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Investigation of porous graphite formation during milling process by gravitational field flow fractionation and Brunauer-Emmett-Teller techniques

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Field flow fractionation is a family of separation techniques applicable to characterize various particulate materials of different nature. In this paper, formation of porous graphite during milling has been investigated by gravitational field flow fractionation. The results from gravitational field flow fractionation were compared to those from Brunauer-Emmett-Teller. The both techniques have shown that particles fracturing and formation of porous graphite was occurred until 50 h milling. Further milling resulted in formation of agglomerated species. There was a good accordance between the results obtained from gravitational field flow fractionation, Brunauer-Emmett-Teller and scanning electron microscopy. Moreover, fractions of porous and non-porous species could be separated by gravitational field flow fractionation technique. Results demonstrated that gravitational field flow fractionation is a simple method with satisfactory results to investigate the evolution of graphite powder during milling process.

Key words: Gravitational field flow fractionation, Porous graphite, Milling

Introduction

Graphite is an attractive precursor for synthesis of carbon-related porous materials because of its very high specific surface area. Normally, all carbonaceous materials can be converted into porous carbons, although the properties of the final product could be different, depending on the nature of the used raw materials [1, 2]. Previous works were investigated the effect of mechanical grinding on microstructure of graphite and they demonstrated that the porous graphite was formed during milling process [3, 4].

Brunauer-Emmett-Teller (BET) is a useful technique to investigate the formation of porous graphite species during milling process [5, 6]. This method, which is based on the physical adsorption of gas molecules on the solid surface is expensive and time consuming.

Field Flow Fractionation (FFF) as a family of separation techniques is applicable to characterize various particulate materials of different nature with size range from 10^{-3} to 10^{2} μm [7-9]. This technique utilizes a combination of the action of a non-uniform flow velocity profile of a carrier liquid with a transverse field to separate the particles as shows figure 1.

Different external fields used for analyzing various types of samples give rise to FFF sub-techniques, including gravitational [10], sedimentation [11], flow, electrical, and thermal FFF.

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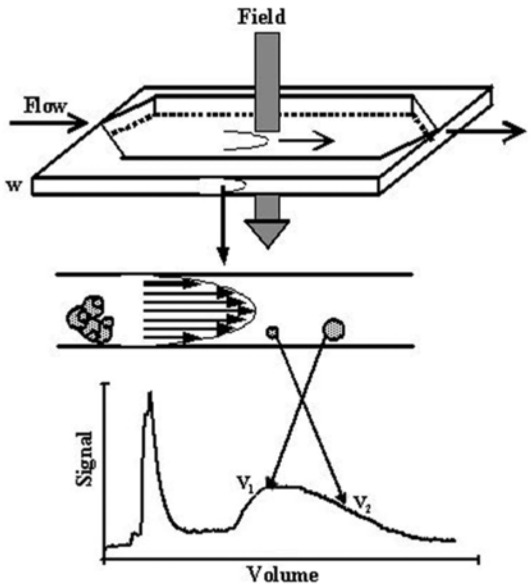

Fig. 1. Principals of gravitational FFF and elution concepts of large particles.

Gravitational FFF (GFFF), using the Earth's gravity (G) as transversal field, is the simplest and the cheapest technique among all of FFF family. In GFFF, the retention volume (V_r) of large particles having diameter $d > 1$ μm is given by equation 1 [figure 1, 12]:

$$V_r = \frac{wV_0}{3\gamma d} \quad (1)$$

where w is the FFF channel thickness, Vo the channel void volume, and γ a dimensionless "steric correction factor". If G is assumed to be constant, *Vr* is inversely proportional to *d*.

In this study, formation of porous graphite during milling was studied by GFFF. BET, laser diffraction particle size analyzer (LDpsa) and scanning electron microscopy (SEM) were used for specific surface area, size and shape characterization of the samples.

Experimental

The GFFF set up has been explained previously [13]. The void volume of the system was determined to be 2.9 ml by measuring the elution volume for a non-retained peak of benzoic acid. The integrated uv-visible detector in compact HPLC apparatus operated at 280 nm.

A laser diffraction particle size analyzer (LDpsa Mastersizer 2000 Malvern instrument Ltd., malvern, UK) was used to obtain information about the particle size distribution of the crude sample. A scanning electron microscopy (LEO, UK) was used to investigate the morphology of raw material and collected fractions.

Ethanol (Merck), was used as surfactant. A mixture of Milli-Q water, EtOH 10% (v/v), and NaN_3 as bactericide was used as the carrier liquid and was introduced to the channel with a velocity of 20 cm/min.

Graphite powder with purity of > 99.8% was used as starting material. Crude sample was sieved by using two sieves (mesh 325 and 500) and the particles placed between the sieves were collected. An equal amount (5 g) of the as-sieved graphite powder was ball milled using a ball mill system at room temperature and different times by alumina balls. The specific surface area of the powders was determined by BET technique (Micromeretics Gemini 2375, USA). Size and morphology characterization of the crude sample by laser diffraction particle size analyzer (LDpsa) and scanning electron microscopy after sieving showed a mean particle size of 30 ± 0.3 μm particles with flaky-irregular shape.

The density of the crude sample was measured via a Helium Pycnometric method (Accupyc 1330, USA) which was 2.21 ± 0.03 g/cm^3.

Results and Discussion

Injection of 100 ml of 1% (w/w) suspension of the sieved graphite powder into the GFFF channel have led to a characteristic mono modal profile shown in figure 2.

The mean particle size was calculated from figure 2 and equations 1 at 30.95 μm, assuming $\gamma \approx 1$. From SEM micrograph particles of flaky shape was observed as shows figure 3.

Specific surface areas (S.S.A.) of the as-sieved graphite sample after milling for 24, 50 and 100 hours were investigated by BET technique and the results are presented in figure 4.

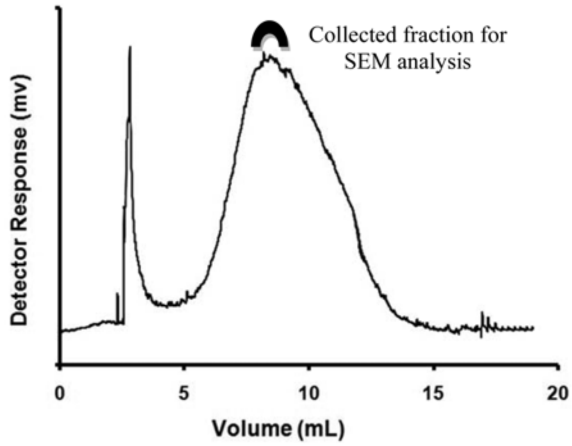

Fig. 2. Obtained curve for injection of 100 ml of 1% (w/w) suspension of the sieved graphite powder into the GFFF channel.

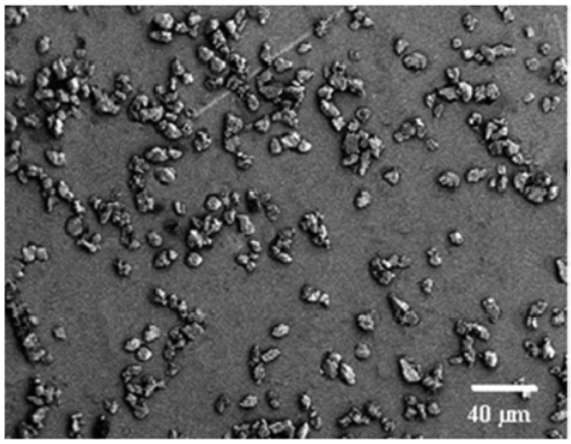

Fig. 3. SEM micrographs of the crude sample injected into the GFFF channel.

According to the figure 4 after 24 h milling S.S.A. increases which can be related to the particle fracturing induced by the ball impacts. A significant increase in SSA after 50 h ball milling is a results of fracturing and formation of the porous species phenomenon. However, the formation of pores is dominant which is demonstrated by an important increase in S.S.A. Chen *et al.* [14] reported the same results for 15 h milling of the graphite powder in a steel ball mill system. In our experiments, this trend in S.S.A. occurs after 50 h because of the less mechanical impact force of alumina balls. Further milling up to 100 h favorites the formation of agglomerates and S.S.A. decreases.

A 100 ml of 1% (w/w) suspension of the resulting powders after different milling time was injected to the GFFF channel separately. Figure 5 presents a comparison of the obtained curves. From figure 5, it seems that after 24 h milling the elution curve began to broadening which can be related to the fracturing of the large particles. After 50 h, a characteristic bimodal peak was obtained which may be related to the presence of two kinds of particles, porous and non-porous-fractured particles. In fact, after 50 h, fracturing

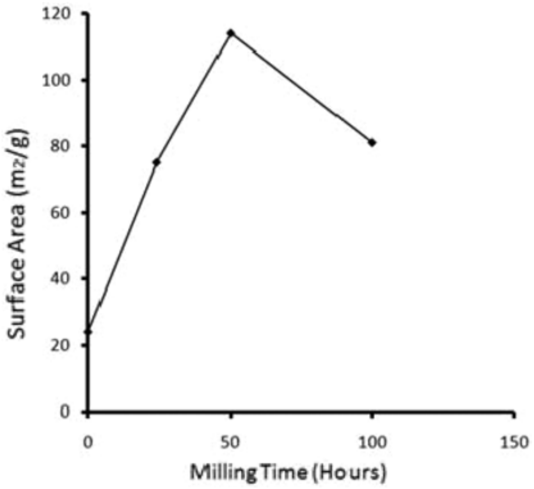

Fig. 4. Specific surface areas (S.S.A.) of the samples by BET technique after different milling time.

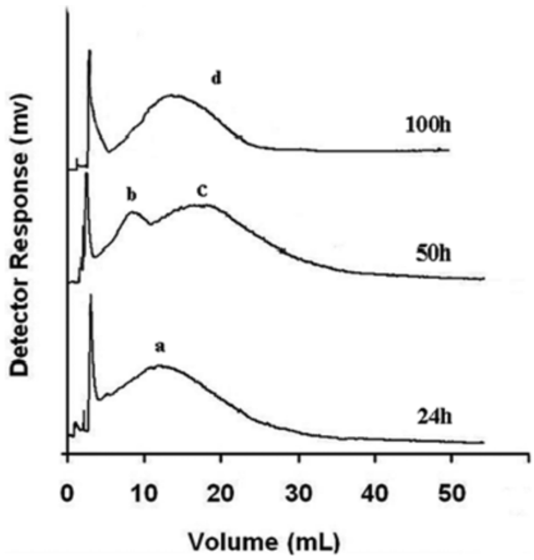

Fig. 5. Obtained curves for injection of 100 ml of 1% (w/w) suspension of the milled graphite powders into the GFFF channel.

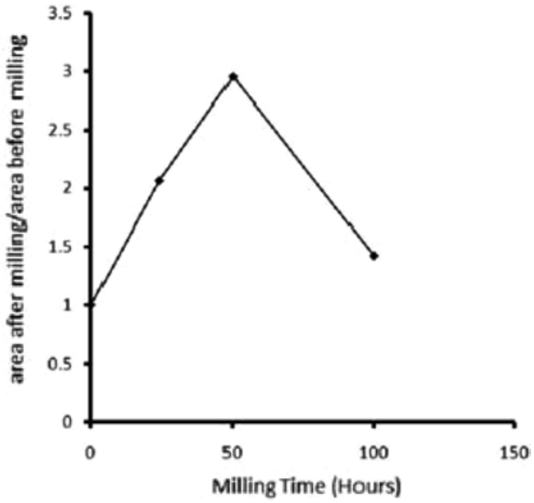

Fig. 6. Trend of *area after milling/area before milling* ratio for the milled samples via milling time.

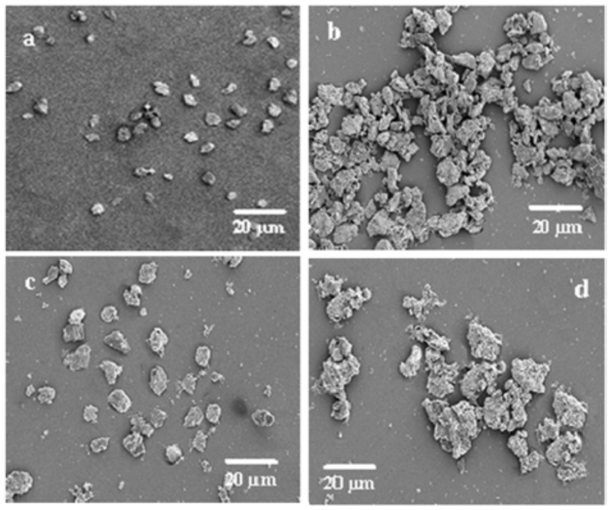

Fig. 7. SEM micrographs of the collected fractions on the GFFF curves.

and formation of porous graphite species occur which are demonstrated by a bimodal FFF peak and a sharp increase in S.S.A. Finally, after 100 h milling, a mono modal peak with smaller retention volume is observed.

In GFFF the effective particle weight (m_{ef}) can be influenced by any change in particle (ρ_p) and carrier liquid (ρ_{cl}) density according to equation 2 [15]:

$$F_G = Gm_{ef} = GV_p(\rho_p - \rho_{cl}) \tag{2}$$

where F_G presents the gravitational force, V_p the volume of the particle and G the gravitational constant. When porous graphite is formed during milling, the total density of the particles decreases. This can be explained by a decrease on the effective particle weight (F_G), leading to a smaller value of the retention volume. On the other hand, those particles that have been subjected to the fracturing phenomena have led to a bigger retention volume (in the steric elution time smaller particles are more retained in the channel). All of these phenomena together have led to broadening and separation of the peaks.

According to the principles of uv-visible spectroscopy in which the magnitude of the detector signal is related to the sample concentration, *area after milling/area before milling* ratio has been considered to follow the trend of porous formation using FFF curves. Peak area of the curves on figures 5 and 2 were calculated by the common numerical methods and variation of *area after milling/area before milling* ratio via milling time is presented in figure 6.

From figure 6 peak area increases after 50 h milling and then it decreases. As the population of the fractured and porous particles increases after 50 h, the separation volume increases and peak broadening occurs. This result is in good agreement with figure 4.

Fractions were collected at the end of the FFF channel (shown as a, b, c and d on figure 5) and were investigated by electron microscopy. Figure 7 shows the obtained micrographs.

Figures 7-a and 7-c present the non-porous graphite particles for which particle size was reduced in comparison with the crude sample. Figures 7-b and 7-d show the porous and porous-agglomerated particles respectively.

Conclusions

GFFF was used as an alternative to expensive and time consuming BET technique for investigation the formation of porous graphite during ball milling. GFFF curves showed that fracturing phenomena and formation of porous graphite species occurred during milling which was demonstrated by a bimodal FFF peak. Results from GFFF, BET and SEM indicated that for 50 h milling, porous species became dominant. The GFFF results were in good agreement with BET and SEM, showing the GFFF ability for investigating of the porous graphite formation during milling process. Moreover, the possibility of separation the porous and non-porous species in the end of the FFF channel can be one of the great advantages of this technique.

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