

COAL IN A MODERN WORLD

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INTRODUCTION

This Henry H. Storch Award review summarizes the research programme of the author during his professional career in the subject area of coal and carbon science. Marsh is a native of North East England well known for its coal-fields and for the massive transportation of coal into Newcastle upon Tyne for shipment to the open-fires of the City of London. Marsh as a schoolboy grew up within a quarter mile of one of the largest collieries in Co. Durham. The noise and dirt of coal mining became part of his life. On leaving school and entering University he had no intention at all of continuing this association with coal. But the British Association for the Advancement of Science held its annual meeting at the University and organized works visits. Marsh, as an undergraduate, was asked to lead one of these visits, yes to a coal mine, and so he became the "expert" of the graduate year in matters of coal. After graduating, Professor H. L. Riley was asked to undertake a study of dangerous swelling coals so modified by an igneous dyke. Marsh was offered the research contract, he accepted, and so inevitably commenced a career in coal.

IGNEOUS DYKE INTRUSIONS

This study of a Durham coal formed the basis of the PhD Thesis (1948) but was not published until 1971 (1). The Hutton seam (32.7 wt.% volatile (daf) and 86.3 wt.% C (daf)) had been penetrated by a whinstone dyke, 30 m thick and coals had been modified to about 65 m away from the dyke interface. Simulations by very slow carbonizations gave indications of maximum temperatures of <500 °C reached by coal during this thermal metamorphosis. The dangerous swelling properties in coke ovens appear to be associated with a mild softening of the coal involving breakage of the hydrogen-bonding with some release of small molecules, followed by cooling with the re-establishment of a higher branch-point density, this maintaining a high coal viscosity and creating swelling dangers.

MICROPOROSITY

Following some years of research into microporosity of carbon, attention was directed to coal materials which were obviously much more difficult to characterize. Microporosity in coals exhibits three aspects of study (a) effective surface area (b) pore shape and size distributions and (c) variations in surface functionality. Coal is not of course a rigid structure. In an initial paper Marsh (2) reviewed the methods of surface chemistry then available, of heats of wetting, neon adsorption and adsorption of nitrogen and carbon dioxide. The use of nitrogen at 77 K is unsatisfactory because of slow activated diffusion effects, isotherms of this gas not describing thermodynamic equilibria. Heats of wetting by methanol had to be adjusted because of different polarities of coal surfaces. The need was to obtain isotherms of molecules such as carbon dioxide at temperatures above 273 K. If adsorbate pressures were < .01 MPa then the maximum p/p₀ values were only of the order of 0.02 and clearly Langmuir or BET equations could not be applied.

Two events changed the course of this research. First the Russian literature describing the use of the Dubinin-Polanyi (D-P) and later the Dubinin-Radushkevich (D-R) equations was filtering into the laboratories of Western Europe. Second, Dr. Teresa Siemieniewska of Poland came to the NCRL for a period of study financed by the British Council. Together we were able to interpret adsorption isotherms, 0 to 0.02 p/p⁰, of carbon dioxide, 273 K and 293 K and compare with isotherms at 195 K (3). It was concluded that this method of adsorption of carbon dioxide gave surface area values agreeing with accepted values for low rank coals but which with increasing rank became progressively greater, rising to 300 m²g⁻¹ for the high rank anthracites. Here the replacement of hydrogen-bonding in the bituminous coking coals by carbon-carbon covalent bonding had reduced the sizes of the microporosity into the range of ultramicroporosity which is accessible to small molecules only at 273 K and above. Marsh and O'Hair (4) took the subject somewhat further by adsorbing nitrous oxide and carbon dioxide on coals and comparable microporous carbons. The D-R plots of log n_a (n_a = amount adsorbed in mmol g⁻¹) against log² (p/p⁰) are sensitive to non-equilibrated sections of the isotherm, usually at the low relative pressure end. The point was made of the futility of attempting to accommodate such isotherms mathematically to provide "correct" surface area data. Working now with French colleagues (5), studies were extended to cokes from coals where the gradients of the D-R plots were related to an average pore size.

Even to those working in the subject area, the reasons for the general acceptability of the D-R equation were not always apparent. Using carbonized anthracite as a material from which to obtain isotherm data, Marsh and Siemieniewska (6) attempted to explain the applicability of this equation. The linearity of the D-R equation is the direct result of the frequency distribution of free energies of adsorption obeying, e.g. a Rayleigh or Gaussian form of distribution. It is difficult to know from the Russian literature if this was their starting point in the development of the D-R theory. With the arrival of new students, Freeman, Rand and Campbell (7-12), the interpretations and uses of the D-R approach were explored. In more recent times, the pragmatic use of the D-R equations has been set out (13,14) in a simplified form to explain how gradients of D-R plots, intercepts and deviations from linearity are interpretative devices to characterize and distinguish porosities. Rodriguez and Marsh (15) compared adsorption isotherms of iodine and carbon dioxide. Iodine induces swelling of coals without solubilization. FTIR spectra of iodinated coals indicate changes in hydrogen-bonding within the macromolecular network (16). Thus the adsorption of iodine is indicative of flexibility in the walls of the microporosity in coals. Jackson (17) and Butler (18) in their Theses describe studies of a rank range of coals by the polar NH₃ and SO₂ adsorbates in attempts to characterize surface functionalities in fresh and oxidized coals. Amounts of NH₃ adsorbed by coals are used to calculate contents of carboxylic acid, phenolic, total hydroxyl and carboxyl groups on coal surfaces. Bromine (18) induces swelling of coals and measurements of cross-link densities indicate a minimum in coals of 80-85 wt.% C.

COAL CARBONIZATIONS

Coking principle

During coal pyrolyses the lignites, sub-bituminous and anthracites do not pass through a fluid phase. Resultant chars are pseudo-morphs of parent coal. The caking and coking coals form a plastic/fluid stage on carbonization out of which develop anisotropic components which eventually constitute structure in the resultant cokes (most often metallurgical cokes). The study of the growth of these anisotropic components (later called the mesophase) became a major contribution to coal science. It began with a study in Penn. State University U.S.A. (19) of carbonizations of anthracene and biphenyl under pressure of 300 MPa. Instead of formation of a compact coke, SEM revealed clusters of spheres, the botryoidal structures, now called mesocarbon beads. These were later identified as spheres of mesophase, i.e. the discotic, aromatic, nematic liquid crystal systems, by Brooks and Taylor (20). The next stage was to examine the chemistry of formation of other graphitizable carbons, i.e. from Gilsonite pitch and polyvinylchloride (21). At the same time, Evans and Marsh (22) initiated studies of the mass spectrometry of formation of anisotropic carbons from model organic compounds. The role of heteroatoms in cyclic systems and enhancement of graphitizability were published by Marsh *et al.* (23) followed shortly by the first of a major series of papers describing the role of mesophase during the carbonization of coking coals (24). Earlier workers (25,26) had long recognized the need to explain the coking principle. Whereas in pitch and model compound carbonizations, when the process of dehydrogenative polymerization established mesogen systems, molecular weights > 800 amu, it was the fragmentation of the macromolecular system of coking coals in a fluid matrix which established comparable molecular mesogen systems. Thus the concepts of liquid crystal chemistry were related to coke formation from coals (24).

Optical textures

Inter-relating with this approach to coal chemistry were discussions taking place into the chemistry of the delayed coker, needle coke versus shot coke (27,28), the development of mesophases for carbon fibre manufacture and the explanation of the Dominant Partner Effect (DPE) in terms of hydrogen donor facility. In the late '70s, I. Mochida and A. Grint took up senior positions in the NCRL and together with Marsh made significant contributions to understanding the chemistry controlling size, shape, viscosity and coalescence behaviour of the wide range of liquid crystal systems. Several reviews were prepared (30-37). The findings of the liquid crystal study were published over several years (38). In the final stages of coal or pitch carbonizations, the size, shape and ability to coalesce dictate the resultant optical texture of the cokes. By optical texture is meant the characterization by optical microscopy of the isochromatic units within the overall anisotropic appearance of polished coke samples. The growth of liquid crystals is a function of the size and shape of mesogen molecules in the fluid pitch matrix, the viscosity of both the fluid and liquid crystals and the time/temperature dependence of viscosity of the liquid crystals. Chemical cross-linking continues to develop between molecules in the liquid crystals. Dominantly, the relative reactivities of mesogen molecules are all important. The presence of functionality and heteroatoms enhances reactivity so promoting increases in average molecular weight of pitch constituent molecules at that stage of carbonization processes where the overall viscosity of the fluid matrix is too high to allow effective growth. Thus the growth process is restricted. The molecular reactivity persists within the liquid crystals which rapidly increase in viscosity within themselves. Coalescence is severely restricted and surface fusion results to establish the fine-grained mosaics, < 5 μm , of optical textures often

found in metallurgical cokes. The absence of functionality, (sub-bituminous to bituminous coals) enhances the stability of polycyclic aromatics which now dominate pitch chemistry. Much lower viscosities are attainable, the liquid crystals are more stable and can undergo coalescence resulting in larger sizes of optical texture, about 20 μm , within coke structure.

Blending

Effective up-grading of rank of coal can be achieved by co-carbonization of weakly caking coals with suitable additives, petroleum or coal-based. The Dominant Partner Effect, i.e. where small quantities of additives can disproportionately up-grade sizes of optical texture of cokes, essentially is the introduction of hydrogen transfer compounds which stabilize free radical intermediates so promoting stable mesophase to the higher temperatures of lower viscosities.

The chemistry of stabilization of pyrolysis products of coal (to form anisotropic carbon ultimately) is essentially similar to that of coal-derived liquids where early coking in the process is to be avoided (39). Advances made in the understanding of coal carbonization techniques benefited from the simultaneous and related studies of coal liquefaction, delayed coking and mesophase fibre production.

A major thrust in coal carbonization is towards the use of cheaper coals of lower rank than the coking coals. Hence coal blending has been introduced into coke making for many years. The use of pitch as an additive, added directly or as pellets to improve coke quality, is now industrial practice. Coals are a heterogeneous composite of macerals and mineral matter. The wide variation in coal genesis, origin of plant, swamp conditions, tectonic disturbance, etc. have created very specific chemistry within macerals. This complexity requires empirical searches for suitable coal blends which may contain from 10 to 20 coals. The purpose of coal blending is to create a "coal soup" in the fluid phase with just sufficient aromaticity, hydrogen transfer facility, etc. to form an anisotropic coke with minimum size of optical texture, i.e. about 1 μm in size. The interlocking interfaces of these small mosaics of isochromatic units of mesophase create the required toughness in the cokes to resist degradation caused by pressure, attritional forces and chemical attack (40). The additions of pitches are essentially equivalent to adding coking coals to blends, coking coals having excess coking capacity and hence can be considerably diluted without loss of coke properties. Here this available hydrogen donating capacity promotes stability in the system and a larger size of optical texture. Totally isotropic cokes, without anisotropic constituent units derived from mesophase, tend to be glass-like and fracture similarly.

Oxidation

Oxidation of coals involves removal of hydrogen and chemisorption of oxygen. On initial heating the surface oxygen complexes can interact to establish a cross-linkage. This enhances branch-point density in the macromolecular structure of coal and the reduced ability for radical capping by mobile hydrogen transforms a coking coal into a non-coking coal.

The co-carbonization of oxidised coals with pitches and decacyclene, one of the strongest of hydrogen transfer model compounds, restores, to some extent, the coking properties of an oxidized coking coal. Fluidity is restored, reduction of oxygen groupings probably occurs and stability is re-introduced to the radical systems from the hydrogen donating additive (41). However although coal-tar pitches are all good blending agents, not all petroleum pitches are as effective (42). Structural components, fractionations and elemental analyses cannot predict hydrogen donating facility in pitches. So it is necessary to carry out tests involving, e.g. co-carbonizations with anthracene or phenanthrene and using ^1H NMR to monitor hydrogenated derivatives.

STRUCTURE, GASIFICATION, COMBUSTION.

Working with Stadler, Marsh (43) reviewed critically the methodology of structural analyses of coal carbonizations, with special reference to interpretations based on the X-ray a- and c- dimensions of the hypothetical "crystallite". Later with Crawford (44) the powerful technique of phase contrast fringe imaging by TEM provided a more satisfactory explanation, in terms of lattice distortion, of the increase and decrease in c- dimensions of crystallites of X-ray diffraction data, with increasing carbonization temperature.

Marsh maintained a simultaneous interest into mechanisms of coke gasification, in 1978 reviewing the carbon-oxygen reaction (45), and in 1979 reviewing how reactivities of cokes may be enhanced by co-carbonizing coals with alkali salts (46). The development of structure in cokes and coals and effects on resultant coke properties were set out by Marsh and Clarke in 1986 (47). Aspects of gasification kinetics and hydrogasification are more recent studies (48,49). During this period collaborative studies with Japanese laboratories examined coal carbonizations by ^1H NMR and esr techniques looking at the macromolecular structure of coals and the effects of iodine uptake (50). Most recently, interests have moved towards maceral analysis of coals, with rank, on combustion behaviour of pulverized coals in power stations. Crelling is a most supportive collaborator (51,52). Correlations are being sort between detailed petrographic analyses of coals and reactivity of coal chars (53). A brief excursion was made into coal genesis because of the enthusiasm of Butler and Goodarzi (54) and we are having another look into solvent swelling of coals to relate to physical adsorption behaviour and peculiarities in carbonizations (55).

COAL IN A MODERN WORLD

Without doubt, coal as a combustible material will remain the principal source of industrial and domestic energy. But this energy conversion process is not without problems. Globally, the greenhouse effect is a catastrophic potential problem; acid rain, although a major problem can be resolved. Major thrusts for coal utilization in a modern world are towards more efficient and pollution free combustion. Other routes, e.g. combined cycle using say pressurized fluidized bed gasification, will utilize coals as feedstocks. The carbonization and gasification behaviour of coals and cokes therefore needs precise study. Although the future of metallurgical coke appears limited, the blast furnace will remain for the immediate future with coal providing energy and a reducing atmosphere by tuyere injection. Coal liquefaction and conversion should remain in research schools not only as an insurance for the chemical industry and for liquid fuels but also for the knowledge it provides of coal material.

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