CARBON NANOFIBERS FROM COAL LIQUEFACTION RESIDUE

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Abstract

Coal hydroliquefaction is an important process for converting coal to desired liquids products, in which a large amount of coal liquefaction residue (CLR) is also produced as by-products. CLR consists of carbonaceous materials and mineral matter from raw coal as well as catalyst residue, as such it may become a precursor for preparing new carbons. In the present paper, we report a novel feasibility study of producing carbon nanofibers (CNFs) directly from CLR under arc jet plasma conditions. CLR was used without any pretreatment, and no additional catalyst was added. The CNF products were examined by scanning electron microscopy and transmission electron microscopy. The results show that a large amount of curly fibers are obtained directly from CLR by arc plasma technique. The CNFs have smooth surface, and quite uniform diameters centering at ca.700 nm. The length of CNFs is about several tens microns. The inner structure of CNFs is similar to CNTs, consisting of many coaxial seamless tubes made of graphite sheets.

Introduction

Coal hydroliquefaction is an important technique in non-fuel use of coal. In addition to desired liquid product, a large amount of coal liquefaction residue (CLR) is produced as by-product in the process of coal direct liquefaction. As a general rule, the production yield of CLR is about (20-30) wt% of raw coal. From the viewpoints of the resource conservation and effective utilization, CLR as the valuable-added carbon resources should be studied for reasonable development of coal direct liquefaction technique. In a conventional case, the CLR are used as a feedstock for gasification to produce hydrogen needed in the process of hydroliquefaction. There are high content of carbon, ash from raw coal and residue catalyst in CLR, it may provide a practical application as a carbon precursor for preparing new carbons. In the present paper, we report a novel feasibility way to deal with CLR that have never been reported by others before. Carbon nanofibers (CNFs), a novel carbon material, which has been intensively studied theoretically and experimentally because of its unique properties, has been successfully synthesized under arc jet plasma condition from CLR without any pretreatment or any additional catalyst.

Experimental

The whole apparatus employed to prepare the CNFs consists primarily of two parts, which are an arc plasma generator and a reactor. The plasma jet used in the experiment is a non-transferred arc plasma torch and was operated on a direct current of 220-240A and a voltage of 140-150V. The behavior of plasma torch could be controlled by adjusting the anode working gas (N_2, purity 99.5%), while the cooling of electrodes is carried out by role of the cathode working gas (N_2, purity 99.5%). The flux of the cathode working gas and the anode working gas is $4m^3/h$ and $5m^3/h$, respectively. The whole system can be operated under atmospheric pressure rather than vacuum condition.

In the present study, a typical CLR without any pretreatment and any additional catalyst from a Direct Coal Liquefaction Pilot Equipment for Shenhua coal in China was used. The proximate and ultimate analysis date of the CLR sample is given in Table 1.

Table 1. Proximate and Ultimate Analysis of CLR

Sample	Proximate analysis /(%)			Ultimate analysis /(daf %)				
	M_{ad}	A_d	V_{daf}	C	H	N	S	O*
CLR	0.20	21.17	31.37	84.08	6.40	1.46	3.07	4.99

*by difference

CLR powder was packed into a pot that was put into the reactor under the nozzle of plasma jet. The distance between the torch plasma nozzle and the pot is about 40mm. For each run, 15g CLR powder was used and the experiment lasted no more than 150 seconds. When the reaction was finished, the products in the pot was collected and examined by scanning electron microscopy (SEM, JSM-5600LV) and transmission electron microscopy (TEM, JEM-2000EX).

Results and Discussion

A group of typical SEM images of the freshly synthesized sample are shown in Fig.1. These images were at different magnifications to show the abundance and cleanness of the product. It has been found that products contain a large amount of curly fibers from Fig.1. Fig. 1a, a low-magnification SEM image, shows lots of fibers-liked products, which entangle with each other, can be seen yet. Fig. 1b and Fig. 1c are higher magnification SEM images of the fibers-liked product. Other impurities such as carbon particles can't be seen, indicating that the purity of the products is quite high. SEM observations show that the CNFs have a columned morphology, with an outer diameter in ca.700 nm. The diameters are quite uniform. These fibers are tens of microns long, and have smooth surfaces. The size of length is much larger than those CNTs produced by traditional arc discharge method. EDX pattern (fig. 2) exhibits the products are consisted by carbon. Typical TEM images of the CNFs produced from CLR is shown in Fig. 3. This TEM examination reveals type of basic structures involved with the as-grown fiber formation: thick twisted fibers. The wall of the CNFs shown in Fig .3 was investigated with HRTEM for further structure analysis as an inset in Fig .3. It can be found from Fig.3 that its structure is similar to that of CNTs, which is made up of many coaxial seamless tubes of graphite sheets with parallel wall alignment and tube axis.

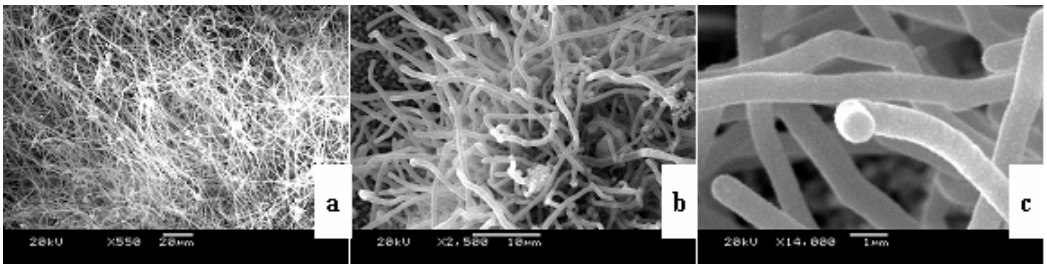

Figure 1. Typical SEM Micrographs of CNFs
(a) A low magnification image of SEM image showing numerous high-purity CNFs,
(b) and (c) Higher magnification SEM images of the fiber-liked CNFs

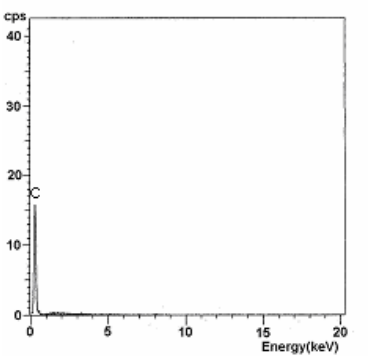

Figure 2. Typical EDX Image of CNFs

Figure 3. Typical TEM Image of Thick Twisted Fibers CNFs

The detailed mechanism involved in the process is not clear so far, but it can be speculated on some possible processes. Based on hydroliquefaction process of coal, the residue contains organic and inorganic components, the former includes unreacted organic substance of coal and heavy products

formed from both condensation and hydrogenation, and the latter includes most of the minerals in the coal and liquefaction catalyst which exist as $Fe_{1-x}S$. When heated by the plasma jet, CLR undergoes decomposition reactions and the organic components released volatile matters and leaving coke behind. In the same time, the inorganic components, $Fe_{1-x}S$ converted to Fe particle. During this stage, the released volatile matters would decompose further to form some smaller active species. The carbon-containing active species would first dissolve into Fe catalyst particles which converted from $Fe_{1-x}S$ to form an over-saturated solution at high temperature, as time goes on, more carbon-containing species are released and continuously take part in the formation of nano-materials. With this in mind, it can be easily envisaged that every cavity in the coke which converted from CLR via plasma jet would function as a constrained reactor in which the formation and growth of carbon nano-materials takes place.

We also have found that the experience lasting time is a crucial factor for the formation of CNFs in the present work. When the operation time is less than 120s, little CNFs are obtained and the optimum time for the growth of CNFs under the experimental condition is about 150 seconds. It seems that a suitable time is necessary to get such the optimum condition as partial pressure, temperature and catalyst for the growth of CNTs.

Conclusion

CNFs has been successfully synthesized using CLR as starting material by non-transferred arc-jet plasma. It is a new approach to utilize CLR from direct coal liquefaction process. The work is still ongoing in our lab to further optimize the experimental conditions for making high quality carbons from CLR in high yield.

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