

Chemical and wettability studies on coal, humic acid and cyclized humic acid

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Investigation of properties such as wettability of coal is often complicated by variations in the surface chemistry of coal samples during their preparation, storing and pretreatments. It is the aim of this study to prepare hydrophobic and hydrophilic derivatives of a single parent coal by chemical methods selected for rupturing and closing cyclic rings in order to understand the mechanisms of hydrophobicity of the coal surface.

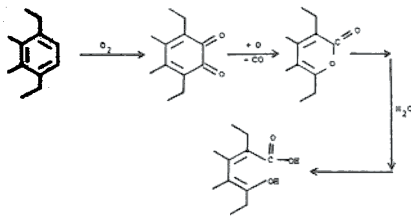
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Various theories have been put forward in the past to explain floatability of coal¹⁻³. These theories are based essentially on the bulk carbon and hydrogen content of the coal and were generated mostly using empirical curve fitting techniques. They do not account for the wide variations in the flotabilities

even in coals from the same seam. This is not surprising, since floatability should depend on the functional groups present on the surface rather than the bulk composition or rank.

Flotation recovery and contact angle of coals have been shown to decrease upon weathering and oxidation^{4,5}. Oxidation of coal, even under mild

conditions yields alkali soluble products called humic acids⁶⁻⁹ and is considered to involve chemisorption in the initial stages^{6,7,9}. The mechanism of oxidation initially involves cleavage of aliphatic chains and has been correlated to loss of Gieseler fluidity¹⁰. In the presence of inherent moisture oxidation has been suggested to proceed as follows⁷.



The humic acids extracted at various stages in the progress of oxidation were similar as regards elementary composition, functional group analyses and i.r. spectra⁶. The composition of alkali insoluble residue approached that of humic acids⁶. Humic acid studies have established a structure resembling the end product of oxidation shown above^{7,8}. This suggests that the mechanism of oxidation initially involves cleavage of aliphatic chains and subsequent rupture of aromatic rings giving rise to products resembling humic acids.

The maturation of humic substances to higher rank coals have been suggested to proceed with loss of polar groups, possibly by a condensation polymerization reaction⁷. There is however, no data at present to support this hypothesis except that of van Krevelan¹¹. Based on the above it was thought that chemical treatment of open ring structured humic acid to remove polar groups, possibly by cyclization, should yield a product of higher hydrophobicity, similar to that obtained during natural coalification. It has been a major aim of this study to test the above hypothesis.

EXPERIMENTAL

Synthesis

Humic acid was prepared by nitric acid oxidation of a coal sample (see Table 1) followed by extraction with an acetone water mixture¹² and freeze drying. The Sherman modified Clemmensen reduction and Friedel Crafts acylation¹³⁻¹⁶ reactions were carried out on humic acid to prepare cyclized humic acid. The experimental procedure is shown schematically in Figures 1 and 2.

Characterization

Hydrophobicity. The hydrophobicity of humic acid particles and cyclized

Table 1 Analysis of coal sample used (high volatile bituminous)

Constituents	Amount (%)
Total carbon	64.6
H ₂ O	1.2
Ash	16.8
Volatile matter	34.2
Fixed carbon	47.2
Silicon in ash	27.1

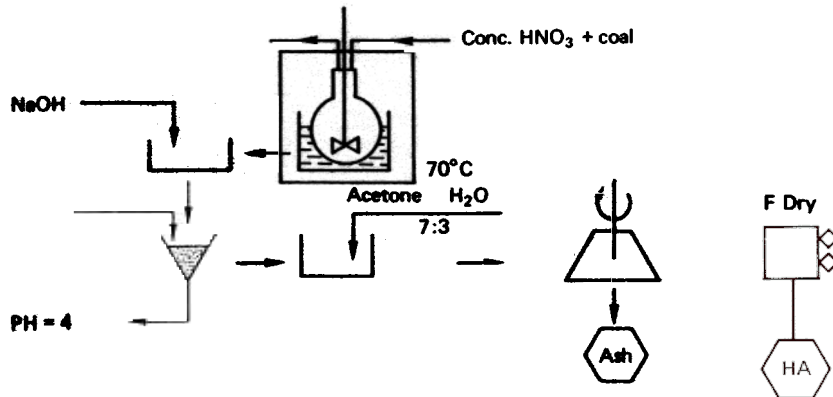


Figure 1 Conversion of coal to humic acid

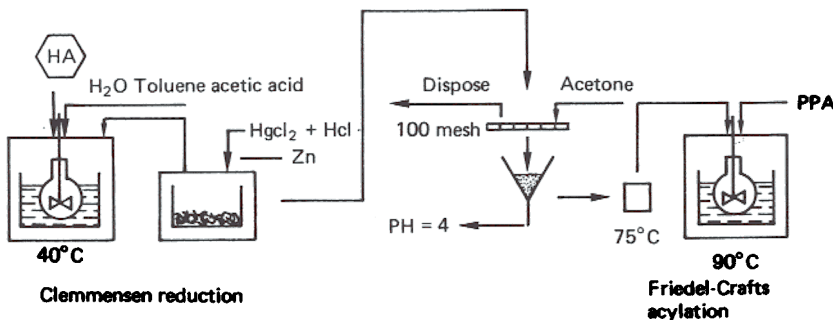


Figure 2 Cyclization of humic acid

humic acid particles was determined using techniques involving particle pick up by single bubbles¹⁷ and by moving air/water interface and by flotation.

Bubble pick up. Single bubbles were generated in water contained in a cell with a syringe. Each bubble was allowed to contact a bed of particles held in a spout under the water in the cell and lifted and moved to detach the particles into the bottom of the cell. Particles were collected from 100 bubbles and then weighed after drying.

Moving air/water interface. The experiment is shown schematically along with the apparatus used in Figure 3. The water/air interface in the fritted funnel was brought below the bed of particles by lowering the separatory funnel. The water level was then allowed to rise slowly and the overflow was collected in a basin surrounding the funnel and transferred to a beaker. Floating particles were removed by decanting and the weight of the particles settled at the bottom of the beaker was recorded.

Flotation. Flotation was conducted in a modified Buchner funnel with provision for introducing nitrogen through the frit, using starvation quantity (1 drop) of amyl alcohol as frother. The nitrogen was passed at a low rate of about 60 bubbles min⁻¹ to minimize turbulence and elutriation of particles.

Acidity. Apparent acidity of humic acid and cyclized humic acid was determined

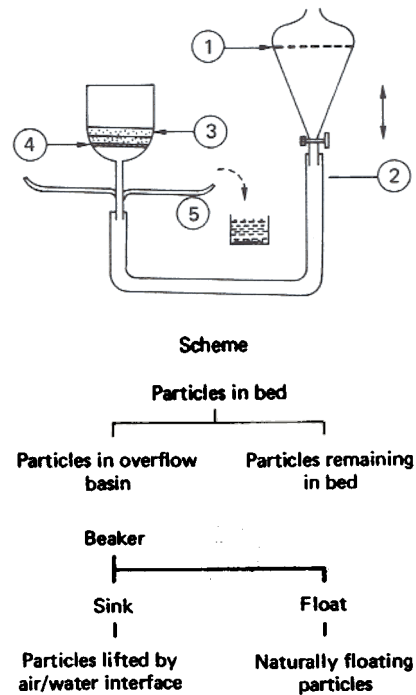


Figure 3 Apparatus for determining hydrophobicity by moving water/air interface. Modified bubble pick up equipment: 1, separatory funnel; 2, rubber tube; 3, particle bed; 4, frit; 5, overflow basin

using barium exchange method as described in Ref. 18.

Spectroscopy. FT-i.r. spectra of humic acid and cyclized humic acid were obtained by standard KBr pellet technique.

RESULTS AND DISCUSSION

Results obtained for the hydrophobicity of the particles as measured by the above methods are given in Table 2. The apparent acidities of the humic acid and cyclized humic acid are given in Table 3. The infrared spectral results are summarized in Table 4.

Sherman modification of Clemmensen reduction and Friedel Crafts acylation are non substitution reactions. The former results in the reduction of double bonds and the latter in cyclodehydration^{13,19}. These reactions when carried out on beta benzoylpropionic acid, which has a structure similar to humic acids, yield tetralin which has a closed ring structure²⁰. These reactions are therefore expected to produce cyclization of humic acids. The decrease in acidity of cyclized humic acid indicated that it has fewer polar groups than humic acid. Polyphosphoric acid used in Friedel Crafts acylation is a cyclodehydrating agent, and is possibly responsible for the reduction in the polar groups and hence acidity.

Table 4 indicates the infrared peak assignments and the relative peak shifts of humic acid and cyclized humic acid. The shifts are relative to the normal carbonyl peak at 1710 cm^{-1} ,²¹ which is the maximum in both cases. In the present study the band at 1530 cm^{-1} is assigned to the carboxylate anion shifted from its characteristic peak at 1563 cm^{-1} due to M^{2+} . The band at 1600 cm^{-1} is assigned to $C=C$ ^{22,23}. The methyl band is normally observed at around 1356 cm^{-1} .²⁴ The peak at 1325 cm^{-1} in the present study is attributed to methyl group. The relative increase in the $C=C$ band, the decrease in the COO^- band and the aliphatic methyl band are all indicative of the ring closure reaction which was expected.

The results of the bubble pick up, moving air/water interface and flotation tests all show that cyclized humic acid is more reactive to air than humic acid. Cyclized humic acid was also observed to undergo spherical agglomeration in oil water medium, whereas humic acid was found to go into colloidal state in water under ambient conditions. This further shows that cyclized humic acid is relatively hydrophobic and humic acid is relatively hydrophilic.

The above results thus show that oxidation of coal causes humic acid to be formed on coal surfaces with polar groups. Cyclization treatment of humic acid reduces its hydrophilicity by

Table 2 Particle pick-up by 100 single bubbles and moving water/air interface and bubble swarms (flotation)

Sample	Pick-up by 100 bubbles (g)	Pick-up by moving water/air interface (%)	Flotation (%)
Humic acid	0.00034	0.4	2
Cyclized humic acid	0.00470	2.26	20

removal of polar groups by reduction of double bonds and cyclodehydration.

CONCLUSION

The surface of coal essentially consists of polar groups formed by the rupture of cyclic rings during oxidation. The extent of polar groups on the surface is responsible for the observed decrease in hydrophobicity on oxidation. The hydrophobicity depends on the relative amounts of open and closed ring structures on the surface of coal.

Since increased hydrophobicity is obtained by cyclodehydration, it is possible that maturation of low rank coals to higher rank coals is a condensation reaction as suggested by van Krevelen. The exception of anthracite could be due to reactions other than cyclization during its formation.

ACKNOWLEDGEMENT

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REFERENCES

- 1 Taggart, A. F., DelGiudice, G. R. M., Sadler, A. M. and Hassialis, M. *Trans. AIME* 1939, 134, 180
- 2 Wilkin, F. T. Conference on pulverized fuel, Hansgate, England, 1974, pp. 398
- 3 Sun, S. C. *Trans. AIME* 1954, 199, 67
- 4 Roberts, C., *MS Thesis*, 'The effects of various oxidising methods on the flotation of coal', Henry Krumb School of Mines, Columbia University, New York, 1982
- 5 Horsley, R. M. and Smith, H. G. *Fuel* 1951, 33, 54
- 6 Conrow, R. B., Durie, R. A., Shanon, J. S. and Sternhell, S. *Fuel* 1963, 42, 275

Table 3 Results for acidity tests

Sample	Apparent acidity m eq acid groups g^{-1}
Coal	0.04
Humic acid	0.42
Cyclized humic acid	0.31

- 7 van Krevelen, D. W. and Schuyer, J. in 'Coal Science', Elsevier, 1957
- 8 Bhowmik, J. N., Mukerjee, P. N. and Lahiri, A. *Fuel* 1959, 38, 211
- 9 Smith, J. W. and Mapstone, G. E. *Fuel* 1957, 36, 191
- 10 Carol, A. R., Senville, J. T., Coleman, M. M., Davis, A. P. C. *Fuel* 1983, 12, 1387
- 11 Meyers, R. A. (Ed.) in 'Coal Structure', Academic Press, 1982
- 12 Bailey, A. E. W., Kimberly, I. E., Turner, L. and Ward, S. G. *Fuel* 1955, 34, 209
- 13 Adams, R. (Ed.) in 'Organic Synthesis', Vol. I, John Wiley and Sons, 1928, 162
- 14 Snyder, H. R. and Werber, F. X. in 'Organic Syntheses', Coll. Vol. 3, (Ed. E. C. Hering, John Wiley and Sons, 1967
- 15 Theitheimer, W. in 'Synthetic Methods of Organic Chemistry', Interscience Publishers, 1951 Vol. 5, 51
- 16 Adams, R. (Ed.) in 'Organic Reactions', Vol. II, John Wiley and Sons, 1947, 130
- 17 Somasundaran, P., Chandar, P. and Chari, K. C. *Colloids and Surfaces* 1983, 8, 121
- 18 Schafer, H. N. S. *Fuel* 1970, 49, 197
- 19 Mazumdar, B. K. and Ganguly, S. *Fuel* 1962, 41, 305
- 20 Morrison, R. T. and Boyd, R. N. in 'Organic Chemistry', 3rd edition, Allyn and Bacon, 1974, 1058
- 21 Painter, P. C., Snyder, R. W., Pearson, D. E. and Kwong, J. *Fuel* 1980, 59, 282
- 22 Painter, P. C. and Coleman, M. M. *Fuel* 1979, 58, 301
- 23 Handy, C. I. and Stock, L. M. *Fuel* 1982, 61, 700
- 24 Rao, H. S. and Gupta, P. L. *Fuel* 1962, 41, 417

Table 4 Infrared peak assignments and peak shifts of humic acid and cyclized humic acid products

Group	Wave number	Humic acid	Cyclized humic acid
$C=C$	1600		
COO^-	1530		
$C-H$, aliphatic methyl	1325		

