Towards an organic chemistry of the hydrogenation of coal

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Abstract – Coals consist of vitrinite, exinite and fusinite. In British carboniferous coals vitrinite and exinite contain alkanes, alkyl benzenes, alkyl phenols and alkyl naphthalenes trapped in an organic matrix; alkyl naphthalenes and alkyl phenols being the predominant aromatics in vitrinites and exinites respectively. The vitrinite matrix consists of substituted aromatic nuclei linked through hydroaromatic groups whilst the exinite matrix is aliphatic with aromatic substituents. When vitrinite is heated the trapped molecules generate small volumes of fluid within which hydrogen is transferred so as to break C–C and C–O bonds in the matrix. Hydroaromatic compounds hydrogenate coal more readily than does hydrogen. The chemical reactions are rapid, the rate of pyrolysis is diffusion controlled. Pyrolysis of exinites ruptures the aliphatic matrix and about half of the material volatilises. In the liquefaction of coals the heart of the process is the transfer of hydrogen from a hydroaromatic solvent to the coal matrix. Evidence is adduced that this may be achieved by the continuous, rapid pyrolysis of an intimate mixture of coal with a relatively small quantity of hydroaromatic material.

PERSPECTIVE AND AIMS

Let us oversimplify. Aromatic chemistry started from Faraday's isolation of benzene from coal tar (Ref. 1) and burgeoned with the development of the coal tar, dyestuff industry. In Europe throughout the first half of the twentieth century, much of chemical engineering and technological organic chemistry continued to be dominated by the carbonisation of coal. Subsequently, and particularly in America, the flowering of the oil industry created an aliphatic chemical engineering emphasising continuous, catalytic processing. More recently, interest in the properties of living material, in heredity and in fermentation have combined to produce bioengineers who, in a very real sense, are inward looking. In terms of tonnage, however, their activities are peripheral. In this lecture I return to coal and I shall try to see to what extent a chemical engineering can be developed from its hydrogenation. Traditionally coal has been hydrogenated to produce substitutes for oil and natural gas. Continued study of the process is based on four postulates, that

1. As Table 1 shows, in terms of energy much of the world lives below the poverty line and demands for energy are therefore certain to increase
2. Reserves of coal permit its exploitation for many decades
3. In much of the world the price of a ton of oil is more than ten times the price of a ton of coal
4. In the beautiful future when we all get our energy from the sun there will still be a need for a cheap feedstock for organic chemicals.

F.K.R. Bergius was awarded the Nobel Prize in 1931 for the invention of the high pressure autoclave and its application during the previous twenty years to the hydrogenation of a variety of materials including coal. The association of the extraction and hydrogenation of coal was reported by Pott and Broche in 1933 (Ref. 2). The most dramatic exploitation of these discoveries was the production of a petroleum substitute by Germany during the Second World War.

TABLE 1. Energy consumption per head of population per year (Tons of coal equivalent)

	1970	1981
USA	10.8	10.2
UK	4.9	4.6
USSR	4.1	5.7
CHINA	0.4	0.6
INDIA	0.1	0.2

UN Statistics

TABLE 2. Simple molecules present in coals

%C in carbon-iferous vitrin-ite (d.a.f.)	81.3	82.2	84.1	86.7	92.5

Identified by GC/MS of fractionated pyridine extracts (Ref. 26)

n-alkanes:	$C_{10}-C_{19}$	$C_{10}-C_{17}$	$C_{10}-C_{25}$	$C_{16}-C_{25}$	$C_{10}-C_{18}$
aromatics:	naphthalene	C_1 naphthalenes	naphthalene	naphthalene	none could be isolated
	C_1 naphthalenes	C_2 naphthalenes	C_2 naphthalenes	C_1 naphthalenes	
	C_2 naphthalenes	C_2 benzene	C_3 naphthalenes	C_2 naptalenes	
		C_4 benzene	C_1 benzene	C_3 naptalenes	
			C_2 benzene	C_1 benzene	
			ethyl phenyl ether	C_5 benzene	
			phenol	C_1 biphenyl	
			biphenyl	hydroxy biphenyl	
			hydroxy biphenyl	dibenzofuran	
			dibenzofuran	phenanthrene/anthracene	
			C_1 dibenzofuran		
			C_2 dibenzofuran		
			phenanthrene/anthracene		

Notes : C_2 benzene means a hydrocarbon containing two aliphatic carbon atoms and a benzene ring. Napthalenes are listed first since they occurred in largest concentrations.

Identified by GC/MS analysis of fractionated pyridine extracts of the associated exinites

n-alkanes:	$C_{10}-C_{19}$	$C_{10}-C_{19}$	C_9-C_{19}	$C_{10}-C_{22}$	The anthracite gave no exinite
aromatics:	benzaldehyde	phenol	phenol	C_1 phenols	
	phenol				
	dihydroxy phenol	C_1 phenols	C_1 phenols	C_2 phenols	
		C_2 phenols	C_2 phenols	C_3 phenols	
		C_3 phenols	C_3 phenols	C_4 benzene	
		C_4 phenols	C_4 phenols	C_2 benzene	
		dihydroxy-phenol	C_2 hydroxy biphenyl	naphthalene	
		naphthalene	naphthalene	C_2 naphthalene	
		C_1 phenol	C_1 naphthalenes	C_3 naptalene	
		C_1 naphthalene	C_2 naphthalenes	C_3 naptalene	
			C_1 quinoline	C_4 biphenyl	
				Hydroxy biphenyl	

Phenols are listed first since they occurred in largest concentration

Identified by GC/MS analysis of fractionated supercritical toluene extracts of a typical carboniferous coal (data supplied by Coal Research Establishment of National Coal Board

alkanes: several normal alkanes and two cycloalkanes isolated but not identified

aromatics:	naphthalene	C_8 benzene	C_1 phenols	C_1 biphenyls	1:2 diphenyl ethane	C_2 indane	C_1 fluorene
	C_1 naphthalenes		C_2 phenols	C_2 biphenyls		C_3 indanes	
	C_2 naphthalenes		C_3 phenols	C_3 biphenyls		hydroxy indane	
	C_4 napthalenes		C_4 phenols	C_4 biphenyls			
				C_2 hydroxy biphenyl			
	C_1 phenanthrenes						
	C_2 phenanthrenes						
	C_3 phenanthrenes						

This conference will not need reminding that society is endangered whenever technology is not founded on the principles of scientific investigation. A passionate concern for truth, unfettered publication of information and a willingness to admit the possibility of error are essential for the safety of the earth's ecosystem.

Recently, Neavel (Ref. 3) stated that there had been little improvement in Bergius' original technique despite the great advance in our understanding. I shall endeavour to show that our increased understanding suggests corresponding advances in technology.

THE CHEMICAL STRUCTURE OF COAL

Great advances in knowledge of the chemical structure of coals occurred thirty to forty years ago when the British coal industry encouraged the application of such techniques as X ray diffraction (Ref. 4), infra red spectrometry (Ref. 5), magnetic resonance (Ref. 6) and at the same time Van Krevelen and his colleagues at the Dutch State mines conducted a series of chemical and physical investigations (Ref. 7) which generated the concept of an average structure for coal in which
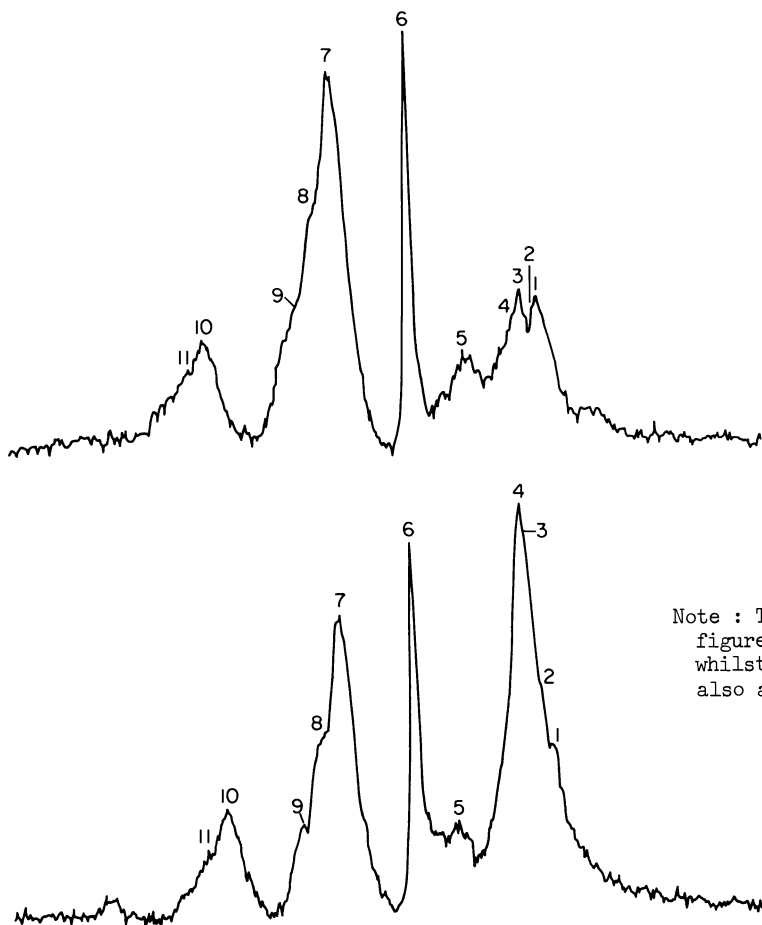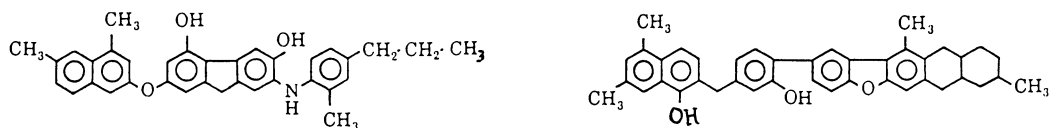
1. 70-80% of the carbon atoms but only 10-20% of the hydrogen atoms in bituminous coal were aromatic, the percentages increasing with the carbon content of the coal.

2. Most of the oxygen in bituminous coals was present as phenolic hydroxyl groups.

3. Much of the structure was hydroaromatic (and here one should pay tribute to the Indian school (Ref. 8) and acknowledge also Fischer (Ref. 9) who was the first to show that hydrogen bromide was released in the bromination of coal).

The concept of an average structure is misleading. First, it conceals the distribution of both molecular weights and chemical structures which are essential facets of the composition of coals. Secondly, it neglects the heterogeneity of coals in being composed of organic minerals or macerals.

Coals consist of simple molecules trapped in an organic matrix. (Refs. 10,11). Many of the simple compounds and some of the lower molecular weight components of the organic matrix can be extracted by solvents (Ref. 12)Thus 25-30% of a bituminous coal can be extracted by pyridine and by supercritical gases and fractionation and gas-chromatography - mass spectrometry (GC/MS) of the simpler molecules present shows them to consist predominantly of n alkanes, alkyl benzenes, alkyl phenols and alkyl naphthalenes (Refs. 13,14) (Table 2) and these classes of compound have also been identified in coal liquefaction products (Ref. 15). The exact mix of compounds present varies from coal to coal and whether there are systematic changes which parallels the amount of carbon in the coal has still to be determined. nmr analysis and molecular mass determination of the more complex molecules present in supercritical extracts suggest that they contain characteristic structures with hydroaromatic and ether linkages (Ref. 16). Some postulated structures satisfying the analyses are shown in Table 3. In as much as it is well established that supercritical gas extraction does not cause major degradation of the coals, these structures must be regarded as similar to those constituting the organic matrix. Confirmation and further understanding og this chemistry has been obtained from reductive alkylation of coals. This remarkable reaction yields products which are markedly soluble in organic solvents (Ref. 17). When coking coals or lignites were reductively alkylated, virtually complete solubility has been obtained (Refs. 18,19) though it is still difficult to isolate individual molecules present in the solution. The reaction has been studied extensively (Ref. 20) and when naphthalene structures - for example - are reductively ethylated the products consist of ethyl dihydro naphthalenes, diethyl dihydro naphthalenes and tetralin. The first and second of these contain olefinic double bonds which may, of course, be cleaved by oxidation. When alkaline nitrobenzene is used as the oxidant an olefinic double bond is also introduced into tetralin and subsequently oxidised (Ref. 21). Such oxidation of reductively ethylated fuels is sufficient to yield products sufficiently volatile to identify by GC/MS (Ref. 22). Table 4 shows products obtained from a lignite. Products lacking oxygen have clearly not been oxidised, though they may have been dehydrogenated and it seems that these were the compounds which were trapped within the coal matrix and indeed many of the structures found in the reductively ethylated coal were again identified when samples of the same coal were subjected to superscritical gas extraction (Ref. 23). It should also be noted that before reductive ethylation the samples were 'cleaned' by extraction with benzene - ethanol so that the alkanes subsequently observed must have truly been trapped within the matrix and released only when reductive ethylation and mild oxidation disrupted the fuels. Compounds containing carbonyl groups are clearly fragments of larger species and it is here that one seeks information about the structures of the organic matrix. Care is needed since oxidation of model compounds with alkaline nitrobenzene (Ref. 21) shows that benzaldehyde - to take an obvious example - is produced from many different compounds. Nevertheless it is obvious that the lattice is composed of many different structures and from the position of the carbonyl groups it appears that aromatic rings are frequently connected by single methylene bridges but that in general branching or structures susceptible to oxidation occurred at a

variety of positions along the chain linking the nuclei. The frequent occurrence of ether linkages confirms the results of investigation by supercritical gas extraction (Table 3) which suggests their presence in the lattice. Although a coherent description of coal structure is already apparent this still needs refining to include an account of the chemical differences between the maceral groups. This problem has recently been put into perspective by Given (Ref. 24). Maceral groups have distinct morphologies (Ref. 25) and thus, presumably, distinct structural chemistries. Davis (Ref.14) has distinguished between the pyridine extracts of vitrinites (telocollinites) and exinites (sporinites) of British carboniferous coals and demonstrated that whereas extracts of both vitrinites and exinites contained the same classes of simple molecule, alkyl naphthalenes and alkyl phenols were the predominating aromatics in vitrinite and exinite extracts respectively. Figure 1 shows ^{13}C CPMAS spectra (Ref. 26) of residues from a vitrinite and its associated exinite after all soluble material has been removed. The diminished aromaticity of the exinite is apparent as is the predominance

TABLE 3. Structures satisfying analyses of benzene soluble materials of
supercritical gas extracts of coals (Ref. 16)

Fig. 1.

Upper Figure : [13]CPMAS nmr of vitrinite residue remaining after pyridine extraction and mild solubilisation (Ref. 26)

Lower Figure : [13]CPMAS nmr of the associated exinite residue remaining after pyridine extraction and mild solubilisation (Ref. 26)

Note : The left hand peak in both figures is a spinning side band whilst the sharp central peak is also an instrumental artefact

TABLE 4. Chemical structures found in Turkish lignites (Ref. 22)
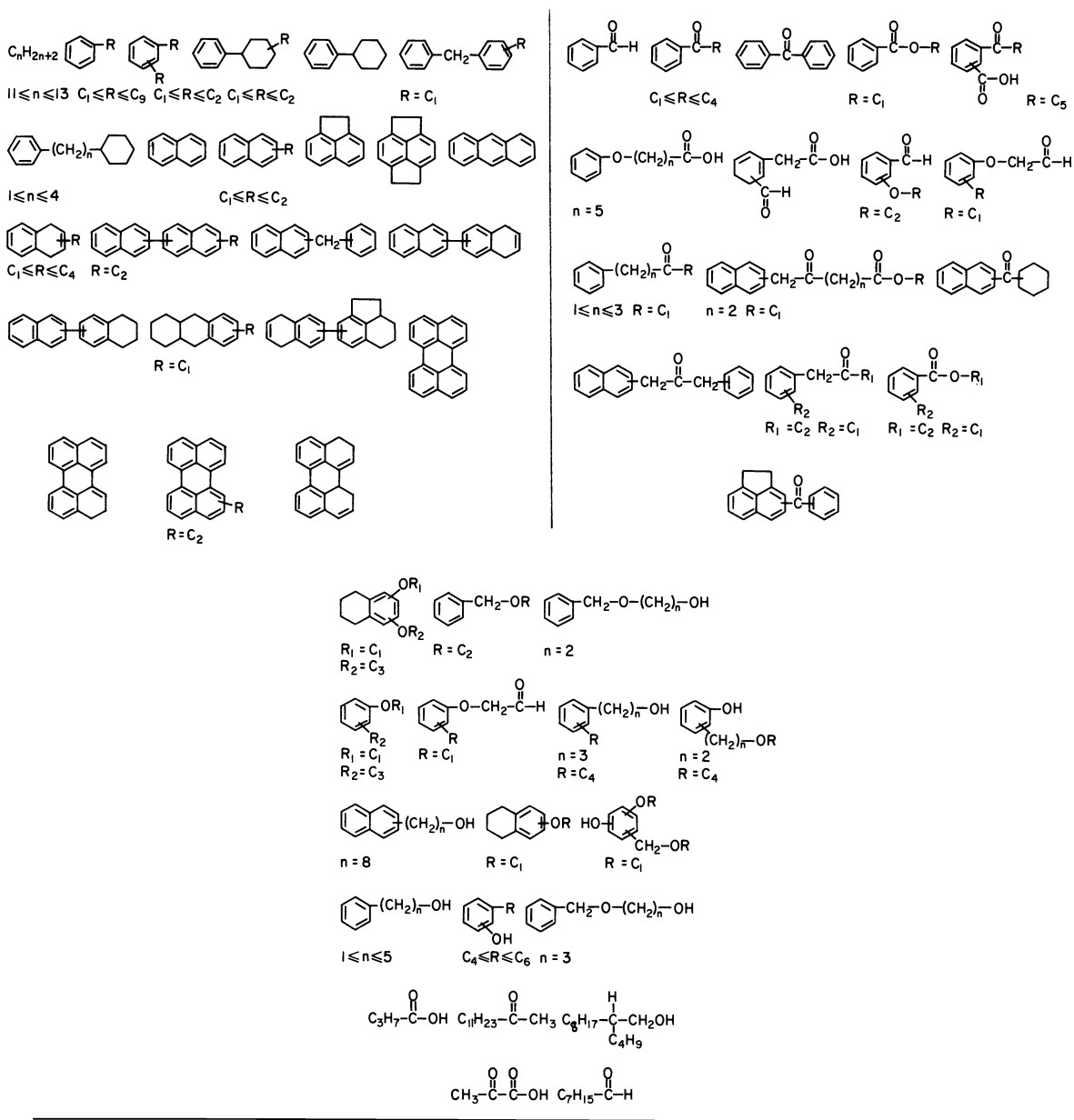
of methylene chains in the aliphatic portion of the spectrum. This is much less pronounced in the vitrinite residues which clearly possess a different distribution of aliphatic (hydro-aromatic !) material. Thus in the vitrinites the matrix consisted of substituted aromatic material linked by hydroaromatic structures as described in previous paragraphs whilst in exinites the matrix was essentially aliphatic with aromatic substituents, there being about nine aliphatic carbon atoms for each (benzenoid) aromatic ring.
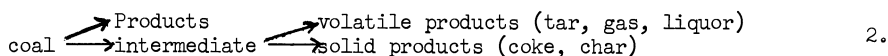
MECHANISM OF PYROLYSIS AND HYDROPYROLYSIS

The modern study of coal pyrolysis started when Fitzgerald and van Krevelen (Ref. 27) recognised that since coking (and caking) coals become fluid or plastic during pyrolysis and subsequently resolidify, the pyrolysis must involve consecutive reactions

$$\text{coal} \longrightarrow \text{intermediate} \longrightarrow \text{products} \qquad 1.$$
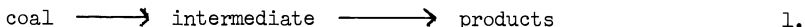
The concentration of intermediate, supposed to be moderate molecular weight material formed by the bond scissions typifying pyrolysis, was postulated to determine the plasticity developed by the system. This view has gained wide acceptance (Refs. 28,29, 30).

Tchukanov (Ref. 31) extended Equation 1. so that it fitted thermogravimetric studies of coal pyrolysis. It is necessary to write a reaction scheme at least as complicated as
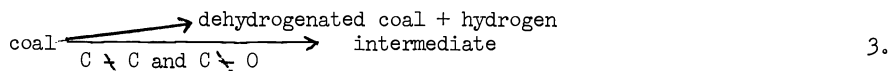
$$\text{coal} \longrightarrow \text{intermediate} \overset{\nearrow \text{Products}}{\underset{\searrow}{}} \overset{\nearrow \text{volatile products (tar, gas, liquor)}}{\underset{\searrow \text{solid products (coke, char)}}{}} \qquad 2.$$

in order to explain

1) the regular increase in yields of volatile material obtained when coals are pyrolysed to increasingly higher temperatures
2) the shape of the thermograms at the start of pyrolysis when the coals are heated rapidly.

Both the development of fluidity and the loss of weight occurring during pyrolysis are described quantitatively by Scheme 2 if all the reactions are first order. The orders of magnitude of the four frequency factors and activation energies obtained by fitting 2 to experimental thermograms suggest all the reactions in 2 to be diffusion controlled though the kinetic factors vary from coal to coal. Nevertheless the formation and decay of intermediate (or the formation and decay of plasticity) is paralleled by increase and decrease of the concentration of free radicals present in the system (Ref. 32) and it is abundantly clear that the four reactions in 2 involve the scission and formation of covalent bonds. More detailed schemes than 2 have been used in modelling of low temperature pyrolysis especially in taking account of the fact that the system is never homogeneous but contains gaseous, liquid and solid components through which heat transfer is difficult (Refs. 28,29).

Since the work of the Indian school it has been apparent that the low temperature pyrolysis of coal is essentially the pyrolysis of a hydroaromatic system. (Refs. 33,34). The initial pyrolysis of a coal may therefore be written (Ref. 35)

$$\text{coal} \underset{C \updownarrow C \text{ and } C \updownarrow O}{\overset{\nearrow \text{dehydrogenated coal + hydrogen}}{\longrightarrow}} \text{intermediate} \qquad 3.$$

3.implies that the complicated pyrolysis of a hydroaromatic system such as tetralin may be approximated d by two types of reaction, dehydrogenation yielding hydrogen and the scission of aliphatic C-C (and where they occur, C-O) bonds. Hydrogen is often spoken of as capping radicals during the pyrolysis (or liquefaction) of coal but much of the bond scission which occurs during pyrolysis is the result of attack by hydrogen on the C-C and C-O bonds (Ref. 35) One is averse to using the term propogation of radicals by hydrogen atoms only because existing evidence suggests chain lengths to be short. The initial reactions generate hydrogen but little of this is evolved as molecular gas since it attacks aliphatic structures before it can diffuse from the system. About as much coal material dehydrogenates to give an extended aromatic system as aromatic material escapes in the tar (Ref. 34).

Recently (Ref. 36), nmr spectrometry has shown that the molecular mobility of coals starts at temperatures as low as 400K. This is particularly noticeable in lignites and kerogens but it is also significant in bituminous coals. A second (and in bituminous coals, major) increase in molecular mobility is observed around 720K when pyrolysis is most rapid (and the concentration of intermediate and the development of plasticity are at their maximum). The melting points, and even some of the boiling points of the simple molecules trapped in the organic matrix of the coal often lie below the temperature of 620K at which coal (and tetralin (Ref. 37)) pyrolyses. These molecules will therefore give localised regions of fluid material trapped within the organic matrix. It seems reasonable to equate the formation of fluid regions with the nmr observation of enhanced molecular mobility in the same temperature range. In addition the aliphatic chains which compose the lattice of exinite material will also become mobile at these temperatures. Hydrogen atoms and radicals formed from hydroaromatic material at the commencement of pyrolysis will be trapped within and between the regions of molecular fluidity. That is they will react with nearby material before they can diffuse out of the system (Reaction 3). In so reacting they will disrupt the organic matrix thereby generating the second increase in molecular mobility. As has been seen, it is this which causes coking coals to become plastic. The plasticity acts as a semi permeable seal preventing the external atmosphere from entering the system and further trapping reactive species within the pyrolysing system. Reaction can be extensive. A study of the pyrolysis of a coking coal in an atmosphere of deuterium (Ref. 38) suggested that pyrolysis affected complete scrambling of hydrogen atoms within the hydrocarbon gases (certainly within the methane) and aldo within those tar molecules which remain trapped in the coal/coke. Hydrogen exchange occurred within the coke through the intermediacy of   complexes.In this study the coal was pyrolysed under pressure and in such circumstances the interaction between pyrolysis and the generation of plasticity is subtle since it is found that the plasticity developed depends not only on the coal and the rate of heating (as Scheme 2 would lead one to expect) but also on the nature and pressure of the external gas (Ref. 39). External pressures of hydrogen usually increase the plasticity of the pyrolysing system (and, in consequence, diminish the accessible internal surface of the resulting coke) but, <u>large</u> external pressures of hydrogen diminish the observed plasticity.

As hydrogen atoms become more scrambled so that the system becomes more thermodynamically stable and as stable molecules slowly diffuse out of the pyrolysing coal thereby removing

hydrogen from the pyrolysis, condensation reactions between reactive species become more prominent. Plasticity diminishes; the system dries up. There is a sense in which this process is autocatalytic since the disappearance of fluidity permits hydrogen to diffuse out of the system rather rapidly – and this is indeed observed – thus preventing even more successfully the continued generation of mobile material. The nmr studies show that 'drying up' occurs relatively soon after the maximum plasticity has been achieved (Ref. 36) and it may be assumed that complete loss of plasticity corresponds to complete loss of simple molecules and, in particular, to the complete depletion of sources of hydroaromatic hydrogen. Bituminous coals contain similar amounts of hydroaromatic hydrogen and it is not surprising that the observed temperatures of 'drying up' are rather independent of the carbon content of the coal.

Two points remain to be stated. First, the interpretation of the nmr studies given here is not that favoured by the investigators themselves and their own interpretation should obviously be considered carefully (Ref. 36). Secondly, the present description of coal pyrolysis is essentially a description of the pyrolysis of vitrinite and possibly of Gondwanaland inertinite, Bituminous exinite becomes completely fluid during pyrolysis and gives yields of more than fifty per cent of volatile material.

COAL LIQUEFACTION AND HYDROGENATION

In modern coal liquefaction particles of coal are digested in a hydroaromatic solvent at temperatures near 670K when the coal pyrolyses. Scanning electron microscopy (Ref. 40) shows that the particles break down in a matter of minutes to give a slurry – colloidal suspension. As it pyrolyses the coal is hydrogenated, not so much by the external atmosphere of hydrogen but by the hydroaromatic hydrogen present in the solvent. The products are further hydrogenated if a high grade liquid fuel is required and hydrogenation is essential to rejuvenate the solvent. Industrial plants differ according to the way they separate and handle the various stages. The factors controlling the success of the process have been analysed very lucidly by Whitehurst (Ref. 41).

In the presence of excess hydroaromatic solvent pyrolysis is rapid and, if of a short duration, is accompanied by little polymerisation. Hydrogenation of pyrolysis products may be controlled by mass transfer when the viscosity of the slurry – colloidal solution is high or by chemical kinetics when the viscosity is low. It is customary to mix catalysts with the coal to be hydrogenated but in fact it is practical to catalyse neither the pyrolysis of the coal nor, when it is mass transfer controlled, the transfer of hydrogen to the pyrolysis products. A variety of catalysts has been employed including cobalt molybdate, molybdenum disulphide, pyrite, colloidal iron oxide and red mud from the aluminium industry. These catalysts are generally used but once and are not recycled and the emphasis has therefore been on finding cheap catalysts, preferably those inherent in the mineral matter of the coal, rather than on catalyst mechanism and efficiency.

One's understanding of the structure and hydropyrolysis of coals suggests that the traditional use of high pressure in liquefaction may be necessary only to refine the products and rejuvenate the solvent. Maximum yields of liquid products were obtained by pyrolysing a coking coal in an atmosphere of hydrogen (no solvent present) when an optimum ratio of hydrogen to coal was selected but high pressure was necessary only if one wished to produce gas (Ref. 42). In fact, as has been seen, the key feature of the disruption of coal by pyrolysis is the attack by hydrogen from hydroaromatic material trapped within the matrix on C-C and C-O bonds and hydroaromatic compounds hydrogenate coal more successfully than does molecular hydrogen. It has been found (Ref.14) that as little as 5% of isopropyl naphthalene added to coals previously extracted with pyridine was sufficient to double their volatile content. This suggests that, to achieve hydrogenation of a coal, it may be sufficient to ensure close association of the coal with relatively small quantities of hydroaromatic material during rapid pyrolysis at atmospheric pressure. The process is readily made continuous by the application of fluidised bed or dispersed phase techniques of chemical engineering. It is seen that, in such a process great use is made of hydroaromatic material present in the coal structure and relatively little external hydrogen donor seems required. Efficient pyrolysis could necessitate cleaning and blending of coals and this might lead one into the organic chemistry of flotation agents. In determining the conditions of pyrolysis one notes that there is no need for the complete conversion of coal to volatile material. Solid product would be used to furnish hydrogen for any desired refining of the volatiles and for partial synthesis of the hydroaromatic material consumed in the pyrolysis. These two processes are kinetically controlled and may be suitable for continuous catalysis.

CONCLUSION

The modern liquefaction of coals is more flexible and more efficient than that envisioned by Bergius (Ref. 41). However, one's understanding of the complicated structures which are coals and, in particular, of the ways in which those structures can be disrupted, indicates new chemical engineering processes for furnishing fuels and chemicals. From these processes new and, hopefully, surprising developments in organic chemistry are certain to emerge. Perhaps only now is one beginning to see how to realise the full potential of coal. With that concern for truth mentioned in the introduction let us assess the future.

REFERENCES

1. The history of the first investigations of aromatic compounds is given, for example, in G.M. Dyson, A Manual of Organic Chemistry I,Longmans, London (1950).
2. A. Pott and H. Broche et al., Gluckauf, 69, 903 (1933).
3. R. Neavel, Coal Science : an idiosyncratic view. Opening lecture to the Int. Conf. on Coal Science, Sydney (1985).
4. H.E.Blayden , J. Gibson and H.L. Riley, Proc. Conf. Ultrafine Structure of Coals and Cokes, BCURA, London, 176 (1944).
    J.K. Brown and P.B.Hirsch, Nature, 175, 229 (1955).
5. C.G. Cannon and G.B.B.M. Sutherland, Trans. Faraday Soc., 41, 279 (1945).
6. P.C. Newman, C. Pratt and R.E. Richards, Nature, 175, 645 (1955).
    J.K. Brown and W.R. Ladner, Fuel, 39, 87 (1960).
    D.J.E. Ingram et al., Nature, 174, 797 (1954).
7. D.W. van Krevelen, Coal, Elsevier, Amsterdam (1961).
8. B.K. Mazumdar et al., J. Sci. Industr. Res., 17B, 509 (1958).
9. Fischer, Z. Angew. Chem., 33, 787 (1899).
10. M.Vahrman , Chemistry in Britain,8, 16 (1972).
11. P.H. Given et al., Fuel, 65, 155 (1986) and refs. therein.
12. I.G.C. Dryden in Chemistry in Coal Utilisation, Supplementary Vol.I, Ed. by H.H. Lowry, Wiley, New York, 232, (L963).
13. K.D. Bartle, T.G. Martin and D.F. Williams, Fuel, 54, 226 (1975).
    T. Tugrul and A. Olcay, Fuel, 57, 415 (1978).
14. M.R. Davis, J.M. Abbott and A.F. Gaines, Fuel, 64, 1362 (1985).
15. J.S. Youtcheff et al., Org. Geochem., 5, 157 (1983).
    Z. Mudamburi and P.H. Given, Rept. to US Dept. of Energy No.DOE 40784-T1 (1983).
16. A.A. Herod, W.R. Ladner and C.E. Snape, Phil. Trans. Roy. Soc. London, A300, 3 (1981).
17. H.W. Sternberg et al., Fuel, 50, 434 (1971).
    H.W. Sternberg and C.L. Delle Donne, Fuel, 53, 172 (1974).
18. R. Dogru et al., Fuel, 57, 399 (1978).
19. L.M. Stock, N. Mallya and R.S. Willis, The contrasting reduction, alkylation and reductive alkylation of low and high rank bituminous coal, Proc. Int. Conf. on Coal Science, Sydney, p722 (1985).
20. J.M. Abbott, O.Erbatur and A.F. Gaines, Fuel, 63, 1441 (1984).
21. N. Owen, University of Aston, Personal Communication (1984).
22. R. Dogru et al., Fuel, 58, 823 (1979).
23. R. Ceylan and A. Olcay, Fuel, 60, 197 (1981) see also Ref. 13.
24. P.H. Given, Organic Geochemistry of Coal, in Coal Science, 3, Ed. by M.L. Gorbaty, J.W. Larsen and I. Wender, Acad.Press, New York, p179 (1984).
25. M.R. Davis, A. White and M.D. Deegan, Fuel, 65, 277 (1986).
26. M.R. Davis, PhD Thesis, University of Aston (1985).
27. D. Fitzgerald, Trans. Faraday Soc., 52, 362 (1958).
    H.A.G. Chermin and D.W. van Krevelen, Fuel, 36, 85 (1957).
28. G.R. Gavalas, Coal Pyrolysis, (Coal Science and Technology), Elsevier, Amsterdam (1982).
29. J.B. Howard in Chemistry of Coal Utilisation Suppl.vol.2, Ed. by M.A. Elliott, Wiley, New York (1981).
30. W.S. Fong, W.A. Peters and J.B. Howard, Fuel, 65, 254 (1986).
31. Tchukanov : Refs given in Chemistry of Coal Utilisation Suppl. vol. 1, Ed. H.H. Lowry, Wiley, New York (1963).
32. J. Uerbersfeld, A. Etiene and J. Combrisson, Nature, 174, 614 (1954).
    L. Petrakis, D.W. Grandy and G.L. Jones, Fuel, 61, 21 (1982).
    See also Ingram Ref. 6.
33. B.K. Mazumdar et al., Fuel, 41, 105 (1962) and Refs. therein.
34. P.H. Dicker, A.F. Gaines and L. Stanley, J. Appl. Chem., 13, 455 (1963).
35. A.F. Gaines and Y. Yurum, Fuel, 55, 129, (1976).
36. L.J. Lynch et al., The molecular basis of coal thermoplasticity, Proc. Int. Conf. on Coal Science, Sydney, p887, (1985).
37. H. Adkins and W.A. Reid, J. Amer. Chem. Soc., 63, 741 (1941).
38. N.S. Noor, A.F. Gaines and J.M. Abbott, Fuel, 65, 67 (1986).
39. M.R. Khan and R.G. Jenkins, Thermoplastic properties of coal at elevated pressures : effects of gas atmospheres, Proc. Int. Conf. on Coal Science, Sydney, p903 (1985).
40. See, for example, A. Wilhelm, K. Hedden and M. Canel, Physical and Chemical effects of hydrogen and hydrogen donors in coal dissolution, Int. Conf. on Coal Science, Sydney, p87, (1985).
41. D.D. Whitehurst, Coal Liquefaction Fundamentals, ACS Symposium 139, particularly p133, (1980).
42. N.S. Noor, A.F. Gaines and J.M. Abbott, Fuel, 64, 1274 (1985).