



PB83128181

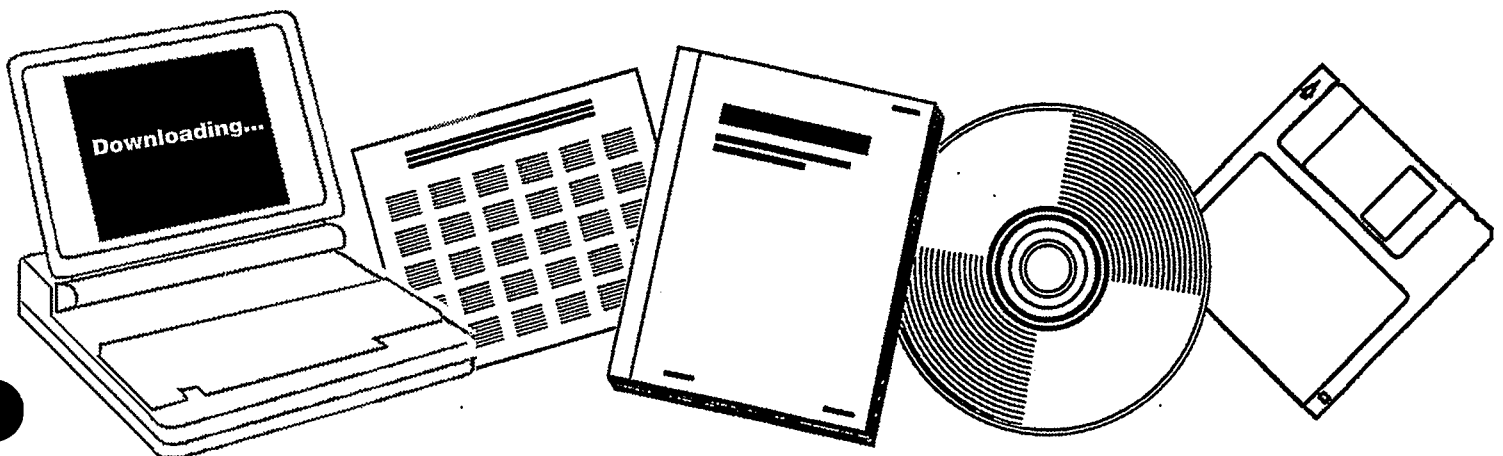
NTIS

One Source. One Search. One Solution.

**PROCEEDINGS OF SYMPOSIUM ON ENVIRONMENTAL
ASPECTS OF FUEL CONVERSION TECHNOLOGY -
VI: A SYMPOSIUM ON COAL-BASED SYNFUELS
HELD IN DENVER, COLORADO ON OCTOBER 26-30,
1981**

MISSOURI UNIV.-ROLLA

SEP 1982



U.S. Department of Commerce
National Technical Information Service

One Source. One Search. One Solution.

NTIS



Providing Permanent, Easy Access to U.S. Government Information

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.



Search the NTIS Database from 1990 forward

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on www.ntis.gov. You now have access to information on more than 600,000 government research information products from this web site.

Link to Full Text Documents at Government Web Sites

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

Download Publications (1997 - Present)

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

www.ntis.gov



U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161

United States
Environmental Protection
Agency

Industrial Environmental
Laboratory
Research Triangle Park NC 27711

EPA-600/9-82-017
September 1982

Research and Development

PB83-128 18 1



Symposium Proceedings:

Environmental
Aspects of Fuel
Conversion Technology—
VI, A Symposium on
Coal-Based Synfuels
(October 26-30, 1981)

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA		
<i>(Please read instructions on the reverse before completing)</i>		
1. REPORT NO. EPA-600/9-82-017	2.	3. RECIPIENT'S ACCESSION NO. PB83-128181
4. TITLE AND SUBTITLE Proceedings: Symposium on Environmental Aspects of Fuel Conversion Technology--VI, a Symposium on Coal-based Synfuels (October 1981)	5. REPORT DATE September 1982	6. PERFORMING ORGANIZATION CODE
	8. PERFORMING ORGANIZATION REPORT NO.	
7. AUTHOR(S) F.A. Ayer and N.S. Jones (Compilers)	10. PROGRAM ELEMENT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P.O. Box 12194 Research Triangle Park, North Carolina 27709	11. CONTRACT/GRANT NO. 68-02-3170, Tasks 43 and 56	
	13. TYPE OF REPORT AND PERIOD COVERED Proceedings; 3/81-3/82	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	14. SPONSORING AGENCY CODE EPA/600/13	
	15. SUPPLEMENTARY NOTES IERL-RTP project officer is N. Dean Smith, Mail Drop 61, 919/541-2708.	
16. ABSTRACT The document summarizes or contains an abstract of each presentation made at the EPA-sponsored symposium, October 26-30, 1981, in Denver, CO. The symposium provided a forum for the exchange of ideas and for discussion of environmentally related information on coal gasification and liquefaction. Process developers and users, research scientists, and government officials reported on results achieved from research projects, synfuels process development, inter-agency programs, control technology evaluation, and regulatory actions. The program included sessions on environmental source test and evaluation results for gasification, indirect liquefaction, and direct liquefaction processes, and water-, air-solid-waste-, multimedia-, and product-related environmental considerations. Approximately 215 participants attended the 5-day symposium.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Coal Gasification Coal Liquefaction Manufactured Gas	Pollution Control Stationary Sources Synthetic Fuels Fuel Conversion	13B 13H 08G, 21D 07D
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 556
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

NOTICE

THIS DOCUMENT HAS BEEN REPRODUCED FROM THE BEST COPY FURNISHED US BY THE SPONSORING AGENCY. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE.

Symposium Proceedings:
Environmental Aspects of Fuel Conversion Technology - VI,
A Symposium on Coal-Based Synfuels
(October 26-30, 1981)

F. A. Ayer and N. S. Jones, Compilers

Research Triangle Institute
P. O. Box 12194
Research Triangle Park, NC 27709

Contract No. 68-02-3170
Task No. 56
Program Element No. CCZN1A

EPA Project Officer: N. Dean Smith

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

PREFACE

These proceedings for the symposium on "Environmental Aspects of Fuel Conversion Technology-VI" constitute the final report submitted to the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, (EPA/IERL-RTP), Research Triangle Park, NC. The symposium was conducted in Denver, Colorado, October 26-30, 1981.

This symposium provided a forum for the exchange of ideas and for discussion on environmentally related information on coal gasification and liquefaction. The program included sessions on environmental source test and evaluation results for gasification and indirect liquefaction, and for direct liquefaction, on water-related environmental considerations, on solid waste-related environmental considerations, on multimedia environmental considerations, and on product-related environmental considerations.

Process developers and users, research scientists, and state and federal officials participated in the symposium, the sixth to be conducted on this subject by IERL-RTP since 1974.

N. Dean Smith, Gasification and Indirect Liquefaction Branch, EPA/IERL, Research Triangle Park, NC, was the Project Officer and the Technical Chairman. William J. Rhodes, Synfuels Technical Coordinator for EPA/IERL-RTP, was General Chairman.

Franklin A. Ayer, Manager, and N. Stuart Jones, Analyst, Technology and Resource Management Department, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, NC, were symposium coordinators and compilers of the proceedings.

In these proceedings, the title of each paper that has resulted from an EPA-funded project is marked with a (†) to indicate that it has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

The absence of a (†) in the title of a paper in these proceedings indicates that the paper is not the result of EPA-funded work and, therefore, its contents do not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

TABLE OF CONTENTS

	<u>Page</u>
OPENING SESSION	1
Session I: ENVIRONMENTAL SOURCE TEST AND EVALUATION RESULTS.	1
PART A: GASIFICATION AND INDIRECT LIQUEFACTION	1
Robert C. Lagemann, Chairman	
William C. Yee, Cochairman	
Characterization of Process Liquids and Organic Condensates from the Lurgi Coal Gasification Plant at Kosovo, Yugoslavia†	2
Karl J. Bombaugh,* Kenneth W. Lee, Ronald G. Oldham, and Slobodan Kapur	
Application of Kosovo (Lurgi) Gasification Plant Test Results to Pollution Control Process Design†	23
G. C. Page, W. E. Corbett, and R. A. Magee*	
Environmental Aspects of the GKT Coal Gasification Process†	42
R. E. Wetzel,* K. W. Crawford, and W. C. Yee	
Source Test of the Texaco Gasification Process Located at Oberhausen-Holtent, West Germany†	57
Robert G. Wetherold,* Robert M. Mann, John Morgan, William Yee, Peter Ruprecht, and Ranier Dürfield	
Source Test and Evaluation of a Riley Gas Producer Firing North Dakota Lignite†	66
Fred L. Jones,* William P. Earley, M. R. Fuchs, and V. A. Kolesh	
PART B: DIRECT LIQUEFACTION.	94
W. Gene Tucker, Chairman	
Morris H. Altschuler, Cochairman	
Environmental Program and Plans for the EDS Coal Liquefaction Project	95
Richard L. Thomas	
Sampling and Analysis of Process and Effluent Streams from the Exxon Donor Solvent Coal Liquefaction Pilot Plant†	107
Mark Notich* and Jung Kim	

*Denotes speaker

	<u>Page</u>
Health and Environmental Studies of H-Coal Process	124
K. E. Cowser,* J. L. Epler, C. W. Gehrs, M. R. Guerin, and J. A. Klein	
Chemical Characterization and Bioassay of SRC Process Materials	148
W. Dale Felix,* D. D. Mahlum, B. W. Wilson, W. C. Weimer, and R. A. Pelroy	
Session II: WATER-RELATED ENVIRONMENTAL CONSIDERATIONS	149
N. Dean Smith, Chairman William E. Corbett, Cochairman	
Coal Conversion Wastewater Treatment/Reuse - An Overview.	150
F. E. Witmer	
Characterization of Coal Conversion Wastewaters Using On-Site GC/MS†	170
C. J. Thielen* and R. V. Collins	
Treatment of Wastewater from a Fixed-Bed Atmospheric Coal Gasifier†	186
Philip C. Singer* and Eli Miller	
Treatment of Fossil Fuel Derived Wastewaters with Powdered Activated Carbon/Activated Sludge Technology.	203
R. B. Ely* and C. L. Berndt	
Land Treatment of Coal Conversion Wastewaters	218
R. C. Sims* and M. R. Overcash	
Session III: AIR-RELATED ENVIRONMENTAL CONSIDERATIONS.	231
Theodore G. Brna, Chairman	
Removal of Acid Gases and Other Contaminates from Coal Gas Using Refrigerated Methanol†	232
J. K. Ferrell, R. M. Kelly, R. W. Rousseau, and R. M. Felder*	
Advanced Techniques for Flue Gas Desulfurization†	256
Charles C. Masser, Theodore G. Brna, and Michael A. Maxwell*	
Health and Environmental Studies of Coal Gasification Process Streams and Effluents	282
C. A. Reilly, Jr.* A. S. Boparai, S. Bourne, R. D. Flotard, D. A. Haugen, R. E. Jones, F. R. Kirchner, T. Matsushita, M. J. Peak, V. C. Stamoudis, J. R. Stetter, and K. E. Wilzbach	

*Denotes speaker

	<u>Page</u>
Gaseous Fugitive Emissions from Synfuels Production - Sources and Controls†293
R. L. Honerkamp	
Control Systems for Air Emissions from Coal Gasification.313
Sid Thomson	
Session IV: SOLID WASTE-RELATED ENVIRONMENTAL CONSIDERATIONS328
David A. Kirchgessner, Chairman	
Kimm W. Crawford, Cochairman	
Health Effects Bioassay Results from Coal Conversion Solid Wastes.329
M. P. Maskarinec,* F. W. Larimer, J. L. Epler, and C. W. Francis	
A Comparison of RCRA Leachates of Solid Wastes from Coal-Fired Utilities and Low- and Medium-Btu Gasification Processes†341
Michael R. Fuchs,* Donnie L. Heinrich, Larry J. Holcombe, and Kishore T. Ajmera	
Characterization of Solid Wastes from Indirect Liquefaction Facilities†358
Cora A. Hunter, Kar Y. Yu, and Kimm W. Crawford*	
Ash/Slag Residuals and Wastewater Treatment Plant Sludges from Synfuels Facilities: Characterizations and Implications for Disposal.380
Ronald D. Neufeld,* Georg Keleti, J. Bern, C. Moretti, S. Wallach, and H. Erdogen	
Update of EPA's Regulatory Views on Coal Conversion Solid Wastes†.397
Yvonne M. Garbe	
Session V: MULTIMEDIA ENVIRONMENTAL CONSIDERATIONS398
T. Kelly Janes, Chairman	
John T. Dale, Cochairman	
A Permitter's View of Synfuel Commercialization†.399
George L. Harlow	
Comparison of Environmental Design Aspects of Some Lurgi-Based Synfuels Plants†.400
Milton R. Beychok* and William J. Rhodes	
Session VI: PRODUCT-RELATED ENVIRONMENTAL CONSIDERATIONS421
Robert P. Hangebrauck, Chairman	
Minh Triet-Lethi, Cochairperson	

*Denotes speaker

	<u>Page</u>
Risk Assessment of Synfuel Technology†422
A. Alan Moghissi	
Premanufacture Review of Synfuels under TSCA†423
Matthew Hale, Jr.* and Carl Mazza	
Methanol as a Clean Major Fuel.440
Paul W. Spaite	
Methanol as an Alternative Transportation Fuel†466
Richard Rykowski, Dwight Atkinson,* Daniel Heiser, John McGuckin, David Pletcher, Jeff Alson, and Murray Rosenfeld	
Project Summary - A Compendium of Synfuel End Use Testing Programs†489
Masood Ghassemi,* Sandra Quinlivan, and Michael Haro	
Comparative Testing of Emissions from Combustion of Synthetic and Petroleum Fuels†.509
W. Gene Tucker* and Joseph A. McSorley	
UNPRESENTED PAPERS.523
Problems Associated with the Analysis of Synfuels Product, Process, and Wastewater Streams†.524
H. C. Higman, D. K. Rohrbaugh, R. H. Colleton, and R. A. Auel	
Solvent Extraction Processing for Coal Conversion Wastewaters . .	.535
James R. Campbell, Richard G. Luthy, and Manuel J. T. Corrono	
APPENDIX: Attendees.545

*Denotes speaker

Session I: ENVIRONMENTAL SOURCE TEST AND EVALUATION RESULTS

Part A: Gasification and Indirect Liquefaction

Chairman: Robert C. Lagemann
U.S. Environmental Protection Agency
Research Triangle Park, NC

Cochairman: William C. Yee
Tennessee Valley Authority
Knoxville, TN

CHARACTERIZATION OF PROCESS LIQUIDS AND ORGANIC †
CONDENSATES FROM THE LURGI COAL GASIFICATION
PLANT AT KOSOVO, YUGOSLAVIA

by: Karl J. Bombaugh, Kenneth W. Lee and Ronald G. Oldham
Radian Corporation
8501 Mo-Pac Blvd.
Austin, Texas 78766

and

Slobodan Kapor
Institut za Primenu Nuklearne Energy
Baranjska 15
11080 Beograd - Zemun
Yugoslavia

ABSTRACT

Process liquids and gaseous stream condensates from the Lurgi Coal Gasification plant at Kosovo were characterized to define their organic composition. Samples of entrained liquids and condensates were collected during Phase II of the Kosovo source test that was described at the preceding Syn-fuel Symposium. These samples were characterized by Liquid Chromatographic fractionation using EPA's protocol for a Level I source assessment. In addition, GC-MS analyses were performed on key samples to quantify their levels of potentially hazardous PNA's, and GC with selective detection was used to characterize sulfur and nitrogen bearing species.

This presentation will provide a discussion of the analytical results and of the impact that these condensates have on the plant's discharge stream severity. It will also include a comparison of the composition of liquids from the Lurgi process with the compositions of liquids from other processes.

INTRODUCTION

Process liquids, gas stream condensates and solid wastes from the Kosovo Coal Gasification Plant were characterized to determine their organic composition. Samples were taken from fourteen gas streams, plus five liquid and two solid phase streams during Phase II of the source test that was sponsored jointly by the United States Environmental Protection Agency and the Government of Yugoslavia. Sampling and analyses were conducted as a cooperative effort by American and Yugoslav scientists (1, 2).

The 21 streams selected for organic characterization are identified in Table 1. These streams provided a representative cross section of the Lurgi technology that is used at Kosovo. The locations of these streams are included in the plant's description.

TABLE 1. ANALYSES PERFORMED ON KOSOVO GAS STREAM CONDENSATES, PROCESS LIQUID AND SOLID WASTES

Stream	Analyses						
	Particulate Determination	TCO	Grav	LC	GC Sulfur	GC Nitrogen	GCMS PNA'S
<u>Gas Stream</u>							
Fleissner Autoclave Vent	x	x	x	x			
LP Coal Lock Vent	x	x	x	x	x	x	x
HP Coal Lock Vent	x	x	x	x	x	x	
Start-up Vent	x	x	x	x			x
H ₂ S-Rich Waste Gas		x	x	x		x	x
CO ₂ -Rich Waste Gas		x	x				x
Crude Product Gas		x	x			x	
Tar Tank Vent		x	x	x		x	x
Medium-Oil Tank Vent		x	x	x		x	x
Tar Separation Waste Gas	x	x	x	x		x	
Phenolic Water Tank Vent		x	x	x		x	x
Ammonia Stripper Vent		x	x	x	x	x	x
Naphtha Storage Tank Vent		x	x	x			x
Waste Gasses to Flare	x	x	x				
<u>Other Streams</u>							
Fleissner Condensate			x				
Gasifier Ash			x				
Heavy Tar	x	x	x				
Phenolic Water	x	x	x		⊕	⊕	⊕
Tar		x	x	x	⊕	⊕	⊕
Medium Oil		x	x	x	+	+	⊕
Naphtha		x			⊕		⊕

x - analyzed in Yugoslavia.

+ - analyzed in US using grab samples taken at random.

⊕ - Data not included in this report, but included in Reference 2.

The gasification plant consists of nine operational units as illustrated in Figure 1. The plant consumes dried lignite and produces two primary products (a medium Btu fuel gas and hydrogen) plus four by-products (tar, medium oil, naphtha and crude phenol). The plant's operation is as follows: run of the mine coal is dried in steam autoclaves by the Fleissner process and then sized to select particles suitable for the Lurgi gasifiers (dp = 6 - 60 mm). The dried coal is fed through a pressure lock system (Coal Lock Vents) to a 3.5 M diameter Lurgi gasifier where it is reacted with steam at 2.5 MP (25 atm) pressure to produce a crude gas which is quenched, cooled and then cleaned by the Rectisol process prior to its transport to the utilization site. As the hot gas is quenched and cooled, organic matter consisting of phenols, tars and oils are removed with quench liquor and hot gas condensate. In the gas cleaning operation, condensable organics are removed from the cooled gas by refrigeration after which the acid-gases (H₂S and CO₂) are removed by sorption in cold methanol. The acid-gas rich methanol is regenerated by depressurization and heating, releasing H₂S-rich Waste Gas which is flared and CO₂-Rich Waste Gas which is vented into the atmosphere.

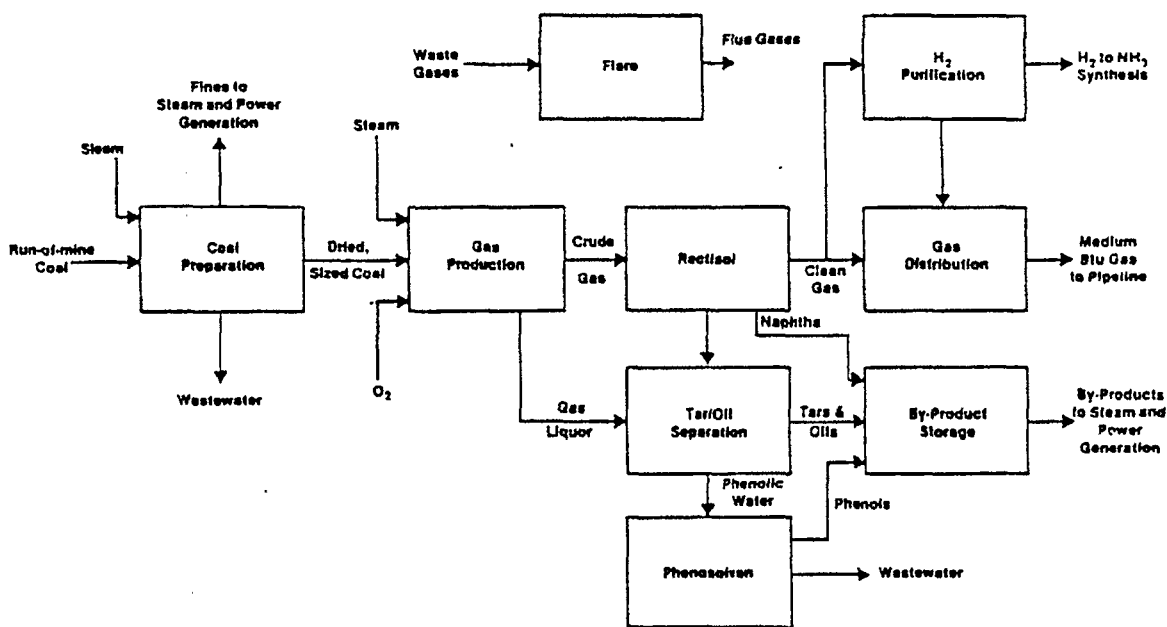


Figure 1. Simplified Flow Diagram of the Kosovo Coal Gasification Plant.

Tar, heavy tar and medium oil are each separated from their aqueous phase by decantation after which the combined waters are depressurized (Phenolic Water Tank) then stripped to remove ammonia (Ammonia Stripper Vent) and then extracted with disopropyl ether to remove extractable organics (Crude Phenol) prior to disposal.

EXPERIMENTAL

The sample characterization program consisted of a combination of the following methods: gas and liquid chromatographic fractionation using EPA's protocol for a Level 1 Environmental Source Assessment to determine the mass distributions of volatile and non-volatile organics; gas chromatographic analyses with both universal and selective GC detections to characterize organics; and GC-MS analysis to quantify certain potentially hazardous polynuclear aromatic compounds. The distributions of volatile and non-volatile organics were determined by the EPA protocol as Total Chromatographable Organics (TCO) and Gravimetrically Determined Organics (Grav) respectively (3).

Condensable organics were collected from gaseous streams with a sampling train that consisted of an entrainment separator, an ice cooled condenser, and a resin filled absorber in series. In some cases, sample collections were made in conjunction with a particulate measurement for which the entrained and condensed liquids were combined and then divided equally for the particulate determination and the organic characterization. In most cases, collections were made specifically for the organic characterization. All samples were refrigerated during the storage period between collection and work-up for analysis.

Sorbed vapors from the respective streams were recovered from their collection resin by soxhlet extraction with methylene chloride and were

combined with the organic extracts from their stream's condensates prior to analysis by the EPA protocol for TCO. The strategy followed for these determinations is illustrated in Figure 2.

To supplement the information provided by the TCO and Grav determinations, the extracts from selected streams (Table 1) were analyzed by gas chromatography with element specific detection to obtain profiles of the sulfur and nitrogen-containing species.

Polynuclear aromatics (PNA's) were determined on several streams by GC-MS. A liquid crystal GC column was used to isolate Benzo(a)pyrene from other isomeric PNA's.

The streams sampled and the analyses performed are summarized in Table 1.

RESULTS AND DISCUSSION

The concentrations of organics in the thirteen major gaseous streams of the Kosovo gasification plant (shown in Table 2) indicate that the phenolic water tank discharges the highest concentration of organics in the Kosovo plant (1.2×10^5 mg/m³) and that a major portion (92%) of the emission is due to TCO. The TCO value obtained from this measurement is a factor of five higher than the level indicated by light aromatic concentrations that were determined during the Phase II test. The significant difference between these two values is not explained. The discharge from the ammonia stripper vent also contains a high concentration of organics but in this stream the mass concentrations of the TCO hereafter called volatile organics (VO) and Grav hereafter called non-volatile organics (NVO) are about equal (57% volatiles). Excluding the two high concentration streams, the average concentration of combined organics in tested streams was 5,800 mg/m³ with most values falling in a range between 1,000 and 20,000 mg/m³. As expected, the lowest concentration of combined organics was found in the CO₂-rich waste gas. The value obtained in this stream for non-volatile organics may not be significant since it is based on a single determination and probably is within the noise level of the analytical method. A more accurate measurement is required to establish, definitively, the level of condensable organics in this stream.

A comparison of the concentration levels of VO's with the concentrations of light aromatics, as determined during Phase II of the source test, is shown in Table 3. The light aromatic values shown are the sum of phenol plus C₁ and C₂ alkyl aromatics. These light aromatics are included in the volatile organics determination and appear to represent a significant portion (30 to 60%) of the materials determined as VO. In cases where the concentrations of light aromatics are greater than the concentration of VO, it is not known whether the difference is due to variations in the stream's composition or to analytical error. However, the VO and light aromatic concentration values, when considered together, provide a reasonable indication of the quantities of volatile organics in the respective streams.

A similar comparison is made in Table 4 between the concentration values of NVO and the Tar and Oil (T&O) values that were reported for particulates in several streams. In this comparison, most values fall within a factor of 2

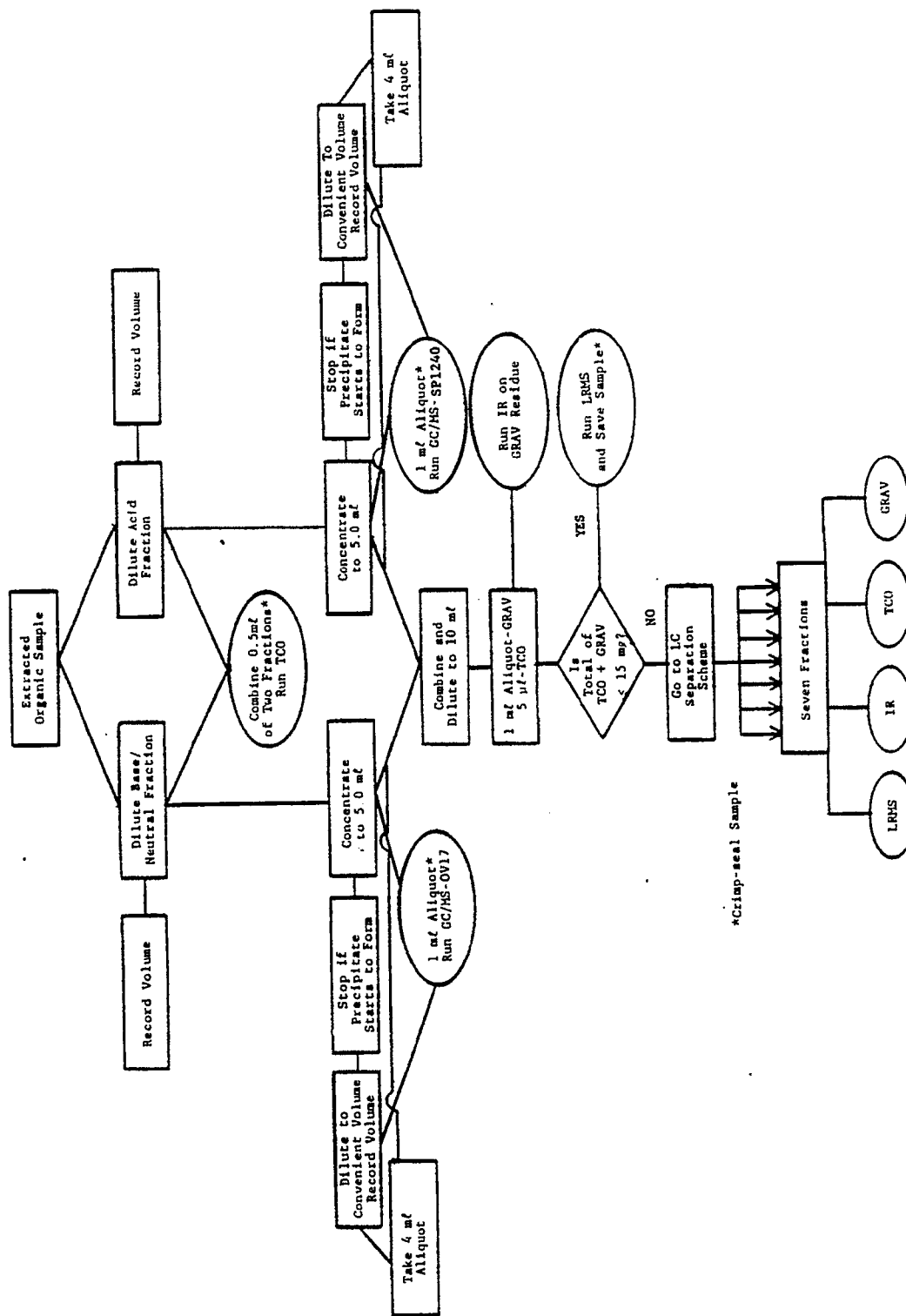


Figure 2. Strategy Followed for the Characterization of Kosovo Organics.

TABLE 2. CONCENTRATIONS OF VOLATILE AND NONVOLATILE ORGANICS IN KOSOVO PLANT GAS STREAM CONDENSATES

Source	mg/m ³			% Volatile Organics	% Non-Volatile Organics
	Volatile Organics ¹ (TCO)	Non-Volatile Organics ² (Grav)	Total Organics ³		
Fleissner Autoclave Vent	306	807	1,113	27	73
LP Coal Lock Vent	3,732	4,007	7,739	48	52
HP Coal Lock Vent	1,622	1,250	2,872	57	43
Start-up Vent	2,670	7,053	(9,723)	27	73
H ₂ S-Rich Waste Gas**	40	90	130	31	69
CO ₂ -Rich Waste Gas	5	9	14	36	64
Tar Tank Vent	10,785	3,628	14,412	75	25
Medium Oil Tank Vent	19,921	1,197	21,118	94	6
Tar Separation Waste Gas	2,335	967	3,302	71	29
Phenolic Water Tank Vent	115,012	9,869	124,881	92	8
Ammonia Stripper Vent	56,167	43,051	99,218	57	43
Naphtha Storage Tank Vent	5,089	499	5,588	91	9
Combined Gas to Flare	312	290	602	52	48

¹ Volatile organics were determined as total chromatographable organics (TCO's) using EPA's Protocol which is based on a gas chromatographic determination of substances eluting in the range of C₇ to C₁₆ hydrocarbons representing a boiling range between 100 and 300°C.

² Non-volatile organics were determined gravimetrically using EPA's Protocol for "Grav" which includes all substances retained from a 24-hour ambient evaporation. The Protocol may allow the same mid-range volatiles to be included in both determinations; consequently the total may be higher than the true value.

³ These values are a summation of toluene, xylene, and phenol as determined during the Phase II test and are included for comparison.

**No XAD-2 value included.

TABLE 3. COMPARISON BETWEEN VOLATILE ORGANICS (TCO) AND SUMMED LIGHT AROMATICS (C₁ + C₂ ALKYL AROMATICS + PHENOL) AS DETERMINED DURING PHASE II OF THE KOSOVO SOURCE TEST

Source	Volatile Organics	Σ Light Aromatics
LP Coal Lock Vent	3,732	1,170
HP Coal Lock Vent	1,622	1,730
H ₂ S-Rich Waste Gas	40	30
CO ₂ -Rich Waste Gas	5	10
Tar Tank Vent	10,785	3,790
Medium Oil Tank	19,921	6,060
Tar Separation Waste Gas	2,335	5,190
Phenolic Water Tank	115,012	21,670*
Ammonia Stripper Vent	56,167	23,800
Naphtha Storage Tank	5,089	7,410

*Phenol value was calculated from its vapor pressure over a saturated aqueous solution at 65°C.

TABLE 4. COMPARISON BETWEEN ORGANICS COLLECTED BY PARTICULATE TRAIN AND THOSE COLLECTED VIA ORGANIC TRAIN

Source	Tar & Oil	Non-Volatile Organics	Total Organics Σ VO + NVO
Fleissner Autoclave Vent	534	808	1,114
LP Coal Lock Vent	7,920	4,007	7,739
HP Coal Lock Vent	953	1,634	3,753
Start-up Vent	9,800	7,051	9,721
Tar Separation Waste Gas	723	967	3,302

of each other (mean = 1.2 ± 0.5). As with the previous comparison, these results provide a reasonable indication of the level of non-volatile organics (Tars and Oil) which are transported by the respective streams.

The mass flow of combined organics in each stream is shown in Table 5. These results show that two streams (the start-up vent and the ammonia stripper vent) transport, by far, the greatest quantity of organic matter (98%). Either of these streams, when operating, transports more condensable organics than all of the other streams combined.

TABLE 5. MASS FLOW OF CONDENSABLE ORGANICS IN KOSOVO GASEOUS STREAMS

Source	Stream Flow m ³ /hr	Mass Flow g/hr	% Non-Volatile
LP Coal Lock Vent	21	163	52
HP Coal Lock Vent	230	660	43
Start-up Vent	12,500	121,538	73
H ₂ S-Rich Waste Gas	3,600	468	69
CO ₂ -Rich Waste Gas	3,600	50	64
Tar Tank Vent	0.55	8	25
Medium Oil Tank Vent	1.7	36	6
Gar Separation Waste Gas	28	92	29
Phenolic Water Tank Vent	5.5	687	8
Ammonia Stripper Vent	260	25,797	43
Naphtha Storage Tank Vent	4.5	25	9

Since both the composition and the flow rate of the discharge from the start-up vent varies considerably over the start-up period, the values presented here may represent a worst-case; nevertheless, the discharge is significant because a large gasification complex having many gasifiers can be expected to have at least one gasifier in a start-up mode at all times. Under such conditions, the start-up stream could flow continuously.

The ammonia stripper vent, reported previously as the most environmentally significant stream in the Kosovo Plant (1), is also the major

source of condensable organics. This stream is intermittent at Kosovo because the Phenosolvan plant is operated on demand, whereby phenolic water is accumulated in two large tanks and processed at a rate that is independent of the gas production rate. However, when the plant is operated at design capacity, continuous operation is necessary and the stripper vent is then a continuous discharge stream.

The phenolic water tank discharge contains the highest concentration of condensable organics, but because of its lower stream volume, its organic mass discharge rate is comparable to lower concentration but higher volume streams, e.g., the HP coal lock vent and the H₂S-rich waste gas stream.

The naphtha tank discharge which contained high concentrations of benzene, contained comparatively little volatile organics as defined by the protocol for Total Chromatographable Organics.

LC FRACTIONATION OF CONDENSABLE ORGANICS FROM KOSOVO STREAMS

The mass distribution of organic matter in the Kosovo condensates, as determined by the EPA Level 1 fractionation protocol, is shown in Table 6. All data are given as stream concentration, expressed in mg/m³. In this form, the values shown for each fraction do not indicate the mass recovered from the column, but rather the computed mass concentration in one cubic meter of gas. Therefore, fraction concentrations are directly relatable to stream concentrations.

TABLE 6. CONCENTRATIONS OF ORGANICS FOUND IN EACH LIQUID CHROMATOGRAPHIC FRACTION AND IN THE SAMPLE STREAM

Source	LC Fraction (mg/m ³)							Total Recovered mg/m ³	Concentration* in Stream mg/m ³
	1	2	3	4	5	6	7		
Fleissner Autoclave Vent	229	47	80	47	73	203	20	699	1,114
LP Coal Lock Vent	167	79	426	1,456	1,281	2,297	266	5,981	7,739
HP Coal Lock Vent	395	285	145	168	282	563	67	1,912	2,872
Start-up Vent	458	430	1,743	160	268	1,595	302	4,956	5,540
H ₂ S-Rich Waste Gas	19	5	12	7	8	18	4	73	130
Tar Tank Vent	3,734	449	410	652	753	2,179	225	8,402	14,412
Medium Oil Tank Vent	2,275	229	246	250	335	1,061	76	4,471	21,118
Tar Separation Waste Gas	266	105	154	129	183	649	38	1,525	3,302
Phenolic Water Tank Vent	32,190	3,335	2,458	3,650	4,185	10,847	857	51,737	124,884
Ammonia Stripper Vent	1,880	2,607	2,222	16,923	17,692	27,949	4,145	73,419	99,218
Naphtha Storage Tank Vent	342	25	40	44	34	380	37	902	5,589

All values computed to stream concentration and expressed as milligram per normal cubic meter of gas

*From Table 2.

Recoveries of organics from the LC fractionation averaged about 50% (Table 7). Recoveries of VO and NVO were computed separately, consequently the values shown for combined organics are weighted values. These results show that NVO recovery, generally, was better than VO's recovery; probably because the component loss to evaporation was more significant than loss through non-elution.

The composition of each chromatographic fraction is defined, in part, by the polarity of the eluting solvent. Consequently, all components in a given chromatographic fraction should have similar polarity, but they may represent widely differing chemical classes. Some chemical classes which could be found in the respective fractions are shown in Table 8. Fraction 5, which shows no entry should contain overlap from adjacent fractions.

TABLE 7. RECOVERIES OF ORGANICS FROM THE LIQUID CHROMATOGRAPHIC PROCEDURE

Stream	Percent Recovery		
	Volatile Organics	Non-Volatile Organics	Combined Organics
Fleissner Autoclave Vent	41	70	62
LP Coal Lock Vent	109	47	77
HP Coal Lock Discharge	66	67	66
Gasifier Start-up Vent	45	54	49
H ₂ S-Rich Waste Gas	40	65	58
Tar Tank Vent	58	58	58
Medium Oil Tank Vent	17	93	21
Tar Separation Waste Gas	38	93	46
Phenolic Water Tank Vent	42	91	46
Ammonia Stripper Vent	98	43	74
Naphtha Storage Tank Vent	9	83	16
Mean	43	69	53
SD	+25	+18	+19

TABLE 8. PROBABLE LC FRACTION IN WHICH VARIOUS COMPONENT CLASSES APPEAR

Eluting Solvent	Possible Chemical Classes in Fraction						
	1	2	3	4	5	6	7
Pentane	Aliphatics						
20% Methylene in Pentane	Aliphatics	Fused-Ring Hydrocarbons					
50% Methylene Chloride in Pentane		Aromatic Hydrocarbons					
Methylene Chloride				Ethers			
5% Methanol in Methylene Chloride				Aldehydes			
20% Methanol in Methylene Chloride				Heterocyclic Oxygen			
50% Methanol in Methylene Chloride				Nitriles			
				Indoles & Carboxoles			
				Thiophenes			
						Alcohols	
						Esters	
						Amines	
						Quinolins	
						Alkyl Sulfur	
						Sulfonic Acids	
						Carboxylic Acids	

The relative distributions of the eluted organics across the seven fractions are shown in Table 9. These results indicate that fraction 6, which should include phenols and nitrogen heterocyclics, contains the largest portion of the eluate (Ave = 31% \pm 8) followed by fraction one [Ave = (27% \pm 19)] which should contain only paraffins.

TABLE 9. PERCENT OF ELUTED ORGANICS FOUND IN EACH LC FRACTION AND PERCENT RECOVERY FROM THE LC SEPARATION PROCESS

Source	Total Elution mg/m ³	Fraction Number							Percent Recovered
		1	2	3	4	5	6	7	
Fleissner Autoclave Vent	699	33	7	11	7	10	29	3	63
LP Coal Lock Vent	5,981	3	1	7	24	21	38	4	77
HP Coal Lock Vent	2,499	21	15	7	9	15	29	4	67
Start-up Vent	-	9	(9)	(35)	(3)	(5)	(32)	(6)	51
H ₂ S-Rich Waste Gas	59	25	7	17	10	11	24	6	56
Tar Tank Vent	8,402	44	5	5	8	9	26	3	58
Medium Oil Tank Vent	4,471	51	5	5	6	7	24	2	21
Tar Separation Waste Gas	1,525	17	7	10	8	12	43	3	46
Phenolic Water Tank Vent	57,522	56	6	4	6	7	19	2	46
Ammonia Stripper Vent	59,880	3	4	3	23	24	38	6	74
Naphtha Storage Tank Vent	902	38	3	4	5	4	42	4	16

A three-dimensional view of the relative distribution of chemical classes across the key streams in the Kosovo plant is shown in Figure 3. From this view, it is evident that a significant portion of the condensable organics from each stream is found in fraction 6 which contains phenols and nitrogen heterocyclics and that most streams contain relatively large proportions of alkyl aromatics as found in fraction 1. Fraction 3 is seen to be larger in the Start-Up Vent and H₂S-Rich Waste Gas's condensate. This fraction could contain thiophenes, indols, nitriles, and oxygen heterocyclics which are normally found in fraction 4 but probably overlap.

The low level of alkyl aromatics in the ammonia stripper vent condensate supports substantially the Phase II source test results which showed virtually no benzene or toluene in that vent's discharge.

A COMPARISON OF CONDENSABLE ORGANICS IN KOSOVO STREAMS WITH THOSE OF OTHER TYPES OF GASIFIERS

A comparison of the levels of condensable organics in vent gases from the Kosovo plant with those in "similar" streams from other types of gasifiers indicates that the organics concentration levels generally are comparable. The comparison data are shown in Table 10. The lower level of volatile organics in the Chapman coal vent discharge may be because the Chapman gasifier was using bituminous coal whereas all others listed were using lignite.

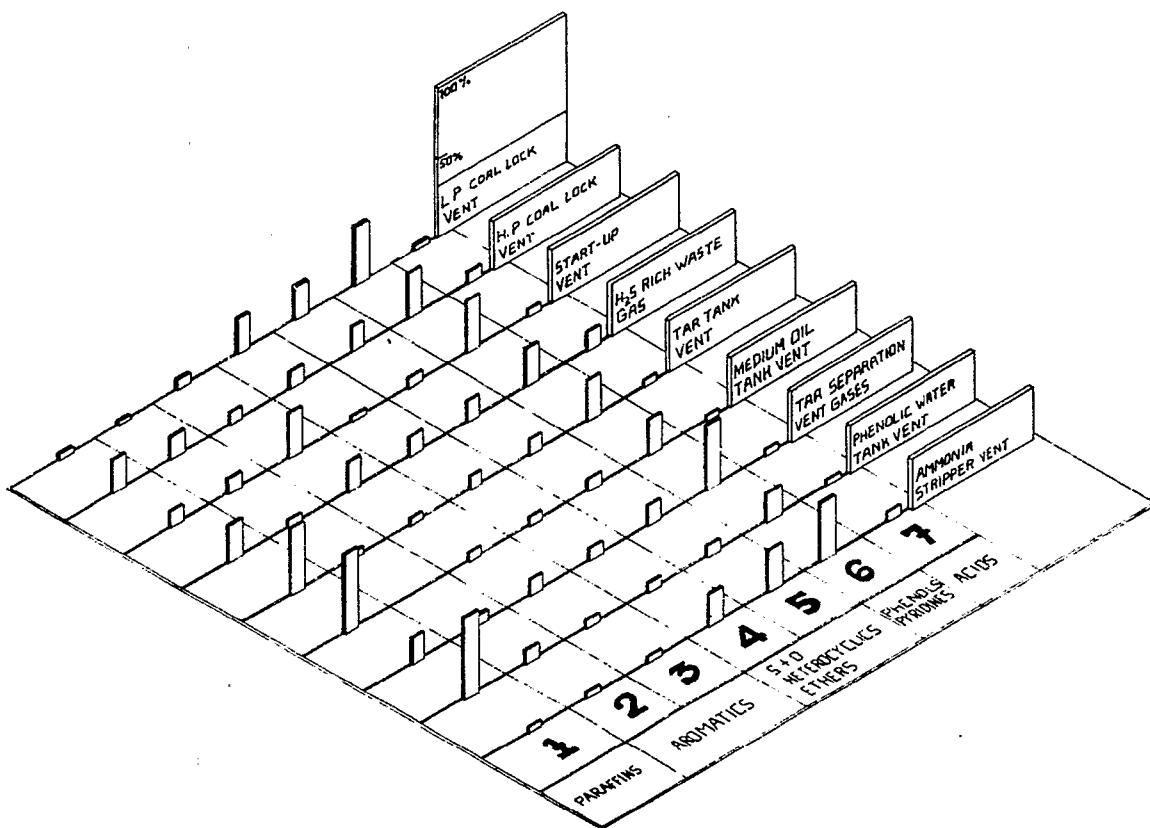


Figure 3. Distribution of Chemical Classes across the LC Fractions of Kosovo Gas Stream Condensates.

TABLE 10. A COMPARISON OF ORGANICS IN "SIMILAR" STREAMS FROM DIFFERENT GASIFICATION PLANTS (4-6)

Source	mg/m ³		
	Volatile Organics	Non-Volatile Organics	Total Organics
Lurgi (Kosovo) LP Coal Lock	3,732	4,007	7,739
Lurgi (Kosovo) HP Coal Lock	2,121	1,632	3,753
Chapman (Holston) Coal Feeder Vent	378	2,002	2,380
Riley Product Gas	3,643	2,186	5,829
Wellman-Galusha (Ft. Snelling) Product Gas	5,900	2,100	8,000
Kosovo Tar Separation Offgas	2,335	967	3,302
Chapman Separator Vent	1,897	2,303	4,200

CHARACTERIZATION OF KOSOVO PROCESS LIQUIDS AND SOLID WASTES

The concentrations of organics in Kosovo process liquids and solid wastes are summarized in Table 11. These results indicate that phenolic water is transporting approximately 11 g/l of organics of which 32% are volatile. Heavy tar consists of about 86% organics - the balance probably being a combination of error in the determination and inorganics in the coal; heavy tar is known to contain a considerable amount of coal dust (26% insoluble particles). Gasifier ash, also listed in Table 11, contains minimal organic matter (.04%) of which none was volatile.

TABLE 11. CONCENTRATIONS OF VOLATILE AND NON-VOLATILE AND TOTAL ORGANICS IN KOSOVO PROCESS LIQUIDS AND SOLID WASTES

	Units	Volatile Organics	Non-Volatile Organics	Total Organics	Percent Volatile	Percent Non-Volatile
Phenolic Water	mg/l	3,569	7,556	11,225	32	68
	mg/l	3,774	7,371	11,145	34	66
Medium Oil	mg/g	389	439	828	47	53
	mg/g	334	452	786	42	58
Tar	mg/g	567	778	1,345	42	58
Heavy Tar	mg/g	460	404	864	53	47
Gasifier Ash	mg/kg	-	400	400	0	100

For definition of volatile and non-volatile, see Table 2.

The by-products, tar and medium oil, show very similar distributions between volatile and non-volatile organics. When their vastly differing boiling point ranges are considered, this similarity is surprising. However, the low recovery of total organics from the medium oil suggests that a significant amount of sample was lost in the determination (~20%). If a correction for this loss were applied to the volatile organics, a more reasonable value would be obtained (55%).

The distribution of organics in various Kosovo tars and oils as determined by liquid chromatography is shown in Table 12. Although these materials can be expected to have vastly different compositions, as would be indicated by their differing solubilities and boiling point ranges, they have surprisingly similar chromatographic profiles.

The close similarity in the LC profiles from the Kosovo streams, whose chemical compositions may differ significantly indicates that more discriminating methods of separation and detection are needed to obtain descriptive profiles of these streams.

GAS CHROMATOGRAPHIC ANALYSIS WITH ELEMENT SPECIFIC DETECTORS

As a supplement to the information that was provided by the LC Fractionation, the condensable organics from several streams were examined by gas

TABLE 12. PERCENT ELUTED ORGANICS FOUND IN EACH LC FRACTION FROM THE LC SEPARATION OF SEVERAL KOSOVO LIQUIDS AND HEAVY TAR

Fraction	Percent in Each Fraction			
	Phenolic Water	Heavy Tar	Tar	Medium Oil
1	19	10	17	12
2	15	6	2	6
3	19	16	15	16
4	4	11	9	4
5	10	14	9	10
6	31	39	39	45
7	2	4	9	7

chromatography with element specific detectors. Chromatograms of the sulfur-containing species and of the nitrogen-containing species that were obtained in this manner show that the Kosovo streams contained complex mixtures of both types of compounds.

The sulfur-specific chromatograms of condensable organics from three streams in Figure 4 show both similarities and differences in these materials. For example, the chromatograms of the LP and the HP coal lock vent have many peaks in common, while the chromatogram of the ammonia stripper condensate is distinctly different from those of the coal lock condensates. The stripper condensate may contain a relatively larger amount of the more water soluble sulfur-containing species.

The condensate from the HP coal lock shows considerably less background matrix effect which may relate in part to the influences of the Venturi scrubber through which the gas had passed. The peaks labeled 1-4 have been identified as thiophenes. Peaks labeled 5-8 are unidentified; however, their intensity suggests that they represent materials which contain a higher sulfur to carbon ratio than the thiophenes (possibly two or more sulfurs per molecule, e.g., disulfides or dithiols). Their uniform difference in retention suggests that they may be an homologous series of isomers.

Nitrogen-specific chromatograms of the stream condensates indicate that the Kosovo condensable organics contain several classes of organic nitrogen compounds. The chromatogram of the condensates from four streams, shown in Figure 5, indicate that these samples contained many of the same components. Several peaks have been identified tentatively as isomers of pyridine and quinoline. In contrast, the chromatograms in Figure 6 indicate that the nitrogen species in some streams differ significantly from the others. For example, the chromatogram of the condensable organics from the stripper vent (A) and the medium oil tank (C) differs significantly from that of the phenolic water tank vent (B). (The latter chromatogram (B) is similar to those in Figure 5). These results indicate that the major components in the two groups of samples are different compounds rather than the same compounds which have distributed differently between the two groups of streams.

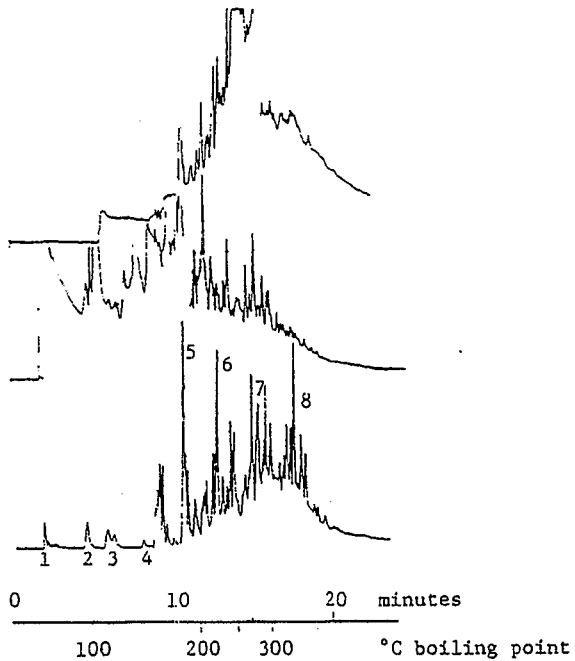


Figure 4. Chromatograms of Sulfur Species in Condensates from 3 Kosovo Gas Streams.
 Top - LP Coal Lock
 Center - Ammonia Stripper Vent
 Bottom - HP Coal Lock

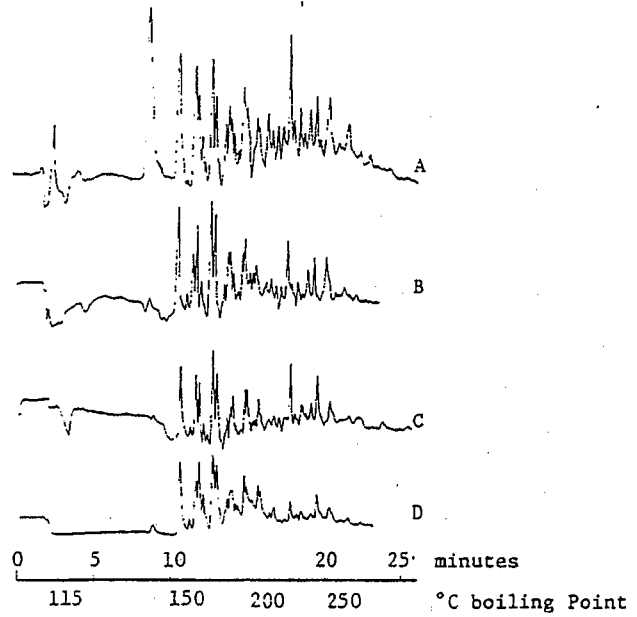


Figure 5. Chromatograms of Nitrogen Species in Condensates from 4 Kosovo Gas Streams.
 A - LP Coal Lock Vent
 B - HP Coal Lock Vent
 C - Tar Separation Waste Gas
 D - Tar Tank Vent

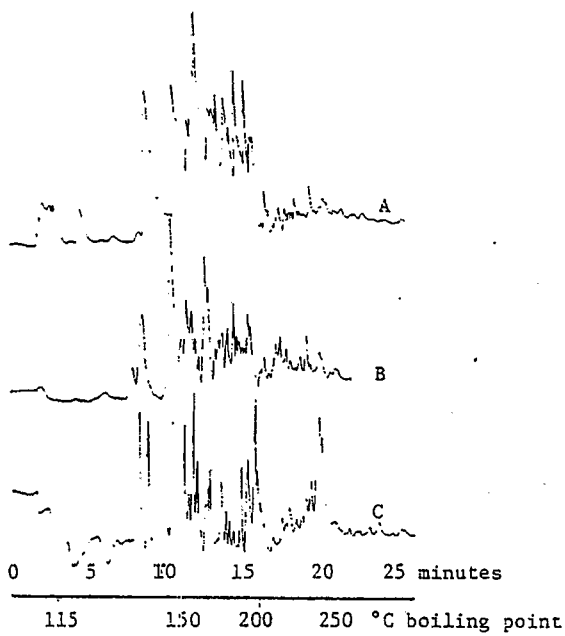


Figure 6. Chromatograms of Nitrogen Species in Condensates from 3 Kosovo Streams.
 A - Ammonia Stripper Vent
 B - Phenolic Water Tank Vent
 C - Medium Oil Tank Vent

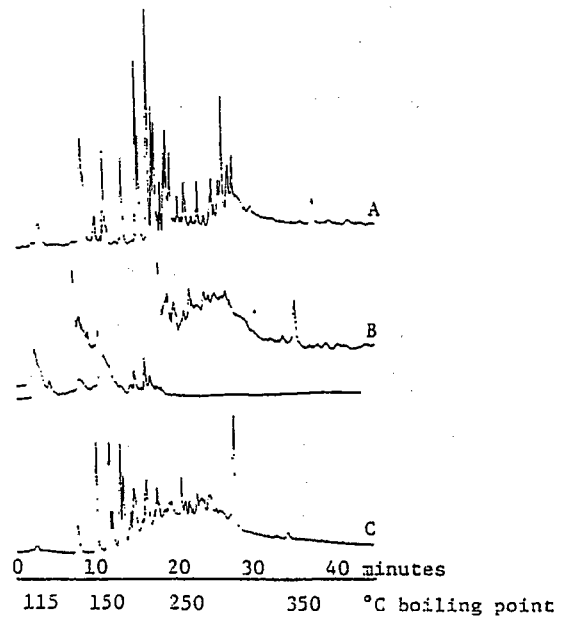


Figure 7. Chromatograms of Nitrogen Species in Kosovo Medium Oil.
 A - Neutral Fraction
 B - (2) Base Extractable Fraction (contains acids & phenols)
 C - Acid Extractable Fraction (contains organic bases)

A most surprising result is the chromatogram of the condensable organics from the medium oil tanks. This nitrogen-specific chromatogram differs from those of the other streams and from previously prepared chromatograms of the nitrogen species in Kosovo medium oil. Since the chromatogram of the condensed discharge differs from that of the tank's oil, this condensate must not be a product of simple vaporization.

INVESTIGATION OF KOSOVO MEDIUM OIL

A brief study was conducted on Kosovo medium oil using a combination of physical/chemical separations and gas chromatography with element specific detectors in an attempt to gain some insight into the cause of the observed difference between the elemental chromatograms of the various stream condensates. The Kosovo medium oil was separated into an acid-extractable fraction, a base-extractable fraction and a neutral fraction. A water-oil co-distillate was also obtained. Element specific chromatograms of each of these fractions provide significant information about the medium oil which can be applied to the condensable organics which are transported by the various Kosovo gaseous streams.

The nitrogen-bearing species in Kosovo medium oil were found to be more complex than the sulfur species in that they consisted of a complex mixture of several different classes of compounds whose solubilities were markedly affected by pH. The chromatograms in Figure 7 show that three distinctly different sets of compounds are found in the respective neutral, base extractable and acid extractable fractions, and that each fraction contains numerous (40-60) compounds. Since very few peaks show common retention times between fractions, it is reasonable to conclude that there is minimal, if any, overlap between fractions.

The acid extractable fraction should contain proton acceptors such as pyridines and quinolines: the neutral fraction should contain the pyrazine (diazines) and/or other more neutral nitrogen species including possibly oxazoles and thiazoles; and the base extractable fraction should contain proton donors such as acids, alcohols and phenols.

The chromatogram in Figure 8 was obtained with the NaOH soluble material that precipitated during the acid-extraction of the medium oil. Since pyroles are known to polymerize in an acid medium and since the peak at 35 min. matches that of cabazole (dibenzopyrole) it is conceivable that this fraction contains pyroles.

A chromatogram of the water/oil co-distillate is shown in Figure 9 along with a chromatogram of the vapor over a closed container of medium oil at about 50°C. This comparison shows that except for the broad early eluting peaks in the vapor, the two samples contain many of the same compounds. The broad early eluting peaks in the vapor suggest that the vapors contain low boiling, strongly polar nitrogen species which are interacting with the column. These materials have not been identified or quantified in the Kosovo gas streams.

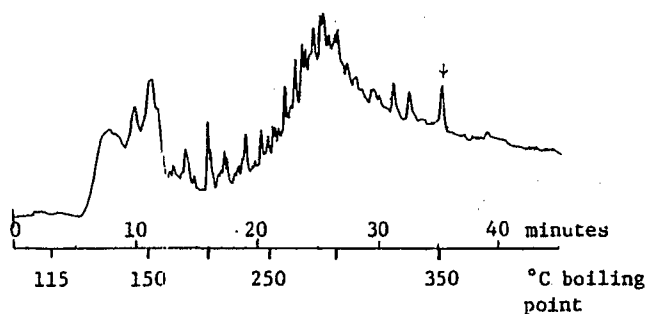


Figure 8. Chromatogram of Acid Insoluble Fraction from Kosovo Medium Oil. Identified peak (+) has same retention time as Carbazole.

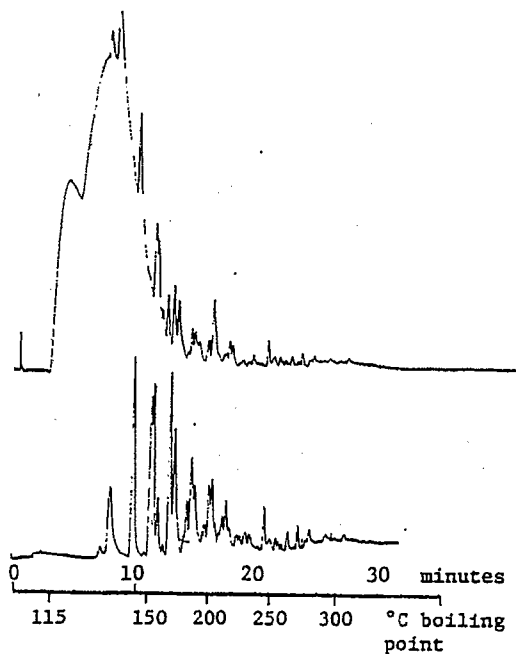


Figure 9. Chromatograms of Nitrogen Species in Medium Oil Head Space Vapor (top) and in Water-Oil Co-distillate (bottom).

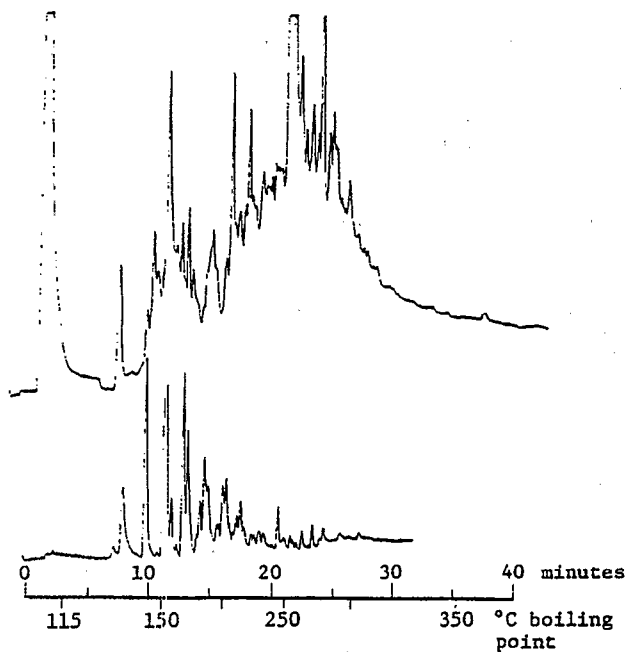


Figure 10. Chromatogram of Nitrogen Species in Residual Water from Co-distillation of Kosovo Medium Oil (top) Compared with Chromatogram of Nitrogen Species in Water-Oil Co-distillate (bottom).

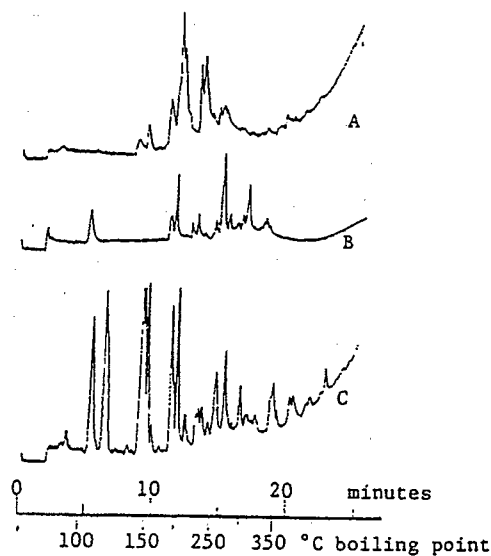


Figure 11. Chromatograms of Sulfur Species in Fractions of Kosovo Medium Oil.

A - Acid Extractable Fraction
 B - Base Extractable Fraction
 C - Neutral Fraction

A chromatogram of the residual water from the co-distillation (still pot) is shown in Figure 10 along with a chromatogram of the steam distillate. These chromatograms also have many peaks in common, but the two materials differ greatly in composition. Significant quantities of high molecular weight materials have partitioned into the water layer from the medium oil producing a fraction that is rich in high-boiling water soluble components. A portion of the water layer chromatogram (5-15 min) is very similar to the chromatogram of the condensate from the ammonia stripper vent shown in Figure 6.

The chromatograms of the several fractions of medium oil shown in Figures 6 through 10 show that the organic nitrogen species in the Kosovo organics represent an extremely complex mixture of compounds covering a wide range of boiling points, solubilities, polarities and dissociation potentials. However, when these compounds are fractionated according to solubility, pH, and finally vapor pressure, a set of profiles is obtained which defines the composition of the mixture. Because these fractionation methods are not absolute, the composition of each fraction depends upon the separation method used, as well as on the sample's compositions. Consequently, the influence of the separation method must be considered when interpreting results.

A major factor in the complexity of the mixture of nitrogen compounds is that the nitrogen species are influenced by so many different properties. The stream's composition can be altered significantly by a slight change in pH, or by the presence or absence of water or by an increased organic layer in an aqueous process stream. Further, a sample's composition can also be influenced by a vapor collection method as well as by a vapor recovery method. As was demonstrated here, exposing a sample to a strong acid can remove an entire class of components. Consequently, a characterization based on a well defined methodology, that takes into consideration the specific properties of these nitrogen compounds, is needed before the composition of the Kosovo organics can be defined quantitatively.

The sulfur species in Kosovo medium oil also represent a range of solubilities and dissociation potentials. However, the mixture appears to be somewhat less complex than the mixture of nitrogen compounds. The neutral fraction of medium oil contains many more components (Figure 11) than either the acid extractable or the base extractable fractions. The neutral fraction contains primarily the thiophenes and the mercaptans. The base extractable fraction which should contain organic acids, and phenols probably contains bifunctional (oxygen and sulfur) compounds also. The acid extractable fraction, which was shown to contain the nitrogen bases, must also contain bifunctional compounds such as thiozoles. Both the acid extractable and the base extractable sulfur compounds appear to fit into a comparatively well defined boiling point range.

When the sulfur specific chromatograms of Kosovo medium oil fractions are compared with those of the plant's discharge stream condensates, it is apparent that the neutral components are dominant in the gas streams associated with the product gas. In contrast, the chromatogram of the ammonia stripper vent shows numerous peaks which match the profiles of the acid and base extractable fractions of medium oil, supporting the earlier premise that the ammonia stripper condensate contains higher concentrations of the water

soluble sulfur species. Bifunctional compounds such as thiozoles (S & N) and thiophenols (S & O), exhibit higher water solubilities than thiophenes and may well be present in the stripper vent's discharge.

POLYNUCLEAR AROMATICS (PNA'S) IN KOSOVO STREAM CONDENSATES

The concentrations of four hazardous polynuclear aromatics (PNA's) in several Kosovo discharge streams are shown in Table 13. Highest concentration levels were found in the LP coal lock discharge. The higher sensitivity levels achieved for the naphtha storage tanks were achieved by concentrating the sample enough to obtain a measurable level of PNA. The concentration of BAP in the naphtha storage tank was thereby measured at a level of $0.085 \mu\text{g}/\text{m}^3$. For the remaining streams, PNA concentrations were measured to a sensitivity level of 0.1 ppm on the extracts as defined by the protocol shown in Figure 3. The resulting minimum detectable concentrations calculated for each stream are listed in Table 13.

TABLE 13. CONCENTRATIONS ($\mu\text{g}/\text{m}^3$) OF SELECTED HAZARDOUS POLYNUCLEAR AROMATICS IN KOSOVO GASEOUS DISCHARGE STREAMS

Source	BaA	BaP	dBahA	BhF
LP Coal Lock Vent	163	670	52	670
Ammonia Stripper Vent	85	20	<2.1	12
Naphtha Storage Tank Vent	<0.06	0.085	0.06	0.11
Start-up Vent	-	139	<2.1	-
Tar Tank Vent	-	252	<10	-
Phenolic Water Tank Vent	-	<50	<50	-
Medium Oil Tank Vent	-	<6.5	<6.5	-
H ₂ S-Rich Waste Gas	-	<0.6	<0.6	-
CO ₂ -Rich Waste Gas	-	<0.7	<0.7	-

All (<) values are calculated from a minimum detectable concentration of 0.1 ppm in the measuring solution.

- not determined.

BaH - Benzo(a)anthracene
 BaP - Benzo(a)pyrene
 dBahA - dibenz(ah)anthracene
 BhF - Benzo(h)Fluoranthene

In a previous report (1) the concentration level of PNA in the Kosovo coal lock discharge was estimated from the concentration of PNA in by-product oil using the measured level of tars and oils in the discharge as a base for calculation. The level for BAP in the LP coal lock discharge was estimated to be between $500 \mu\text{g}/\text{m}^3$ (the oil based value) and $1500 \mu\text{g}/\text{m}^3$ (the tar based value). The measured value on the stream is $670 \mu\text{g}/\text{m}^3$ which is very close to the estimate that was based on medium oil. This agreement indicates that the reasonable estimates of the levels of PNA in discharge streams can be made with the combined use of the concentration of tar/oil aerosols in the streams and the PNA concentration of medium oil.

Estimated values that were reported previously for 7,12 Dimethylbenz(a)-anthracene could not be confirmed because difficulty was experienced in the determination. Reproducible results could not be obtained.

ENVIRONMENTAL SIGNIFICANCE OF CONDENSABLE ORGANICS IN KOSOVO STREAMS

In a previous work, the environmental significance of each of these Kosovo streams was determined using the SAM-1/A model to compute the streams' Total Discharge Severities (TDS). To make these determinations, the concentrations of each potential pollutant in the gas phase was divided by its D-MEG value to obtain component DS values which could be summed to obtain the streams' TDS value (7).

To include the contributions of the condensable organics in the stream's TDS determination, it is necessary to adopt a representative D-MEG value with which to calculate Discharge Severity (DS) values for these heterogeneous mixtures of organic substances. Use of a representative D-MEG value is the only reasonable alternative since a rigorous treatment based on individual component concentrations and D-MEG values is impractical, if not impossible.

A D-MEG (air-health) value of 2.5×10^4 was adopted as being representative of higher molecular weight components thought to be present in the Kosovo organic condensates. This value was used to calculate DS values as shown in Table 14 for condensates in each stream. Also shown are: the previously reported TDS values that are based on the stream's major and minor components, and the percentages by which each stream's TDS would be increased by the addition of the DS due to condensable organics. No percentage value exceeded 20% and several were less than 1%.

TABLE 14. EFFECT OF CONDENSABLE ORGANICS ON TOTAL DISCHARGE SEVERITY (TDS) OF KOSOVO STREAMS

Source	Previously Reported TDS	Added DS*	% Increase
Fleissner Autoclave Vent	1.00E04	4.50E01	<1
LP Coal Lock Vent	7.88E03	3.10E02	4
HP Coal Lock Vent	5.92E03	1.15E02	2
Start-Up Vent	7.19E03	3.89E02	5
H ₂ S-Rich Waste Gas	1.11E04	5.20E00	<1
CO ₂ -Rich Waste Gas	7.32E02	5.60E01	<1
Tar Tank Vent	4.31E03	5.76E02	13
Medium Oil Tank Vent	2.82E04	8.44E02	3
Tar Separation Waste Gas	2.06E04	1.32E02	6
Phenolic Water Tank Vent	3.67E04	5.00E03	14
Ammonia Stripper Vent	2.07E04	3.97E03	19
Naphtha Storage Tank Vent	7.08E04	3.23E02	<1

*Based on an average D-MEG (air-health) of 2.5E04
1.00E04 represents 1.00×10^4

These results indicate that the "condensable" organics are environmentally significant in all streams except the CO₂-Rich Waste Gas but, in all cases, their contributions to the TDS values of these streams are relatively small.

ENVIRONMENTAL SIGNIFICANCE OF HAZARDOUS PNA'S IN KOSOVO STREAMS

DS (air-health) values for the potentially more significant PNA's are listed in Table 15 along with the percentages by which these DS's would increase the previously reported TDS values of each stream. As with the condensable organics, all DS values greater than unity are potentially significant environmentally. However, significant increases in stream TDS value were found in only three of the nine streams tested. The greatest increase (430%) was seen in the LP coal lock vent; followed by the tar tank vent (300%) and the start-up vent (100%). A most significant observation is that the PNA's contribution to stream TDS is dominated by the contribution from Benzo(a)pyrene.

TABLE 15. DISCHARGE SEVERITY DUE TO HAZARDOUS PNA'S IN KOSOVO STREAMS

Source	BaA	BaP	dBahA	Total	%
LP Coal Lock Vent	3.62E00	3.35E04	5.59E02	3.41E04	433
Ammonia Stripper Vent	1.89E00	1.00E03	2.26E01	1.02E03	5
Naphtha Storage Tank Vent	-	4.25E00	<1	4.25E00	nil
Start-Up Vent	-	6.95E03	<2E1	6.97E03	97
Tar Tank Vent	-	1.26E04	<1E2	1.27E04	297
Phenolic Water Tank Vent	-	<2E3	<5E2	<2.5E3	<7
Medium Oil Tank Vent	-	<3E2	<7E1	<3.7E2	<1
H ₂ S-Rich Waste Gas	-	<3E1	<6E0	<3.6E1	<1
CO ₂ -Rich Waste Gas	-	<4E1	<8E0	<4.8E1	<7

All DS values for Benzo(h)fluoranthene were <1 and are not shown.

ACKNOWLEDGEMENT

This work was sponsored by the Industrial Environmental Research Laboratory of the United States Environmental Protection Agency. The authors express their thanks to the following organizations and individuals for their contributions to this work: U.S. EPA, T. Kelly Janes and W. J. Rhodes; Radian Corporation, R. V. Collins and W. E. Corbett; Rudarski Institute, M. Mitrovic and D. Petkovic; Kosovo Institute, A. Kukaj and M. Milesavljevic; Elektroprevreda Kosovo, S. Dyla and E. Boti.

REFERENCES

1. Bombaugh, K. J., W. E. Corbett, K. W. Lee, and W. S. Seames. An Environmentally Based Evaluation of the Multimedia Discharges from the Lurgi Coal Gasification System at Kosovo. In: EPA Symposium on Environmental Aspects of Fuel Conversion Technology V, September 16-19, 1980. Radian Corporation, Austin, Texas.
2. Lee, K. W., W. S. Seames, R. V. Collins, and K. J. Bombaugh. Environmental Assessment: Source Test and Evaluation Report--Lurgi (Kosovo, Yugoslavia) Medium-Btu Gasification. In press. Radian Corporation, Austin, Texas. March 1981. 354 pp.
3. Lentzen, D. E., D. E. Wagoner, E. D. Estes, and W. F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment, (Second Edition). EPA-600/7-78-201, PB-293 795. Research Triangle Institute, Research Triangle Park, NC. October 1978. 277 pp.
4. Page, G. C. Environmental Assessment: Source Test and Evaluation Report--Chapman Low-Btu Gasification. PB-289 940. EPA-600/7-78-202. Radian Corporation, Austin, Texas. October 1978.
5. Fuchs, M. R., R. A. Magee, and P. M. Jeans. Environmental Assessment: Source Test and Evaluation Report--Riley Gas Producer, Low-Btu Gasification. IERL-RTP Contract No. 68-02-31317. April 1981.
6. Kilpatrick, M. P., R. A. Magee, and T. E. Emmel. Environmental Assessment: Source Test and Evaluation Report--Wellman-Galusha (Ft. Snelling) Low-Btu Gasification. EPA-600/7-80-097. Radian Corporation, Austin, Texas. January 1980.
7. Cleland, J. G. and G. L. Kingsbury, Multimedia Environmental Goals for Environmental Assessment, Volumes I and II (final report). Research Triangle Institute. Research Triangle Park, North Carolina. Report Number EPA-600-7-77-136a, b, NTIS Number PB 276-920 (Volume II). EPA Contract Number 68-02-2612. November, 1977.

APPLICATION OF KOSOVO (LURGI) GASIFICATION †
PLANT TEST RESULTS TO POLLUTION CONTROL PROCESS DESIGN

by: G. C. Page, W. E. Corbett, R. A. Magee
Radian Corporation
8500 Shoal Creek Blvd.
Austin, Texas 78766

ABSTRACT

This paper describes a test program performed by Radian Corporation to obtain process data to define the pollution control technology requirements for Lurgi-based coal gasification plants. This program was sponsored by the Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency conducted at a Lurgi-based gasification plant in the Kosovo region of Yugoslavia. It should be emphasized that the Kosovo plant does not reflect state-of-the-art Lurgi technology especially in pollution control practices. However, the "uncontrolled" process discharge streams from the Kosovo plant are representative of those from Lurgi-based gasification plants.

From an assessment of the Kosovo data, the following discharge streams were selected to be "key" based on flow rate and/or concentration of pollutants (1) high- and low-pressure coal lock vent gases and ash from the gas production section, (2) liquid depressurization gases and surge tank vent gases from the tar/oil separation section, (3) H₂S- and CO₂-rich vent gases from the Rectisol acid gas removal section, and (4) extracted wastewater from the Phenosolvan unit.

The conclusions reached from an engineering evaluation of the components in those key discharge streams and the effects those components may have on pollution control processes were as follows: (1) pollution control processes are commercially available for treating these streams, (2) the effects of minor and trace components on the performance of those control processes have not been demonstrated and there may be problems in the direct transfer of technology from other industries (e.g., coke ovens), (3) the design and selection of pollution control processes during transient and normal operation should occur in parallel with the base plant design, and (4) the variability of the components in the discharge streams must be determined and included in pollution control process design.

INTRODUCTION

An international program, sponsored by the Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency, was conducted in the Kosovo region of Yugoslavia. The major objective of this program was to characterize process discharge streams associated with a Lurgi-based gasification plant and to assess how components in those streams may affect pollution control process design and operation. The study, conducted over a three year period, was a cooperative endeavor between scientists from Yugoslavia, the EPA, and Radian. The program was undertaken because the Lurgi gasification process has significant potential for use in the United States.

The purpose of this paper is to address the key process discharge streams from the Kosovo plant that will require pollution control in a Lurgi-based plant constructed in the United States. The potential impacts of specific components in those key uncontrolled discharge streams on the design and operation of pollution control process are examined.

It should be emphasized that the Kosovo plant does not reflect state-of-the-art Lurgi technology and that it has essentially no pollution control processes that would be acceptable for Lurgi-based plants built in the U.S. However, the "uncontrolled" process discharge streams from the Kosovo plant contain compounds that will be present in discharge streams from U.S. Lurgi plants. Many of these species will affect the design and operation of pollution control processes in the first generation Lurgi-based gasification plants.

DESCRIPTION OF THE KOSOVO GASIFICATION FACILITY

The Kosovo gasification plant is an integral part of a large mine-mouth industrial complex located near the city of Pristina in the Kosovo Region of Southern Yugoslavia. The industrial complex consists of a coal mine, a coal preparation plant, the gasification plant, an ammonia plant, an air separation plant, and a steam and power generation plant. The gasification plant consumes dried lignite and produces two primary products: a fuel gas with a net heating value of 14 MJ/m^3 @ 25°C (360 Btu/scf) and hydrogen for ammonia synthesis. Several hydrocarbon by-products are also produced and are used as fuel. These by-products include: light tar, medium oil, naphtha, and crude phenols.

The design flow rates for the major streams in the Kosovo plant are shown in Figure 1. These flow rates are for five of the six Lurgi gasifiers in operation. As shown in Figure 1, the plant is designed to produce 24 Mg ($65,000 \text{ m}^3$ @ 25°C) of product gas for 80 Mg of dried lignite consumed.

The unit operations employed at the Kosovo gasification plant are typical of the operations in several proposed U.S. Lurgi-based plants. Figure 2 is a simplified flow diagram of the unit operations in the Kosovo facility.

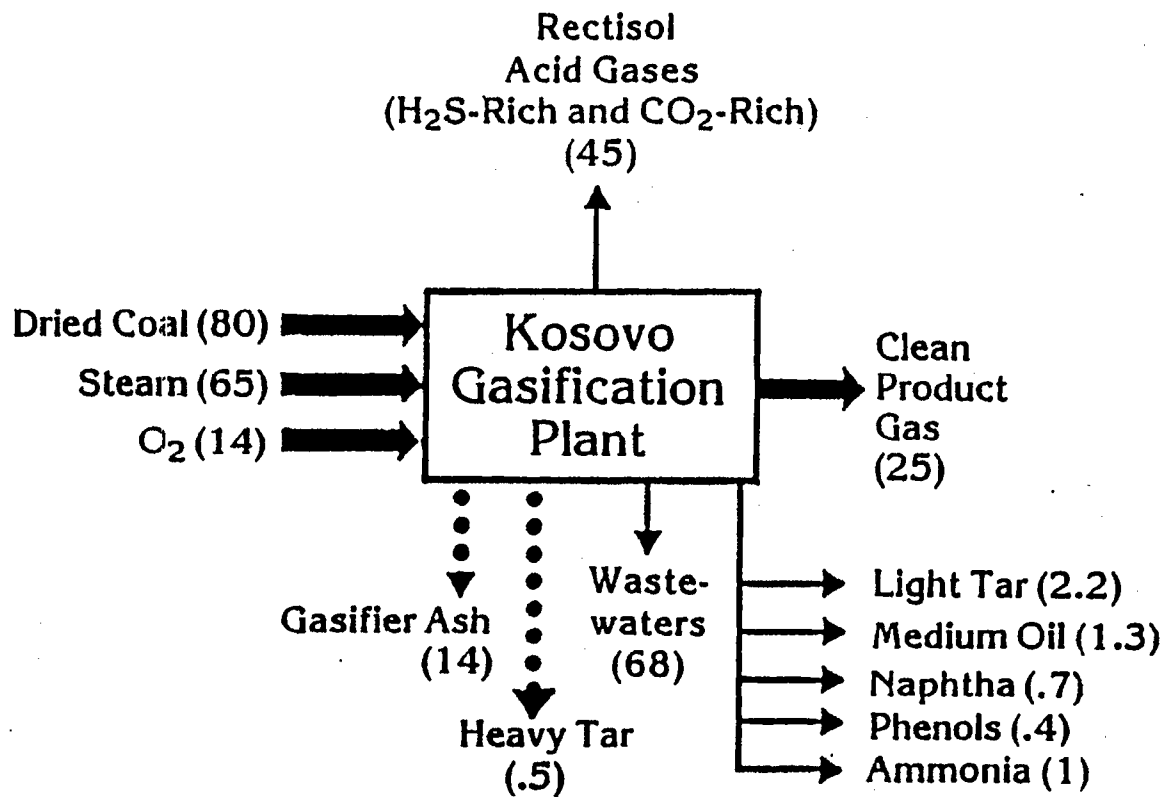


Figure 1. Design Flow Rates of Major Streams for the Kosovo (Lurgi) Gasification Plant (Flow Rates in Megagrams/hr.)

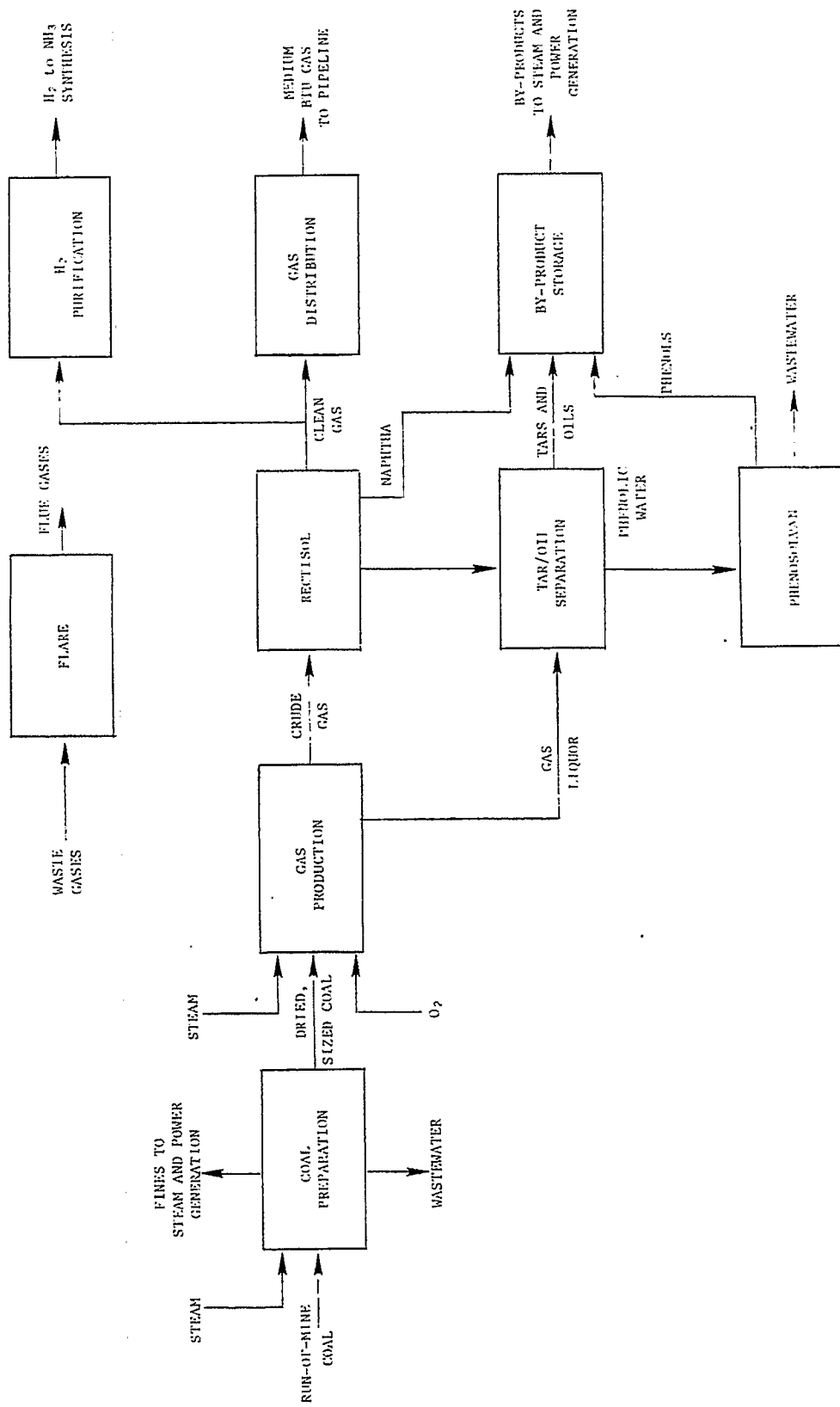


Figure 2. Simplified Flow Diagram of the Kosovo Coal Gasification Plant

The following summarizes the function of each unit operation, its discharge streams, and those discharge streams considered to be key. Key discharge streams were selected based on two criteria: mass flow rate and/or high concentrations of pollutants.

COAL PREPARATION

Run-of-mine coal containing approximately 50 weight percent moisture is dried by the Fleissner process to approximately 25 weight percent moisture. The dried coal is then crushed and particles between 6 and 60 mm are stored in the gasifier coal feed hopper. Table 1 shows a typical composition of the dried coal feedstock. Coal fines (less than 6 mm) are routed to the on-site steam and power plant.

Although the Fleissner process is used in foreign countries, the process is not likely to be used in U.S. Lurgi plants. Therefore, the discharge streams from this process were not considered "key" with respect to the evaluation of pollution control requirements for U.S. facilities.

GAS PRODUCTION

In the gas production section, dried coal is reacted with steam and oxygen at a pressure of 25 atm to produce a crude product gas. This reaction occurs in the gasifiers (3.5m in diameter) used at Kosovo. The crude product gas is then cooled and scrubbed to remove coal fines, tars, oils, and other condensibles. Ash produced during gasification is collected from the bottom of each gasifier in a lock hopper. The ash is water-quenched and routed to a landfill.

The discharge streams from the gas production section are: coal room vent, high-pressure coal lock vent, low-pressure coal lock vent, start-up vent, gas liquor tank vent, ash lock vent, gasifier ash, and ash quench water. Of these discharge streams, the following are considered to be key streams:

- o low-pressure coal lock vent,
- o high-pressure coal lock vent, and
- o gasifier ash.

TAR/OIL SEPARATION

In the tar/oil separation section, heavy tar, light tar, and medium oil are separated from the crude gas quench liquor and from the condensates produced by cooling the crude gas. Depressurization of quench liquor and condensates followed by a series of phase separators are used to accomplish this. Light tar and medium oil are sent to by-product storage to be used as boiler fuel. Heavy tar is landfilled at Kosovo; however, current plans for U.S. plants are to recycle this tar to the gasifier or to use it as boiler fuel. The aqueous phase from the separators is routed to Phenosolvan for phenol recovery.

TABLE 1. TYPICAL COMPOSITION OF THE DRIED COAL
FEEDSTOCK FOR THE KOSOVO PLANT

<u>Ultimate Analysis (wt. %)</u>	
Moisture	20
Ash	14
Carbon	45
Sulfur	0.89
Hydrogen	3.5
Nitrogen	1.1
Oxygen	16

<u>Heating Values (kcal/kg)</u>	
Proximate HHV	3900
Proximate LHV	3700

The discharge streams from this unit operation are: depressurization gases, surge tank vents, phenolic water, and heavy tar. The key discharge streams include depressurization gases and surge tank vents.

ACID GAS REMOVAL (RECTISOL)

Acid gases, such as H_2S , COS , CO_2 , HCN , and mercaptans are selectively removed from the cooled product gas by sorption in cold methanol. The product gas enters the Rectisol process at about $22^\circ C$ and 23 atm. The gas is cooled by a cold water wash followed by a cold methanol wash. Condensates from this initial cooling are a light organic phase (naphtha) and aqueous phase. Naphtha is sent to by-product storage to be used as fuel while the aqueous phase is routed to tar/oil separation. After the initial gas cooling step, the gas is scrubbed with cold methanol in the H_2S absorber. The H_2S -lean product gas is then sent to CO_2 absorption for final purification. During methanol regeneration, the acid gases removed from the product gas stream are stripped from the methanol which results in two waste gas streams H_2S - and CO_2 -rich vent gases.

Discharge streams from the acid gas removal unit operation are:

- o H_2S -rich vent,
- o CO_2 -rich vent,
- o naphtha, and
- o aqueous condensate.

Of these streams, the H_2S - and CO_2 -rich vent gases are considered key.

PHENOL REMOVAL (PHENOSOLVAN)

In the phenol removal section, phenolic water from the tar/oil separation section is extracted with diisopropylether (DIPE) to remove phenolic compounds. To accomplish this, residual tars and oils are removed by phase separation and filtration, followed by removal of dissolved gases by steam stripping. After dissolved gas removal, the water is extracted with DIPE to remove phenolic compounds. Recovered phenol is sent to by-product storage to be used as a fuel. The extracted water is discharged.

The discharge streams from the Phenosolvan section include:

- o stripped gases,
- o surge tank vents,
- o by-product phenol, and
- o wastewater.

The key discharge stream from this unit operation is wastewater from DIPE extraction.

KEY DISCHARGE STREAMS

As discussed above the key discharge streams from the Kosovo plant that are of primary concern for proposed Lurgi-based plants in the U.S. are:

- o Gas production
 - High-pressure coal lock vent
 - Low-pressure coal lock vent
 - Gasifier ash
- o Tar/Oil Separation
 - Depressurization gases
 - Surge tank vents
- o Acid Gas Removal (Rectisol)
 - H₂S-rich vent gas
 - CO₂-rich vent gas
- o Phenol Recovery (Phenosolvan)
 - Extracted wastewater

These streams were selected as key discharge streams based on their flow rates and/or their concentration of pollutants. Tables 2 and 3 summarize the flow rates and compositions of these streams. The data in these tables are a portion of the results from the environmental test program performed at the Kosovo plant.

The following text contains a discussion of these key discharge streams which emphasize the components in each stream that will affect the design and operation of processes used for pollution control in U.S. Lurgi-based plants. The use of the hydrocarbon by-products as fuel and/or as feedstocks for petrochemical manufacturing is also addressed.

GAS PRODUCTION

High-Pressure Coal Lock Vent

The flow rate of the high-pressure coal lock vent stream is approximately 2 percent of the crude product gas flow rate. This stream will contain all of the compounds found in the crude product gas exiting the gasifier including coal fines, tars, oils, reduced sulfur compounds, HCN, NH₃, CO, H₂, etc.

Because of the high flow rate and energy content of this stream, viable control alternatives include recycle to the product gas or use as a fuel. For recycle to the product gas, entrained particulate matter and tar/oil aerosols need to be removed prior to compression to product gas pressure. Particulate and aerosol removal also will be necessary prior to combustion to minimize equipment fouling and buildup of tar in the gas lines. Flue gas control of gases resulting from the combustion of the high-pressure vent stream also will be necessary because of the high levels of sulfur compounds in this stream.

Low-pressure Coal Lock Vent

The flow rate of the low-pressure coal lock vent gas is low (less than 0.2 percent of the crude product gas flow), however this gas will contain

TABLE 2. KEY GASEOUS DISCHARGE STREAM COMPOSITIONS

Stream Parameter	Low-Pressure Coal Lock Vent	High-Pressure Coal Lock Vent (after scrubbing)	Tar/Oil Separation Depressurization Gases (after scrubbing)	Medium Oil Surge Tank Vent	H ₂ S-Rich Tail Gas	CO ₂ -Rich Tail Gas
Dry Gas Flow Rate (m ³ /gasifier-hr @25°C)	21**	230**	28**	1.7**	3600***	3600***
Moisture Content (wt %)	44	11	7.7	8.4	3.9	5.1
Dry Gas Molecular Weight	23.5	24.9	39.0	32.5	43.0	42.2
Dry Gas Composition						
Fixed Gases (Vol %)						
H ₂	37	32	11	<0.01	0.11	<0.01
O ₂	0.27	0.24	<0.01	0.45	<0.01	<0.01
N ₂	0.18	0.14	<0.01	1.1	<0.01	<0.01
CH ₄	8.6	10.5	3.5	7.6	4.3	1.2
CO	14.6	12	1.1	5.9	1.1	<0.01
CO ₂	36.5	42	77.5	56	88	94
Sulfur Species (ppmv)						
H ₂ S	13,000	3500	9000	26,000	45,400	39
COS	110	120	120	96	420	62
Methyl Mercaptan	420	460	2500	5200	2100	8.5
Ethyl Mercaptan	220	210	1600	2100	780	4.4
Hydrocarbons (vol %)						
C ₂ H ₆	0.22	0.42	0.33	0.34	0.82	1.60
C ₂ H ₄	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
C ₃ 's	0.14	0.25	0.41	0.30	0.63	0.28
C ₄ 's	0.05	0.11	0.41	0.25	0.32	<0.01
C ₅ 's	<0.01	0.01	0.09	0.09	0.04	<0.01
C ₆ ⁺ 's	0.12	0.08	1.3	2.4	0.21	NF
Light Aromatics (ppmv)						
Benzene	760	550	9600	7650	110	1.0
Toluene	220	100	1200	1400	8	< 1
Xylene, Ethylbenzene	75	38	150	140	NF	< 1
Phenols	5.7	2.5	4.2	110	< 1	NF
Higher Aromatics	NF	NF	4.9	NF	NF	NF
Nitrogen Species (ppmv)						
NH ₃	2400	NF	19,300	19	2200	4.6
HCN	600	170	64	57	200	13
Particulate Matter (mg/m ³ @ 25°C)						
Total Particulates	8100	960	920	NS	NS	NS
Organics Contained in Particulate Matter*	7300	660	660	NS	NS	NS

*Organics include tars and oils which contain significant amounts of polynuclear aromatics as found in the Kosovo tar and medium oil by-products.

**Measured flow rates

***Design flow rates

NF: Not found

NS: Sample not obtained during the test program

TABLE 3. KEY LIQUID AND SOLID DISCHARGE STREAM COMPOSITIONS

Key Liquid Stream		Key Solid Stream	
Stream Parameter	Extracted Wastewater from Phenosolven	Stream Parameter	Gasifier Ash before Quenching
Design Flow Rate (m ³ /gasifier-hr)	13	Design Flow Rate (Mg/gasifier-hr)	2.8
pH	9.6	<u>Ultimate Analysis (wt %)</u>	
<u>Solids Analysis (mg/L)</u>		Moisture	2.1
Total Solids	1,350	Ash	94
Suspended Solids	1,160	Volatile	-
Dissolved Solids	190	Fixed Carbon	1.7
		Carbon Dioxide	-
<u>Water Quality Parameters</u>		Total Sulfur	0.15
COD (as mg O ₂ /L)	7,910	Free Sulfur	-
Permanganate (mg/L)	4,040	Fixed Sulfur	-
BOD ₅ (as mg O ₂ /L)	2,350	Hydrogen	0.25
		Nitrogen	0.03
<u>Aqueous Composition Data (mg/L)</u>		Oxygen (By Difference)	2.3
		Chlorine	0.04
		<u>Proximate Analysis (wt %)</u>	
TOC	1,470	Moisture	2.1
Total Phenols	230	Ash	94
Volatile Phenols	130	Volatiles	6.5
Free Ammonia	Tr	Fixed Carbon	-
Fixed Ammonia	205	Total Sulfur	0.15
Cyanide	0.019		
Nitrites	Tr	<u>Trace Elements (mg/kg) by AA</u>	
Nitrates	11.4	As	75
Pyridines	--	Be	2.5
Chlorides	60	Cd	69
Fluorides	Tr	Co	17
Total Sulfur	84	Cr	180
Sulfites	-	Cu	40
Sulfates	110	Hg	0.30
Sulfides	-	Mo	8.9
Thiocyanates	<75	Ni	320
Thiosulfates	Tr	Pb	52
		Sb	NF
<u>PNA Analysis (mg/L)</u>		Se	24
Benz(a)anthracene	NF	Sr	370
7,12-dimethylbenz(a)anthracene	NF	Tl	NF
Benzo(a)fluoranthrene	NF	V	100
Benzo(a)pyrene	NF	Zn	2.1
3-methylcholanthrene	NF		
Dibenz(a,h)anthracene	NF		
252 Group (as BaP)	0.19		

Tr = Trace
 NF = Not Found
 - = Not Analyzed
 AA: Atomic Adsorption Spectroscopy

pollutants found in the crude product gas (e.g., tars, oils, reduced sulfur compounds, HCN, CO, etc.). Even if these gases are diluted with air, they still will contain significant levels of tar/oil aerosols and reduced sulfur species and, therefore, should not be directly vented to the atmosphere.

A viable control of the low-pressure coal lock stream involves first minimizing its flow rate by controlling the pressure at which the low-pressure lock vent is opened (approximately 2 atm) followed by particulate and aerosol collection and then combustion (flaring). The major concern in controlling this stream is the pressure drop required to remove particulates and aerosols. To attain the required pressure for this, a blower may have to be installed in the vent line. If a blower is required, an explosive gas mixture may result due to the influx of air. Precautions must be taken to eliminate exposing the gas mixture to ignition sources.

Gasifier Ash

The gasifier ash is a key waste stream because of its high flow rate and the potential for the leaching of trace elements contained in the ash. However, leaching tests (RCRA and ASTM, Ref. 1 and 2) performed on the unquenched gasifier ash from Kosovo and on ashes from other gasifier processes show that the concentration of trace metals in the leachates are well below RCRA limits for hazardous wastes. Table 4 shows the results of the RCRA and the ASTM leaching tests on the gasifier ash from the Kosovo plant. As shown in this table, the trace element concentration in the leachates was between 10 and 1000 times lower than the RCRA limits for hazardous wastes.

There are two disposal alternatives for gasifier ash resource recovery or disposal in a nonhazardous waste landfill. It should be emphasized that the leaching tests were conducted on unquenched ash and the leaching properties of the ash could be significantly different if untreated process wastewaters were used to quench the ash. If process water is used for ash quench, the water should be treated to remove any toxic organics or trace elements that may render the ash to be classified as hazardous under RCRA.

TAR/OIL SEPARATION

Liquid Depressurization Gases and Surge Tank Vents

The combined flow rate of depressurization gases and surge tank vents is less than one percent of the crude product gas flow rate. However, these streams contain high levels of pollutants (e.g., H₂S, COS, mercaptans, HCN, and nonmethane hydrocarbons) which must be controlled.

Two viable control alternatives for these gaseous streams are.

- o containment and collection followed by combustion with flue gas controls and
- o containment and collection followed by the sulfur recovery process used to treat the H₂S-rich gas from Rectisol.

TABLE 4. GASIFIER ASH TRACE ELEMENT LEACHING RESULTS

<u>Element</u>	<u>Leachate Concentration/RCRA Limits</u>	
	<u>RCRA Leachate</u>	<u>Neutral Leachate</u>
As	0.001	0.002
Ba	0.03	0.001
Cd	<0.001	<0.004
Cr	0.06	0.10
Pb	0.002	0.01
Hg	<0.005	<0.020
Se	0.01	0.007
Ag	<0.0002	<0.0008

Use of the first control alternative may be complicated by the pressure differences of the gas streams and the physical location of vents in the plant. Routing these gases to sulfur recovery also may cause operational problems in the sulfur recovery process due to the presence of reduced sulfur compounds (COS, mercaptans), HCN, and hydrocarbons. These potential problems are discussed in the control alternatives for the H₂S-rich vent gas from Rectisol.

ACID GAS REMOVAL (RECTISOL)

H₂S-Rich Vent Gas

The H₂S-rich vent gas from the Rectisol acid gas removal process has a high flow rate (approximately 30 percent of the clean product gas flow rate) and contains pollutants. Table 5 summarizes the compounds of concern in this stream. As shown in this table, the H₂S-rich gas contains significant levels of H₂S, mercaptans, COS, HCN, and nonmethane hydrocarbons.

Of the many viable methods to control this stream, two methods were selected for discussion in this paper:

- o H₂S concentration (e.g., routing the gas to an amine-based acid gas removal process to concentrate the H₂S to approximately 10 to 15 volume percent in the gas) followed by sulfur recovery using a Claus with a Claus tail gas cleanup process, or
- o H₂S removal using a Stretford process followed by tail gas combustion.

If the first control alternative is used, problems may be caused by the production of organic sulfur compounds in the Claus process because of the high levels of hydrocarbons in the gas (ref. 3). Also, the effectiveness of the Claus and the Claus tail gas treatment processes in removing high levels of reduced sulfur and nitrogen compounds has not been demonstrated.

The Stretford process will not remove COS from the stream and HCN in the stream will cause formation of nonregenerable compounds in the Stretford solution (ref. 4). The fate of mercaptans in the Stretford process is uncertain (e.g., the removal of mercaptans by the Stretford solution and how mercaptans distribute between the Stretford tail gas and the oxidizer vent gas). Another concern with the Stretford process is the effect of contaminants in the gas on the purity of the by-product sulfur (e.g., organics in the gas may end up in the by-product sulfur) thus reducing the marketability of the sulfur.

CO₂-Rich Vent Gas

The CO₂-rich vent gas from the Rectisol process is a high volume stream (approximately 30 percent of the clean product gas flow) and contains pollutants as shown in Table 6. In certain designs of Lurgi-based plants, the CO₂-rich vent stream is vented directly to the atmosphere. However,

TABLE 5. POLLUTANTS IN THE H₂S-RICH GAS FROM
RECTISOL TO BE CONTROLLED

Component	Concentration
<u>Major (vol. %)</u>	
H ₂ S	2-5
CH ₄	4
Nonmethane Hydrocarbons	2
CO	1
<u>Minor (ppmv)</u>	
COS	400
Mercaptans	3,000
NH ₃	2,000
HCN	200

TABLE 6. POLLUTANTS IN THE CO₂-RICH GAS FROM
RECTISOL TO BE CONTROLLED

Component	Concentration
<u>Major (vol. %)</u>	
Nonmethane Hydrocarbons	2
<u>Minor (ppmv)</u>	
COS	50
Mercaptans	10
NH ₃	5
HCN	10
H ₂ S	40

based on the results obtained at Kosovo, the amount of nonmethane hydrocarbons and mercaptans in the CO₂-rich stream may not allow direct discharge of this stream.

Venting of the CO₂-rich tail gas directly to the atmosphere would involve operating the Rectisol process such that the levels of nonmethane hydrocarbons and reduced sulfur compounds are significantly lower than levels found at Kosovo. If this cannot be accomplished, a nonselective Rectisol process configuration may be used which has only one vent gas containing components in both the H₂S- and CO₂-rich vent gases. Viable control alternatives for this stream would be similar to those for the H₂S-rich vent gas.

PHENOL RECOVERY (PHENOSOLVAN)

Extracted Wastewater

The extracted wastewater from the Phenosolvan process has a flow rate of approximately 0.8 kg of wastewater per kg of coal fed to the gasifier and contains significant levels of pollutants. These compounds include phenols, organic acids, refractory organics, cyanides, and ammonia.

A viable control alternative for this wastewater is removal of organics by biological oxidation followed by trace organic removal by carbon adsorption and possibly incineration. Biological oxidation and carbon adsorption will be effective in removing the major portion of the organics; however, removal of high molecular weight "refractory" organics by these processes has not been demonstrated.

Direct transfer of biological oxidation and carbon adsorption technologies from other industries (e.g., coke ovens) may not be entirely applicable. This is illustrated by comparing the organic fractions in wastewaters from the Kosovo plant, the Chapman low-Btu gasification plant, and a coke oven plant. Figure 3 shows the relative amounts of total organic carbon (TOC) remaining in these wastewaters after extraction with DIPE to simulate the phenosolvan process and after analytical extraction with methylene chloride. Both of the gasification wastewaters contain significantly higher amounts of nonextractable (refractory) organics than the coke oven wastewater. These organics are very polar and/or ionic in nature since extraction (including pH adjustment) would not remove them.

Some preliminary data on carbon adsorption of wastewaters from the Chapman low-Btu gasification plant indicate that carbon adsorption cannot reduce the level of total organic carbon (TOC) below 150 to 200 ppm (ref. 5). Therefore, if significant levels of organics remain in the wastewater after biological treatment and carbon adsorption, incineration of the wastewater to destroy these organics may be necessary. It should be emphasized that incineration is necessary if these organics are toxic. At this time there are no data concerning the toxicity of these organic constituents.

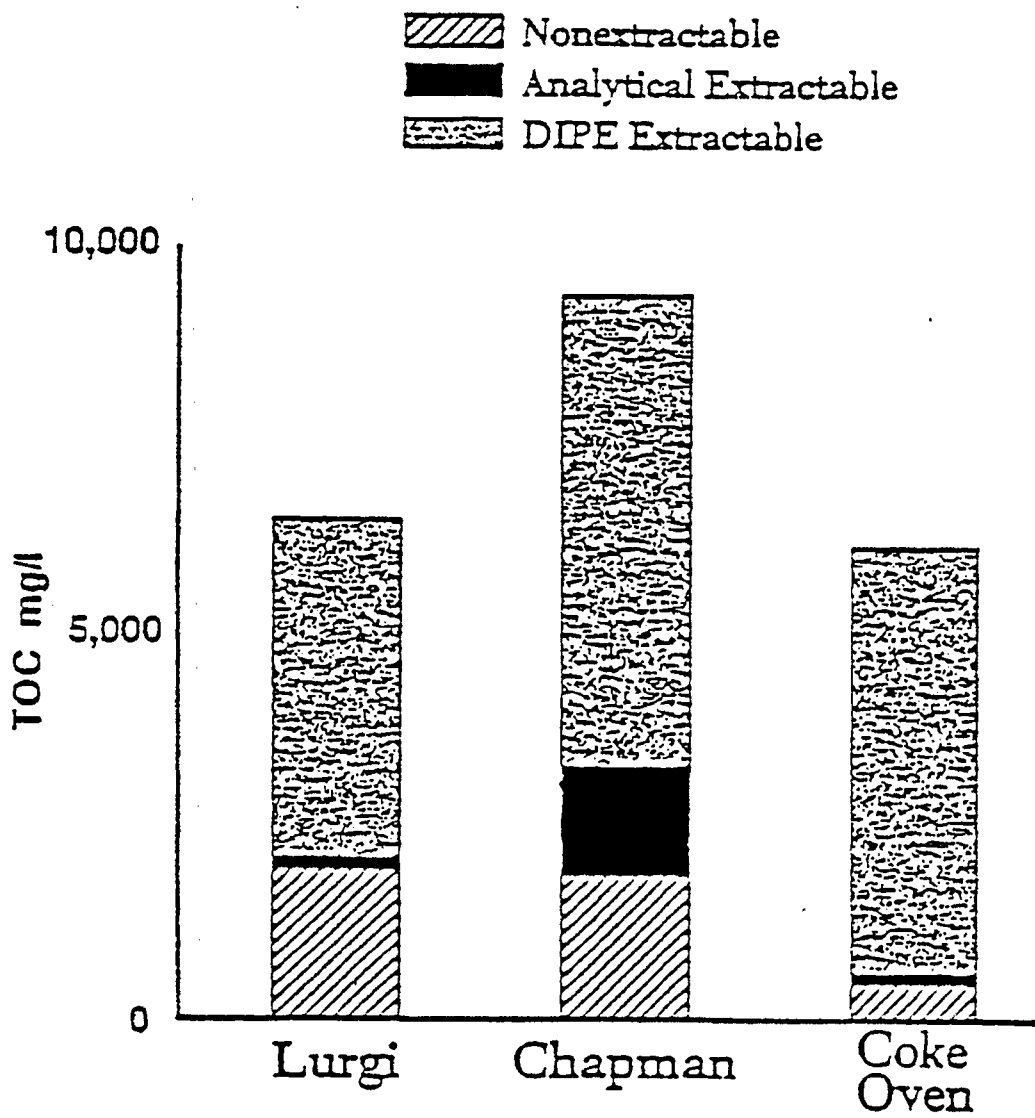


Figure 3. Extractable and Nonextractable Organics in Gasification and Coke Oven Wastewater (Ref. 5)

By-Products: Tar, Oil, Naphtha and Phenol

The composition of the by-products (tar, medium oil, naphtha and phenol) will affect their end use. Chemical analysis data for Kosovo by-products are shown in Table 7. Analysis of the phenol is not reported because a sample was not obtained during the test. Table 7 indicates that the sulfur contents of the liquid by-products become progressively higher in the "lighter" fractions. In contrast, the trend in the nitrogen values is reversed. These data indicate that heavy hydrocarbon by-products similar to those generated at Kosovo, could be used to satisfy some of the on-site fuel needs (e.g., for steam generation) of a U.S. Lurgi plant without flue gas desulfurization. This assumes that current SO₂ emissions standards consistent with those for large fossil fuel fired steam generators are applicable.

Table 7 also shows that the naphtha by-product contained none of the heavy polynuclear aromatics (PNA's) found in the tar and medium oil. Use of the tar and oil as fuel would destroy those PNA's by combustion. However, the naphtha could be used as a chemical feedstock with minimal risk of worker exposure to heavy PNA's.

CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations derived from the results of the Kosovo test program and from an assessment of the pollution control processes to treat key discharge streams from a Lurgi-based plant are presented in four areas:

- o availability of controls,
- o applicability of controls,
- o integrated plant concerns, and
- o discharge stream variability

AVAILABILITY OF CONTROLS

Pollution control processes for all of the key discharge streams are commercially available. Most of these processes have been proven in related industries (e.g., coke oven, refinery, etc.).

APPLICABILITY OF CONTROLS

Even though pollution control processes are commercially available, minor and trace components in discharge streams from gasification plants will affect the operation of those processes. Because many of these components are unique to gasification technology, direct transfer of pollution control process design from other industries may not be applicable.

INTEGRATED PLANT CONCERNS

Pollution control costs will be a significant portion of the base plant cost. The control of discharge streams by recycling or process modification should be considered in the total plant design, especially if significant cost savings for pollution control can be realized.

TABLE 7. CHEMICAL AND PHYSICAL DATA FOR KOSOVO BY-PRODUCTS

By-Product	Light Tar	Medium Oil	Naphtha
Specific Gravity (g/cm ³)	1.06	0.97	0.85
Higher Heating Value (kcal/kg)	8910	9500	9940
Lower Heating Value (kcal/kg)	8280	9400	8925
Ultimate Analysis (wt. %)			
Carbon	82	82	86
Hydrogen	8.4	8.9	9.9
Nitrogen	1.3	1.00	0.18
Sulfur	0.49	0.83	2.2
Ash	0.22	0.03	---
Oxygen (difference)	7.8	8.2	2.2
Moisture Content (wt. %)	1.1	0.8	---
PNA Analysis (mg/kg)			
Benz(a)anthracene	490	160	NF
7,12-dimethylbenz(a)anthracene	1100	62	NF
Benzo(b)fluoranthrene	310	120	NF
Benzo(a)pyrene	210	68	NF
3-methylcholanthrene	26	NF	NF
Dibenz(a,h)anthracene	23	6.6	NF
252 Group (as BaP)	950	280	NF

NF = not found.

--- = no data available.

DISCHARGE STREAM VARIABILITY

Every Lurgi-based plant will have unique discharge stream characteristics resulting from differences in coal feedstock properties, process operation, and plant configuration. Pollution control processes must be designed to handle worst case transients as well as "normal" operating conditions. Therefore, during the testing phase to obtain operating parameters on a specific coal feedstock, characterization of discharge streams during steady-state and transient conditions should be performed to define the bases for pollution control process design.

As stated previously, pollution control technology is available for Lurgi-based gasification plants, but the application of this technology is not completely straightforward. For this reason, pollution control process designs must be based on design data obtained over a broad spectrum of operating conditions. It is particularly important that data be obtained under both transient as well as steady-state conditions.

ACKNOWLEDGEMENT

This work was sponsored by the Industrial Environmental Research Laboratory of the United States Environmental Protection Agency. The authors express their thanks to the following organizations and individuals for their contributions to this work:

U.S. EPA - T. Kelly Janes, W. J. Rhodes
Radian Corporation - K. J. Bombaugh, K. W. Lee
Rudarski Institute - M. Mitrovic, D. Petkovic
Kosovo Institute - B. Shalja, A. Kukaj, M. Milesavljevic
REMHK Kosovo - S. Dyla, E. Boti
INEP - S. Kapor

REFERENCES CITED

1. Federal Register Vol. 46, No. 24, Proposed Rules for Land Disposal Facilities, (Feb. 5, 1981).
2. Bombaugh, K.J., et al. "An Environmental Based Evaluation of the Multimedia Discharges from the Kosovo Lurgi Coal Gasification System" presented at the 5th IERL/EPA Symposium on Environmental Aspects of Fuel Conversion Technology, St. Louis, MO (Sept. 1980).
3. Goar, G. "Impure Feeds Cause Claus Plant Problems" Hydrocarbon Processing. 53(7), 129-32 (1974).
4. Cavanaugh, E.C., et al. Environmental Assessment Data Base for Low/Medium-Btu Gasification Technology. Vol. I and II, EPA-600/7-77-125a and b (Nov. 1977).
5. Collins, R.V., et al. "Comparison of Coal Conversion Wastewaters" presented at the 5th IERL/EPA Symposium on Environmental Aspects of Fuel Conversion Technology, St. Louis, MO, (Sept. 1970)

ENVIRONMENTAL ASPECTS OF THE GKT COAL GASIFICATION PROCESS†

R.E. Wetzel

GKT Gesellschaft für Kohle-Technologie mbH
29 Moltkestraße
43 Essen, FRG

K.W. Crawford

TRW Systems and Energy
One Space Park
Redondo Beach, CA 90278

W.C. Yee

Tennessee Valley Authority
300 Corroon and Black Building
Chattanooga, Tennessee 37401

INTRODUCTION

Thermal Conversion of coal is always accompanied by the production of pyrolysis products, of solid wastes like ash, slag or flydust, of different sulfur compounds and a number of undesired trace compounds in the gas. Quality and quantity of these components depend on the applied process principle, the composition of the reactants and on the main process parameters like temperature and pressure. The high temperature entrained coal gasification process according to GKT, a well established commercial process since 30 years, offers a coal conversion system with minimum environmental impact.

To evaluate the operating conditions and the environmental impact when gasifying American coal, TVA and GKT agreed to conduct a large scale test with about 5000 short tons of Illinois No. 6 coal in a commercial coal to ammonia plant in Greece. TRW, funded by TVA, cooperated in the extensive test programme regarding the environmental aspects. The favourable results of the test runs, carried out in March/April 1981, and the extraordinary low

environmental impact demonstrated, have led to TVA's decision to built its Murphy Hill plant basing on GKT's technology.

THE GKT PROCESS

In 1936/42 Friedrich Totzek and his coworkers developed a new gasification principle, the gasification of pulverized coal in an entrained bed reactor, using oxygen and steam as gasification media.

In this GKT PROCESS coal dust and oxygen are reacted within one second in a flame reaction to carbon monoxide and hydrogen, at close to atmospheric pressure and temperatures of 1400 to 1600 °C. Under these conditions, the coal ash converts to liquid slag and Flyash.

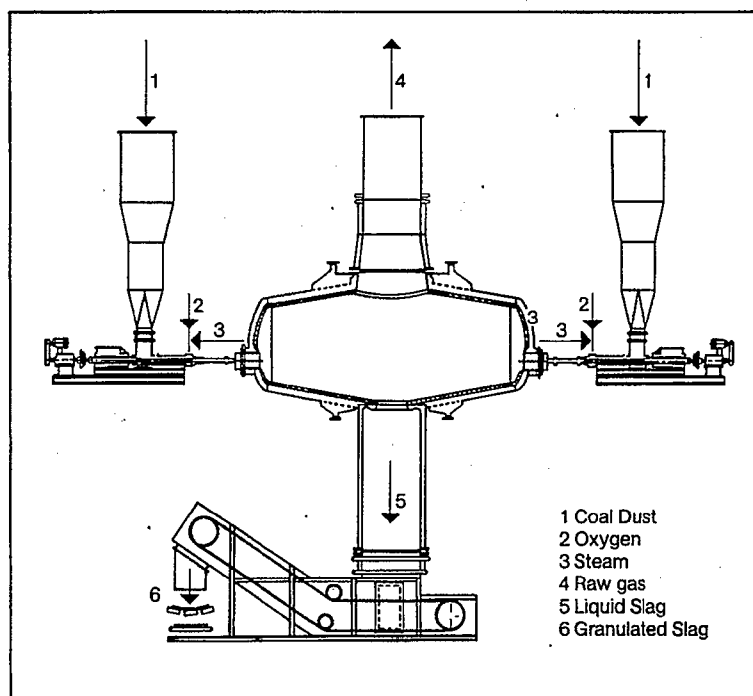


Figure 1 The GKT gasifier

The reaction vessel is shown in Figure 1. Coal dust metered via dosing screw conveyors, is injected with oxygen and steam through opposite burners. Liquid slag accumulating at the reactor wall, flows down through the bottom opening into a water bath, granulates and is discharged via chain conveyor. The reactor wall is cooled by raising steam in the double-wall jacket. The product gas exiting at the top is quenched to about 1000 °C by water injection in order to solidify slag droplets before entering the waste heat boiler.

The reactions of the coal with the gasifying agents are sum-

marized in Table 1. Most important are Reactions (1) to (3) which lead to a product gas with approximately 90 % CO and H₂ at a ratio of 2/1 to 2.5/1. Formation of methane, Reaction (4), is of no importance at the high gasification temperatures. However, traces of methane are always present in the gas.

TABLE 1 REACTIONS OF THE SYSTEM C/H/O/N/S

Gasification reactions:		
C	+ O ₂	= CO ₂ (1)
C	+ CO ₂	= 2 CO (2)
C	+ H ₂ O	= CO + H ₂ (3)
C	+ 2H ₂	= CH ₄ (4)
Side reactions:		
C	+ 2S	= CS ₂ (5)
CO	+ S	= COS (6)
H ₂	+ S	= H ₂ S (7)
2 CO ₂	+ S	= SO ₂ + 2 CO (8)
3 H ₂	+ N ₂	= 2 NH ₃ (9)
C	+ NH ₃	= HCN + H ₂ (10)
O ₂	+ N ₂	= 2 NO (11)

The sulphur contained in the coal in form of organic and inorganic compounds, is almost completely converted to H₂S and COS at a molar ratio of 9/1. Further reactions of the system C/H/O/S permit the formation of traces of CS₂, SO₂ and elemental sulfur, reactions (5) to (8). The nitrogen in the coal and the nitrogen content of the gasification oxygen lead by a number of side reactions to the formation of traces of HCN, NH₃ and NO, reactions (9) to (11).

The reactions shown in Table 1 represent the minimum number which describe the system. Their combinations result in a large number of heterogeneous and homogeneous reactions occurring simultaneously.

Besides these reactions, also coal ash components will react under the prevailing conditions.

The coal ash contains practically all chemical elements in small traces, similar to all natural ores and minerals used for industrial purposes. Under gasification conditions accordingly many trace element side reactions as reduction reactions, vola-

tilization reactions, so-called transport reactions and condensation reactions are experienced.

SYNTHESIS GAS VIA THE GKT PROCESS

The flow diagram of a GKT coal gasification plant for the production of synthesis gas is shown in Figure 2. All important streams entering and leaving the plant are marked.

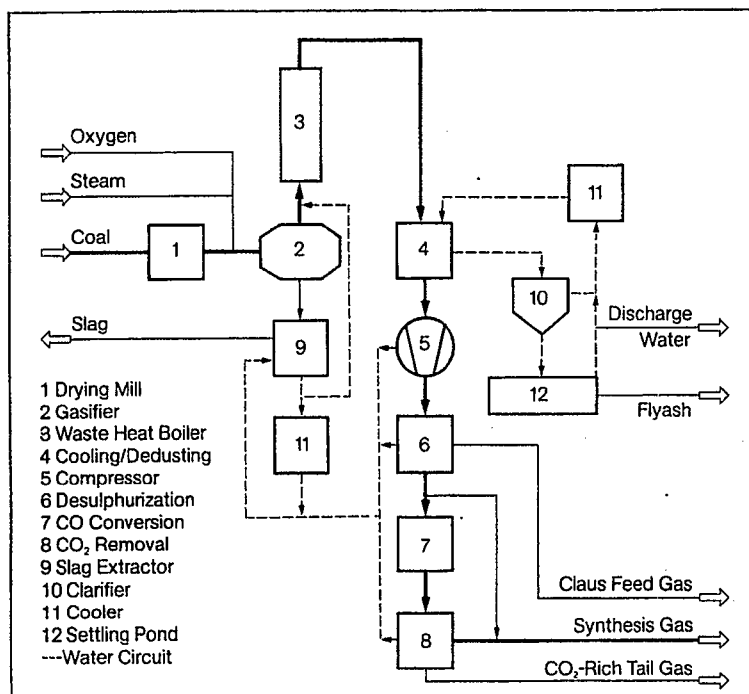


Figure 2 Flowsheet of a synthesis gas from coal plant

The raw coal entering the plant is crushed and pulverized to the necessary particle size (< 0.1 mm) and is simultaneously dried in a mill. The coal dust is pneumatically conveyed to the feed bunkers of the individual gasifiers. With oxygen and steam admixture the coal dust is injected into the gasifiers and gasified autothermally.

The slag leaving the reactor at the bottom is quenched in the water seal of the gasifier and discharged as a granulate. The raw gas after quenching is cooled to about 300°C in a waste heat boiler, where saturated steam at 100 bar is raised.

Cooling of the raw gas to ambient temperature and compressor grade dedusting is attained in a series of steps comprising a washer cooler, a disintegrator stage and a wet electrostatic precipitator. The flyash and the sensible heat are absorbed by the wash water which is recycled via a clarifier and a cooling stage. The flyash is pumped as a slurry from the clarifier to a settling pond.

The cooled and dedusted raw gas is compressed to 20-60 bar for desulphurization by a chemical or physical wash, a CO shift conversion and a CO₂ removal. According to the application of the synthesis gas the sulfur free gas is partly or totally entering the CO shift reactor and the CO₂-removal stage.

THE TEST UNIT

For the large-scale test operation the fertilizer plant of "Nitrogenous Fertilizer Industry S.A." in Ptolemais, Greece, was chosen. This plant started operation in 1963. Extensions increased production in 1971 and 1973. The coal gasification section of this plant is shown schematically in Figure 3.

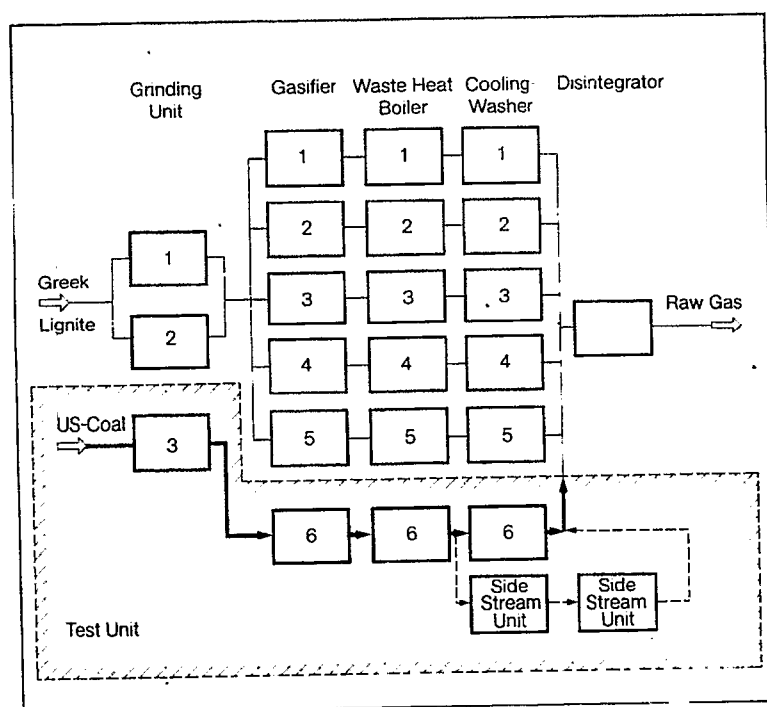


Figure 3 The Test unit at the NFI plant

Three grinding units and six gasifiers are available. For the test operation

- the drying and grinding unit no. 3 and
- the gasifier no. 6

of the plant were required.

From Figure 3 the limitations of the system are apparent. The raw gas produced in the test gasifier is mixed with the gas produced in the other gasifiers before entering the second washing stage. The washing water entering the cooling washer is recycle water from the operation of the total gasification and

gas cleaning section of the plant.

For the determination of the chemical composition of the washing water in a scrubbing system not affected by the parallel operation of the gasifiers 1 to 5 with Greek lignite a wet gas cleaning side stream unit including

- a washer cooler
- a Theisen disintegrator
- a drop separator and
- a closed water circuit with clarifier and cooler

was installed, Figure 4.

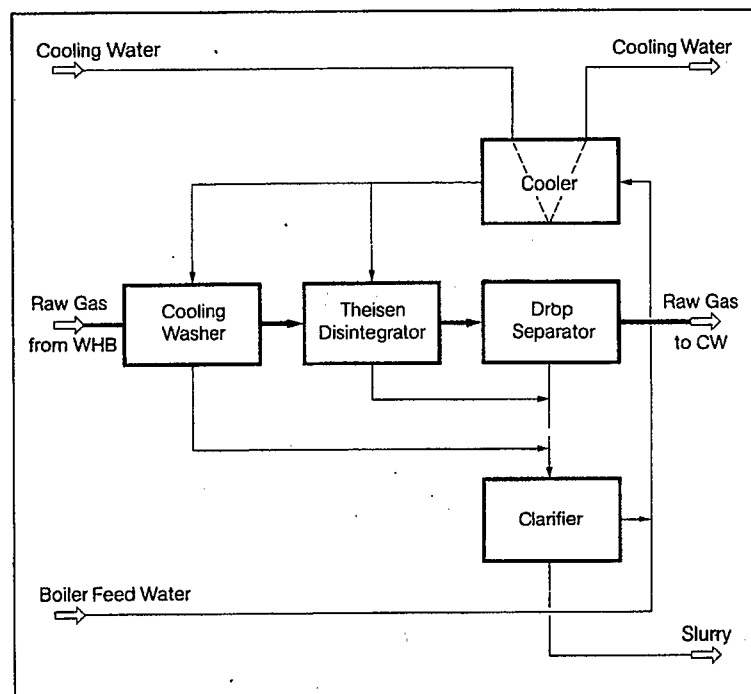


Figure 4. The side stream gas cleaning unit

TEST RESULTS AND DISCUSSION

The following discussion will focus on the streams which are shown in Figure 2. Especially

- the coal feedstock
- the slag
- the flydust
- the wash water from the washing unit and
- the raw synthesis gas before entering the compression stage

will be discussed.

Further streams, as

- the final synthesis gas
- the sulfur rich Claus gas and
- CO₂-rich off gas from the CO₂-removal stage

will be characterized.

TABLE 2 TEST GASIFICATION DATA

Operating Conditions	
Illinois No. 6 coal	6,300 kg/h
O ₂ /Coal (maf) ¹ -ratio	1.08 kg/kg (maf)
Steam/Coal (maf)-ratio	0.11 kg/kg (maf)
Operating Results	
Raw gas (dry)	10,900 m _n ³ /h
(CO + H ₂)/coal(maf)-ratio	1.73 m _n ³ /kg (maf)
Coal conversion: %C	94.6%
Efficiency: $\eta_{th, chem}$	77.8%

1.) maf = moisture and ash free
2.) excluding steam production in waste heat boiler

For orientation operational conditions and results are summarized in Table 2. The flow rates of all product and discharge streams are presented in Table 3. All the results presented are obtained at these test conditions.

The composition of the coal gasified is given in Table 4. The Illinois no. 6 coal has a high sulfur content, a medium ash content and a low chlorine content of 0.05 to 0.07 %. The moisture content of the coal dust prepared for gasification is 1 %. The solid by-products, slag and flyash comprise the coal ash and the unconverted coal, their composition is shown in Table 5.

The slag, recovered from the gasifier in granular form is environmentally harmless as it has been fused at high temperatures. According to the high SiO₂-content it has a vitreous and dense structure. Traces of dissolved carbon are responsible for its black colour. Leaching tests according to the RCRA procedure demonstrate, that practically no priority pollutants are develo-

TABLE 3 SPECIFIC FLOW RATES

Flow Rates of Product and Discharge Streams Basis: 1 t Illinois No. 6 Coal (moisture free):	
Synthesis Gas	1730 m ³ /t
Claus Feed Gas	71 m ³ /t
CO ₂ -Off Gas	831 m ³ /t
Discharge Water ¹⁾	1.3 m ³ /t
Flydust (dry)	120 kg/t
Slag	46 kg/t

¹⁾ Side Stream Unit only.
Commercial Operation ~ 0.5 m³/t

TABLE 4 COAL ANALYSIS

Ultimate Analysis, wt.-% mf		Ash Analysis, wt.-%	
H	4.6	Fe ₂ O ₃	17.0
C	69.6	SiO ₂	49.8
S _{combustible}	2.6	Al ₂ O ₃	21.5
N	1.4	CaO	3.2
Ash	12.7	MgO	1.2
O _(by difference)	9.1	Na ₂ O	0.4
		K ₂ O	2.4
Total Sulphur	2.7	TiO ₂	1.0
		P ₂ O ₅	0.1
		SO ₃	3.4

Amax Delta Mine, Illinois No. 6 Coal

TABLE 5 SLAG AND FLYDUST ANALYSES

Component	Concentration in wt.-% (dry)	
	Slag	Solids in Wash Water
C	0.2	32.9
Ash	99.5	66.3
S	0.3	1.3
Ash: SiO ₂	50.1	49.3
Al ₂ O ₃ + TiO ₂	25.5	23.5
FeO	10.8	-
Fe ₂ O ₃	4.5	16.8
CaO	3.9	3.6
MgO	1.2	1.2
Na ₂ O+K ₂ O	2.5	3.0
P ₂ O ₅	0.1	0.1
SO ₃	-	1.9

TABLE 6 SLAG LEACHING TEST

Element	Concentration in mg/kg		
	RCRA Extract P _{1,5}	Neutral Extract P _{1,7}	RCRA Standard
Ag	<0.01	<0.01	5
As	<0.4	<0.4	5
Ba	<0.01	<0.01	100
Cd	<0.007	<0.007	1
Cr	<0.04	<0.04	5
Hg	<0.0002	<0.0002	0.2
Pb	<0.05	<0.05	5
Se	<0.4	<0.4	1
NH ₃		0.7	None ¹¹
SCN ⁻		<0.1	None ¹¹
COD		4.8	None ¹²

¹¹ No Standard Available

ped, Table 6. Values below the analytical detection limit are marked by the sign "smaller than" (<) in Table 6 and the following relevant Tables. Traces of NH₃ result from the adsorbed quench water. Limited washing during extraction by chain conveyers will reduce this contaminant further. The use of the slag for road construction or other applications is therefore principally possible.

The flyash entrained in the raw synthesis gas is removed in the wet washing and cooling stage of the process. The fine grain size, the unconverted carbon content and the water content from the wet cleaning operation hinder an economic application. Therefore it has to be deposited. The exposition to the high temperature of the gasification results in an inert material. The carbon content is mainly graphitized, volatiles are limited. A hydrogen content up to 0.1 % was analysed. Leachable components from the flyash but also from the raw gas are transferred to the discharge water, which is an important stream from the environmental point of view, as it is necessary at least to discharge surplus water resulting from coal moisture and steam input into the gasification stage as well as quenching water used for raw gas cooling before entering the waste heat boiler.

TABLE 7 INORGANIC PRIORITY POLLUTANTS

Element	Concentration, mg/l	
	Boiler Feed Water	Wash Water to Clarifier
Antimony	<0.06	<0.06
Arsenic	<0.1	<0.1
Beryllium	-	<0.02
Cadmium	<0.007	0.015
Chromium	<0.015	<0.015
Copper	0.025	0.02
Lead	<0.1	<0.1
Mercury	<0.0002	<0.0002
Nickel	<0.03	0.06
Selenium	<0.5	<0.5
Silver	<0.01	<0.01
Thallium	<0.4	<0.4
Zinc	<0.005	0.29

The inorganic priority pollutants in the discharge water in comparison to the boiler feed water, that was used as make up water during the test operation, are shown in Table 7.

It has to be stated, that a small increase in nickel most probably results from the low pH-water attack on the steel piping and the clarifier material. The increase in zinc content possibly result from the volatilization of zinc traces in the coal and the transportation as gaseous $ZnCl_2$ to the washing system.

The analyses of the discharge water and the boiler feed water are given in Table 8.

TABLE 8 WATER ANALYSES

Components	Concentration in mg/l	
	Boiler Feed Water	Wash Water to Clarifier
pH	11.2	3.8
COD	9	118
Dissolved Solids	98	812
Cl ⁻	9	306
F ⁻	<0.1	37
NH ₃	<1	120
CN ⁻	<1	1.7 - 6
SCN ⁻	<1	3
S ⁻	<1	1
S ₂ O ₃ ⁻	<1	83
SO ₃ ⁻	<1	11
SO ₄ ⁻	25	217

The main components needing further treatment are NH_4^+ , CN^- and also the sulfur compounds in lower state of oxidation. Especially from the relatively high amount of sulfate ions it is evident, that the dissolved sulfur compounds are oxidized finally to the sulfate stage. The chlorine content in the coal is nearly totally transferred to the discharge water. In actual operation at the TVA plant the discharge water will be minimized to less than half of the amount of the water that was actually discharged at the "Test Unit". The resulting concentrations in the discharge water stream will increase accordingly. Ammonia and cyanide result from the earlier discussed gasification reactions and are transferred from the raw gas to the discharge water.

The washing effect for the trace components in the raw gas is limited, as is demonstrated in Table 9, which presents the raw gas analysis after the washing stage in the side stream unit.

The remaining impurities are removed in the downstream gas

TABLE 9 RAW GAS ANALYSIS

Main Components Vol.-% (dry)		Impurities mg/m ³ (dry)	
CO ₂	9.4	H ₂ S	13,896
CO	62.2	COS	2,653
H ₂	25.6	CS ₂	80
N ₂ +Ar	1.8	SO ₂	18
		NH ₃	19
		HCN	89
		NO	4
		Solids	50

TABLE 10 PRODUCT AND BYPRODUCT GASES

Components	Concentration in vol.-%		
	Synthesis Gas	CO ₂ -Off Gas	H ₂ S Claus Gas
CO ₂	3	75.82	73.39
CO	28.48	0.02	1.32
H ₂	67.52	0.02	0.08
N ₂ + Ar	0.99	24.14	
CH ₄	0.01		
H ₂ S		4 ppmv	22.21
COS			2.47
CS ₂			0.09
HCN			0.19
Methanol		300 ppmv	0.25

handling stages. In the Rectisol unit, according to GKT's concept, H₂S, COS, CS₂ and also HCN are removed and transferred to the Claus unit for sulfur production. The components SO₂ and NO are virtually completely reduced to H₂S and N₂ in the gas treatment system. Remaining traces will be removed with condensates and waste water from the gas treatment stages.

These combined water streams are used for slag quenching and finally as raw gas quenching water before the waste heat boiler, Figure 2. From the CO₂ removal a CO₂-rich stream is generated, which is vented to the atmosphere. The final clean synthesis gas stream, the CO₂-rich off gas and the H₂S-rich Claus gas are characterized in Table 10. According to calculating results it seems possible to reduce the CO-content of the CO₂ off-gas by changing the flash conditions in the CO₂ removal stage to still lower values.

A further analytical effort was aiming for evaluation of the organic compounds present in the waste streams of the GKT PROCESS.

Table 11 shows the results obtained for the raw gas after cooling and washing. Practically no higher hydrocarbon than methane and this also at a rather low level were detected.

TABLE 11 ORGANICS IN RAW GAS

Components	Concentration ppmv
CH ₄	10
C ₂ H ₄ +C ₂ H ₂	<0.5
C ₃ H ₆	<0.5
Benzene	<0.5
Toluene	<0.5
Xylene	<0.5
C ₃ H ₈	<0.5
C ₂ H ₄	<0.5
CH ₃ SH	<0.5
C ₂ H ₅ SH	<0.5

To collect organics in the hot raw gas before entering the washer group XAD resin traps were used. No resin sample contained sufficient extract to perform liquid chromatography. Infra-red analysis of each gravimetric residue indicated no organics other than those found in the resin blank. Low resolution mass spectrometry revealed that elemental sulfur (S_8) was the only species not found in the blank, Table 12.

TABLE 12 ORGANICS IN GASIFICATION STREAMS

Components	Raw Gas before Washer	Wash Water to Clarifier	Slag	Solids in Discharge Slurry
	mg/m ³	mg/l	mg/kg	mg/kg
Oil/Grease		1.3		
Formate		<0.1		
Phenols		<0.001		
TCO ¹⁾	1.6	<0.1	0.1	7.2
Grav. ²⁾	3.8	13.2	32.0	780
S ₈ in Grav.	~98%	97.2%	94.4%	94.3%
TCO+Grav. ³⁾	1.7	0.4	1.9	52

1.) Total chromatographable organics
2.) Gravimetric organics
3.) Sulfur free

In the discharge water small amounts of formate are present and traces of grease and oil were found in the side stream washer system. Essentially all of the organic extracts of the sample could be attributed to elemental sulfur (S_8). No other organics could be identified in the extracts by infrared analysis and low resolution mass spectrometry. The resulting residue was insufficient for liquid chromatography.

Slag and solids in the washing water (flydust) were subjected to methylene chloride extraction, followed by gas chromatography on the extract. Low resolution mass spectrometry again indicated almost entirely elemental sulfur. The higher gravimetric residue of the flydust indicate also some organics with boiling points higher than that of the C₁₆ normal alkane, which may result from the carbon content of the flydust, not fully graphitised, or dust fines, having passed through the filter.

CONCLUSIONS

From the results achieved it is evident, that special interest is directed towards the flydust slurry and the discharge water. The GKT concept for handling this streams is shown in Figure 2. The flydust slurry is transferred from the clarifier to a settling pond where it is slowly dewatered. The effluent from the pond is partly recycled to the main washing system. The surplus water in the system is discharged and will be treated further, especially for ammonia reduction. It has to be pointed out, that the impurities of the wash water react with each other and with the flyash. Sulfide ions are converted to $S_2O_3^{2-}$ and SO_4^{2-} . HCN reacts with sulfur compounds to form SCN^- and with the flyash to form insoluble complexes. Additional oxidation reactions occur in the settling pond. These oxidation reactions, which are catalysed by flyash components, involve $S_2O_3^{2-}$, SO_3^- , CN^- , SCN^- and also NH_4^+ . This experience is demonstrated in Table 13, which shows water analyses from the GKT coal gasification plant in Modderfontein, Republic of South Africa. This Figure, excluding the wash water stream to the clarifier, was presented by TRW and GKT in 1980.

TABLE 13 WATER ANALYSES FROM GKT COAL GASIFICATION IN MODDERFONTEIN, RSA

Components	Concentration in mg/l			
	Make-up Water		Wash Water to Clarifier	Settling Pond Discharge
	PSE ¹⁾	CW ²⁾		
pH	6.8	8.5	8.0	8.0
NH ₃	73	2.4	134.0	38
CN	<0.2	1.2	8.6	<0.2
SCN	2.1	2.1	6.9	1.3
S ⁻	<0.1	<0.1	0.7	<0.1
S ₂ O ₃ ⁻	<1	<1	3.6	<1
SO ₃ ⁻	<1	<1	1.4	<1
SO ₄ ⁻	584	853	746	752

¹⁾ Municipal Purified Sewage Effluent
²⁾ Cooling Water

The changes in composition from the wash water stream before the clarifier to the final water discharge stream from the pond are remarkable, no further treatment of the discharge water is carried out.

SOURCE TEST OF THE TEXACO GASIFICATION PROCESS †
LOCATED AT OBERHAUSEN-HOLTEN, WEST GERMANY

by:

Robert G. Wetherold and
Robert M. Mann
Radian Corporation
8501 MoPac Boulevard
Austin, Texas 78766

Dr. Peter Ruprecht
Ruhrchemie AG
4200 Oberhausen-Holten, West Germany

and

John Morgan and William Yee
Tennessee Valley Authority
1070 Chestnut Street
Chattanooga, Tennessee 37401

Dr. Ranier Dürfield
Ruhrkohle Ol und Gas GmbH
4250 Bottrop, West Germany

ABSTRACT

A comprehensive environmental characterization of water and solids from the Ruhrkohle/Ruhrchemie Coal Gasification Pilot Plant in Oberhausen-Holten, West Germany has been conducted. Coal is gasified at the plant with a modified Texaco coal gasification process. The pilot plant tests were conducted in November, 1980, during gasification of Illinois No. 6 coal. A test plan was prepared including stream selection, sample collection and chemical analyses. Multiple samples of six process water and four process solid streams were collected during two twelve-hour environmental balance periods. Normal pilot plant operation was maintained during the first period; the second incorporated water recycle to observe dissolved levels of components with minimized makeup water.

Samples of liquid and solid process streams have been subjected to comprehensive analyses including water quality parameters, trace elements, organic characterization, physical testing, radioactivity analyses and bioassay testing.

These efforts, conducted under contract with the Tennessee Valley Authority, have been performed to provide support information for both process operation and environmental impact associated with a 10,000 ton per day coal gasification plant proposed by TVA for a northern Alabama site. Topics to be addressed in the presentation include pilot plant configuration and operation, sample collection, analytical testing and results of the characterization program.

ENVIRONMENTAL TEST RESULTS
FOR THE RUHRKOHLE/RUHRCHEMIE/COAL GASIFICATION PILOT PLANT

Under a contract with the Tennessee Valley Authority, Radian Corporation has performed a comprehensive environmental characterization of the process water, effluent water and solid waste from the Ruhrkohle/Ruhrchemie Coal Gasification Pilot Plant in Oberhausen-Holtens, West Germany. At this plant, coal is gasified with a modified Texaco coal gasification process.

During a recent test in November and December, 1980, samples of process water streams, effluent water streams, slag, raw coal and coal slurry were collected. The samples were obtained during two 12-hour environmental balance periods on November 14 and November 18, 1980.

The liquid and solid samples have been subjected to comprehensive analyses. Some analyses were carried out on-site at the Ruhrchemie plant in Oberhausen-Holtens while others have been performed at the Radian laboratories in Austin, Texas.

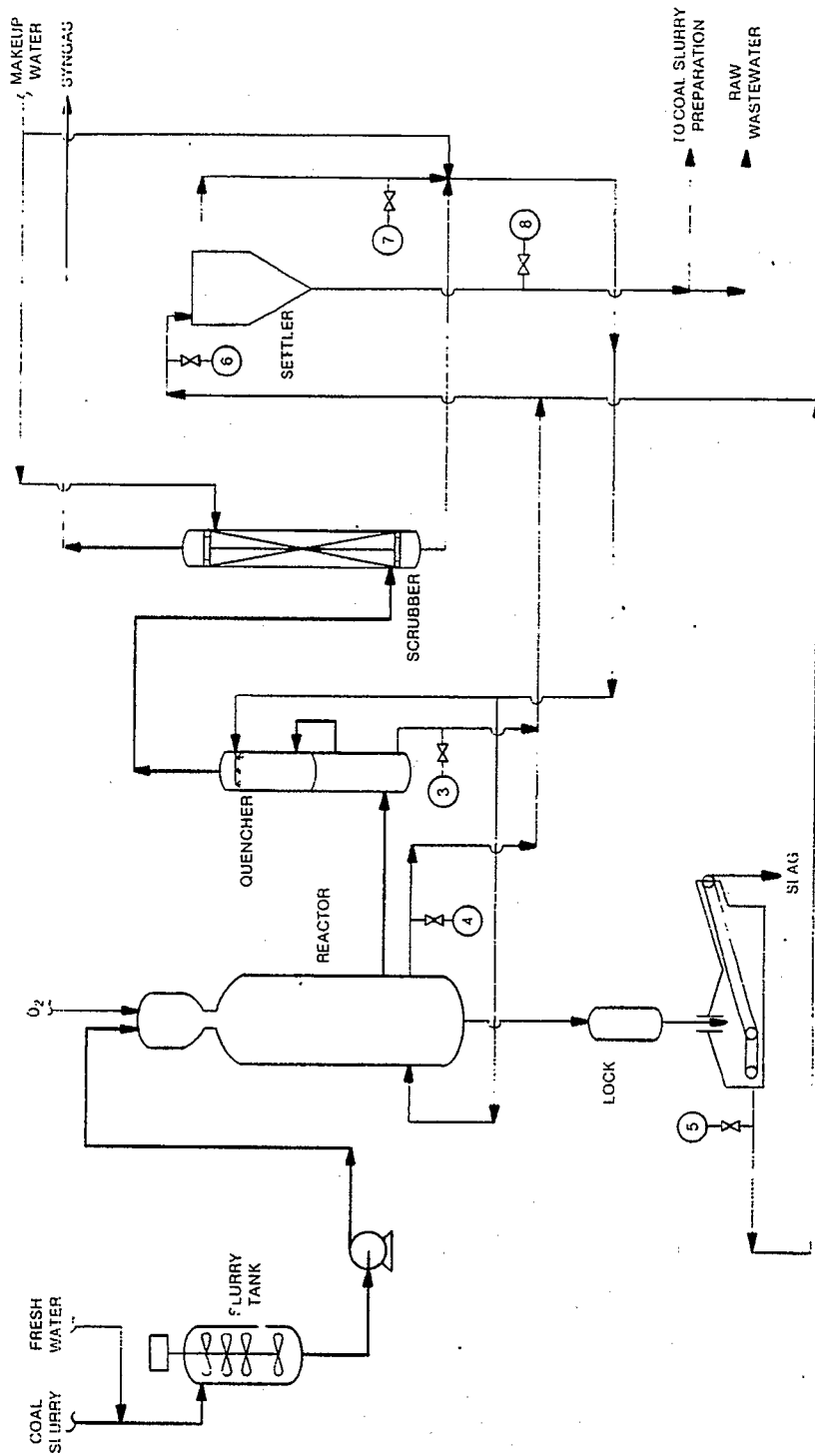
Some of the results of the program are briefly summarized in this paper. The process is described and the overall mass balance is presented. Many of the key characteristics of the process effluent water are defined, and some of the results from the wastewater treatability study are presented. The solid wastes from the process were subjected to RCRA leaching tests, and these results are given.

PROCESS DESCRIPTION

The testing took place at the Ruhrkohle/Ruhrchemie demonstration coal gasification plant located in Oberhausen-Holtens, West Germany. This plant contains a Texaco gasifier and has a nominal coal capacity of 5,700 to 6,100 kg/hr [150-160 tons/day]. A simplified flow scheme of the Ruhrkohle/Ruhrchemie demonstration plant is shown in Figure 1. The numbered points on this diagram identify the locations from which solid and liquid samples were taken during the environmental balance periods.

In the plant, coal is fed from a storage bunker to a grinding mill. There it is pulverized and combined with fresh water or, alternatively, effluent water recycled from the settler. The resulting coal slurry is pumped to agitated run tanks and from there into the gasification reactor.

The Texaco Coal Gasification Process reactor is a pressurized, entrained bed, downflow slagging gasifier. It operates under pressures of 2 to 10 Mpa [300 to 1,500 psia] and at high temperatures, generally in the range of 1,200 to 1,400°C. These temperatures are above the melting point of the coal ash.



021152

FIGURE 1. FLOW SCHEME FOR THE RUHRKOHLE/RUHRCHEMIE COAL GASIFICATION PLANT DURING THE ENVIRONMENTAL TESTING

The coal slurry and oxygen are fed into the top of the gasification reactor vessel. This vessel is lined with refractory, and it consists of two zones, a gasification zone and a radiant zone. The basic combustion and gasification reactions occur in the gasification section. The raw synthesis gas from the gasification section passes into the radiant cooler or quench section of the vessel. Here the gas is partially cooled and process steam generated. Synthesis gas from the gasifier is routed into a quench tower, where recycled process water is used to additionally cool the gas and remove particulate matter. The synthesis gas leaves the quench tower and passes into a water scrubber where the final gas cooling and particulate removal takes place.

Most of the slag produced in the reactor is solidified in a water bath in the bottom of the radiant cooler section. It is then removed from the reactor through an electronically-controlled lockhopper system. The slag and sluice water fall into a covered bin where the granulated slag is continuously removed by a conveyor belt. The slag water, containing some fine particulates, is sent to the settler. The water from the radiant cooler section of the gasifier and from the quench tower is routed to a flash tank where dissolved gases are flashed off during depressurization. The water from the flash tank then passes into the settler. The residence time in the settler is sufficient to allow settling of most of the fine particulate matter.

Two water streams are taken from the settler. The overflow water stream, taken off near the top of the settler, contains a relatively low concentration of solids. The underflow stream, taken from the bottom of the settler, contains the residual fines at a much higher concentration.

The settler overflow is combined with the scrubber blowdown stream and makeup water stream. This combined water stream is used as slag sluice water and also recycled to the quench tower and the radiant zone of the gasification reactor.

The underflow [or at least a portion of it] from the settler serves as the water blowdown stream from the coal gasification unit. The blowdown stream is first sent to an open holding tank before being routed to the plant water treatment system.

MASS BALANCES

The environmental balance periods took place on November 14, 1980 [EB-1] and November 18, 1980 [EB-2]. During the tests, Illinois No. 6 coal was processed at a rate of 6,900 to 7,200 kg/hr [180 to 190 tons/day]. The composition of the test coal is shown in Table 1. The major difference in the operating conditions between the two environmental balance periods was the disposition of the clarifier underflow [bottoms] stream. During the first environmental balance period [EB-1], all of the settler underflow stream was sent to the holding tank and then to water treatment; no underflow was recycled. During the second environmental balance period [EB-2], the fresh water requirements to the plant were minimized. Approximately half of the settler underflow stream was recycled to the coal slurry preparation area to satisfy

the water requirements to slurry the fresh coal which was sent to the gasifier. The remainder of the settler underflow was sent to the plant water treatment facilities.

TABLE 1. COMPOSITION OF ILLINOIS NO. 6 COAL

Component	Concentration*
Ash	11.21
Volatile	28.54
Fixed Carbon	50.25
Energy Content [Btu/lb]	12686
C	70.94
H	4.94
N	1.28
Cl	0.05
S	3.37
Ash	11.21
Oxygen (difference)	8.21
	100.00

*Values as percent [%] except Energy Content

Some of the operating conditions, as reported by Ruhrkohle/Ruhrchemie for the environmental balance periods, are summarized in Table 2.

TABLE 2. OPERATING CONDITIONS DURING ENVIRONMENTAL BALANCE PERIODS

Solids Feed Rate, kg/hr	6,000-6,300
Carbon Conversion [Once-Through], %	89-95
Dry Syngas Production, NM ³ /hr	11,800-12,200
[H ₂ +CC] Production, NM ³ /hr	9,000-9,400

Total material balances for both environmental balance periods were developed. These are shown in Table 3. The balances [or closures] are quite good for both test periods. Ruhrkohle/Ruhrchemie reported material balances for oxygen, carbon, water, sulfur, and nitrogen. The oxygen, carbon, water, and sulfur balances closed within $\pm 4\%$. The nitrogen balances were within $\pm 7\%$ of closure.

TABLE 3. RUHUKOHLLE/RUHRCHEMIE COAL GASIFICATION PLANT -
TOTAL MATERIAL BALANCE

	Stream Flow Rates, kg/hr			
	Environmental Balance Period 1		Environmental Balance Period 2	
	In	Out	In	Out
Coal Feed	7,157		6,923	
Water	8,312		4,600	
Other Inlet Streams	6,226		5,921	
Synthesis Gas		11,597		11,542
Effluent Water		7,708		3,706
Slag & Other Outlet Streams		1,863		1,833
TOTAL	21,695	21,168	17,444	17,081
Balance [Out/In], %		97.6		97.9

WASTEWATER CHARACTERISTICS AND TREATABILITY

Samples of seven water streams were obtained during the two environmental balance periods. These streams were:

- Inlet Streams - fresh water
- Process Streams - gasifier quench water
 - quench tower bottom stream
 - slag water
 - settler inflow water
- Outlet Streams - settler overflow water
 - settler underflow water

During the environmental testing, the settler overflow water stream was recycled to the process. The settler underflow stream served as a purge stream, and was sent to wastewater treatment. During the second environmental balance period, some of the settler underflow was recycled to the coal slurry preparation area.

Several hundred gallons of the pilot plant settler underflow stream were collected during the two environmental balance periods. Settler underflow water from the second environmental balance period was subjected to treatability tests in a screening study performed by AWARE, Inc., of Nashville, Tennessee. The goal of this screening study was to define the treatability of wastewater from the Texaco coal gasification process. A conceptual wastewater treatment system was simulated on a laboratory-scale in the study. This system utilized conventional existing water treatment technology. Bench-scale

simulation of wastewater treatment processes is an accepted and often the only means of obtaining treatment system design criteria when a "new" industrial wastewater is involved.

In the study, each treatment process was individually simulated using a portion of the wastewater to determine optimum process conditions. After the optimum conditions for a process were defined, the remainder of the wastewater was treated at those conditions. The next treatment process in the sequence was then evaluated.

A summary of the water quality characteristics of the raw settler underflow water stream is presented in Table 4. The raw wastewater characteristics are either average values of samples taken from the drums of wastewater to be treated or the value of a composite of samples from the drums. The sulfide and cyanide concentrations had the greatest variations among drum samples. Sulfide results were biased low because the samples were hot when collected, and some off-gasing occurred during cooling.

TABLE 4. CHARACTERISTICS OF WASTEWATER TO TREATMENT

Parameter	Concentration [ppm]
COD	540
BOD	202
Phenolics	<0.018
NH ₃ -N	1,550±98
CN ⁻	15±14
SCN ⁻	11
S ⁼	128±80
SO ₄ ⁼	5
TSS @ 105°C	152±42
TDS @ 180°C	960
Alkalinity [as CaCO ₃]	4,070
pH[units]	8.3

A relatively high ammonia concentration was observed in the raw wastewater samples. Minimal concentrations of nitrate or nitrite were found. The total alkalinity was found to be high. Bicarbonate alkalinity was the predominant form.

The wastewater treatability screening study was directed toward the reduction of the major wastewater quality parameters including BOD, COD, TSS, NH₃, and H₂S levels. The laboratory treatment system, consisting of conventional solids removal, steam stripping, and oxidation, was effective in reducing these parameters. The reductions are summarized in Table 5. The removal efficiency across the total treatment process for both COD and TSS was in the range of 70-80%. The removal efficiency for most other constituents was in

excess of 90%. Total dissolved solids increased substantially due to caustic and acid additions required for pH adjustment during the treatment sequence.

TABLE 5. TREATABILITY RESULTS

Component	Reduction [%]
BOD	91
COD	68-86
TSS	67-86
NH ₃	>99
H ₂ S	~99
Fe	83
TDS	*
Sulfate	*
Arsenic	0
Fluoride	3
Selenium	0
Chloride	0

*The use of NaOH and H₂SO₄ for pH adjustment increased the levels of sulfate and dissolved solids.

The effect of the treatment process on the levels of various metals was also determined. Elements whose concentrations are reduced by the treatment system include Al, Ba, Be, Ca, Fe, Mg, Mn, Pb, Si, and Ti. On the other hand, the concentrations of several metals were virtually unaffected in the treatment process. Included in this category are As, B, Cd, Ni, Sb, and Se. The levels of a number of elements, including Ag, Co, Cr, Mo, Tl, and V, were below detectable limits in both the raw wastewater and the effluent from the treatment system.

SOLIDS CHARACTERIZATION

Two process solid wastes and two solid wastes from the bench-scale wastewater treatment system were subjected to RCRA extractions. The solid wastes were:

- process wastes - slag
settler fines
- treatment wastes - primary sludge
biosludge

An elemental analysis was performed on the RCRA leachates. The results of these analyses are shown in Table 6. None of the RCRA limits for metals was exceeded in the leachates of any of the solids stream.

TABLE 6. RCRA LEACHING RESULTS OF SOLIDS*

Element	Process Samples		Treatability Samples		RCRA Limit
	Slag	Settler Fines	Primary Sludge	Biosludge	
Ag	<0.001	<0.001	<0.001	<0.001	5.0
As	<0.003	<0.003	0.031	0.039	5.0
Ba	0.094	0.10	0.21	0.29	100
Cd	0.008	0.014	0.010	0.35	1.0
Cr	<0.001	<0.001	0.074	0.055	5.0
Hg	<0.0005	<0.0005	<0.0005	<0.0005	0.2
Pb	<0.002	0.024	0.003	0.008	5.0
Se	<0.004	<0.004	<0.004	0.078	1.0

*Concentration in $\mu\text{g/ml}$ (ppm)

SUMMARY OF RESULTS AND CONCLUSIONS

Some of the major results and conclusions of this study are:

- The gasification pilot plant appeared to be operating at steady-state conditions during the environmental testing.
- The total mass balance showed very good closure.
- Existing conventional wastewater treatment technology is effective in reducing the significant effluent water quality parameters including BOD, COD, TSS, NH_3 , and H_2S .
- The concentrations of many of the trace metals are significantly reduced in the wastewater treatment system.
- The quality of most receiving waters should not be adversely affected by the treated effluent if properly treated with existing wastewater treatment technology.
- The solid wastes are not classified as toxic wastes according to RCRA extraction procedures.

ACKNOWLEDGEMENT

The coal test run was sponsored by the Electric Power Research Institute and we wish to acknowledge the assistance which they provided during our sampling activities. We would especially like to express our appreciation and thanks to the staff and operating personnel at the Ruhrkohle/Ruhrchemie gasification plant for their considerable efforts in support of our sampling program.

The assistance and cooperation of the Texaco Development Corporation is gratefully acknowledged.

SOURCE TEST AND EVALUATION OF A RILEY †
GAS PRODUCER FIRING NORTH DAKOTA LIGNITE

by: Fred L. Jones
American Natural Service Company
Detroit, MI 48226

William P. Earley
Riley Stoker Corporation
Worcester, MA 01613

M. R. Fuchs
Radian Corporation
Austin, TX 78766

V. A. Kolesh
Riley Stoker Corporation
Worcester, MA 01613

ABSTRACT

A ten-foot six-inch diameter Riley Morgan gasifier was operated for 14 days to convert North Dakota lignite to low-Btu gas. During that period, the gasifier was operated at a range of load conditions, and the product gas was transported to a commercial-scale kiln burner mounted in a large combustion test chamber. Process stream conditions and compositions were recorded throughout the test and were submitted to an SAM/1A analysis. Gaseous effluent streams were found to be well controlled due to the unique Riley coal feed and poke hole systems. Solid wastes from the process (gasifier ash and cyclone dust) were found to be nontoxic, noncarcinogenic and nonmutagenic. Gasifier wastewater effluent (ash pan water) was similarly found to be nonhazardous. Although combustion stack gases were not monitored, sulfur and particulate loadings in the gasifier product gas indicated that the stack gases would comply with current EPA New Source Standards. If all reduced nitrogen compounds were converted to NO_x, however, these emissions would exceed New Source Performance Standards^x.

"SOURCE TEST AND EVALUATION OF A RILEY GAS PRODUCER
FIRING NORTH DAKOTA LIGNITE"

In 1979, American Natural Service Company commissioned the Riley Stoker Company to perform a full scale test of the low Btu gasification of North Dakota lignite in the Riley coal gasifier. Co-sponsors of the test were the Riley Stoker Company, The Hanna Mining Company and the Environmental Protection Agency through a contract with Radian Corporation. This report summarizes the results of that test and more specifically the environmental assessment of the Riley gas producer carried out by Radian Corporation.

PROCESS DESCRIPTION

The Riley gasifier is a modern, modified version of the Morgan gas producer, workhorse of the steel, glass, lime, pulp and chemical industries during the first fifty years of this century. Of the nearly 1,100 of these first generation units manufactured, at one time installations could be found on every continent in the world.

Since 1974, Riley Stoker Corporation has been operating a commercial sized demonstration unit at its Worcester, MA., R & D facility, the primary goal being the refinement of the successfully established first generation technology to the standards imposed by both environmental and operational constraints of the synfuels industry. A secondary, but no less important goal, has been the gaining of hands on experience in an area long treated as more an art than a science, and in which hard data is generally lacking.

During this time, a total of twenty-two demonstration runs with various eastern coals was carried out on the gasifier, together with an equal amount on a smaller one-fifth scale gasifier. Results of this program, together with a summary of practical operating experiences have been presented before other bodies (References 1, 2, 3).

THE GASIFIER

The Riley gasifier is depicted in Figure 1. This unit is an example of that group of gas producers classified as thin-bed, atmospheric. The entire fuel bed, including ash, never exceeds 140 cm. (55 inches), and slowly rotates, at a speed of one revolution in six and one-half minutes.

The height of the active fuel bed, 76 to 91 cm. (30-36 inches), differentiates this gasifier from moderately deep bed gasifiers (Wellman-Galusha, Lurgi), and very deep bed gasifiers (two-stage units). This design resulted from the need to accommodate swelling bituminous coals in the steel

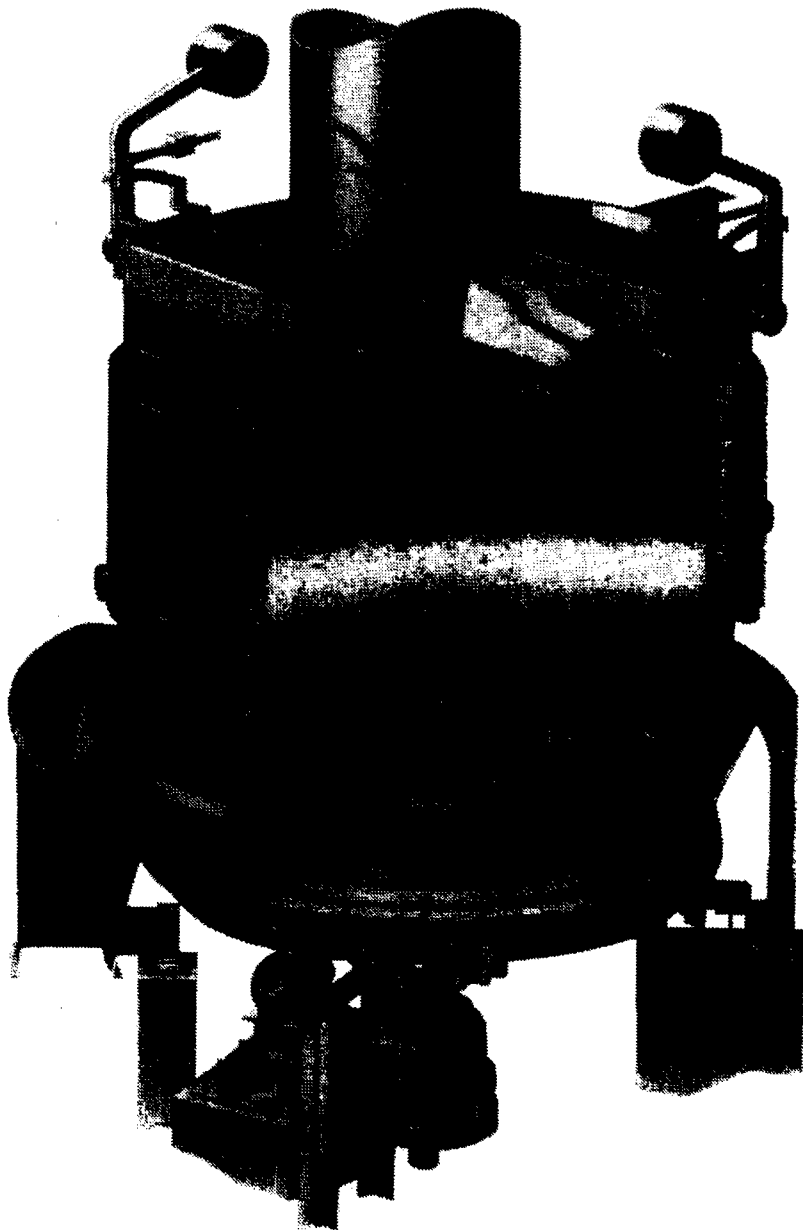


Figure 1. The Riley Gasifier

industries of the United States and the United Kingdom.

As has been found (Reference 1), coal particle heating rate is the controlling factor in managing swelling coals, and the ability to vary bed height allows the time-temperature history of the individual coal particle to be preselected and governed, resulting in minimal swelling. In general, thin-bed gasifiers operate with considerably higher exit temperatures than do the other classes of gasifiers, so that the distillation/pyrolysis environment which is first seen by the coal is more severe. This difference must be kept in mind in comparisons of yields and distribution of some of the minor families of compounds evolved from different gasifiers. Ash retention characteristics may also be influenced.

Continual rotation of the entire 3.2 meter (10'-6") I.D. unit accomplishes a number of purposes. Primarily, it is to assure even coal distribution across the entire fuel bed, a crucial factor in thin-bed management. This is accomplished without the use of an internal distributor by means of a slot drum feed across an entire radius of the unit. Thus, a continuous curtain of the fuel is evenly laid upon the advancing fuel bed.

Second, two horizontally fixed but vertically moveable water-cooled bars perform the function of fuel bed agitation, another requirement for swelling coals.

Third, ash is removed intermittently thru the use of a plow mechanism which is periodically stopped, scooping ash from the integral pan and discharging it over the ash pan lip. Some of the seal water will be carried over with this ash, and means for its treatment must be considered.

The Riley gasifier utilizes a blast hood for air/steam admission, rather than a grate, the ash bed acting as the diffuser.

THE SYSTEM

The demonstration facility at Riley Stoker is shown schematically in Figure 2. Coal is fed to the unit from a 60 ton nitrogen sealed bunker thru a three-valve lock hopper system, and is gasified by the countercurrent air/steam mixture. Gas exits thru a .9 meter (36 inch) insulated line, is cleaned of particulate in a high efficiency cyclone and transported to a 300 million Btu/hour test furnace where it is combusted. Char is removed from the cyclone dry, thru a lock hopper arrangement. A photograph of the installation is shown in Figure 3.

DESIGN FOR EMISSIONS

Much of the work at RSC during the past seven years has been devoted to design improvements of those parts of the system responsible for fugitive emissions. Historically, most gas producer manufacturers paid scant attention to the two areas most responsible for such emissions of raw gas: the coal feed system and access ports.

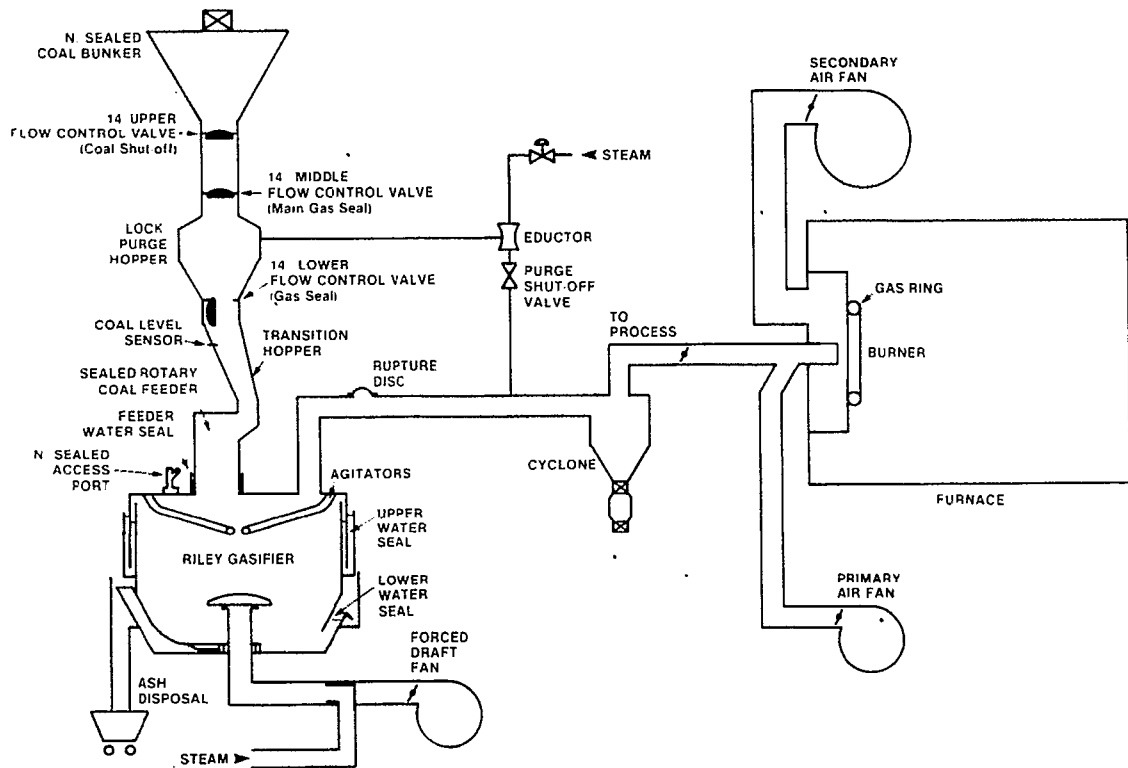


Figure 2. Schematic of the Test Facility

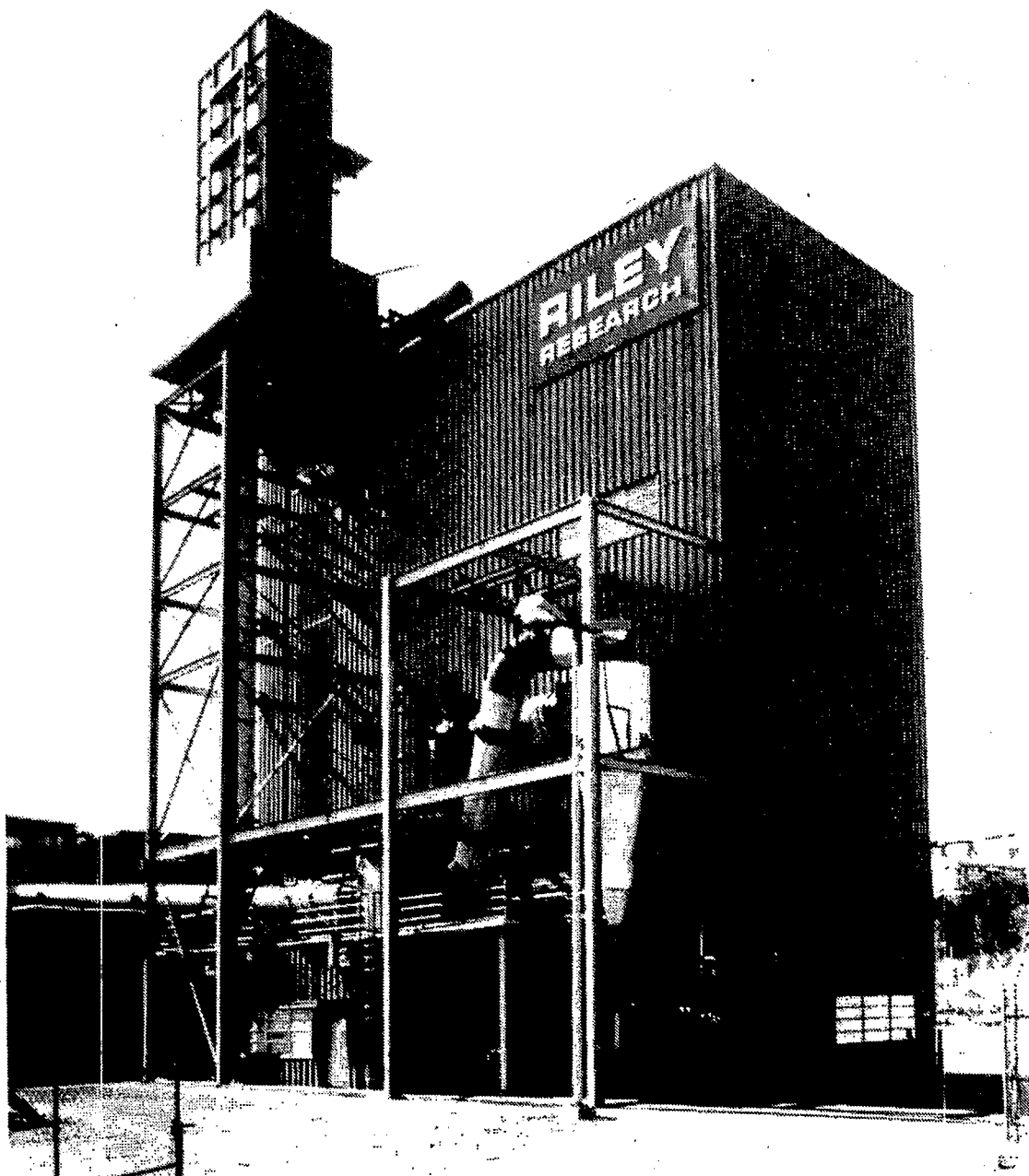


Figure 3. Riley Installation

Coal Feed System

In the Riley Stoker lock-purge coal feed system as shown in Figure 2, fuel is inventoried up to a level just below the middle valve, with the valves positioned as shown. The top valve must support a head of coal up to 6.4 meters (21 feet). The middle valve is closed to contain system gases. The lower valve is open to admit lock hopper coal to the gasifier feeder. All valves are of a semi-ball type, with ground seats.

As gasification proceeds the fuel in the lock hopper falls to a level just below the lower valve, where its absence is detected by means of a sonar device. This triggers a sequence as follows: following closure of the lower valve, a short burst of steam is admitted into the line from the eductor to the lock hopper cleaning that line of any residual tar or dust from the previous cycle. After an interval, the purge shut-off valve opens, and the steam eductor begins evacuating the lock hopper of gas and discharging it into the downstream gas piping system. The pressure in the lock hopper eventually becomes sub-atmospheric (660 mm. Hg. or less). At this time, the steam and purge shut-off valves close, and the upper two flow valves open, admitting coal from the main storage bunker to the lock hopper. These valves remain open until the lock hopper is filled to the previous level (approximately 1 ton). At this time the upper valve closes, interrupting coal flow, followed by the middle valve closing, creating a gas tight seal. The lower valve opens with middle valve closure, and the cycle is completed. Total elapsed time for this entire cycle is approximately one minute.

Throughout this sequence, gasifier feed has been maintained continuously, from the inventory of coal located between the coal feeder and the lower lock valve.

By the maintenance of a nitrogen blanket just slight above atmospheric pressure in the storage bunker above this system, together with the eductor system, migration of gases is always toward the gasifier, and never from it.

Access Ports

After a number of trials, RSC has perfected a nitrogen-sealed (any inert will do), universal joint access port, to be used during those times when access to the gasifier bed is a necessity. This unit is shown in Figure 4. Mounted atop a machined ball that moves within a gland seal fixed to the gasifier deck is another ball valve, a packing gland and a flexible hose conveying inert gas at approximately 1.4 kg/cm^2 (20 psig).

Insertion of a rod thru the upper gland to the ball valve is followed by opening the inert gas line. The ball valve is then opened and the rod inserted into the gasifier thru the assembly, inert gas flowing into the gasifier, and also around the upper gland to the environment.

This arrangement assures no leakage of producer gas into the environment,

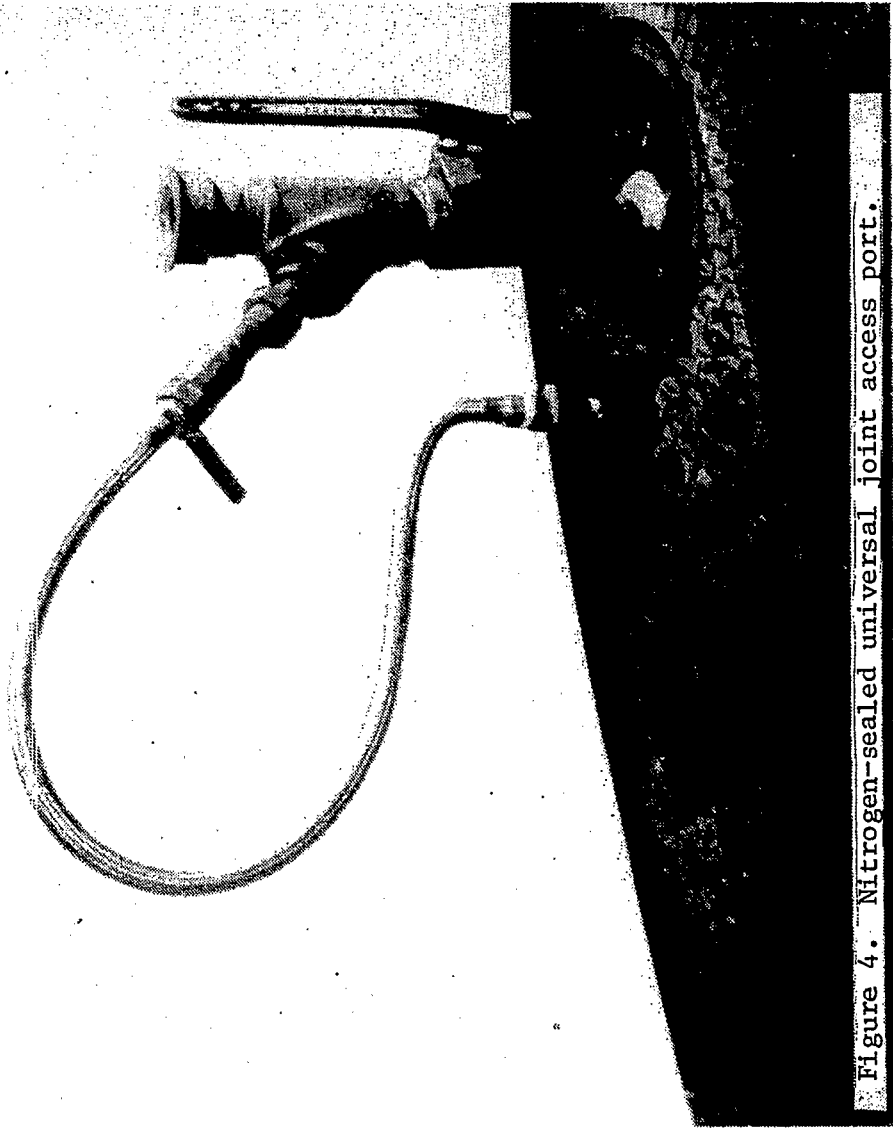


Figure 4. Nitrogen-sealed universal joint access port.

and also makes possible viewing of the fuel bed by the substitution of a plexiglass plate for the rod or other device.

ABSTRACT OF RUN

The gasifier test facility was operated from December 4 to 15, 1979. During this period a total of 374 metric tons of North Dakota lignite was gasified. Because of some non-gasifier problems, two interruptions caused shutdowns early in the test. The major portion of the test fuel was processed in the last five days of operation, and the results presented herein represent data taken from this continuous period. More specifically, data for the environmental assessment were taken over a 25 hour period extending from 0900 hours on December 13 through 1000 hours December 14.

Tables 1 and 2 present the heat and material balance around the gasifier at a time near the end of the 25 hour period. Table 3 shows a summary of the concentrations of the major species of the product gas over the 25 hour operating period. Table 4 summarizes the chemical compositions of the feed coal, tar and cyclone dust.

Over the total two week test period, the gasifier was operated at feed rates up to 4550 Kg/hr (10,000 lb/hr) of coal, and produced a high quality low Btu gas with a heating value of approximately 160 Btu/cubic foot. A summary of process conditions during the 25 hour sampling period is given in Figures 5 and 6.

ENVIRONMENTAL RESULTS

For the purposes of a source analyses model evaluation, five effluent or process streams are considered coming from the gasifier: product gas vapors; product gas particulates, tars and oils; gasifier ash; cyclone dust; and ash pan water. Product gas vapors are distinguishable from product gas particulates, tars and oils by a characterization temperature of 115 C (240 F). The product gas is separated into two fractions at this temperature by the sampling procedure. The separation makes it possible to assess the potential health and ecological effects of fugitive emissions. It also allows an evaluation of appropriate control technologies. The phase condensed and collected at 115 C (particulates, tars and oils) was collected in an electrostatic precipitator. The remaining portion of the product gas (vapors) was collected in a condenser at approximately 15 C (60 F), followed by an organics absorption resin for organics collection, or an impinger train for trace elements, ammonia or hydrogen cyanide.

The results of the source analysis model (SAM/1A, Reference 4) evaluation of the five effluent or process streams are presented in Figure 7. By this evaluation procedure there are potentially harmful health and ecological effects for all total discharge severity (TDS) and total weighted discharge severity (WDS) values above 1. Each of the five streams exhibited potentially harmful health and ecological effects. The SAM/1A approach indicated that potential health and ecological effects were primarily due to organic compounds. However, the total DS for the streams (except gasifier ash and product gas vapors) include significant contributions from "worst case assump-

TABLE 1. OVERALL HEAT & MATERIAL BALANCE

	Mass Flow Rate		Temperature		Type of Heat	Enthalpy* kJ/kg (Btu/lb)	KW	Heat Flow Rate	
	kg/s	(lb/hr)	°C	(°F)				(1000 Btu/hr)	Percent
Inputs									
Coal	1.045	(8,292)			Potential	16,205 (6,967)	16,932	(57,700)	96.0
Net Stream	0.274	(2,174)	-2 (29)		Sensible	-33 (-14)	-34	(-116)	-0.2
Air	1.554	(12,334)	164 (328)		Sensible	2,847 (1,224)	780	(2,661)	4.4
Total	2.837	(22,800)	-2 (29)		Sensible	-28 (-12)	-43	(-148)	-0.2
							17,635	(60,167)	100.0
Outputs									
Dry Gas	2.299	(18,245)			Potential	6,020 (2,588)	13,840	(47,218)	78.5
Moisture	0.440	(3,492)	270 (518)		Sensible	265 (114)	609	(2,080)	3.5
Tars and Oils	0.0215	(171)	270 (518)		Potential	26,193 (11,261)	1,280	(4,368)	7.3
					Sensible	205 (88)	566	(1,926)	3.2
Cyclone Dust	0.0043	(34)	270 (518)		Potential	20,139 (8,658)	86	(294)	0.5
					Sensible	205 (88)	1	(3)	---
Ash	0.108	(858)	93 (200)		Potential	8,806 (3,786)	952	(3,248)	5.4
					Sensible	58 (25)	6	(21)	---
Heat to Cooling Water							128	(437)	0.7
Unaccounted for Losses							163	(557)	0.9
TOTAL	2.873	(22,800)					17,635	(60,167)	100.0

* Enthalpy is 25°C (77°F) and H₂O liquid. Potential heats are based on higher heating value (HHV).

TABLE 2. POTENTIAL ENERGY FLOWS BY LOWER HEATING VALUE

	Mass Flow Rate kg/s	LHV kJ/kg	LHV Heat Flow Rate kJ/s
Lignite Feed	1.045	14,783	15,448
Dry Gas	2.299	5,636	12,957
Tars and Oils	0.0215	24,398	525
Cyclone Dust	0.0043	19,821	85
Ash	0.108	8,706	940

TABLE 3. MAJOR GAS COMPONENTS

Time Hrs	Volume Percent on Dry Basis						
	CO	CO ₂	H ₂	O ₂	N ₂	CH ₄	
Dec. 13	1000	NA	NA	NA	NA	NA	NA
	1100	NA	NA	NA	NA	NA	NA
	1200	NA	NA	NA	NA	NA	NA
	1300	NA	NA	NA	NA	NA	NA
	1400	26.9	7.0	16.6	1.1	46.8	NA
	1500	24.1	8.6	16.6	1.1	48.2	0.6
	1600	26.1	7.2	16.5	1.0	47.3	1.0
	1700	28.0	6.8	16.7	1.2	45.8	0.7
	1800	27.1	6.6	16.7	1.1	46.5	1.2
	1900	27.4	6.7	16.9	1.2	46.4	0.7
	2000	24.6	8.3	16.5	1.1	47.6	1.0
	2100	25.3	8.0	16.5	1.1	47.5	0.7
2200	27.3	7.1	16.8	1.0	45.7	1.2	
Dec. 14	2300	27.4	7.2	16.9	1.0	45.6	1.1
	2400	27.6	7.1	16.6	1.1	45.3	1.4
	0100	26.6	7.7	16.0	0.9	46.6	1.4
	0200	27.0	7.1	17.1	1.0	45.6	1.3
	0300	27.7	6.4	18.0	1.1	44.5	1.5
	0400	28.2	6.2	17.4	1.2	44.8	1.5
	0500	28.9	6.3	17.3	1.2	44.7	0.9
	0600	25.7	7.7	18.3	1.3	45.4	0.9
	0700	28.8	6.3	18.7	1.3	43.3	0.9
	0800	29.2	5.9	19.0	1.1	43.2	NA
0900	28.9	5.3	17.3	1.0	45.9	NA	
1000	26.4	8.9	17.2	1.2	44.8	NA	

Notes: * Compositions are Radian process gas chromatograph readings normalized to 100 percent.

** Argon was not measured and is assumed to be 0.54 volume percent for all periods.

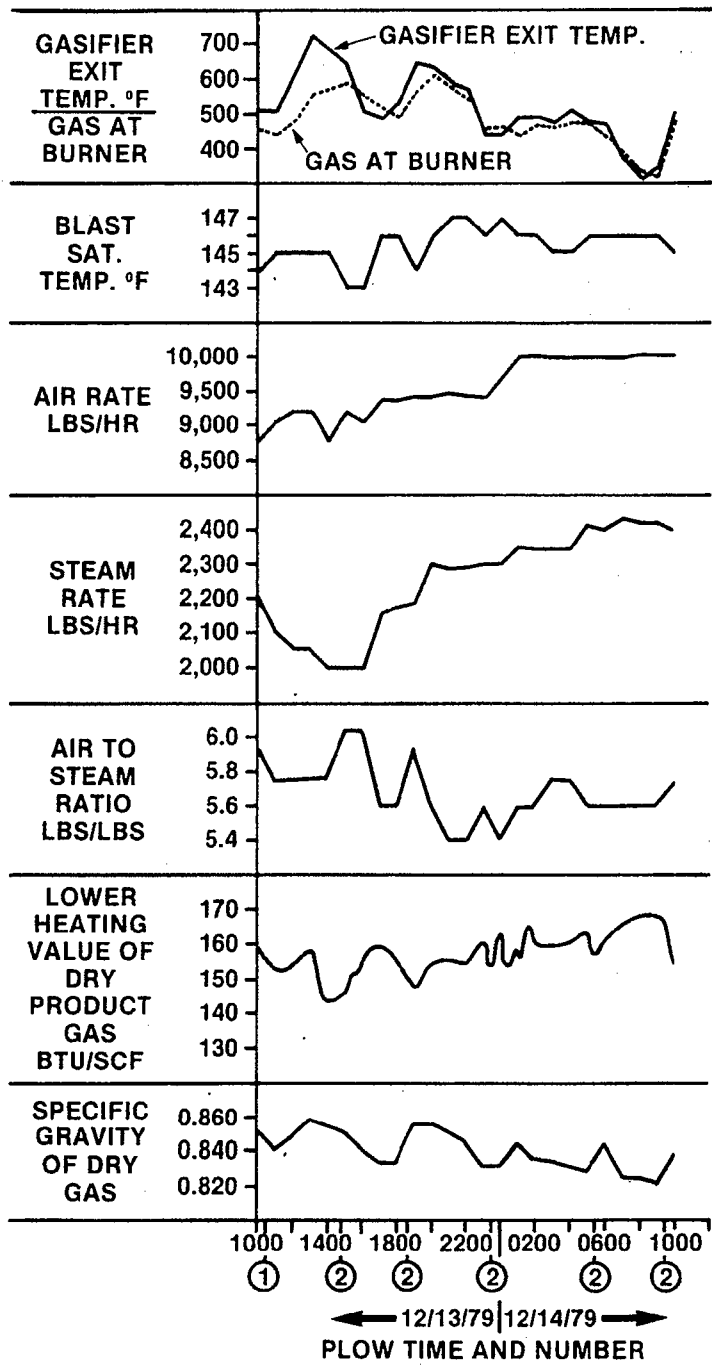


Figure 5. Process Variable for 24 Hour Period

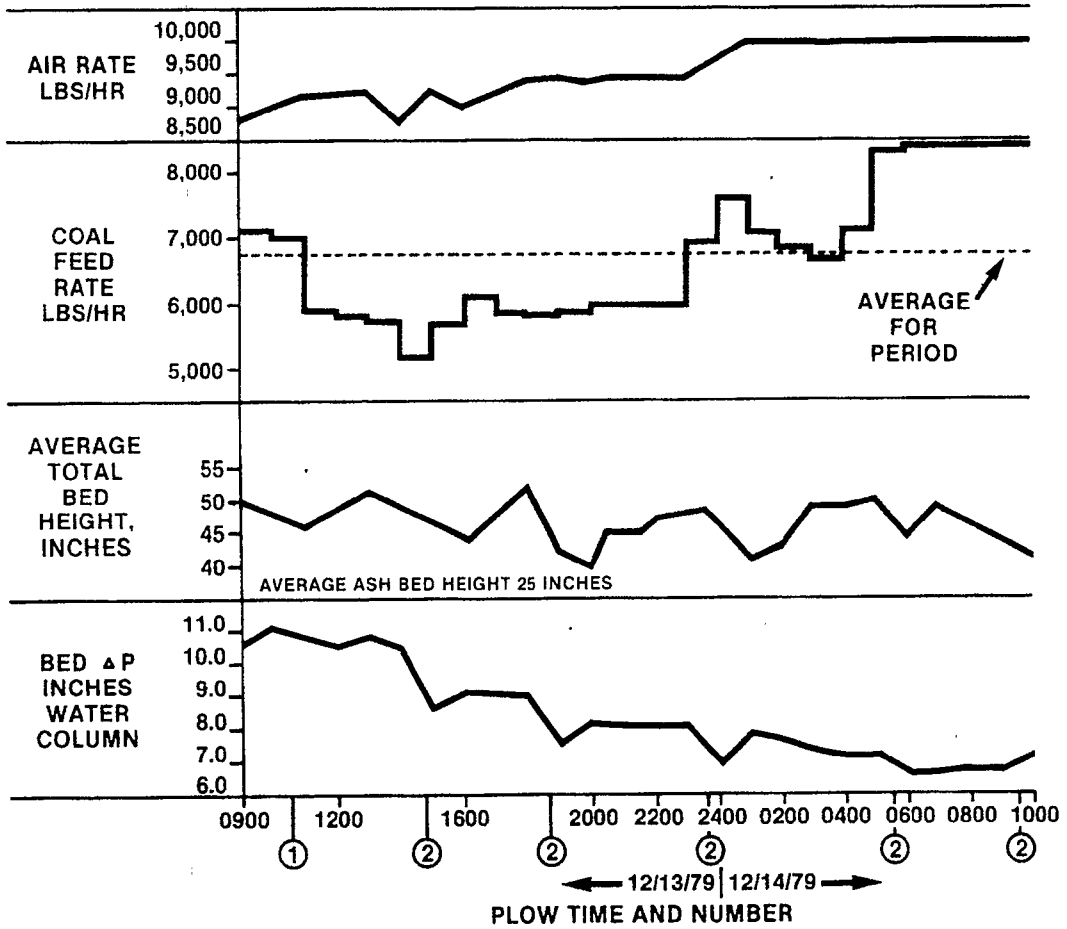


Figure 6. Bed Related Process Variable Plots for 25 Hour Lignite Run

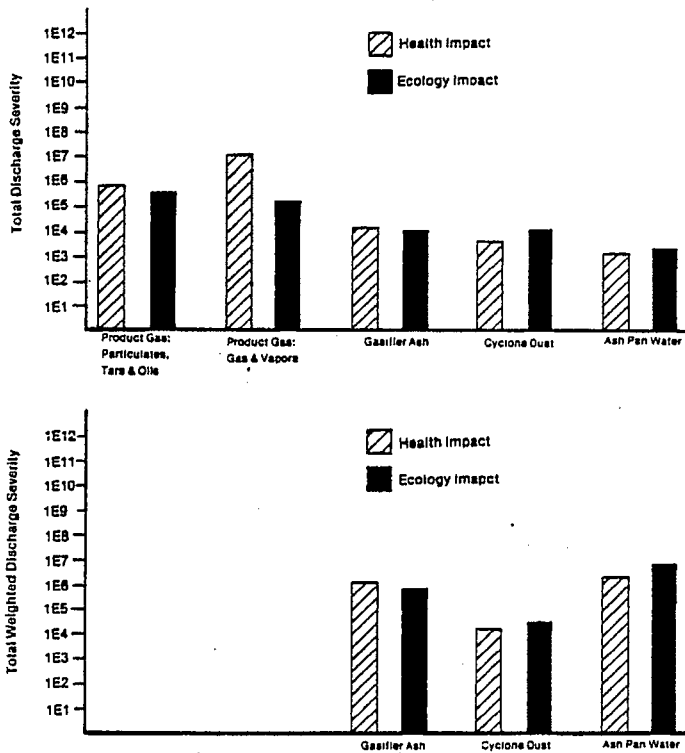


Figure 7. Total Discharge Severities and Weighted Discharge Severities of Effluent Streams

TABLE 4. SELECTED CHEMICAL ANALYSES

	Feed Coal		Cyclone		Tar WT. %
	(as received)%	Dust WT. %	Dust WT. %	Tar WT. %	
Moisture	34.10	0.59			--
Ash	7.54	38.21			0.20
Carbon	41.82	54.48			59.57
Hydrogen	2.83	1.48			8.40
Oxygen	12.70	2.82			30.75
Nitrogen	0.70	0.83			0.69
Sulfur	0.31	1.59			0.33
V.M.	30.68	--			--
F.C.	27.68	--			--
HHV, Btu/lb		6,967			
HHV, kJ/kg		16,205	8,607		11,261
LHV, kJ/kg		14,669	20,020		26,193

TABLE 5. CONTRIBUTIONS TO TOTAL DS AND TOTAL WDS BY WORST CASE ASSUMPTIONS
GC/HECD DATA, AND EXPERIMENTALLY DETERMINED RESULTS

EFFLUENT STREAMS	Health			Ecology		
	WCA*	GC/HECD	EXP. / INORG.	WCA*	GC/HECD	EXP. / INORG.
Product Gas: Particulates, Tars and Oils	~97%	~3%	99.9%/0.1%	~99%	1%	99.7%/0.3%
Product Gas: Gas and Vapors	~100%	<1%	100%/0%	<1%	~100%	100%/0%
Gasifier Ash	~1%	~2%	18%/82%	<1%	~4%	~95%
Cyclone Dust	~83%	~17%	83%/17%	~23%	~77%	23%/77%
Ash Pan Water	~74%	~5%	99.9%/0.1%	~76%	~3%	79%/21%

*Worst Case Assumptions

tions" for the organics, which should be greatly reduced by more extensive analysis for specific organics (Table 5).

Inorganic elements, on the other hand, had the most significant contribution to the health and ecological impacts of the gasifier ash stream, with iron having the most significant health impact and phosphorus the most significant ecological impact. Inorganic elements did not contribute significantly to total DS or WDS for product gas or ash pan water health effects. However, phosphorus did make a significant contribution to the ecological effects of the ash pan water.

The findings in this source test evaluation indicate that the potential health and ecological effects of the ash pan water are significant. Even though the organic loading of the ash pan water was very low, the health and ecological DS and WDS of the stream were the result primarily of organics, other than the contribution of phosphorus to ecological impact. During the test program, ash pan water was continuously purged. Therefore, the concentrations of many parameters of concern in the stream were possibly held below anticipated levels of design operation using recycle, thereby reducing the total DS. However, continuous purging of the ash pan water provided a flow rate higher than design operation flow rate for the ash pan water and thereby raised the total WDS values to a level representative of commercial operation of the gasifier (Table 6).

Since organics provide the most significant contribution to the total DS of the product gas, these values would be reduced for the product gas combustion effluent due to the vast reduction in organic content following combustion. It should be noted that the SAM/1A approach treated the product gas as an effluent stream, which it is not, other than as a fugitive emission.

The SAM/1A results for gasifier ash and cyclone dust also showed potentially harmful health and ecological effects. On the other hand, bio-assay tests conducted on the solid gasifier ash and cyclone dust indicated little or no health hazard. A neutral leaching of the two solid streams provided a liquid for bio-assay testing that showed a high level of ecological hazard. However, subjecting the gasifier ash and cyclone dust to (RCRA) leaching procedures (Reference 5) resulting in the solids being classified as non-hazardous (Tables 7, 8).

EMISSIONS FOLLOWING COMBUSTION

Presently, the main concern about the utilization of coal and coal-derived fuels in industry centers above emissions of oxides of sulfur, oxides of nitrogen, and particulates. While the actual emissions of SO₂ and NO_x due to low Btu gas combustion are dependent on application, the Riley test provided some indication of what the expected levels of these emissions might be.

During the two week test period, product gas from the gasifier was passed through a single stage cyclone for clean-up and transported directly to the large kiln burner. Because the temperature of the gas was maintained very close to that observed at the gasifier exit, not one gallon of product

TABLE 6. COMPARISON OF LIQUID STREAMS TO DRINKING WATER STANDARDS*

	NIPDWS*** µg/l	NSDWR**** µg/l	ASH PAN WATER**		ASH PAN CARRY-OVER WATER µg/l	SERVICE WATER µg/l
			RANGE µg/l	AVERAGE µg/l		
As	50		11 - 30+	21+	9+	<10
Ba	1,000		91 - 230	170	250	100
Cd	10			<1	<10	<10
Cl-		250,000	48,000-110,000	78,000	2,000	300
Cr	50			<1	<1	<30
Cu		1,000	3 - 10	6	<1	70
F-	1,800		300 - 710	530	~1,000	~20
Fe		300	540 - 3,400	1,900	910	3,000
Pb	50		<1 - 2	<1.3	300	<10
Mn		50	27 - 96	58	11	40
Hg	2			<0.5+	<0.5+	
Se	10		<5 - 10+	<7	<5+	<10
Ag	50		2 - 30	14	20	<10
Zn		5,000	<3 - 12	<5.3	<3	80
NO ₃ - (as N)		10,000		<20		
SO ₄ = (mg/l)		250	540 - 1,870	1,260		6.1
pH		6.5-8.5	10.2 - 11.3	10.8	5.0	4.3
TDS (mg/l)		500	1,250 - 2,050	2,250		52

*ICPES analytical results unless noted otherwise. Analysis performed by SSMS.

**Samples RM-18, RM-23, RM-49

***National Interim Primary Drinking Water Standards (Federal Register, 8/27/80).

****National Secondary Drinking Water Regulations (Federal Register, 7/19/79).

+Analysis performed by AAS.

TABLE 7. BIOASSAY TEST MATRIX

	Ames* (Health)	CHO** (Health)	RAM*** (Health)	RAT**** (Health)	Fresh- water Alga***** (Ecology)
Cyclone Dust	Negative	Low Toxicity	No Detectible Toxicity		
Gasifier Ash	Negative	No Detectable Toxicity	Low Toxicity		
Gasifier Ash Neutral Leachate	Negative	Low Toxicity		Not Toxic	Toxic
Cyclone Dust Neutral Leachate	Negative	No Detectable Toxicity		Not Toxic	Toxic

*Salmonella Mutagenesis Assay (Ames)
 **Chinese Hamster Ovary Clonal Toxicity Assay (In Vitro Cytotoxicity Assay)
 ***Rabbit Alveolar Macrophage Assay (In Vitro Cytotoxicity Assay)
 ****Rodent Acute Toxicity (Acute in Vivo Toxicological Test)
 *****Freshwater Alga (Selenastrum capricornutum) Toxicity Assay

TABLE 8. COMPARISON OF SOLID EFFLUENT EXTRACTS
AND RCRA EXTRACT LIMITS

	RCRA Extract Limits* (5/19/80)	Gasifier Ash Leachate*	Cyclone Dust Leachate*
As	5,000	33	4
Ba	100,000	680	390
Cd	1,000	<0.5	<0.5
Cr	5,000	<1	<1
Pb	5,000	<2	<2
Hg	200	<0.5	<0.5
Se	1,000	6	2
Ag	5,000	<0.5	<0.5
Endrin	20	<2.0	<2.0
Lindane	400	<0.2	<0.2
Methoxychlor	10,000	<2.0	<2.0
Toxaphene	500	<100	<100
2,4-D	10,000	<0.8	<0.8
2,4,5-TP Silvex	1,000	<0.3	<0.3

*Concentrations in µg/liter.

gas tars and oils was condensed from the gas, nor was any significant amount of water-based condensate produced. With the exception of a light coating of dust which formed on the inside of the gas main, all product gas effluents leaving the gasifier cyclone outlet proceeded to the gas burner for combustion.

Combustion of the product gases was achieved in a low pressure baffle burner operating with combustion in the primary air zone at 33% of theoretical air and 213% of theoretical air overall. The theoretical adiabatic flame temperature for this mixture was 1077 C (1970 F). The flame produced was a long diffusion flame, ranging from 1.2 to 2 meters (4-7 feet) in diameter and 9 to 12 meters (30-40 feet) in length. Figure 8 illustrates several temperature profiles measured in the flame using a suction pyrometer.

No measurements of actual stack emissions were made. However, by analyzing the composition of the product gas being fed to the combustor, it was possible to make the following correlations.

The North Dakota (Indian Head) lignite gasifier feedstock for the 24 hour test period had an average sulfur concentration of 0.44g/10⁶J (1.02 lb S/10⁶ Btu). Some 53% of the sulfur being fed to the gasifier was being converted to reduced sulfur species in the product gas, with the majority of the remainder being retained by the gasifier ash stream. If 100% of the reduced sulfur species in the product gas were converted to sulfur dioxide during combustion, the resulting SO₂ emission level would be 0.49g/10⁶J (1.10 lb SO₂/10⁶ Btu) based on the heat value of the lignite feed. The New Source Performance Standards emission limit for SO₂ is 0.52g/10⁶J (1.20 lb SO₂/10⁶ Btu) for coal-fired boilers (Reference 6, Subpart D: Fossil Fuel Fired Steam Generators).

The average ammonia content of the product gas was 7.8 X 10⁵ µg/Nm³ and the average HCN concentration was 1.8 x 10⁵ µg/Nm³. About 26% of the nitrogen in the lignite feedstock was converted to reduced nitrogen species. Assuming that 100% of the reduced nitrogen species in the product gas was converted to NO_x during combustion, the resulting NO_x emission (as NO₂) would be 0.36g NO₂/10⁶J (0.84lb NO₂/10⁶ Btu) based on the heat value of the lignite feedstock. The NSPS emission level (Subpart D) for NO_x is 0.26g NO₂/10⁶J (0.60 lb NO₂/10⁶ Btu) for coal fired boilers. While estimated NO_x emissions may be biased high, assuming 100% conversion of reduced nitrogen species to NO_x, it does not provide for the additional NO_x created due to thermal reaction of nitrogen and oxygen during combustion, which for many applications may be a significant contribution. For the specific test described here, the low combustion temperatures observed would likely minimize thermal production of NO_x, but high excess air levels would likely favor conversion of reduced nitrogen species to NO_x.

The particulate loading of the product gas stream was 4.76 x 10⁵ µg/Nm³ downstream of the cyclone. Particulate was assumed to be of the same composition as the cyclone dust, and the cyclone dust ash content was used for calculations to determine the particulate emissions after combustion. Basing the adjusted particulate loading upon the heat value of the lignite feedstock, the particulate emission after combustion would be 0.026g particulate/

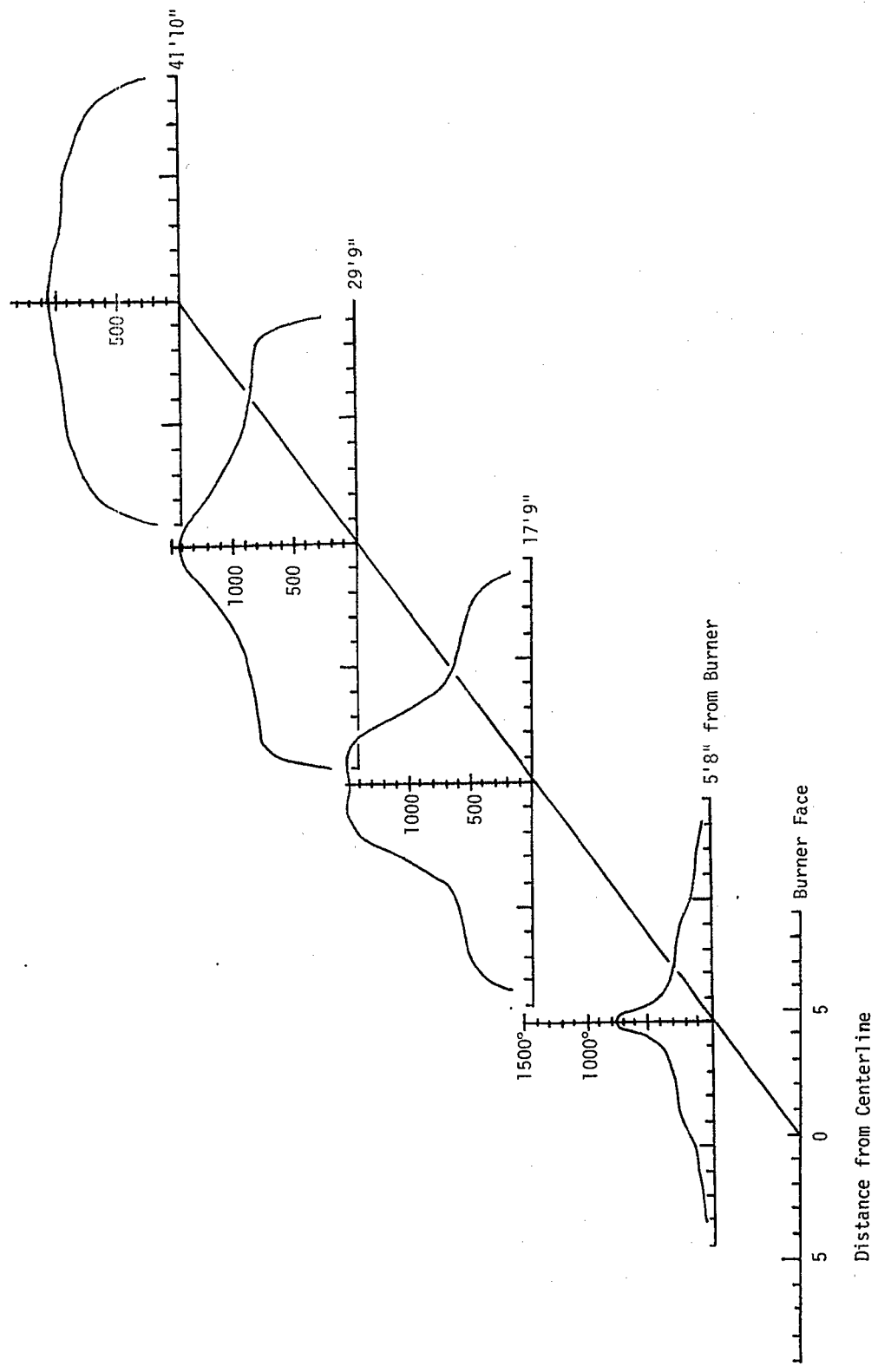


Figure 8. Low Btu Gas Flame Temperature Profile (9300 lb/hr rate)

10⁶J (0.06 lb particulate/10⁶ Btu). This particulate emission estimate does not consider particulate resulting from incomplete combustion of tars and oils. The NSPS (Subpart D) for particulate is 0.043g particulate/10⁶J (0.10 lb particulate/10⁶ Btu) for coal-fired boilers.

FUGITIVE EMISSIONS

The North Dakota lignite gasification test provided an opportunity for testing the effectiveness of the unique Riley coal feed and poke hole designs for minimizing fugitive emissions from the gasifier. Fugitive emissions of hydrocarbons were measured in the vicinity of the gasifier by several methods. Hydrocarbon concentrations, reported as methane, were less than one part per million as summarized in Table 9. Hydrocarbons were also measured in the off-gases from the nitrogen-pressurized coal bin. Concentrations here were 5-6ppm as methane. Readings of two carbon monoxide monitors maintained by Riley Stoker were recorded during the sampling period, and are summarized in Table 10. The maximum recorded CO concentration was 24 ppm with readings generally below this value. The Occupational Safety and Health Administration (OSHA) permissible exposure limit for CO is 50 ppm (see Reference 7). There is no OSHA regulation for hydrocarbons as a compound class. Propane is the lightest hydrocarbon regulated by OSHA and has a permissible exposure limit of 1,000 ppm.

Radian Corporation has performed STE's for a Chapman low Btu gasifier with a bituminous coal feedstock and a Wellman Galusha gasifier with an anthracite coal feedstock. The Chapman STE Report (Reference 8) presents coal feeder vent gas hydrocarbons concentrations of $2.5 \times 10^6 \mu\text{g}/\text{Nm}^3$. Similar measurements at the Wellman Galusha facility (Reference 9) resulted in coal hopper gas hydrocarbon concentrations of $1.4 \times 10^6 \mu\text{g}/\text{Nm}^3$ as methane. Related values measured at the Riley gas producer are many orders of magnitude less. These data demonstrate the relative reduction of fugitive emissions achieved by the controls employed on the coal bin at the Riley gas producer.

A sample was taken of the poke hole gas discharge during a simulated poking operation on the gasifier, to determine the effectiveness of the Riley poke hole design in keeping product gas sealed within the gasifier. Table 11 summarizes the results of that test, and shows the high degree of effectiveness of the Riley poke hole.

TRACE ELEMENTS

Trace elements enter the gasification process with the lignite feedstock and are subjected to the high temperatures of the process. Many elements, especially the more volatile ones, undergo volatilization in the hot areas of the system, and may either remain a vapor in the product gas, condense homogeneously, or condense upon aerosol particles. Other elements are chemically transformed into gaseous species and are emitted in the product gas. Most trace elements remain in the coal solids and are emitted in the gasifier ash. Even though the majority of most elements are emitted with the solid effluent streams, RCRA extraction procedures analyses result in the classification of these solids as non-hazardous.

TABLE 9. ORGANIC VAPORS ANALYSIS

DATE	TIME	LOCATION	CONCENTRATION (ppm as CH ₄)
12/13	1100 hrs	Gasifier Building --all walkways	1.5 ppm
12/13	2200 hrs	Gasifier Building --all walkways	1 ppm
12/13	2200 hrs	Gasifier Building --top of gasifier during poking operation	1 ppm
12/13	2223 hrs	Coal Bin --2-inch gate on top	5-6 ppm

TABLE 10. CARBON MONOXIDE MONITOR READINGS

Date	Time	Monitor 1*	Monitor 2**
12/13	1100		20 ppm
12/13	1500	1 ppm	
	1502		12 ppm
	1506		15 ppm
	1750	1 ppm	24 ppm
	1808		1 ppm
	2213		<0 ppm
12/14	0035		<0 ppm
	0235	1 ppm	<0 ppm

*Located in gasifier building on ground level, west wall.

**Located in gasifier building on gasifier poke hole level,
north wall.

TABLE 11. POKE HOLE DISCHARGE DURING SIMULATED POKING OPERATION

DATE: 12/14
TIME: 0645 hours
FLOWRATE: 0.022 m³/sec (actual)

GAS ANALYSIS:

N ₂	95.4%
H ₂	1.1%
O ₂	0.2%
CO	Below detection limit
CH ₄	Below detection limit
CO ₂	Below detection limit

Minor and trace elements can be grouped according to the mechanism by which each is emitted. The elements primarily in the product gas can be considered highly volatile or transformed into gaseous compounds. Moderately volatile elements are predominately in the cyclone dust or product gas particulate and can be evaluated on the basis of volatilization and recondensation. Elements emitted predominately in the gasifier ash can be considered to be non-volatile elements.

For this source test evaluation, an element was considered to be highly volatile if 25% or more of its total mass was found in the gas and vapors portion of the product gas. These highly volatile elements were: bromine, cesium, chlorine, fluorine, gallium, iodine, selenium, silicon, sulfur and tellurium. An element was classified as moderately volatile if 25% or more of its total mass was found in the cyclone dust and particulates, tars and oils portion of the gas. These elements were: antimony, arsenic, chromium, germanium, lead, tin, and zinc.

The following elements were possible volatile and will acquire additional data to characterize their behavior definitively: beryllium, bismuth, cadmium, dysprosium, erbium, europium, gold, holmium, iridium, neodymium, osmium, palladium, platinum, praseodymium, radium, rhodium, ruthenium, silver, tantalum, terbium, thallium, thulium, uranium and ytterbium.

Figures 9 and 10 graphically present the elemental distribution in the effluent streams. The elements are listed in the order of increasing boiling points. In general, as the elemental boiling points increase, the predominance of elemental distribution shifts from the product gas to the gasifier ash. Although a general trend is evident, there is no direct correlation between elemental boiling point and distribution. The distribution of individual elements in the system is dependent not only on elemental boiling point, but also on much more complex properties, including chemical reactions within the gasifier, the volatility of compounds containing the elements, and solubility of compounds in the tars and oils.

Most of the elements classified as highly volatile from their distribution in the effluent streams were depleted in both the gasifier ash and cyclone dust. Cesium and gallium were exceptions and were enriched in both solids. This behavior is more characteristic of non-volatile elements.

Those elements considered to be moderately volatile from distributions fell into two major categories. Lead, chromium and zinc followed the expected behavior of being depleted in the gasifier ash and enriched in the cyclone dust. Arsenic and antimony, however, were depleted in both solids. The distribution results show that both of these elements were found in the particulates, tars and oils fraction of the product gas. This indicates somewhat greater volatility than that of other moderately volatile elements. The behavior of germanium and tin was more characteristic of non-volatile elements, for germanium was enriched in both solids, and the enrichment ratios for tin were very close to the ash contents.

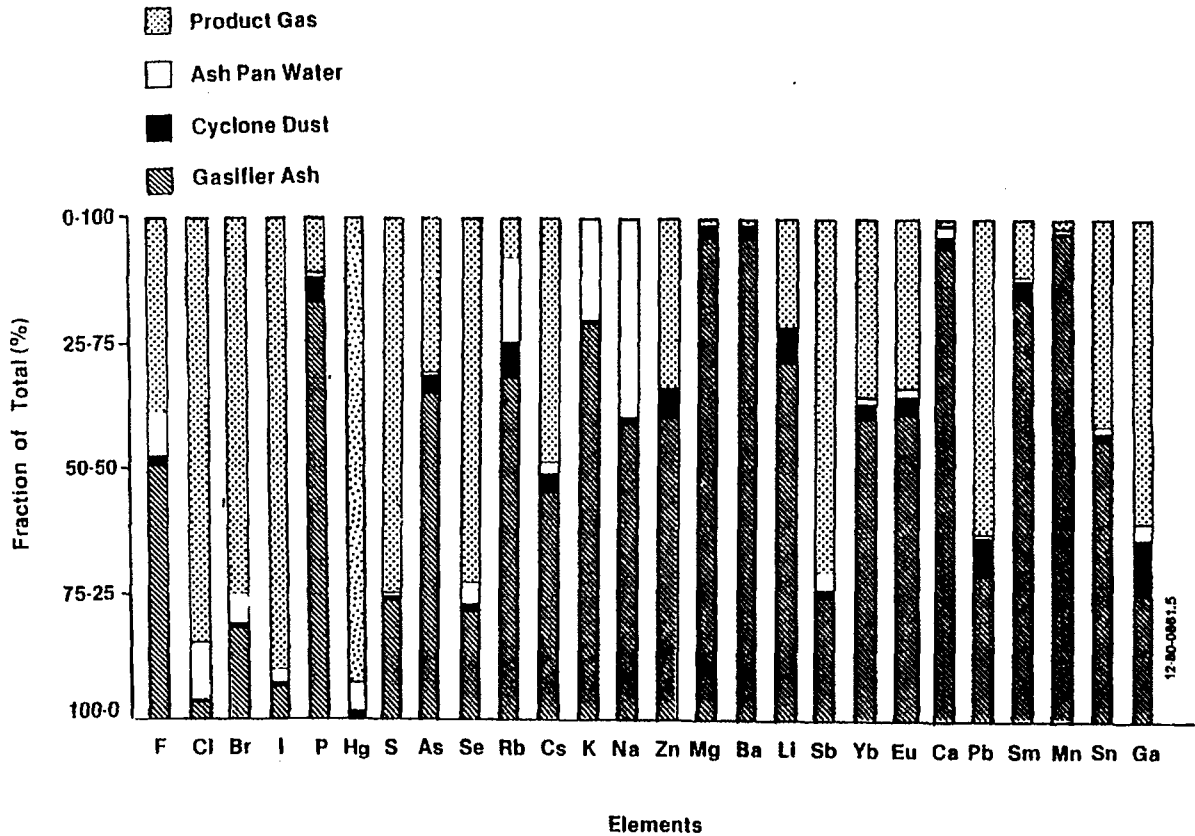


Figure 9. Stream Elemental Distributions as Percentage of Combined Effluent Streams Emission (Ordered by Increasing Elemental Boiling Points)

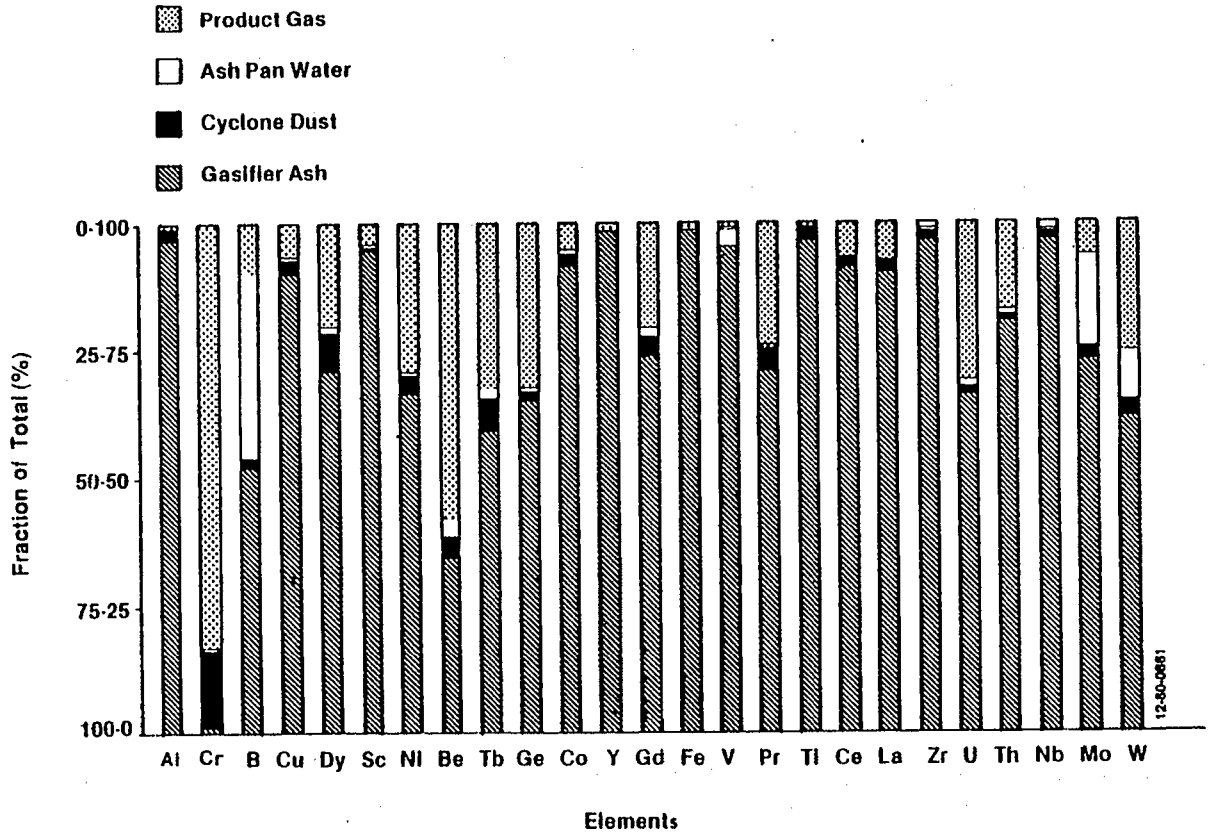


Figure 10. Stream Elemental Distributions as Percentage of Combined Effluent Streams Emission (Ordered by Increasing Elemental Boiling Points)

CONCLUSIONS

The major findings of this program are summarized below.

- Acute bio-assay tests of the gasifier ash and cyclone dust solids and neutral leachates of the gasifier ash and cyclone dust indicated no adverse health effects. Environmental bio-results of neutral leachates of the gasifier ash and cyclone dust showed significant toxic effects.
- Leaching studies conducted on the gasifier ash and cyclone dust to determine the effects of solid waste disposal, indicated that the materials are non-hazardous according to Resource, Conservation and Recovery Act (RCRA) protocol and standards.
- Although the gasification process emits over 50% of the lignite sulfur in the product gas, it will not require additional sulfur removal to meet New Source Performance Standards for coal fired boilers.
- Assuming that 100% of the ammonia and HCN present in the product gas are converted to NO_x during combustion, and not considering the contribution of thermally created NO_x in the boiler, additional NO_x controls will be necessary to meet the New Source Performance Standards for coal fired boilers.
- Additional particulate control measures will not be necessary to meet NSPS for particulate. This conclusion is based upon the particulate loading of the product gas downstream of the cyclone and the heat value of the lignite feedstock.
- Enclosed and pressurizing the coal bin, together with the nitrogen purge poke hole mechanism developed by Riley Stoker significantly reduce fugitive emissions.

REFERENCES

1. Earley, W. P., Lisauskas, R. A., and Rawdon, A. H. "Practical Operating Experience on a Riley-Morgan Gasifier." 88th AIChE Meeting, Phila., Pa. June 8-12, 1980.
2. Rawdon, A. H., Lisauskas, R. A., and Johnson, S.A. "Operation of a Commercial Size Riley-Morgan Coal Gasifier." American Power Conference Chicago, Ill. April 19-21, 1976.
3. Lisauskas, R. A., Johnson, S. A., and Earley, W. P. "Control of Condensable Tar Vapors for a Fixed-Bed Coal Gasification Process." Fourth Energy Resource Conference, Institute of Mining and Minerals Research. Lexington, Ky. Jan. 7-8, 1976.
4. Schalit, L. M., and K. J. Wolfe. SAM/1A: A Rapid Screening Method for Environmental Assessment of Fossil Energy Process Effluents. EPA-600/7-78-015. Acurex Corporation/Aerotherm Division, Mountain View, CA, February, 1978.
5. Environmental Protection Agency. Hazardous Waste Management System- Identification and Listing of Hazardous Waste, Federal Register, 45(98):33084-33135, May 19, 1980.
6. Environmental Protection Agency. New Stationary Source Performance Standards: Electric Utility Steam Generating Units. Federal Register, 44(113):33580-33624, June 11, 1979.
7. Occupational Safety and Health Administration. Industrial Hygiene Field Operational Manual. U.S. Department of Labor. Washington, D.C., April, 1979.
8. Page, G. C. Environmental Assessment: Source Test and Evaluation Report -- Chapman Low-Btu Gasification. EPA-600/7-78-202 (NTIS-PB289940). Radian Corporation, Austin, TX, October, 1978.
9. Thomas, W. C., K. N. Trede, and G. C. Page. Environmental Assessment: Source Test and Evaluation Report -- Wellman-Galusha (Glen-Gery) Low-Btu Gasification. EPA-600/7-79-185. Radian Corporation, Austin, TX, August, 1979.