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The Chemical Nature of Supercritical Gas Extracts from Low-Rank U.K. Coals [and Discussion]

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The chemical nature of supercritical gas extracts from low-rank U.K. coals

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Two processes are being developed by the National Coal Board for producing liquids from coal. Both involve extraction of the coal to produce an extract, freed from mineral matter, which is then catalytically hydrocracked. This approach is particularly suitable for producing transport fuels and chemical feedstocks.

One process uses as solvent a process-derived liquid. The other uses a compressed supercritical gas to extract the more hydrogen-rich parts of the coal, leaving a reactive char which can provide the necessary hydrogen, heat and power for the process.

As part of the development programme, extracts have been prepared by gas extraction over a range of conditions, and their chemical structures investigated by elemental and spectroscopic analysis. The average structures so derived consist of small aromatic clusters joined by methylene, ether and diphenyl linkages. Extracts produced by the liquid solvent route contain larger aromatic clusters.

1. Introduction

In the U.K. a requirement is foreseen for premium liquid products from coal, principally transport fuels and chemical feedstocks. It is not envisaged that it will be necessary to convert coal to liquid boiler fuels as it would probably be cheaper to burn coal with appropriate measures for pollution control. Two conversion processes are being developed by the National Coal Board, one using a supercritical gas as solvent and the other a process-derived liquid. The use of liquid solvents in direct coal liquefaction is well established (Kölling; Schmid *et al.*; Neavel; all this symposium), but the properties of supercritical gas solvents have not hitherto been exploited.

2. The coal extraction processes

(*a*) *Supercritical gas extraction process*

To serve as a solvent, the supercritical fluid has to be compressed so that intermolecular forces similar to those present in a liquid can come into effect (Paul & Wise 1971). It is preferable for the fluid to be close to its critical temperature, otherwise the pressures required are excessively high. After extraction, a reduction of the pressure causes the solvent molecules to move apart, the solvent capacity is lost, and the extracted material is precipitated, thus freeing the solvent for re-use.

Coal extraction is normally carried out at 400–450 °C while the coal is undergoing thermal decomposition. The supercritical extractant is therefore chosen such that its critical temperature is near this value. Suitable fluids include coal tar or petroleum naphtha fractions, and it is found that aromatic compounds are more effective than aliphatic compounds because coal decomposition products are primarily aromatic in character.

It has been shown that supercritical fluids selectively extract from the coal decomposition products the smaller molecular species, which contain more hydrogen than the rest of the coal, and are therefore more suitable for conversion to the required liquid products (Whitehead & Williams 1975). The more carbonaceous material that remains is suitable for gasification with steam and oxygen to provide hydrogen for conversion of the extract, and fuel gas to provide the process heat requirement. It can also be used to generate power and steam for the process. One such integrated flow-sheet, in which the feedstock is a high-volatile bituminous coal, is shown in figure 1. In this example about 45% of the organic matter in the coal is extracted and it is estimated that petrol and diesel fuel could be produced, together with synthetic natural gas (s.n.g.) and liquefied petroleum gas (l.p.g.), at an overall thermal efficiency of about 65%. The extraction and hydrocracking steps have been demonstrated in small pilot plants, and a design has been prepared, with Government support, for a larger pilot plant to process coal at 1 t/h.

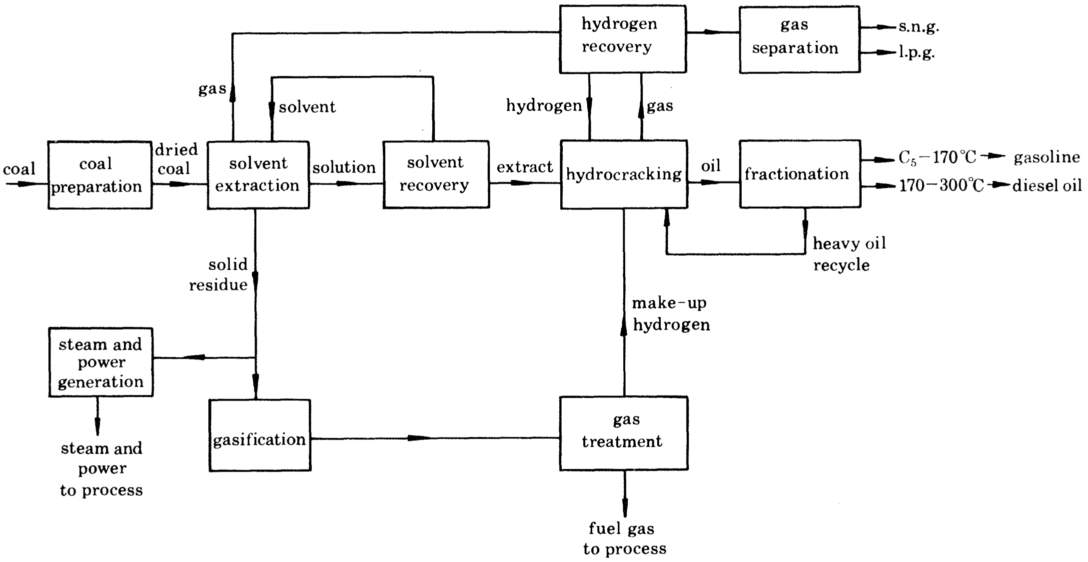


FIGURE 1. N.C.B. supercritical gas extraction process.

As part of this programme, extracts have been prepared from high volatile coals over a range of conditions and their chemical structures have been investigated. For comparison, the chemical composition of an extract prepared in 82% yield by the N.C.B. liquid solvent extraction route has also been determined.

(b) *Liquid solvent extraction process*

The distinctive feature of the liquid solvent extraction process is that the extraction step is effected at a pressure close to atmospheric, thus avoiding the complications involved in handling solids at the elevated pressures adopted in most other direct liquefaction processes. Conditions are chosen to simplify the subsequent removal of insoluble material by filtration. The filtered coal solution is then reacted with hydrogen over a catalyst at about 425 °C, 20 MPa, as in the supercritical gas extraction process, as a result of which the aromatic structures present are hydrogenated and cracked, and oxygen, nitrogen and sulphur are removed. The oil that is produced is distilled at about 300 °C and the distillate is converted to transport fuels and chemical feedstocks, while the distillation residue is recycled to the extraction stage as the solvent. The overall flow-sheet is shown in figure 2. Extra coal is brought in to supplement the small amount of insolubles from the extraction stage for gasification to provide the hydrogen and process heat requirements. The overall thermal efficiency is estimated to be about 70 %. Conversion to petrol, diesel fuel and chemical feedstocks has been shown to be feasible and a design for a 1 t/h pilot plant has been prepared.

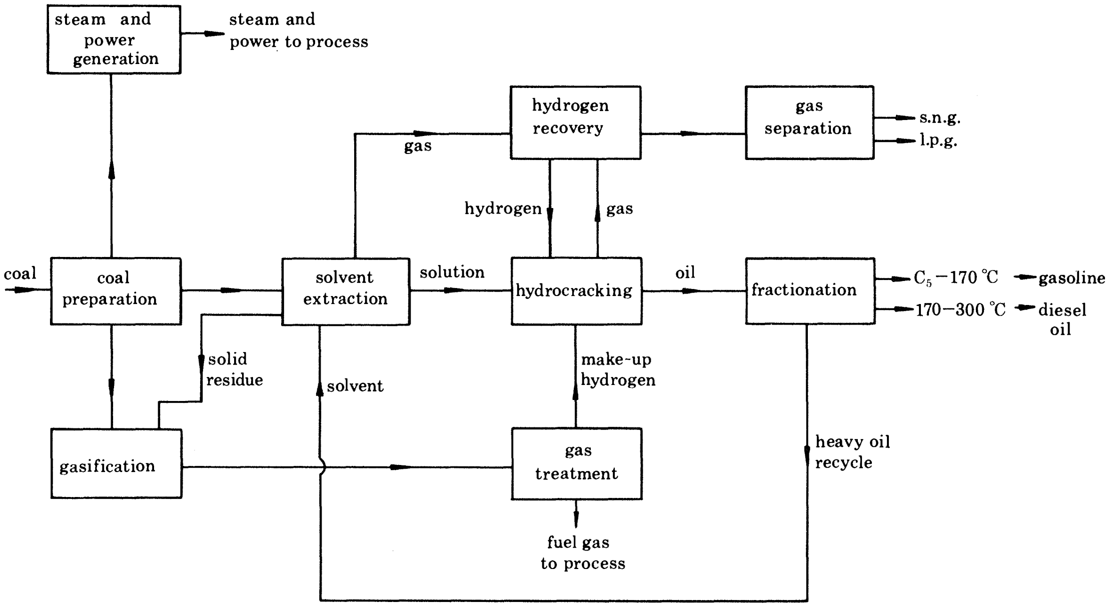


Figure 2. N.C.B. liquid solvent extraction process.

3. Preparation of coal extracts

(a) *Supercritical gas extracts*

Extracts were prepared in the laboratory by passing a compressed stream of supercritical fluid through a bed of < 1.6 mm coal at extraction conditions for a predetermined time. Other extracts were prepared in a small pilot plant by passing a stream of solvent and < 210 μm coal through a preheater and then through an extraction vessel. The insoluble matter, in the form of a particulate char, was separated from the product stream leaving the vessel, and the extract was recovered by depressurizing the fluid. Typical analyses of coal, extract and char are shown in table 1.

Ten different bituminous coals were extracted, of N.C.B. Coal Rank Code 702–902. They contained 4–36 % ash, 37–42 % volatile matter (dry ash-free basis), 60–80 % vitrinite, 11–25 % inertinite and 5–12 % exinite. Their ultimate analyses on a dry ash-free (d.a.f.) basis were within the range 81–85 % carbon, 4.9–5.3 % hydrogen, 3.5–10.5 % oxygen, 1.4–2.0 % nitrogen and 1.4–2.9 % sulphur (dry basis). The oxygen content of the extract varied with the oxygen content of the coal but over a narrower range, 6.1–8.4 %. The sulphur contents of the coals varied mainly as a result of differences in the composition of the mineral matter, with the result that the sulphur contents of the extracts varied only from 0.9 % to 1.1 %.

Nine supercritical solvents were used. One was a pure compound, toluene, and the others were mixtures of aromatic hydrocarbons, apart from one that consisted of aliphatic hydrocarbons. The extraction conditions covered pressures from 10 to 30 MPa, temperatures from 380 to 450 °C, coal residence times from 4 to 20 min (gas residence times were generally much less than this), and solvent/d.a.f. coal mass ratios of 3:1 to 10:1. The mass of extract recovered varied from 16 to 47 % of the d.a.f. coal. The ultimate analysis of the extract showed little change with change in extraction conditions.

Table 1. Typical analyses of coal, supercritical gas extract and char

	coal	extract	char
C (% d.m.m.f.)	81.2	83.6	87.4
H (% d.m.m.f.)	5.2	6.4	3.6
O (% d.m.m.f.)	11.4	8.0	6.7
N (% d.m.m.f.)	1.4	1.15	1.5
S (% a.r.)	1.65	0.95	1.1

(b) *Liquid solvent extract*

An extract was prepared for comparison by digesting Annesley coal (CRC 702, 3 % ash, 37 % volatile matter; 84.0 % carbon, 5.4 % hydrogen, 8.0 % oxygen, 1.9 % nitrogen, 0.7 % sulphur) in a liquid solvent, containing hydrogen donor compounds, similar to that produced by the liquid solvent extraction process described above. The digestion was carried out for 1 h at 400 °C and the product was filtered to remove insoluble material. The extract yield corresponded to 82 % of the d.a.f. coal. Although the extract is not normally isolated at this stage, it was recovered on this occasion by distilling off the appropriate amount of solvent. Because of the overlap in boiling range, some of the solvent may have remained in the extract and some of the extract may have been distilled.

4. Fractionation and analysis of the extracts

As the extracts were extremely complex mixtures, with components of molecular masses from 200 to over 2000, a crude molecular mass fractionation was effected by extraction with refluxing benzene and then by addition of *n*-pentane to the benzene solution. Aliphatic compounds, present in the *n*-pentane soluble fraction in amounts corresponding to less than 1 % by mass of the coal, were separated by adsorption chromatography on silica gel. Details of the fractionation procedure are given by Herod *et al.* (this symposium). For the supercritical gas extracts, the yields of *n*-pentane soluble material and of asphaltenes (insoluble in *n*-pentane, soluble in benzene) each amounted to up to 10 % d.a.f. coal and the yield of benzene-insoluble material was up to 30 % d.a.f. coal. For the liquid solvent extract corresponding yields were 13, 24 and 45 % respectively.

The fractions were subjected to ultimate analysis and to determination of phenolic hydroxyl content by enthalpimetric titration. Typical analyses are shown in table 2. The low molecular mass pentane-soluble fraction contained more hydrogen and less oxygen and nitrogen than the other fractions. However, little change in elemental composition was observed with change in extraction conditions.

The number average molecular masses of the fractions were determined isopiestically; the results are plotted against extraction temperature in figure 3, the variation with the nature of the solvent also being indicated in the diagram. The more powerful supercritical solvents, as indicated by their density under extraction conditions, were capable of extracting higher molecular mass material than the weaker solvents. Increasing the extraction temperature decreased the average molecular mass of the benzene insoluble fraction, possibly because the high molecular mass material polymerized at the higher temperatures before it could be extracted from the coal. The asphaltenes were readily extracted, except by the weakest solvents, and the pentane solubles were readily extracted by all the solvents. Their molecular masses did not change with extraction conditions. The effect of coal residence time does not appear on the diagram, as it was observed that the material extracted near the start of extraction had a similar molecular mass to that extracted later.

TABLE 2. TYPICAL ANALYSES OF EXTRACT FRACTIONS

	pentane solubles	asphaltenes	benzene insolubles
C (%)	83.5	81.7	79.8
H (%)	8.3	6.4	5.9
O (%)	6.4	9.1	9.5
N (%)	0.5	1.3	2.0
S (%)	0.9	1.0	1.1
OH (%)	3.4	6.6	5.5
n.p.O (%)	3.2	3.4	4.3
molecular mass	340	570	980

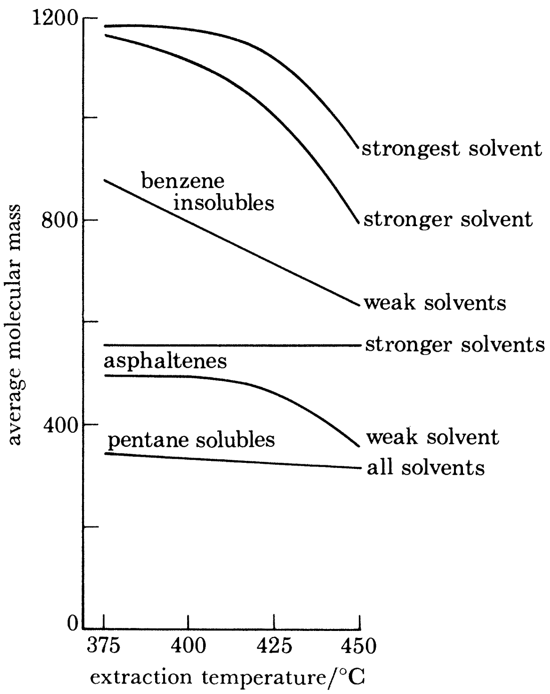


FIGURE 3. Average molecular masses of extract fractions.

5. AVERAGE CHEMICAL STRUCTURE OF THE EXTRACTS

The structural analysis scheme adopted is that described by Herod *et al.* (this symposium). It is based on the assignment of the bands in the ^{1}H n.m.r. and ^{13}C n.m.r. spectra of the fractions to specific hydrogen and carbon bonds and structural environments.

TABLE 3. STRUCTURAL PARAMETERS OF EXTRACT FRACTIONS

	pentane solubles	asphaltenes	benzene insolubles
number of aromatic rings, R_a	3	7	12
aromaticity (aromatic C/total C), f_a	0.65	0.74	0.79
aromatic H/total H, $n_{\mathrm{Har+OH}}/n_{\mathrm{H}}$	0.24	0.35	0.42
degree of aliphatic substitution, σ	0.34	0.26	0.21
condensed structure parameter, $k_{\mathrm{c.s.}}$	0.4	0.4	0.4
open structure parameter, $k_{\mathrm{o.s.}}$	0.7	0.7	0.7

The first step in the scheme is to calculate the numbers of different atoms and groups in an average molecule from the hydrogen and carbon distributions, ultimate analysis, phenolic hydroxyl content and average molecular mass of each fraction. The second step is to derive a series of structural parameters of the average molecule for each fraction, namely:

the total number of carbon atoms, $n_{\mathrm{C}} = n_{\mathrm{Car}} + n_{\mathrm{Cal}} + n_{\mathrm{Cm}}$;
the number of aromatic carbon atoms, n_{Car};
the number of alkyl and naphthenic carbon atoms n_{Cal};
the number of methylene bridge carbon atoms, n_{Cm};
the number of aromatic and phenolic hydrogen atoms, $n_{\mathrm{Har+OH}}$;
the number of alkyl and naphthenic groups, $n_{\mathrm{a.g.}}$;
the number of ring-joining groups, $n_{\mathrm{r.j.g.}}$;
the number of carbon atoms in aromatic rings and in ring-joining groups, $n_{\mathrm{Cr}} = n_{\mathrm{Car}} + n_{\mathrm{r.j.g.}}$;
the number of ring-joining carbon atoms, $n_{\mathrm{Cj}} = n_{\mathrm{Cr}} - n_{\mathrm{Har+OH}} - n_{\mathrm{a.g.}} - n_{\mathrm{r.j.g.}}$ (i.e. the carbon atoms common to two rings or attached to a ring-joining group); and
the number of hydrogen atoms joined to aromatic rings and ring-joining groups when substituents are replaced with hydrogen, $n_{\mathrm{Hr}} = n_{\mathrm{Har+OH}} + n_{\mathrm{a.g.}} + 2n_{\mathrm{r.j.g.}}$ (this is also numerically equal to the number of peripheral carbon atoms, $n_{\mathrm{Cp}} = n_{\mathrm{Cr}} - n_{\mathrm{Cj}} + n_{\mathrm{r.j.g.}}$).

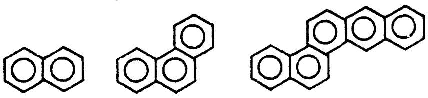
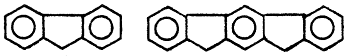
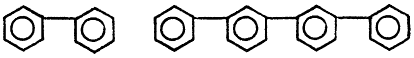
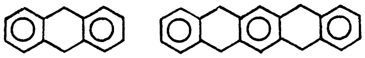
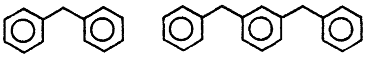
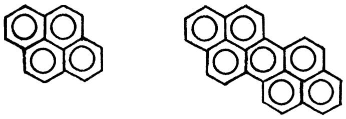
The non-phenolic oxygen is known to be present in aromatic ethers, and it is assumed that the small numbers of nitrogen and sulphur atoms are present in heterocyclic carbazole and dibenzothiophene structures. For convenience, therefore, these atoms have been added to the number of methylene bridges in calculating the number of ring-joining groups, $n_{\mathrm{r.j.g.}}$. Following from this, $n_{\mathrm{r.j.g.}}$ is included in the number of atoms in the basic skeleton, n_{Cr}, which therefore includes all carbon, oxygen, nitrogen and sulphur atoms except those in substituent aliphatic and phenolic hydroxyl groups.

A further series of parameters can be calculated now, which are of more immediate value in defining the average molecular structure. These are listed, together with typical values for the fractions, in table 3.

The total number of aromatic rings and rings containing ring-joining groups, n_{ra}, is given by $\frac{1}{2}(n_{\mathrm{Cj}} + 2)$. This parameter varies with extraction conditions in the same way as the molecular mass.

The aromaticity, f_{a}, and the fraction of aromatic plus phenolic hydrogen are obtained directly from the n.m.r. spectra, and, for both, the benzene-insoluble fraction gives the highest value and the pentane-soluble fraction gives the lowest value. The degree of alkyl and naphthenic substitution, σ, which equals $n_{\mathrm{a.g.}}/(n_{\mathrm{a.g.}}+n_{\mathrm{H_{ar}+OH}})$, decreases from 0.34 for the pentane solubles to 0.21 for the benzene insolubles. None of these parameters is affected by changes in the operating conditions, and the fractions from the liquid solvent extract give similar results.

TABLE 4. DEGREE OF CONDENSATION OF AROMATIC NUCLEUS

family of aromatic structures	$k_{\mathrm{o.s.}}$	$k_{\mathrm{c.s}}$
	0.50	0.50
	0.57	0.57
	0.67	0.33
	0.75	0.50
	0.86	0.29
average of the above structures	0.69	0.44
	0.40	0.60

The condensed structure parameter, $k_{\mathrm{c.s.}} = n_{\mathrm{C_j}}/(n_{\mathrm{C_r}}-6)$, and the open structure parameter, $k_{\mathrm{o.s.}} = (n_{\mathrm{H_r}}-6)/(n_{\mathrm{C_r}}-6)$, were chosen because the aromatic structures likely to be present in the extracts can be grouped into families for each of which the values of these parameters are constant. For example (see table 4), for cata-condensed aromatics, $k_{\mathrm{o.s.}} = 0.50$ and $k_{\mathrm{c.s.}} = 0.50$, while for benzene rings joined by methylene bridges, $k_{\mathrm{o.s.}} = 0.86$ and $k_{\mathrm{c.s.}} = 0.29$. From the examples shown in table 4 it can be seen that as the proportion of ring-joining carbon is increased and the structure becomes more condensed, $k_{\mathrm{c.s.}}$ increases. Conversely, as more hydrogen is introduced into the structure and it becomes more open, so $k_{\mathrm{o.s.}}$ increases. An average structure containing an equal mixture of all the cata-condensed structures has $k_{\mathrm{o.s.}} = 0.69$ and $k_{\mathrm{c.s.}} = 0.44$. More condensed structures such as pyrene and higher members of that family have lower $k_{\mathrm{o.s.}}$ values and higher $k_{\mathrm{c.s.}}$ values.

It is therefore possible to prepare graphs of $n_{\mathrm{C_j}}$ against $n_{\mathrm{C_r}}$ and of $n_{\mathrm{H_r}}$ against $n_{\mathrm{C_r}}$ (see figures 4 and 5 respectively), for which each of the families of structures appears as a straight line. As the number of rings is given by $\frac{1}{2}(n_{\mathrm{C_j}}+2)$, the larger the value of $n_{\mathrm{C_j}}$ the more rings there are in the structure. In addition, as the angle from the $n_{\mathrm{C_r}}$ axis increases in figure 4, so the structure becomes more condensed. Thus, if a point corresponding to the average $n_{\mathrm{C_j}}$ and $n_{\mathrm{C_r}}$ values for an extract fraction is plotted on this diagram, its position will indicate how condensed, and how large, the average structure is. It is found that the points for the gas extract fractions fall in much the same position with respect to the lines, irrespective of the conditions under which the extracts were prepared or from which coal they were derived or indeed whether the fraction is pentane-soluble, asphaltene or benzene-insoluble. Thus, the average structure is apparently a continuous function of molecular mass, with the benzene-insoluble fractions appearing to be equivalent to 'polymers' of the pentane-soluble and asphaltene fractions. The points fall near to the average for the cata-condensed structures and well away from the more condensed structures. Thus the relatively open average structure previously reported by Bartle *et al.* (1975, 1979) for extracts obtained in 17 and 27% yield is now seen to apply to extracts representing up to half of the coal. The only exception is a point corresponding to an extract prepared under conditions where condensation reactions are most likely to have occurred on extraction.

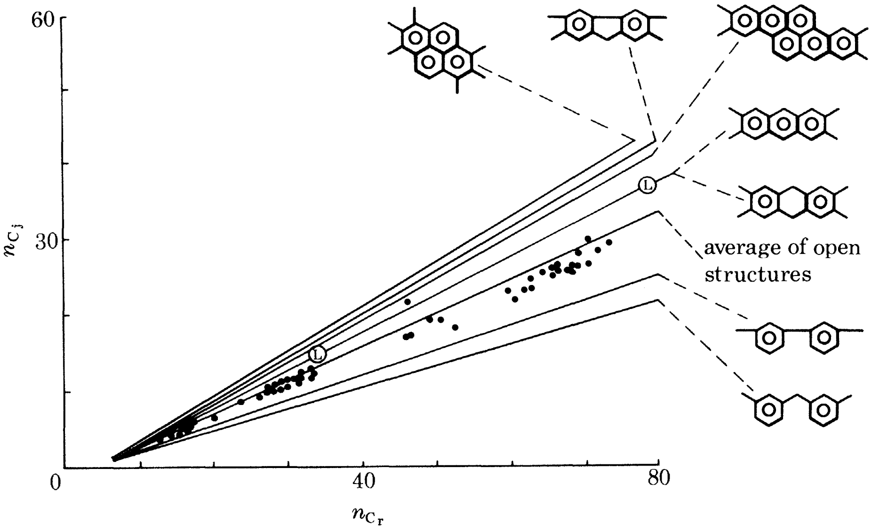


FIGURE 4. Plot of n_{C_j} against n_{C_r} for extract fractions.

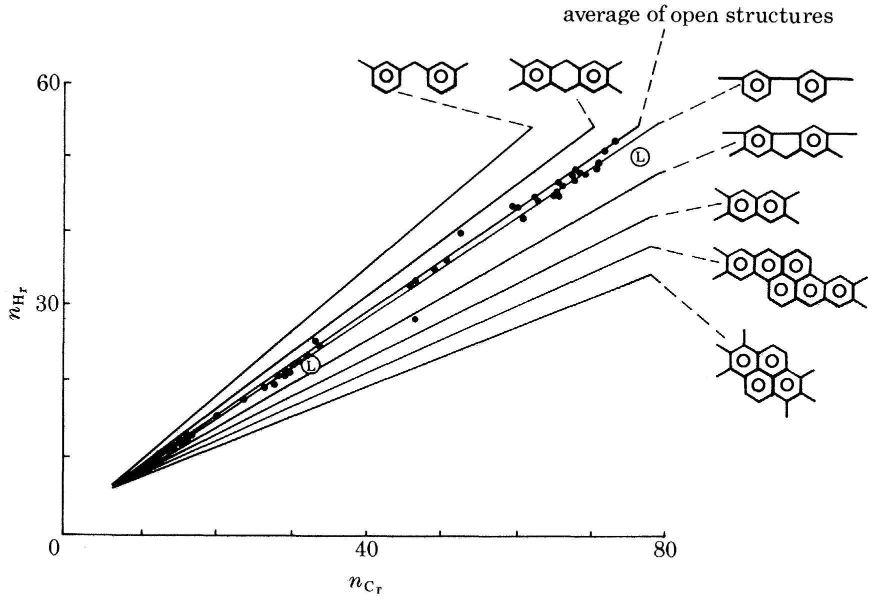


FIGURE 5. Plot of n_{H_r} against n_{C_r} for extract fractions.

The points for the fractions of the liquid solvent extract, corresponding to 82% of the coal, are indicated on the graph by the letter L. These points correspond to average structures which are more condensed than those for the gas extracts.

The graph of n_{H_r} against n_{C_r} is shown in figure 5. In this diagram as the angle from the n_{C_r} axis increases, so the amount of hydrogen in the structure increases and it becomes more open.

Separate lines are shown for cata-condensed aromatic and hydroaromatic structures, whereas they were coincident in figure 4, so this figure provides additional information about the extract structure. However, the points for the gas extract fractions again fall close to the line corresponding to the average for the cata-condensed structures, and the points for the liquid solvent extract correspond to somewhat more condensed structures, so similar conclusions are reached to those drawn from figure 4.

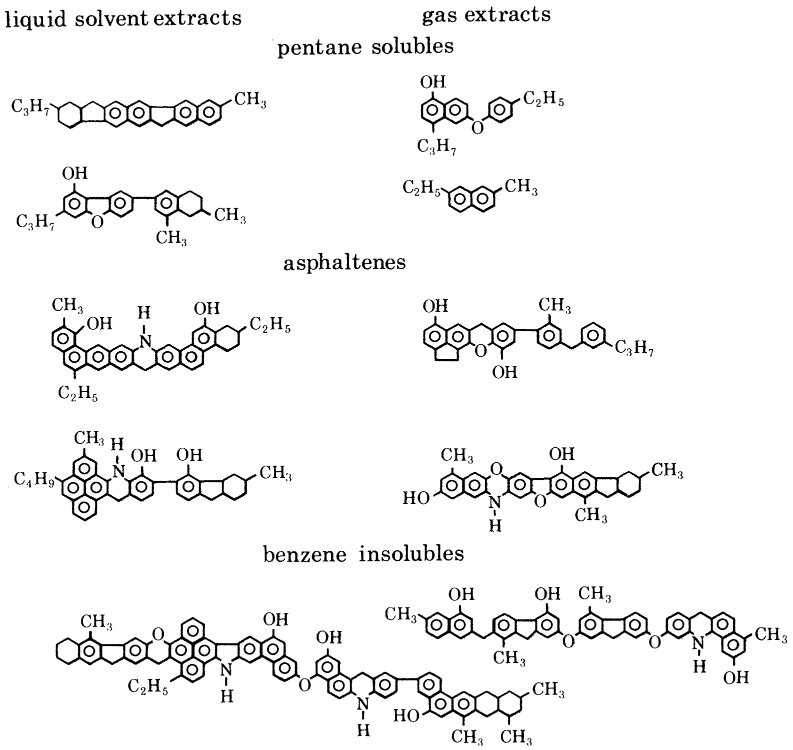


Figure 6. Average structures of extract fractions.

By making use of these diagrams and the values for the structural parameters described earlier, it is possible to draw molecules whose structures correspond to these values. These molecules are statistical averages of chemical type and size of the very large number of individual types present in the extract fractions. Structures representing each of the fractions of the supercritical gas extracts and the liquid solvent extract are shown in figure 6. The average structures of the gas extracts contain benzene and naphthalene units joined by methylene bridges, ether bridges and 5-membered rings. Methyl is the most common alkyl constituent. The liquid solvent extract is somewhat more condensed, containing phenanthrene and pyrene units in its average structures, but its structure is still relatively open compared, for example, with coal tar pitch. It also contains more hydroaromatic rings, possibly because these structures were stabilized during extraction by the hydrogen donor compounds present in the solvent. It is concluded that both types of extract would be amenable to hydrocracking, and this has been shown experimentally to be so.

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European Coal and Steel Community for financial support. The views expressed are those of the authors and not necessarily those of the Board.

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Discussion

H. SCHULZ (*Engler-Bunte-Institut, Universität Karlsruhe, Germany*). The process of supercritical gas extraction suffers from low yields of extracts due to the non-hydrogen-transferring properties of the solvent to be used. The large amount of residue of extraction must also be regarded as a costly substance, owing to its expensive mode of production. My question is: From the side of the properties of the extract and of the residue, can the authors claim outstanding benefits that might compensate for these disadvantages?

D. F. WILLIAMS. I am glad to have the opportunity to answer this question, because it gives us an opportunity to provide a justification for aiming at a relatively low extract yield of 40–50 %.

In all direct liquefaction processes it is necessary to provide a gasification feedstock from which the hydrogen and fuel gas required by the process may be generated. In the circumstances for which these processes are being developed, where petroleum and natural gas are in short supply, this feedstock will be derived from coal. The power requirements of the process may also be derived from coal. Thus, in processes with a high yield of extract for conversion to liquid products, it will be necessary to consume additional coal to provide the hydrogen and energy requirements.

An alternative approach can therefore be envisaged in which a smaller extract yield is obtained, and the extraction residue provides the gasification feedstock. In certain circumstances this could prove the better approach. For example, it would seem to be advantageous if the extract produced in this way consisted of molecules that required less hydrogen and energy to convert them to the required products, and if the residue was more carbonaceous than the coal and contained that part of the coal that is more difficult to break down to liquid products, yet was still suitable for gasification. As implied in the question, some advantage of this kind is needed to offset the additional expense involved in extracting all the coal fed to the plant.

Meaningful conclusions about the value of this approach can be reached only by considering specific processes. Supercritical gas extraction is an example of the 'lower extract yield' approach. The expected overall thermal efficiency of this process is similar to that for other direct liquefaction processes. The capital cost of the equipment, which as for the other processes has at present to be estimated from data from small pilot plants, also seems to be similar to the general level. The process seems to have advantages in terms of the premium value of its products: transport fuels, with some l.p.g. and s.n.g. In this respect it is similar to the liquid solvent extraction process that we are developing, which happens to adopt the 'high extract yield' approach.

To summarize, then, the supercritical gas extraction process appears to have high potential, and it will be possible to make a more complete judgement when the 25 t/day pilot plant that we are planning has been in operation for some time.