GAS CHROMATOGRAPHY APPLIED TO THE STUDY OF THE LIQUID PRODUCTS OF THE LOW-TEMPERATURE FLUIDIZED-BED CARBONIZATION OF COAL

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INTRODUCTION

Economic considerations in many countries at the present time are not favourable for the large scale conversion of coal into liquid fuels and chemicals. But this situation is bound to change in the future as the proved reserves of coal are many times greater than the most optimistic estimates of petroleum. The Department of Fuel of the University of New South Wales has therefore adopted as one of its research projects the investigation of low-temperature carbonization of coal and the products obtained by various processes for this purpose.

The programme of the Department includes both static- and fluidized-bed carbonization techniques. The latter involves the application of heat to the coal particle "boiling" or suspended in a turbulent state in the reaction chamber by a stream of gas (usually air) for a time interval commensurate with maximum tar-oil yield. The volatile material moves out of the carbonizing zone at a rate that approaches the velocity of the transport gas with the result that the tars produced are considered to represent the most nearly primary tars produced by industrial processes[1].

From the practical point of view fluidized processes have the advantages of high throughput for a given size of plant, high yield of liquid products and better control than is possible with batch processes in static beds.

Various workers have described gas chromatographic examinations of fractions from low-temperature coal tars. KARR *et al.*[2,3] analysed phenols boiling up to 234° from the low-temperature fluidized carbonization of a West Virginia bituminous coal, at 160° on a di-*n*-octyl phthalate column using helium as carrier gas. FITZGERALD[4,5] studied the application of gas chromatography to the analysis of phenols using a number of stationary phases, and concluded that for the best resolution of mixtures both polar and non-polar phases should be used. He found Apiezon L and sodium dodecylbenzene sulphonate (as a spray-dried mixture with sodium sulphate in an industrial detergent) to be the most useful stationary phases and employed them to analyse the lower-boiling phenols from Lurgi brown coal tar. BROOKS[6] studied the relative effectiveness of phosphate esters of various phenols for the separation of close-boiling phenol isomers, *e.g.* 2,4- and 2,5-xylenols and *m*-ethylphenol and *p*-ethylphenol. PAYN[7] used a di-*n*-octyl sebacate column at 178° for routine analysis of phenols.

In the case of the neutral oil most work has been done on the aromatic fraction. This is a natural consequence of earlier work on high-temperature tars. DUPIRE AND BOTQUIN[8] developed a chromatograph which employed silicone grease as the stationary

phase and helium as carrier gas, and this was later used by DUPIRE[9] to determine quantitatively forty-five components of a tar using column temperatures from 130° to 360°. CHANG AND KARR[10] analysed aromatic hydrocarbons boiling up to 218° in the low-temperature tar mentioned above[2,3] at 150° on a 15 ft. long column using Apiezon L as stationary phase.

Although not available to the author until the present work was in its concluding stages, the papers by COPPENS, BRICTEUX AND NEURAY[11] and BOYER et al.[12] are of particular interest. COPPENS et al. worked on tar obtained by carbonization of a high volatile coal at about 600° in a fixed bed. The fraction of the neutral oil boiling below 280° was separated into paraffins (and naphthenes), olefins and aromatics by a modification of the fluorescent indicator adsorption (F.I.A.) method of column chromatography. The paraffin and olefin fractions were then submitted to gas chromatography at 190° on a column containing silicone grease on firebrick with helium as carrier gas. The paraffin fraction, which consisted of 16.5 % of the neutral oil boiling below 280°, was shown to consist predominantly of normal paraffins from C9 to C16 together with minor components corresponding to five homologous series of different isoparaffins of the same range of carbon numbers. The olefin fraction, which consisted of 11.0 % of the neutral oil boiling below 280°, was found to consist essentially of normal olefins C9 to C16 in three series decreasing in amount in the order 1-, trans-2- and cis-2-olefins. Members of up to six homologous series of branched olefins also appeared to be present in minor amounts. It should be noted that over two-thirds of this neutral oil fraction was aromatic.

BOYER et al. carbonized to 550° vitrinite and exinite concentrates from a Lorraine high-volatile coal in a laboratory apparatus under conditions of high heating rate and low secondary cracking. They considered the tar obtained to be somewhat analogous to that obtained from semi-carbonization in a fluidized bed. The tar was subjected to counter-current extraction to remove polar compounds, distilled, separated into hydrocarbon types by column chromatography on silica gel, and these fractions analysed on a gas chromatograph analogous to that described by DUPIRE[9]. Infrared and ultraviolet spectroscopy were used to identify components trapped out after separation. Paraffins and olefins up to about thirty carbon atoms were identified. Most of these were straight-chain compounds and the authors claimed that these came "almost only from exinite" (a petrographic maceral* group in coals comprising remains of spores, cuticles, algae and resin bodies). They further stated that aromatic compounds were abundant in all the tars, but were more highly substituted in the exinite tar.

The liquid products in the present study were examined on the invitation of the Australian Joint Coal Board, and were produced for the Board in a fluidized-bed pilot plant operated by the United States Bureau of Mines in Denver, Colorado, U.S.A. The coal carbonized was a high-volatile bituminous coal from the Liddell Seam, Foybrook Open Cut, New South Wales, and conditions of the run were adjusted to produce a char of 16.0 % volatile matter.

The general properties of 20 tars obtained from a variety of coals in this pilot plant have been described by GOMEZ, GOODMAN AND PARRY[1]. Six of these were from

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* Macerals are defined as the elementary homogeneous microscopic constituents of micro-lithotypes in coals, and are analogous to minerals in rocks.

TABLE I

	Range	Mean
Primary distillation yield (weight %)	28.0–60.6	43.2
Composition of distillate (volume %)		
Acids	18.0–34.8	26.5
Bases	1.4– 3.4	2.5
Neutral Oil	62.6–80.6	71.0
Composition of neutral oil (volume %)		
Olefins	30.3–69.5	40.3
Aromatics	14.0–37.3	28.6
Paraffins (includes naphthenes)	16.5–39.1	31.1

high-volatile bituminous coals, and some results of interest for them are given in Table I.

The analytical procedures for these determinations were those described by REYNOLDS AND HOLMES[13]. The various fractions thus obtained were not studied in further detail.

EXPERIMENTAL

(a) Samples

(i) Light oil distillate

The light oil had been recovered from the secondary condenser of the carbonization plant. It was a dark brown to black mobile liquid with a tarry smell. 100 ml was distilled in an A.S.T.M./I.P. standard distillation apparatus to yield a distillate (93 %) of boiling range 90–285° (60 % between 190° and 280°).

Phenols in light oil distillate. These were extracted in the conventional way with 10 % sodium hydroxide solution. The yield was 18.8 % v/v of the distillate.

Neutral oil from light oil distillate. The phenols-free light oil distillate was extracted with 25 % w/w sulphuric acid to remove bases (0.5 % v/v of the distillate) so that the neutral oil amounted to 80.7 % v/v of the distillate.

(ii) Tar distillates

The tar had been recovered from the primary condenser and precipitator of the carbonization plant. It consisted of a mixture of mobile and viscous material which was not homogeneous even after heating at 80° for a week. It was therefore distilled

	Yields of tar distillates (% w/w)		
	(A)	(B)	Original tar (calc.)
Pitch	62.2	69.5	68.0
Distillate to 310°	35.6	27.0	28.8
Liquor	0.4	0.0	0.1
Loss	1.8	3.5	3.1

in two lots representative of the mobile (A) and viscous (B) portions and the yields for the original tar calculated. The standard apparatus for crude tar distillation was used

with a charge of approximately 4 kg in each case. The specific gravity of distillate (A) was 0.887 (15.5/15.5°).

The softening point of pitch (A) was determined as 70° by the "Ring and Ball" method.

Phenols in tar distillates. These were extracted by 10 % sodium hydroxide solution. Portions of the wet phenols were mixed with ether and dried with anhydrous sodium sulphate. The ether was then allowed to evaporate.

| | Yields of phenols (% v/v) | | |
	(A)	(B)	Composite (calc.)
Wet phenols	16.6	38.0	33.7

Neutral oil in the tar distillates. Bases were removed by 25 % w/w sulphuric acid. Emulsion formation, interfacial solids and the very dark colour made the separation difficult.

| | Yield of neutral oil (% v/v) | | |
	(A)	(B)	Composite (calc.)
Tar bases	1.1	6.4	5.3
Neutral oil	79.3	55.6	61.0

(b) Gas chromatograph

A Beckman GC2 instrument fitted with a fraction collector was used. Hydrogen and, more frequently, helium were the carrier gases employed and detection was by means of a katharometer.

Columns

Silicone. (Beckman 74346) Dow-Corning Silicone Fluid Type 550 on 42–60 mesh C22 Johns Manville firebrick in the ratio 30:100 in a 6 ft. × ¼ in. column.

Apiezon L. (Beckman 70013) Apiezon L on C22 firebrick in the ratio of 30:100 in a 6 ft. × ¼ in. column.

The total weight of column filling material was 22.5 g.

Molecular sieve 5A. (Beckman 70020) 29.2 g in a 6 ft. × ¼ in. column.

(c) Chromatographic procedures

For analytical separations samples varied in size from 2–20 μl and were injected by Hamilton syringe. The gas inlet pressure was kept constant at 25 lb./sq.in., and the flow rates corresponding to different columns and conditions were measured at the exit. For the phenols the reference was phenol itself. In the case of the neutral oils toluene, mesitylene and diphenyl were used at 100°, 160° and 220° column temperatures respectively so that sufficient accuracy without excessively long retention time was obtained. In all cases the reference was run immediately before and after each unknown mixture or series of known substances.

When collection of components was desired the sample size was increased up to 200 μl (0.2 ml), but the same columns were used. Up to this volume separation was still good, but one test using 300 μl flooded the column. The inlet was heated by a cartridge heater during injection and the exit line to the collector was kept above column temperature to prevent premature condensation. Ice water was found to be adequate for cooling the traps in the Dewar flask, which were inserted on the exit only when the peak concerned was being traced on the recorder. For individual peaks the component condensed almost completely in the inner tube, and was easily washed out with a few drops of spectroscopic grade carbon tetrachloride. For larger cuts the liquid collected in the narrow bottom of the tube and could be sucked into a syringe fitted with a long needle. It was not found necessary to centrifuge the tube.

(d) Infrared spectroscopy

Most spectra were determined on a Perkin Elmer "Infracord" instrument. Several samples were run on a Perkin Elmer Model 421.

RESULTS AND DISCUSSION

Phenols

Separation of the phenols was found to be reasonable on the silicone column with either hydrogen or helium as carrier gas. The peaks tended to be somewhat tailed. Temperatures of 100°, 160° and 190° were tried. At 100° resolution was good, but the retention times were too long, e.g. phenol itself took about 24 min to pass through. The best compromise between resolution and time of analysis appeared to be at 160°. A typical chromatogram for the phenols from the light oil run at this temperature is shown in Fig. 1. The phenols from tar distillate (A) gave a very similar chromatogram. Apiezon L was found much less satisfactory for separation of the phenols mixtures.

Tentative identification of the phenols by means of relative retention times is shown in Table II for the light oil and Table III for tar distillate (A). Several pairs of phenols could not be resolved under the conditions used. Other stationary phases
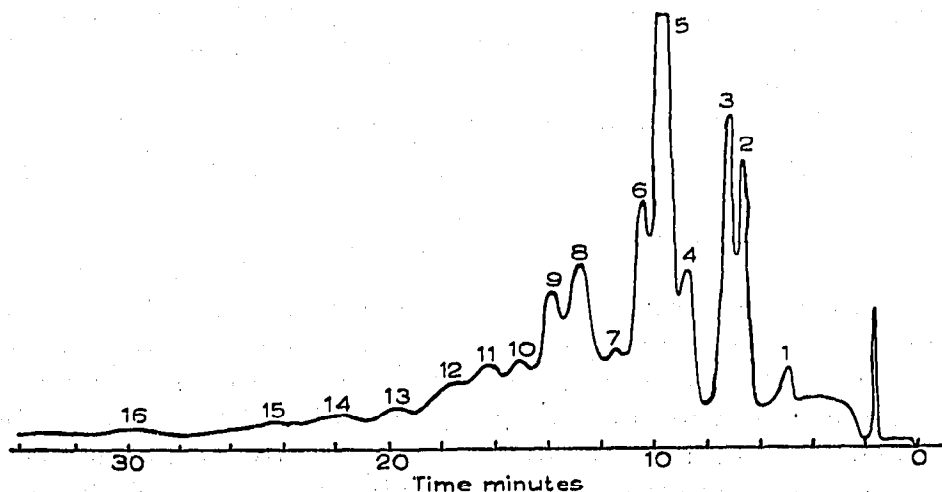

Fig. 1. Chromatogram of phenols from light oil on silicone column at 160°. Sample size: 2 μl; carrier gas: He; inlet pressure: 25 lb./sq. in.; outlet pressure: atmospheric; flow rate: 46 ml/min.

TABLE II

PHENOLS FROM LIGHT OIL DISTILLATE AT 160° ON SILICONE

Peak No.	R.R.T. to peak No. 1	Identification	R.R.T. of known compounds	Relative strength*
1	1.00	Phenol	1.00	w
2	1.37	o-Cresol	1.41	m
3	1.50	m- and p-Cresol	1.55, 1.52	s
4	1.88	2,6-Xylenol	1.90	w
5	2.07	2,4-Xylenol; 2,5-xylenol	2.14, 2.13	vs
6	2.25	4-Ethylphenol; 3,5-xylenol	2.32, 2.32	m
7	2.49	2,3-Xylenol	2.53	vw
8	2.80	2-n-Propylphenol	2.84	m
9	3.05			m
10	3.32	4-n-Propylphenol; 3-ethyl-5-methylphenol	3.42, 3.40	w
11	3.60	2,3,5-Trimethylphenol	3.71	w
12	3.92			w
13	4.40			w
14	4.9	4-Indanol	5.08	w
15	5.5			vw
16	6.7			w

* w = weak; m = medium; s = strong; vs = very strong; vw = very weak.

would no doubt be able to do this. Separation was considered insufficient to attempt quantitative analysis. All that was thought justifiable was a rough division of peaks into "very strong" (vs), "strong" (s), "medium" (m), "weak" (w) and "very weak" (vw) as is shown in the tables.

The work demonstrates that with a general purpose column, even though the ultimate in separation is not achieved, much valuable information can be easily

TABLE III

PHENOLS FROM TAR DISTILLATE (A) AT 160° ON SILICONE

Peak No.	R.R.T. to peak No. 1	Identification	R.R.T. of known compounds	Relative strength*
1	1.00	Phenol	1.00	m
2	1.40	o-Cresol	1.41	m
3	1.52	p- and m-Cresol	1.52, 1.55	s
4	1.90	2,6-Xylenol	1.90	w
5	2.10	2,4-Xylenol; 2,5-xylenol	2.14, 2.13	s
6	2.29	3,5-Xylenol; 4-ethylphenol	2.32, 2.32	m
7	2.5	2,3-Xylenol	2.53	vw
8	2.84	2-n-Propylphenol	2.84	m
9	3.09			m
10	3.37	4-n-Propylphenol; 3-ethyl-5-methylphenol	3.42, 3.40	m
11	3.65	2,3,5-Trimethylphenol	3.71	vw
12	4.0			vw
13	4.4			vw
14	5.0	4-Indanol	5.08	w
15	5.6			w
16	6.7			w
17	7.5			vw
18	8.0			vw
19	8.7			vw

* For abbreviations see Table II.

obtained from tar acid fractions. In the case of the light oil eleven of the sixteen peaks have been tentatively identified. If "major components" are defined as those of medium strength or stronger then only one major component (No. 9 peak) remains unknown. (From its position it is almost certainly a C9 phenol.)

The same phenols are apparently present in tar distillate (A) and their quantitative distribution follows almost the same pattern. There are three more components in minor amounts at the high end of the boiling point range.

The following phenols could not be detected in either the light oil or tar distillate (relative retention times to phenol given in brackets): O-ethyl-phenol (2.00); 3,4-xylenol (2.71), 1-naphthol (13.0) and 2-naphthol (13.8).

Neutral oils

A typical chromatogram of the neutral oil from tar distillate (A) on the silicone column at 220° is shown in Fig. 2. Separation was quite good at this temperature whilst lower temperatures led to very long retention times and flattened peaks. The neutral oil
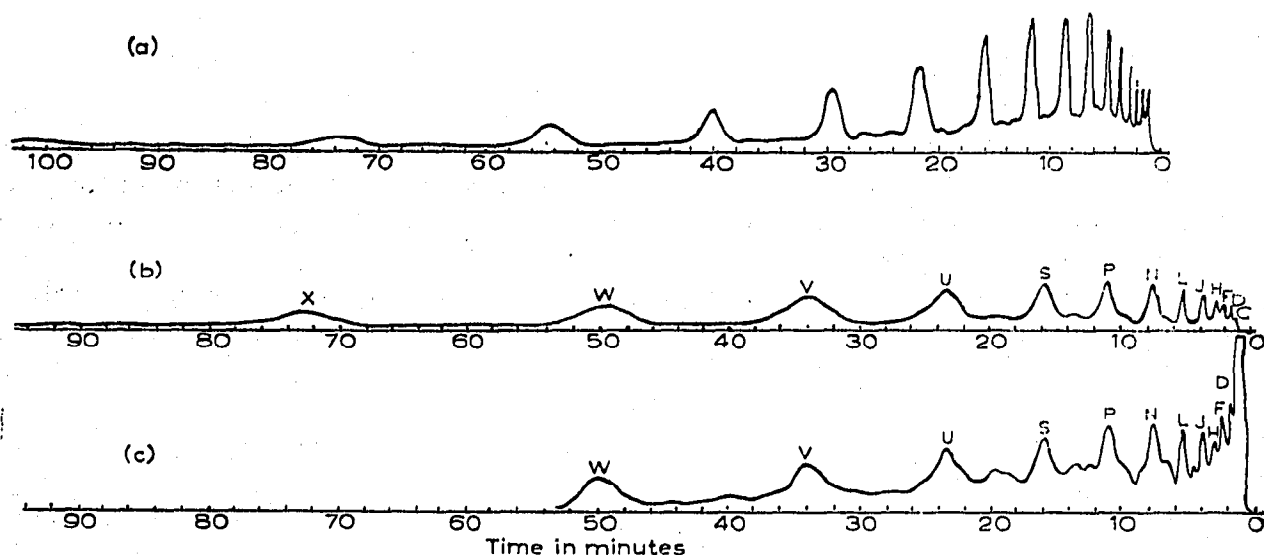
Fig. 2. (a) Chromatogram of neutral oil from tar distillate (A) on silicone column at 220°. Sample size: 4 μl; carrier gas: He; inlet pressure: 25 lb./sq.in.; outlet pressure: atmospheric; flow rate: 41 ml/min. (b) Chromatogram of neutral oil from tar distillate (A) on Apiezon L column at 220°. Sample size: 5 μl; carrier gas: He; inlet pressure: 25 lb./sq.in.; outlet pressure: atmospheric; flow rate: 43.5 ml/min. (c) Chromatogram of neutral oil from tar distillate (B) on Apiezon L column at 220°. Sample size: 20 μl of ethereal solution; carrier gas: He; inlet pressure: 25 lb./sq.in.; outlet pressure: atmospheric; flow rate: 43.5 ml/min.

from the light oil gave a chromatogram similar to the early part of the tar distillate at 220°. If the column temperature was reduced to 160° the same peaks were obtained with better separation.

Comparison with the relative retention times of known neutral substances was not helpful. These reference compounds were mostly aromatic hydrocarbons. Nine of the major components of the tar distillate were collected for examination by infrared spectroscopy. The spectra were all similar (Fig. 3b) showing very strong bands corresponding to aliphatic carbon–hydrogen bonds at about 2800–3000 cm^{-1}, 1460 cm^{-1} and 1370 cm^{-1}. Minor bands were also present, e.g. at 965 cm^{-1}, 910 cm^{-1} and 720 cm^{-1}.

The neutral oil itself from tar distillate (A) was very similar except that there were additional weak bands at about 1600 cm^{-1}, 810 cm^{-1} and 745 cm^{-1} (Fig. 3a). For comparison the spectrum of paraffin oil is shown in Fig. 3c. It is evident that the components of the neutral oil are very aliphatic in nature.
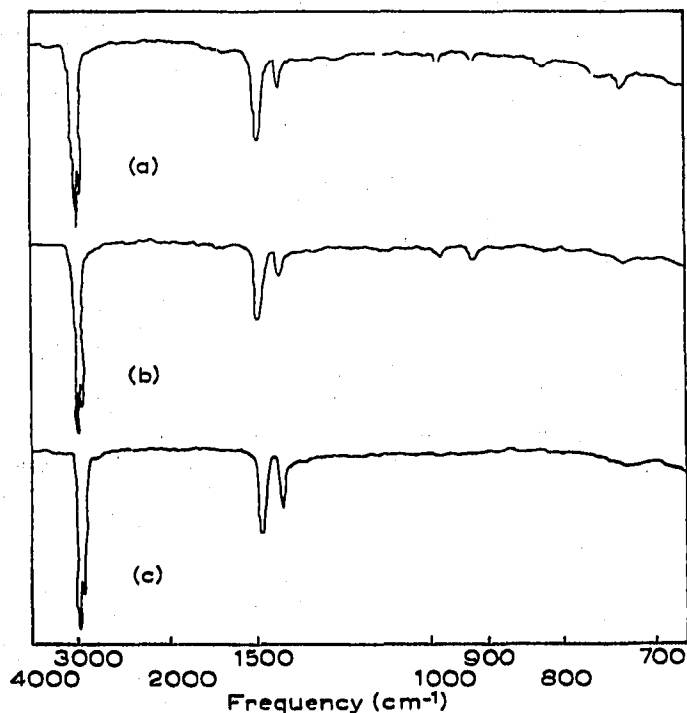

Fig. 3. Infrared spectra of: (a) Neutral oil from tar distillate (A). (b) Typical major peak trapped from tar distillate (A) neutral oil on silicone column at 220°. (c) Paraffin oil.

When the same sample was run on the Apiezon L column at 220° (Fig. 2) the peaks were more spread out, but the same regularity, which suggested an homologous series, was apparent. Fig. 2 also shows part of a run on the neutral oil from tar distillate (B), showing differences from (A) in minor early components, but having all the same major components. (N.B. The very strong front peak is due to added ether as solvent.) If the major components were assumed to be normal paraffins then peaks D, H and U corresponded to n-octane, n-decane and n-hexadecane, by relative retention time to diphenyl as reference. The graph of log (relative retention time × 100) versus carbon number on this basis for the major peaks was a straight line as can be seen from Fig. 4. However, collected components above C17 were liquids, which was inconsistent with their being normal paraffins, so it appeared that they were either isoparaffins of about the same relative retention time, or mixtures.

As mentioned earlier it was impractical to run the neutral oil from the tar distillate below 220°, and at 160° on silicone the neutral oil from the light oil showed the same peaks as at 220° except that at the lower temperature they were more widely spaced. However, when the latter oil was run on Apiezon L at 160° all the major peaks were split in two, the first of each pair being somewhat stronger. This is shown in Fig. 5a.

The infrared spectrum of the light oil neutral oil (Fig. 6a) showed strong bands corresponding to aliphatic carbon–hydrogen bonds and a number of other bands
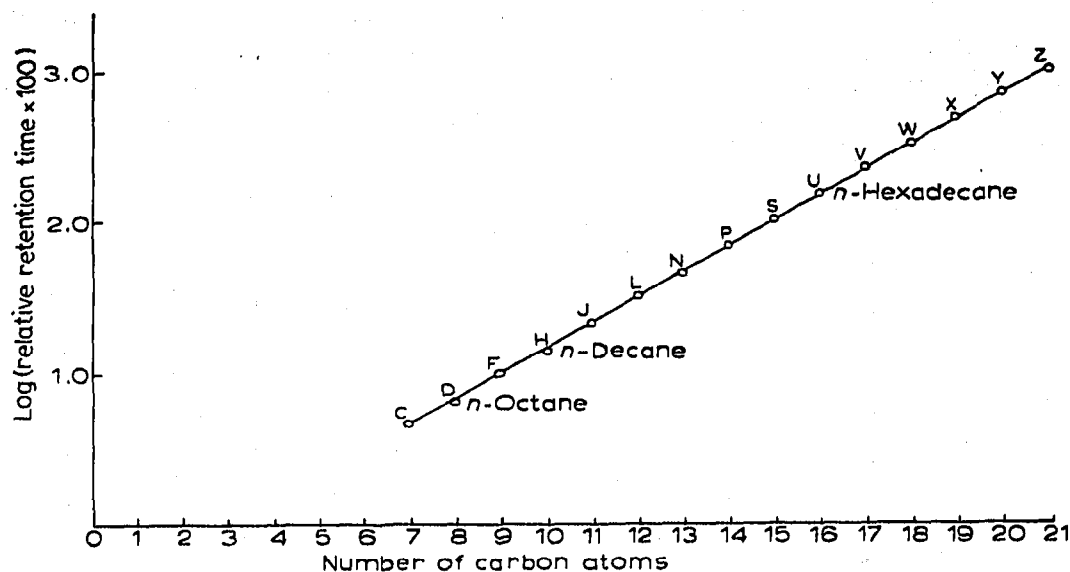
Fig. 4. Graph of log [relative retention time (to diphenyl reference) × 100] *versus* number of carbon atoms for the major peaks from tar distillate (A) neutral oil on Apiezon L column at 220°.
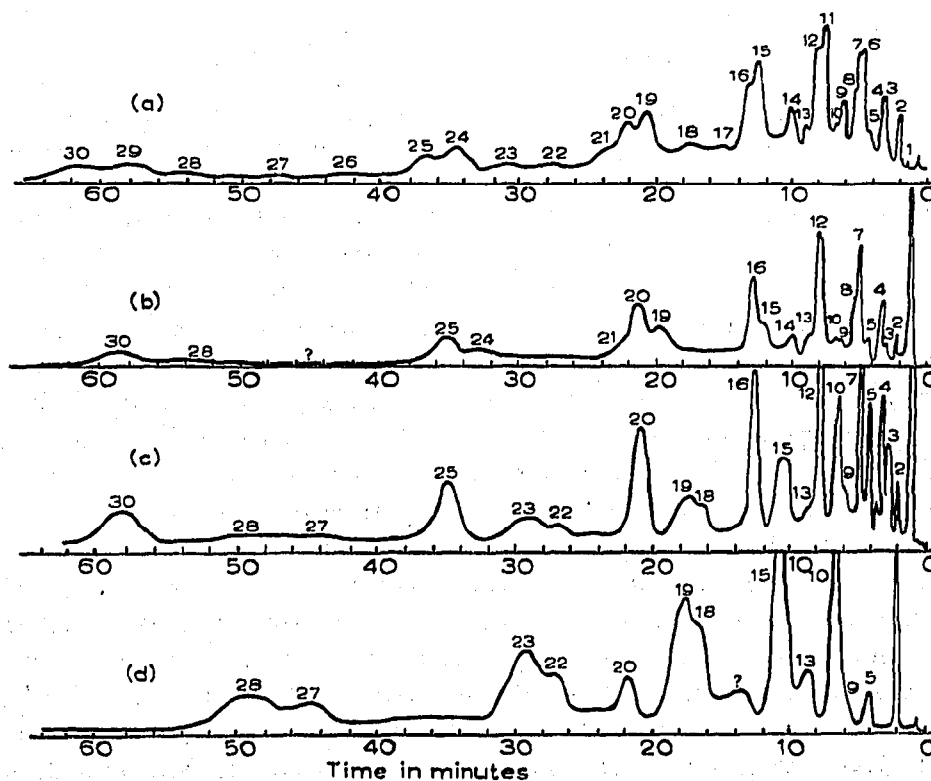

Fig. 5. Chromatograms of light oil neutral oil (a), and the residual oil from it after successive treatment with 80 % sulphuric acid (b), 98 % sulphuric acid (c), and passage through molecular sieve 5A column at 220° (d). The chromatograms are all on Apiezon L column at 160°. Sample size (a) 5 μl, (b) 8 μl ethereal solution, (c) 10 μl ethereal solution, (d) 6.5 μl benzene solution; carrier gas: He; inlet pressure: 25 lb./sq. in.; outlet pressure: atmospheric; flow rate: 48 ml/min.

consistent with olefinic and aromatic structures. These were also present to varying degree in six components trapped out of it at 160° on silicone (e.g. Fig. 6b). Advantage was taken of the splitting of these peaks on Apiezon L at 160° to collect the first of each of a number of pairs separately from the second of each. The spectra are shown in Fig. 6c and 6d. It can be seen that (c) shows bands at about 3050 cm^{-1} (w), 1650 cm^{-1} (m), 995 cm^{-1} (m) and 910 cm^{-1} (s), which are absent or much weaker in (d). These bands are consistent with a vinyl type alkene structure as in a 1-olefin.
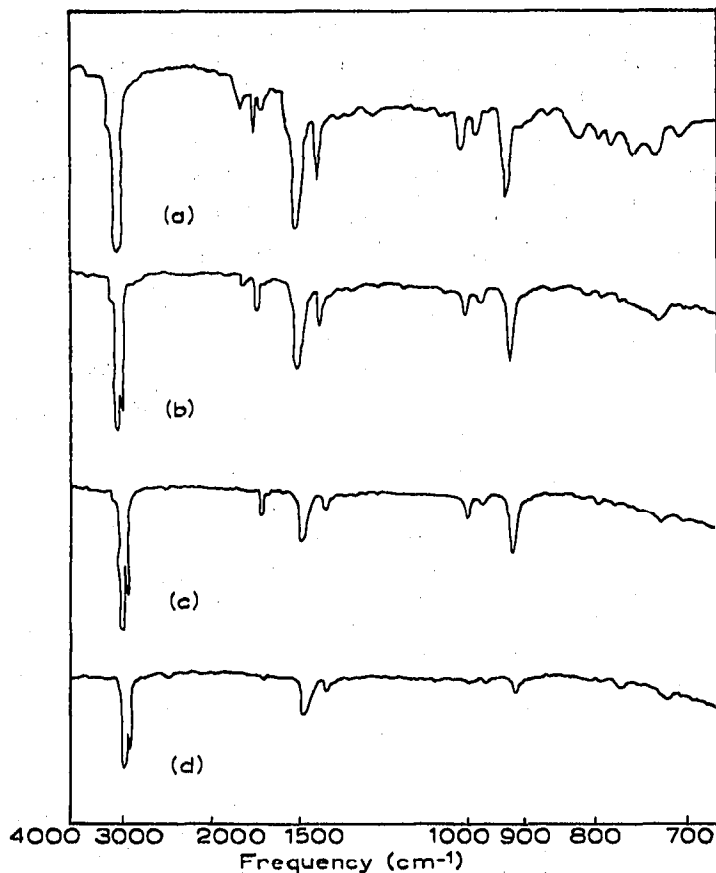

Fig. 6. Infrared spectra of: (a) Neutral oil from light oil. (b) Typical major peak trapped from light oil neutral oil on silicone column at 160°. (c) Combined peaks 11, 15, 19, 24 and 29 trapped from light oil neutral oil on Apiezon L column at 160°. (d) Combined peaks 12, 16, 20, 25 and 30 trapped from light oil neutral oil on Apiezon L column at 160°.

Successive removal of components from light oil neutral oil

This oil was subject to treatment designed to remove successively olefins, aromatics and normal paraffins. The oil was examined after each such treatment. The resulting chromatograms on Apiezon L at 160° are shown in Fig. 5b, 5c and 5d.

The oil was first extracted with 80 % sulphuric acid, giving a volume reduction of 23.3 %. The first of each double peak was either eliminated or drastically reduced. This indicated the presence of a series of olefins (peaks 3, 6, 11, 15, 19, 24, 29 and 31).

Further extraction with 98 % sulphuric acid removed only a few minor peaks (8, 14, 21 and rest of 24), although the reduction in volume corresponded to 51.7 % of the original light oil. This high figure is believed to be the result of the extremely long contact time between the oil and the acid necessitated by emulsion formation,

and is therefore not considered a true indication of the aromatic content. FOWKES *et al.*[14] have noted that a considerable amount of the lower boiling material from the neutral oil from a lignite tar was removed by successive extraction with sulphuric acid of increasing strength.

A sample of 100 µl of the residual oil was next passed through the molecular sieve 5A column at 220° in order to remove the normal paraffins, after the manner of BRENNER AND COATES[15] and WITHAM[16]. The residue was collected and was chromatographed on Apiezon L at 160°. Fig. 5d shows that the peaks eliminated were 3, 4, 7, 12, 16, most of 20, 25, 30 and 32. All of these except 3 were second peaks in the major pairs originally, and were thus shown to correspond to a series of normal paraffins. The part of peak 3 eliminated does not appear to be a normal paraffin, and its origin is unknown.

The graph of log (relative retention time × 100) *versus* carbon number for these peaks is shown in Fig. 7. The straight-line relationship is quite good. On the same graph is a similar line for the peaks 3, 6, 11, 15, 19, 24, 29 and 31, previously shown
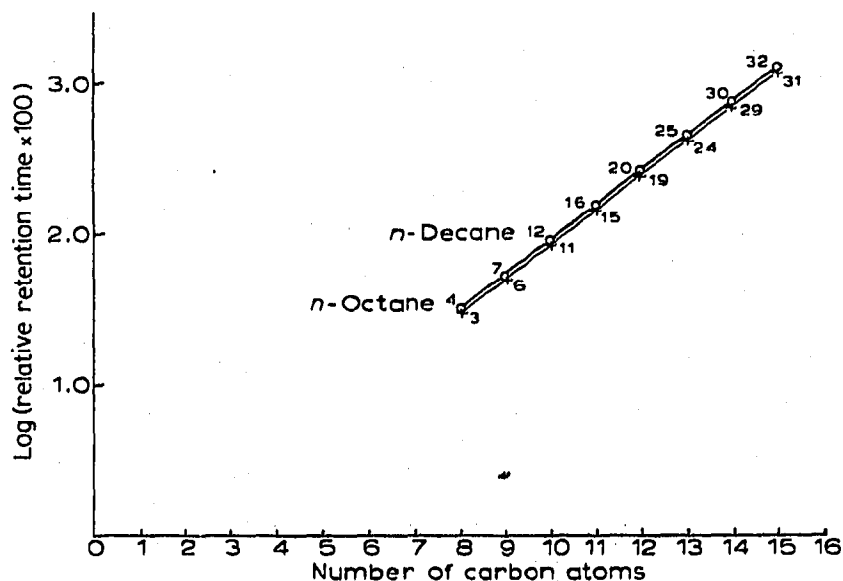

Fig. 7. Graph of log [relative retention time (to mesitylene reference) × 100] *versus* number of carbon atoms for the two series of major peaks from the light oil neutral oil on Apiezon L column at 160°.

to be olefins, on the assumption that the carbon number is the same as the normal paraffin associated with it (no reference substances available). Again the relationship is linear.

The final residual oil showed as major peaks components which were very minor in the original neutral oil. These would be either isoparaffins or naphthenes. It may be noticed that three double peaks, each with the second stronger than the first, are present (18–19; 22–23 and 27–28). These may well be members of two series of iso-paraffins.

These results are summarized in Table IV, where the relative retention times of the various peaks to mesitylene as reference are given. Identification of the various components is proposed in the final column. For the branched paraffins and isomeric

TABLE IV

NEUTRAL OIL FROM LIGHT OIL DISTILLATE AT 160° ON APIEZON L

Peak No.	Original relative strength	Relative retention time (mesitylene reference)				Identification proposed
		Originally	After 80% H₂SO₄	After 98% H₂SO₄	After 5A molecular sieve	
1	vw	0.110	Masked by added solvent			?
2	w	0.187	0.184 (w)	0.187 (w)	Masked	n-Heptane (0.175) + cyclohexane (0.182) etc.
3	w	0.297	0.273 (w)	0.274 (w)	—	n-Octane + ?
4	w	0.319	0.319 (m)	0.314 (m)	—	n-Octane
5	vw	0.446	0.447 (w)	0.443 (m)	0.451 (w)	Isononane or naphthene + ?
6	m	0.506	—	—	—	1-Nonene
7	m	0.532	0.531 (m)	0.533 (s)	—	n-Nonane
8	vw	0.571	0.570 (vw)	—	—	m- and p-Xylenes (0.567, 0.570)
9	w	0.685	0.678 (vw)	0.675 (vw)	0.675 (vw)	Isodecene + isodecane or naphthene
10	vw	0.743	0.740 (vw)	0.740 (s)	0.745 (s)	Isodecane or naphthene
11	s	0.858	—	—	—	1-Decene
12	m	0.904	0.897 (s)	0.902 (s)	—	n-Decane
13	vw	1.01	0.993 (vw)	1.05 (vw)	1.00 (w)	Isoundecane or naphthene
14	w	1.15	1.15 (w)	—	—	Aromatic e.g. pseudocumene (1.16)
15	s	1.44	1.41 (w)	1.25 (s)	1.25 (s)	1-Undecene + isoundecane or naphthene
16	m	1.53	1.52 (s)	1.52 (s)	—	n-Undecane
17	vw	1.76	—	—	—	Isododecene
18	vw	2.03	?	2.02 (w)	2.01 (m)	Isododecane or naphthene
19	s	2.43	2.35 (m)	2.09 (m)	2.11 (s)	1-Dodecene + aromatic + isododecane or naphthene
20	m	2.59	2.56 (s)	2.56 (s)	2.65 (m)	n-Dodecane + isododecane or naphthene
21	vw	2.76	2.73 (vw)	—	—	Aromatic
22	vw	3.3	?	3.3 (vw)	3.31 (m)	Isotridecane or naphthene
23	vw	3.6	?	3.54 (m)	3.56 (s)	Isotridecane or naphthene
24	m	4.10	3.96 (w)	—	—	1-Tridecene + aromatic
25	w	4.35	4.28 (s)	4.29 (s)	—	n-Tridecane
26	vw	5.1	—	—	—	Isotetradecene
27	vw	5.6	?	5.6 (vw)	5.50 (m)	Isotetradecane or naphthene
28	vw	6.4	6.4 (vw)	6.0 (w)	6.05 (m)	Isotetradecane or naphthene
29	w	6.9	—	—	—	1-Tetradecene
30	w	7.3	7.2 (m)	7.20 (s)	—	n-Tetradecane
31	vw	11.5	—	—	—	1-Pentadecene
32	vw	12.3	12.0 (w)	12.0 (m)	—	n-Pentadecane

olefins the carbon number has been taken in general as the same as the next higher normal member of the series, on the assumption that branched molecules usually have lower boiling points.

An attempt to carry out a similar series of experiments on the tar distillate neutral oil was unsuccessful because the chromatograms could not be run successfully at 160°, which would have been necessary to resolve the peaks. However, the neutral oil from tar distillate (A) was split into three fractions on the silicone column at 220°, and the lowest cut from this was examined by infrared and also chromatographed at 160° on Apiezon L. The spectrum was almost identical to that of the light oil (Fig. 6a) and the chromatogram, part of which is shown in Fig. 8, had the same major peaks as the

light oil except that the second peak (the normal paraffin) in each pair was stronger. These peaks are numbered to correspond with the equivalent peaks in the light oil as shown in Fig. 5a.

The spectra of the two higher boiling fractions of the tar distillate neutral oil tended towards that of paraffin oil which may indicate that olefins are present in
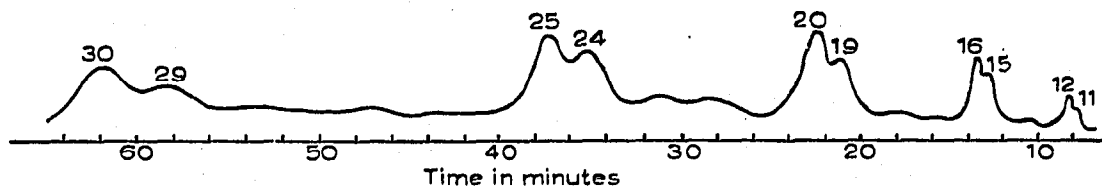

Fig. 8. Part of chromatogram of low-boiling fraction trapped from tar distillate (A) neutral oil on silicone column at 220°, rechromatographed on Apiezon L column at 160°. Sample size: 5 μl; carrier gas: He; inlet pressure: 25 lb./sq.in.; outlet pressure: atmospheric; flow rate: 48 ml/min.

lower amount in these fractions. However, the extent of the decrease is most probably misleading when estimated from the spectra as isolated double bonds would tend to be "swamped" by the long aliphatic chains present in both olefins and paraffins.

CONCLUSIONS

The neutral oils appear to be remarkably aliphatic, consisting of homologous series of normal paraffins and 1-olefins with minor amounts of branched isomers. They resemble the aliphatic fractions from the tars examined by COPPENS, BRICTEUX AND NEURAY[11], but are not associated with a large aromatic fraction as was found by these authors.

The same applies to comparison with the results of BOYER et al.[12] while, in addition, the coal carbonized in the present instance has generally a low proportion of the exinite macerals which BOYER et al. claimed were responsible for such straight-chain compounds in the tars they obtained.

The composition of the neutral oil would be a most important consideration in its utilization, e.g. mild hydrogenation may be used to produce diesel oil.

From the fundamental point of view of coal constitution the presence of such long carbon chains in such a "primary" tar gives rise to interesting questions, e.g.: Are there still longer chains in the pitch or is it aromatic in nature? Are such chains present in the coal itself, contrary to present opinion, or are they formed by polymerization of small fragments during carbonization? If so, is low-temperature tar from fluidized beds really so "primary" after all?

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SUMMARY

Acidic and neutral fractions of a light oil distillate and tar distillates produced by the low-temperature fluidized-bed carbonization of a New South Wales bituminous coal were examined by gas chromatography using silicone, Apiezon L and Molecular sieve 5A columns up to 220°.

The separation of the phenols was incomplete, but eleven peaks were tentatively identified. The distribution of phenols in the light oil distillate and in the tar distillate was very similar, the major components being the cresols and certain xylenols.

The neutral fractions were highly aliphatic as shown by infrared spectra of the whole oils and of components collected after chromatographic separation. Successive removal of olefins, aromatics and normal paraffins from the light oil followed by chromatography of the residue in each case showed that normal paraffins and 1-olefins ranging from C_7 to C_{15} (mainly C_9 to C_{13}) were the major constituents. The tar distillate appeared to be similarly constituted except that the proportion of olefins was somewhat less. The range was C_7 to C_{21} approximately (mainly C_{11} to C_{20}). Iso-paraffins, isomeric olefins and perhaps naphthenes were also present in minor amounts in both cases. Very little aromatic material appeared to be present.

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