COMPOSITION OF SELECTED FRACTIONS FROM COAL TARS PRODUCED FROM AN UNDERGROUND COAL GASIFICATION TEST

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INTRODUCTION

The remaining fossil energy resources contained within the United States are comprised primarily of coal. These resources have been estimated at 3.9 trillion short tons (1) or enough coal to provide this country with all of its energy needs for the next two hundred years. One drawback with this vast potential is the difficulty in utilizing this resource. Estimates indicate that only 10-25 percent (1) is recoverable using present day techniques. The remaining coal seams are either too deep or too low in quality to mine economically.

In an effort to develop this inaccessable resource ERDA has sponsored several different research programs in underground coal gasification. The Laramie Energy Research Center has been developing a technique called the linked vertical well (LVW) process to produce a low-Btu gas by gasifying a coal seam in situ.

The field tests conducted at Hanna, (2,3) Wyoming, have shown that a low-Btu gas can be produced and a great deal of control can be achieved in directing the underground reaction systems, thereby resulting in high utilization of the coal. The most recent field test conducted from April through July of 1976 showed a total of 6700 tons of coal utilized and production rates up to 12 MM scf/day. (4) The highest heating value obtained for a substantial period was approximately 175 Btu/scf. In addition to this low-Btu gas an organic condensate was co-produced with the gas. For lack of a better term, this organic liquid has been called a coal tar. Its composition has been studied for various reasons, one of which is to ascertain its value as a petrochemical feedstock or fuel.

Another consideration is the possible changes in composition due to changes in reaction conditions. Additionally, the possible environmental effects of such a by-product on groundwater quality must also be accounted for since the seam is considered to be a low-grade aquifer. With these thoughts in mind, the characterization was started to possibly answer these questions.

DESCRIPTION OF THE LINKED VERTICAL WELL (LVW) PROCESS

The coal seam at the Hanna site is 30 feet thick, approximately 300 feet deep and of subbituminous rank, a coal typical of most Western coals.

Numbers in parentheses refer to references at the end of the text.

The LVW process involves two distinct and separate steps. The first is a linkage step to achieve the desired permeability necessary for the subsequent gasification. This linkage is achieved through a reverse combustion process as shown in Figure 1 and then the gasification step using a forward combustion process follows. The produced gases flow through the previously formed linkage path to the production well and finally to the surface. The coal tars are produced within the reaction zone and carried to the surface with the produced gas.

The particular sample to be discussed in detail was produced during the first test at Hanna (collected on December 10, 1973) but reference to other samples from more recent tests will be made.

EXPERIMENTAL

Nonaqueous titration of nitrogen was performed in acetic anhydride and benzene with $HClO_4$ as described by Buell. (5) GLC analyses of tar acids were done on a 10' x .055" 10% SP-1200/1% H_3PO_4 on Chromosorb W AW column. With a helium carrier gas, a flow rate of 70 ml/min, isothermal for 2 min at 130° C, then 2° C/min increase to 200° C, a usable separation of components resulted. GLC analyses of the aliphatics were done on a 20' x .055" 3% SP-2100 on Supelcoport column. With a flow rate of helium carrier gas at 70 ml/min, isothermal at 50° C for 4 minutes, then a 2° C/min increase to 300° C, a usable separation was achieved. GC-MS data were collected on a system using a HP-5712 gas chromatograph interfaced to an AEI MS-12 mass spectrometer.

Simulated distillations were performed with use of gas chromatography with residue defined as any material that does not boil below 1000° F.

Fractionation into basic, acidic and neutral fractions was accomplished by aqueous mineral acid, sodium bicarbonate, and caustic soda extraction, pH adjustment to regenerate the species and extraction with diethyl ether. Neutrals were also separated into aliphatic and aromatic fractions with the use of silica gel. Hexane was used to elute the aliphatics and methanol to remove the aromatics.

PHYSICAL PROPERTIES

The following range of physical properties were determined from many samples collected during the three different tests conducted at Hanna, Wyoming.

Table 1 - Physical Properties

Specific gravity at 60° F	-	0.960 - 0.977
Viscosity at 100° F	-	3.5 - 13.2 centistokes
Heat of combustion	-	14,000 - 17,300 Btu/lb

As shown in Table 1 the physical parameters of these coal tars are desirable, in particular, they are very mobile compared to typical coal tars.

CHEMICAL PROPERTIES

The elemental analysis (Table II), for the sample collected on December 10, 1973, is typical for most of the tars produced from the underground coal gasification tests at Hanna.

Table II - Elemental Analysis

C	-	86.33 %
H	-	10.43
N	-	0.79
S	-	0.18
O[a]	-	2.27

[a]Percentage determined by difference

The maximum values for nitrogen and sulfur that have been observed are 1 percent and 0.5 percent respectively.

Another technique used for analysis is simulated distillations. The simulated distillation of the coal tar (collected December 10, 1973) is shown in Figure 2. The interesting point is the fact that none of the material boils above 950° F. When compared with the simulated distillation of a coal tar produced by laboratory carbonization (Figure 3), the obvious difference is in the boiling point distribution. With use of internal standard, it was determined that the carbonized laboratory sample was 24 percent (weight) residue or material boiling above 1000° F versus 0 percent for the UCG sample (Table III).

Table III - Boiling Range Distribution

Sample	Amb-400°F	400-500	500-600	600-700	700-800	800-900	900-1000	Residue
Carbonized	0	11.3	16.3	13.1	15.2	12.4	7.5	24.2
UCG sample	6.2	16.9	25.6	28.2	16.0	5.3	1.8	0

This demonstrates an important point about the UCG coal tar. It is a fractionated portion of the total produced coal tar. The passage through the production path up to the surface from the reaction zone acts as a preliminary separation step before presenting the coal tar at the production wellhead. This also explains the rather low viscosity of the tar since the more volatile components are produced at the surface. This provides a rather unique product for characterization when compared to typical coal tars.

Non-aqueous titration of the sample is shown in Table IV.

Table IV - Non-Aqueous Titration Results

Sample from December 10, 1973	0.524% WB	0.186% VWB

Strong, weak and very weak bases are defined by their half neutralization potential (HNP), with very strong bases having an HNP less than 150 mV, weak bases between 150 and 350 mV, and very weak bases greater than 350 mV. Pyridines and quinolines will titrate as weak bases and amides as very weak bases. Primary and secondary anilines titrate as very weak bases since they will acetylate and then titrate as amides.

The separation of numerous samples into tar bases, tar acids (strong and weak acids) and neutrals gave the following range of results (Table V).

Table V - Compositions Wt % of Tar

Tar Bases	2.5 - 8.0%	
Tar Acids	.1 - 1 %	- Strong Acids
	12 - 31%	- Weak Acids
Neutrals	55 - 77%	- 70% Aromatic
		30% Aliphatic

In addition, the neutrals were separated into aliphatic and aromatic fractions. The interesting point was that after looking at many samples, the relative amount of aliphatics vs. aromatics was essentially constant (30:70). Previous work (6) on the bases indicate them to be primarily quinolines with some pyridines and anilines, much as would be expected in a liquid product produced from coal.

The results presented in this paper are concerned with the composition of the weak acid and aliphatic fractions of this one sample as identified by GC-MS and NMR analysis. Although complete analyses have not been finished on other samples, a comparison of the weak acid and aliphatic fractions from other samples will be made.

The sample from December 10, 1973, was 14.5 percent (by weight) weak acids and 23 percent (by weight) aliphatics.

WEAK ACIDS

The composition of the weak acid fraction is almost exclusively phenolic in nature. With the use of GC-MS a reasonable separation (Figure 4) and subsequent analysis was obtained. Table VI lists the resulting components determined. In some cases the GC resolution was adequate enough to provide a mass spectra "clean" enough to identify specific isomers but in most cases only enough information was available to determine molecular weight and/or degree of alkylation.

Table VI - Weak Acids

phenol
p - cresol
o - cresol
m - cresol
4 different xylenols
7 C_3 - phenols
5 C_4 - phenols
small amount of aromatic aldehyde or ketone

Additional spectral information was obtained by manually trapping peaks eluted from the GLC and using H^1 and C^{13} NMR techniques to identify the components. Without the presentation of the data, the H^1 and C^{13} NMR spectral data support the conclusions of the GC-MS analysis.

ALIPHATICS

The aliphatic fraction showed very little in the way of unsaturation or cyclic compounds but a very high concentration of saturate components. The results (Table VII) show a normal hydrocarbon series going from C_{10} all the way to C_{32}.

Table VII - Composition of Aliphatics

1.	n-C_{10} through n-C_{32} series	
2.	Branched Saturates	2,11 - Dimethyl tridecane ($C_{15}H_{32}$) 2 - Methyl tetradecane ($C_{15}H_{32}$) 4,11 - Dimethyl pentadecane ($C_{17}H_{36}$) 6 - Methyl octadecane ($C_{19}H_{40}$) 7 - Methyl octadecane ($C_{19}H_{40}$) 3 - Methyl octadecane ($C_{19}H_{40}$) 3,6 - Dimethyl heptadecane ($C_{19}H_{40}$) two polybranched $C_{19}H_{40}$ 2,4 - Dimethyl octadecane ($C_{20}H_{42}$)

A small amount of branched saturates are also observed with a rather large concentration of C_{19} branched saturates. As seen in Figure 5, the GLC trace for this sample shows the distinct normal series with the branched C_{19} series at about 70 minutes retention time. No C^{13} or H^1 NMR spectra were run on this sample since the GC resolution was sufficient to provide reasonable GC-MS analysis.

COMPARISON OF SAMPLES

Although analysis by GC-MS and NMR of other weak acid and aliphatic samples are not complete and ready for presentation, the author feels that the following evidence of similarity between samples will be of interest.

The only data presented is the very noticeable resemblance between GLC traces for the weak acids and aliphatics from different samples (Figures 6, 7, 8 and 9). The coal tars represented by these fractions were collected during different tests at the Hanna, Wyoming site. The sample previously discussed was collected in the first test during December of 1973. The next tar (Figures 6 and 8) was produced in the second test operated from April til August of 1975. The third sample (Figures 7 and 9) was collected during the most recent test from April through July 1976. Simple observation of the three GLC traces (Figures 4, 6 and 8) for the weak acids show a very strong similarity, indicating a very similar composition for the three fractions. A corresponding similarity is noticed for the aliphatics (Figures 5, 7 and 9) except for the concentrations of what appears to be the n-C_{25} component in the 6-25-75 sample (Figure 7). Other than that one difference, which the author cannot provide an explanation for, the fractions all have a normal saturate series from about C_{10} to C_{31} or C_{32} and a C_{19} branched series at 70 minutes retention time.

Other samples have shown this same general character within all their fractions although they are not presented here. The overwhelming conclusion is that the coal tar is fairly constant in composition, not only during the life of an experiment, but also from one test to another as long as the tests are in the same coal seam.

This would appear to be a very desirable by-product of the gasification process due to its constancy. Additionally, the consistency of composition would indicate a process approaching steady-state conditions since there does not appear to be variation in one of its products, the coal tar.

EXPLANATION OF COAL TAR FORMATION

The following discussion is based not only on the composition of the coal tars but also on the other available information pertaining to UCG and in particular the work conducted at Hanna, Wyoming.

The air reacts exothermically with the coal and/or char to provide heat for the then hot gases CO_2 and H_2O to react with the char to form CO and H_2. The still relatively hot gases pass into or by fresh coal which is then devolatilized to produce the coal tars. These coal tars are then fractionated according to boiling point since they continue to cool as they flow with the product gas away from the combustion zone or heat source. The heavier components remain within the seam until they are eventually consumed or thermally cracked to lighter compounds. This fractionation is based on the temperature of the passage and the velocity of the gas stream since entrained droplets might also be carried to the surface.

This might also provide a very convenient method of disposing of these heavy molecular weight materials that would be hard to handle on the surface. It also helps to decrease the environmental effects on the ground water quality, if the more soluble products (the volatiles) are produced at the surface and the less water soluble (the heavy ends) remain behind and are eventually consumed. The actual fate of these organics in the ground water within the seam will be determined in a test to be conducted during the spring of 1977.

CONCLUSIONS

Analysis of the weak acid and aliphatic fractions of a coal tar produced from an underground coal gasification test reveal interesting results. The composition of the weak acids is much as would be expected, alkylated phenols. The aliphatics have a normal saturate series running from C_{10} to C_{32} with some branched saturates and a particularly heavy concentration of C_{19} branched saturates.

The most important point is the similarity of samples over the life of a system or from test to test. Referring to the three questions proposed earlier, this similarity or constancy would indicate the following:

1. As a fuel or petrochemical feedstock, a constant feedstock would be very desirable.

2. The unchanging composition suggests a system approaching steady-state conditions.

3. Environmental problems would be reduced if the effluent was constant in composition, thereby limiting the number of components to be monitored.

As a by-product, the coal tar appears to be advantageous which only increases the attraction of underground coal gasification as a commercial process.

REFERENCES

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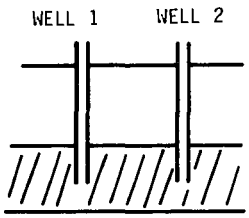
3. C. F. Brandenburg, R. P. Reed, R. M. Boyd, D. A. Northrop and J. W. Jennings, "Interpretation of Chemical and Physical Measurements from an In Situ Coal Gasification Experiment," 50th Annual Meeting of the Society of Petroleum Engineers of AIME, SPE 5654, September 1975.

4. D. D. Fischer, C. F. Brandenburg, S. B. King, R. M. Boyd and H. L. Hutchinson, "Status of the Linked Vertical Well Process in Underground Coal Gasification," presented at the 2nd Annual Symposium on Underground Coal Gasification, Morgantown, WV, August 1976.

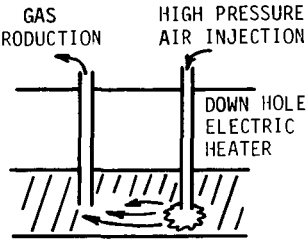
5. B. E. Buell, Anal. Chem., 39, 756 (1967).

6. S. B. King, C. F. Brandenburg and W. J. Lanum, "Characterization of Nitrogen Compounds in Tar Produced from Underground Coal Gasification," presented at the Spring ACS meeting (Fuel Chemistry Division) in Philadelphia, PA, April 1975.

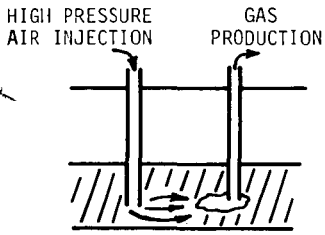
NOTE: Any reference to specific brand names does not imply endorsement by the Energy Research and Development Administration.



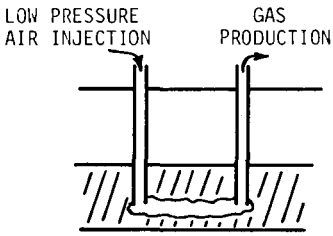
(A) VIRGIN COAL



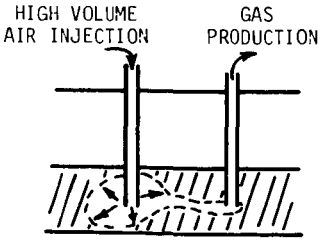
(B) IGNITION OF COAL



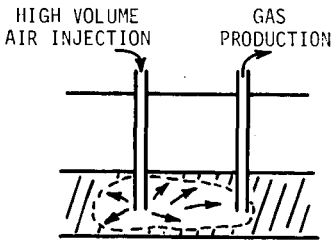
(C) COMBUSTION LINKING FRONT PROCEEDS TO SOURCE OF AIR



(D) LINKAGE COMPLETE WHEN COMBUSTION ZONE REACHES INJECTION WELL (SYSTEM READY FOR GASIFICATION)

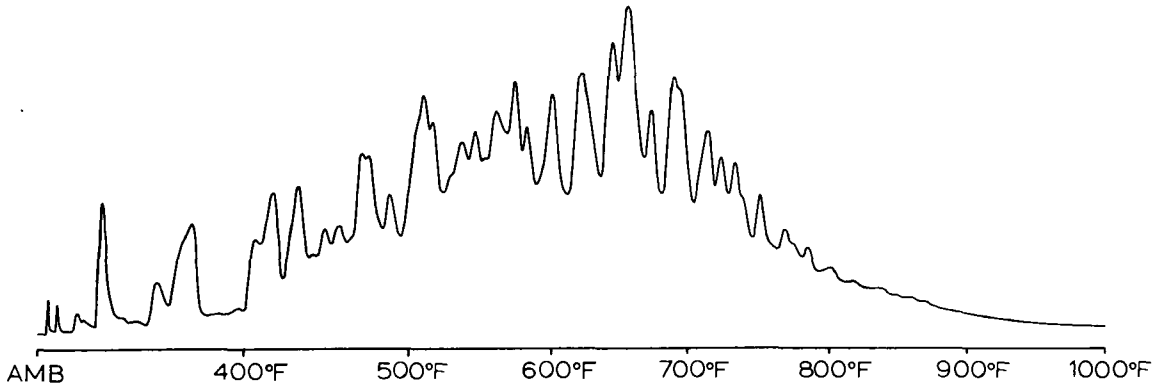


(E) COMBUSTION FRONT PROCEEDS IN THE SAME DIRECTION AS INJECTED AIR



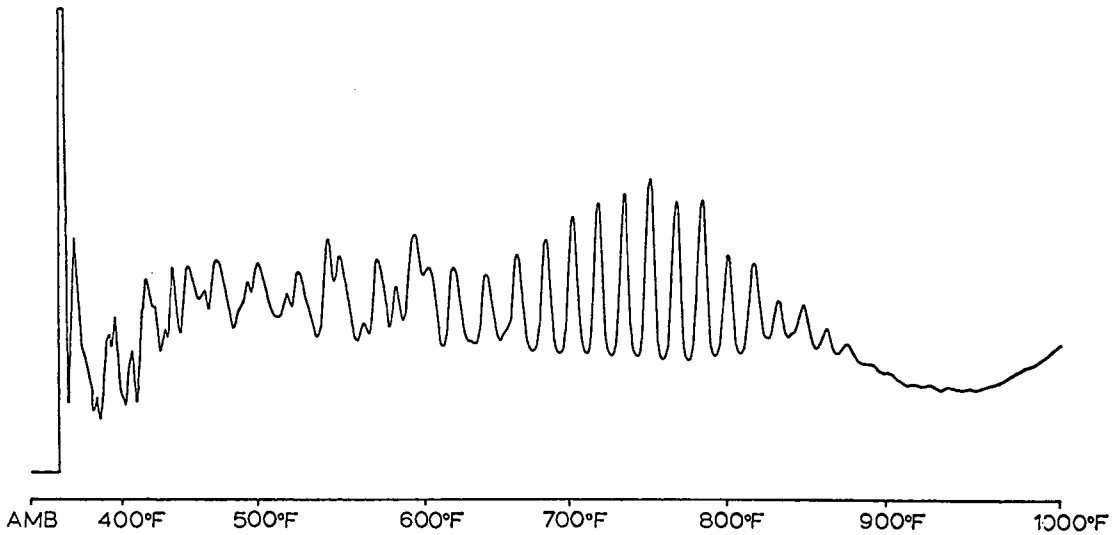
(F) COMBUSTION FRONT EVENTUALLY REACHES PRODUCTION WELL

FIGURE 1



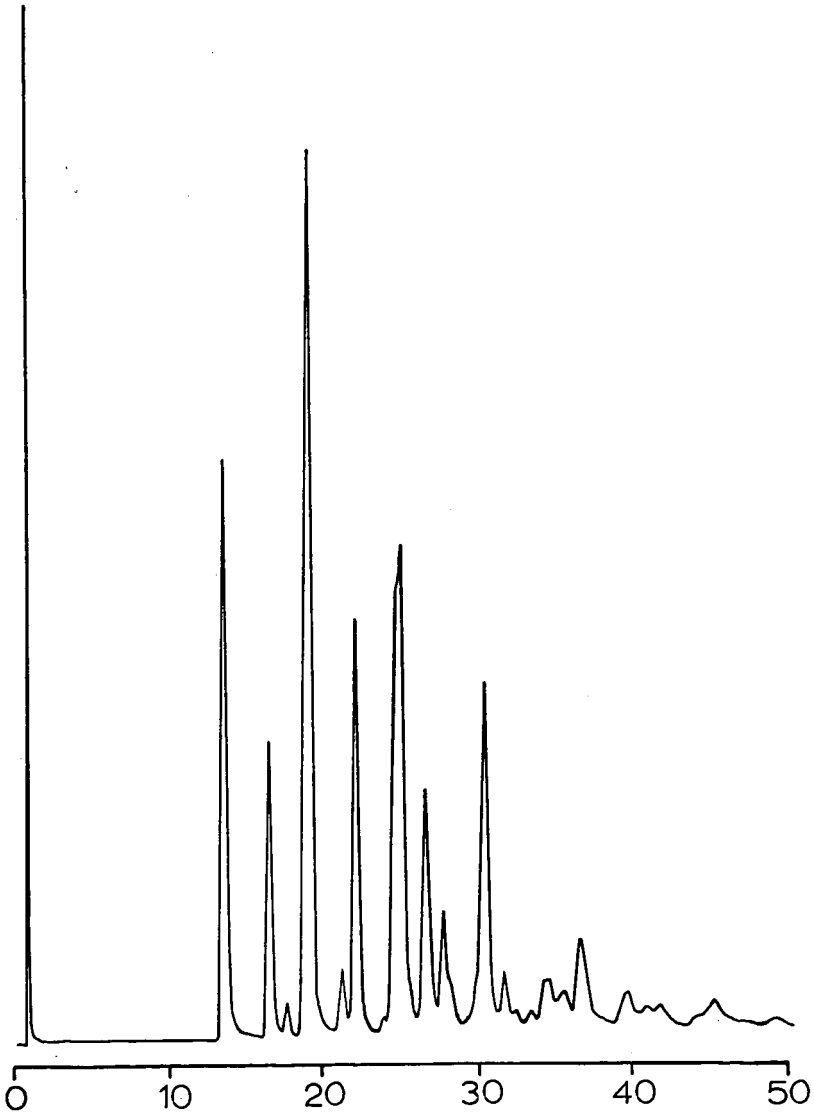
SIMULATED DISTILLATION OF TAR (12-10-73)

FIGURE 2



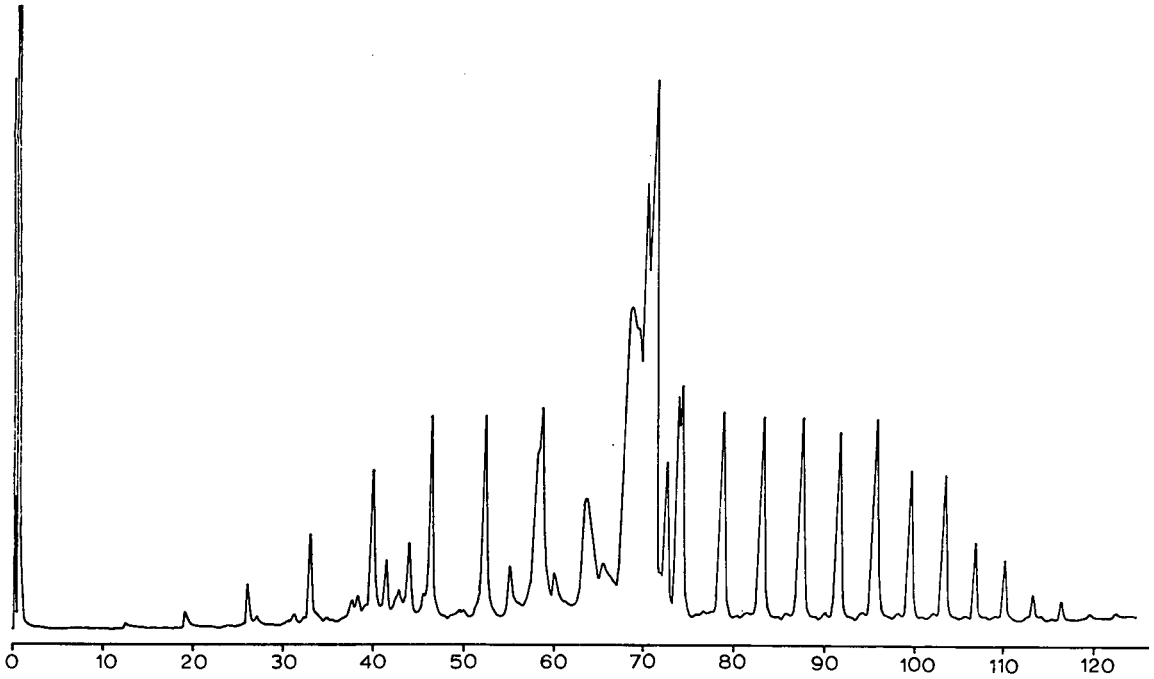
SIMULATED DISTILLATION OF COAL TAR
PRODUCED BY CARBONIZATION AT 500°C

FIGURE 3



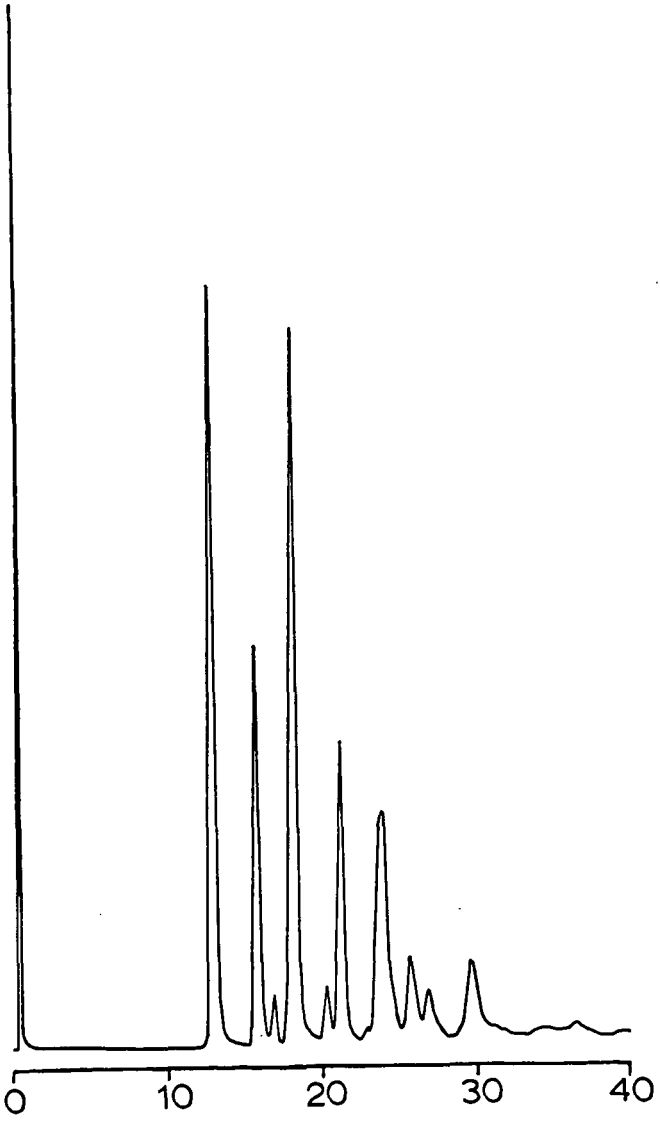
TAR ACIDS FROM (12-10-73)

FIGURE 4



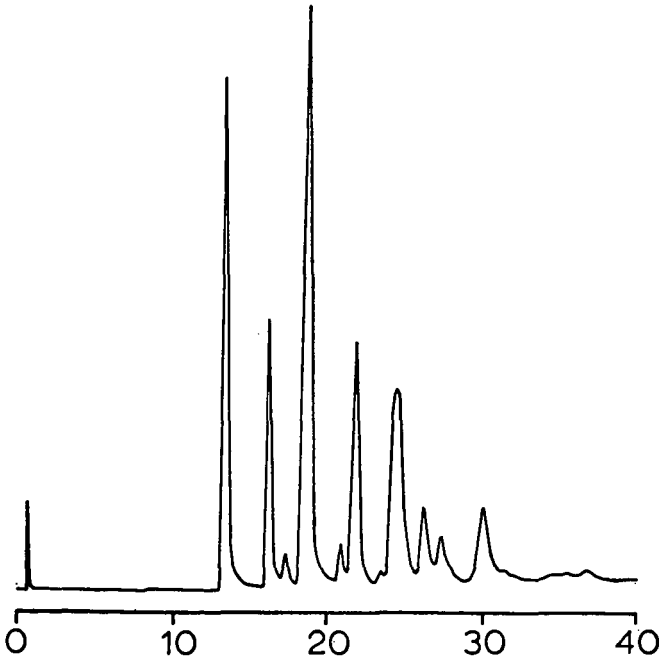
ALIPHATICS FROM (12-10-73)

FIGURE 5



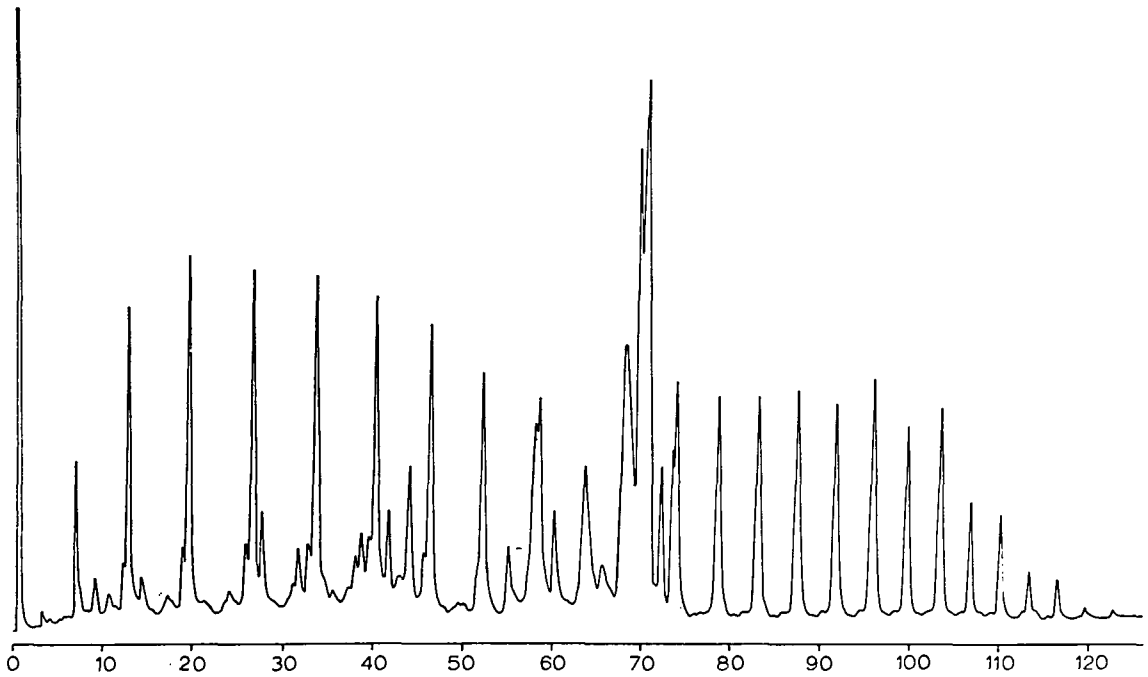
TAR ACIDS FROM (5-21-76)

FIGURE 6



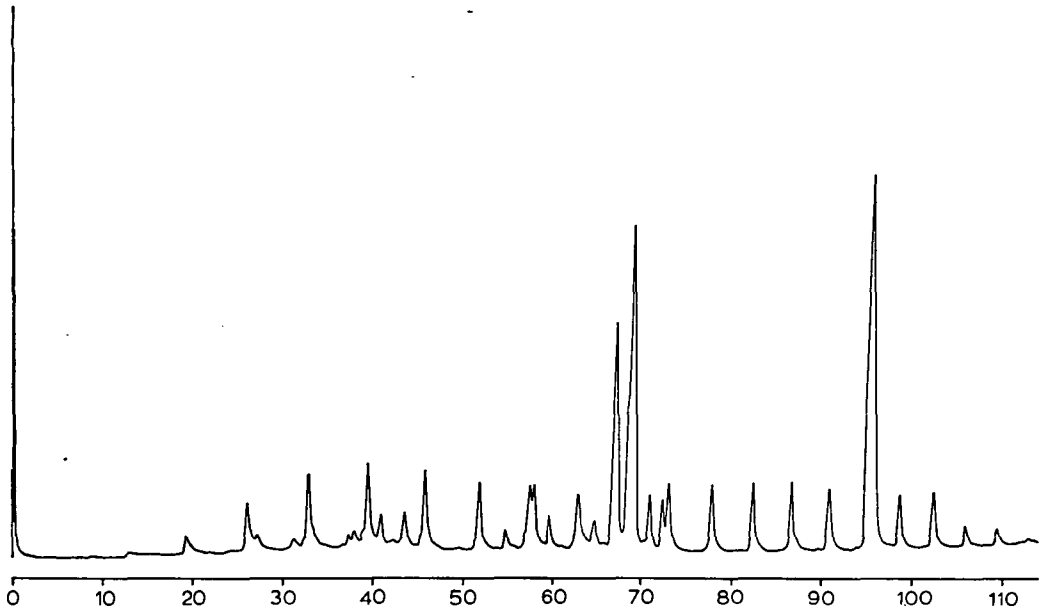
TAR ACIDS FROM (6-25-75)

FIGURE 7



ALIPHATICS FROM (5-21-76)

FIGURE 8



ALIPHATICS FROM (6-25-75)

FIGURE 9