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**CHEMICALLY MODIFIED COAL MACERALS.**

**SEPARATION, DENSITY AND SURFACE AREA VARIATIONS\***

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# Chemically Modified Coal Macerals. Separation, Density and Surface Area Variations

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## ABSTRACT

Two Argonne Premium Coals were O-alkylated and O-acylated using a variety of different reagents, and then separated using density gradient centrifugation (ADGC). The separation data suggested that the hydroxyl groups are fairly evenly distributed in the maceral particles. However, several reagents produced results counter to this generalization, and exhibited enhanced maceral separation. Comparison of ADGC densities and He densities of the modified coals showed several reactivity "families" that appear to be based on wettability differences. Surface areas were also measured; areas as high as 200 m<sup>2</sup>/g were obtained for some modified coals. The data suggest that there is an optimum molecular size for the added group that leads to the large areas.

**Keywords:** maceral, chemical modification, surface area.

## INTRODUCTION

We know that the chemistry of even a single maceral type, such as vitrinite, varies as a function of density.<sup>1</sup> However, there is little understanding of how this gross analysis translates to differences in chemical structure and functional group variation. In the approach considered here, two coals were chemically modified and then separated, looking for changes in the density distributions as a measure of the heterogeneity of the functional groups. Choi et al. started this approach with O-methylation and O-butylation of coal hydroxyl groups, and found in one case that a narrow inertinite density fraction was changed into a new density distribution with three new bands.<sup>2</sup> The present work extends this approach using well known O-alkylation and O-acylation reactions with a wide variety of alkyl and acyl groups.

## EXPERIMENTAL

The starting coals were fluid energy mill ground (average particle size 1-2 microns), chemically demineralized<sup>3</sup>, and exhaustively extracted with pyridine. The alkylation

reactions were done following a procedure similar to that reported by Liotta.<sup>4</sup> Acetylations were performed according to standard practices.<sup>5a,b</sup> Density gradient separations were performed according to standard practices.<sup>3</sup> Helium density measurements were done using a model MPY-2 micropycnometer (Quantachrome Corp.). Surface area measurements were carried out on using an Autosorb-6 model AS-6 (Quantachrome Corp.).

## RESULTS AND DISCUSSIONS

Two bituminous coals from the Argonne Premium Coal Sample Program were chosen for this study: Pittsburgh #8 (APCS 4), and Upper Freeport (APCS 1).<sup>6</sup> Both contain high amounts of vitrinite (>82%).

From density distribution information, and a knowledge of the hydroxyl content of each maceral density fraction, the general trends in density can be calculated for different groups added to the coal.<sup>1,6-8</sup> With hydrocarbon groups, the density distribution bands are expected to shift to lower density and become narrower. With heteroatom or aromatic groups, there will be a shift to higher density with some broadening. To experimentally reflect the expected density shift, the density distribution is integrated. To reflect the width of the density distribution data, the distribution is normalized to the maximum point, and the curve integrated to obtain the peak area.

**Table 1. Reagents Used in Modification of Coals**

<i>Alkylations:</i>	<i>Acylation (Pyridine Catalyst)</i>
1-iodobutane	acetic anhydride
1-iodohexane	trimethylacetic anhyd.
1-iodooctane	trichloroacetic anhyd.
benzyl bromide	pentafluoropropionic anhyd.
a-bromometylnaphthalene	heptafluorobutyric anhyd.
bromomethylpyrene	n-butyric anhyd.
2-bromobenzyl bromide	
perfluoro-n-butyl iodide	
carbon tetraiodide	

Table 1 is a compilation of the groups used. Most of these reagents show narrower peaks (smaller peak areas) than the starting coal. Moreover, even though narrowed, the new density distributions retain much of the character of the original density distribution. This suggests that the hydroxyl content may follow the total oxygen content of the macerals with a high degree of fidelity. However, there were some exceptions. Adding  $-Cl_3$ ,

$-CF_2(CF_2)_2CF_3$ , and  $-OCCF_2CF_3$  groups to APCS 4 coal produced high peak areas, and even evidence of new peaks. Each coal has its own reaction character; for the APCS 1 coal only the  $-Cl_3$  and  $-CF_2CF_2CF_2CF_3$  groups showed an increase in band

area. This contrasting reaction behavior for different added groups suggests two things. First, the hydroxyls appear to be homogeneously distributed in both coal vitrinites, and for those groups that produce broader distributions, the chemical reaction is likely limited by other factors.

To provide additional information on what drives the ADGC density changes, Figure 1 is a plot of the ADGC and He derived specific volumes for the coals. The simplest analysis is to assume that the He

specific volumes are a good measure of the "true" specific volume of the coal, and the ADGC specific volumes are the sum of the He volumes and an invariant excluded volume. The latter volume is that portion of the void space that is not filled by the aqueous CsCl/surfactant solution.

With this simple interpretation, we expect that the data will fall on a straight line with a slope of one and an intercept which represents the excluded volume. Although the data in Figure 1 appears linear, the slopes are not unity, ranging from 0.6 - 0.7. The low slopes imply that the low specific volume points (halogen containing reagents) have too high a specific volume. This suggests that less solution is entering the void spaces than expected. Fluoropolymers, for instance, have some of the highest water contact angles. Thus, they would be expected to decrease the wettability of the internal and external coal surface. However, this interpretation does not fit all cases. The data for  $-Cl_3$  is not clear at all; nor is it clear why the introduction of hexyl or octyl groups does not appear to have an adverse effect on the data in the high specific volume region. We suspect that part of the problem is that each homologous series of reagents, e.g. the perfluoro's, the aliphatics, and the aromatics, have separate curves.

Surface areas were also measured for the modified coals; the data is shown in Figure 2. Both coals exhibit a maximum in surface area with groups having molecular

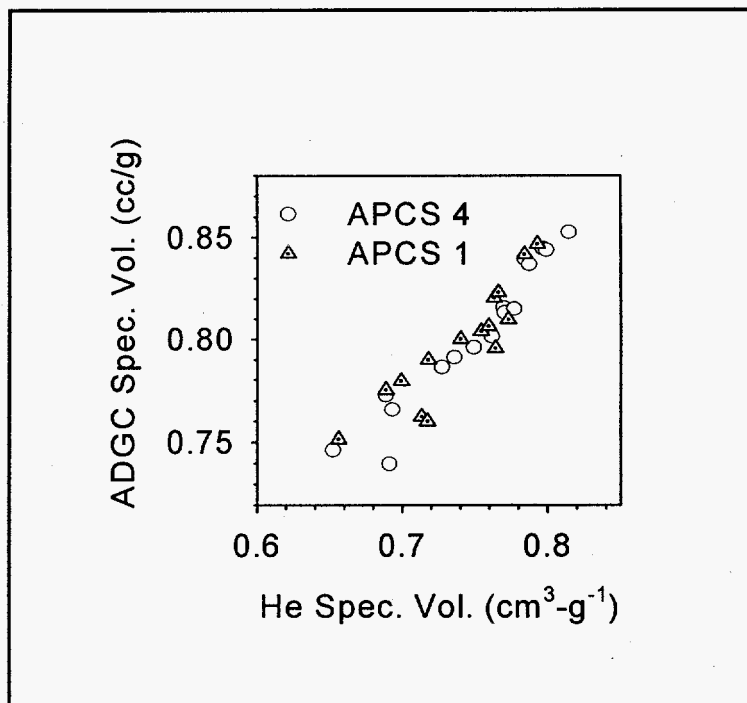
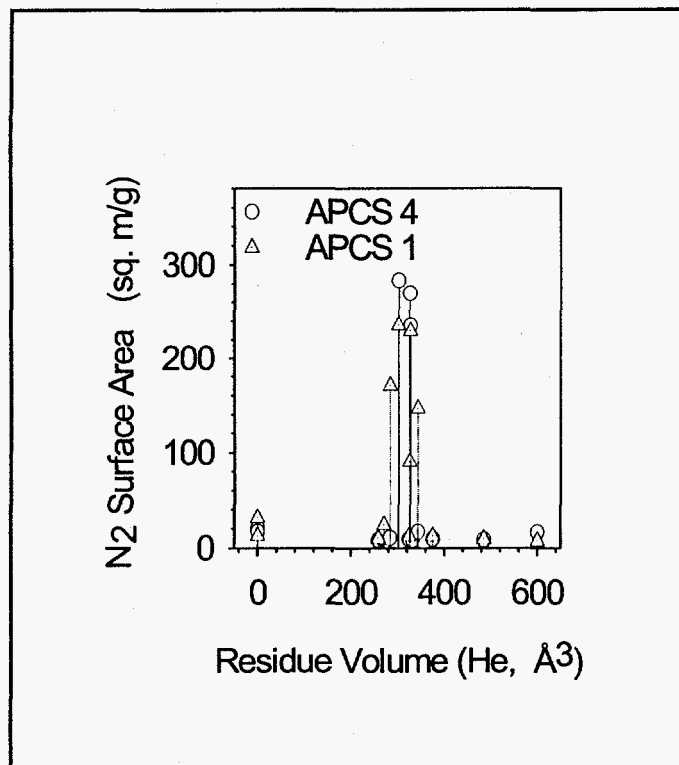


Figure 1. Comparison of ADGC derived densities and He densities for APCS 4 and APCS 1.



**Figure 2.** Correlation of surface area and molecular volume of added groups.

volumes in the range of 300-350 Å<sup>3</sup> (-Cl<sub>3</sub>, -OCC(CH<sub>3</sub>)<sub>3</sub>, -OCCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>) of coals. The reason for this behavior is not clear at this time.

## CONCLUSIONS

The hydroxyl groups in coal appear to be fairly homogeneously distributed in individual maceral particles. In several cases where there seemed to be enhanced separation, the density variation appears to be due to wetting phenomena, and other physical changes to the coal structure.

## ACKNOWLEDGMENT

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