

Classes of Compounds Responsible for Mutagenic and Cytotoxic Activity in Tars and Oils Formed During Low BTU Gasification of Coal

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Summary

The Lovelace Inhalation Toxicology Research Institute (ITRI), in cooperation with the Morgantown Energy Technology Center (METC), has completed toxicity screening of vapors, liquids and solids formed during operation of an experimental pressurized, stirred-bed, coal gasifier at METC. Vapors collected from the cooled process stream on Tenax resins had no mutagenic activity in the Ames *Salmonella* assay. Dichloromethane extracts of liquids and solids collected from the effluent or process streams were fractionated by gel chromatography into fractions containing mostly aliphatic compounds; neutral polycyclic aromatic hydrocarbons (PAH); polar PAH and heterocyclic compounds; and salts. The polar fraction was partitioned into acids, bases, water soluble compounds and phenols. Bacterial mutagenic activity was highest in the basic fraction with additional activity in the neutral PAHs. Highest cytotoxicity toward both the bacteria and canine alveolar macrophages was in the phenolic fraction. Treatment of the gasifier tars by nitrosation or by acetylation to remove primary aromatic amines (PAA) reduced the bacterial mutagenicity by 50-60%, indicating that some, but not all, of the mutagenicity was due to PAA.

Introduction

The Lovelace Inhalation Toxicology Research Institute (ITRI), working in cooperation with the Morgantown Energy Technology Center (METC), has completed studies to obtain information on the possible inhalation toxicity of airborne effluents associated with low BTU coal gasification (1-4). Such information is needed to enable an improved assessment of potential health risks to man arising from this technology.

The METC coal gasifier is an experimental pressurized, stirred-bed coal gasifier (Figure 1) and differs from commercial fixed-bed producers in its smaller size (1.1 m ID) and its provisions for stirring the bed. The gasifier uses a Lurgi process for low BTU coal gasification using heat, air, steam and coal. The gas cleanup devices are experimental and evolving and are designed to produce a low BTU gas suitable for use in combined cycles with turbines.

The main process stream cleanup devices in use at the time of this research program included a cyclone to remove dust; a humidifier, tar trap and Venturi scrubber to remove tar; a muffler and a flare. Other cleanup devices indicated in Figure 1 were bypassed during sampling periods for this project.

Experimental

Sampling

Vapors, liquids, and solids were sampled from both the process and effluent streams. The process stream was sampled at points A, B, C, D, and E (Figure 1) using two sampling systems. An analytical system extracted cooled, diluted process stream material and measured the concentration (by filters), the size of aerosols (by cascade impactors) and the concentration of vapors (by adsorption on Tenax traps). Condensor traps were used to collect larger samples of tars and oils. In addition to the process stream material, bulk quantities of bottom ash from the gasifier, dust from the cyclone, and tar from the humidifier, tar trap and Venturi scrubber were collected.

Fractionation of Tars and Oils

Tars from the tar scrubbing devices and condensed oils from the process stream were fractionated on Sephadex LH-20 gel columns using tetrahydrofuran (THF) to elute separate fractions containing, 1) mainly aliphatic and polymeric material (F1, F2); 2) neutral polyaromatic hydrocarbons (PAH) (F3, F4); and 3) polar compounds including nitrogen heterocyclic compounds and PAH with polar fractional groups (F5) (See Figure 2). The polar fraction was subfractionated into acidic, basic and neutral components.

Mutagenicity Testing

The potential mutagenicity of each subfraction was assessed using the Ames Salmonella bacterial mutagenicity assay, using strain TA-98 (detects frame-shift mutations) both with and without addition of liver metabolizing enzymes (S-9). Cytotoxicity toward the bacterial cells and toward canine alveolar macrophages was also measured.

Effect of Removal of Primary Aromatic Amines (PAA) on Mutagenicity

To determine the contribution of PAA to the mutagenic activity of gasifier tar, the PAA were removed by nitrosation at pH 2.5 or by acetylation. Several PAA, one aza-arene and a coal oil sample from the Fossil Fuels Research Matrix Program, Oak Ridge National Laboratory, were included as control samples. The treated samples were then re-tested for mutagenic activity.

Results

The vapor phase material collected on Tenax traps did not have mutagenic activity in the bacterial mutagenicity assay used. All tar and oil samples collected from the process or potential effluent streams had mutagenic activity when S-9 metabolizing enzymes were included. The subfractions showing the most activity were the neutral PAH (F3, F4) and the polar fraction (F5) in both process stream samples and the potential effluent material (Tables 1, 2, 3). The basic and neutral portions of the polar fraction had

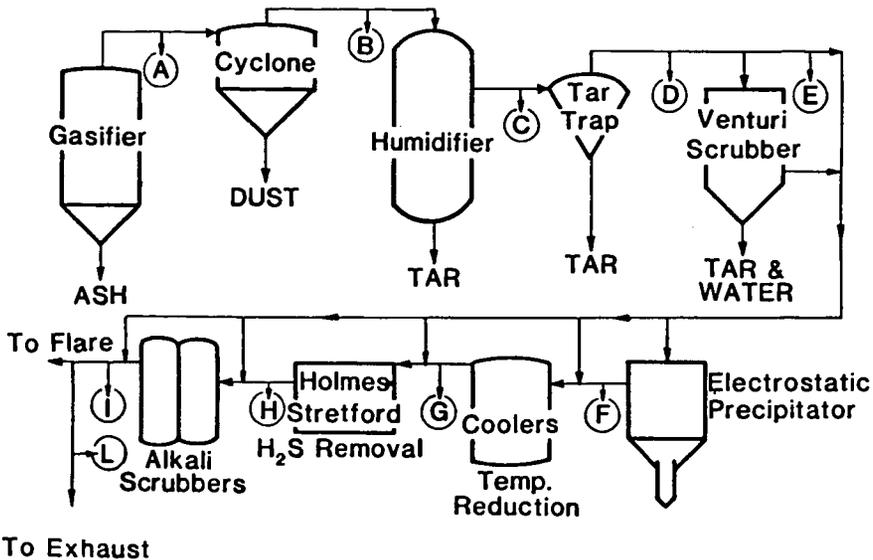


Figure 1. Schematic diagram of the METC low Btu coal gasifier and cleanup system.

LH-20 - THF ELUTION PROFILE

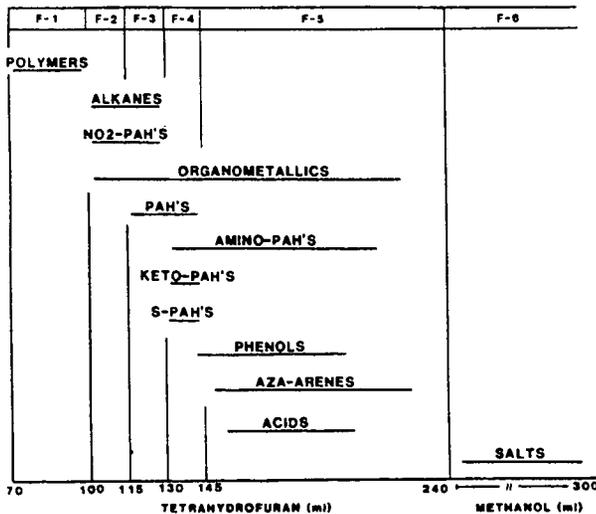


Figure 2. Elution profiles of compounds from Sephadex LH-20 column using tetrahydrofuran (THF) as eluant. The lines for each compound indicate the volume of THF in which the compounds eluted. The dot indicates the center of the elution peak.

TABLE 1

Mutagenic Activity of Process Stream Samples
and their Sephadex LH-20 Fractions

<u>Fraction</u>	<u>Mass^a Percent</u>	<u>Revertants^b per μg (with S-9)</u>	<u>Mutagenicity^c Percent</u>	<u>Revertants per L Process Stream</u>
<u>Position B -- Raw Gas</u>				
Crude	100.0	6.7 \pm 0.6	100	50,000
LH-20 Fraction				
1	27.8	0.7 \pm 0.2	3	1,600
2	6.5	2.8 \pm 0.3	3	1,900
3	21.8	10.4 \pm 1.1	39	17,000
4	16.7	5.0 \pm 0.6	14	6,200
5	21.7	10.4 \pm 1.0	38	17,000
6	5.5	2.8 \pm 0.2	3	1,100
<u>Position D -- After Tar Trap</u>				
Crude	100.0	3.7 \pm 0.2	100	9,700
LH-20 Fraction				
1	35.4	0.0	0	0
2	8.4	3.2 \pm 0.4	14	700
3	18.6	1.9 \pm 0.6	18	900
4	15.6	4.5 \pm 0.4	35	1,900
5	15.3	4.1 \pm 0.2	31	1,600
6	6.7	0.5 \pm 0.3	2	80
<u>Position E -- After Venturi Scrubber</u>				
Crude	100.0	4.1 \pm 0.3	100	2,200
LH-20 Fraction				
1	7.0	0.2 \pm 0.2	0	10
2	5.0	2.8 \pm 0.4	6	70
3	23.0	1.8 \pm 0.3	24	200
4	14.0	2.3 \pm 0.4	18	200
5	29.0	2.9 \pm 0.2	49	400
6	21.0	0.2 \pm 0.2	3	25

^a Mass percent of material fractionated.

^b TA-98 revertants/ μ g determined from slope of dose-response curve by linear regression analysis.

^c Mutagenicity percent is the percent of the mutagenicity each fraction contributes to the crude material.

TABLE 2
 Mutagenic Activity of Process Stream LH-20
 Fractions 5 and their Subfractions

<u>Fraction</u>	<u>Mass^a Percent</u>	<u>Revertants^b per μg with S-9</u>	<u>Mutagenicity^c Percent</u>
<u>Position B -- Raw Gas</u>			
LH-20 Fraction 5	21.7	9.7 \pm 0.5	100
Acids	0.9	1.0 \pm 0.5	1
Bases	4.1	5.5 \pm 1.0	20
Neutrals	1.6	46.7 \pm 2.6	79
Amphoterics - Water solubles	15.2	Not tested	-
<u>Position D -- After Tar Trap</u>			
LH-20 Fraction 5	15.3	2.1 \pm 0.2	100
Acids	0.03	0.4 \pm 0.1	0
Bases	3.8	4.2 \pm 0.4	50
Neutrals	4.6	5.2 \pm 0.3	50
Amphoterics - Water solubles	6.6	Not tested	-
<u>Position E -- After Venturi Scrubber</u>			
LH-20 Fraction 5	29.0	2.3 \pm 0.3	100
Acids	0.7	0.0	0
Bases	1.6	12.4 \pm 0.7	83
Neutrals	2.1	2.2 \pm 0.2	17
Amphoterics - Water solubles	24.6	Not tested	-

^a Mass percent of material fractionated.

^b TA-98 revertants/ μ g determined from slope of dose-response curve by linear regression analysis.

^c Mutagenicity percent is the percent of the mutagenicity each fraction contributes to the crude material.

TABLE 3

Mutagenic Activity of Tar Trap Tar and Venturi Scrubber Water and their LH-20 Fractions

<u>Fraction</u>	<u>Mass^a</u> <u>Percent</u>	<u>TA-98 Revertants^b</u> <u>per μg (with S-9)</u>	<u>Mutagenicity^c</u> <u>Percent</u>
<u>Position B -- Raw Gas</u>			
Tar Trap Tar	100	21.6 \pm 1.8	100
LH-20 Fraction			
1	16	2.9 \pm 0.2	2
2	18	2.9 \pm 0.5	2
3	34	2.5 \pm 0.8	3
4	14	107.0 \pm 49.1	60
5	14	56.6 \pm 8.0	32
6	3	10.2 \pm 0.5	1
Venturi Scrubber			
Inlet Water			
Lyophilized (50ml)	100	0.0	0
Venturi Scrubber			
Outlet Water			
Lyophilized (50ml)	100	1.14 \pm 0.06	100
Outlet Water			
Dichloromethane-			
Solubles (0.07%)	100	0.72 \pm (0.18)	100
LH-20 Fraction			
1	6	0.8 \pm 0.2	7
2	2	1.1 \pm 0.3	3
3	3	1.7 \pm 0.3	7
4	5	1.8 \pm 0.4	13
5	75	0.6 \pm 0.2	64
6	10	0.4 \pm 0.2	6

^a Mass percent of material fractionated.

^b TA-98 revertants/ μg determined from slope of dose-response curve by linear regression analysis.

^c Mutagenicity percent is the percent of the mutagenicity each subfraction contributes to the total.

the greatest mutagenicity (Table 2). Nitrosation or acetylation of the tar-trap tar removed some (50-60%) of the mutagenic activity (Table 4) but not as much as was removed by similar treatment of a coal oil.

The most cytotoxic fractions of the coals and tars were the polar fractions containing phenols.

Discussion

Tars and oils produced during a low BTU coal gasification process were mutagenic toward Salmonella bacteria. The mutagenic activity could be attributed to PAH and to neutral and basic compounds in the polar fraction. In contrast to coal liquids, in which most of the mutagenic activity has been attributed to PAA (5), the mutagenic activity of the tars was reduced by only approximately one-half after treatment to remove PAA.

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TABLE 4
Mutagenic Activity Remaining After Treatment
(%)

<u>Chemical</u>	<u>Nitrosation</u>	<u>Acetylation</u>
2-Aminoanthracene	4	7
3-Aminofluoranthene	0	20
2-Aminofluorene	0	21
6-Aminochrysene	13	6
9-Aminophenanthrene	0	0
Phenathridine	100	86
Coal oil A ^a	9	30
Tar trap tar	39	52

^a Obtained as a comparative research material from the Fossil Fuels Research Matrix Program, Oak Ridge National Laboratory.