AN INVESTIGATION OF AROMATIC FRACTIONS FROM COAL TAR PRODUCED BY AN UNDERGROUND COAL GASIFICATION TEST

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INTRODUCTION

As most people are well aware, the majority of fossil energy resources in the United States are in the form of coal. Current estimates place these resources at approximately 4 trillion short tons (1), yet only 10-25 percent of this resource is recoverable using present day technology.

The Energy Research and Development Administration is currently funding several projects to develop the technology of underground coal gasification. The objective of these projects is to increase the total recoverability of this vast resource. One of these projects is being conducted by the Laramie Energy Research Center and is referred to as the linked vertical well (LVW) process. This process is being developed at the Hanna, Wyoming, field site and has been under development since 1972.

The most recent test was completed in the summer of 1976. The results showed a total of 6700 tons of coal utilized and production rates up to 12 MM scf/day (2). 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 produced. This organic condensate or coal tar comprised 1-1½ percent (by weight) of the gas stream. Its composition has been studied for various reasons, not the least of which is its value as a petrochemical feedstock or as a fuel. Another consideration is its possible environmental implications whether due to surface handling or effect on groundwater quality.

DESCRIPTION OF THE LINKED VERTICAL WELL PROCESS (LVW)

The coal seam at the Hanna site is a subbituminous coal, 30 feet thick and approximately 300 feet deep.

The LVW process is a two-step operation. The first step is to prepare the seam for gasification, since the virgin coal has a permeability too low to accept the high volumes of air necessary for gasification. This preparation is called "linking" and involves the drawing of a combustion front from the bottom of one well to an adjacent well using a reverse combustion technique. After this "linking" is complete, the permeability between these two wells is sufficient to proceed with the second step or the gasification process. This involves injecting large volumes of air into one well and the gasification products being produced at the other well. It is during this step that the coal tars are produced and carried to the surface as a by-product of the overall gasification process.

EXPERIMENTAL

GLC analysis of the aromatic fractions were done on a HP-5712 chromatograph using a 10' x 0.093" 3% SP-400 on 80/100 Supelcoport column. With a flow rate of 30 ml/min, isothermal at 50° C for 2 minutes, then a 2° C/min increase to 300° C, a usable separation was obtained. Combined gas chromatography-mass spectroscopic studies were performed using a HP-5700A gas chromatograph coupled directly to an AEI MS-12 mass spectrometer. The GC separation was obtained using support coated open tabular columns.

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

The tar was separated into tar acids, tar bases and neutrals by acid-base extraction. The fractions were regenerated by pH adjustment 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

Table I lists some of the physical properties of the sample to be discussed in detail. These are properties of the whole sample, not just the aromatic fraction.

Table I - Physical Properties

Specific gravity at 60° F	- 0.977
Viscosity at 100° F	- 13.16 centistokes
Heat of combustion	- 17,256 Btu/lb

Similar values have been measured for other samples collected during other tests. Their mobility (low viscosity) would make them easily handled in a surface facility and their heating value would qualify them as a possible fuel.

CHEMICAL PROPERTIES

The elemental analysis (Table II) is typical of the tars produced from the Hanna tests.

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. An interesting point is demonstrated by this technique, this being that none of the coal tar boils above 950° F. When compared with a coal tar produced by laboratory carbonization, the obvious difference is in the boiling point distribution. With the use of an internal standard, it was determined that the carbonized laboratory sample was 24 percent (by weight) residue 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 illustrates an important point about the UCG coal tar. It is a fractionated portion of the total coal tar produced underground in the seam. The passage through the production path, including the linkage path and well casing, acts as a preliminary separation step. The fate of the heavier components is questionable but there is certainly some cracking and perhaps eventual combustion of the remaining components.

These more volatile components that reach the surface provide a rather unique product for characterization when compared to "standard" coal tars produced in surface units.

The separation of numerous samples into tar bases, tar acids (strong and weak acids) and neutrals (aromatic and aliphatic) gave the following range of values (Table IV).

Table IV - 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

An interesting point was that after looking at many samples the relative amount of aliphatics versus aromatics was essentially constant (30:70). Previous investigations (3) of the tar bases indicate the composition to be primarily quinolines with some pyridines and anilines. The tar acids have been described (4) as alkylated phenols. The aliphatics (4) are mostly saturated with a C_9 to C_{31} normal series and a predominate C_{19} branched series.

AROMATICS

The aromatic fraction did not show any unusual components but did lack any alkylated benzenes, which were expected. The reason for this is believed to be the volatile nature of the methyl and polymethyl substituted alkylbenzenes and the technique that was used to collect the coal tar sample from the production stream. The collection procedure discriminated against the volatile components. The predominate type of alkylation found in the remaining aromatics was methylation. Table V lists the various compound types, or in some cases isomers, that were determined by GC-MS analysis.

Table V - Components of the Aromatics

Naphthalene
2 - Methyl Naphthalene
1 - Methyl Naphthalene
3 different Dimethyl Naphthalenes
Acenaphthalene or Biphenyl
A 1, 2, 3, 4 - Tetrahydronaphthalene w/ C_4H_8 substitutent
A Dipropyl Thiophene
4 different Trimethyl Naphthalenes
A Dimethyl - Ethyl Naphthalene
A Penta - Methyl Naphthalene
Anthracene and/or Phenanthrene
A Methyl Anthracene and/or Phenanthrene
An Ethyl Anthracene and/or Phenanthrene

The results presented in Table V show there is no evidence of PNA components and the majority of the alkylation is methyl.

COMPARISON OF AROMATIC FRACTIONS

As has been reported in a previous paper (4), the similarity of the separate fractions is remarkable. The same is true of the aromatic fractions. The three aromatic fractions that will be discussed are from three different tests. The first from December 10, 1973, during the Hanna I test, the second from June 25, 1975, during the Hanna II, Phase I test and the third from May 21, 1976, during the Hanna II, Phase II test.

Without doing a complete GC-MS analysis of all these samples and considering only the GC trace the striking similarity is obvious. The assumption at present is that the aromatic fractions are similar in composition both qualitatively and quantitatively. This indicates a very constant liquid by-product from UCG.

CONCLUSIONS

Analysis of an aromatic fraction from a coal tar produced from an underground coal gasification test shows mostly methylated naphthalenes, anthracenes and phenanthrenes. The similarity between various aromatic fractions and the corresponding similarity of acid, base and aliphatic fractions suggests that the liquid product is very constant in composition with respect to time. This would in turn indicate that the LVW process approaches steady state conditions. The constancy of such a product would certainly be compatible and desirable with any facility that might utilize such a liquid for either a feedstock or as a fuel.

The lack of evidence for any PNA's in the aromatic fraction is certainly encouraging from an environmental standpoint and would probably be expected when considering the way in which the coal tar is produced.

As a by-product, the coal tar appears to be a desirable product which only enhances the outlook for underground coal gasification becoming a commercial process.

REFERENCES

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