

Activated Carbons from Bituminous Coals by Reaction with H_3PO_4 : Influence of Coal Cleaning

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Introduction

Previous publications have described the results of research in this laboratory to investigate the conversion of coals to activated carbons through reaction with phosphoric acid (1-5). These studies have examined the compositional, morphological, and porosity changes in subbituminous and bituminous coals, resulting from reaction with H_3PO_4 at temperatures up to $650^\circ C$.

Most of the present studies has been concerned with the use of Illinois bituminous coals as activated carbon precursors. These coals have high sulfur and high mineral matter contents. Phosphoric acid reacts with both of these components, promoting the substantial removal of organic and inorganic sulfur as H_2S (5), and combining with mineral matter constituents, thereby increasing the ash content of the carbon.

The second of these effects is particularly undesirable from the standpoint of producing a quality adsorbent carbon. A possible solution is to lower the coal mineral matter content, by some physical separation process, prior to carbon synthesis. This paper describes the effects of coal cleaning by pentane agglomeration, for three bituminous coals with ash contents between about 8 to almost 40%, on the synthesis and properties of activated carbons.

Experimental

Three bituminous coals, IBC 101, IBC 104 and IBC 106, were studied as precursors. The coals were obtained from the Illinois Basin Coal Sample Program and were of high volatile C rank, as determined by vitrinite reflectance measurement. Properties of the coals are summarized in Table 1. The coals were selected to show significant differences in ash content and organic and inorganic sulfur: IBC 104 is a high ash content coal (39.3%) in which about two-thirds of the sulfur is in the pyritic form; IBC 101 and 106 both have lower ash contents (10.5 and 8.9%, respectively) but the first coal has a high proportion of organic sulfur and the second has an organic/pyritic sulfur ratio of about one.

The parent coals were ground to -20 mesh before reaction with phosphoric acid. Finer grinding (-200 mesh) was required for coal cleaning. Physically cleaned coal samples were produced using a laboratory scale flotation unit. Fuel oil or pentane was vigorously mixed with a coal/water slurry to render the coal particles hydrophobic and to selectively agglomerate them. The agglomerated slurry was then screened; the free ash particles flowed through the screen and the agglomerated coal was retained.

The procedure for preparing chemically activated carbons from both parent and cleaned coals has

been described in detail elsewhere (5). Briefly, a 20 g sample of coal was thoroughly mixed with 30 cm³ of 50% strength phosphoric acid solution. The mixture was then heated to 170°C and held at this temperature for 30 minutes in flowing nitrogen (80 ml.min⁻¹). Each sample was then heated to the higher heat treatment temperature of 550°C for 60 minutes in the same inert atmosphere. The solid products were leached with distilled water to pH=6 and vacuum dried at 110°C before further analysis.

Results and Discussion

The compositions of the cleaned coals are shown in Table 1. The reduction in ash content ranges from around 60%, for IBC 101 and IBC 106, to 90% for the high ash coal IBC 104. With all three coals, cleaning produces a significant rejection of pyritic sulfur. There is effectively no change in organic sulfur. For IBC 106, Si is also removed, and for IBC 104, there is substantial removal of both Si and Al.

The compositions of carbons produced from parent and cleaned coals by acid treatment, are shown in Table 2. In all cases, the carbons have much higher ash contents, by a factor of about two, than the corresponding precursor. Some increase is to be expected due to the loss of material to volatile products. However, the ash contents of the chemically-activated carbons are much higher than expected from devolatilization, and the trend is paralleled by increases in phosphorus content, as observed previously (5,6). Iron, silicon and aluminum can all form insoluble phosphates when reacted with phosphoric acid, and X ray diffraction data have shown that P is present as FePO₄, Si₂P₂O₇, Al(PO₃)₃ in carbons produced from both parent and clean coals. The formation of such species can account for the increased ash content and high phosphorus content of the synthesized carbons, even after extensive leaching.

The carbon phosphorus content is found to correlate almost linearly with both the total ash content of the parent coal and that of the carbon product, Figure 1, although the slopes of the curves differ. A high ash content is detrimental to the mechanical strength of the carbon product and its specific adsorptive capacity, and to the effective use of phosphoric acid: its consumption through these reactions means that less acid is available to promote the synthesis process, and less will be recoverable for recycle in an industrial process. The significant reductions in mineral matter, that are effected by coal cleaning, certainly help to minimize phosphorus retention and produce adsorbent carbons with much lower ash contents.

The data in Table 2 show that acid treatment causes extensive removal of sulfur: the concentrations of pyritic and organic sulfur are lowered by as much as 100% and 88%, respectively. The pyritic sulfur content is reduced to lower levels in the carbons from the parent coals and is almost completely eliminated in the carbons from the cleaned coals. More organic sulfur is also removed from the cleaned coals. The greater extent of S removal from the cleaned coals may relate to their smaller particle size and lower mineral matter content, both of which could facilitate access of the acid to the interior of the particles. The data for the parent high ash coal, IBC 104, provide evidence that the consumption of acid, by reaction with mineral matter, limits the extent of its reaction with the organic matrix, shown here by the extent of sulfur removal. After cleaning, the reduced mineral matter content allows more acid to be available for the removal of organic and pyritic sulfur, and other reactions involved in carbon synthesis.

The greater part of the coal sulfur is released in the form of H₂S, Figure 2. Approximately 60% of the sulfur in the starting coal is converted to H₂S for IBC 101, 47% for IBC 104, and 40% for IBC 106. This is considerably higher than can be attained by thermal treatment, as shown by other published data (5,7). Interestingly, the proportion of sulfur in the precursor that is removed as H₂S remains the same, irrespective of whether the coal has been cleaned or not.

Coal cleaning increases both the total (BET) surface area and the mesopore surface area of the synthesized carbons, Table 3. The bulk of the surface area is contained in the micropores. For the medium ash content coals, IBC 101 and IBC 106, the surface area is increased by 11 and 24%, respectively. However, for IBC 104, the surface areas of the carbon from the cleaned coal were about three times higher than for the carbon from the parent coal, corresponding to a major reduction in the ash content of the precursor from 39 to 4%.

The micropore, mesopore and macropore volumes are also significantly higher in the carbons from the cleaned coals, Figure 3. An exception is the macropore volume of IBC 106 which actually decreases after cleaning. The last observation may signify that, for this particular coal, the ash in the carbon made an appreciable contribution to the macroporosity.

One reason for the increased surface area and porosity in carbons from cleaned coals is considered to be that more of the phosphoric acid is available to react with the organic structure, since less will be consumed by reaction with coal mineral matter, as discussed. In the case of IBC 104, the high ash content of the parent coal could severely restrict the amount of available acid. Previous work has shown that acid concentration can be important to the development of porosity. By increasing the acid concentration from 15 to 50%, for the carbonization of coal IBC 101 at 550°C, the micropore volume was increased by a factor of four while the meso- and macropore volumes increased by a factor of two (6).

Mineral matter and ash constituents can also block the pore structure of coals and chars, which may also help to explain why coal cleaning prior to carbonization enhances porosity. Mahajan and Walker (8) examined the effects on pore structure of a number of coals by removing soluble inorganic constituents by acid washing of coals before carbonization, or the resulting chars. The results were apparently random with the surface area being increased in some cases and decreased in others, suggesting that the distribution of the mineral matter in the coal is an important parameter.

Ehrburger et al. (9) found that the micropore volume of chars was increased after demineralization of the parent coal. In these experiments, demineralization was effected by chemical treatment with HCl/HF prior to carbonization. Some of the increase in microporosity in these cases may well be due to the action of the acid on the organic structure of the coal, rather than simply the removal of mineral matter. The same authors found that acid pretreatment increased the carbonization yield which is indicative of the acid promoting crosslinking reactions. Similar phenomena may also account for some of the results obtained by Mahajan and Walker (8), where the coal structure is modified during acid washing, or during subsequent heat treatment in the presence of residual acid. It is known that acid treatment with HCl and HCl/HF modifies coal thermoplasticity and eliminates swelling during pyrolysis, Lee and Jenkins (10), Lu (11), and leads to increased microporosity in the carbon products.

It is supposed that the role of phosphoric and other acids is to initiate the cleavage of weak connecting bridges between coal structural units at sub-pyrolysis temperatures. Subsequently, bond cleavage reactions are followed by the re-combination of radical fragments to form stronger linkages or larger structural units, leading to the formation of a rigid crosslinked solid. This modified structure will be less susceptible to volume contraction upon heat treatment. Restricted shrinkage and limited volatile loss may facilitate the development, or perhaps more accurately, conservation of the elements of porosity that are present in the starting material. Consequently, factors that influence the availability of the reagent to the precursor will impact upon the pore structure of the carbon.

Summary

It has been shown that high mineral matter content can adversely influence the process of carbonization and the properties of carbons produced by chemical activation of coals. In thermal processing, it is desirable to keep the coal mineral matter content low as carbon is removed during carbonization and activation, thereby increasing the ash content. Around 8-10% ash in the activate is probably an acceptable maximum for many applications; higher concentrations can adversely affect the physical strength of the carbon and specific adsorption capacity. Ash constituents may also catalyze unwanted reactions when the carbon is in service and could reduce its ignition point.

In chemical activation with phosphoric acid, there are additional disadvantages in that acid is consumed by reaction with mineral matter. This leads to: reduced availability of acid for reaction with the organic structure, which may severely limit the extent of porosity development; the loss of recoverable acid for recycle; and an increase in the ash content of the carbon. Lowering the mineral matter content of the carbon precursor by coal cleaning techniques can provide a solution to these problems.

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Table 1. Composition of parent and cleaned coals (wt.%).

Coal	ash	Fe	Si	Al	Pyr.S	Org.S	S
101	10.5	1.4	2.5	0.9	1.6	4.0	5.7
101 clean	4.1	0.8	2.5	1.2	0.8	3.6	4.4
104	39.3	3.2	10.8	3.6	4.4	3.0	7.5
104 clean	3.9	0.7	1.5	0.8	0.9	3.1	4.0
106	8.9	1.7	1.9	0.9	2.4	2.4	4.8
106 clean	3.7	0.8	1.1	1.3	1.0	2.4	3.4

Table 2: Composition of carbons from parent and cleaned coals (wt.%).
(Carbons produced at HTT=550°C, 50% phosphoric acid)

Sample	ash	P	Fe	Si	Al	Pyr.S	Org.S	S
101	20.8	3.2	0.1	10.9	4.0	0.3	0.9	1.2
101 clean	7.0	1.3	0.3	0.1	0.2	0.1	0.8	0.9
104	67.0	8.7	2.5	34.8	8.8	2.3	2.0	4.4
104 clean	8.9	1.5	0.1	0.2	0.1	0.0	0.8	0.9
106	22.7	3.2	1.2	9.8	3.7	0.5	0.3	0.8
106 clean	9.2	1.7	0.2	0.3	0.1	0.1	0.3	0.5

Table 3: Surface areas of carbons from parent and clean coals.
(Carbons produced at HTT=550°C, 50% phosphoric acid)

Sample	BET s.a. (m ² /g)	Mesopore s.a. (m ² /g)
101	575	87
101 clean	638	82
104	155	24
104 clean	652	98
106	660	92
106 clean	820	113

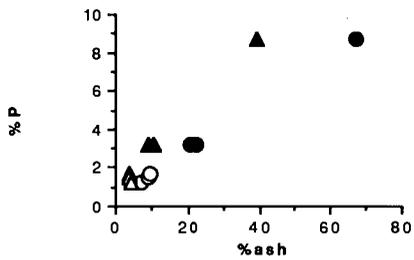


Figure 1: Correlation of P with mineral matter (parent coals) and ash (derived carbons).

(Carbons produced at 550°C, 50% phosphoric acid.)

- △ clean coal
- ▲ carbon from clean coal
- parent coal
- carbon from parent coal

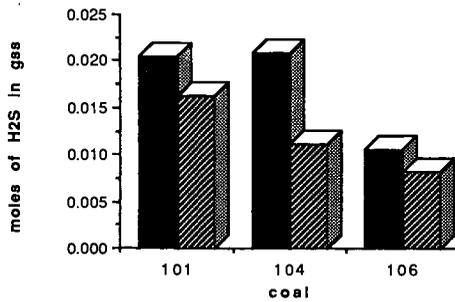
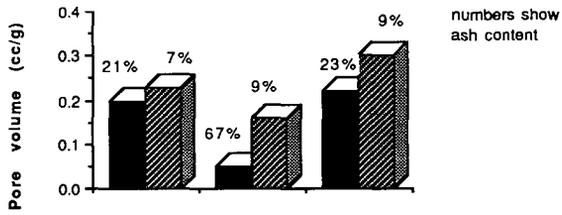


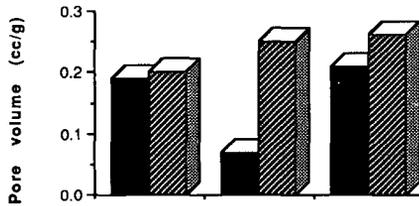
Figure 2: Moles of H₂S released during heat treatment (HTT=550°C, 50% acid).

- carbon from parent coal
- ▨ carbon from clean coal

a) micropore volume



b) mesopore volume



c) macropore volume

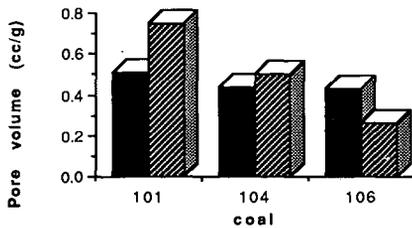


Figure 3: Pore volumes for carbons heat treated to 550°C, 50% acid.

■ carbons from parent coal ▨ carbons from clean coal