

## Full Length Research Paper

# The effects of phosphoric acid and pyrolysis temperature to the formation of flaky graphite from lignite

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**The flaky graphites were prepared from lignite. The effects of phosphoric acid ratios and pyrolysis temperatures on flake formation were studied by SEM, TEM and XRD. The results showed that the flaky graphite occurred at a pyrolysis temperature of 600°C with a 1.0:1.0 ratio of carbon to phosphoric acid. The flaky formation was almost completed by pyrolysis at 800°C and with a 1:2.0 ratio of carbon to phosphoric acid. The flaky graphite had a thickness and lateral dimension of about 50 nm and 2 µm.**

**Key words:** Flaky graphite, phosphoric acid, pyrolysis temperature, lignite.

## INTRODUCTION

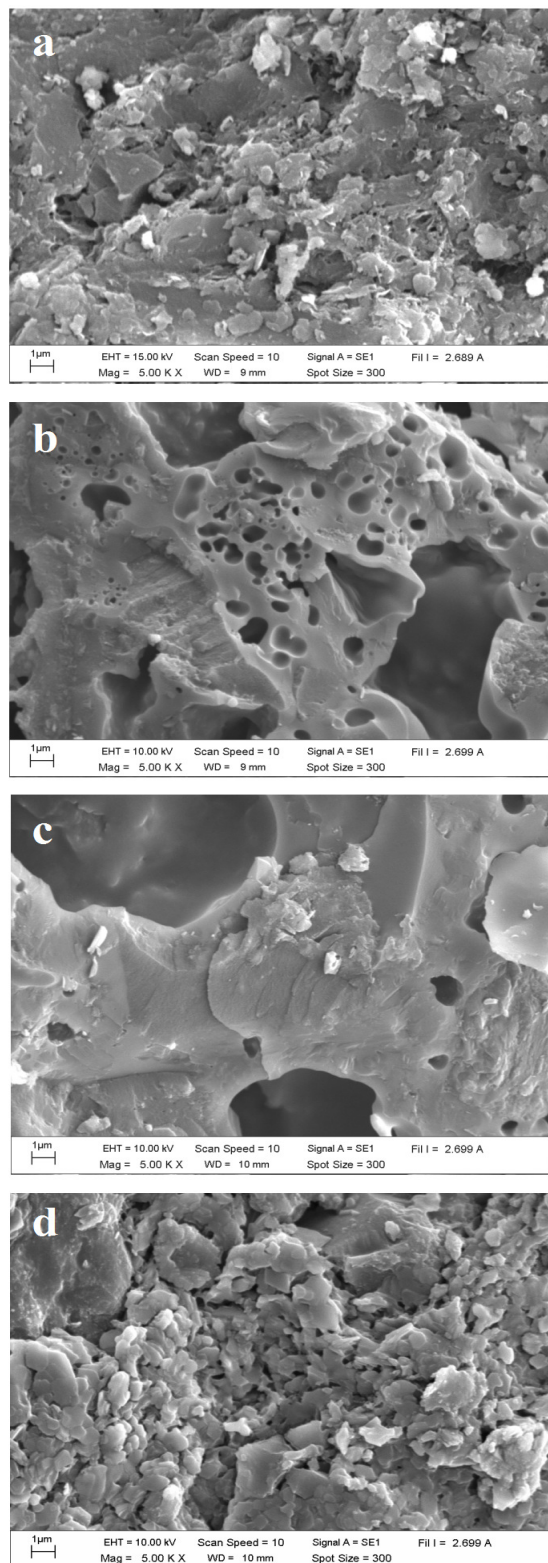
Flaky graphites are used as a precursor in electrically conductive materials (Han et al., 1998; Kuga et al., 2004) and lubricants (Kuga et al., 2004; Dienwiebel et al., 2005). In addition, the flakes can be mixed with cast iron for erosion resistance (Dai et al., 2000) prepared for graphite platelet/epoxy composite fabrication (Yasmin and Daniel, 2004) and graphite nanosheets/resin shielding coatings (Wang et al., 2007). The flaky graphite powder is also used for the nanodeposition of iron on its surface by a gas-liquid-solid method. The product from this process showed a spherical and nonspherical, conductive and insulated substrate-supported metal (Chen et al., 2008). In contrast to graphite, it is difficult to ground finely due to softness and lubricant properties (Kim et al., 2002). Graphitization in the product occurred above 700°C (Miyaoka et al., 2006). Flaky graphite has been produced by a dissolution-precipitation method from a carbon-rich cast iron melt at 1600°C (Lee et al., 2003), grinding in a low-pressure attrition mill (Kim et al., 2002) and under low energy pure shear milling using water as a lubricant (Antisari et al., 2006). Another way for the preparation of flaky graphite is an oxidation reaction using acid, metal oxides and alcoholic vapors such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, hexachloroplatinic acid (Dunaev et al., 2008), Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiO, Co<sub>3</sub>O<sub>4</sub> (Inagaki et al., 2001), *i*-C<sub>3</sub>H<sub>8</sub>OH, *n*-C<sub>3</sub>H<sub>8</sub>OH, C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>OH (Kuga et al., 2004). With phosphoric acid activation at 800°C, activated lignite showed the creation of more pores which

were quite irregular. The XRD pattern for activated lignite at 800°C corresponded to graphite (Mopoung et al., 2008). The flakiness of the natural graphite could be increased with the decrease in the particles' sizes by controlling the grinding atmosphere (Kuga et al., 2002) and by grinding in alcohol vapors (Kuga et al., 2004).

The flaky graphite from these methods had a high electrical conductivity. However, these processes of flaky graphite production may be difficultly produced for high yield. This research studied the effects of different concentrations of phosphoric acid and pyrolysed temperatures on flaky graphite formation from lignite. The pyrolytic lignites were characterized for surface morphology by SEM, TEM and crystallinity analysis by XRD.

## MATERIALS AND METHODS

The lignite (obtained from the Mae Moh basin, Lampang province, Thailand) was carbonized at 500°C and agitated 85 wt. % H<sub>3</sub>PO<sub>4</sub> (UNIVAR, AR) at a ratio of 1.0:0.5 to 1.0:2.0 (lignite:H<sub>3</sub>PO<sub>4</sub>) on a prepared weight by volume basis. After that, the slurry was left overnight at room temperature and dried at 110°C for 24 h. The samples were then activated in a closed system. The samples were pyrolysed at three consecutive temperatures ranging from 600 to 800°C. They were then maintained at a constant temperature for 1 h before cooling. After cooling, the activated lignite was washed several times with 5 N HCl (BDH, AR.), 22N HF (MERCK, pro analysi), then with hot water until the pH became neutral and finally



**Figure 1.** SEM micrograph of: (a) pyrolysed lignite, (b) pyrolytic lignite with 1.0:0.5 ratio of lignite:  $\text{H}_3\text{PO}_4$  and pyrolysed at  $500^\circ\text{C}$ , (c) pyrolytic lignite with 1.0:0.5 ratio of lignite:  $\text{H}_3\text{PO}_4$  and pyrolysed at  $800^\circ\text{C}$ , (d) pyrolytic lignite with 1.0:1.0 ratio of lignite: $\text{H}_3\text{PO}_4$  and pyrolysed at  $500^\circ\text{C}$ .

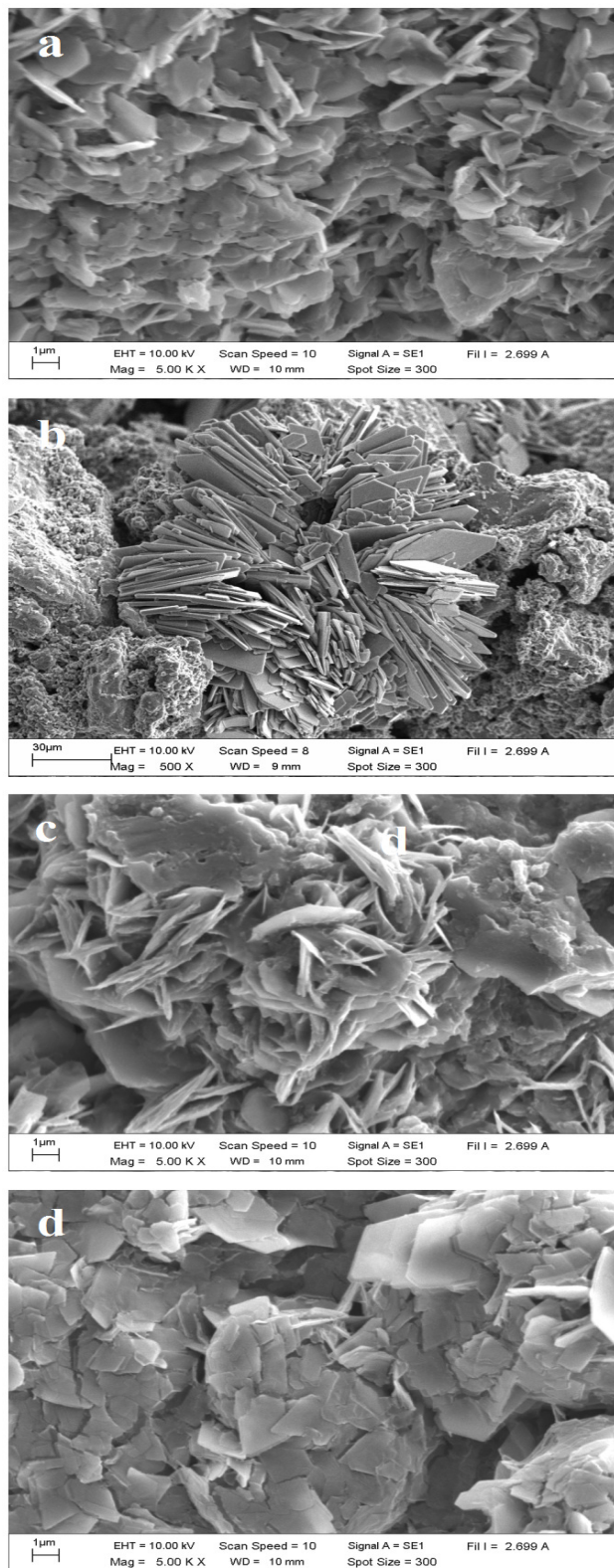
with cold water to remove the excess phosphorous compounds. The washed samples were dried at  $110^\circ\text{C}$  to get the final product. The flaky shape of the graphite was visually confirmed by scanning electron microscopy (SEM, LEO 1455 VP), transmission electron microscopy (TEM, Phillips, Tecnai12) and X-ray diffraction (XRD, PW 3040/60, X' Pert Pro MPD).

## RESULTS AND DISCUSSION

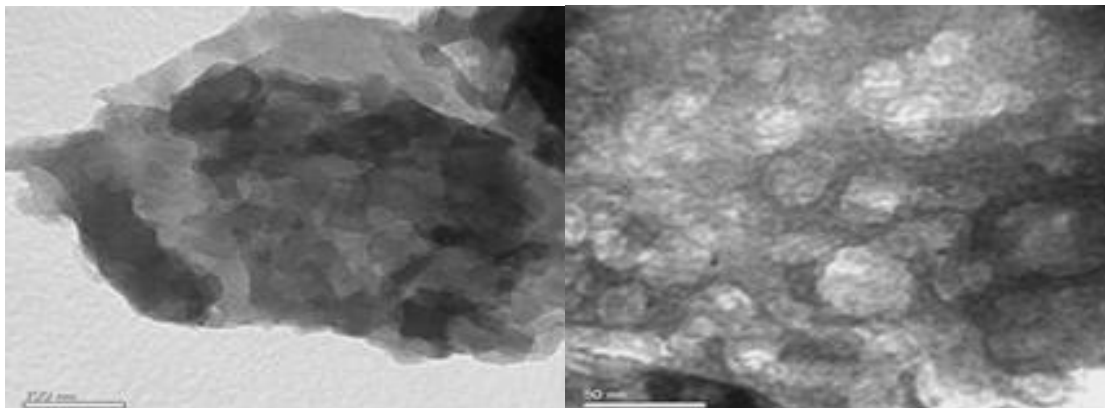
The surface morphology from SEM of pyrolytic lignite is shown in Figures 1 and 2. The samples had a flaky appearance in the pyrolytic samples heated above  $600^\circ\text{C}$  and a 1.0 phosphoric acid ratio (Figure 2a). However, the pyrolytic lignites which carbonized at  $500^\circ\text{C}$  or ratio of phosphoric acid  $\leq 0.5$  were showed a tight texture with some porosity on the surface (Figures 1a - d). These results suggested that the flaky character increased when the concentration of phosphoric acid and pyrolysis temperature increased (Figures 2a - d). As shown in Figure 2d, the flaky formation was almost completed by pyrolysis at  $800^\circ\text{C}$  and 1.0:2.0 ratio of carbon to phosphoric acid. The flaky graphite shows a uniform distribution, dislocation and stake together on the surface. The thickness and lateral dimension of the flakes of graphite were about 50 nm and 2  $\mu\text{m}$ , respectively. It can be concluded that the formation of a flaky structure is caused by the weak bonding between the hexagonal sheets which are dissociated in agreement with report of Lee et al. (2003). Phosphoric acid plays important role to the formation of flaky graphite, since phosphoric acid diffused into the interlayers of graphite in the lignite and accelerated the bond cleavage reaction. This result has been reported by using metal oxide (Inagaki et al., 2001). This acceleration involved the loss of hydrogen, sulfur and oxygen leading to a rupture of the weak bond between the layers of graphite (Teng et al., 1998). Additionally, at a high temperature, the flaky graphite formation can contribute to the separation of the weakly bonded layers. The increase in pyrolysis temperature causes the bond to break between the layers of graphite. Figure 3 shows a TEM micrograph image of the pyrolytic lignite with 1.0:2.0 ratio of lignite: $\text{H}_3\text{PO}_4$  and pyrolysed at  $800^\circ\text{C}$  and confirms that a flaky structure is formed. Finally, the XRD pattern (Figure 4a) shows that the flaky graphite and fullerenes peaks appeared after pyrolysis of lignite. A sharp peak at  $26.5^\circ$  shows the presence of a graphitic crystalline. The corresponding values of d-spacing were in the range of 3.35 to 3.45 angstrom.

## Conclusion

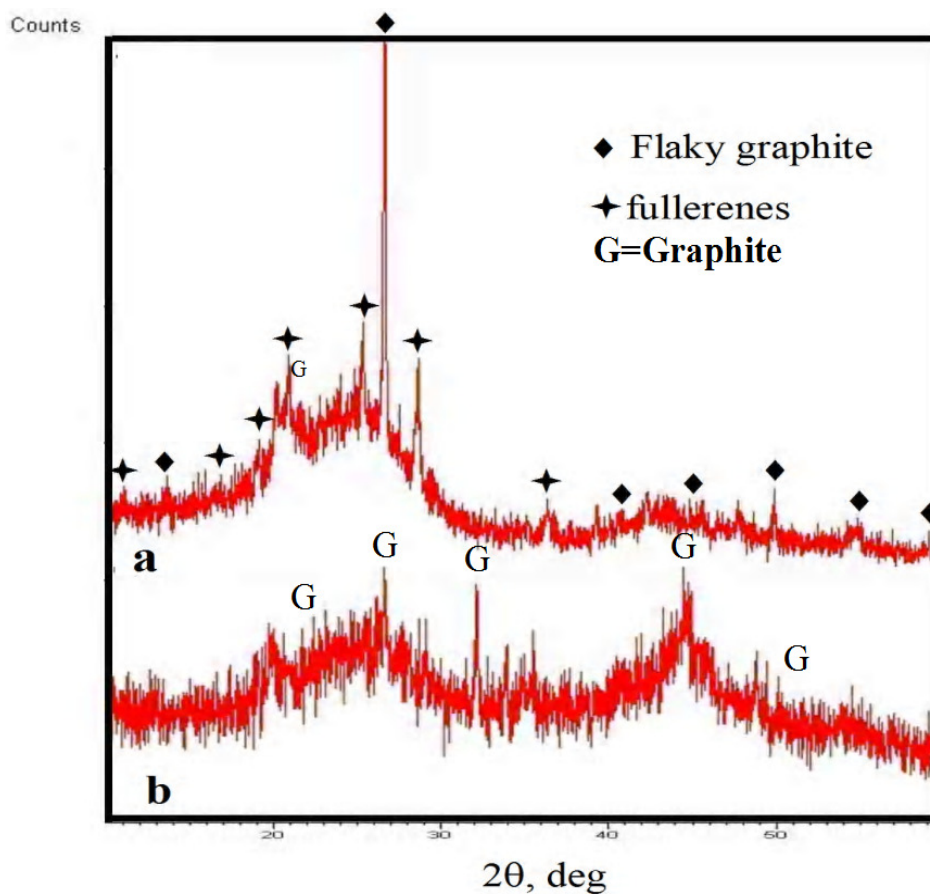
The development of flaky graphite in lignite depends on the pyrolysis temperature and the content of phosphoric acid. Increased pyrolysis temperature above  $600^\circ\text{C}$  and a 1.0:1.0 ratio of carbon to phosphoric acid effected the flaky graphite formation. The flake formation was



**Figure 2.** Flaky surface morphology of: (a) pyrolytic lignite with 1.0:1.0 ratio of lignite:  $H_3PO_4$  and pyrolysed at 600°C, (b) pyrolytic lignite with 1.0:1.5 ratio of lignite:  $H_3PO_4$  and pyrolysed at 600°C, (c) pyrolytic lignite with 1.0:2.0 ratio of lignite:  $H_3PO_4$  and pyrolysed at 700°C and (d) pyrolytic lignite with 1.0:2.0 ratio of lignite:  $H_3PO_4$  and pyrolysed at 800°C.



**Figure 3.** TEM morphology of pyrolytic lignite with 1.0:2.0 ratio of lignite:H<sub>3</sub>PO<sub>4</sub> and pyrolysed at 800°C.



**Figure 4.** XRD pattern of pyrolytic lignite at 800°C (a) and lignite (b).

completed by pyrolysis at 800°C and a 1.0:2.0 ratio of carbon to phosphoric acid. This condition is enough to impart flaky sheets to the original graphite particles. The flaky graphite shows uniform distribution, dislocation and stake together on the surface. The thickness and lateral dimension of the flaky graphite are about 50 nm and 2

μm, respectively.

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