-1} , respectively in the raw coals. Some prominent aliphatic vibrational frequencies are also observed in the region of aliphatic stretching at 2800 cm^{-1} and 3000 cm^{-1} . The aliphatic chains were broken up in the MCL process which is depicted by a decrease in its intensity after treatment in the MCL process. The coal samples reveal long chain aliphatic with higher intensities centered at 2920 and 2850 cm^{-1} demonstrating aliphatic chains of longer dimensions (Varma et al., 2015). The existence of aromatic carbon (C=C)

indicated by the absorption band at 1600 cm^{-1} which shows lower intensity before the MCL process. Various semi-quantitative ratios like A-factor, Index of aliphaticity (I_{AL}), and Index of aromaticity (I_{AR}) are derived from FTIR spectra and used for this study (Ganz and Kalkreuth, 1991; Misra et al., 2018). The values of these parameters of A-factor, I_{AL} , I_{AR} are exhibited in Table 4.

$$A - \text{Factor} = [(2860 + 2930\text{ cm}^{-1}) / (2860 + 2930 + 1630\text{ cm}^{-1})] \quad (2)$$

$$I_{AL} = [(2950 + 2920 + 2850\text{ cm}^{-1}) / (3030 + 2950 + 2920 + 2850 + 1600\text{ cm}^{-1})] \quad (3)$$

$$I_{AR} = [(3030 + 1600\text{ cm}^{-1}) / (3030 + 2950 + 2920 + 2850 + 1600\text{ cm}^{-1})] \quad (4)$$

A-factor is the ratio of aliphatic/aromatic intensities bands. Plotting the A-factor with CNPs yield shows a linear positive relationship (Fig. 11A), which suggests with increase in aliphaticity, CNPs development enhances. Index of aliphaticity (I_{AL}) is calculated (Misra et al., 2018) to determine the abundance of aliphaticity. The plot between the Index of aliphaticity (I_{AL}) and CNPs yield ($R^2 = 0.75$; Fig. 11B) also shows a linear trend. Similarly, Index of aromaticity (I_{AR}) is also calculated (Misra et al., 2018) to determine the relative richness of aromaticity ($3030 + 1600\text{ cm}^{-1}$) over the sum of total aromatics and aliphatics. The plot between CNPs yield and indices of aromaticity (I_{AR}) indicates ($R^2 = 0.75$; Fig. 11C) a negative relationship. The aliphatic chains are more susceptible to reaction with the alkalis than the aromatics used in MCL process. The aliphatic substituents in coal molecular structure may be oxidized during the MCL process. This may facilitate the development of some moderately ordered and disordered carbon microlayers. Further, on the treatment of MCL products with

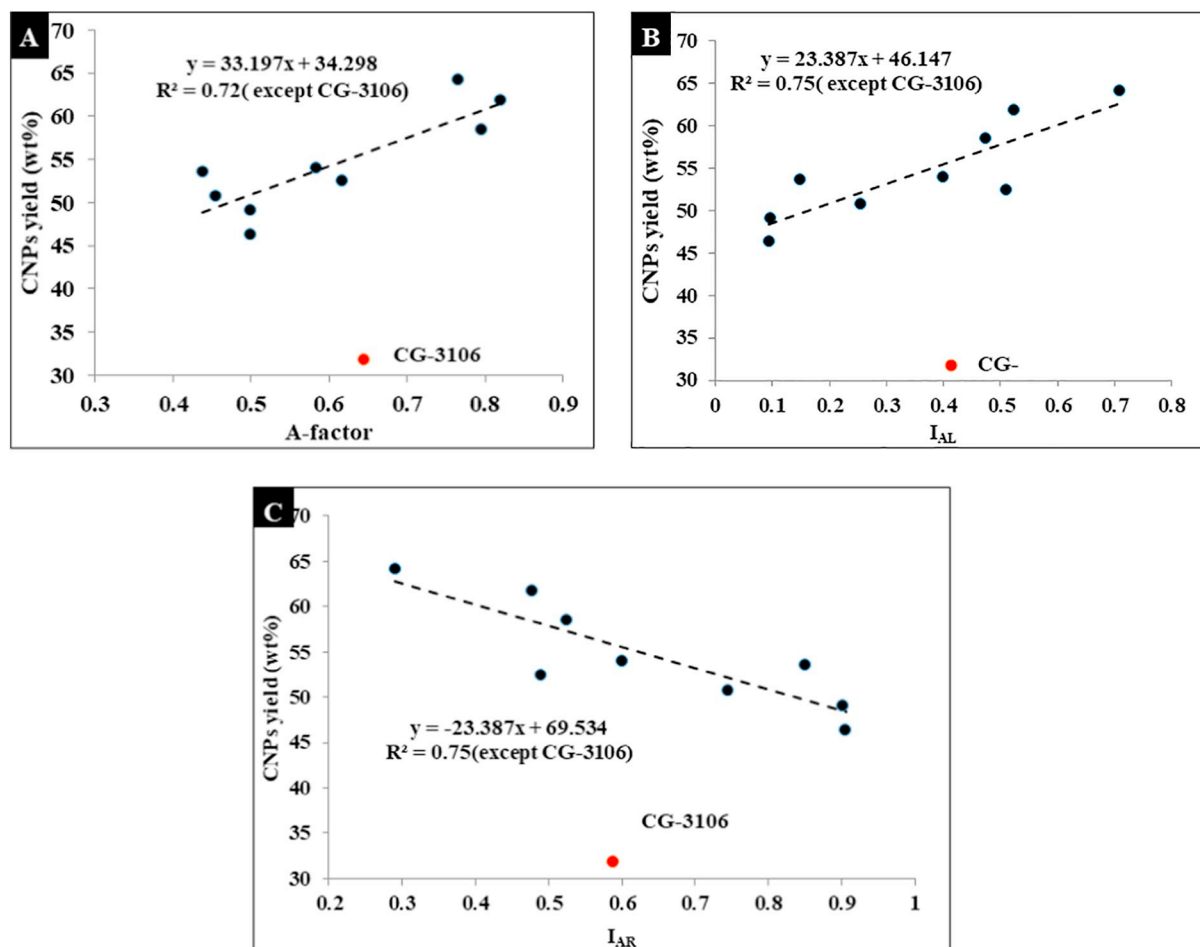


Fig. 11. Relationship between CNPs yield and semi-quantitative ratios of FTIR analysis viz. A = Relationship between A- factor of the coal samples and CNPs yield (wt%); B = Relationship between I_{AL} of the coal samples and CNPs yield (wt%); C = Relationship between I_{AR} of the coal samples and CNPs yield (wt%). Explanations: I_{AL} = index of aliphaticity, I_{AR} = index of aromaticity, CNPs = carbon nano-products.

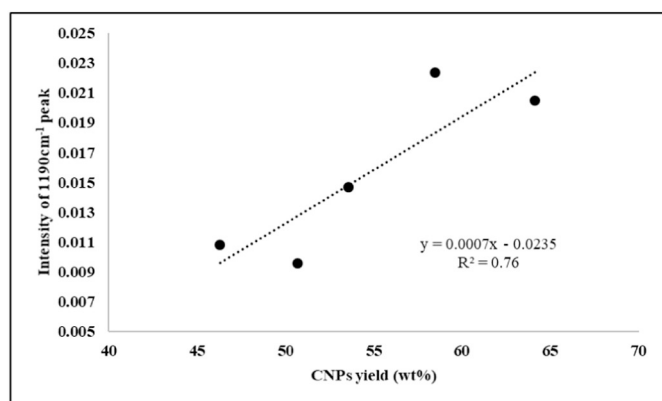


Fig. 12. Relation between CNPs yield and intensity of 1190cm^{-1} peak.

HCl, the weak cross-links of coal may easily break up, with liberating the alkynes and aromatic reactive hydrocarbons. These reactive hydrocarbons along with catalytic ions of Fe_2O_3 , FeS_2 , Co, Ni, Cu, etc. usually occurring in coal might help in carbon nano-materials

formation (Dosodia et al., 2009; Hernadi et al., 1996; Saikia et al., 2009). The aromatic bonds are most stable and stronger than aliphatic bonds and less reactive, so they have little participation in the reaction with alkali mixture added in the MCL process. Thus, it limits to CNPs formations in the MCL process. The sample CG-3106 is deviated from the trend line due to a large amount of ash yield that might have hindered the CNPs synthesis.

4.5.2. MCL products

FTIR spectra of MCL products exhibit a broad peak located around 1190cm^{-1} with strong intensity signifying the occurrence of carbon nano-tubes. This band is a characteristic feature of carbon nano-tubes (Bantignies et al., 2006). The relation between CNPs yield and peak intensities of absorbance for 1190cm^{-1} is plotted. A good positive correlation ($R^2 = 0.76$; Fig. 12) is observed. Some amorphous carbon in the MCL products is observed through small peaks at 1045 and 1090cm^{-1} (Bantignies et al., 2006). The distinct functional group(s) at 1600 and 860cm^{-1} can be assigned as the presence of single-walled carbon nanotube (SWNT). The aromatic $\text{C}=\text{C}$ at 1600cm^{-1} band shows an increase in intensity. This may result from an enhancement in the organization of aromatic rings in the MCL products. Similar

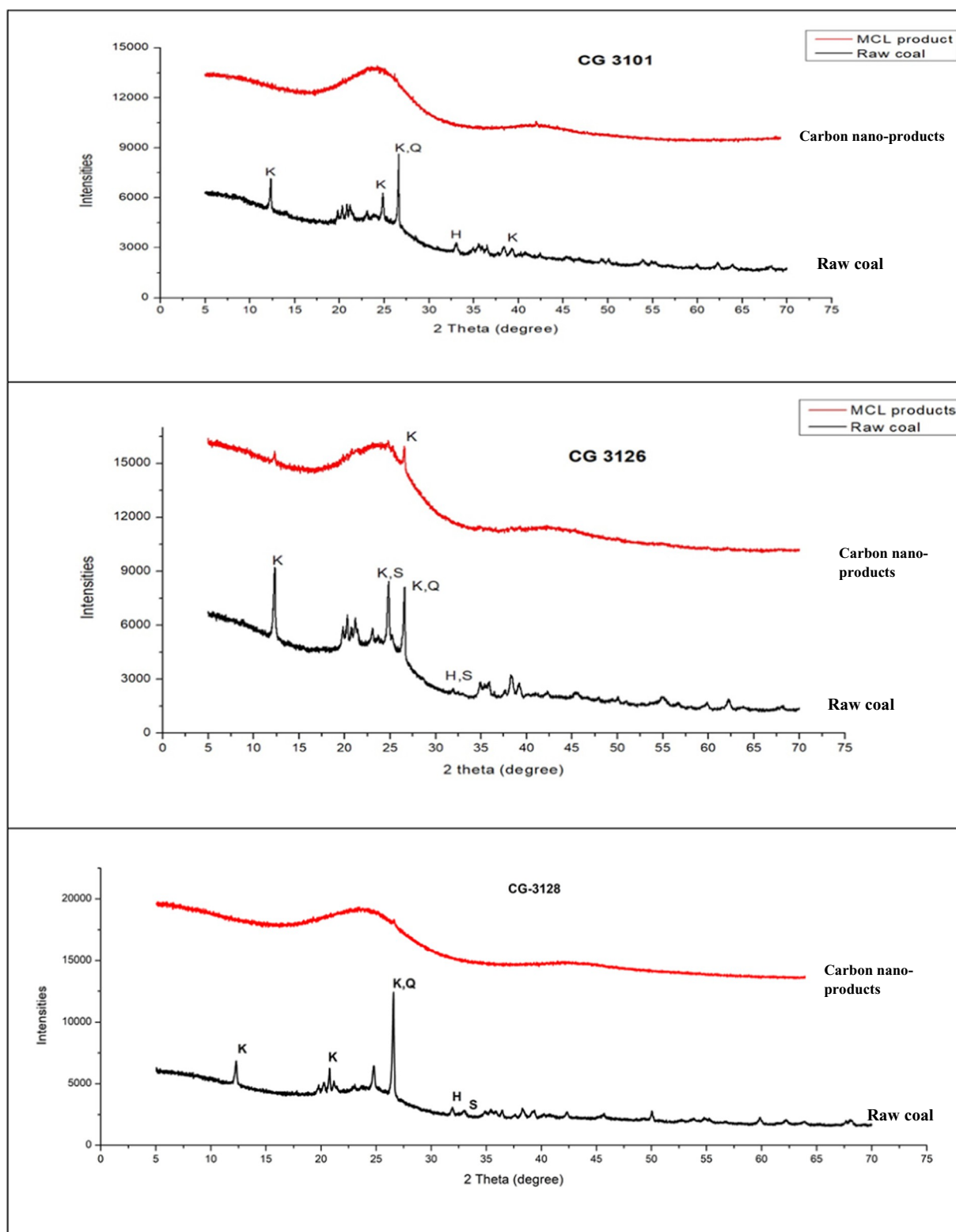


Fig. 13. XRD analysis of raw coal samples and carbon nano-products of sample CG-3101, CG-3126 and CG-3128 respectively. Explanations: K = Kaolinite; Q = quartz; H = Hematite; S = siderite.

Table 5
Maceral composition (vol%) of the coal samples.

Sample no.	V ^{mmf}					L ^{mmf}					I ^{mmf}					MM									
	Te	Co	Vd	Cod	Ge	CoG	Total	Spo	Cut	Res	Alg	Ld	Exd	Sub	Bitu	Total	Sf	F	Mac	Mic	Fun	InD	Sec	Total	
CG-3101	5.37	47.52	3.52	1.64	0.29	0.22	58.57	5.90	1.12	0.00	0.08	0.97	0.00	0.00	0.00	8.07	26.95	0.99	1.88	0.28	0.00	3.27	0.00	33.36	15.13
CG-3105	2.42	43.84	5.08	3.18	0.08	0.00	55.61	3.06	0.78	0.45	0.06	3.75	0.00	0.00	0.00	8.10	26.06	1.34	0.40	2.83	0.00	5.66	0.00	36.29	15.80
CG-3106	0.23	32.08	5.86	2.32	0.00	0.00	40.50	0.99	0.21	0.00	0.00	0.85	0.00	0.00	0.00	2.05	45.18	2.27	1.07	0.01	0.00	8.92	0.00	57.45	44.91
CG-3113	2.67	48.86	2.97	3.15	0.01	2.37	60.04	6.65	2.46	0.30	0.05	0.32	0.00	0.00	0.00	9.78	23.03	2.40	0.59	2.08	0.00	2.08	0.00	30.17	32.75
CG-3117	3.50	43.48	5.03	2.04	0.58	0.29	54.91	6.65	1.00	0.28	0.07	0.04	0.00	0.00	0.00	8.04	24.19	2.67	0.29	2.91	0.00	6.99	0.00	37.05	32.95
CG-3121	0.79	40.56	5.02	0.74	0.00	5.53	52.65	5.50	0.13	0.00	0.09	2.72	0.00	0.00	0.00	8.44	26.21	5.85	1.05	1.32	0.00	4.48	0.00	38.91	24.37
CG-3122	2.68	51.90	1.87	0.54	0.07	0.00	57.05	5.15	0.33	1.07	0.13	0.74	0.00	0.00	0.00	7.42	24.19	2.25	1.87	2.68	0.00	4.55	0.00	35.53	25.24
CG-3125	0.70	61.01	1.16	0.23	0.93	0.00	64.02	10.42	0.40	0.23	0.16	0.27	0.00	0.00	0.00	11.48	13.37	2.27	5.38	1.85	0.00	1.62	0.00	24.49	16.14
CG-3126	1.19	63.02	0.95	0.47	0.19	0.71	66.53	11.31	1.23	0.24	0.15	0.99	0.00	0.00	0.00	13.92	11.92	1.71	2.37	1.19	0.24	2.13	0.00	19.56	16.80
CG-3128	2.44	52.90	0.49	0.56	0.09	0.24	56.72	9.22	1.00	0.00	0.11	0.25	0.00	0.00	0.00	10.58	27.60	1.68	0.73	0.73	0.00	1.95	0.00	32.70	18.41

Explanations: ^{mmf} = mineral matter free basis (vol%); V = vitrinite macerals; L = liptinite macerals; I = inertinite macerals; Te = telinite; Co = collotelinite; Vd = vitrodetrinite; CoD = collodetrinite; Ge = gelinite; CoG = corpogelinite; Spo = sporinite; Cut = cutinite; Res = Resinite; Ld = liptodetrinite; Exd = exsudatinite; Sub = suberinite; Bit = bituminite; Sf = semifusinite; F = fusinite; Mac = macrinite; Mic = micrinite; Fun = funginite; InD = inertodetrinite; (all macerals of vitrinite, inertinite and liptinite groups were determined on mineral matter free basis) MM = mineral matters.

observations were reported by Kuhlmann et al., 1999. Reduction in the intensity of kaolinite peaks corresponding to 3652 cm^{-1} , 3641 cm^{-1} and 3694 cm^{-1} in the MCL products, has been depicted (Fig. 10). This might be due to some alumina and silica-bearing minerals which were dissolved from the clay after treatment of the coal samples with alkali mixture (Das et al., 2016).

4.6. X-ray diffraction (XRD) analysis

Coal samples and MCL products were studied under X-ray diffraction (XRD) to investigate mineral matters. Kaolinite (K), quartz (Q), hematite (H), and siderite (S) are noticed in coal samples. Hematite, pyrite, and siderites (naturally occurring iron content) are favorable mineral matters promoting the carbon nanotube formations (Hernadi et al., 1996; Qiu et al., 1998). The iron group metals may react with carbon to form metal carbides that may become largely active as a catalyst, with dissociative chemisorption of carbon. Further, the adequate continuous supply of carbon is required for the development of carbon nano-products. X-ray diffractogram records reduction in kaolinite, hematite, siderite, and quartz after MCL process (Fig. 13). The alkali mixture (NaOH + KOH) and HCl treatment possibly have broken the macromolecular structure of coal into smaller shattered portions and rearrange the broken parts into orderly carbon layers as carbon nano-materials which is already discussed in section 4.5.1.

4.7. Petrographic Analysis

The abundance of macerals was determined by using the point counting method in the maceral analysis (Table 5). Vitrinite (V^{mmf}) content varies from 40.50–66.53 vol% and is differentiated into telinite, collotelinite, collodetrinite, vitrodetrinite, gelinite, and corpogelinite. A significant amount of liptinites (L^{mmf}) ranges from 2.05–13.92 vol%. All samples except CG-3105 and CG-3106 exhibit considerable amount of sporinites and cutinites. Inertinite (I^{mmf}) content extends from 19.56–57.45 vol%. The inertinite maceral group is separated into fusinite, semifusinite, funginite, secretinite, macrinite, micrinite and inertodetrinite. Microphotographs of various macerals are shown in Fig. 14. The mineral matter content varies from 15.13 to 44.91 vol%. The dominant constituents of mineral matter are clays along with a small amount of pyrites. The role of the microscopic organo-petrographic constituents (macerals) in coal appears to be significant in CNPs formations. The relation of vitrinite content (V^{mmf}) with CNPs yield shows a positive linear correlation ($R^2 = 0.83$; Fig. 15A). Liptinite (including alginite, sporinite, and cutinite) also shows a positive correlation to CNPs yield ($R^2 = 0.86$; Fig. 15B). The occurrence of branched-aliphatic contents, higher aliphatic chains, and bridges with some alicyclic parts in liptinites and vitrinites and their reactions in CNPs formation, explains the above-mentioned observations. The aliphatic chains are more susceptible to reaction with the alkalis used in MCL process and they catalyze the reaction. The weak bonds and cross-links break down and release the reactive hydrocarbons like alkynes and aromatic species. The used alkalis and acid treatment may facilitate the disordered bonds to be ordered as fullerene structures during the MCL process. Similar observations have been reported in Baruah and Khare, 2007; Viswanathan et al., 2009. Therefore, liptinite and vitrinite macerals favor the formation of carbon nano-products (CNPs). Liptinite has highest aliphatic bonds among all macerals subgroups and alginite contains the highest among all liptinite macerals. Alginite maceral of liptinite, having largest aliphatic components shows a good linear positive correlation with CNPs yield ($R^2 = 0.79$; Fig. 15D). However, a small amount of alginite is observed, that might have played as a significant facilitator in CNPs formations. In addition, liptinite (L^{mmf}) exhibits a fairly good correlation with the index of aliphaticity ($R^2 = 0.40$). In contrast, liptinite plays a negative correlation with the index of aromaticity. Similar observations were made by Misra et al., 2018. Further, a negative correlation of CNPs formation with inertinite

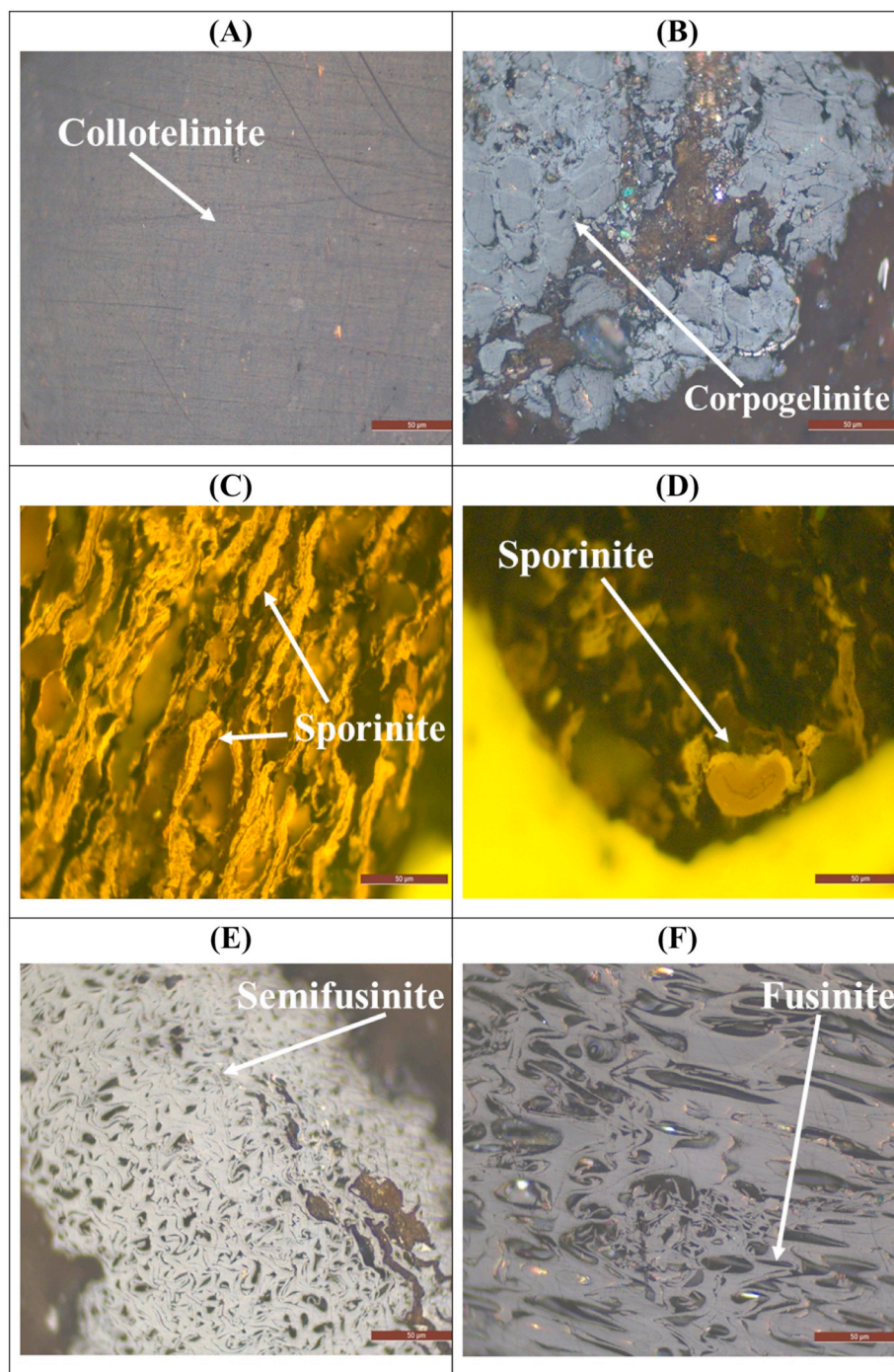


Fig. 14. (A) = Microphotographs of collotelinite; (B) corpogelinite; (C, D) = sporinite under fluorescent light; (E) = semifusinite; (F) = fusinite.

content is observed ($R^2 = 0.86$; Fig. 15C). The inertinite macerals are characterized by high aromaticity with aromatic rings of large size. The aromatic bonds are most stable and stronger than aliphatic bonds and are less reactive, therefore do not take part in reaction with alkalis/acid treatment. Additionally, inertinites contain a large amount of oxygen-rich functional groups. These oxygen functional groups are not conducive for CNPs synthesis. Similar observations were reported in

Kidena et al., 2002; Patney et al., 1999; Smith, 1994. Moreover, Inertinite (I^{mmf}) indicates a fairly negative correlation with index of aliphaticity ($R^2 = 0.36$). In addition, Inertinite depicts fairly good positive correlation with the Index of aromaticity ($R^2 = 0.36$). Hence vitrinites and liptinites appear to be favorable organo-petrographic entities for CNPs formation in coal as they facilitate major molecular rearrangement.

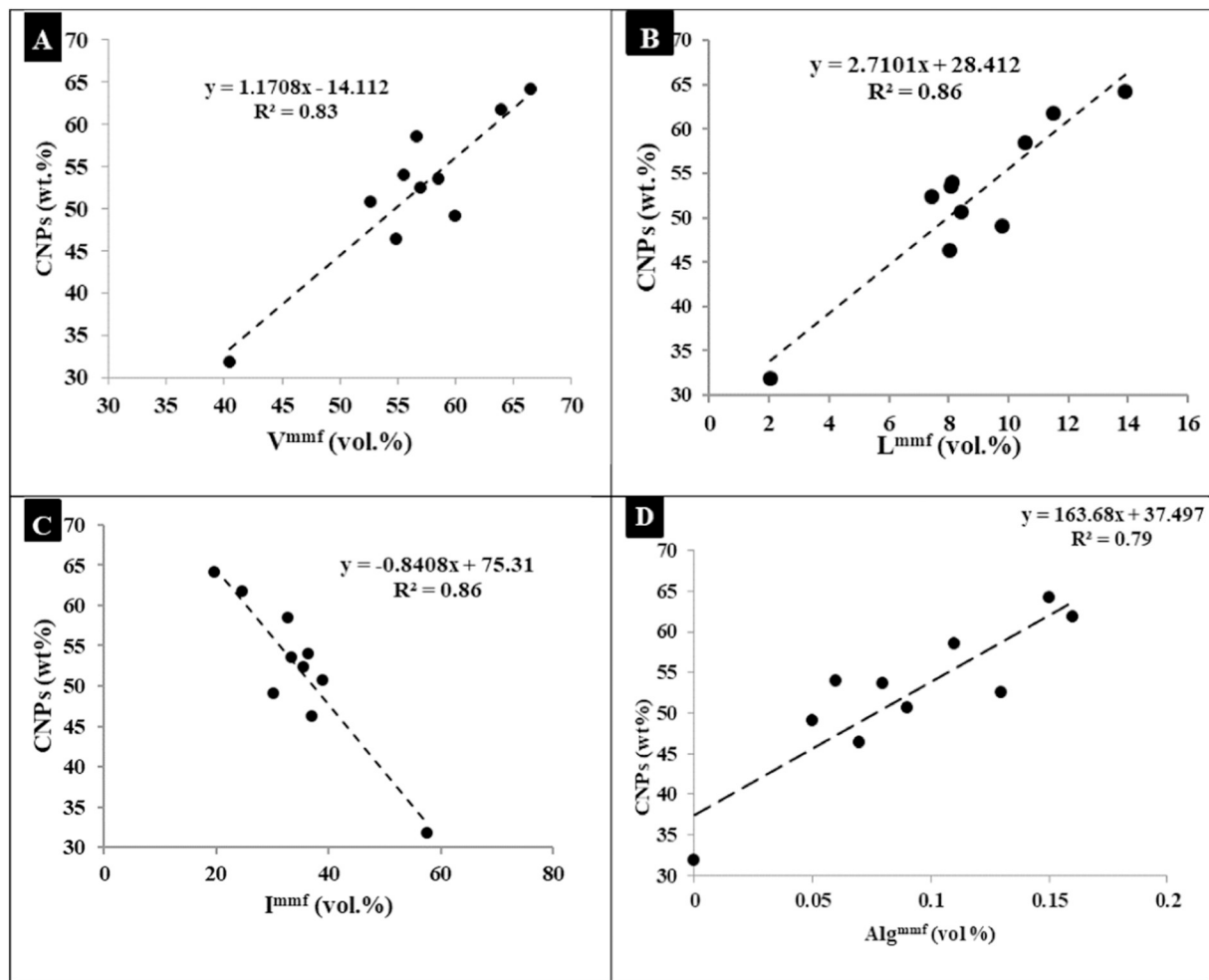


Fig. 15. Relation between organopetrographic entities of the coal samples and CNPs yield viz. (A) = Relation between vitrinite (V^{mmf} vol%) of the coal samples and CNPs yield (wt%); (B) = Relation between liptinite (L^{mmf} vol%) of the coal samples and CNPs yield (wt%); (C) = Relation between inertinite (I^{mmf} vol%) of the coal samples and CNPs yield (wt%); (D) = Relation between alginite (Alg^{mmf} vol%) of the coal samples and CNPs yield (wt%).

Explanations: CNPs = carbon nano-products yield, ^{mmf} = in mineral matter free basis.

The petrographic estimate of CNPs production (PEC) is empirically proposed for determining the relative reactivity of macerals and calculation of CNPs yield through the MCL process. It may help to select the suitable coal samples for CNPs synthesis. The PEC is estimated from the following Eq. (5):

$$PEC = 0.23V^{mmf} + 0.54L^{mmf} + 0.16C^{daf} - 0.17I^{mmf} - 0.28VM^{daf} + 40.31 \quad (5)$$

where, PEC = Petrographic estimate of CNPs production (wt%); V = vitrinites (vol%); L = liptinites (vol%); I = inertinites (vol%); C = carbon (wt%), VM = volatile matter yield, ^{mmf} = on mineral matter free basis, ^{daf} = on dry ash free basis.

The PEC exhibits a good coefficient of determinations with CNPs ($R^2 = 0.96$; Fig. 16). The equation depicts higher reactivity of liptinites and vitrinites in CNPs formation, whereas inertinites and volatile matter yield play a negative role in CNPs development. The authors have proposed this equation based on limited number of 10 samples. However, authors recommend for testing of the equation with large

number of samples. The proposed empirical equation, PEC also provides probable amount of CNPs yield. These observations support earlier observations made in 4.2 and 4.7.

5. Conclusions

An empirical equation, PEC is proposed to predict the amount of nano-products yield through the MCL process. Carbon nano-products (CNPs) including carbon nanotubes and carbon nanoballs can be synthesized from sub-bituminous to bituminous coals. MCL process appears to be an effective method for the synthesis of CNPs. Vitrinites and liptinites favor the formation of CNPs, whereas inertinites hinder the synthesis of CNPs. Generally, mineral matters do not favor the CNPs formation, but the presence of some iron contents in the mineral matter may increase the formation of CNPs. Authors recommend for systematic investigations with various types of coals with varying composition, belonging to different ranks for CNPs synthesis through the MCL process.

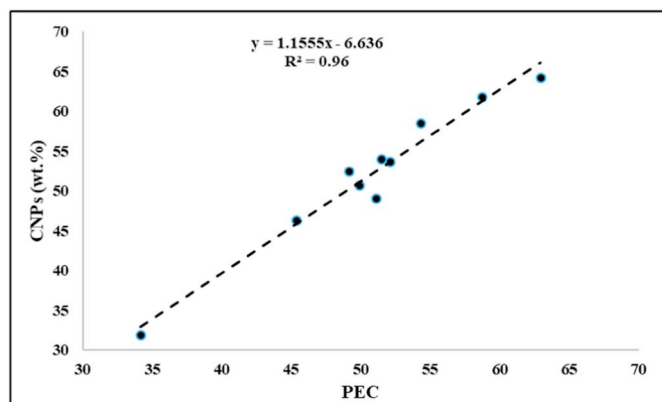


Fig. 16. Relation between PEC (Petrographic estimate of CNPs) and CNPs yield.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.coal.2019.103211>.

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