

## PRODUCTION OF ACTIVATED CARBONS FROM A VITRAIN CONCENTRATE FROM THE STOCKTON COAL.

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**Keywords:** Activated carbon, chemical activation, phosphoric acid

### Introduction

Earlier, related studies have shown that porous carbons can be produced by phosphoric acid activation of coals and hardwood [1-4]. One of the findings was that the development of surface area appears to be rank-dependant. It is also supposed that maceral composition will affect the response to phosphoric acid activation, although there is no available information on this subject.

In this context, a study has been initiated of the phosphoric acid activation of coal macerals. The objectives are to examine the effects of maceral composition and rank on porosity development, and to understand the individual and collective contributions of maceral groups to the activation of coals by phosphoric acid.

In this study, a vitrinite concentrate from an hvA bituminous coal (Stockton) was used as starting material for the production of activated carbons by  $H_3PO_4$  activation. The chemical, morphological, and surface area changes were followed as a function of reaction temperatures and are compared to the results of previous studies.

### Experimental

#### Maceral Separation

Bench samples of Stockton coal (hvA bituminous) were collected from fresh highwall exposures in the field in eastern Kentucky. Samples were chosen for their high vitrain content. In the laboratory, vitrain-rich benches were chosen to facilitate hand picking of vitrains. The samples were coarsely ground in a mortar and pestle to about 4 mesh and then split into approximately 10g samples for later experiments.

Petrographic pellets were made from a representative split of the vitrain concentrate to ascertain maceral content and purity. Standard preparation and polishing techniques were used. The Stockton sample was found to have a mineral matter-free vitrinite content of 93.5%. Table 1 shows maceral composition for this sample as determined by point-count analysis.

#### Carbon Synthesis

Activated carbons were produced according to procedures described in earlier carbon studies [1-4]. A split of the vitrinite concentrate was placed in a quartz crucible with a known volume and concentration of phosphoric acid to give an acid/dry coal ratio of approximately 0.96. The quartz boat was placed in a stainless steel oven tube, which was then flushed with nitrogen gas. It was then reacted at a low temperature (170°C) for 0.5h after which it was heated to a final heat treatment-temperature (HTT) ranging from 350°C to 550°C, and allowed to react for 1h at temperature. After the sample had cooled to room temperature it was leached with hot distilled water until the pH of the leachate was at or near neutral. Leached samples were then dried in a convection oven at about 100°C for 1.5 to 2h. Prior to nitrogen BET analysis, these samples were further dried in a vacuum oven at 110°C to insure complete outgassing. For comparison thermal counterparts were also run. These splits were treated as already described except that no acid was added prior to heat treatment.

#### Characterization

Proximate and ultimate analyses were performed following standard procedures. Fourier-transform infrared spectroscopy (FTIR) data were collected on a Nicolet 20SX spectrometer at  $4\text{ cm}^{-1}$  resolution using pressed KBr pellets which contained approximately 0.5wt % sample. Spectra were normalized to a 1/200 concentration of sample/KBr to allow direct comparison between spectra.

Epoxy impregnated pellets of each activated carbon were prepared for petrographic and vitrinite reflectance analysis. Optical characterization was performed on a Zeiss microscope equipped with a 40x oil immersion lens. Modal maximum vitrinite reflectance ( $\%R_{\text{max}}$ ) measurements were collected from 25 samples/pellet. Measurements were taken at 546nm wavelength and standardized against a set of glass standards. Photographs were taken of several of the fields of view using the same microscope equipped with a 40x Antiflex lens. In several instances, the polars were crossed to determine the extent of anisotropy in the carbons.

Surface area measurements were obtained from nitrogen adsorption isotherms at 77K using a Quantachrome Autosorb 6. Macro and meso-pore volumes and surface areas were measured using a Quantachrome Autoscan-60 mercury porosimeter.

## Results and Discussion

### Optical Characteristics

The maximum vitrinite reflectance of the vitrinite-rich samples heat treated in the presence and absence of acid increases with increasing HTT (Fig. 1). As found in earlier studies, up to HTT of 450°C the acid-treated carbons exhibit higher vitrinite reflectances than their thermal analogs, while above 450°C this relationship is reversed. Vitrinite rich samples follow the same trends that were observed for whole coals [1-4].

In most of the carbons, it was noted that the desmocollinite reflectance was slightly lower than that of telocollinite, throughout the range of activation temperatures.

Reflectance data reported here were measured on telocollinite. The apparent difference in reflectance between the two submacerals lessened with increasing HTT. At HTTs above 350°C it became more difficult to differentiate between desmocollinite and telocollinite, and this, as well as misidentification of semifusinite, may account for the spread in vitrinite reflectance values that were found in taking measurements. Resinite occurs in the desmocollinite of the vitrinite-rich samples up to HTTs of 350°C, after which it was no longer evident, having been either transformed or removed.

Some degree of anisotropy was observed in the vitrinites at higher HTTs, changes in reflectance of up to 0.1% were noted upon rotation of the stage. This anisotropy was clearly visible when the antilex lens was used. The anisotropy did not develop to a great extent even at 450°C or 550°C, rather it occurred around vacuoles in the vitrinites.

These vacuoles (approximately 50 µm in diameter) were formed in both the thermal and acid-treated samples and become far more prevalent with increasing HTT. In the acid-treated samples at HTT of 350°C, some of the larger pieces of vitrinite showed evidence of a reaction front, usually associated with some of the vacuoles as well as with cracked edges. There was a visible difference in reflectance of the vitrinite by as much as 0.3% across these aureoles, with the higher reflectances being in the outer region. Examination of these aureoles with the antilex objective suggested that they were reaction fronts rather than anisotropic zones. At the maximum HTT (550°C) the acid treated samples appeared much more macerated and friable, exhibiting many small pits between the larger vacuoles.

### Chemical composition

Both the acid-treated and thermal suites of samples show a loss of hydrogen with increased HTT (Fig. 2); however, the loss of hydrogen with HTT is more extensive upon reaction with H<sub>3</sub>PO<sub>4</sub>. This result supports the FTIR observation that the acid treated samples lost aliphatic hydrogen more quickly than the thermal samples as found in previous studies with whole coals [1-4]. A negative relationship is found to exist between %R<sub>max</sub> and H/C ratio. As the samples in both suites lose hydrogen there is a corresponding increase in %R<sub>max</sub> (Fig. 1).

FTIR analyses show good correspondence with the elemental data with respect to loss of hydrogen. As can be seen in Figure 3, the overall trend of decreasing aliphatic content with increased HTT can be seen by the disappearance of peaks in the 2900 cm<sup>-1</sup> wavenumber range. The existence of various inorganic phases present in these samples obscures many of the peaks in the lower wavenumber range.

In the acid-treated samples there is a very strong peak around 1200cm<sup>-1</sup> that in previous studies has been assigned to phosphate esters [3-4]. In these samples it appears that there is significant overlap in this region with inorganics that appear in the thermal control samples as a peak only slightly shifted up from the 1200 cm<sup>-1</sup> peak.

The carbonyl peak at 1700cm<sup>-1</sup> decreases in intensity and shifts to lower wavenumbers with increasing HTT in both the thermal and acid-treated samples. It disappears completely above 350°C. This shift is greater in the thermal blanks, between the parent and 350°C, than in the acid-treated samples. This may indicate that the carbonyl functions in the acid-treated samples are more strongly bound, perhaps by resonance with nearby double bonds.

Aliphatic peaks at about 2900cm<sup>-1</sup> decrease in both of the sample suites and are virtually eliminated above 350°C. These peaks decrease more quickly for the acid-treated samples than for the thermal samples, and the aromatic C-H peak at 3000cm<sup>-1</sup> appears more well developed in the acid runs. This latter effect may be more a function of greater intensity of the -OH broad peak which may be overlapping this peak in the thermal runs.

### Surface Area Measurements

Table 2 shows that the thermally treated vitrinite samples develop virtually no porosity or surface area. Upon acid treatment, porosity starts to develop after 350°C, with most of the porosity residing in the microporous range.

The data on the development of surface areas of acid treated samples with HTT are shown in figure (4) which also shows results obtained by Jagtoyen et al. [6] for different starting materials. In each case there is a maximum in the surface area with HTT which decreases with rank and shifts to higher temperatures.

The extent of surface area development decreases in the order: hardwood > subbituminous coal > hvC bituminous coal > hvA vitrain, which tends to confirm the supposition that the extent of metamorphism reduces the response to phosphoric acid activation [6].

### Conclusions

A study has been made of the chemical activation of a vitrain concentrate, hand-picked from the Stockton hvA bituminous coal. Reactions were conducted at HTT from 350°C to 550°C. Thermal blanks were generated under similar conditions for comparison.

Changes in chemical composition were followed by elemental analysis and FTIR. With increasing HTT, acid-treatment promotes more extensive loss of hydrogen. The infrared spectra show the early loss of aliphatic groups and increasing aromaticity for samples reacted with H<sub>3</sub>PO<sub>4</sub>. Shifting behaviour of the carbonyl peak at 1700cm<sup>-1</sup> in the spectra suggests greater resonance stabilization of carbonyl functions in the acid-treated samples than in the thermal control samples.

Corresponding to these chemical changes, there is an increasing maximum vitrinite reflectance with HTT: this is higher for acid-treated than thermal carbons up to about 450°C, above which temperature the reverse is the case. These changes are in keeping with the findings of earlier studies.

Surface area development with HTT is less than found for lower rank materials, which is also in keeping with the suggestion that metamorphic changes reduce the response to H<sub>3</sub>PO<sub>4</sub> activation. Hence, at this stage of the research, it is not yet possible to distinguish maceral from rank effects on pore structure development.

### Acknowledgments

This study was made possible with the assistance of the DOE EPSCoR traineeship. Thanks go to the University of Kentucky Department of Geological Sciences and the University of Kentucky Center for Applied Energy Research for significant contributions of funds and access to equipment.

### References

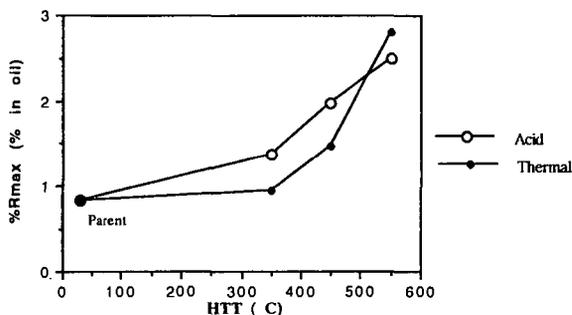
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**Table 1.** Maceral composition of hand-picked Stockton bench 2.

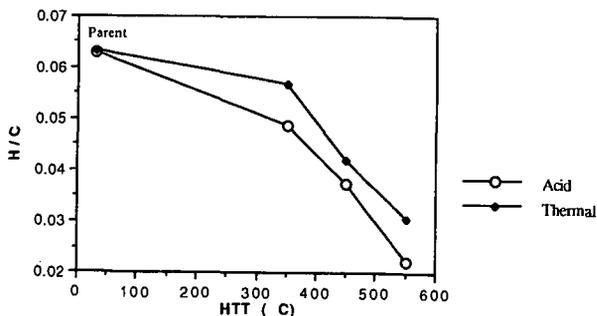
Maceral	% Composition (mineral matter free)
Telocollinite	70.5
Desmocollinite	23.0
Pyrofusinite	2.5
Semifusinite	2.0
Exinite	2.0

**Table 2.** Composition and porosity of samples in this study.

HTT/Treatment	%Rmax	Atomic H/C	BET S.A. (m <sup>2</sup> /g)
Parent	0.8	0.06	000
350°C/Acid	1.4	0.05	000
350°C/Thermal	1.0	0.06	000
450°C/Acid	2.0	0.04	110
450°C/Thermal	1.5	0.04	000
550°C/Acid	2.5	0.02	361
550°C/Thermal	2.8	0.03	000



**Figure 1:** Relationship between reflectance and HTT for carbons produced from Stockton vitrinite-concentrate



**Figure 2:** Relationship between H/C and HTT for Stockton vitrinite-concentrate

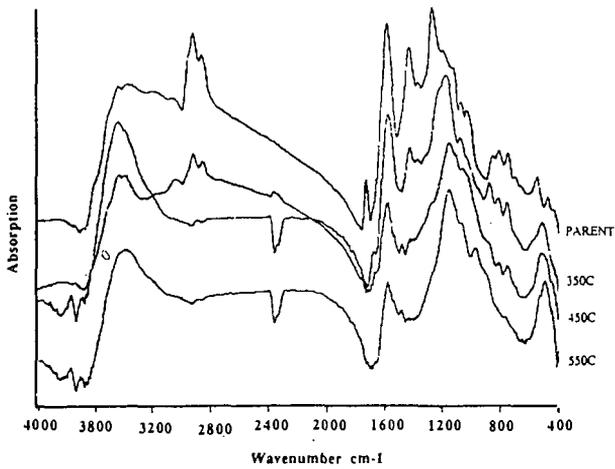


Figure 3: FTIR spectra for acid treated carbons (top) and thermal counterparts (bottom) from vitrain concentrates.

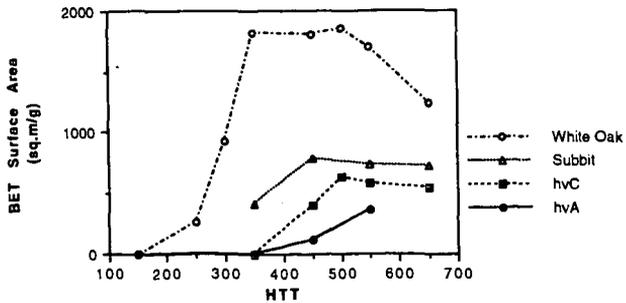


Figure 4: Surface area related to parent material [modified after ref. 6]