INDIAN COAL TAR

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The possibility of the development of the coal tar industry in India is remote, as the quantity of tar available is small, only two fair-sized gas works, at Bombay and Calcutta, being in operation. Coal of good quality is found only in the Gondowana fields of Behar and Bengal, while the deposits in the adjacent areas of Central India consist of an inferior coal characterised by high ash and low calorific value. Coal of tertiary age generally inferior in quality is also found in Bikanir, the Punjab and Baluchistan. This low grade coal is not suitable for metallurgical purposes and only the best varieties are treated in coke ovens. Very little information is available regarding the tar which is at present manufactured and as it appeared that a comparison with material from different sources would be of interest, it was decided to examine any available samples and determine their chief constituents.

The two main sources of coal tar, *viz.*, gas tar and coke oven tar, in the West are also produced in India and specimens were obtained from the Oriental Gas Company, Calcutta, the Bombay Gas House, and the Jamshedpur coke ovens. The coal from which these were produced was obtained from the Raniganj coalfield, Dhemo Main and Parbelia, and the Jharia coalfield respectively. Coal tar being a product of destructive distillation, its composition varies with the varieties of coal used, plant and details of distillation and there are marked differences between the tar obtained in the manufacture of coal gas and that collected at the coke ovens. In gas works, vertical retorts which are gradually displacing the horizontal, give a tar having a lower specific gravity, less free carbon and pitch and more of tar oils. The gas tars examined are of normal quality and comparable with tars produced in a similar way in Europe the coke oven tar from Jamshedpur being an exception.

The first treatment of coal tar on a large scale consists in distilling it and collecting the distillate in four or five fractions. A few distillations with 25 lb. charges in a small iron still designed for the purpose were made but as larger quantities of some fractions were required, it was found more convenient to employ the fractions obtained by the Bengal Chemical and Pharmaceutical Works from the Oriental Company's gas tar.

EXPERIMENTAL

The two specimens of tars from the gas works were obtained in 20 gallon drums while that from Jamshedpur in a large barrel containing 500 lbs. They were thoroughly mixed in the containers and 3 litre samples withdrawn from each and kept in wide mouthed bottles.

Estimation of water.—The tar (100 g.) was mixed with benzene (50 c.c.) in a glass retort (250 c.c.) and distilled until a temperature of 200° was reached. The volume of water which separated was read off from the measuring cylinder into which the distillate had been received (Atack, *The Chemists' Year Book*, 1932, p. 982). This determination was also made by directly distilling the tar and the volume of water passing over with the distillate up to 170° was collected and measured.

Specific gravity.—The tar was dehydrated before the specific gravity was determined as follows. An open beaker containing the tar was placed in a water-bath kept at 50° for 24 hours. The water which separated was decanted and the last traces removed with filter paper. The specific gravity of the dehydrated tar was determined using a specific gravity bottle (50 c.c.) with a vertical groove in its stopper (Illingworth, *The Analysis of Coal and its By-products*, 1921, p. 139).

Free carbon.—The tar (10 g.) was introduced into a fat-free thimble (previously washed with xylene and dried and weighed) and extracted with xylene in a soxhlet apparatus until the solvent flowed out clear and no further change occurred in the weight of the thimble after drying. The weight of the free carbon in the thimble was determined and the percentage calculated.

Ash.—The tar (5 g.) was weighed in a porcelain crucible provided with a lid, heated cautiously to expel volatile matter and then ignited, cooled and weighed (*Standard Methods for testing Tar and its products*. By 'Standardisation of Tar Products Tests Committee'. W. Heffer & Sons, 1929, p. 41).

Distillation test.—The procedure and the conditions suggested by Illingworth (*ibid.*, pp. 133-137) for the distillation of the tar were adhered to throughout, as a slight change in the rate of distillation or the variation of half-an-inch in the position of the thermometer causes a difference of about 5 per cent. in the amount of distillate (*ibid.*, p. 135). The proportion of the various fractions is a rough estimate of the quantities of several products obtainable in works practice. The temperatures at which receivers are changed, differ considerably in the practice of different analysts and the following has been adopted in this

TABLE I.

Analysis of Coal tars.

[illegible]	[illegible]	[illegible]	Coke oven tar from Jamshedpur	Gas tar horizontal retort	Gas tar vertical retort	Coke oven tar
[illegible]	[illegible]	[illegible]	1·2445	1·213	1·103	1·142
[illegible]	2·0	4·0	...	3·9	3·8	2·0
[illegible]	[illegible]·4	2·6	17·4	22·0	2·4	4·0
Ash	0·07	0·12	0·07	...	...	...
Light oil (–170°)	3·2	8·2	*Nil*	3·4	9·1	4·1
Carbolic oil (170–230°)	12·5	12·5	*Nil*	6·0	10·2	8·0
Creosote oil (230–270°)	10·8	10·4	6·2	6·0	11·2	16·2
Anthracene oil (above 270°)	8·2	10·2	10·8	15·1	16·6	[illegible]
Pitch	[illegible]	[illegible]	80·0	[illegible]	51·9	53·0

investigation, figures in brackets giving the percentage of each fraction obtained from Calcutta gas tar: ammonia liquor, -110° (2-0); light oil, 110-170° (2-3); carbolic oil, 170-230° (8-10); creosote oil, 230-270° (8-10); anthracene oil (light), 270-350° (10); anthracene oil (heavy), above 350° (5); pitch, residue (62-65). The results obtained during the analysis of the several tars are given in Table I along with the constants for some typical gas and coke oven tars for comparison.

Tars are liable to vary from many causes and the results given for comparison in the table must therefore be looked upon only as a guide. The gas tars from Calcutta and Bombay compare well with vertical retort gas tars produced in other countries. Coke oven tar from Jamshedpur does not contain any of the lower boiling hydrocarbons or the lower phenols. The product does not compare well with those obtained from any of the different kinds of coke ovens.

The information obtained so far gives a general basis for the evaluation of the crude tars. Further examination is now necessary to determine the quantity of refined products obtained. The gas tar from Calcutta alone has been further examined. The tar (25 lb.) was distilled from a 5 gallon iron still designed for the purpose with a convex bottom and a stop-cock for running off the molten pitch, using a Fletcher burner during the distillation.

Larger quantities of the various fractions of the Calcutta gas tar were made available to us by the Bengal Chemical and Pharmaceutical Works to whom our best thanks are due for thus facilitating the work.

LIGHT OIL

The light oil fraction formed 2.5 per cent. of the whole tar, had a [illegible] 0.9971 and contained 0.5 per cent. water. The crude light oil (1030 g.) on cooling gave naphthalene (85.5 g.) or 0.2 per cent. on the whole tar. The light oil was analysed for its constituents according to the methods of Colman and Yeoman (*J. Soc. Chem. Ind.*, 1919, 38, 567).

Phenols and bases.—The crude light oil (600 c.c.) was fractionated once using a 12-pear Young column and 387 c.c. (65 per cent. crude light oil or 1.63 per cent. of the whole tar) distilled over below 200°. This fraction is hereafter called the prepared light oil. The prepared light oil (150 c.c.) was shaken with 10 per cent. aqueous caustic soda (40 c.c.) for five minutes and allowed to settle for half-an-hour. It was washed again with caustic soda. The loss of volume (31 c.c. or 20.7 per cent by volume on prepared light oil or 0.3 per cent. on the whole tar) represents the phenols or tar acids present.

The tar (119 c.c.) freed of the phenolic bodies was shaken with three separate volumes of 25 c.c. sulphuric acid (1 :2) (Illingworth, *ibid.*, p. 206) the acid extracts mixed, washed with ether and basified with 20 per cent. caustic soda solution. The liberated bases measured 14 c.c. or 0.15 per cent. on the whole tar or 9.3 per cent. on the prepared light oil.

Unsaturated hydrocarbons.—The tar devoid of phenols and bases was shaken with 95 per cent. sulphuric acid (13 c.c.) for exactly 5 minutes and a diminution of 18 c.c. (0.2 per cent. on whole tar or 12 per cent. on prepared light oil) was observed.

Determination of benzene, toluene and xylene.—Phenols, bases and unsaturated hydrocarbons having been removed, the oil (300 c.c.) was fractionated with a 12-pear Young column at the rate of 4 c.c. per minute and the following fractions were obtained :

Fraction	B. P. at 685 mm.	B. P. at 760 mm.	Vol. of oil in c.c.
A	-91·7	-95	45
B	91·7–136·5	95–140	76
C	136·5–156·3	140–160	39
D	156·3–196·3	160–200	100
E	Above 196·3	Above 200	37

90's *benzol.*—On fractionating A (45 c.c.), the oil boiling upto 90° was 37 c.c. which represents 90's benzol, i.e., the fraction upto 90° (7.1 per cent. on prepared oil).

Benzene and toluene.—90's benzol (100 c.c.) on fractionation gave 84.2 c.c. boiling below 81.7° (85° at 760°). The amount of benzene read off from Colman and Yeoman's graph was 91.3 per cent. and toluene 8.7 per cent.

The fraction 90-140° (fraction B + residue from 90's benzol) gave on distillation at 685 mm. the following results :—

-101·5 (105° at 760 mm)	...	45·5 c. c.
101·5–112·2 (116° at 760 mm)	...	9·8 c. c.
Residue	...	44·2 c. c.

The benzene, toluene and xylene read off from the graph were 24, 55 and 21 per cent. respectively.

Solvent naphtha.—Fraction C (39 c.c.) along with xylene in fraction 90-140° represents solvent naphtha, i.e., 6.9 per cent. on prepared light oil or 0.17 per cent. on the whole tar.

Heavy naphtha.—The fraction 160-200° (100 c.c. or 12.5 per cent. as prepared light oil or 0.3 per cent. on the whole tar) represents heavy naphtha.

The percentage composition of the prepared light oil is as follows :—phenols, 20.7 ; pyridine bases, 9.3 ; unsaturated hydrocarbons, 12.0 ; benzene, 9.8 ; toluene, 9.2 ; solvent naphtha, 6.9 ; heavy naphtha, 12.5 ; naphthalene, 8.2.

CARBOLIC OIL OR MIDDLE OIL

Specific gravity d^{25}_{25} 0.9876 ; $d^{15.5}_{15.5}$ 0.9947. On distillation at 685 mm. up to 170°, 1.8 per cent. water was collected. Between 140-195° and 195-210°, 27 and 44 per cent. distilled over or 71 per cent. below 210°. According to Lunge and Keane a good quality carbolic oil should contain 60 per cent. distilling below 210°.

Naphthalene.—The oil (197.5 g.) kept at ordinary temperature (21-25°) for 24 hours deposited naphthalene (22.5 g.) or 11.4 per cent. of the carbolic oil (1.0 per cent. on whole tar).

Phenols.—The oil (400 c.c.) shaken with 20 per cent. warm sodium hydroxide (80 c.c.) showed a diminution in volume of 120 c.c. or 30 per cent. by volume. The phenols (100 c.c.) on distillation at 685 mm. yielded the following fractions :

Fraction	B. P.	Volume in c. c.	Remarks
A	170–186°	23·5	50 per cent. phenol.
B	186–195°	34·0	31 per cent. *m*-cresol.
C	195–210°	3·4	...
D	210–220°	0·6	...

According to Fox and Barker's method (*J. Soc. Chem. Ind.*, 1917, **36**, 842 ; 1920, **39**, 169) fraction *a* was found to consist of 50 per cent. phenol or 3.6 per cent. on the middle oil ; fractions *b* and *c* mixed together (10 g.) gave trinitro-*m*-cresol (5.4 g.) by Raschig's method (Illingworth, *ibid.*, p. 192) showing the *m*-cresol content to be 31 per cent. or 3.4 per cent. on the middle oil ; *o* and *p*-cresols formed 11.2 per cent. on the middle oil.

CREOSOTE OIL

This portion of the tar boiling mainly between 230-270° had water 0.1 per cent., d^{25}_{25} 1.0244, d^{38}_{38} 1.0147 and deposited no naphthalene on cooling to 15.5° (Illingworth, *ibid.*, p. 204) ; fraction 220-230/685 mm. of the neutral oil, however, deposited 13.9 per cent. naphthalene on creosote oil. On distillation at 685 mm. 67.5 and 21.2 per cent.

distilled over between 210-250 and 250-300 respectively. The creosote oil contained phenols (13.5 per cent. by volume) and bases (3.1 per cent. by volume). The neutral oil (100 c.c.; d^{25}_{25} 1.0156) on distillation at 685 mm. gave the following results:

Fraction	B. P.	Volume in c. c.	Remarks
1	-220°	18·0	From 1 and 2, 16.7 naphthalene
2	220-230°	16·3	...
3	230-250°	29·3	Liquid
4	250-260°	6·3	Liquid
5	260-270°	3·4	Partial solidification
6	270-320°	5·5	3·7 g. yellow solid

ANTHRACENE OIL

The anthracene oil (light) on analysis gave the following results: d^{25}_{25} 1.0373; phenols 13.9 per cent.; bases (extracted with 9 per cent. hydrochloric acid) 4.2 per cent. On cooling no naphthalene or anthracene separated. The neutral oil (81 per cent.) gave 14.56 per cent. respectively between 240-270°, 270-300° and 300-340°. The last fraction partially solidified and yielded 16 per cent. crude anthracene or 8.9 per cent. of the anthracene oil.

Bases.—The liberated bases (246 g.) were distilled with a 8-pear Young column at 685 mm. pressure and the following fractions obtained:

Fraction	B. P.	Weight in g.	Yield per cent. in total bases
I	170-230°	14·0	5·3
II	230-260°	65·5	22·8
III	260-275°	19·8	8·0
	Residue	143·0	58·1

Isolation of quinoline and isoquinoline.—The bases (220 g.) boiling between 230-255° were obtained by fractionation of the crude bases twice. The isoquinoline which is a stronger base than quinoline was isolated from the above fraction by the method of Harris and Pope (*J. C. S.*, 1922, **121**, 1029). The fraction was shaken with sulphuric acid (4 N) for half a minute and the unattacked portion removed with benzene. The bases were then fractionally precipitated, adding enough ammonia (4 N) to the acid solution to liberate only 20 per cent. of its content in bases and extracting them with benzene every time. After eleven repetitions of the ammonia treatment, the whole of the remaining base was precipitated with excess of ammonia. The last benzene extract contained isoquinoline. The benzene is distilled and the residue mixed with twice its volume of alcohol and concentrated sulphuric acid added, keeping the temperature at 25-30°. The crystalline isoquinoline sulphate (m.p. 206°; 1.5 g.) separated out on standing, the yield of isoquinoline being 0.08 per cent. on the anthracene oil. From the earlier fractions quinoline (144.5 g.) was liberated or 1.3 per cent. of the anthracene oil.

Heavy anthracene oil.—This fraction boiled above 350° and had d $^{45}_{45}$ 1.0758 ; bases 2.5 per cent. (extracted with 9 per cent. hydrochloric acid) ; phenols 6.7 per cent. (with 25 per cent. aqueous caustic soda).

Anthracene.—On cooling the heavy anthracene oil (200 g.) to 10°, a solid separated, which was washed with alcohol and dried and found to be crude anthracene (18.2 g.) or 9.1 per cent. of the anthracene oil. The anthracene in this crude material was estimated by Luck's process (Illingworth, *ibid.*, p. 199). From crude anthracene (1 g.) anthraquinone (0.35 g.) was obtained or 2.7 per cent. anthracene on heavy anthracene oil.—

SUMMARY

1. The gas tars from Calcutta and Bombay gas houses are of normal quality and compare well with similar tars produced in Europe.

2. The coke oven tar from Jamshedpur was of poor quality and contained no light oil. 80 per cent. being pitch.

3. The different fractions of the gas tar from Calcutta had the following percentage composition :

(a) *Light oil*—Amoniacal water 0.6 ; benzene 6.8 ; toluene 7.2 ; solvent naphtha (xylene and others) 6.7 ; heavy naphtha 12.2 ; pyridine bases 5.6 ; phenol 1.3 ; cresols 14.1 ; naphthalene 6.3.

(b) *Middle oil.*—Phenol 3.6 ; *o* and *p*-cresols 11.2 ; *m*-cresol 3.4 ; naphthalene 11.4.

(c) *Creosote oil.*—Phenols 13.5 ; bases 3.1 ; naphthalene 13.9.

(d) *Anthracene oil.*—Quinoline 0.9 ; isoquinoline 0.03 ; anthracene 2.7.

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