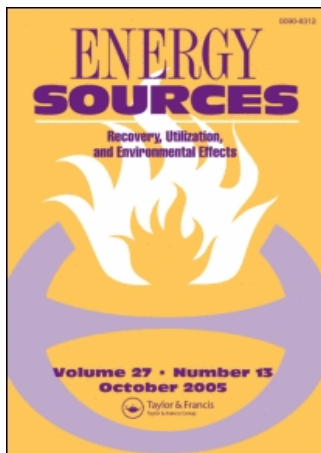


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## Formation of Carbon Deposits from Coal in an Arc Plasma

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**Abstract** *The issue of deposited carbon (DC) on a reactor wall during the producing of acetylene by the coal/arc plasma process is a potential obstacle for the industrialization process. The formation mechanism of DC is very difficult to reveal because the high complexity of coals and the volatile matter. Combining with quenching technique, the methane, liquid petroleum gas and benzene were employed as the model materials to roughly act as the light gas, chain and aromatic subcomponents of volatile matter, and then the reasonable formation mechanism of DC was subtly speculated accordingly.*

**Keywords** arc plasma jet, coal, deposited carbon

### Introduction

Arc plasma jet is a hot super-fast gas flow containing lots of active species. When coal is injected into plasma jet, the acetylene is the main hydrocarbon product; therefore, this technique is attractive for directly manufacturing acetylene from coal, which has been demonstrated by Bond et al. (1966), Chakravarty et al. (1976) and Baumann et al. (1988). However, during the running of the process, some amount of deposited carbon (DC) is gradually formed and grows thicker on the reactor wall, which causes the reduction of the reactor diameter and finally breaks down the successive running of the process. This problem might be one of the potential obstacles for the industrialization of the technique. Up to now, little attention has been paid to this issue, except for Veb Chem. Leipzig (1989) and Akad Wiss Phys. Chem. (1991), who considered removing the DC in their patents. For the purpose of reducing or eliminating the generation of DC, it is very important to study the formation behavior, properties and formation mechanism of DC. Considering the complexity of coals, and the volatile matter released as coals are heated,

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**Table 1**  
Typical experimental conditions

Power of plasma generator	42 kW
Flow rate of working gas	Ar: 2.2 m <sup>3</sup> /h; H <sub>2</sub> : 5.2 m <sup>3</sup> /h
Flow rate of carrying gas	Ar: 1.7 m <sup>3</sup> /h
Feeding rate of coal	0.5–4.0 g/s
Feeding rate of LPG	0.5–2.0 m <sup>3</sup> /h
Feeding rate of methane	1.0–4.5 m <sup>3</sup> /h
Feeding rate of benzene	1–10 ml/s
Reaction time	10–15 min
Residence time of coal in reactor	4–8 ms

we employed methane, liquid petroleum gas (LPG) and benzene as model materials to roughly simulate their subcomponents of light gas, chain and aromatic, and the sound formation mechanism was deduced accordingly.

### Experimental

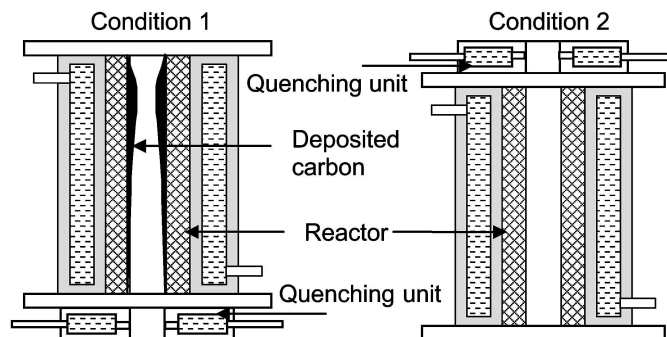
The experiment equipment mainly consists of plasmatron, feeder (when solid feedstock is used), feedstock distributor, reactor, quenching unit and separator. Tian et al. (2001) has shown the equipment sketch in their previous work. Arc plasma is generated when the arc is ignited between the water-cooled copper electrodes and the plasma jet is formed after the working gases (mixture of argon and hydrogen) pass through the arc. Feedstock is injected into the plasma jet through an injector and mixed with the jet. Reactions occur within the graphite-wall reactor with a diameter of 20 mm and length of 350 mm, and then quenched by water in quenching unit installed downstream from the reactor. The gaseous products are vented from the upper outlet of separator, and the slurry of solid residue is discharged from the bottom tube of separator to be filtered. Baode coal with grain a size of 5–25  $\mu\text{m}$  is used as raw material for preparation of acetylene. It is fed into arc jet when the system reaches a stable state; its chemical analyses are referred to in (Tian et al., 2001), and the typical operational conditions are listed in Table 1. Accompanying with reactions, the DC is deposited on the reactor wall inch by inch.

Methane (99.999%), LPG and benzene (chemically pure) are used as model materials as mentioned above. The chemical composition of LPG is shown in Table 2.

A special quenching technique is used to capture the direct precursors of the DC. Practically, the quenching unit was installed at the upstream position of reactor, so that the precursor of DC could be frozen and preserved by quenching water (flow rate at 0.81 m<sup>3</sup>/h) before forming DC. The experimental condition when the quenching unit is installed downstream reactor is called Condition 1, and upstream-reactor installation is

**Table 2**  
Chemical composition of LPG

	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>5</sub> H <sub>12</sub>
Mol%	0.4	0.82	17.9	48.2	13.0	19.5	0.18

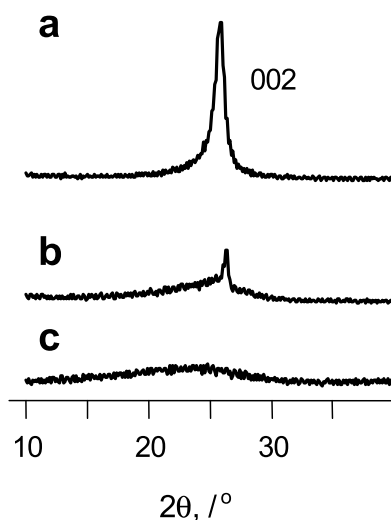


**Figure 1.** Illustration of experiment Condition 1 and Condition 2.

called Condition 2. These two conditions are illustrated in Figure 1. The solid products are characterized by X-ray diffraction (XRD, Regaku-D/max 250, Cu-K $\alpha$  radiation of  $\lambda = 0.15418$  nm, 40 kV, 40 mA) and scanning electronic microscope (SEM, Hitachi-S520, 15Kv) and BET (SORPTMATIC-1990).

### Results and Discussion

Figure 2 shows the comparison of XRD patterns of parent coal, DC and residue. It is noticed that the intensity of (002) peak of the DC is the strongest (Figure 2a), indicating that the graphitization degree of the DC is the highest. The calculated crystal cell parameters of  $d$ ,  $L_a$ ,  $L_c$  are 0.3481 nm, 4.019 nm, 1.494 nm, respectively, reveal that the structure of the DC is close to graphite. Figure 2b also presents a noticeable stronger (002) peak, implying that graphite or graphite-like structure may exist in the residue.



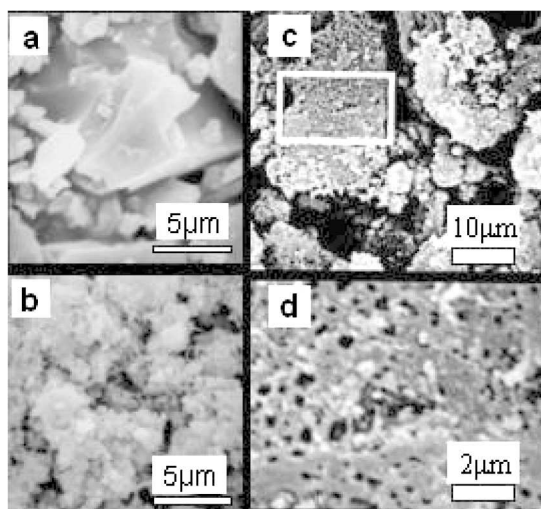
**Figure 2.** Comparison of XRD patterns of (a) deposited carbon, (b) reaction residue and (c) parent coal. The structure of parent coal is amorphous absolutely, that of deposited carbon closes to graphite.

Anyhow, the amorphous carbon structure of coal becomes ordered in certain degree after the treatment by the high temperature plasma jet.

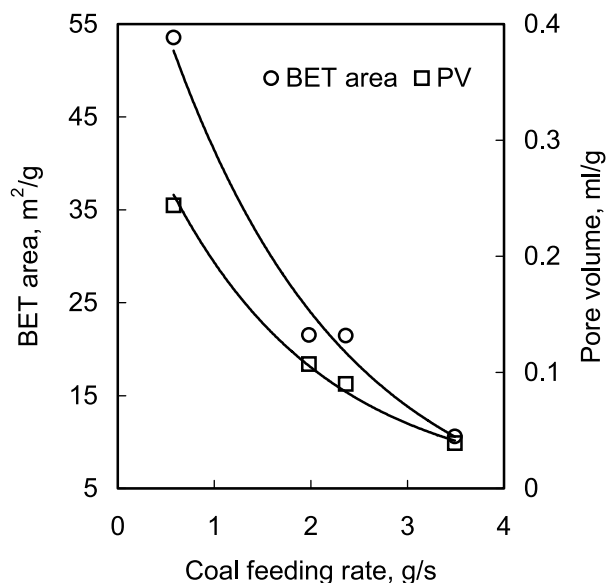
The morphology observation illustrates that parent coal powder with an amorphous carbon structure is comprised of rock-like particles, as shown in Figure 3a, and the DC (Figure 2b) is compactly aggregated by small blocks. Some thread-like wires are also found between the crevices. It's interesting that the morphology of the residue is mainly porous particles, as shown in Figure 3c and 3d. As coal was rapidly pyrolyzed in plasma jet with an initial temperature of about 3700 K, the volatile matter would be released from coal particles, resulting in the formation of a porous structure. Compared with the BET area ( $3.01 \text{ m}^2/\text{g}$ ) and pore volume ( $0.012 \text{ ml/g}$ ) of parent coal, the porous structure is improved largely after reactions. However, with an increase of the coal feeding rate, the BET area and pore volume would decrease, as shown in Figure 4. In practice, the increase of the coal feeding rate caused the decrease of the average temperature and hence reduced the amount of released volatile matter, resulting in the diminishing of porous structure. In addition, a small amount of carbon nanotubes (Tian *et al.*, 2001) and onion fullerene (Tian *et al.*, 2004) that has well-graphited structures have been observed within DC and the residue, respectively, which consists with the XRD patterns in Figure 2.

We defined the amount of DC formed within unit time by unit mass of feedstock as the formation capacity of DC (FCDC). Figure 5 illustrates that the FCDC of coal decreases as the coal feeding rate increases, which is very similar to the tendency of coal conversion. Xie *et al.* (2002) suggested that the volatile matter played an important role in the coal conversion. It's reasonably deduced that the volatile matter released from coal is the direct starting material for the DC formation.

Since coal is a well-known complex super-macro molecular solid, a simplistic approach is employed as Fletcher *et al.* (1992) did, with broad definition of aromatic cluster, bridge, side chain and loops. Moreover, the released volatile matter from coal is as complex as coal which could be roughly classified into light gases, chain and aromatic

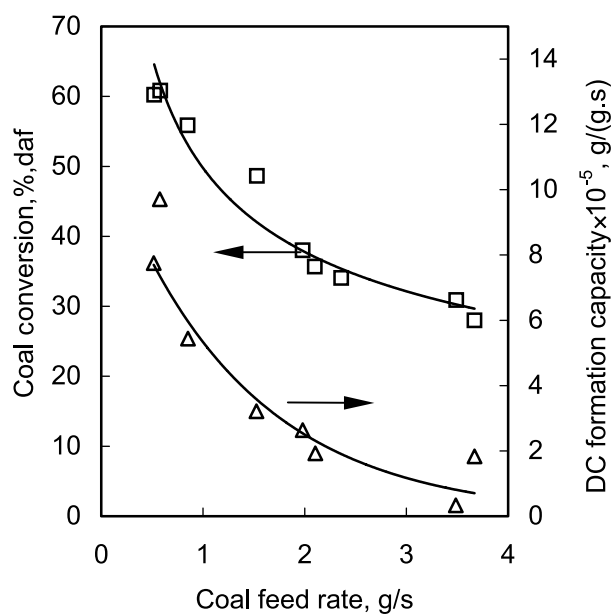


**Figure 3.** The SEM morphology of (a) parent coal, (b) DC and (c) reaction residue; the enlargement of a porous particle in residue is shown in (d).



**Figure 4.** The changes of BET area and pore volume of residue as a function of coal feeding rate.

components. Its rational to take the methane, LPG and benzene to approximately act as the role of light gases, chain and aromatic components of volatile matter, respectively, for disassembling the formation mechanism of DC. Table 3 shows their maximum FCDC under typical conditions. It is implied that benzene and LPG easily formed DC and the methane's FCDC was the smallest. Accordingly, it is deduced that the aromatic and



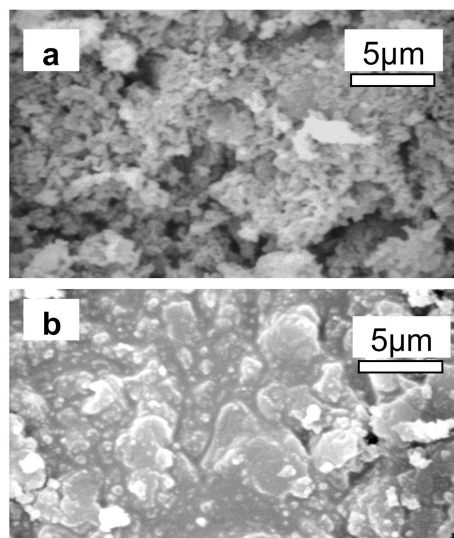
**Figure 5.** Coal conversion and DC formation capacity vs coal feed rate.

**Table 3**  
Maximum DC formation capacities of various carbonaceous materials

	DC formation capacity [g DC/(g feedstock·s)]	Corresponding feeding rate	Corresponding feeding rate [g/s]
Benzene	1.80	0.7 ml/s	0.62
LPG	0.15	1.3 m <sup>3</sup> /h	0.76
Baode coal	$9.71 \times 10^{-5}$	0.58 g/s	0.58
Methane	$5.23 \times 10^{-6}$	3.2 m <sup>3</sup> /h	0.63

chain compositions of volatile matter were the main contributors of DC. Due to the C-C bonding of benzene, molecules are highly similar to that of graphite layer, they are very liable to aggregate together to form graphene sheets and then develop to fullerene-like or other poly-carbon products with graphite-like structures according to the six-membered-ring-based growth model (Tian et al. 2004). If more aromatic clusters were contained in parent coal, it's inferred that a larger amount of DC would be generated.

For LPG, the chemical analyses of the residue collected at the flow rate of 1.3 m<sup>3</sup>/h under Condition 1 and Condition 2 shows that the residue of Condition 2 has more volatile content (28.99 wt%, daf) and hydrogen content (2.01 wt%, daf) than that of Condition 1 (13.88 wt%, 1.54 wt%, daf), implying that some amount of volatile hydrocarbon, which should be the precursor of DC, is frozen and preserved under Condition 2. The SEM morphology (Figure 6) shows that porous structure is the main characteristic of the residue of Condition 1, but lots of oil-like morphology is observed within the residue of Condition 2. This kind of oil-like matter should be the preserved precursors.



**Figure 6.** SEM morphology images of reaction residua under (a) Condition 1 and (b) Condition 2.

In  $H_2/Ar$  arc plasma jet, partial LPG was cracked into smaller molecules. Meanwhile, many kinds of free radicals were also derived. The combination and recombination of radicals could generate hydrocarbons with heavier molecular weight. Once the evaporation pressures of these heavy hydrocarbons were lower than pressure of reaction system, they existed as the format of droplet at that time. As the droplets run into the reactor wall, they were adhered and then were carbonated to DC by the high temperature plasma jet, which is probably another route of DC formation. When the quenching technique was adopted (Condition 2), the droplets were preserved and formed the oil-like matter, as imaged in Figure 6b. Comparing with the FCDC of methane, it's concluded that the heavier the molecular weight of chain hydrocarbon the more easily the DC is generated.

In summary, in terms of our experimental results and analyzing, the FCDC of coal dominantly depends on its aromatic and side chain subcomponents of volatile matter. Under the experimental conditions, it seems impossible to prevent the formation of precursors of DC. For the purpose of long running, it's suggested that the probable effective measure is to prevent the precursors from running into reactor wall.

## Conclusions

When coal was taken as starting material to prepare acetylene by arc plasma process, it's believed that the pyrolysis was the first step under the circumstances of hot plasma jet, and the released volatile matter was the direct source of DC. On the basis of the experimental results and analysis of above mentioned model materials, the formation mechanism of DC was accordingly speculated that the aromatic components of volatile matter had the biggest contribution due to the aromatic radicals were liable to be directly polymerized without the dissociation of C–C bonds of aromatic rings, as suggested by Wilson et al. (2002). The chain components also had noticeable influence by the easily coupling together to generate macro-molecular matter as direct precursors, but the influence of light gaseous component could be negligible.

## Acknowledgments

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## References

- Akad Wiss Phys. Chem. DD Pat, 294-497-A, 1991-10-02.
- Baumann, H., Bittner, D., Beiers, H. G., Klein, J., and Jüntgen, H. 1988. Pyrolysis of coal in hydrogen and helium plasmas. *Fuel* 67:1120–1123.
- Bond, L. R., Ladner, W. R., and Mcconnel, G. I. T. 1966. Reactions of coal in a plasma jet. *Fuel* 45:381–395.
- Chakravartty, S. C., Dutta, D., and Lahiri, A. 1976. Reaction of coals in plasma conditions: Acetylene production. *Fuel* 55:43–46.
- Fletcher, T. H., and Kerstein, A. R. 1992. Chemical percolation model for devolatilization. 3. Direct use of  $^{13}C$  NMR data to predict effects of coal type. *Energy Fuels* 6:414–431.
- Tian, Y. J., Xie, K. C., and Zhu, S. Y. 2001. Simulation of Coal Pyrolysis in Plasma Jet by CPD Model. *Energy Fuels* 15:1354–1358.
- Tian, Y. J., Xie, K. C., and Fan, Y. S. 2001. New technique for synthesis of carbon nanotubes from coal directly. *Chem. J. Chinese Universities* 22:1456–1458.



- Tian, Y. J., Zhang, Y. L., Yü, Q., Wang, X. Z., Hu, Z., Zhang, Y. F., and Xie, K. C. 2004. Effect of catalysis on coal to nanotube in thermal plasma. *Catalysis Today* 89:233–236.
- Tian, Y. J., Hu, Z., Yang, Y., Wang, X. Z., Chen, X., Xu, H., Wu, Q., Ji, W. J., and Chen, Y. 2004. In Situ TA-MS Study of the Six-Membered-Ring-Based Growth of Carbon Nanotubes with Benzene Precursor. *J. Am. Chem. Soc.* 126:1180–1183.
- Veb Chem. Leipzig. DD Pat, 270-315-A, 1989-07-26.
- Wilson, M. A., Moy, A., Rose, H., Kannangara, G. S. K., Young, B., McCulloch, D., and Cockayne, D. 2002. Fullerene blacks and cathode deposits derived from plasma arcing of graphite with naphthalene. *Fuel* 79:47–56.
- Xie, K. C., Lu, Y. K., Tian, Y. J., and Wang, D. Z. 2002. Study of coal conversion in arc plasma jet. *Energy Sources* 24:1093–1098.