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GAS CHROMATOGRAPHIC INVESTIGATION OF RAW WASTEWATER FROM COAL GASIFICATION

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SUMMARY

Tars produced from a fixed-bed laboratory coal gasifier were characterized using two glass capillary gas chromatography systems. In one system, sulfur heterocyclics and polycyclic aromatic hydrocarbons were simultaneously monitored by splitting the column effluent to a sulfur specific dual-flame photometric detector and a flame ionization detector. In the other system, nitrogen heterocyclics and polycyclic aromatic hydrocarbons were simultaneously monitored using a nitrogen-specific detector and a flame ionization detector. Typical dual-detector profiles for tars produced from gasification of a bituminous coal and a lignite are presented and discussed.

INTRODUCTION

The shortage of crude oil and increased foreign dependence has triggered the development of synthetic fuel production processes in the United States. Coal conversion to clean liquid and gaseous fuels is receiving the maximum attention because of vast U.S. coal reserves. Side by side with the development of coal gasification and liquefaction processes, assessment of environmental problems associated with these processes is also receiving major emphasis.

The Research Triangle Institute (RTI) has undertaken a five-year study to determine pollution problems associated with coal gasification. Several coals ranging in rank from lignite to anthracite have been gasified in a laboratory reactor under a variety of conditions. Both coal type and operating conditions have been shown to influence pollutant production. Details of the reactor and the associated sampling system are available in various reports[1-4]. A variety of analytical techniques[1] including gas chromatography (GC), high-performance liquid chromatography (HPLC), GC–mass spectrometry (MS), atomic absorption spectroscopy, Fourier transform infrated spectroscopy, ion chromatography, and wet chemical procedures have been used to characterize the gaseous, liquid, and solid effluent streams from the coal gasifier.

In this paper, GC characterization of the tar portion of the liquid effluent stream that is produced from fixed-bed gasification is described. Typically, one gram of the liquid stream is produced per gram of coal gasified, of which *ca.* 2–4% is tar and the rest aqueous. Simulated GC distillation shows that this tar boils between

150 and 650°C[1] and has a number-average molecular weight of *ca.* 180 to 200, as measured by vapor phase osmometry[5]. In the interest of space, only typical results are presented, with emphasis placed on experimental details. Detailed results are available elsewhere[2].

EXPERIMENTAL

Preliminary characterization of wastewater consisted of first separating the aqueous portion and tar by filtration. The aqueous portion was then exhaustively extracted using methylene chloride. At this point, mainly phenolics remained in the aqueous portion and were characterized by a reversed-phase HPLC technique[1]. The tar was subjected to a solvent partitioning scheme similar to one used by Novotny *et al.*[6]. This scheme separated the tar into five fractions including acids, bases, polar neutrals, non-polar neutrals, and polynuclear aromatic hydrocarbons (PAHs). Qualitative characterization of these fractions was carried out by GC–MS. The entire procedure was rather tedious; however, enough background information was now available about the nature of the tar sample so that a more direct and rapid GC technique could be used. This technique was based on high-resolution glass capillary GC and was initially only applied for the quantitation of the polynuclear aromatic fraction of the tar[1]. Recently, the technique has been extended for simultaneous detection of specific heterocyclic compounds and PAHs in tar directly; the technique is described below.

Two Varian 3700 glass capillary GC systems are used, one consisting of a flame ionization detector (FID) and a flame photometric detector (FPD), and the other consisting of a FID and a nitrogen–phosphorus detector (NPD). The systems are all-glass from the injector to the detector. Wall-coated OV-101 capillary columns are used in each system, and the column effluent is split 50:50 by means of a zero-dead volume splitter. All sample-wetted parts are made of glass. Helium is used as carrier gas as well as makeup gas. The FPD for specific detection of sulfur species is of a novel design consisting of two hydrogen-rich flames. The first flame is used to destroy the organic matrix so that a more uniform S-emission response can be produced from the second flame[7]. This reduces the problem of organic quenching of the response. The NPD is specific to organic nitrogen with a specificity of greater than 1000:1 for nitrogen *versus* carbon. The principle, based on an electrically heated alkali bead, is described in detail by Patterson and Howe[8]. These authors claim longer bead life and more stable response than for beads used in the past.

The tars are dissolved in methylene chloride at concentrations of *ca.* 15–20 µg/µl, and a 2–3-µl sample is injected following the "splitless technique" outlined by Grob and Grob[9]. Identification of peaks is carried out by combining information from GC–MS results, boiling point, and retention time of pure standards. Chromatographic conditions and typical results are described below.

RESULTS AND DISCUSSION

In Fig. 1, dual-detector FID–FPD chromatograms for tars from gasification of an Illinois No. 6 bituminous coal and a lignite coal are shown. In Fig. 2, the corresponding dual-detector FID–NPD chromatograms are shown. Compound identifica-
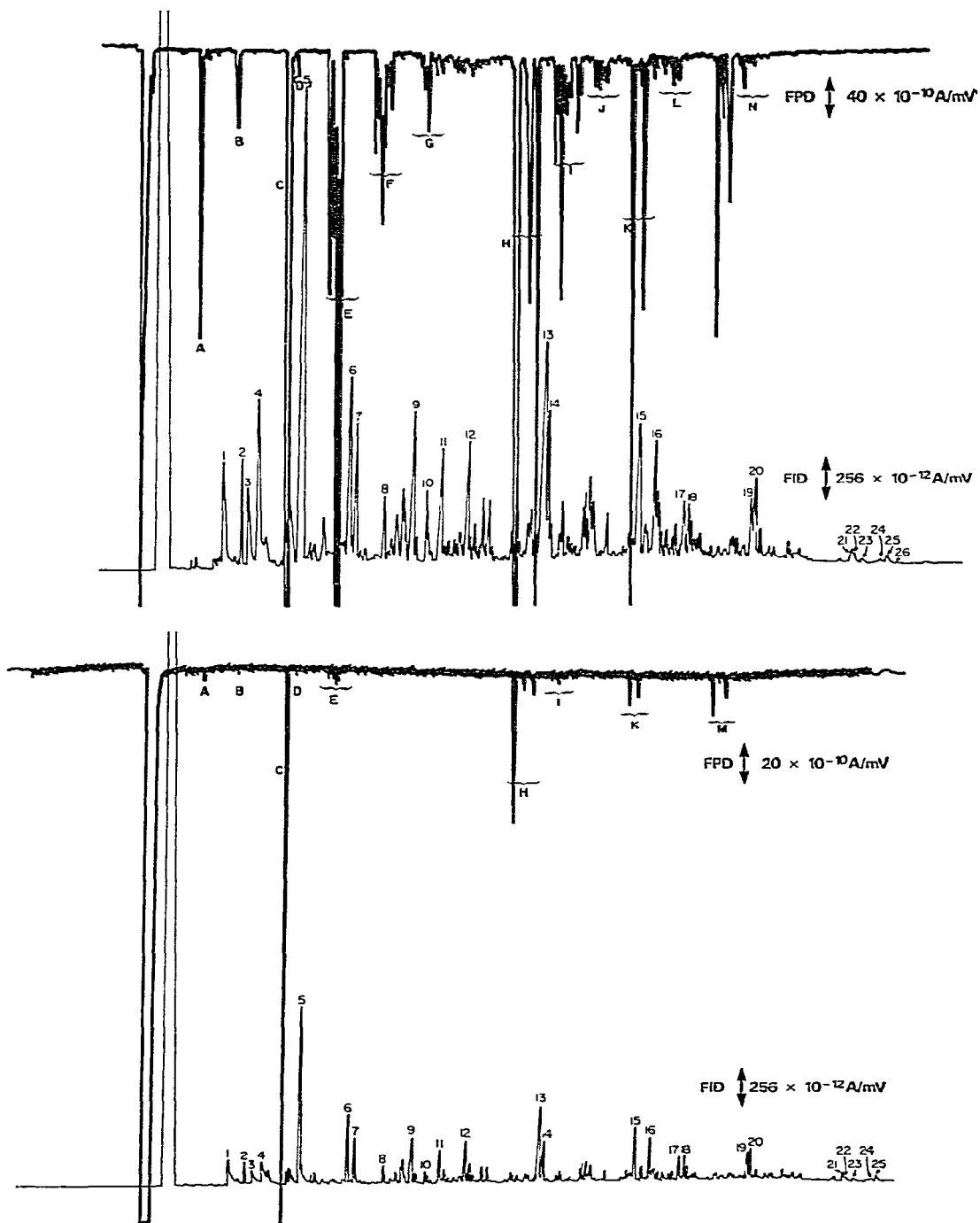
Fig. 1. Dual-detector FID–FPD chromatograms of Illinois No. 6 tar, 46 μg in methylene chloride (top) and N. Dakota lignite tar, 35 μg in methylene chloride (bottom). Conditions: instrument, Varian 3700 gas chromatograph; injector temperature, 250°C; detector temperature, 280°C; "Grob" splitless injection; column, 30 m × 0.25 mm OV-101 wall-coated open tubular; pressure, 21 p.s.i.; temperature, 70°C (1 min), programmed at 4°C/min to 260°C; FID–FPD split, 1:1.
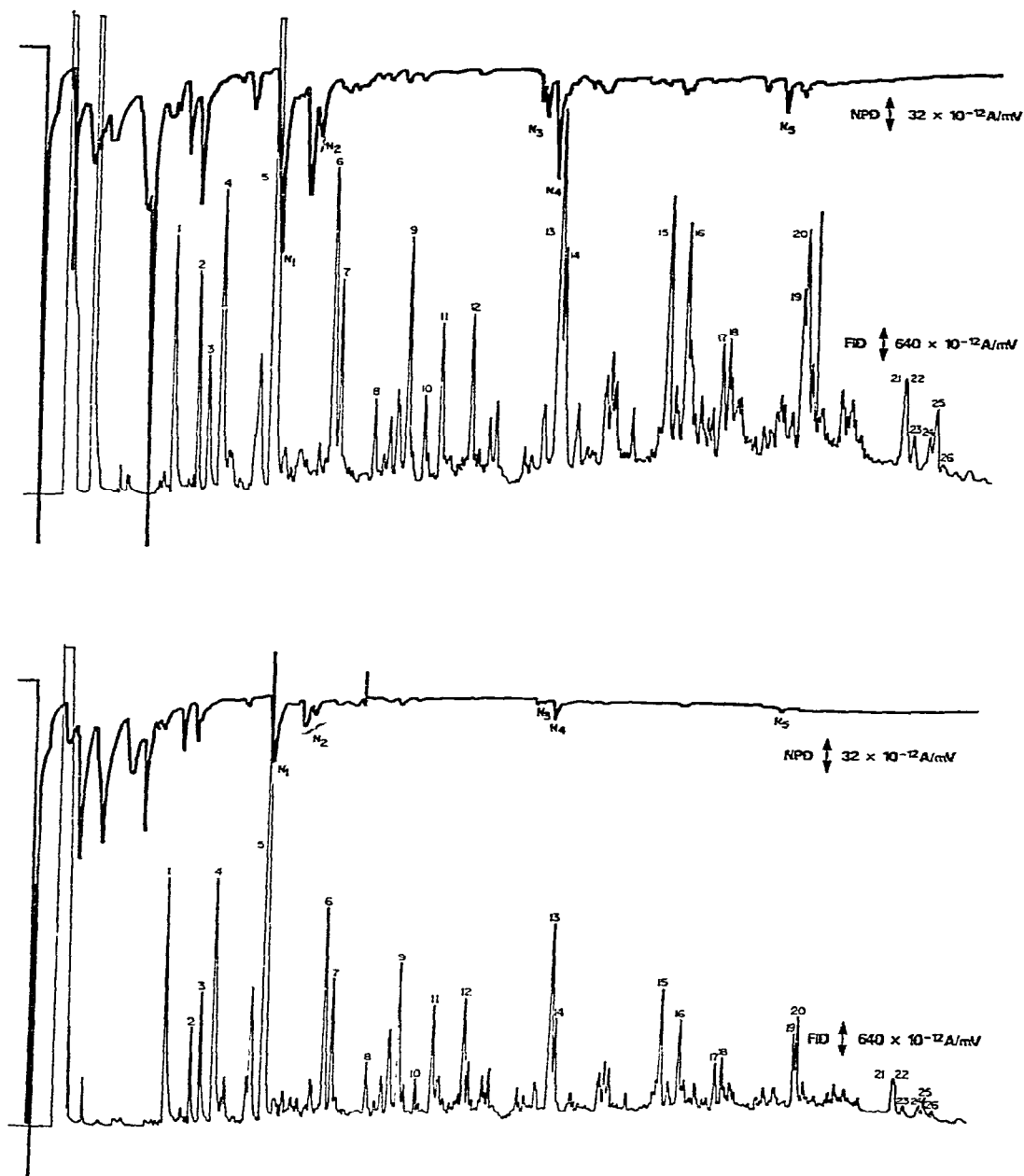
Fig. 2. Dual-detector FID–NPD chromatograms of Illinois No. 6 tar, *50 μg* in methylene chloride (top) and N. Dakota lignite tar, *60 μg* in methylene chloride. Conditions: column, 20 m × 0.25 mm OV-101 wall-coated open tubular; pressure, 16 p.s.i.; temperature, 50°C (1 min), programmed at 4°C/min to 260°C; FID–NPD split, 1:1, other conditions as in Fig. 1.

TABLE I

COMPOUND IDENTIFICATION

FID	FPD	NPD
1 Phenol	A Benzenethiol	N_1 Quinoline
2 Indene	B Toluenethiol or benzyl mercaptan (tent.)	N_2 Methylquinolines
3 O-Cresol	C Benzothiophene	N_3 Benzoquinolines
4 m- and p-Cresols	D Dihydrobenzothiophene (tent.)	N_4 Acridine
5 Naphthalene	E Methyl benzothiophenes	N_5 Benzoacridine
6 2-Methylnaphthalene	F C_2 and dimethyl benzothiophenes	(tent.)
7 1-Methylnaphthalene	G C_3 and trimethyl benzothiophenes	
8 Biphenyl	H Dibenzothiophene and naphthothiophene	
9 Acenaphthylene	I Methyl dibenzo- and methyl naphtho-	
10 Acenaphthene	thiophenes	
11 Dibenzofuran	J C_2-dibenzothiophenes	
12 Fluorene	K Fluoranthene and pyrene sulfur	
13 Phenanthrene	derivatives (tent.)	
14 Anthracene	L Methyl substituted (K) (tent.)	
15 Fluoranthene	M Naphthobenzothiophenes	
16 Pyrene	N Methyl naphthobenzothiophenes	
17 Benzo[a]fluorene		
18 Benzo[b]fluorene		
19 Benz[a]anthracene		
20 Chrysene + triphenylene		
21 Benzo[b]fluoranthene		
22 Benzo[k]fluoranthene		
23 Benzo[f]fluoranthene		
24 Benzo[e]pyrene		
25 Benzo[a]pyrene		
26 Perylene		

tions are presented in Table I. The Illinois No. 6 coal contained 3% sulfur and 1.38% nitrogen, and the lignite contained 0.56% sulfur and 0.73% nitrogen. The relative intensities of the nitrogen and sulfur profiles of the two tars reflects these differences. The profiles are generally similar qualitatively. The majority of the nitrogen hetero-cyclics are smaller than quinoline. These molecules are presumably (as indicated by GC–MS) mainly pyridine and methyl-, dimethyl-, and ethyl-substituted pyridines. The other major nitrogen peaks are quinoline, acridine, benzoacridine and methyl derivatives of these compounds. Sulfur compounds are mainly thiophenic, ranging from benzothiophene to naphthobenzothiophene. Small amounts of benzenethiol and toluenethiol are also present. A striking feature of the results is the absence of

TABLE II

COMPARISON OF PAH CONCENTRATIONS IN RAW WASTEWATER WITH THEIR CORRESPONDING (DMEG)ᵥ VALUES

PAH	Concentration ($\mu g/l$)	$(DMEG)_v$ ($\mu g/l$)
Phenanthrene	$8.76 \cdot 10^5$	$2.39 \cdot 10^4$
Benz[a]anthracene	$1.00 \cdot 10^6$	$6.72 \cdot 10^2$
Pyrene	$2.05 \cdot 10^5$	$3.45 \cdot 10^6$
Benzo[a]pyrene	$7.04 \cdot 10^4$	$3.00 \cdot 10^{-1}$
Dibenzo[a,h]anthracene	$5.50 \cdot 10^4$	1.40

aromatic compounds with long aliphatic side-chains, presumably because of their absence from the original coal structure. PAHs range from two to five rings, although some six-ring compounds have also been observed[1]. The PAHs are of major importance because of their adverse health effect and biological activity. In fact, sixteen PAHs ranging from naphthalene to benzo[ghi]perylene are on the priority pollutant list issued by the U.S. Environmental Protection Agency[10]. The concentrations of various PAHs in raw wastewater are compared with their corresponding $(DMEG)_w$ values in Table II. Here $(DMEG)_w$ is defined as the maximum concentration of the compound in an aqueous stream which is not expected to have adverse health effects[11]. The environmental severity of the wastewater stream is reflected by the fact that the concentrations for various PAHs far exceed, or are near to, their $(DMEG)_w$ value.

CONCLUSIONS

Dual detection with FID–FPD and FID–NPD of a capillary column effluent is feasible and represents a rapid method of characterization of tars produced from coal gasification. Background information from GC–MS on the nature of tars supplements identification by specific detection and retention time.

ACKNOWLEDGEMENT

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