ABSTRACT

This research program has investigated the utility of Illinois coals as precursors for the synthesis of activated carbons by chemical activation, using a combination of coal cleaning by column flotation, followed by reaction with phosphoric acid or potassium hydroxide.

With phosphoric acid activation, carbons with surface areas around 800 m²g⁻¹ are produced at HTT to about 500°C. The carbons are dominantly microporous, with low mesopore surface areas. Above 500°C, the specific surface area decreases, when the acid may be converted to an inactive form. Extending the reaction time at high HTT can increase the micropore surface area. Increasing HTT increases the carbon ash content, commensurate with a reduction in yield, and reduces the organic sulfur and hydrogen contents. The carbon properties are strongly dependent upon the ratio of reagent to precursor. Increasing the ratio to about 1.0 increases both the micropore and mesopore surface areas. Further increase lowers the micropore surface area. The reduction can be attributed to increases in ash content. Increasing the ratio also promotes the removal of hydrogen and organic sulfur. The adjustment of the low HTT reaction parameters, over the ranges studied, appear to offer little prospect for significantly modifying the final carbon properties.

The surface area of KOH carbons increases steadily with increasing HTT, attaining a value of about 1600 m²g⁻¹ at HTT=800-900°C. The carbons are also highly microporous. The effect of KOH:coal ratio is also important to surface area development. A sharp increase in surface area is obtained by increasing the ratio at low values. At higher ratios, there is a reduction in specific surface area which can be accounted for increased carbon ash content.

Activation with H₃PO₄ and KOH produces some similar changes including partial dissolution of the coal structure at low HTT, and the removal of sulfur and hydrogen. The gaseous products could provide sources of H₂ (KOH activation), and S (phosphoric acid activation). The liquids could be used as low-sulfur fuels or as a source of phenolics.

Standard test methods have shown that these microporous carbons are suitable for the adsorption of small molecules but, not for the adsorption of large molecules such as color bodies. The KOH activated carbons are able to adsorb phenol to a similar extent as a commercial water treatment carbon. The acid activated carbons are much less effective. Further study is recommended.
EXECUTIVE SUMMARY

The primary aims are of this research program have been to investigate the utility of Illinois coals as precursors for the synthesis of activated carbons by chemical activation, using a combination of coal cleaning by column flotation, followed by reaction with phosphoric acid or potassium hydroxide. Coal cleaning reduces the contents of mineral matter and inorganic sulfur. Subsequent reaction in the presence of a chemical reagent produces an adsorbent carbon as the principal product, with by-product liquids and gases. The production of high surface area carbons has been realized by reaction with these reagents at temperatures up to 900°C. Detailed studies have been made to determine: the influence of reaction parameters on the composition and pore structure of the carbons; the accompanying chemical, structural, and morphological changes to the starting coal; the composition and potential utility of the gaseous and liquid by-products; and the performance of the carbons in relation to commercially available products.

With phosphoric acid activation, it has been found that carbons with surface areas around 800 m² g⁻¹ (in the range of commercial interest), are produced by heat treatment to temperatures of about 500°C. The carbons are dominantly microporous, with mesopores contributing only about 10% to the total surface area. At HTT above 500°C, the specific surface area decreases or, if considered on an ash-free basis, the surface area appears to reach a plateau. At high temperatures, the acid may be converted to an inactive form, and in the absence of a mechanism for stabilizing or enhancing the pore structure, dimensional contraction will reduce the accessible pore structure.

Extending the reaction time at high HTT can appreciably increase the micropore surface area. Increasing HTT also increases the carbon ash content, commensurate with a reduction in yield, and reduces the organic sulfur and hydrogen contents.

The carbon properties are strongly dependent upon the ratio of reagent to precursor. Increasing the acid to coal ratio increases both the micropore and mesopore surface areas. A minimum ratio of about 1.0 is required to develop maximum surface area. Further increase lowers the micropore surface area, while the mesopore surface area remains unchanged. The reduction in microporosity at high ratios can be attributed to increases in ash content. Increasing the ratio also promotes the removal of hydrogen and organic sulfur.

Studies of low HTT (170-245°C) reaction with phosphoric acid have shown that there are small but consistent changes in certain properties with increasing reaction severity. However, it is concluded that the adjustment of the low HTT reaction parameters, over the ranges studied, offers little prospect for significantly modifying the final carbon properties.

In contrast to H₃PO₄, the surface area of KOH carbons increases steadily with increasing HTT, attaining a value of about 1600 m² g⁻¹ at HTT=800-900°C. The KOH carbons are also highly microporous, with still lower mesopore surface areas than the phosphoric acid activated carbons. Increasing the rate of heating to the final HTT is found to increase the BET surface area.

The effect of KOH: coal ratio is also important to surface area development. As with phosphoric acid, a sharp increase in surface area is obtained by increasing the ratio at low values. At higher ratios, there is a reduction in specific surface area which can be accounted for increased carbon ash content.
Activation with $\text{H}_3\text{PO}_4$ and KOH produces some similar changes. At low temperatures, the reagents cause partial dissolution of the coal structure. This phenomenon appears to be relevant to the process of chemical activation and warrants further investigation.

Both reagents promote the removal of sulfur and hydrogen. They completely remove pyritic sulfur, even at low HTT, and are similarly effective for the removal of organic sulfur. However, the mode of sulfur removal is different. During phosphoric acid activation, most of the sulfur is released as $\text{H}_2\text{S}$. For KOH activation, most of the parent coal sulfur is transformed to water-soluble sulfides that are recovered during leaching. Dehydrogenation is more extensive than is attained thermally, and some hydrogen is released as $\text{H}_2$. Much more hydrogen gas is evolved during KOH activation than with $\text{H}_3\text{PO}_4$.

The gaseous and liquid by-products have been analysed to assess their potential commercial value. The gases could provide a valuable source of $\text{H}_2$ for KOH activation, and $\text{S}$ (from $\text{H}_2\text{S}$) for phosphoric acid activation. The liquids have reasonably high hydrogen contents, and lower sulfur contents. They also contain high proportions of phenolic oxygen and may be a viable source of these chemicals, as well as possibly finding direct use as a fuel.

Standard test methods have been applied to assess the utility of the carbon products. Iodine number and methylene blue values confirm that these microporous carbons are suitable for the adsorption of small molecules but, having low mesopore surface areas, neither is an appropriate choice for the adsorption of large molecules such as color bodies. The KOH activated carbons proved to have the ability to adsorb phenol to a similar extent as a commercial water treatment carbon. The acid activated carbons were much less effective. Further study is recommended.
1. OBJECTIVES

The primary goals of this research have been to investigate the utility of selected Illinois coals as precursors for the synthesis of activated carbons by chemical activation, using a combination of coal cleaning by column flotation, followed by reaction with phosphoric acid or potassium hydroxide.

Specific objectives are:

to examine the cleaning of selected Illinois coals by column flotation;

to conduct research with phosphoric acid and cleaned coals that will involve: a study of the influence of low temperature reactions on activated carbon properties; establishing reliable mass balances and compositional information on the reaction products; studying the composition, yield and potential utility of the liquid products; determining the importance of sulfur forms to \( \text{H}_2\text{S} \) formation; relating processing behavior to coal characteristics;

to investigate KOH as an alternative reagent to \( \text{H}_3\text{PO}_4 \) and to address: its applicability to bituminous coals; the potential advantages in ease of reagent recovery for recycle; the ability to exert further control in tailoring the adsorptive properties and capacities of the carbons; the effect of KOH on sulfur redistribution.

2. INTRODUCTION AND BACKGROUND

The direction of this work emanates from the results of a previous program (Derbyshire and others, 1991a) to investigate the potential of Illinois coals as precursors for activated carbons by chemical activation with phosphoric acid. The research successfully established that activated carbons can be synthesized from these coals, and that there is substantial removal of organic and inorganic sulfur. The findings led to the development of a conceptual process that combines the elements of coal cleaning and chemical activation to generate a range of marketable products.

In this concept, coals are first cleaned to reduce their mineral matter content and to substantially remove inorganic sulfur. The cleaned coal is then heat treated in the presence of phosphoric acid to afford an adsorbent carbon as the principal product. Most of the remaining sulfur is liberated as hydrogen sulfide, allowing the recovery of by-product sulfur, and low-sulfur hydrocarbon liquids are generated for use as a fuel or feedstock for upgrading.

This research has examined the cleaning of selected Illinois coals by column flotation. Chemical activation studies have employed both phosphoric acid and potassium hydroxide as reagents. The inclusion of KOH was made to evaluate the potential advantages of more facile reagent recovery and extended flexibility in tailoring the adsorptive properties and capacities of the carbons. The focus has been to: understand how reaction parameters influence the carbon structure and can be used to control adsorptive properties; evaluate the modes of sulfur release; establish reliable mass balances over the system; examine the potential uses of the liquid products; and investigate the comparative influences of the two reagents.

The ultimate goals are to identify alternative products and processing routes for the use of
Illinois coals. The market for activated carbons will continue to grow, with increasing emphasis and legislation on air pollution and water quality. Moreover, the concept now developed offers the prospect of generating premium by-products, in addition to high-value adsorbents. The research could further benefit the economics of other coal utilization processes where this technology can be usefully integrated. The studies will also help to provide an improved understanding of the chemistry of coal and coal sulfur behavior, and their relationship to coal characteristics. The results should be of value both to basic coal science and to developing alternative approaches to coal utilization.

Progress over the first nine months of this program was described in three quarterly reports. This final report deals principally with new data, with due references to the earlier results.

3. EXPERIMENTAL

3.1 Program of studies

The experimental program was divided into 6 Tasks: in Task 1, sufficient quantities of cleaned coals were prepared for the programs of work in other Tasks; Tasks 2 and 4 involved investigations of low temperature reactions, over a temperature range of 170-245°C for H₃PO₄ and up to 120°C for KOH; Tasks 3 and 5 were corresponding studies of combined low and high temperature (350-900°C) heat treatment on the properties of the final carbon product; Task 6 deals with characterization of the raw materials, reaction intermediates and final products.

3.2 Materials

The coals selected for this research were Illinois Basin bituminous coals, supplied by the Illinois Basin Coal Sample Program. The coals were selected to provide samples with: high organic sulfur content, IBC 101; high pyritic sulfur content, IBC 102; and moderate sulfur content with a 1:1 ratio of pyritic to organic sulfur, IBC 106. The coals were obtained as lumps stored under nitrogen. They were ground to an average particle size of 10 microns before they were cleaned by column flotation (Parekh, 1990). Coal cleaning has been found to improve the properties of the activated carbons (Jagtoyen and others, 1992a). All three coals were cleaned by column flotation. For carbon synthesis studies, cleaned IBC 106 was used exclusively. The chemical composition of the IBC 106 cleaned coal is shown in Appendix 1.

Chemical activants: Phosphoric Acid 85%, AR, from Mallinckrodt. Potassium Hydroxide AR, ACS Pellets, from Mallinckrodt.

3.3 Synthesis Apparatus and Procedure

The apparatus and procedure have been described previously (Derbyshire and others., 1991 b). Briefly, low and high temperature reactions are conducted in a stainless steel reactor tube that is contained within a tubular furnace. A sample of coal or coal-reactant mixture is contained in a 230 cm³ quartz glass boat inside the reactor tube. For KOH activation an inconel crucible was used.
The reactor tube is longer than the furnace, allowing samples to be stationed in a cool position while heating the furnace, and to be cooled rapidly after heat treatment. The reactions are carried out under an inert atmosphere of flowing nitrogen. At the start of the experiment, the sample is placed in the cool end of the reactor tube. After heating the furnace to the required temperature, the sample is introduced into the hot zone. When the sample has experienced the desired time-temperature progression, it is withdrawn into the cool zone. The same procedure is used for both low and high temperature heat treatment.

The tar and oil products are collected in cold traps at the reactor outlet. The first trap is immersed in an ice/water slurry, and the second trap in dry ice/methyl alcohol. The gaseous products are collected in a calibrated graduated gas cylinder. The volume of gas is recorded, along with the room temperature and atmospheric pressure. The gas composition and concentration of each component is determined using a HACH Carle gas chromatograph, using standard procedures for calibration.

The reactor incorporates three thermocouples attached to a Molytek Model 2700 Multipoint recorder to monitor: the reactor cool end temperature; the atmosphere directly above the sample; and the sample temperature. The inconel thermocouple also acts as a push rod for moving the sample to different positions inside the reactor tube.

3.4 Tasks 2 & 3, Treatment with H₃PO₄ Low and High Temperature

Work in Task 2 examined the influence of synthesis parameters on the reaction of IBC 106 coal with H₃PO₄ at low temperatures. The experimental part of this research was essentially completed by the end of January, 1992 and subsequent research has been concerned with the characterization of the products.

The procedure for these reactions was to prepare a slurry of the coal and acid solution, using 30g of dry coal, and selected solution volumes and acid concentrations. The coal moisture content was taken into account in preparing the acid solution. The slurry was then heated to temperature (170 - 245°C) in flowing nitrogen and held for the required time before cooling.

The solid products were leached with distilled water to pH = 7 and vacuum dried at 110-120 ºC for a minimum of 4h before further analysis. For comparison, a parallel series of thermally carbonized coals were prepared by heat treatment under the same conditions.

In Task 3, the effects of low temperature treatment on the properties of the final product were investigated by heating low temperature slurries (prepared in the same way as described above) to a higher heat treatment temperature (HTT) of 500°C for a holding time of 1 h. The experimental work originally planned under this Task was completed by the end of February. Some further experiments were subsequently made to complete a study of varying acid concentration, and of upper HTT and hold time.

3.5 Tasks 4 & 5, Treatment with KOH at Low and High Temperature

Task 4 was a study of the reactions of KOH and coal, at temperatures up to 100°C, using a reactor that allows the slurry to be stirred during low temperature treatment. The experiments involve reaction at a selected temperature, with stirring, in nitrogen for 2 h, following which the sample is dried overnight (24 hr) at 115°C. The work on this Task was
completed on schedule at the end of April. Subsequent work was concerned with the analysis of the reaction products.

Task 5 examined the influence of low temperature treatment on the products generated at heat treatment temperatures up to 900°C.

3.6 Task 6, Analysis and Characterization

A range of analytical techniques was applied to determine the composition and properties of the coals, intermediate, and final solid, liquid and gaseous products. These include: elemental analysis; surface area and porosity by gas adsorption and mercury porosimetry; FTIR; scanning electron microscopy and optical microscopy. A more detailed description of the techniques has been given previously (Derbyshire and others, 1991a).

4. RESULTS AND DISCUSSION

Full details of all the experiments conducted to date and the available results are provided in Appendices 1-8. Tables and Figures given in the main text provide more specific illustrations.

4.1. Task 2, Low Temperature Treatment with H₃PO₄.

The experimental program and results of the low temperature studies with H₃PO₄ are given in Appendix 1.

Porosity and composition

As previously reported (Derbyshire and others, 1992b), the compositional changes produced by low temperature treatment are generally quite small. Nonetheless, reaction in the presence of phosphoric acid produces certain consistent effects when compared to thermal treatment. With increasing time and/or temperature over the ranges studied, the reflectance of the altered vitrinite increases; the BET surface areas, which are very low, decrease, as does the macropore volume; and there is an overall trend to reducing the H/C atomic ratio. Equivalent thermal treatment has a negligible influence on these properties.

The progressive loss of surface area and macropore volume with reaction severity may be explained by increasing solubilization or digestion of part of the coal structure in the reagent solution, as suggested by other studies (Guy and others, 1990), and is supported by examination of these reaction products by optical microscopy (see below).

The parent coal contains 0.5% pyritic sulfur and 2.1% inorganic sulfur. Thermal treatment produces little change in either of these sulfur forms. Low temperature acid treatment also has little influence on the organic sulfur content, but causes a significant reduction in the pyritic sulfur content as the temperature is increased from 170 to 245°C.

Increasing the acid to dry coal ratio from 0.24 to 1.76 was found to have little effect upon the composition of the low HTT carbons produced by reaction at 170°C for 0.5h.

For the solid products generated under similar conditions, the fixed carbon content is consistently higher, and the volatile matter content lower, after acid treatment than thermal reaction. It is considered that this represents the onset of the crosslinking reactions that are
pivotal to the formation of high porosity carbons, and result in higher carbon yields. The ash contents of acid-treated carbons are also higher, consistent with the retention of phosphorus, Jagtoyen and others, (1992a).

**Optical microscopy**

Thermal- and phosphoric acid-treatment (0.96 acid:coal ratio) of IBC-106 at temperatures of 170 and 210°C for 0.5 hrs caused essentially no change in the morphology or measured reflectance of the altered vitrinite, whereas treatment at 245°C caused a significant reflectance increase, but only in the acid-treated coal (Appendix 6). The increase in reflectance, in the absence of any porosity development, is consistent with the loss of hydrogen and increased aromaticity, Jagtoyen and others (1992b). Accompanying the higher reflectivity was an increased degree of apparent dissolution and subsequent agglomeration of the coal particles, to form larger, coherent masses. The presumed collapse or occlusion of existing pores during chemical digestion, also suggested by the decrease in BET surface area and macroporosity, would both be consistent with a reflectance increase, Derbyshire and others (1992b). No such trends were observed in the thermally pretreated samples.

The contrast between phosphoric acid and thermal pretreatment was also evident when the reaction time was increased from 0.5 to 3.0 hours. Thermal treatment at 170°C for 3 hours did not significantly alter the reflectance of the vitrinite component, whereas acid-treatment at the same temperature for 0.5, 1.5, and 3.0 hours caused a slight, but progressive increase in the reflectance of the altered vitrinite (Appendix 6), again consistent with slight decreases in hydrogen content, BET surface area, and macropore volume. It is apparent that increasing the severity of low temperature treatment in the presence of phosphoric acid can have a pronounced influence on coal microstructure, whereas thermal pretreatment alone leaves the coal structure, for all practical purposes, unchanged.

4.2 Task 3, High Temperature Treatment with \( \text{H}_3\text{PO}_4 \).

**Effect of low HTT reaction parameters**

**Porosity and composition**

The results of experiments to examine the influence of low temperature reaction conditions on the properties of carbons produced after final heat treatment to 500°C, for 1h are shown in Appendices 2 and 3. Data are presented for acid treated carbons and thermal blanks. Most of the findings have already been reported in previous quarterly reports (Derbyshire and others, 1992a and b). A brief summary review is presented here for completeness, in addition to new information.

At 170°C, the BET surface area passes through a shallow maximum with increasing reaction time, with a corresponding minimum in mesopore surface area. It appears that extended reaction at lower temperatures may be detrimental to micropore surface area, at the expense of increasing the mesopore surface area. However, for the range of conditions studied (170 - 245°C, and 0.5 to 3h), it seems that there is little latitude for exerting any significant degree of control over the pore structure of the high temperature carbons through modification of the low temperature reaction parameters.
Neither was there any significant effect of varying the low temperature conditions on the composition of the high HTT carbons. However, the compositions of the high HTT acid treated carbons were clearly different to those of the thermal blanks. Acid treatment gave: higher carbon yields; lower volatile matter content; higher fixed carbon content; lower H/C atomic ratio; and essential elimination of the pyritic sulfur and a high proportion of the organic sulfur.

**Optical microscopy**

Some of the effects of low temperature pretreatment on carbon morphology are manifest after final activation at HTT 500°C (0.96 acid:coal), as evidenced by a study of the high HTT carbon products by optical microscopy. Increasing the low temperature reaction time from 0 to 1.5 hours, resulted in a reflectance increase of the altered vitrinite, followed by a decrease after reaction for 3 hours. The maximum reflectivity in this series was obtained after 1.5 hrs at 170°C pretreatment. This carbon exhibited a smooth optical texture compared to the other carbons which had a submicron granular appearance. It is possible that this granular appearance is caused by submicron-sized pores, and that reflectance is negatively affected by the small pores (below the resolution of the optical microscope), especially those in the mesopore range that have been proposed to cause increased scattering and absorption of the incident light (Derbyshire et al., 1992 b).

The product morphology also shows some correspondence to porosity development. With increasing pretreatment temperature, reflectivity exhibits a trend which is the inverse of that shown by the mesopore volume, Figure 4.2.1 (see also the discussion at the end of this section). For a given upper HTT, it may be assumed that the aromaticity and structural order are similar for these carbons, in which case, the observed reflectance changes are largely related to the proportion of mesopores.

![Figure 4.2.1 Inverse relationship between reflectance and mesopore volume (IBC 106 precursor; acid:coal=0.96)](image)
Effect of high HTT reaction parameters

The influence of high temperature reaction conditions on the properties of carbons first reacted at 170°C for 0.5h is considered in this section. Data are tabulated in Appendices 2 and 3.

Acid to coal ratio

Increasing the acid to coal ratio increases both the micropore and mesopore surface areas of carbons produced at HTT 500°C (Derbyshire and others, 1992b). A minimum ratio of about 1.0 (dry coal basis) is required to develop the maximum surface areas. Further increase in the proportion of acid appears to lower the micropore surface area, while the mesopore surface area remains unchanged. The changes in micropore and mesopore volume with acid: coal, Figure 4.2.2 reflect these same phenomena. The reduction in microporosity at high ratios could be attributed to the increasing ash content. When expressed on an ash-free basis, the micropore surface areas attained at ratios of 1.0 and higher, are more or less the same.

![Figure 4.2.2 Dependence of pore volume on acid to coal ratio (IBC 106 coal; HTT 500°C, 1h)](image)

The macropore volume data are more scattered but the weight of evidence suggests that there is a general decrease in macropore volume with acid: coal, which may relate to the digestion (partial dissolution) of the coal in the reagent solution and the subsequent redistribution of dissolved material into the larger pores (see Task 2).

With respect to compositional changes, increasing the acid to coal ratio effects a proportional lowering of the H/C atomic ratio of the carbon (Derbyshire and others, 1992b). Acid treatment, under all conditions at temperatures of 350°C and above, eliminates pyritic sulfur, while it is much more difficult to remove by purely thermal treatment. The other notable compositional change upon acid treatment is the extensive removal of organic sulfur. The organic sulfur content of the parent coal is 2.1%. As shown
in Figure 4.2.3, the organic sulfur content of the carbon is strongly dependent upon the ratio acid: coal up to a value of about 0.6, when the organic sulfur content is 0.5%. At higher values, there is no further sulfur removal at this heat treatment temperature (500°C). The extent of organic sulfur removal is further increased at higher HTT (see below). In comparison, thermal treatment to 550°C only reduces the carbon organic sulfur content to 1.9%.

![Effect of acid: coal on organic sulfur content of carbon (IBC 106 coal; HTT 500°C, 1h)](image)

**Heat treatment temperature and reaction time**

A study has been made to examine the effects of HTT in the range 350 to 650°C, and for reaction times of 1 and 3h. The compositional and pore structural information on the product carbons are summarized in Appendices 2 and 3.

The influences of time and HTT on the surface areas of carbons produced from cleaned IBC 106 coal are illustrated in Figure 4.2.4, where data are also shown for carbons synthesized from IBC 101 (obtained under the previous contract, Derbyshire and others, 1991a). The BET surface areas of the carbons from IBC 101, produced by reaction for 1h, pass through a maximum at about HTT 500°C. The reported mesopore surface areas (Derbyshire and others, 1991a) also pass through a shallow maximum at about HTT 550°C. The carbons produced from IBC 106, after 1h reaction, behave in similar manner. Analogous behavior has been reported for carbons produced from coconut shell by phosphoric acid activation (Laine and others, 1989), and for carbons produced from a wood precursor (Jagtoyen and Derbyshire, 1992). In both of these cases, the maximum surface areas were attained at HTT 450°C, and it may be that the location of the maximum is rank dependent.

As with the changes caused by increasing the ratio acid: coal, the maxima obtained with the coal-derived carbons could be attributed to the simultaneous increases in carbon ash content. However, in the cited studies with coconut shell and wood, these precursors have very low ash content. The sharpness of the maxima, and the inferred low ash content of the
products, makes it unlikely that increased ash content can account fully for the loss of surface area at high HTT. The more likely causes are considered to be due to the acid becoming inactive for further porosity development, and dimensional contraction of the carbon at high HTT (Jagtoyen and Derbyshire, 1992).

It is also to be noted that the surface areas are higher for the IBC 106 carbons, than when IBC 101 is used as the precursor, as reported previously (Jagtoyen and others, 1992a). After reaction for 3h, the BET surface areas of the IBC 106 carbons are higher than those obtained at the shorter reaction time. This behavior has not been previously observed in these studies of H₃PO₄ activation. The absence of a data point at HTT 500°C precludes confirmation that a maximum, or the beginning of a plateau, exists at about this temperature. However, the considerable weight of supporting evidence produced in this research makes it probable that the curve shown by the dotted line is a reasonably accurate representation.

The mesopore surface areas of the IBC 106 carbons appear to be little influenced by reaction time and, as in the studies with the IBC 101 precursor, they pass through a shallow maximum at about HTT 550°C. The pore volume data, Figure 4.2.5, parallel the preceding comments relating to surface area.

The carbon composition is found to depend upon HTT, but does not seem to be affected by reaction time, as shown in Figure 4.2.6 for the organic sulfur content. The H/C atomic ratio of the carbon similarly decreases with HTT but is also unaffected by reaction time. The carbon ash content, and associated phosphorus incorporation (Jagtoyen and others, 1992b), both increase in a linear manner with HTT, Figure 4.2.7, commensurate with a decrease in carbon yield.

![Figure 4.2.4 Dependence of surface area on HTT](image_url)
Figure 4.2.5 Dependence of pore volume on HTT
(IBC 106 coal, acid: coal = 0.96)

Figure 4.2.6 Effect of HTT on organic sulfur removal
(IBC 106 precursor; acid: coal = 0.96)
As a general comment, it is found that the acid treated products have higher fixed carbon contents than those produced by equivalent thermal reaction. The yields of solid product are also higher after acid treatment. An example of the yield of carbon product is 69.6% after thermal treatment and 72.7% after acid treatment.

Optical microscopy

Acid treatment at 500°C and 550°C produced a carbon with a finely granular appearance and submicron mosaic anisotropy, whereas the thermally-activated carbons exhibited a smooth, isotropic optical texture. As discussed previously (Derbyshire et al., 1991b) the thermally activated carbons produced at these temperatures were more highly reflecting than the acid-activated equivalents.

Increasing the acid:coal ratio, at constant HTT of 500°C, produced a monotonic decrease in carbon reflectivity and a progressive increase in mesoporosity, Figure 4.2.8. At the same time, the H/C atomic ratio is found to decrease as the proportion of reagent is increased, and it is supposed that this corresponds to increased aromaticity and structural order which, in turn, would increase reflectance. Further, it has already been shown (Derbyshire and others, 1992b) that increasing the HTT, at constant acid concentration, also results in a decrease in H/C atomic ratio. Changes in both acid to coal ratio and/or activation temperature also affect carbon porosity. Consequently their influence on carbon reflectance is complicated by competing processes; increasing structural order, which would result in a higher measured reflectance, and the development of significant porosity which can decrease the reflectance by light scattering and absorption, particularly by those pores in the mesopore range (Derbyshire and others, 1992b).
The effect of increasing HTT on reflectance and mesopore volume for IBC 106 carbons is shown in Figure 4.2.9. Increasing the HTT from 350 to 450°C results in a significant increase in reflectance (temperatures around 350°C are usually considered to herald the onset of thermal cracking). At HTT 500°C, the reflectance goes through a shallow minimum and then increases again at 550 and 650°C. The initial rise in reflectance corresponds to the initial stages of porosity development. However, over this temperature range (350 to 450°C), the structural alterations appear to dominate the reflectance.

At 500°C, the mesopore volume passes through a maximum, and it is here that the porosity can contribute to depressing the measured reflectance. At still higher temperatures, the porosity of the carbon decreases or if corrected for ash content reaches a plateau (as now shown several times: this is believed to be due to the phosphoric acid becoming inactive for the development of pore structure at temperatures much above 500 - 550°C) and a positive relationship between reflectance and HTT is reasserted. Some insight into the reflectance trend is also provided by qualitative microscopical observations. The lowest reflecting carbon in the series has a highly granular appearance (and relatively high measured porosity), whereas the carbon exhibiting the highest reflectance has a smooth optical texture, and a comparatively low mesoporosity.
4.3: Task 4, Low temperature treatment with KOH

Under this Task, a study has been made to examine the compositional and structural changes taking place during the low temperature stage reaction with KOH, and to determine how these might impact upon the structure and properties of high HTT carbons.

A particularly significant finding is that the bituminous coal structure is partially digested in the KOH solution at moderate temperatures (75 - 115°C). This phenomenon has also been found in studies of low temperature reaction with H₃PO₄, and in other research on the KOH activation of brown coal, where the degree of solubilization is very extensive (Guy and others, 1990). The extent of digestion has been determined by measuring the yield of solid material remaining after low temperature reaction, separation of the soluble (humic acid) fraction, and subsequent washing. The solid yield, as expected, decreases with increasing digestion temperature at a constant ratio of KOH: coal, Figure 4.3.1a, and is surprisingly low (c. 20%) after reaction at 300°C.

Increasing the ratio of KOH:coal up to about 2.4, at a reaction temperature of 75°C, has a rather unexpected effect, in that it appears that there is a minimum solid yield (maximum digestion) at a ratio around 1.0, Figure 4.3.1b. At higher ratios, there is a reversal of the digestion effect, and the solubility decreases leading to a higher yield of insoluble material. It might be speculated that some equilibrium exists between the KOH and soluble material, and that this is adversely affected at higher KOH loadings.

The changes in H/C ratio of the insoluble solid material (runs 4-1 to 4-46 in Appendix 5) support this proposition. The H/C ratio of the solid product is at a minimum at a ratio of around 1.0, Figure 4.3.2, and below that of the parent coal, suggesting that the digested material is somewhat richer in hydrogen than the insoluble portion.
In each of the low HTT digestion experiments, the reacted product was dried for 20h at 115°C, which effectively extends the digestion time and makes it difficult to ascertain the influence of this variable. However, it is assumed that increasing the reaction time will normally increase the yield of solubilized product.

The apparent inverse solubility at high KOH loadings may bear some relation to the effect that is found with surface area development in high HTT carbons: the surface area when expressed on an ash-free basis reaches a plateau at a KOH: coal ratio around 1.42 and higher (see section 4.4).

The effect of partial digestion of the coal was investigated in an experiment in which the coal was digested for 2h at 75°C at a KOH to coal ratio of 2.37. The extracted fraction and the insoluble fraction were chemically activated at 800°C, (the weight ratio of KOH to dry material was kept at 2.37). The humic acid (extract) fraction gave a surface area of only 305 m²/g (sample 5-46a in Appendix 4) while the insoluble fraction (which was re-mixed with KOH before activation) gave a surface area of 1979 m²/g (run 5-46b in Appendix 4). This is over 400 m²g⁻¹ higher than the surface area obtained by activation of the whole coal under the same conditions (surface area = 1501 m²g⁻¹).

**Optical microscopy**

Pretreatment in the presence of KOH causes a slight, but consistent increase in reflectance which does not vary significantly as the pretreatment conditions are changed. For example, pretreatment with a KOH: coal ratio of 0.4:1 at 75°C caused an increase in the reflectance of the altered vitrinite from 0.50 to 0.55%, which is very similar to the increase brought about by pretreatment with a KOH: coal ratio of 2.4:1. Similarly, there is no effect on vitrinite reflectance due to increasing the pretreatment temperature to 100°C. The only other comment of note is that, as discussed in a previous report (Derbyshire et al., 1992b), the polished particulate surfaces of the KOH-treated coals tended to develop cracks during the dessication of the polished surface. This is a phenomenon often observed in low-rank coals and is probably due to shrinkage of the altered coal particles upon drying. This was not observed in the feed coal.
Figure 4.3.1: Yield of water insoluble material after low temperature reaction of KOH and coal as a function of reaction temperature (a), ratio=1.42, and ratio of KOH:coal (b), HTT=75°C. (Reaction time = 2hrs).

Figure 4.3.2: H/C ratio of water insoluble material after low temperature reaction of KOH and coal as a function of KOH:coal ratio (HTT=75°C, reaction time = 2h).
4.4 Task 5, High Temperature Treatment with KOH

A series of experiments has been made to investigate the influence of reaction parameters during high temperature treatment: HTT, heating rate and KOH:coal weight ratio. A summary of the experiments and result is provided in Appendices 4 and 5. Data are presented for KOH activated samples and some thermal blanks. Many of the findings have already been reported in previous quarterly reports (Derbyshire and others, 1992 a and b.). Where appropriate, a brief summary is presented for completeness, in addition to new information.

Effect of low HTT reaction parameters

The influence of the low temperature reaction parameters on the development of surface area at high HTT (800°C) is shown in Figure 4.4.1, for constant heating rate and ratio KOH: coal = 1.42. Increasing the pretreatment temperature or extending the reaction time both result in lower surface areas. The reasons for this behavior are not clear, but stress the point that the reactions and structural alterations occurring at low temperatures are important to the structure and properties of the final high temperature carbon product. Changes in the other low temperature conditions do not have any apparent influence on the composition or porosity of the high HTT carbons.

Effect of high HTT reaction parameters

Porosity development
The influence of HTT on carbon yield and surface area development is illustrated in Figure 4.4.2. The yield decreases with increasing HTT, while the surface area starts to develop at temperatures between 400-500°C and increases steadily with further increase in HTT. Thus, the choice of HTT effects a compromise between the surface area attainable and the yield of product that is desired. The ash content of the carbons actually decreases with HTT, presumably due to the solubilization of mineral matter constituents, which will somewhat enhance the value of the specific surface areas.

The effect of KOH: coal ratio on surface area development is shown in figure 4.4.3. A sharp increase in surface area is obtained by increasing the ratio from 1-1.4. On going to still higher ratios, there is a reduction in surface area. Parallel behavior was observed with phosphoric acid, section 4.2. As noted, a possible reason for this reduction is that there is
a corresponding increase in the ash content of the carbon from 2.0 to 11.2. If it is assumed that the ash makes no contribution to the surface area, then expressing the surface area on an ash-free basis should compensate for the reduction in specific surface area. Calculation shows that this appears to be the case. However, studies of the effects of coal cleaning on carbon porosity suggest that the assumption of negligible ash surface area may not always be valid (Jagtoyen and others, 1992c).

Figure 4.4.1: Dependence of low temperature reaction conditions on surface area development on KOH activation at 800°C. (Low reaction temperature indicated on figure)

Figure 4.4.2: Influence of heat treatment temperature on yield and surface area, open circles show yield, filled circles show surface area.

As a general comment, it is found that the KOH carbons are generally somewhat less mesoporous than the phosphoric acid activated carbons: the maximum measured mesopore
surface areas are 55 m²g⁻¹ for KOH and 114 m²g⁻¹ for H₃PO₄. The relevance of this observation to the utility of the carbons is discussed further under Task 6.

![Graph showing surface area dependence upon KOH:coal ratio. (HTT=800°C)](image)

**Figure 4.4.3: Surface area dependence upon KOH:coal ratio. (HTT=800°C)**

**Hydrogen Content**

The H/C atomic ratio of the KOH and H₃PO₄ activated carbons is plotted against HTT in Figure 4.4.4. Data for the phosphoric acid carbons produced in the previous program are also included (Derbyshire and others, 1991b), as well as data for thermally treated carbons. The addition of more recent results allows the correlation to be fully extended over the whole temperature range of study. Both reagents act similarly in promoting dehydrogenation at a much faster rate than is attained thermally.

![Graph showing change in H/C ratio for carbons synthesized from bituminous coals.](image)

**Figure 4.4.4: Change in H/C ratio for carbons synthesized from bituminous coals.**
Gas analyses have shown that hydrogen is evolved during chemical activation and that the H\textsubscript{2} released during thermal treatment is significantly lower. These findings support the low H/C ratio found in the chemically activated carbons. In some cases, the yield of H\textsubscript{2} amounts to as much as 100% of the hydrogen in the parent coal.

**Optical microscopy**

Thermal activation of IBC-106 at temperatures of 700, 800, and 900°C produced carbons with consistently higher reflectivities than the corresponding KOH-activated carbons (Appendix 7). As was discussed for phosphoric acid activation, the higher reflectance of the thermally-activated carbons corresponds to a significantly lower mesoporosity than that of the KOH-activated carbons.

Increasing the KOH:coal ratio in the final activation step (HTT 800°C) from 1.0:1 to 1.4:1 resulted in a marked decrease in carbon reflectance, followed by smaller decreases as the ratio was further increased. Although sample 5-9 (1.4:1 KOH:coal) has a mean reflectance lower than that of the 1.9:1 carbon (5-14), Figure 4.4.5 shows that a large proportion of the reflectance readings are higher in sample 5-9 than 5-14, with the distribution skewed towards the lower values. In the absence of any significant changes in elemental composition, it appears that the initial decrease in reflectance corresponds to a marked increase in total and mesopore surface area, whereas the subsequent and smaller decreases in reflectance at higher KOH:coal ratios correspond to smaller increases in porosity.

However, the carbon prepared at a ratio of 2.4:1 (5-15) has a slightly lower mesopore and total surface area than the 1.9:1 (5-14) carbon (Appendix 4). In this case, the further decrease in reflectance may be less due to porosity than other factors: the occurrence of anisotropic semicoke and a relatively high proportion of inorganic material.

As with phosphoric acid-activation, increasing the HTT resulted in a carbon reflectance trend which is complex and probably a result of the competing effects of increased aromaticity, and porosity development. The relationship between reflectance and HTT for these carbons was discussed at some length in the last quarterly report (Derbyshire and others, 1992b).
Figure 4.4.5: Reflectance histograms for carbons produced with different KOH:coal ratios (HTT=800°C).
4.5: Task 6, Characterization

4.5.1: Composition of liquid and gaseous by-products

Although the principal aims of this work have been to examine the synthesis of activated carbons from Illinois coals, the liquid and gaseous by-products have also been analyzed to assess their potential commercial value. The liquids show some potential as a fuel and the gases could be a source of H₂ and S (from H₂S). The distribution of carbon between the solid, liquid and gaseous products is shown in Table 4.5.1 for the reaction of IBC 106 with phosphoric acid to HTT 500°C. Between 70 to 80% of the carbon in the parent coal reports to the solid product, 15 to 22% to the liquids, and 2 to 4% to the gases.

<table>
<thead>
<tr>
<th>Run</th>
<th>HTT(°C)</th>
<th>H₃PO₄: coal</th>
<th>char</th>
<th>tar</th>
<th>gas (g)</th>
<th>total</th>
<th>parent</th>
<th>balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>low</td>
<td>high</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-10</td>
<td>170</td>
<td>500</td>
<td>0.24</td>
<td>17.7</td>
<td>2.1</td>
<td>0.8</td>
<td>20.6</td>
<td>24.6</td>
</tr>
<tr>
<td>3-11</td>
<td>210</td>
<td>500</td>
<td>0.96</td>
<td>19.7</td>
<td>3.6</td>
<td>0.7</td>
<td>24.0</td>
<td>24.6</td>
</tr>
<tr>
<td>2-21</td>
<td>170</td>
<td>500</td>
<td>1.61</td>
<td>16.5</td>
<td>5.5</td>
<td>1.1</td>
<td>23.1</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td>Thermal treatment only</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-8</td>
<td>170</td>
<td>500</td>
<td>0</td>
<td>20.8</td>
<td>4.8</td>
<td>0.7</td>
<td>26.3</td>
<td>28.7</td>
</tr>
</tbody>
</table>

**Liquid products**

The yields, and H/C and S/C atomic ratios of the liquids produced by H₃PO₄ activation at HTT 500°C are summarized in Table 4.5.2. Equivalent data for liquids produced by KOH activation at HTT 700°C are shown in Table 4.5.3.

The H/C ratios of the liquids from H₃PO₄ activation are in the range 1.3-1.4, corresponding to 6 to 10% hydrogen content, and are slightly higher than those obtained by thermal treatment (H/C = 1.29). The hydrogen contents are within the range of H/C ratios found in commercial fuels, e.g the commercial fuel oil listed in table 2 has an H/C ratio of 1.4.

<table>
<thead>
<tr>
<th>Run</th>
<th>Ratio H₃PO₄:coal</th>
<th>Yield liquid</th>
<th>H/C ratio liquid</th>
<th>S/C % of H as H₂</th>
<th>% of S as H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>char</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-8</td>
<td>0</td>
<td>32</td>
<td>-</td>
<td>1.28</td>
<td>0.4</td>
</tr>
<tr>
<td>3-15</td>
<td>0</td>
<td>24</td>
<td>71</td>
<td>1.27</td>
<td>0.4</td>
</tr>
<tr>
<td>3-10</td>
<td>0.24</td>
<td>25</td>
<td>69</td>
<td>1.42</td>
<td>0.44</td>
</tr>
<tr>
<td>2-22</td>
<td>0.96</td>
<td>-</td>
<td>64</td>
<td>1.37</td>
<td>0.3</td>
</tr>
<tr>
<td>2-20</td>
<td>1.29</td>
<td>22</td>
<td>76</td>
<td>1.29</td>
<td>0.3</td>
</tr>
<tr>
<td>2-21</td>
<td>1.61</td>
<td>-</td>
<td>67</td>
<td>0.2</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4.5.3: Liquid and gaseous products from KOH synthesis of activated carbons from coal, HTT = 700°C.

<table>
<thead>
<tr>
<th>Run</th>
<th>Ratio</th>
<th>Yield</th>
<th>H/C ratio</th>
<th>S/C ratio</th>
<th>% of H as H₂</th>
<th>% of S as H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KOH:coal</td>
<td>char</td>
<td>liquid</td>
<td>char</td>
<td>liquid</td>
<td></td>
</tr>
<tr>
<td>5-11</td>
<td>0</td>
<td>64</td>
<td>1.0</td>
<td>0.19</td>
<td>0.009</td>
<td>16</td>
</tr>
<tr>
<td>5-3</td>
<td>1.42</td>
<td>63</td>
<td>1.7</td>
<td>0.05</td>
<td>0.002</td>
<td>51</td>
</tr>
<tr>
<td>Commercial</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel Oil #6, no HTT</td>
<td>1.39</td>
<td>-</td>
<td></td>
<td></td>
<td>0.007</td>
<td>-</td>
</tr>
</tbody>
</table>

The H/C ratios of the solid and liquid products are shown as function of the ratio of H₃PO₄ to coal for HTT 500°C in Figure 4.5.1, where it can be seen that the H/C ratio steadily decreases as the proportion of acid is increased. The highest hydrogen content liquids are generated at a ratio of 1.0 or less which is also where the maximum surface area is attained (see Task 3).

Much of the hydrogen may be removed as H₂, rather than in the form of light hydrocarbons. As can be seen from Tables 4.5.2 and 4.5.3, KOH activation at 700°C reduces the carbon (char) hydrogen content much more than H₃PO₄ activation at 500°C. In consequence, there is much greater hydrogen production (approximately 50 % of the parent coal hydrogen is released as H₂), and the liquids too have a high hydrogen content (H/C atomic ratio of about 1.7, compared to 1.0 for an equivalent thermal run).

Figure 4.5.1: H/C ratio in liquid and solid product is decreasing with increasing ratio of H₃PO₄ to coal.

Another interesting aspect of the liquids is their low sulfur content, which is lower than that of the sample of commercial #6 fuel oil, Table 4.5.3. One of the outcomes of this research program has been to show that both H₃PO₄ and KOH activation promote extensive sulfur
release from the coal precursor. In the case of H₃PO₄ most of the sulfur is released as H₂S, which gives an opportunity for recovering elemental sulfur. For KOH activation, sulfur is released as soluble sulfides that appear in the leaching water. A discussion of sulfur balances is given in section 4.5.2.

The $^{13}$C NMR spectra of samples of liquids produced by H₃PO₄ activation and thermal treatment at HTT 550°C are presented in Figure 4.5.2. The spectra are normalized to the polymethylene resonance band at 30 ppm. The large off-scale bands at 136 and 123 ppm are due to the pyridine solvent. The phosphoric acid treated sample is shown to have a significantly higher proportion of aromatic carbon in its structure than the thermal product.

The FTIR spectra of the same samples are shown in Figure 4.5.3 along with a difference spectrum, in which the spectrum of the acid was subtracted from that of the thermally treated sample. The difference spectrum is normalized on aliphatic groups, by multiplying the acid spectrum with a coefficient to eliminate the aliphatic peaks in the subtraction spectrum. The acid treated sample is clearly more aromatic, in agreement with the NMR data. It is also apparent that the acid treated sample contains a much higher proportion of phenolic OH groups.

The existence of high concentrations of phenolic OH groups supports the assumptions presented in last year's final technical report (Derbyshire and others, 1991a) where the disappearance of aromatic C=O linkages was linked with the appearance of carbonyl and phenolic groups in the activated carbons. Hard numbers are not available for the liquid oxygen content. However, the spectral information suggests that, despite the high hydrogen and low sulfur contents of the liquids, some further processing will be necessary to produce a liquid with a conventional fuel oil composition. At the same time, the liquids may have sufficient heating value to be used directly, and might also prove to be a valuable source of phenolics.

**Figure 4.5.2:** $^{13}$C NMR spectra of liquids from thermal treatment and H₃PO₄ activation of coal (IBC 106 coal; HTT = 550°C; 1h reaction)
Figure 4.5.3: FTIR spectra of liquids from thermal treatment and chemical activation of coal (IBC 106 coal; HTT = 550°C; 1h reaction)

Gaseous products

The compositions of the product gases differ significantly for chemical activation and thermal treatment, Table 4.5.4. As noted in the previous section, chemical activation leads to the extensive release of hydrogen as \( \text{H}_2 \) for KOH activation up to 70-90% of the parent coal hydrogen is released as \( \text{H}_2 \), around 7% with \( \text{H}_3\text{PO}_4 \) treatment, and a negligible amount on thermal treatment. Hydrogen gas is therefore a valuable by-product from the KOH activation process.

The most significant gaseous by-product of \( \text{H}_3\text{PO}_4 \) activation is \( \text{H}_2\text{S} \). Up to 55% of the parent sulfur is released as \( \text{H}_2\text{S} \). The actual number may be higher than indicated by the data, due to experimental difficulties in the quantitative determination of \( \text{H}_2\text{S} \). The \( \text{H}_2\text{S} \) release on thermal treatment is about 20-25% at HTT=500°C.

Table 4.5.4: Composition of gaseous products from carbon synthesis, HTT=500°C, rx. time=1hr.

<table>
<thead>
<tr>
<th>Treatm.</th>
<th>( \text{H}_2\text{S} )</th>
<th>( \text{H}_2 )</th>
<th>( \text{CO}_2 )</th>
<th>( \text{C}_2\text{H}_4 )</th>
<th>( \text{C}_2\text{H}_6 )</th>
<th>( \text{CH}_4 )</th>
<th>( \text{C}_3\text{H}_8 )</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_3\text{PO}_4 )</td>
<td>54.3</td>
<td>6.9</td>
<td>0.38</td>
<td>0.05</td>
<td>0.12</td>
<td>0.43</td>
<td>0.25</td>
<td>74</td>
</tr>
<tr>
<td>Thermal</td>
<td>23.5</td>
<td>0.5</td>
<td>0.61</td>
<td>0.07</td>
<td>0.24</td>
<td>0.41</td>
<td>0.24</td>
<td>71</td>
</tr>
<tr>
<td>KOH</td>
<td>0</td>
<td>75.8</td>
<td>2.47</td>
<td>0.01</td>
<td>0.04</td>
<td>0.36</td>
<td>0.00</td>
<td>80</td>
</tr>
</tbody>
</table>
4.5.2: Redistribution of sulfur during activated carbon synthesis

During phosphoric acid activation, up to 85% of the parent sulfur is released from the coal. As much as 97% of the sulfur in the parent material has been accounted for in the solid, liquid and gaseous products, Table 4.5.5. The closing of the sulfur balance ranges from 75-97%. Most of the parent sulfur is released to the gas phase as H₂S which is a great advantage, since it then can be recovered as elemental sulfur. The char typically has a sulfur content of 0.4% after activation to HTT in the range 450 to 650 °C, while that of the liquid products ranges from 0.05-0.25.

For KOH activation, there is no sulfur release to the gas phase. There is some sulfatic sulfur in the char, normally around 0.2-0.4%, and the liquids have very low sulfur contents (around 0.05%). To determine the fate of the original sulfur, the washwater used to leach the excess KOH from the samples after activation was first analysed for sulfatic sulfur, with negative results. The addition of HCl liberated H₂S, indicating the presence of soluble sulfides. In order quantify the sulfide content of the washwater, an oxidizing agent was then added to oxidize the sulfides to sulfates, following which, sulfate analysis confirmed that most of the parent sulfur had been transformed to water-soluble sulfides.

<table>
<thead>
<tr>
<th>Run</th>
<th>HTT (°C)</th>
<th>Parent</th>
<th>Char</th>
<th>Liquid</th>
<th>Gas</th>
<th>Washwater</th>
<th>Total</th>
<th>balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH activation,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-30</td>
<td>800</td>
<td>0.39</td>
<td>0.03</td>
<td>0.003</td>
<td>-</td>
<td>0.266</td>
<td>0.30</td>
<td>78</td>
</tr>
<tr>
<td>5-16</td>
<td>700</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.109</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H3PO4 activation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-19</td>
<td>500</td>
<td>0.78</td>
<td>0.1</td>
<td>0.03</td>
<td>0.42</td>
<td>-</td>
<td>0.55</td>
<td>71</td>
</tr>
<tr>
<td>2-21</td>
<td>500</td>
<td>0.75</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>-</td>
<td>0.70</td>
<td>96</td>
</tr>
<tr>
<td>3-10</td>
<td>500</td>
<td>0.75</td>
<td>0.21</td>
<td>0.03</td>
<td>0.38</td>
<td>-</td>
<td>0.63</td>
<td>84</td>
</tr>
<tr>
<td>Thermal treatment only</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-8</td>
<td>500</td>
<td>0.88</td>
<td>0.43</td>
<td>0.07</td>
<td>0.19</td>
<td>-</td>
<td>0.68</td>
<td>78</td>
</tr>
</tbody>
</table>
The fate of the sulfur during H$_3$PO$_4$ and KOH activation is summarized in Figure 4.5.4.

![Bar chart showing sulfur forms and treatment results](image)

**Figure 4.5.4:** Sulfur forms in carbons synthesized from IBC 106 clean coal by chemical activation with H$_3$PO$_4$ and KOH, HTT=550°C

### 4.5.3: Recycle of H$_3$PO$_4$

The as-synthesized activated carbons are leached with distilled water in order to remove and recover excess phosphoric acid. High recovery efficiencies are pivotal to process economics in large-scale processing. The phosphoric acid recovery in these small scale experiments is normally about 90-95% (Derbyshire and others, 1991b). One experiment was made in order to determine the feasibility of directly re-using the recovered acid. The acid recovered after activation at 550°C for three hours (run 3-32, Appendix 2) was analyzed for phosphorus content, after which the amount of coal used in the second experiment was adjusted to obtain the original phosphorus to coal ratio.

The surface areas of the two activated carbons from the first experiment and the experiment with recycled acid were 782 and 680 m$^2$g$^{-1}$, respectively. The fact that the surface area was slightly lower for the second run could be explained if some of the phosphorus were present in a non-reactive form. The dependence of surface area development on acid to coal ratio (see Task 3) is such that a small decrease in the effective ratio could easily account for the reduction in surface area. In this case, successful recycling of used acid would require the addition of supplementary fresh acid.

### 4.5.4: Characterization of carbons by standard test methods

Several measurements that are used industrially to characterize activated carbons (iodine number, methylene blue and phenol adsorption) were applied to assess the utility of the
carbons synthesized in this program. The experimental methods are given in Appendix 9 and the results are summarized in Appendix 8.

_**Iodine Number**_

The iodine number provides an indication of the adsorption capacity for small molecules. The iodine number determination was made for a suite of KOH activated carbons, possessing a wide range of BET surface areas, having been synthesized at HTT from 400°C-900°C.

The iodine number is usually found to be directly proportional to the BET surface area. As shown in Figure 4.5.5, there is almost a one to one correlation between the two measurements. A commercially produced activated carbon, G210, was analysed in order to verify the technique and provide a point of comparison. The published iodine number for G210 is 1275 m²g⁻¹, and the measured value was 1127 m²g⁻¹. Not surprisingly, the highly microporous KOH carbons give high values for the iodine number.

_**Methylene Blue Value**_

The methylene blue molecule is much larger than that of iodine, and its adsorption is restricted mainly to the mesopores. It is a useful indicator of the ability of the carbons to adsorb larger molecules, such as colour bodies from solution. Most of the carbons tested in this evaluation were produced by phosphoric acid activation at HTT, using a range of acid:coal ratios. These carbons, while somewhat more mesoporous than the KOH carbons, are still dominantly microporous and have low mesopore volumes.

A positive relationship is found between mesopore volume (cc/g) and the methylene blue value, Figure 4.5.6. However, relating to the above comments, the methylene blue values of the carbons were low, and a sample of KOH activated carbon was found to give a still lower value. It may be concluded that these carbons are not ideally suited for the adsorption of larger molecules.
Figure 4.5.5 Correlation of Iodine Number with BET surface area (carbons from IBC106 coal; KOH:coal=1.4)

Figure 4.5.6: Relationship of Methylene Blue Value to mesopore volume.
Phenol Adsorption

Phenol adsorption can be used as a method to assess a carbon's performance for adsorbing polar compound. Many of the KOH activated carbons from this study proved to have an ability to adsorb phenol to a similar extent as the Norit Row Supra carbon, which is a commercial water treatment carbon. The acid activated carbons, usually adsorbed only a third of the phenol of the KOH activated carbons, indicating that these reagents produce carbons with different surface chemistry.

Phenol, being a polar molecule, will be attracted to polar sites in the carbon. The major incidence of such sites will occur at surface oxygen functional groups. It is found that positive relationships exist, for the acid activated carbons from this study, when phenol loading is compared to atomic H/C and O/C ratios, and to the atomic ratio O/H. The increase in phenol adsorption with these ratios suggests that phenol may be preferentially adsorbed on carboxylic acid groups that have higher O/H ratios.

![Graph showing phenol load vs O/C and H/C ratios](image)

Figure 4.5.7: Phenol load has a positive relationship to both H/C and O/C ratios. (carbons from H₃PO₄ activation)
Figure 4.5.8 Phenol load vs O/H ratio indicating selective adsorption on possible acid sites.

5. SUMMARY

The results reported here, and in three previous quarterly reports, describe a study of the utility of Illinois coals as precursors for activated carbons produced by chemical activation. The focus of the program has been to synthesize activated carbons from IBC 106 coal, after first cleaning by column flotation to lower the mineral matter content. The production of high surface area carbons was realized by reaction with phosphoric acid and potassium hydroxide at temperatures up to 900°C. Detailed studies have been made to determine: the influence of reaction parameters on the composition and pore structure of the carbons; the accompanying chemical, structural, and morphological changes to the starting coal; the composition and potential utility of the gaseous and liquid by-products; and the performance of the carbons in relation to commercially available products. The principal findings are summarized below.

Phosphoric acid activation

Carbons with surface areas around 800 m²g⁻¹ (in the range of commercial interest), have been produced by phosphoric acid activation by heat treatment to temperatures of about 500°C. The carbons are dominantly microporous, with mesopores contributing only about 10% to the total surface area. At HTT above about 500°C, the specific surface area decreases; if considered on an ash-free basis, the surface area appears to reach a plateau.
Reasons advanced for this phenomenon are that, at high temperatures, the acid is converted to a form that is inactive for further porosity development. In the absence of a mechanism for stabilizing or enhancing the pore structure, dimensional contraction at high HTT will reduce the accessible porosity.

Extending the reaction time at high HTT has been found to appreciably increase the carbon micropore surface area. Increasing HTT is also found to increase the ash content of the carbon, commensurate with a reduction in carbon yield, and to reduce the organic sulfur and hydrogen contents.

The carbon properties are also found to be strongly dependent upon the ratio of reagent to precursor. Increasing the acid to coal ratio increases both the micropore and mesopore surface areas. A minimum ratio of about 1.0 (dry coal basis) is required to develop maximum surface area. Further increase in the proportion of acid lowers the micropore surface area, while the mesopore surface area remains unchanged. The reduction in microporosity at high ratios can be attributed to increases in ash content. When expressed on an ash-free basis, the micropore surface areas attained at ratios of 1.0 and higher, are more or less the same. Increasing the ratio also promotes the removal of hydrogen and organic sulfur.

Studies of low HTT (170-245°C) reaction with phosphoric acid have shown that there are small but consistent changes in certain properties with increasing reaction severity (increasing time or temperature): increasing reflectance; decrease in surface area (which is very low), and in macropore volume; reducing H/C atomic ratio. However, it is concluded that, while the reactions occurring at low HTT are important to determining the properties of the high HTT product, adjustment of the low HTT reaction parameters over the ranges studied offers little prospect for significantly modifying the carbon properties.

**KOH activation**

In contrast to H₃PO₄, the surface area of KOH carbons increases steadily with increasing HTT, attaining a value of about 1600 m²g⁻¹ at HTT=800-900°C. The KOH carbons are also highly microporous, with still lower mesopore surface areas than the phosphoric acid activated carbons: the maximum measured mesopore surface areas are 55 m²g⁻¹ for KOH and 114 m²g⁻¹ for H₃PO₄.

Heating rate is found to have an influence on porosity. Increasing the rate from 1 to 25°C/min to a final HTT of 600°C leads to a steady increase in BET surface area, and also appears to increase the carbon yield.

The effect of KOH: coal ratio is also important to surface area development. As with phosphoric acid, a sharp increase in surface area is obtained by increasing the ratio at low values (1.0-1.4). At higher ratios, there is a reduction in specific surface area. The observed data can be accounted for by the increased carbon ash content.

**General comments**

Activation with H₃PO₄ and KOH produces some similar changes. At low temperatures, the reagents cause partial dissolution of the coal structure. While this has not been the subject of detailed study in this research, the phenomenon appears to be relevant to the process of chemical activation and warrants further investigation.
Both reagents also promote the removal of sulfur and hydrogen. There is effectively complete removal of pyritic sulfur, even at the lowest HTT used, and both reagents are similarly effective for the removal of organic sulfur. However, the mode of sulfur removal is different. During phosphoric acid activation, most of the sulfur is released as H₂S. For KOH activation, most of the parent coal sulfur is transformed to water-soluble sulfides that are recovered during leaching. Dehydrogenation is more extensive than is attained thermally. In both cases, some hydrogen is released as H₂. Gas analyses have shown that much more hydrogen gas is evolved during KOH activation than with H₃PO₄ at the same HTT.

Gas and liquid by-products

The liquid and gaseous by-products of chemical activation have been analysed to assess their potential commercial value. The gases could provide a valuable source of H₂ for KOH activation, and S (from H₂S) for phosphoric acid activation.

Compared to the analysis of a #6 fuel oil, the liquids have comparable hydrogen content, and lower sulfur contents. The liquids also contain high proportions of phenolic oxygen and may be a viable source of these chemicals, as well as possibly finding direct use as a fuel.

Characterization of carbons

Standard test methods have been applied to assess the utility of the carbon products.

The iodine number provides an indication of the adsorption capacity for small molecules and is proportional to BET surface area. Consistent with the measured values, the highly microporous KOH carbons gave high values for the iodine number, while lower numbers were obtained for the phosphoric acid carbons.

The methylene blue value is a useful indicator of the ability of the carbons to adsorb larger molecules, such as color bodies from solution. Because this depends upon adsorption in mesopores, higher values were obtained for the H₃PO₄ carbons, although neither appears to be suitable for such applications.

Phenol adsorption can be used to assess a carbon's performance in adsorbing polar compounds. Many of the KOH activated carbons proved to have an ability to adsorb phenol to a similar extent as the Norit Row Supra carbon, which is a commercial water treatment carbon. The acid activated carbons, usually adsorbed only a third of the phenol of the KOH activated carbons. The difference in adsorption capacity indicates that the reagents introduce different surface chemistries. Further study is recommended, as this may lead to new routes to alter adsorption selectivity.
6. REFERENCES


