

CHARACTERIZATION OF TAR FROM GASIFICATION OF MAKERWAL COAL

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(Received September 20, 1966)

Tar from the gasification of Makerwal coal was characterized by solvent extraction and elution adsorption chromatography. The whole tar is separated into broad chemically identical fractions. The results of some preliminary evaluation experiments are also discussed, in the light of which it may be possible to find some suitable use for this tar.

Introduction

The tar under investigation is obtained by the gasification of Makerwal coal from Trans-Indus area by the Lurgi process at Daudkhel Fertiliser Factory for the production of hydrogen, for the subsequent manufacture of ammonium sulphate. By this method 2.2 tons per day of a lower boiling fraction (60°-200°C) designated as 'Raw gasoline' and 5 tons per day of a higher boiling tar fraction, are obtained as by-products. A process has been developed to utilise the "raw gasoline" for the production of an insecticide.¹ However, no suitable use appears to have been found to utilise the higher boiling tar fraction. The object of this work is therefore, to characterize this tar with a view to finding some suitable use for this by-product or similar products as and when they are available.

A method for characterization of tar based on solvent extraction and chromatography was used.² It has several advantages over the conventional method of tar analysis based on distillation technique.

Experimental

As a necessary preliminary the tar was distilled by the standard method³ to ensure that it did not contain any lower boiling compounds, (below 150°C) which would otherwise escape during the recovery of solvents from the fractions of tar in the above-noted method of analysis.² The results of tar distillation are given in Table 1. The moisture content of tar was determined by the Dean and Stark method. The analysis of tar in duplicate was carried out by two different solvent extraction methods and subsequent elution adsorption chromatograph on silica gel as follows:—

(a) The method of tar analysis described by Blunt and Vahrman² was followed, excepting that the benzene-insoluble portion was not analysed further. 20 g of *undehydrated* tar were used for each analysis (Table 2).

(b) As an alternate method of analysis, 20 g of undehydrated tar were extracted with successive portions of benzene till the extract was almost colourless. The extracts were mixed and centrifuged at 3000 rev/min to remove suspended insoluble material if any. From the extract, phenols and bases were separated as in (a). The neutral portion after recovering benzene was extracted with light petroleum (40°-60°C) and

TABLE I.—DISTILLATION OF TAR.
(% cumulative yields, v/w)

Temperature °C	Tar distillate
B.p. of tar ..	166
160 ..	1.8 (water)
170 ..	2.2
180 ..	2.3
190 ..	2.5
200 ..	3.5
210 ..	5.3
220 ..	8.2
230 ..	12.7
240 ..	16.5
250 ..	18.0
260 ..	22.4
270 ..	28.7
280 ..	47.4
290 ..	51.7
300 ..	58.8
310 ..	63.0
320 ..	64.0
330 ..	65.6
340 ..	66.6
350 ..	72.1
360 ..	73.1
Pitch > 360 ..	24.3

chromatographed as before on a silica gel column to determine its composition (Table 3).

For the preparation of the bulk sample of total benzene-soluble phenols from tar, the solvent extraction technique as described in (b) was used. The results of distillation of these phenols are given in Table 4.

The refractive indices of hydrocarbon fractions were measured in an Abbe's refractometer. The fractions from tar analysis were also examined by the IR absorption spectroscopy in a recording double beam spectrophotometer.

Olefins were determined in aliphatic fraction (a) by the Wijs method and were quantitatively separated from paraffins by chromatography of the iodine monochloride addition compounds

followed by regeneration to the unchanged olefins by refluxing with alcoholic potassium iodide⁴ (Tables 2 and 3).

Results and Discussion

The initial boiling point of this tar was found to be 168°C and only a very small amount 1.7% excluding moisture, distilled below 200°C. The bulk of this tar distilled between 200° and 360°C (Table 1). Hence the method of tar analysis used was without prior separation by distillation of lower boiling fraction. The examination of different fractions indicated that phenols were evenly distributed in the distillate fractions and the pitch.

The results of tar analysis (Table 2) showed that this tar contained 10.3% w/w phenols, 3.4% w/w bases and the remainder contained neutral

TABLE 2.—ANALYSIS OF WHOLE TAR (A).

Fraction	%w/w; dry tar bases	Remarks
1. Benzene-insoluble	2.89	Moisture content of tar 2.4%w/w.
2. Benzene-soluble, light petroleum-insoluble	(total 19.88)	
Bases (lower mol. wt.)	0.49	
Phenols	1.61	
Bases (higher mol. wt.)	0.30	
Neutral	10.39	
Insoluble	7.09	
3. Benzene-soluble, light petroleum-soluble	(total 71.00)	
Bases (lower mol. wt.)	2.12	
Phenols	8.70	
Bases (higher mol. wt.)	0.46	
Insoluble	3.39	
Neutral		
Chromatographic fraction (a)	9.09	A white soft wax, paraffins 4.0% (n_D^{20} 1.4560) and olefins 5% (n_D^{20} 1.4612).
" " " (b)	4.40	A yellow mobile liquid, substituted hydroaromatic hydrocarbons (n_D^{20} 1.5168).
" " " (c)	33.88	A reddish brown viscous liquid, substituted aromatic hydrocarbons (n_D^{20} 1.6230).
" " " (d)	8.96	A dark brown resinous material, aromatic compounds containing OH.
4. Losses in extraction and chromatography (by difference).	6.23	

TABLE 3.—ANALYSIS OF WHOLE TAR (B).

Fraction	%w/w: dry tar basis	Remarks
1. Benzene-insoluble	3.30	
2. Benzene-soluble	(total 91.22)	
Bases (lower mol. wt.)	1.85	
Phenols	11.20	
Bases (higher mol. wt.)	0.97	
Benzene-insoluble	5.66	
Neutral		
light petroleum-insoluble	15.10	
light petroleum-soluble	(56.44)	
chromatographic fraction (a)	8.70	A white, soft wax-paraffins 3.8% (n_D^{20} 1.4584) and olefins 4.9% (n_D^{20} 1.4624).
" " " (b)	4.63	A yellow mobile liquid-substituted hydroaromatic hydrocarbons (n_D^{20} 1.5312).
" " " (c)	35.10	A reddish-brown viscous liquid, substituted aromatic hydrocarbons (n_D^{20} 1.6314).
" " " (d)	8.01	A dark-brown resinous material-aromatic compounds containing OH.
3. Losses in extraction and chromatography (by difference.)	5.28	

compounds of different molecular complexities. The benzene-insoluble portion of the tar was not analysed further as the yield of this fraction was small. Moreover it contained about 50% free carbon. This indicated that the tar had undergone secondary cracking during its production.

The resinous benzene-soluble, light petroleum-insoluble fraction consisted of phenolic, basic and neutral compounds, which according to Morgan's terminology⁵ are designated as resinols, resinamines and resinenes, respectively. These are complex higher molecular weight materials which had undergone relatively lesser degree of secondary cracking during the production of tar.

As shown in Table 2 the two insolubles noted under benzene-soluble, light petroleum-insoluble and benzene-soluble, light petroleum-soluble fractions are initially benzene-soluble and light petroleum soluble, respectively. This is because of the mutual solubility effects of certain phenolic compounds present in the tar that these are initially soluble in benzene and light petroleum. Once

TABLE 4.—DISTILLATION OF PHENOLS FROM TAR.
(% cumulative yield v/w)

Temperature °C	Distillate	Remarks
B.p. of phenols ..	185°	} No neutrals
190 ..	0.86	
200 ..	2.16	
210 ..	5.62	
220 ..	14.71	
230 ..	18.18	
240 ..	21.64	
250 ..	25.10	
260 ..	28.13	
270 ..	30.83	
280 ..	33.00	} 2% neutrals
290 ..	35.93	
300 ..	41.11	
310 ..	44.58	} 5% neutrals
320 ..	61.25	
Pitch > 320 ..	32.10	} 18% neutrals

the phenols are separated they no more influence the solubility of the solvent and as a result these insolubles are obtained. The results of analysis by two different solvent extraction techniques seem to agree well (Tables 2 and 3).

Out of about 10% total benzene-soluble phenols only 1.5% are resinols and the remainder relatively simpler phenols. The results of distillation of total benzene-soluble phenols are given in Table 4. This fraction contained roughly 18% simpler phenols like phenols, cresols and xylenols distilling upto 230°C. It was noticed that during distillation small amount of phenols distilling in the range of 250°-300°C, had undergone some dephenolation as confirmed by alkali extraction, and IR spectra (absence of band near 3600 cm^{-1} of alkali unextracted distillate fractions).

This tendency of dephenolation was found to increase with the increase in the boiling range of phenolic compounds. In the phenolic pitch it was found that about 18% of this fraction was no more extractable by alkali solution. This can, however, be minimised by distillation under reduced pressure.

Out of the total 3.4% bases 0.8% consisted of more complex resinamines and the remainder contained relatively simpler bases.

The neutrals consisted of about 14% resinenes and 56% of less complex light petroleum-soluble material. The neutral benzene soluble light petroleum-soluble fraction was found by chromatography and subsequent examination of fraction to consist of (a) mixture of n-, iso-, and cycloparaffins and olefins (b) substituted hydroaromatic hydrocarbons (c) substituted aromatic hydrocarbons and (d) neutral oxygen containing aromatic compounds.

On the basis of the above analysis and considering the yield of tar it appears that separation of individual phenols, especially the lower boiling

phenols, would not be a commercially feasible proposition. However, the total phenolic fraction can partially meet the requirements of different chemical industries, such as in the manufacture of disinfectants and phenolic resins etc. The neutral tar, after separating phenols, or tar as such can be chlorinated which can possibly be used in wood preservation. Some of the initial experiments carried out in this connection showed that 20-30% of chlorine can easily be introduced by passing chlorine through tar at room temperature. The tendency of polymerisation of tar can be avoided by keeping the temperature of tar below 20°C particularly at the initial stage of chlorination. The chlorinated product thus obtained is a viscous liquid and has good spreading property.

Different types of hydrocarbons and particularly aromatics can be separated by known solvent extraction techniques⁶ but the quantities of tar available at the moment do not justify this separation on commercial scale.

Acknowledgement.—The authors thank Dr. Salimuzzaman Siddiqui, F.R.S., for his valuable suggestions and interest in this work, and to the West Pakistan Industrial Development Corporation for the sample of tar.

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