Session I: ENVIRONMENTAL SOURCE TEST AND EVALUATION RESULTS

Part B: Direct Liquefaction

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ENVIRONMENTAL PROGRAM AND PLANS FOR THE EDS COAL LIQUEFACTION PROJECT

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ABSTRACT

The Exxon Donor Solvent (EDS) coal liquefaction project is a unique government/industry arrangement for developing EDS technology to the point that commercial plants can be designed with an acceptable level of risk. Project participants are the U.S. Department of Energy (DOE), Exxon Company, U.S.A., Electric Power Research Institute, Japan Coal Liquefaction Development Company, Inc., Phillips Coal Company, ARCO Coal Company, Ruhrkohle A.G., and AGIP S.p.A.

A broad environmental program is being advanced within the project to address plant emission, occupational health, and product-related environmental concerns associated with the direct liquefaction of coal. The current plans, status and outlook for the EDS Environmental Program are described to provide information on the overall strategy being followed for the acquisition of data relating to these concerns.

PROGRAM ORGANIZATION AND MANAGEMENT

The EDS Cooperative Agreement forms the basis upon which the government can participate in developing a technology in the national interest with industrial partners who develop and are the end users of the technology (1). Thus, the EDS Environmental Program Organization and Management reflects this arrangement in terms of the character and direction of the work activities.

Exxon Research and Engineering Company, the developer of the EDS process, has overall technical and execution responsibilities for the EDS project. Construction and operation support is provided by Exxon Company, U.S.A. The various contractual interfaces are shown in Figure 1.

Project direction is carried out by a number of committees consisting of members of sponsoring organizations participating in the cost sharing of the project as shown in Figure 2. The EDS Environmental Program draws upon the various elements of the Exxon organization for carrying out work activities related to their specific areas of expertise. The EDS Project Director has responsibility and authority for work direction, stewardship and communications.

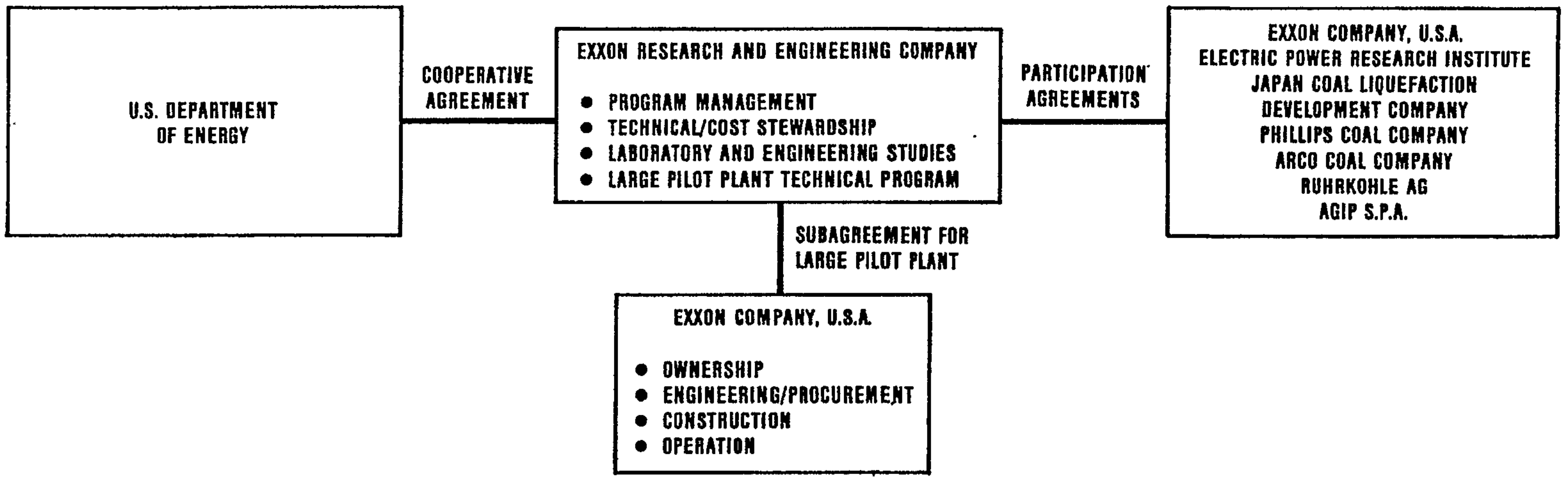


Figure 1. Contractual Interfaces EDS Coal Liquefaction Project

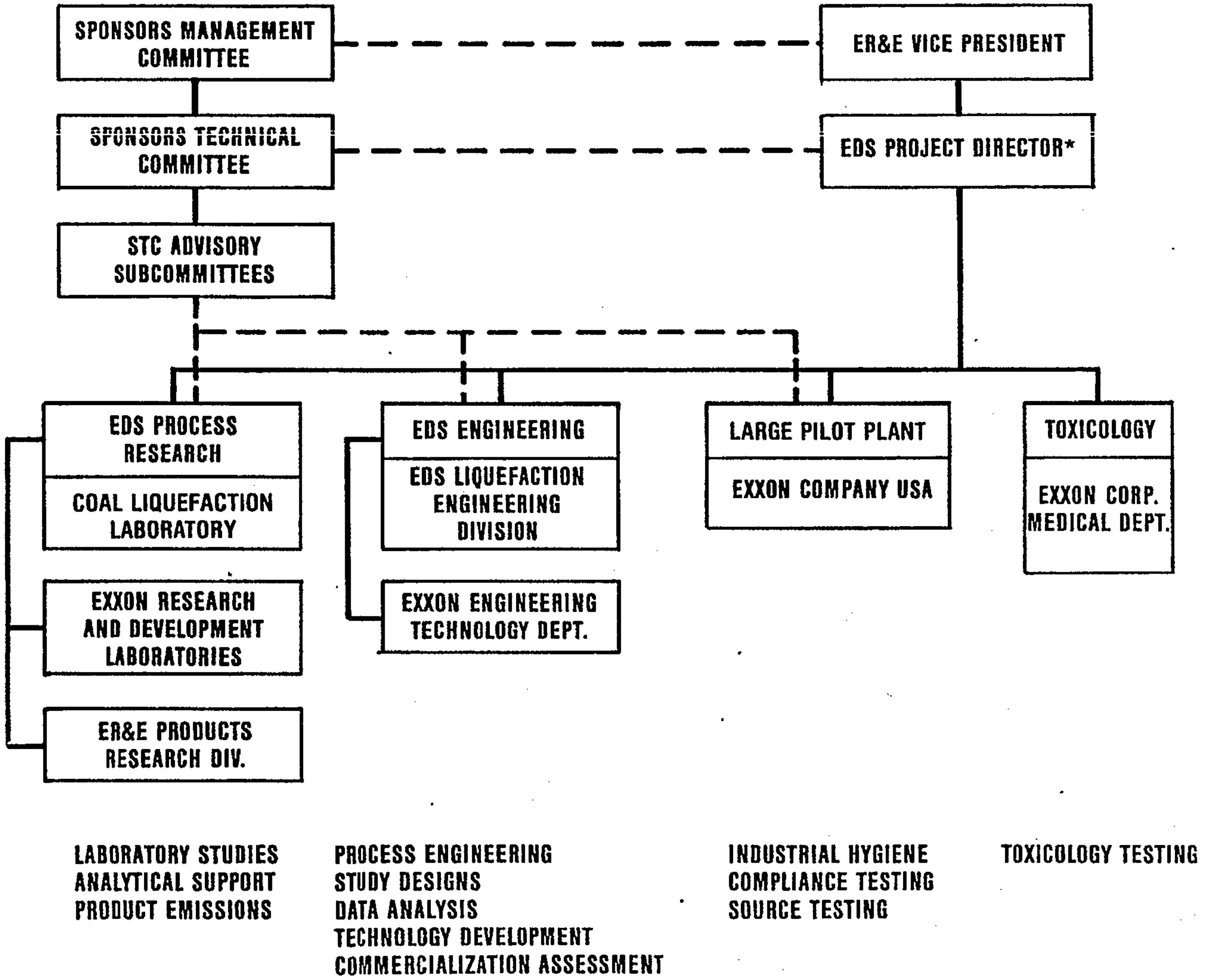
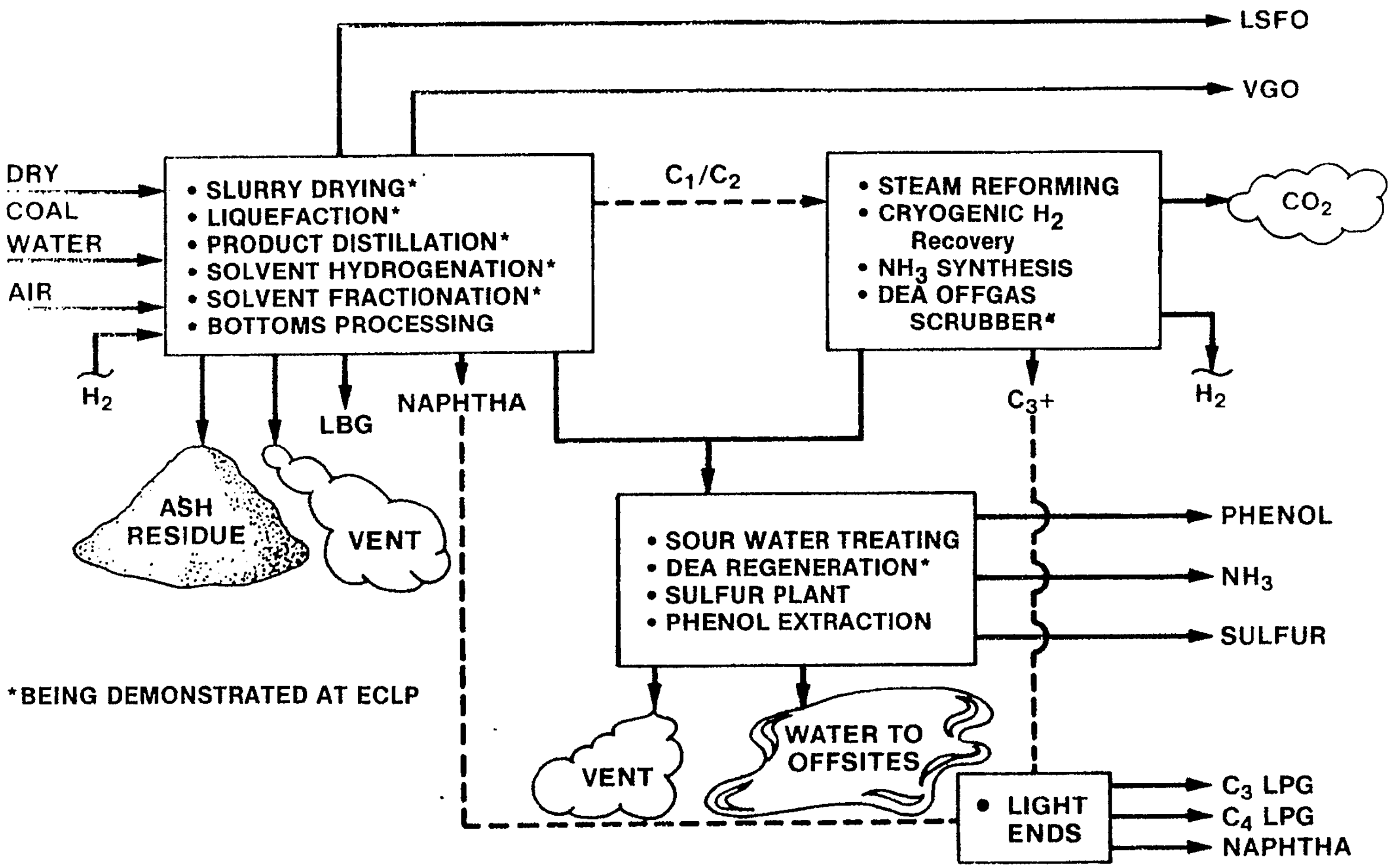


Figure 2. EDS Coal Liquefaction Project Organization for EDS Environmental Program Activities



*BEING DEMONSTRATED AT ECLP

Figure 3. EDS Commercial Plant Study Design Features

IMPLEMENTATION PLAN

The overall objective of the EDS Environmental Program is to assure a safe and environmentally sound process. Bench-scale research, small pilot unit operation, engineering design and technology studies, and operation of a 250 ton-per-day coal liquefaction pilot plant (ECLP) are collectively being utilized to provide an environmental data base to meet this overall objective. This effort is summarized in Table 1.

A conceptual design for a commercial scale plant operating on Illinois bituminous coal has been recently completed for a Western Illinois location (2). This engineering study depicting the state of EDS technology in 1978, after approximately ten years of development work, was carried out in sufficient detail to define environmental control needs and costs for siting a commercial plant. Studies of this type are used for research guidance in the environmental program. A similar study reflecting potential process improvements conceived after 1978, is currently underway for a conceptual plant operating on Wyoming coal in a Western U.S. location.

The large 250 ton-per-day pilot plant at Baytown, Texas plays an important role in providing representative commercial streams for environmental and health studies of EDS materials in the various stages of production from raw materials to products and effluents. Chemical and physical characterization of pilot plant materials in conjunction with bioassay and occupational exposure data from the pilot plant constitute the data base for making judgments on the potential environmental acceptability of the EDS process for commercialization.

Program emphasis is on the aspects of the EDS process which conceivably can be scaled to commercial size facilities. The basic EDS process streams, plant products and commercial plant design features are shown in Figure 3 along with those features undergoing demonstration at the large 250 ton-per-day pilot plant (ECLP).

In the EDS process, coal is dried and slurried with hydrogenated recycle solvent and reacted in a liquefaction reactor at approximately 800°F and 2000 psia. The three phase product stream from the liquefaction is separated by a combination of atmospheric and vacuum distillation. The liquid fuel products are naphtha, a middle distillate (LSFO) and a vacuum gas oil (VGO). If desired, the vacuum gas oil stream may be recycled to extinction in the liquefaction reactors to provide a product slate with a boiling range below 800°F. The basic environmental control units involve sulfur, phenol and ammonia recovery.

The major operating units at ECLP, as they pertain to the EDS process are the coal preparation section, the slurry drying section, the liquefaction section, the product recovery section and the solvent hydrogenation section. Other areas of ECLP are similar in nature to typical support units of any petroleum refinery and include DEA regeneration and gas treating, hydrogen compression, safety facilities, waste handling, sour water collection facilities, utilities and tankage.

TABLE 1. EDS ENVIRONMENTAL PROGRAM IMPLEMENTATION

- Carry out Conceptual Plant Design Studies
    - To Identify Areas Requiring Additional Research
    - To Develop Updated Investment Costs and Economics
    - To Provide Base Point for Initial Commercialization of a Future Pioneer Plant
- Carry out Pilot Plant Demonstrations
    - Stream Characterization and Source Testing
    - Monitor Workplace Exposures
    - Equipment Design and Scale-up Data
    - Representative EDS Products for Combustion Emission Testing
- Develop Integrated Environmental and Health Assessment Data Base
    - Chemical and Physical Properties
    - Bioassay and Occupational Exposure Data

Not included in the ECLP demonstration is processing of the vacuum bottoms material which consists largely of 1000°F+ liquids, unconverted coal and coal mineral matter. Work is in progress to evaluate the use of bottoms partial oxidation processing for hydrogen/fuel gas generation and direct combustion of bottoms for plant fuel. Conceptual Commerical Plant Study designs carried out to date have utilized FLEXICOKING for vacuum bottoms processing. FLEXICOKING, a commercial petroleum process that employs integrated coking and gasification reactions in circulating beds, recovers essentially all of the feed carbon from the bottoms material as product liquid or plant fuel gas. A small amount of carbon is purged from the unit with the coal mineral matter. Leachate tests have been performed on the solids from FLEXICOKING to identify any problems requiring resolution (3). Environmental assessments will need to be carried out for the other bottoms processing/ utilization options being developed for the EDS process.

PROGRAM HIGHLIGHTS

Conceptually the program consists of related environmental and health monitoring, testing, engineering studies and assessments. Specific activities within the EDS Environmental Program include monitoring and testing of process streams and occupational exposures as well as engineering and laboratory studies of environmental controls. The following summarizes the major activities in each of the environmental areas of air, water, solid wastes, human health, ecology and product utilization highlighted in Table 2.

AIR EMISSIONS

The air emissions activity consists of compliance monitoring associated with the large pilot plant (ECLP) operations at Baytown, Texas, design studies to define control technology options for criteria pollutants in conceptual commercial plants and in-plant testing to characterize noise and process emission sources. The focus of the pilot plant test program is to assess fugitive, particulate, and potentially toxic emissions during both normal and intermittent operations to provide a data base for environmental assessments for future plants and the design of emission control facilities where needed.

WASTEWATER TREATMENT

Treatment of all process and other water effluent streams from the ECLP operations is being carried out in the adjacent Baytown Refinery facilities as provided in the environmental permit for the pilot plant. An extensive in-plant test program is underway to monitor and characterize raw process water streams for variability, composition (including trace

TABLE 2. EDS ENVIRONMENTAL PROGRAM HIGHLIGHTS

- Air Emissions
  - Control Technology Options for Criteria Pollutants
  - In-plant Testing
  - Assessment of Fugitive H/C Emissions
- Wastewater Treatment
  - Characterization of Raw Process Streams
  - Treatability Studies
  - Bench Scale Testing
- Solid Waste Disposal
  - Physical and Chemical Properties
  - Solid Waste Management Techniques
- Occupational Health
  - Seven Phase Worker Protection Program
  - Workplace Monitoring
  - Medical Surveillance
- Toxicity
  - Acute, Subchronic, Chronic Testing
  - Environmental and Product Streams
  - Human and Ecological Systems
- Product Utilization
  - Raw EDS Products
  - Combustion Emissions

metals), and treatability. Offsite bench-scale treating tests will be carried out on samples from large pilot plants to establish the water treatment requirements for a commercial plant. This work will serve to confirm the basis for commercial plant design studies being conducted in parallel with the test program to define quantities and streams for a commercial plant. An independent inplant test program has been completed at ECLP by the U.S. Environmental Protection Agency (EPA) to serve as a data base for EPA's research activities in direct coal liquefaction.

SOLID WASTE DISPOSAL

Solid waste management techniques and requirements are being developed as part of a study design activity for a conceptual commercial plant. In addition, in-plant test work to characterize the solid wastes on all project coals will be carried out to determine handling and disposal properties.

OCCUPATIONAL HEALTH

A seven-phase program involving engineering controls, industrial hygiene, operations and laboratory work practices, personal hygiene, medical surveillance, and health education forms the basis for the ECLP Occupational Health Program (4). Specific goals are to assure a safe and healthy work environment at ECLP and to provide an expanded data base for future production facilities. The industrial hygiene data base being generated includes pre-startup and periodic baseline surveys, routine monitoring of process and mechanical personnel, and area monitoring of special operations such as maintenance. Over 1200 personal and area samples have been generated during the first of three program coals. An independent industrial hygiene in-plant survey has been carried out at ECLP by the National Institute of Occupational Health and Safety (NIOSH) to support NIOSH research in direct coal liquefaction.

TOXICITY

The goals of the Toxicity Program are to 1) identify toxic hazards to either human health or ecological systems, 2) assess the risks those hazards present, and 3) assess the commercial readiness of the EDS process technology in the light of those risks and hazards. The program provides for analytical characterization, and in-vitro and invivo testing of samples of EDS product, process and waste streams. The testing will encompass the following: acute oral, dermal and inhalation toxicity; eye and skin irritation; skin sensitization; mutagenicity; carcinogenicity; subchronic toxicity, teratology and reproductive effects; and fish and daphnia toxicity, daphnia and algae growth and inhibition.

PRODUCT UTILIZATION

Downstream processing/refining of EDS products and subsequent marketing and use of such upgraded products is outside the present scope of the EDS project. However, the middle distillate (LSFO) and vacuum gas oil (VGO) products can be used directly or as a blendstock for existing petroleum products. Combustion emission testing of EDS fuel oil blends has been initiated (5). In addition, all products will be evaluated for toxic hazards to human health and ecological systems recognizing the need for handling and transporting of EDS products from a production facility.

STATUS AND OUTLOOK

The environmental data base being generated within the EDS project is designed to complement programs being carried out in cooperation with government agencies. In this manner, the EDS process is expected to meet commercial environmental design requirements and resolve present concerns for the class of materials which exist in coal liquefaction plants.

The program status is highlighted in Table 3. To date, 3900 hours of operation on Illinois No. 6 coal have successfully been completed at the large EDS Pilot Plant in Baytown, Texas (6). All environmental data acquisition objectives for this run have been met and a major data analysis and laboratory investigation effort is underway. Present operating plans for the pilot plant call for operation on a subbituminous and a lignite coal with further environmental testing to establish a data base for three different types of coals.

The EDS process is still evolving with the introduction of bottoms recycle operations at ECLP in August, 1981, and the work in progress to evaluate various bottoms processing and utilization options. Environmental data acquisition efforts will be integrated into these process development areas consistent with the overall strategy of the EDS Environmental Program.

As presently funded, the EDS project will terminate June 30, 1982, with the subsequent dismantling of ECLP and completion of the EDS environmental work outlined in this paper. Under the terms of the EDS Cooperative Agreement, work of a non-proprietary nature is to be made available to the EDS Project Sponsors. The reporting system for the EDS Project consists of monthly, quarterly, and annual technical reports and assures that all technical contract data for the EDS Environmental Program will be in the public domain through DOE sponsorship of the project.

TABLE 3. EDS Environmental Program Status

- Illinois Coal Study Design and Pilot Plant Operations Complete
- Wyoming Coal Study Design and Pilot Plant Operations Underway
- EDS Process Still Evolving
    - Bottoms Processing Studies
    - Bottoms Recycle Under Demonstration at ECLP
    - Product Utilization Emphasis on Distillate Fuels
- Data Analysis and Laboratory Work will Continue for Three Types of Coals

REFERENCES

1. Epperly, W. R., "Running Government-Industry Projects," CHEMTECH, 1981, pp. 220-223.

2. , "EDS Commercial Study Design Update, Illinois Coal," FE-2893-62, February, 1981.

3. Boyer, G. T. et al, "Water Pollution Control in the Exxon Donor Solvent Coal Liquefaction Process," AIChE 87th National Meeting, Boston, Mass., August 21, 1979.

4. Montgomery, C. Hunter, "Coal Liquefaction Occupational Health Program," 65th Annual Meeting of the American Occupational Medical Association, Detroit, Mich., April 21-25, 1980.

5. Ryan, D. F., Panzer, J., "PNA Emissions From Combustion of EDS Fuel Oils," 6th Annual EPRI Contractor's Conference on Coal Liquefaction, May 13-14, 1981.

6. Brackett, R. H., Clunie, T. J., Goldstein, A. M., "Exxon Donor Solvent Coal Liquefaction Process: Exxon Coal Liquefaction Plant Operations," 6th Annual EPRI Contractors' Conference on Coal Liquefaction, May 13-14, 1981.

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SAMPLING AND ANALYSIS OF PROCESS AND† EFFLUENT STREAMS FROM THE EXXON DONOR SOLVENT COAL LIQUEFACTION PILOT PLANT

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ABSTRACT

Under contract to the U.S. Environmental Protection Agency (EPA), Hittman Associates, Inc. performed a sampling and analysis of process discharge streams from the Exxon Donor Solvent (EDS) coal liquefaction plant in Baytown, Texas. Twenty-four streams were sampled and 2,200 samples were returned to Hittman's laboratory for analysis. The chemical analyses of these samples included water quality parameters, GC/MS, GC/FID, and bioassays. Analyses were also performed to determine the accuracy and precision of the data and to determine the variability of stream components due to process variations. Preliminary results are available and data evaluation for the Source Test and Evaluation Report is underway.

INTRODUCTION

The EPA Industrial Environmental Research Laboratory is developing a data base in support of EPA's synfuels program. This data base includes data obtained through sampling and analysis of environmentally significant waste and process streams from existing synfuels facilities. Environmental data acquired in this program will be used to assess the environmental impacts of synthetic fuels plants and evaulate the effectiveness of control technologies.

The Exxon Donor Solvent process is one of several processes used to convert coal to liquid fuel which is under investigation. In this process a "donor solvent" is first hydrogenated and then mixed with pulverized coal and hydrogen. Hydrogen is transferred from the donor to components of the coal, thereby liquefying the coal. Subsequent fractionation of the resulting mixture yields hydrocarbon products. The donor solvent is separated and recycled for hydrogenation. The EDS process is being studied at the Exxon Coal Liquefaction Pilot Plant (ECLP) in Baytown, Texas. Hittman Associates, Inc. performed sampling and analysis of the plant's process discharges. The results of the analysis will be used by EPA to assess the environmental impacts of the EDS process. It should be noted that although the pilot plant represents a commercial facility, there are significant differences. Three major differences are: (1) the pilot plant has no wastewater treatment facility; all sour water streams are combined and sent to the adjacent Baytown Refinery wastewater treatment plant; (2) acid gas (H_2S) removed from the gaseous streams also is treated by the refinery sulfur recovery system, while a commercial facility would have its own sulfur recovery system; and (3) the vacuum bottoms (carbonaceous residue) is drummed and stored at the pilot plant, whereas in a commercial facility this would be either treated in a Flexicoker® or gasified to produce hydrogen.

The criteria used to select the ECLP streams to be sampled are presented in detail in the EDS Test Plan. (Hittman Associates, Inc. Environmental Test Plan for the EDS Pilot Plant in Baytown, Texas. EPA Contract No. 68-02-3147, February 1981). The intent was to select streams which would be found in a commercial facility or would be similar to such streams and were significant either to potential environmental impacts or to control technology evaluation. No internal process streams were sampled. The selected streams are listed in Table 1. They include 15 sour water streams and the combined sour water that leaves the ECLP for treatment, naphtha, light solvent fuel oil, combination product, feed coal, vacuum bottoms, and several gaseous streams relevant to control technology evaluation. The sampling program consisted of three separate efforts: (1) collection of composite samples over a three-day period for each of the selected streams; (2) collection of a set of samples from six of the streams to determine process, sampling, and analytical variability; and (3) collection and on-site analysis of the gaseous samples on a one-time only basis. The primary liquid samples from the ECLP plant were split, composited, preserved, and returned to the Hittman Laboratory for analysis.

The analytical program was based on a combined Level 1/Level 2 methodology using a directed analytical approach. The combined methodology was adopted because in conducting consecutive Level 1/Level 2 analyses, the time interval between the two efforts allows for major changes in the facility, particularly in the case of pilot operations. A directed analytical approach was chosen because it permits complete analyses of a selected group of high-priority streams which guide the analyses of components of the priority streams. A complete discussion of the analytical program is presented in the EDS Test Plan. A paper devoted to the EDS analytical work is included in this symposium (Higman, et al. "Problems Associated with the Analysis of Synfuel Products, Process, and Waste Water Streams").

PROCESS DIAGRAM AND SAMPLE POINTS

The first step of the EDS process is coal preparation. Figure 1 shows the coal preparation area. Coal is transported to the plant via a bottom-dump rail car and taken to a 5,000-ton storage silo. The coal is then crushed and dried before entering the slurry drier tank.

The crushed coal is mixed with recycle solvent and fed to the slurry drier (Figure 2). The coal-solvent mixture is pumped, along with hydrogen, to the preheat furnace and then to the liquefaction reactors. These reactors are kept at 840°F and 1,900 to 2,000 psig. The off-gas from the

TABLE 1. ECLP SAMPLE POINTS

Aqueous Sample Points

Stream	Process Area
Sour Water - Recycle Gas Cold Separator Drum	Slurry Drying and Liquefaction
Rich DEA - Liquefaction DEA Scrubber	Slurry Drying and Liquefaction
Scrubber Water - Recycle Gas Water Scrubber	Slurry Drying and Liquefaction
Sour Water - Atmospheric Fractionator	Product Distillation
Cold Sour Water - Atmospheric Fractionator	Product Distillation
Sour Water - Steam Ejector Condensate Pump	Product Distillation
Scrubber Water - Water Scrubber Unit	Solvent Hydrogenation
Rich DEA - DEA Scrubber	Solvent Hydrogenation
Condensed Water - P-302 & P-304	Solvent Hydrogenation
Rich DEA - Hydrocarbon Skimming Drum	Fuel Gas Treating and DEA Regeneration
Lean DEA - DEA Regenerator	Fuel Gas Treating and DEA Regeneration
Sour Water - Fuel Gas DEA Scrubber Sour Water Pump	Fuel Gas Treating and DEA Regeneration
Scrubber Water - Acid Gas Water Scrubber	Fuel Gas Treating and DEA Regeneration

TABLE 1. (CONTINUED)

Solid Sample Points

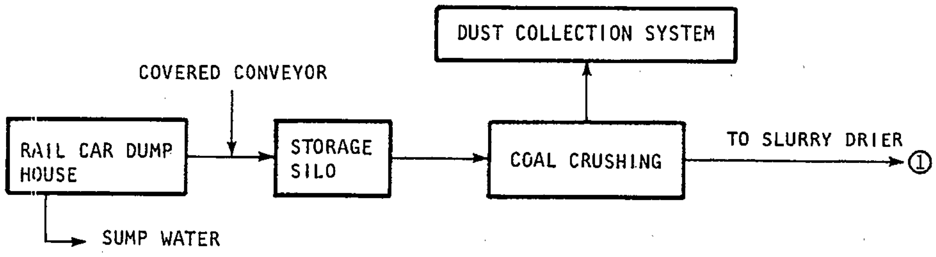
Stream	Process Area
Feed Coal	Coal Prep
Vacuum Bottoms	Product Distillation

Product Sample Points

Stream	Process Area
Naphtha	Solvent Hydrogenation
Light Solvent Fuel Oil	Solvent Hydrogenation
Combined Product	Solvent Hydrogenation

Gaseous Sample Points

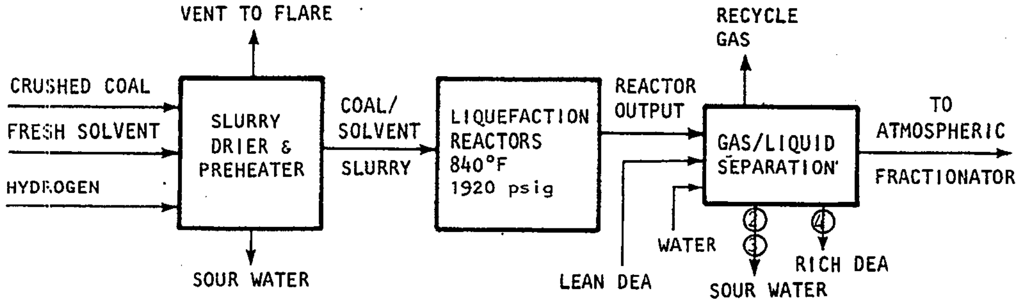
Stream	Process Area
Offgas - DEA Regenerator	Fuel Gas Treating and DEA Regeneration
Offgas - Fuel Gas Condensate Separator Drum	Fuel Gas Treating and DEA Regeneration
Acid Gas to Refinery	Fuel Gas Treating and DEA Regeneration
Offgas - Fuel Gas DEA Scrubber	Fuel Gas Treating and DEA Regeneration



1 - Feed Coal

Figure 1. Coal Preparation Area

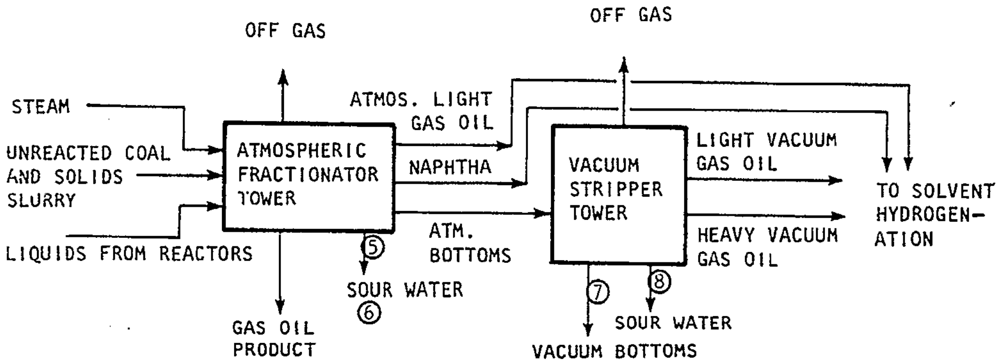
reactors is separated into a vapor stream and a slurry stream. The vapor stream is condensed, yielding sour water, hydrocarbons, and an off-gas stream. The sour water stream goes to the sour water disposal tank. The condensed hydrocarbons are mixed into the slurry stream and sent to the atmospheric fractionator. The off-gas from the separator drums is scrubbed with DEA and water and recycled back to the process.



2 - Sour Water - Recycle Gas Cold Separator Drum
3 - Scrubber Water - Recycle Gas Water Scrubber
4 - Rich DEA - Liquefaction DEA Scrubber

Figure 2. Slurry Drying and Liquefaction Area

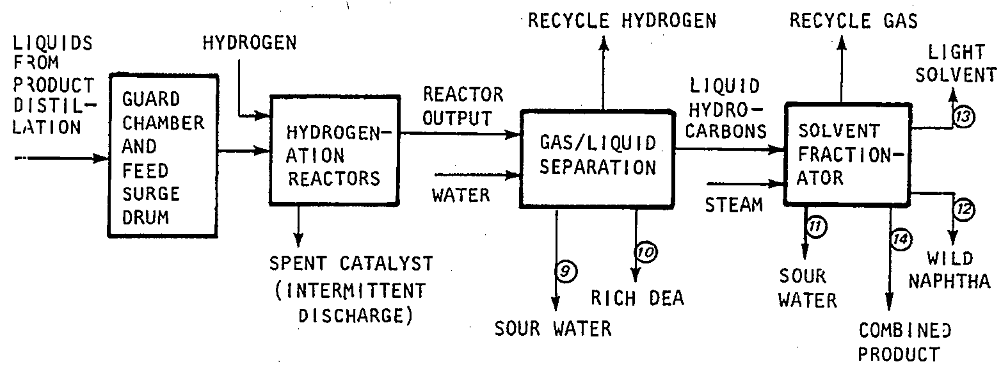
The slurry stream is fed to the atmospheric fractionator, where it is separated into atmospheric bottoms, naphtha, atmospheric light gas oil, and off-gas (Figure 3). The off-gas is condensed and separated into sour water, condensed hydrocarbons, and raw fuel gas. The atmospheric bottoms are fed to the vacuum fractionator, where the off-gas, light and heavy gas oil, and vacuum bottoms are separated. The products from the atmospheric and vacuum fractionators are combined and fed to the solvent hydrogenation section for further processing.



5 - Sour Water - Atmospheric Fractionator
6 - Cold Sour Water - Atmospheric Fractionator
7 - Vacuum Bottoms
8 - Sour Water - Steam Ejector Condensate Pump

Figure 3. Product Distillation Area

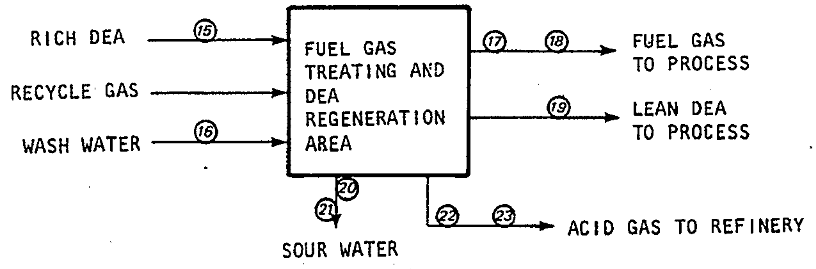
The output from the product distillation area is mixed with hydrogen and fed to the hydrogenation reactors (Figure 4). These reactors consist of four fixed-bed reactors containing a nickel-molybdate catalyst. The reactor output is separated into hydrogen-rich gas, sour water, and a hydrotreated liquid stream after passing through hot and cold separator drums. The hydrogen-rich gas is scrubbed with DEA and water and the hydrogen is recycled back to the process. The solvent fractionator separates the hydrotreated liquids into naphtha, light solvent fuel oil, gas oil product, fresh recycle solvent, and raw fuel gas.



9 - Scrubber Water - Water Scrubber Unit
10 - Rich DEA - DEA Scrubber
11 - Condensed Water from P-302 and P-304
12 - Light Solvent Fuel Oil
13 - Naphtha
14 - Combined Product from E-306

Figure 4. Solvent Hydrogenation Section

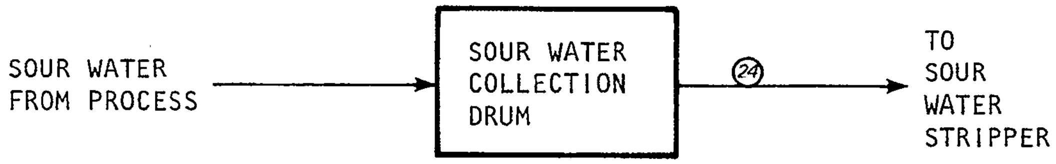
The rich DEA from the DEA scrubbers is pumped to the fuel gas treating and DEA regeneration section (Figure 5). The DEA is fed to the DEA regenerator, where it is stripped of H_2S and SO_2 and then returned to the process. The stripped acid gas is water scrubbed and sent to the refinery for sulfur recovery. The raw fuel gas is water scrubbed and then DEA scrubbed before being used as fuel gas for the process.



15 - Rich DEA - Hydrocarbon Skimming Drum
16 - Wash Water Input
17 - Offgas - Fuel Gas Condensate Separator Drum
18 - Offgas - Fuel Gas DEA Scrubber
19 - Lean DEA - DEA Regenerator
20 - Sour Water - Fuel Gas DEA Scrubber Sour Water Pump
21 - Scrubber Water - Acid Gas Water Scrubber
22 - Offgas - DEA Regenerator
23 - Acid Gas to Refinery

Figure 5. Fuel Gas Treating and DEA Regeneration Section

All of the sour water and scrubber water generated by the process is pumped to the sour water collection section (Figure 6). The sour water is then pumped to the refinery's sour water stripper.



24 - Sour Water - Sour Water Disposal Pump

Figure 6. Sour Water Collection Section

SAMPLING PROGRAM

PRE-SAMPLING ACTIVITIES

To accommodate a sampling effort of this size and scope, a field laboratory had to be established. The chosen facility was an empty, 2,500 sq.ft. warehouse located 1/2 mile from the pilot plant. This building was the central point for all sample splitting, preservation, packaging, shipping, and on-site analysis.

To reduce the work load for the field team, as much preparatory work as possible was done at the home office. A field manual was compiled which provided exact instructions on the handling, preservation, and shipment of each sample. Each sampling team member was assigned a specific task during the sampling effort. All sample bottles, 2,200 in all, were pre-cleaned and labeled before shipment to the field laboratory.

The on-site analysis called for the use of a gas chromatograph to analyze gaseous grab samples. These samples had to be analyzed within one hour after sampling in order to meet holding-time requirements. An experienced chemist with a GC background was assigned to these analyses.

All necessary equipment and chemicals were delivered to the field laboratory at least four days before sampling began. This provided time for the field team to check over the equipment and prepare any necessary reagents.

SAMPLING SCHEDULE

With the exception of the gaseous samples, samples were collected twice daily, at 8:00 a.m. and 8:00 p.m., on three consecutive days. Samples for the process variability program were collected during the appropriate sampling period along with the composite samples. The sampling schedule is detailed in Table 2.

TABLE 2. ECLP SAMPLING SCHEDULE

Day 1	Day 2	Day 3
A.M.	A.M.	A.M.
Composite Samples	Composite Samples	Composite Samples
Process Variability Samples	Process Variability Samples	
P.M.	P.M.	P.M.
Composite Samples	Composite Samples	Composite Samples Process Variability Samples

Composite samples contained equal aliquots from all six sampling periods. The analytical result for each component from this composite is the average value of that component over the six sampling periods. Process variability samples are not composited but are distinct samples representing individual sampling periods. The analytical results from these samples track certain components to determine how the concentration varies with changing process conditions and other factors.

IN-PLANT AND FIELD LABORATORY ACTIVITIES

Liquid samples were collected in 5-gallon and 1-gallon bottles. The 5-gallon bottles were used to collect composite and process variability samples, while the 1-gallon bottles were used only for composite samples. Volatile Organic Analysis (VOA) samples were taken in 40 ml septum-top vials and sampled in duplicate. Feed coal and vacuum bottom samples were collected in 2-liter, brown-glass, wide-mouth bottles.

Once all the samples from a given sampling period were obtained, they were immediately returned to the field laboratory for processing. This phase included sample splitting and preservation. Samples from the 5- and 1-gallon bottles were split into smaller bottles for two reasons, first, to allow for required preservation steps, and second, to make sample handling easier for laboratory personnel. Thus, there was less chance for sample degradation and errors in handling and analysis. Each composite sample bottle and process variability sample bottle was pre-labeled. These labels contained the stream name, intended analysis, preservation method, and aliquot volume required. Having all the bottles labeled with the proper information enabled the field team to perform production-line sample splitting.

Preservation of the samples for shipment and subsequent analysis was very important. Every precaution was taken to properly preserve the samples and to reduce the degradation of the chemical species of interest.

Samples were preserved in accordance with the procedures defined in Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters, (Luthy, Richard G.). Each aliquot that was split into sample bottles had to be preserved, and most of the 2,200 samples required chemical preservation. These preservation procedures were repeated six times on approximately 1,500 bottles.

Packaging and shipment was the last procedure that the samples were subjected to at the field laboratory. Holding-time requirements dictated that the volatile organic analyses samples be delivered overnight to the analytical laboratory. The samples also had to be kept at 4°C during shipping to meet preservation requirements. The samples were packed in styrofoam shipping coolers with packing material and ice just prior to pickup by the shipper. To avoid the loss of a sample due to breakage in transit, all samples were prepared in duplicate and shipped so that duplicates were in separate coolers. Composite samples were stored in ice during the 3-day sampling period while compositing was being completed. With these packaging procedures, only four of the 2,200 bottles were lost or broken.

PROBLEM AREAS AND SOLUTIONS

There are many problems associated with a sampling effort of this size. The best way of avoiding difficulties is to identify potential problem areas and determine what precautions can be taken. Three areas which Hittman identified as potential problems were:

- Fumes and vapors from the acidification of sour water samples containing high levels of sulfur
- Keeping the samples at 4°C for an extended period of time
- Properly packaging and shipping the samples.

Since acidification with concentrated nitric or sulfuric acid is required for several species, any evolution of H_2S from the samples could present a health hazard. A glove box was converted into a sealed-hood system with vacuum pumps to draw the gas out of the box and through two scrubbing bottles containing 15 to 25% NaOH. The scrubbed gas was pumped to the outside of the field laboratory. Industrial fans were located so that H_2S fumes and other hazardous materials were prevented from accumulating in the field laboratory.

Samples were kept in a large walk-in dumpster converted into a cooler. Layers of 1-inch polystyrene were attached to the walls and floor and covered with thick plastic. A roof was installed and insulated with polystyrene and plastic. The dumpster was 24 feet long, 6 feet wide, and 4 feet high. It required between 800 and 1,000 pounds of block ice per day to keep the samples at 4°C. Refrigerated trucks were not suitable because of the danger of contamination in the event of a sample spill.

The packaging and shipment of such a large quantity of bottles is subject to both mishandling and breakage. This problem was addressed by having the samples duplicated, split, and shipped in different coolers. In this way, if a cooler was lost in shipment or damaged, sufficient sample would still be available in the other cooler. Two members of the sampling team were assigned full-time to packaging and coordinating sample shipments.

ANALYTICAL PROGRAM

The EDS analytical program consisted of two areas: composite sample analysis and variability sample analysis. The analyses of the composite samples included a wide range of chemical tests, while the variability analyses were limited to four tests. Results from the composite samples will provide an overall picture of the plants operation during the three days of sampling. Results from the process variability samples will provide information on the sensitivity of certain species to process variations.

The analyses performed on the composite samples are listed in Table 3.

TABLE 3. EDS COMPOSITE SAMPLE ANALYSES

Inorganics and Water Quality Parameters

- CN^-
- NH_3+
- $S^=$
- NO_2/NO_3
- Cl^-
- Fl^-
- Alkalinity
- Acidity
- TSS
- TDS
- Total N
- Total S
- Phenolics
- Oil & Grease
- TOC
- COD
- BOD
- Trace Metals
- SCN^-
- SO_4:

Organics

- VOA
- GC/MS
- GC/FID
- HPLC

Bioassays

- Ames Test
- CHO Cytotoxicity
- RAM Test
- Fathead Minnow
- Daphnia

The variability analyses performed are listed in Table 4.

TABLE 4. EDS PROCESS VARIABILITY ANALYSES

Total sulfur
Total Nitrogen
Trace Metals
GC/FID
Organics
GC/MS

These analyses will aid in defining the cause of differences in test results due to process and sampling variability, analytical accuracy, and analytical reproducibility.

Process variability is the result of variations in process operating parameters during the sampling period. Variations are due to changes in coal feed rate, solvent recycle rate, temperature, pressure, and other operational parameters. If the plant has not reached process equilibrium before sampling is initiated, sample variability will result from non-steady state conditions.

Sampling variability results from non-reproducibile samping technique (e.g., non-isokinetic sampling or sampling of non-homogeneous streams).

Analytical variability in precision results from non-homogeneity of sample, minor variations in technique, etc., while variability in accuracy is normally the result of poor recoverability during extractions.

The determination of the variability due to these four factors is illustrated in the branch diagram in Figure 7.

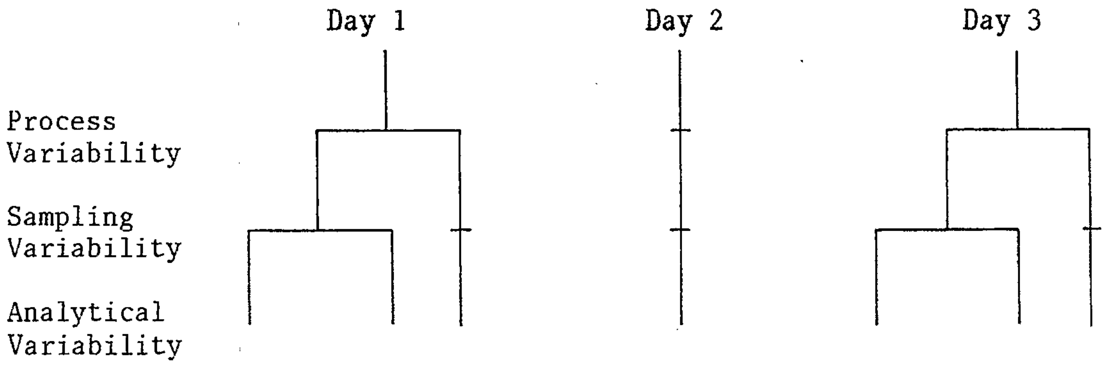


Figure 7. Process Variability Branch Diagram

The application of this diagram can be more clearly seen when analytical results are presented with it (Figure 8).

PRELIMINARY RESULTS

Preliminary results for the sample sour water - atmospheric fractionator are presented in Table 5. This stream is the condensed water from the reflux drum of the atmospheric fractionator. A process block diagram of this sample is provided in Figure 2, Product Distillation Area. The results are from the six-period composite sample.

In the Source Test Evaluation Report on the EDS pilot plant, all results will be presented as a range. This range will be determined on the basis of the analytical error derived from the variability analyses.

		DAY 1 AM			DAY 2 AM	DAY 3 PM			detection limit
		(a)	(b)	(c)		(a)	(b)	(c)	
Aluminum	Al	0.22	0.25	L	0.23	0.28	0.24	0.25	0.15
Antimony	Sb	L	L	L	L	L	L	L	0.15
Arsenic	As	0.004	0.003	0.004	0.003	0.003	0.003	0.003	0.002
Barium	Ba	0.023	0.020	0.024	0.020	0.025	0.025	0.027	0.001
Beryllium	Be	L	L	L	L	L	L	L	0.003
Bismuth	Bi	L	L	L	L	L	L	L	0.50
Boron	B	474.	480.	486.	454.	448.	452.	468.	0.01
Cadmium	Cd	L	L	L	L	L	L	L	0.025
Calcium	Ca	0.92	0.89	0.91	0.95	0.89	0.86	0.96	0.01
Chromium	Cr	L	0.082	L	0.14	L	0.040	L	0.03
Cobalt	Co	L	L	L	L	L	L	L	0.02
Copper	Cu	L	L	L	0.038	L	L	L	0.015
Iron	Fe	1.42	0.35	0.32	0.22	0.20	0.20	0.25	0.03
Lead	Pb	L	L	L	0.10	L	L	L	0.08
Magnesium	Mg	0.089	0.091	0.078	0.110	0.095	0.098	0.110	0.001
Manganese	Ma	0.060	0.026	0.021	0.019	0.019	0.014	0.015	0.003
Mercury	Hg	0.112	0.097	0.087	0.086	0.098	0.088	0.088	0.002
Molybdenum	Mo	L	L	L	L	L	L	L	0.04
Nickel	Ni	0.058	0.031	L	0.043	0.027	L	L	0.025
Phosphorus	PO_4	L	L	L	L	L	L	L	0.40
Potassium	K	0.38	2.92	0.37	0.45	0.38	0.49	0.56	0.01
Selenium	Se	-	-	-	-	-	-	-	
Silicon	SiO_2	4.64	3.82	2.76	4.45	4.52	3.30	5.21	0.08
Silver	Ag	L	L	L	L	L	L	L	0.03
Sodium	Na	1.60	1.72	1.90	2.32	1.66	1.74	2.11	0.10
Strontium	Sr	L	0.004	0.003	0.004	L	L	0.003	0.001
Tin	Sn	L	L	L	L	L	L	L	0.03
Titanium	Ti	L	L	L	L	0.010	0.029	0.010	0.006
Tungsten	W	-	-	-	-	-	-	-	
Uranium	U	-	-	-	-	-	-	-	
Vanadium	V	L	L	L	L	L	L	L	0.01
Zinc	Zn	0.068	0.088	0.066	0.240	0.110	0.150	0.072	0.015

(- = cannot be analyzed by ICAP)
(L = less than detection limit)
(All units are mg/l)

Figure 8. ICAP Analysis of Sour Water From Recycle Gas Cold Separator Drum, Process Variability EDS Samples

TABLE 5. PRELIMINARY ANALYTICAL RESULTS, SOUR WATER - ATMOSPHERIC FRACTIONATOR

Water Quality Parameters	Concentration (mg/l)
COD	93,700
TOC	27,000
TDS	678
TSS	31
Alkalinity (as $CaCO_3$)	5,020
Cl^-	122
Fl^-	8
NH_3	1,730
$S^=$	188
Oil and Grease	<20
NO_3	0.15
$SO_4^=$	63
SCN^-	240
Phenolics	18,000
Aluminum	0.024
Boron	0.054
Calcium	2.61
Iron	1.90
Magnesium	0.085
Potassium	0.16
Sodium	2.16
Zinc	0.091
Total S	1,640
Total N	1,990

Organic Analysis - Major Components

GC/MS - Acid and Base/Neutral Extracts Analysis

Phenol

C_1 Phenol

C_2 Phenol

Aniline/Methyl Pyridine

Benzofuran

Organic Analysis - Major Components (Continued)

GC/MS - Volatile Organic Analysis

- Butane
- Pentane
- C-6 Alkanes
- C-7 Alkanes
- Ethyl Nitrile
- Propyl Nitrile
- Toluene
- Methyl Pyrole
- Methyl iso-butyl ketone

Bioassays	EC_{50}
Ames Test	Not determined
CHO Clonal Cytotoxicity Assay	<6 ul/ml
RAM Assay	<6 ul/ml
Fathead Minnow (LC_{50})	0.047%
Daphnia	0.158%

Figure 9 represents the concentration of phenolics in several process streams. The level of phenolics is the highest in the condensates from the separation drums throughout the process. The sour water-atmospheric fractionator has the highest level of phenolics. Several streams are not represented in this process diagram, such as those from the fuel gas treating and DEA regeneration area and the sour water collection section. These omitted streams generally contain lower levels of phenolics than indicated in Figure 9.

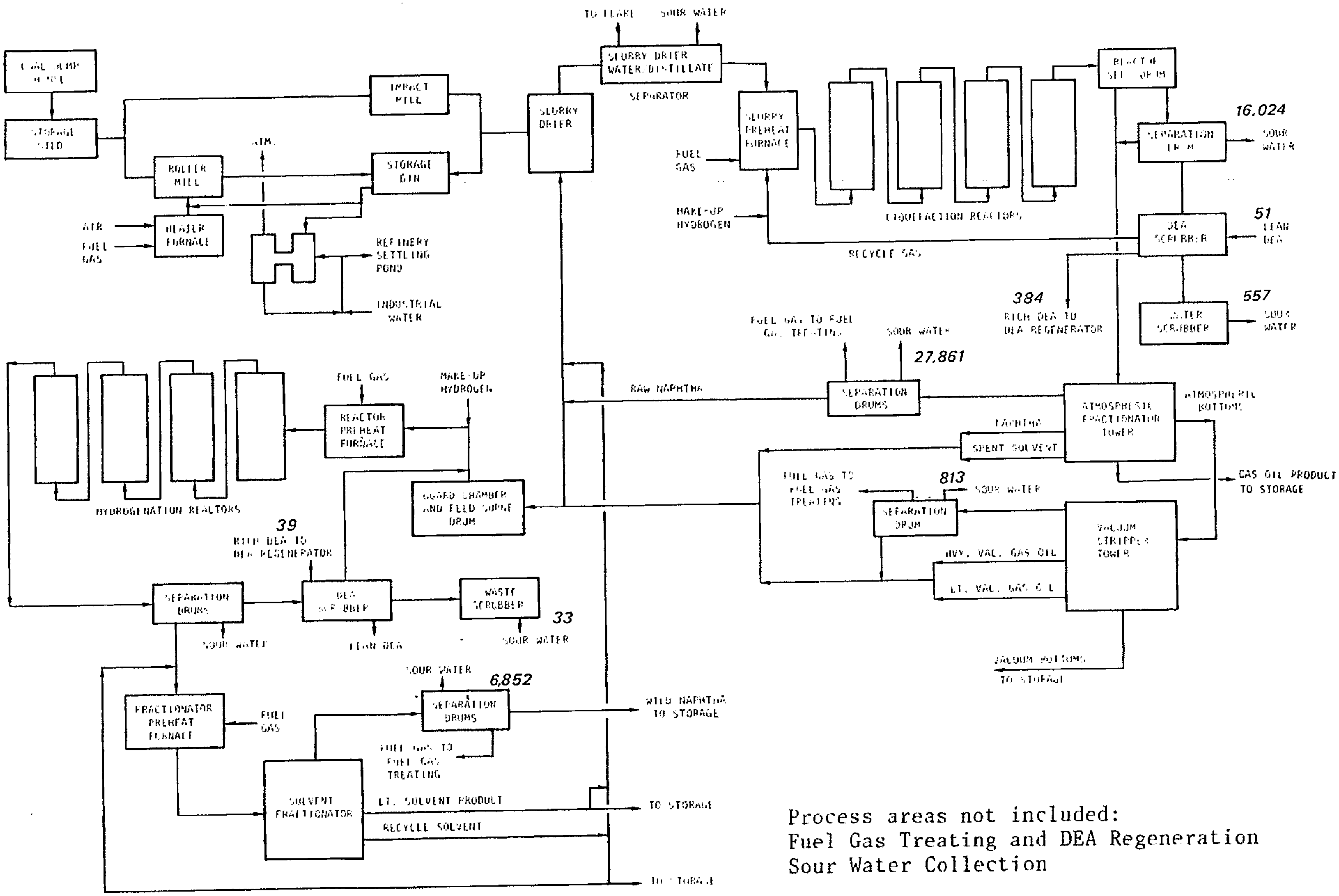


Figure 9. Phenolics in EDS Pilot Plant Process (mg/l)

Process areas not included:
Fuel Gas Treating and DEA Regeneration
Sour Water Collection

SUMMARY

A pilot plant is not fully representative of a commercial facility. To obtain the most representative data possible, we sampled only those streams which we know will be present in a commercial facility. Streams that are unique to the pilot plant were not sampled. The results obtained from the analyses of these samples can be scaled up based on the expected operational conditions of a commercial-scale facility.

The process variability analyses performed as part of this program were mainly a quality control/quality assurance measure. The data obtained from the process variability analyses will be evaluated to determine the accuracy and precision of the analytical results. By identifying the source of variations in the data, it is possible to reduce errors in future sampling and analytical programs.

ACKNOWLEDGEMENTS

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HEALTH AND ENVIRONMENTAL STUDIES OF H-COAL PROCESS*

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ABSTRACT

With the implementation of the Energy Security Act of 1980, coal and oil shale are expected to be principal sources for petroleum and natural gas substitutes. H-Coal is one of several processes under intensive study for the direct conversion of coal to the desired synthetic fuels.

In this paper we describe the health and environmental study program of H-Coal, sponsored by the Department of Energy. Presented are the results of the chemical, biological, and ecological characterization of products and by products derived from the operation of a process development unit. These initial results provide an informed basis for subsequent monitoring and testing activities of the nominal 200- to 600-ton/d pilot plant at Catlettsburg, Kentucky.

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HEALTH AND ENVIRONMENTAL STUDIES OF H-COAL PROCESS

INTRODUCTION

In the next two decades the major production and use of products derived from coal and oil shale is expected. The primary incentive for such development is the imbalance between the domestic supply and demand for oil and gas and the consequent dependence on oil imports.[1] Clearly a synthetic fuels (synfuels) industry will increase flexibility in dealing with any future disruptions in the world oil market.

Over 70 coal liquefaction processes have been proposed.[2] These can be classified as indirect liquefaction, direct liquefaction, and pyrolysis. The Department of Energy (DOE) is devoting considerable attention to direct liquefaction because of its potential for lower cost. H-Coal is one of the attractive methods of reacting coal with hydrogen in the direct production of liquid products such as naphtha and fuel oils.

Accompanying the development of energy-producing technologies is the consideration of potential health and environmental impacts. Recognizing this need, DOE asked Oak Ridge National Laboratory (ORNL) to develop comprehensive environmental and health plans to study the H-Coal process and in particular the pilot plant at Catlettsburg, Kentucky. Components of the pilot plant operation applicable to commercial size facilities are to be emphasized. Similar studies of the solvent refined coal (SRC) process are in progress elsewhere, complementing the H-Coal activity. Together they will provide a basis for technology assessments.[3]

Our study of the H-Coal process is being carried out in two phases. Phase I involves characterizing and testing materials produced by a process development unit (PDU); Phase II is a study of the pilot plant. In this paper we report the results of our Phase I activities and describe the Phase II program, which has just begun.

PROCESS DESCRIPTION

H-Coal is a process for the catalytic hydrogenation of coal under high pressure and temperature to produce liquid hydrocarbon products and fuel gas. The process was developed initially by Hydrocarbon Research, Inc., with the use of bench-scale units and a 3-ton/d PDU located in Trenton, New Jersey. A pilot plant was subsequently constructed at Catlettsburg, Kentucky, with a nominal capacity of 200- to 600-ton/d, depending upon the operating mode. Operation of the plant began in 1980 to demonstrate the commercial viability of the process and develop data for the design of commercial units.

In the H-Coal process (Figure 1), coal is slurried with a process-derived oil, pumped to reactor pressure, mixed with recycle and makeup hydrogen, and fed through a preheater to the catalytic (Co/Mo) ebullated-bed reactor. Typical operating conditions are 2500-3000 psi and 850°F. Catalyst activity is maintained by the periodic addition of fresh catalyst and the withdrawal of spent catalyst, and ebullition is provided by an external pump that recycles the coal-solvent slurry.

The reactor products leave the reactor and are separated for subsequent processing. The vapor from the reactor is cooled and scrubbed to produce a H_2-rich recycle gas and a light hydrocarbon stream fed to the distillation unit. The liquid-solid product from the reactor, containing unconverted coal, ash, and oil, is fed to a liquid flash separator. The flashed-off material is passed to the distillation unit to produce a variety of fuel gases and light and heavy distillate products. The bottoms products from the flash separator are further separated in a hydroclone and then in a vacuum distillation unit. A portion of the heavy distillate is recycled to the reactor, with the heavy bottoms stream from the vacuum distillation unit being utilized for hydrogen production.

By varying the residence time in the reactor, the process can be designed to operate in the synthetic crude (syncrude) or the fuel oil mode. To produce syncrude, more hydrogen is required and there is a lower yield of residual fuel oil. To produce a low-sulfur residual fuel oil as a major product, the temperature and pressure in the reactor are lower and less hydrogen is required. However, a special liquid-solid separation unit, not shown in Figure 1, will be required.

PROCESS DEVELOPMENT UNIT STUDIES

Elements of our synfuels research program concern the chemical, physical, and biological properties of hazardous or toxic materials; the environmental transport and systems to control the release of or to minimize the exposure to such materials; and the assessment of the consequences of exposure. Numerous comparative studies of coal-derived liquids and other related materials such as shale oils, petroleum crude oils, petroleum products, and various polynuclear aromatic compounds have been completed and reported, including research with materials from the H-Coal PDU.[4]

The following discussion is limited to the results of several of the more recent characterization and testing studies of samples from the PDU. These samples are not necessarily representative of coal liquids that will eventually be produced in a commercial facility; consequently they are not adequate for definitive process-specific comparisons. The results are valuable, however, as indicators of potential problem areas. As such, they provide a basis for selecting samples and defining studies to be performed with pilot plant materials.

Characterization and Cellular Bioassays

An important focal point of our research has been the identification of

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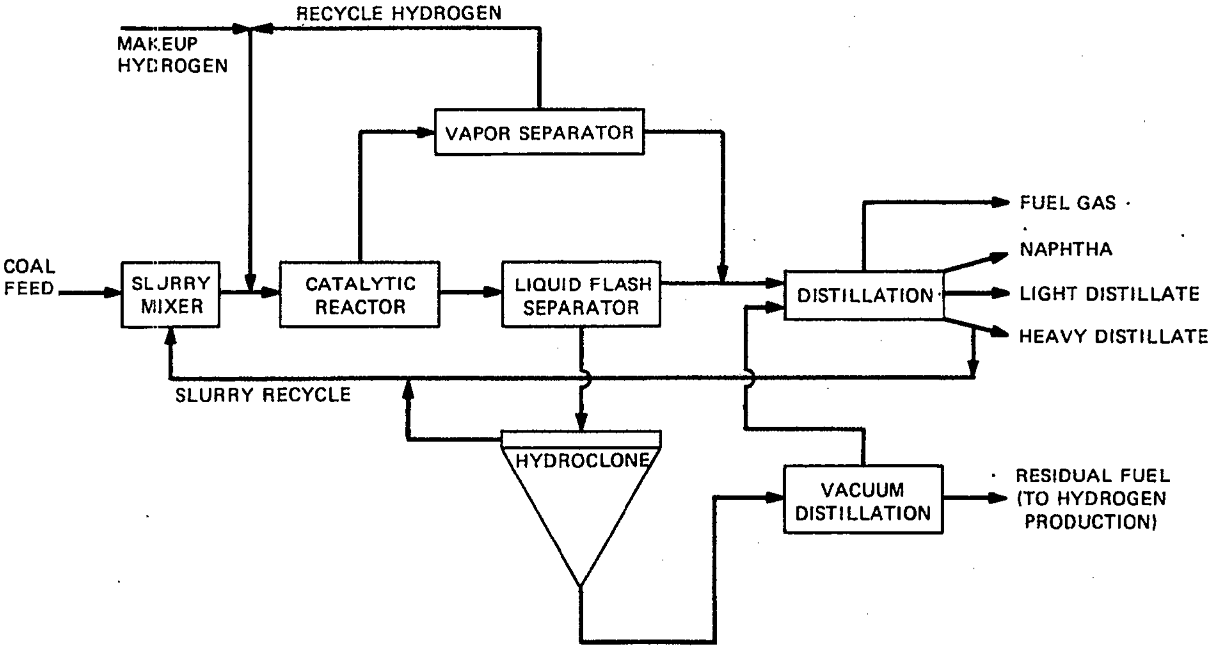

Figure 1. H-Coal Process Schematic.

the chemical constituents responsible for the potential biological effects of synfuel products and processing effluents. An effective approach is to integrate biological testing with a chemical manipulation of the test material. Thus, in our comparative mutagenesis program we have emphasized the combining of chemical class fractionation with biotesting.

Samples examined in this study were provided by Mobil Research and Development Corporation and Hydrocarbon Research, Inc., and incorporated into the Synfuels Research Materials Facility.[5] Both raw distillates and products upgraded by hydrotreatment (HDT) were included. The samples are identified in Table 1, with information given on their boiling point ranges and ultimate analyses. Because these samples were not necessarily representative of the coal liquids that will eventually be produced in a commercial facility, they were used for generic research into the chemical and biological properties of petroleum substitutes.

All samples were treated according to the procedure shown in Figure 2. After removal of the highly volatile matter, the residue was fractionated into chemical classes with a diethyl ether-aqueous acid partitioning and a subsequent Sephadex LH-20 separation of the neutral fraction.[6,7] The resulting volatiles, insoluble matter, and acidic, basic, and neutral subfractions were weighed and subjected to bacterial mutagenic testing. Although biological screening studies with H-Coal materials have included tests in a bacterial system (<u>Salmonella typhimurium</u>) and a protozoan system (<u>Tetrahymena pyriformis</u>),[8] only the former tests are discussed in this paper.

The results of characterization and mutagenic testing are summarized in Table 2 by general chemical class and approximate weight and by mutagenic contribution. These results, useful in identifying general trends as opposed to absolute hazards posed by the test materials, have been discussed extensively in other publications.[9,10] For example, the total mutagenicities (the sum of chemical fractions) of coal-liquid samples that are more volatile (sample No. 1312) or that have been hydrotreated (sample Nos. 1603 and 1604) tend to be lower, and mutagenicity tends to increase with increasing vapor pressure (e.g., sample Nos. 1313-1315). These samples exhibit greater mutagenicity than petroleum crude oils. In addition to the neutral subfractions, the alkaline components can contribute significantly to the mutagenicity of coal liquids. Recent evidence indicates that polycyclic aromatic amines and azaarenes are unusually bioactive alkaline constituents whereas polar-substituted neutral polycyclic aromatics are occasionally responsible for high mutagenicities.

In-Vivo Mammalian Tests

Whole-animal studies have included the preliminary investigation of both the acute and chronic toxic effects of coal-derived liquid materials. A total of five acute toxicity tests was used: determination of the acute toxicity following oral and interperitoneal administration of the test materials to mice, acute dermal toxicity in rats, primary skin irritation and eye irritation in rabbits, and delayed-contact sensitivity in guinea pigs. Skin carcinogenesis tests involved the repeated application of the test material to the shaved skin of mice. Test and data analyses procedures have been described elsewhere.[11,12]

TABLE 1. PROPERTIES OF COAL LIQUID SAMPLES FROM PROCESS DEVELOPMENT UNIT

Identification		Operational		Description	Characteristics					
						Wt. %				(%)**
PDU Run	ORNL Repository	Mode	Coal	Sample Point Location	Boiling* Range(°F)	Hydrogen	Oxygen	Nitrogen	Sulfur	C_A
1	1601	Fuel oil	Ill. No. 6	H-Coal distillate (raw)	300-700	9.65	1.62	0.39	0.107	57
	1602			HDT at low severity		9.87	0.95	0.20	0.002	52
	1603			HDT at medium severity		10.5***	0.39	0.13	<0.002	45
	1604			HDT at high severity	200-650	10.9***	0.21	0.09	<0.002	39
1		Fuel oil	Ill. No. 6	H-Coal fuel oil	375-1000					58
	1617			HDT at low severity		9.17	0.94	0.58	0.059	52
	1618			HDT at medium severity		9.22	0.74	0.55	0.039	51
	1619			HDT at high severity	375-1000	9.67	0.44	0.30	0.011	44
5	1308	Syncrude	Ill. No. 6	Atmospheric overhead (ASOH)	146-590	11.8		0.17	0.07	
	1309			Atmospheric bottoms (ASB)	458-650 (66%)	9.4		0.37	<0.03	
	1310			Vacuum overhead (VSOH)	492-650 (34%)	8.7		0.42	<0.03	
	1311			Vacuum bottoms (VSB)		4.3		0.90	3.0	
7	1312	Fuel oil	Ill. No. 6	Atmospheric overhead (ASOH)	172-565	11.4		0.30	0.2	
	1313			Atmospheric bottoms (ASB)	410-650 (81%)	9.5		0.40	0.5	
	1314			Vacuum overhead (VSOH)	462-633 (46%)	8.7		0.50	0.1	
	1315			Vacuum bottoms (VSB)		4.7		1.5	2.2	

*Parenthetical values are percent of volume distillated at highest indicated temperature.
**Aromatic carbon as percent of total carbon.
***Estimated.

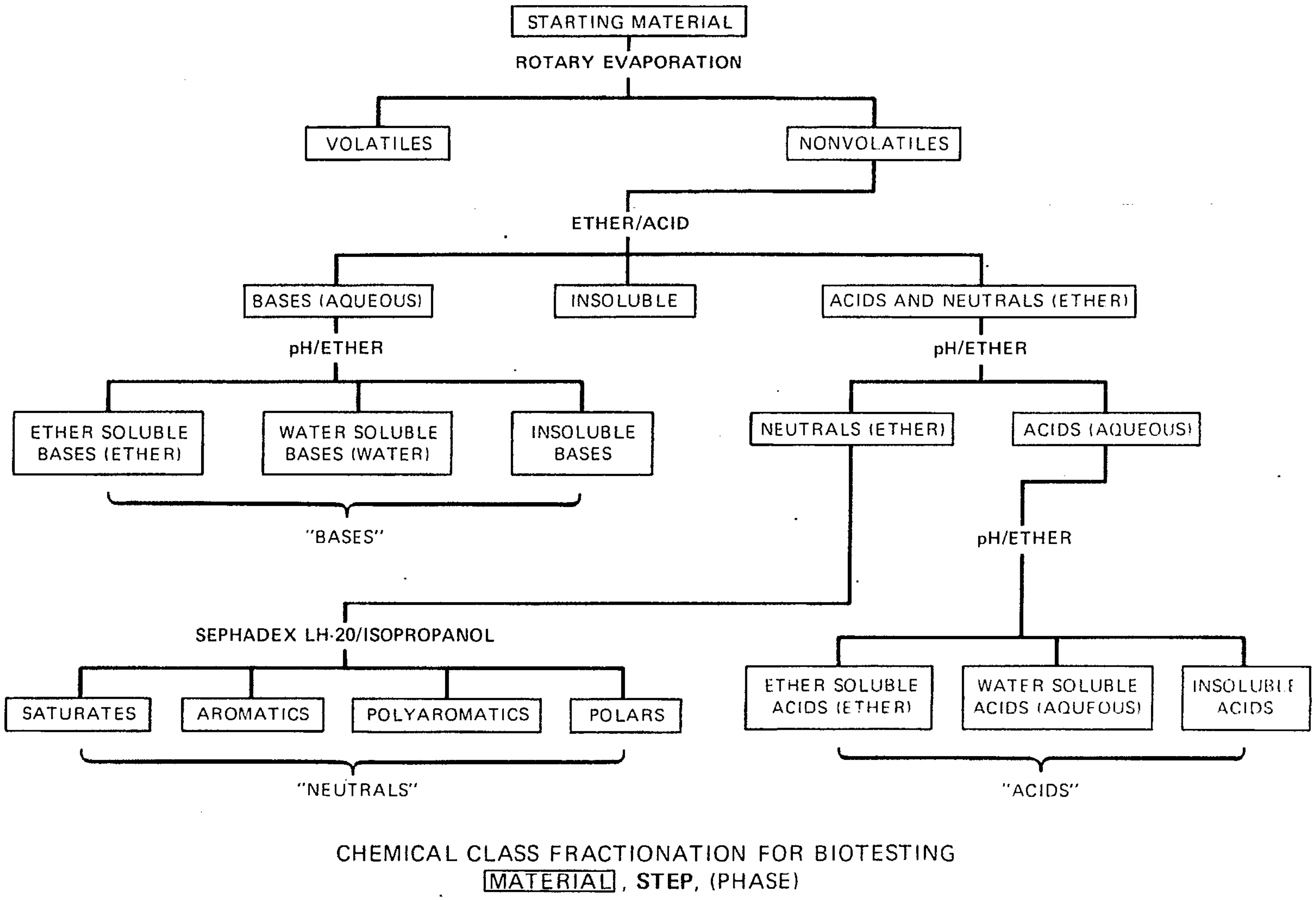

Figure 2. Swain-Stedman Acid-Base Fraction Coupled with LH-20 Separation of Neutral Fraction

TABLE 2. APPROXIMATE MUTAGENICITY AND WEIGHT DISTRIBUTIONS BY CHEMICAL CLASS

	Mutagenic Activity*					Weight Distribution				
		Percentage Contribution				Percent of Total				
Sample	Total (revert mg-1)	Acids	Bases	Neutrals	Other**	Acids	Bases	Neutrals	Other**	Total Recovered
H-Coal ASB (Syn) No. 1309***	970	1	46	53	0	<1	3	95	<1	99
H-Coal VSOH (Syn) No. 1310	2400	0	42	58		1	3	95	1	100
H-Coal VSB (Syn) No. 1311	2000	0	66	17	16	2	5	30	65	102
H-Coal ASOH (FO) No. 1312	0	0	0	0		1	2	55	35	93
H-Coal ASB (FO) No. 1313	140	0	100	0		1	2	95	1	99
H-Coal VSOH (FO) No. 1314	4200	0	25	75		1	2	95	1	99
H-Coal VSB (FO) No. 1315	6300	0	89	9	2	1	10	30	60	101
H-Coal 'Dist' No. 1601	350	0	37	63	0	1	1	85	4	91
H-Coal 'Dist' HDT-L No. 1602	540	0	0	100	0	1	2	85	10	98
H-Coal 'Dist' HDT-M No. 1603	210	0	0	100	0	1	2	80	10	93
H-Coal 'Dist' HDT-H No. 1604	0	0	0	0	0	1	1	80	15	97
Wilmington Crude No. 5301	5	0	0	100	0	2	1	90	7	99

*Determined using *S. typhimurium* strain TA98 and Arochlor-1254-induced rat liver microsome preparation.

**Volatiles and precipitates other than acidic and basic precipitates.

***Numbers following sample names are designations of the ORNL repository. Abbreviations are identified in Table 1.

Consult Ref. 10 for test results with other coal-derived, shale-derived, and petroleum crude oils.

The results of the acute oral toxicity tests are listed in Table 3.[13] The LD_{50}s of the PDU materials were greater than those of the petroleum crude oil, but only of moderate toxicity. The trend suggests that oral toxicity tends to be lower for the more volatile and HDT coal liquids. No coal liquid tested exhibited acute lethality in rats when applied to the skin at a dose of 2 g/kg or produced skin sensitization when applied intradermally. Eye irritation was noted with some materials, although it was a reversible effect.[14]

Chronic dermal exposure studies revealed that coal liquids from the PDU were carcinogenic to mouse skin.[15] The most carcinogenic materials were those of higher boiling range, but a substantial reduction of skin carcinogenic potential occurred even at the lowest severity of hydrotreatment involved. Neurotoxic and systemic toxic effects are now being studied.

Ecological Tests

Parallel studies of the acute and chronic effects of PDU materials on aquatic and terrestrial organisms of different ecological organizational levels have also been completed.[16,17] This discussion will be limited to the test results of liquid products in bioassays with freshwater algae (Selenastrum capricornutum and Microcystis aeruginosa) and freshwater crustacean (Daphnia magna), the basic screening tools for preliminary comparative studies.

Spills of liquid products derived from coal, oil shale, and natural petroleum are a potential source of environmental impact. Comparative information on transport, dissolution and effects is necessary to define the potential impacts and the requirements for cleanup. Of considerable interest is the primary toxic materials which dissolve rapidly into water in the event of an aquatic spill. Thus, one element of research has focused on water-soluble fractions (WSFs) of these materials; the results of testing several PDU materials are listed in Table 4.

The WSFs permit testing of the toxic components of oils, which were prepared by gently stirring the mixture of oil floating on distilled water. Their effect on photosynthesis by freshwater algae was measured as a concentration causing 20% inhibition (EC_{20}) of organic carbon uptake in 4-h exposures.[18] Values for the coal-liquid WSFs were below those for petroleum WSFs or of greater potential acute toxicity. Water soluble fractions were also tested for acute toxicity to Daphnia in standard 48-h bioassays (LC_{50}) and for chronic effects in examinations of the lowest concentrations at which significant change to reproduction was observed in 28-d exposures (LOEC).[19,20] The acute effects for the WSFs of coal liquefaction products were larger (LC_{50}s ranging from 0.2 to 4.6%) than those for the petroleum products; similarly, reproduction effects were also larger.

Generally the toxicity of chemical class fractions from coal-liquid WSFs was found to increase as ether-soluble bases > ether-soluble acids > neutral subfractions. Phenolic compounds and anilines were determined to be the most important water soluble components of the coal liquids in terms toxic effects.

TABLE 3. ACUTE TOXICITY IN MAMMALIAN SYSTEM

Sample	Oral LD_{50}* (g/kg)	95% Confidence Limits
H-Coal ASB (Syn) No. 1309**	3.6	2.4-5.2
H-Coal VSOH (Syn) No. 1310	2.5	1.7-3.1
H-Coal ASOH (FO) No. 1312	5.8	4.7-7.2
H-Coal ASB (FO) No. 1313	2.3	1.9-2.6
H-Coal ASOH (FO) No. 1314	2.6	2.2-3.2
H-Coal 'Dist' No. 1601	3.6	2.8-4.5
H-Coal 'Dist' HDT-L No. 1602	4.0	3.4-4.7
H-Coal 'Dist' HDT-H No. 1604	5.5	2.8-7.2
Wilmington Crude No. 5301	>16	

*Dose in grams of material per kilogram of body weight that kills 50% of animals.

**Numbers following sample names are designations of the ORNL repository. Abbreviations are identified in Table 1.

TABLE 4. TOXICITY IN ECOLOGICAL TEST SYSTEMS

Sample	Algae Acute Toxicity (EC_{20})* Selenastrum capricornutum	Algae Acute Toxicity (EC_{20})* Microcystis aeruginosa	Crustacea Toxicity Acute (LC_{50})** Daphnia magna	Crustacea Toxicity Chronic (LOEC)*** Daphnia magna
H-Coal ASOH (Syn) No. 1308****	0.25	0.46		
H-Coal ASB (Syn) No. 1309	0.30	0.26	4.6	0.58
H-Coal VSOH (Syn) No. 1310	0.063	0.13	2.5	0.92
H-Coal ASOH (FO) No. 1312	0.019	1.4	0.24	0.016
H-Coal ASB (FO) No. 1313	0.16	0.15	1.0	0.25
H-Coal ASOH (FO) No. 1314	0.019	0.13	2.5	
H-Coal 'dist' No. 1601	0.42	0.91	0.4	
H-Coal 'dist' HDT-L No. 1602	0.57	0.75	0.5	
H-Coal 'dist' HDT-M No. 1603	0.68	1.4	1.5	
H-Coal 'dist' HDT-H No. 1604	0.60	1.6	1.7	
Petroleum No. 2 diesel fuel	15.	25.	30.	20.

*WSF concentration (percent dilution) causing 20% inhibition of photosynthesis.

**WSF concentration (percent dilution) that killed 50% of the organisms in 48-h.

***Lowest WSF concentration (percent dilution) at which significant effects on reproduction were observed in 28-d.

****Numbers following sample names are designations of the ORNL repository. Abbreviations are identified in Table 1.

PLANNED STUDIES OF PILOT PLANT

Major areas of health and environmental concern for synfuel development have been described in detail.[21-24] These include consideration of facility siting, potential degradation of air and water quality, solid waste management, worker health and safety, and potential public health risks. Extensive federal legislation exists to cope with these concerns, with the new legislation having increased almost exponentially in number since the passage of the National Environmental Policy Act of 1969.[25] However, additional information in these areas is needed; thus, research programs relate to the perceived issues involving both regulated activities and yet-to-be-defined regulations.

The objective of the H-Coal Environmental and Health Program is to provide data and information to support analyses and assessments of coal liquefaction technology. It is not intended as an environmental compliance activity, because the protection of the worker and environment at the pilot plant is the responsibility of Ashland Synthetic Fuels, Inc. (ASFI).

Program emphasis is on those aspects of the H-Coal process and those units that can conceivably be scaled to commercial-size facilities. Process sampling is thus keyed to the examination of products, effluents, possible occupational exposures, and the information necessary for control technology evaluation. Biological screening activities focus on samples representing material of the greatest potential for human exposure or health effects, tempered with the results of tests on samples from the H-Coal PDU. Environmental studies complement the process and in-plant studies, with the thrust on testing product oils and plant effluents, including solid wastes.

PROCESS MEASUREMENTS AND CONTROLS

Sufficient samples and analyses are provided to characterize a few points in the process streams and nearly all the points of plant effluents and to assess the efficiency of environmental control devices. The details of process sampling and analyses are described in the H-Coal program plan.[26] In general, process sampling strategy provides for the characterization of materials introduced into the process; minimal sampling of intermediate-process streams based on considerations of mass flow, scale-up problems, and the potential for occupational exposure; and final product and waste streams.

Fifty-three sampling points are located to meet our sampling criteria; twenty-four are built into the plant (e.g., hydroclone overhead), and the others can be obtained at several preselected points (e.g., coal pile runoff). Sample collection is targeted to steady-state operation, and because steady-state operation cannot be determined a priori, several sample suites will be collected during each coal run. After operational conditions are evaluated, materials for testing are selected from samples that have been stored under controlled conditions. The frequency and intensity of sampling and monitoring are subject to modification as experience dictates.

The analytical procedures and the constitutents or parameters to be measured were chosen to allow early measurement of traditionally monitored or suspected materials and to maximize the likelihood of detecting unexpected and hazardous constituents. Results must be adequate to document process conditions, to evaluate the efficiency of environmental control technology, to identify limitations in sample size or analytical methodologies, to identify possible biological hazards in potential fugitive emissions, and to assign priorities to materials for subsequent bioassay.

Each sample can be identified as a process sample, a product (or final effluent), a fugitive emission, or a solid waste. As shown in Table 5, each sample is designated a process (I), product (II), fugitive emission (III), or solid-waste (IV) sample. Subsets of each category--gases, tars, solids, etc.-- can then be listed with the chemical and physical characterizations to be performed. Thirty-two classes of analyses are specified, but not for all samples. For example, the study of oils and tars comprises (1) elemental analysis; (2) analyses of Environmental Protection Agency (EPA) priority pollutant trace elements; (3) determination of filterable solids, moisture, volatile organic compounds, volatile organosulfur compounds, benzo(a)pyrene, polycyclic aromatic hydrocarbons, and organonitrogen compounds; (4) organic class analyses; and (5) a bioassay preparation. As with sampling, we view the analyses strategy as flexible because actual measurements may suggest curtailing some studies or expanding others.

Environmental Control Technology--

A complete evaluation of two environmental control methods that are scalable to larger systems will be attempted. One is the diethanolamine absorption towers for CO_2 and H_2S removal from the sour fuel gas and vent gas streams, the other is the sour water strippers for H_2S and NH_3 removal from the wastewater stream. Companion studies will also be made of the remaining wastewater system with the operating contractor. A special study of the treatability of coal liquefaction wastewaters (described below) will also be undertaken.

Sample Collection Status--

Present plans are to operate the pilot plant in the syncrude operational mode with at least three different coals. During a 45-d run initiated on February 17, 1981, using Illinois No. 6 coal, two sets of samples were collected and placed in storage. Early in May the plant was brought on stream with a Kentucky No. 9 coal, and an extensive sample set was taken for the environmental program. Limited characterization and testing of these latter samples began in late August. During September continuous plant operation with Illinois No. 6 coal was achieved, and two additional sample sets were collected. As this run continues, additional samples will be collected. Selection between these sets for subsequent study will be made shortly on the basis of process conditions.

OCCUPATIONAL EXPOSURE AND EFFECTS

The potential exposure of man in the working environment includes consideration of plant area controls and the effects on man if exposures occur. Monitoring and testing activities thus involve the requirements of worker protec-

TABLE 5. DETERMINATIONS CONSTITUTING THE STUDIES

Study	Ultimate analysis[a]	EPA priority elements[b]	EPA drinking water elements[c]	Anionic analysis	Leachable elements	Filterable solids	Total suspended solids	pH	Total organic carbon	Moisture	Extractable organics[d]	XAD-2 extractables - GC/MS analysis	Volatile organic compounds	Volatile organo-sulfur cmpds.	H_2S	SO_2	Stable gases	BaP	Total particulate loading	Leachable organics	Sulfur: organic, pyritic, sulfate	PAHs	Organonitrogen compounds	Organohalogen compounds	Size fractionation	Standard drinking water tests	Organic class analysis	Texax adsorbables[f]	Bioassay preparation	Direct GC/MS analysis[g]	Area samplers[h]	EP extract preparation
Process (I)																																
Solids (IA)	X	X																			X											
Oils and tars (IB)	X	X				X				X			X	X				X				X	X				X		X			
Process waters (IC)			X	X			X	X	X			X[d]																	X			
Oily waters (ID)			X	X			X	X	X		X	X[d]															X		X			
Gases (IE)												X	X	X	X	X	X											X				
Product (II)																																
Solids (IIA)	X	X			X						X							X		X									X			
Naphtha and light oils (IIB)	X	X											X	X															X	X		
Fuel oils (IIC)	X	X											X	X	X	X	X	X				X	X				X		X			
Gases (IID)		X[e]									X[e]	X	X	X					X			X[e]	X[e]					X	X[e]			
Processed water (IIE)												X														X						
Fugitive emissions (III)																																
Solids (IIIA)		X									X								X						X				X			
Liquids (IIIB)	X	X				X				X			X	X				X				X	X				X		X			
Gases (IIIC)																															X	
Solid wastes (IV)	X	X								X	X		X									X		X			X		X			X

---

[a] C, H, N, S, O.
[b] Ag, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Tl, and Zn; also includes Co and Mo plus any other elements which are easily determined by the techniques used.
[c] As, Ba, Cd, Cr, Pb, Hg, Se, Ag.
[d] Includes extractables from suspended solids.
[e] Pertains to the particulate content.
[f] Analysis for chemical smog precursors (e.g., acetaldehyde).
[g] Standard components determined in industrial hygiene surveillance.
[h] EP: RCRA protocol extraction procedure (EPA).

tion and the potential effects of exposure to primary effluents and fugitive emissions.

Plant Area Sampling and Characterization

The primary objective of an industrial hygiene program is to recognize, evaluate, and control exposures that may have the capability of producing untoward health effects. ASFI has prime responsibility for protecting the health of its employees, and we have participated by complementing ASFI's requirements and providing information for occupational health control assessments.

Two types of monitoring of potential exposures are provided. Area monitoring for particulates, fugitive emissions, and various physical and chemical stresses indicates possible exposures whereas personnel monitoring defines the actual exposures. New capabilities in monitoring pollutants associated with tars and oils have been demonstrated and will be used in program implementation.[27] These include portable instruments with the real-time measurement capabilities listed in Table 6 to assist in the selection of sample sites and in the determination of residual worker contamination. A variety of standard industrial hygiene techniques employing filter cassettes and gas badges will also be used to define the time-weighted exposures to organic vapors and particulate contamination.

Occupational Toxicology

The principal focus of our occupational toxicology studies is on the testing of products, primary effluents, and potential fugitive emissions to estimate the effects on man. Questions to be answered concern:

- the relative toxicity of products, by-products, and effluent;
- toxicity variation with process conditions; and
- the potential for work-place toxicity.

A tiered or multilevel approach will be used in the investigation of these questions of toxicity, which will be guided by the results with PDU materials. Level one tests, or cellular mutagenic bioassays, are the initial screens to ascertain the relative toxicity of materials of interest and the need for further testing and to correlate with whole-animal somatic effects. Level two tests, or mammalian somatic toxicity tests, complement the mutagenic and cytotoxic testing and provide validating or confirmatory information on biological potency.

In Table 7 we list the bioassays to be employed, although not all tests will be run on all samples collected at a given point. Cellular bioassays make use of a variety of biological systems including bacteria, yeast, and mammalian cells to investigate mutagenic effects. These shorter-term tests will provide guidance in subsequent testing and be complemented by longer-term validating assays using <u>Drosophila</u>, cultured mammalian cells, and whole-animal (mouse) systems. Toxicity tests involve the use of whole animals to characterize the acute, subacute, and chronic toxicity of products and effuents. They are used in the study of materials of likely high toxicity

TABLE 6. PORTABLE MONITORING INSTRUMENTS

Control Pollutant	
NH_3, NO_x, SO_2, C_6H_6, C_6H_5OH, naphthalene its derivatives	Second-derivative ultraviolet absorption spectrometer with multipass gas cell for real-time monitoring of selected effluents
Tar and oil on contaminated surfaces	Fluorescence spill spotter for general surface contamination including BaP
Tar and oil on contaminated skin	Lightpipe luminoscope for residual skin contamination using very low intensities of UV light
PNA vapors	Passive meter for area or personnel monitoring of selected PNA compounds using room-temperature phosphorescence detection techniques

TABLE 7. BIOASSAY TESTS FOR HEALTH EFFECTS ASSESSMENT

Purpose	Test
Screening	1. Bacteria-- *Salmonella typhimurium* strains
	2. Yeast-- *Saccharomyces cerevisiae*
	3. DNA repair-- *Bacillus subtilis*
	4. Mammalian cell (CHO) cytotoxicity
	5. Invertebrate cytotoxicity-- *Tetrahymena pyriformis*
	6. Embryo toxicity-- *Xenopus laevis*
	7. Mammalian teratogenesis-- mouse
Screening and validation	1. Fruit fly-- *Drosophila melanogaster*
	2. Mammalian cell (CHO) gene mutation
	3. Mammalian cell (CHO) cytogenetic damage
	4. Mammalian cell (leukocyte) chromosomal change
	5. In-vitro cell transformation
Mammalian mutagenesis	1. Mouse-- dominant lethals
	2. Mouse-- heritable translocations
	3. Mouse-- specific locus
	4. Mouse-- spot test, somatic mutation
	5. Mouse-- reproductive capacity
Mammalian toxicity	1. Mouse-- acute oral LD_{50}
	2. Mouse-- intraperitoneal injection LD_{50}
	3. Rat-- acute dermal toxicity
	4. Rabbit-- eye and skin irritation
	5. Guinea pigs - dermal sensitization
	6. Mouse-- maximum tolerated dose
Mammalian carcinogenesis	1. Mouse-- lung tumors
	2. Mouse-- skin tumors

about which little information is available but which have potential for human exposure. A brief description of each bioassay is provided in the H-Coal program plan.

ENVIRONMENTAL FATE AND EFFECTS

Environmental studies emphasize the data base requirements to assess the H-Coal technology rather than the pilot plant. Consequently, the thrust of the program is on characterizing and testing process and plant effluents, solid wastes, and liquid products. The latter studies are concerned with the effects of possible oil spills on terrestrial and aquatic systems.

Ecological tests to be performed on the various materials are identified in Table 8. Toxicity screening tests provide an initial indication of potential ecological effects and include algal photosynthetic inhibition (4-h exposure) and acute toxicity response (48-h LC_{50}), the latter using three different aquatic test organisms. Materials showing high toxicity and high potential for environmental exposure will be tested further. These activities include tests of the reproduction effects on crustacea and insects and of acute toxicity and abnormalities on fish embryo-larval life stages. Chemical and physical characterization (Table 1) is a part of the testing protocol.

The transport and fate of products that may be spilled in aquatic environments will be studied in small field ponds. Aqueous extracts of vacuum bottoms flaked product and filter cake consisting of solids from the wastewater treatment system will be prepared to simulate on-site storage and landfill disposal, respectively, and will be subjected to selected tests. Studies of aqueous wastes will be limited to effluents from the wastewater treatment plant and to the combined discharge (process water, sanitary effluents, and sursurface runoff from the plant site) to the Big Sandy River. All tests will be replicated with equivalent petroleum crude and oil for comparison purposes.

SPECIAL STUDIES

Several special studies will be carried out to examine issues of particular importance in direct coal liquefaction, which involves the H-Coal process. They are summarized as follows.

Advanced Wastewater Control Technology

A 1-gpm wastewater treatment PDU will be designed and constructed for initial use at the H-Coal pilot plant.[28] The treatment unit provides the means to evaluate the efficiency and cost of advanced treatment techniques to achieve zero stream discharge or meet future discharge regulations, to investigate the operational problems of existing systems, and to provide scale-up data for larger facilities. Unit processes in the treatment train will be constructed in transportable, self-contained modules that can be interchanged or bypassed to achieve maximum flexibility. As shown in Figure 3, unit processes will provide for pretreatment and conditioning by distillation stripping of NH_3 and H_2S, setting and flotation for solids and oil removal, and solvent extraction for phenol removal; biological oxidation; and polishing operations

TABLE 3. ECOLOGICAL TESTS OF H-COAL MATERIALS

Sample Description	Photosynthesis, algal-- *Sclenastrum capricornutum* and *Microcystis aeruginosa*	Acute toxicity, crustacea -- *Daphnia magna*	Acute toxicity, midge larva-- *Chironomus tentans*	Acute toxicity, fathead minnow-- *Pimephales promelas*	Reproduction, crustacea-- *Daphnia magna*	Reproduction, cricket-- *Acheta domesticus*	Embryo-larval toxicity, fathead minnow-- *Pimephales promelas*	Transport studies
Light fuel oil*	X	X	X	X	X	X***	X	X***
Heavy fuel oil*	X	X	X	X**	X**		X**	X***
Vacuum bottoms, flaked product*	X	X			X**			
Treated process wastewater	X	X	X	X	X		X**	
Filter cake*	X	X	X	X	X**		X**	X***
Combined aqueous discharge	X	X						
Petroleum crude* ****	X	X	X	X	X	X***	X	X***

*Aqueous extract unless otherwise indicated.

**Tests to be performed if chemical characterization or *Daphnia* acute toxicity indicates potential hazard.

***Whole oil tested rather than aqueous extract.

****For comparison with H-Coal liquid products.

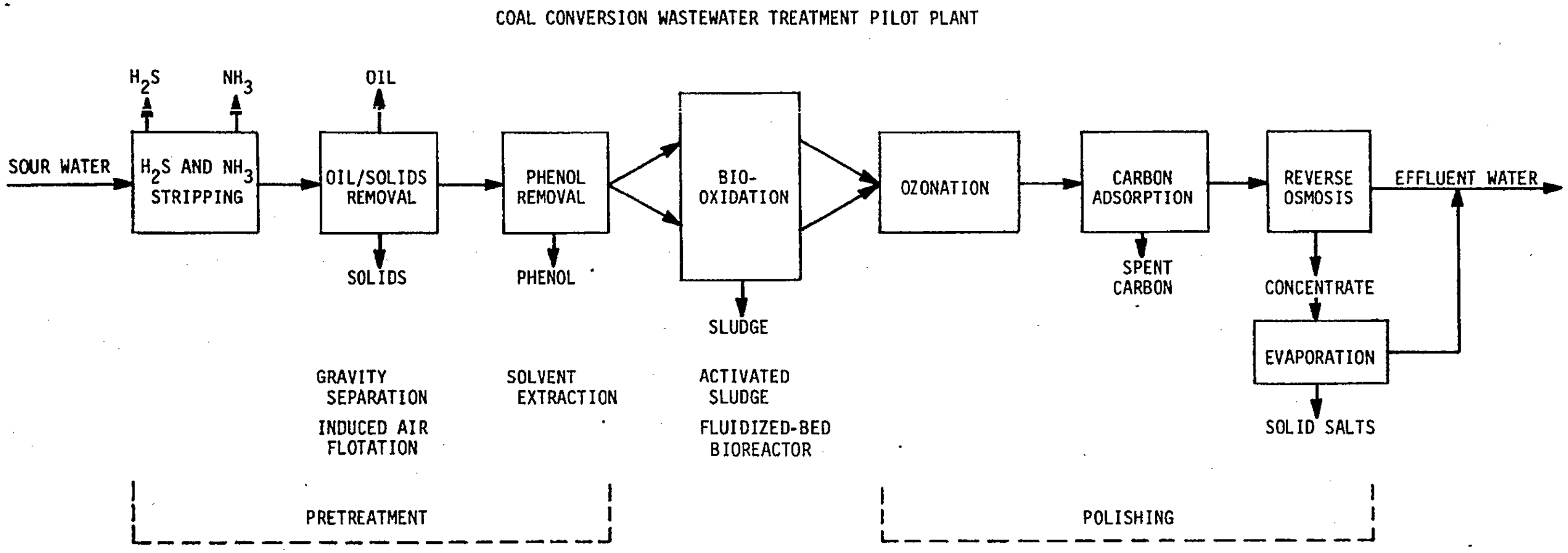

Figure 3. Coal Conversion Wastewater Treatment Process Development Unit

with ozonation and carbon adsorption for refractory and residual organic removal and reverse osmosis for dissolved salt removal.

Product Upgrading

Exploratory research indicates that hydrotreatment and selective distillation of H-Coal PDU liquid products may reduce significantly microbial genotoxicity and mammalian toxicity. Similar findings are reported for SRC-II liquids.[29] Consequently, a systematic study has begun of the effects of hydrotreatment and process conditions on the chemical, physical, and biological properties of liquid products derived from pilot plant operations of H-Coal, SRC-II, and Exxon Donor Solvent (EDS) processes. Blends of distillates will be hydrotreated to three levels of severity and characterized and tested for toxicological response. In a companion effort the status and preliminary cost estimates of process technology for hydrotreatment, boiling-cut fractionation, and other methods of product upgrading (e.g., nitrosation, acid-base extraction, organic solvent extraction, and chromatographic separation) will be investigated.[30]

CONCLUDING REMARKS

Samples of coal-liquid products from the H-Coal PDU have provided initial information on important areas of continuing research. Comparative studies show that crude petroleum substitutes, including the H-Coal materials, generally exhibit greater activity in biological and ecological test systems than petroleum crudes, but this activity is reduced in samples that have been hydrotreated and in low-boiling distillates. Constituents of the alkaline and neutral fractions of coal liquids are responsible for mutagenicity whereas phenolic compounds and anilines cause the greatest toxicity in freshwater algae and zooplankton.

Based upon the initial results of studies with PDU materials and in consideration of the scale-up requirements for a commercial-size facility, the implementation of an extensive health and environmental study of the H-Coal pilot plant has begun. Plans include the characterization and testing of products, by-products, and effluents; collaborative studies with the operating contractor involving plant area monitoring and worker protection; and investigations of environmental controls for plant effluents. Systematic studies have also begun of hydrotreatment and other methods of upgrading liquid products to alleviate biological activity.

REFERENCES

1. U.S. Department of Energy, Securing America's Energy Future: The National Energy Policy Plan, DOE/S-0008 (July 1981).

2. R. S. Livingston et al., Toward a Desirable Energy Future: A National Perspective, ORNL/PPA-81/6 (March 1981).

3. W. D. Felix et al., Chemical/Biological Characterization of SRC-II Product and By-Products, PNL-SA-8813 (September 1980).

4. L. W. Rickert and J. L. Seiber, Publications in Life Sciences Synthetic Fuels of Oak Ridge National Laboratory, ORNL/TM-7680 (June 1981).

5. W. H. Griest, D. L. Coffin, and M. R. Guerin, Fossil Fuels Research Matrix Program, ORNL/TM-7346 (June 1980).

6. I. B. Rubin, M. R. Guerin, A. A Hardigree, and J. L. Epler, "Fractionation of Synthetic Crude Oils from Coal for Biological Testing," Environ. Res. 12:358-365 (1976).

7. A. R. Jones, M. R. Guerin, and B. R. Clark, "Preparative-Scale Liquid Chromatographic Fractionation of Crude Oils Derived from Coal and Shale," Anal. Chem. 49:1766 (1977).

8. T. W. Schultz, J. N. Dumont, T. K. Rao, M. R. Guerin, C. Y. Ma, and J. L. Epler, "Evaluation of Hydrotreatment as a Means of Reducing Biological Activity of Synfuel Related Materials," Environ. Res. (submitted September 1981).

9. J. L. Epler, "The Use of Short-Term Tests in the Isolation and Identification of Chemical Mutagens in Complex Mixtures," Chemical Mutagens: Principles and Methods for Their Detection, New York, Plenum Press (1980).

10. M. R. Guerin, I. B. Ruben, T. K. Rao, B. R. Clark, and J. L. Epler, "Distribution of Mutagenic Activity in Petroleum and Petroleum Substitutes," Fuel 60(4):231-248 (1981).

11. H. R. Witschi, W. M. Huschek, and L. H. Smith, Level 2- - Mammalian Toxicity, University of Minnesota-Duluth Coal Gasification Project Quarterly Progress Report for the Period Ending December 31, 1979, ORNL/TM-7268 (June 1980).

12. J. M. Holland, D. W. Wolf, and B. R. Clark, "Relative Potency Estimation for Synthetic Petroleum Skin Carcinogens," Environ. Health Perspect. 38:149-155 (1981).

13. H. R. Witschi, Acute Oral Toxicity Tests, H-Coal Pilot Plant Environmental Project Semiannual Progress Report for the Period Ending December 31, 1980, ORNL/TM-7741 (June 1981).

14. J. L. Epler, ed., *Health Effects Research in Direct Coal Liquefaction: Studies of H-Coal Distillates, Process Development Unit Samples*, ORNL/TM (in draft).

15. J. M. Holland, *Toxicity and Carcinogenicity Associated with Chronic Dermal Exposure to H-Coal PDU Distillated and Effect of Hydrotreatment on the Chronic Dermal Toxicity of a Blended H-Coal PDU Distillate*, Life Sciences Synthetic Fuels Semiannual Progress Report for the Period Ending June 30, 1981, ORNL/TM-7926 (in press).

16. C. W. Gehrs, *Advanced Fossil Energy Program*, Environmental Sciences Division Annual Progress Report for the Period Ending September 30, 1980, ORNL-5700 (March 1981).

17. J. M. Giddings, *Summary of Research on Coal Liquefaction Product Spills*, ORNL/TM-7966

18. J. M. Giddings and J. N. Washington, "*Coal-Liquefaction Products, Shale Oil, and Petroleum. Acute Toxicity to Freshwater Algae*." Environ. Sci. Technol. 15: (1981).

19. B. R. Parkhurst, C. W. Gehrs, and I. B. Rubin, "Value of Chemical Fractionation for Identifying the Toxic Components of Complex Aqueous Effuents," in *Aquatic Toxicology*, American Society for Testing Materials, ASTM STP-667.

20. U.S. Department of Energy, *Fate and Effects of Coal Liquefaction Products in Aquatic Ecosystems*, Final Environmental Impact Statement, SRC-I Demonstration Project, 2 DOE/EIS-0073 (July 1981).

21 U.S. Department of Energy, *Environmental Development Plan: Coal Gasification*, DOE/EDP-0043 (October 1980).

22. U.S. Department of Energy, *Environmental Development Plan: Coal Liquefaction*, DOE/EDP-0044 (August 1980).

23. U.S. Department of Energy, *Environmental Readiness Document, Oil Shale*, DOE/ERD-0016 (September 1979).

24. U.S. Department of Energy, *Synthetic Fuels and the Environment: An Environmental and Regulatory Impact Analysis*, DOE/EV-0087 (June 1980).

25. C. R. Richmond, "Opening Comments," *Proc. 3rd ORNL Life Sciences Sympo. on Health Risk Analyses*, Gatlinburg, Tennessee, October 27-29, 1980 (in press).

26. K. E. Cowser, ed., *Environmental and Health Program for H-Coal Pilot Plant*, Oak Ridge National Laboratory (November 1980).

27. D. D Schuresko, *Preliminary Field Testing of H-Coal Monitoring Instruments*, H-Coal Pilot Plant Environmental Project Semiannual Progress Report for the Period Ending December 31, 1980, ORNL/TM-7741 (June 1981): 8-18.

28. G. E. Oswald, J. F. Walker, J. A. Klein, and R. K. Genung, *Coal Conversion Wastewater Treatment PDU*, Life Sciences Synthetic Fuels Semiannual Progress Report for the Period Ending June 30, 1981, ORNL/TM-7926 (in press).

29. W. C. Weimer, R. A. Pelroy, and B. W. Wilson, *Initial Chemical and Biological Characterization of Hydrotreated Solvent Refined Coal (SRC-II) Liquids: A Status Report*, PNL-3464 (July 1980).

30. R. Salmon, J. F. Fisher, and K. H. Lin, *An Evaluation of the Technology Available for the Reduction of Bioactivity in the Products of Direct Coal Liquefaction*, ORNL/TM-8039 (in draft).

CHEMICAL CHARACTERIZATION AND BIOASSAY OF SRC PROCESS MATERIALS

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ABSTRACT

Bioassay techniques have shown that certain coal liquefaction process streams and products are both mutagenic (Ames assay) and carcinogenic. These materials have been chemically fractionated using a number of techniques (solvent extraction, alumina column separation, HPLC, Sephadex LH-20) in an attempt to identify the constituents responsible for the biological activity. These studies have shown that primary aromatic amines (PAA's) account for more than 90% of the mutagenic response in the Ames test. Long-term skin painting and initiation-promotion assays indicate that the PAA's may also play a role in the carcinogenicity of the coal-derived materials. However, while the PAA's can be designated as the determinant mutagens in coal liquids, they cannot be assigned a determinant role in skin carcinogenesis. Thus far, carcinogenicity appears to better correlate with increasing molecular weight and boiling point. Our results also suggest that benzo(a)pyrene is not a reliable marker compound for carcinogenic activity.

(Only the abstract is published herein.)

Session II: WATER-RELATED ENVIRONMENTAL CONSIDERATIONS

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U.S. Environmental Protection Agency
Research Triangle Park, NC

Cochairman: William E. Corbett
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PB83-128272

COAL CONVERSION WASTEWATER TREATMENT/REUSE - AN OVERVIEW

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ABSTRACT

Environmentally, the production of synfuels from coal can be classified into two categories: (1) low temperature processes, and (2) high temperature processes. Low temperature processes are characterized by the production of high boiling liquids and tars which tend to retain the multiple-ring structure of the original coal "molecule," while high temperature processes typically produce synthesis gas, methane and/or light liquids. Dry-ash moving-bed gasification and direct l-quefaction processes are representative of low temperature conversion processes. Entrained gasification is an example of high temperature processes. Fluid bed gasification processes that operate at temperatures just below the ash slagging point may produce limited heavy liquids and fall intermediate within the classification regime.

Depending on the process, process steam which is subsequently condensed and/or gas clean-up quench waters come into direct contact with the raw gaseous product stream. As a consequence, the resultant wastewater associated with the low temperature processes is highly contaminated with organics. The production of ammonia in the high temperature processes is generally suppressed and reduced due to "cracking." Condensate waters from high temperature processes usually contain little or neglible NH_3, while the condensate waters from low temperature processes contain high levels of NH_3. The condensate waters from both low and high temperature processes generally contain volatized and entrained mineral matter, trace elements and salts as well as adsorbed H_2S, CO_2, and cyanates.

The treatment of the condensate waters from the low temperature processes poses a special challenge due to the high and variable level and toxic nature of the gross organics. A portion of the total organic carbon is biorefractory and this also causes concern. Laboratory treatability tests have demonstrated that with appropriate dilution and/or pretreatment (e.g., gas stripping, organic extraction, and/or the addition of powdered activated carbon) activated sludge treatment processes do a reasonable job of reducing biological oxygen demands (BOD) and total organic carbon levels (TOC), and coupled with activated carbon treatment, relatively high quality effluent can be produced. In a "zero discharge" mode, subsequent concentration and reuse of the effluent must be effected to ultimately produce a concentrated brine or dry salt.

The questions that remain center on the capability of this rather elaborate treatment train to accommodate variabilities in the raw feed and on the reliability and costs of such a system, i.e., do viable alternatives exist? Options will be outlined with special emphasis on: (1) improvements to biological treatment, and (2) purely physical/chemical systems. The effect of more stringent standards with respect to, say, the control of biorefractory ring-structure compounds, trace elements, ammonia, etc., will be discussed relative

to the state-of-the-art biotreatment and these environmental control options. Areas of uncertainty and future research will be delineated based on a recent synfuel wastewater workship, conducted in June 1981.

INTRODUCTION

The capability to adequately treat and discharge wastewaters associated with coal conversion causes some apprehension primarily because of the lack of treatability data from actual operating facilities, at scale and under stringent discharge standards. A number of concerns exist for the tentative wastewater control systems:

- the possible requirement to meet tighter future effluent discharge standards for ring-structured biorefractory organics, trace elements, ammonia, etc.;
- the high level of contamination, variability of composition, and large and variable volumeric flowrate (variability being a special concern with pioneer type plants);
- the vulnerability of biological treatment systems to toxic effects (either due to high loadings in the feed and/or build-up of toxic agents from recycle); and
- the desirability that the wastewater treatment/reuse system be highly reliable to preclude shutdown or curtailment of production.

If one considers "chemical" pollutants of universal concern, adverse environmental effects include (1) changes in pH by strong acid and bases, (2) increase in water corrosivity and reduced suitability for irrigation due to soluble salts, (3) toxicity caused by heavy metals, phenols and cyanides, (4) depletion of dissolved oxygen by oxygen consuming organics, (5) surface films from trace oils, (6) taste and odor problems associated with phenols and chlorinated derivatives and (7) release of biorefractory materials which can be fatal to fish and aquatic life (note--the effect on man, especially any long term cumulative effects, has not been established).

Representative compositions of condensate waters resulting from low temperature coal conversion processes contain each of these "chemical pollutants" (Figure 1). It is apparent that intensive and specialized treatments are required for such waters.

In the design of wastewater treatment facilities, a variety of sources are encountered, although condensate waters typically account for over half the wastewater produced (Figure 2). General design practice is to segregate streams and use different methods of pretreatment tailored to the composition of the individual streams. The current pollution control design data base is such that the practice is to encourage the incorporation of of enhanced design flexibility within the total system. In this context, "flexibility" refers to parallel units and/or spares, conservative design specifications, bypass lines and space to accommodate additional equipment, if necessary. If one examines the preliminary designs of a number of wastewater treatment trains, one finds a high degree of variation between individual process designs with provisions for "flexibility" reflecting a common design philosophy (Figures 3, 4, 5).

	GASIFICATION	DIRECT LIQUEFACTION		
	LURGI	SRC I	H-COAL	EDS
pH	9.0-9.5	8.4	9.5-10.8	—
BOD	4,000-15,000	17,000	—	—
TOC	4,000-20,000	11,000	—	—
COD	15,000-30,000	60,000	28,000	—
PHENOLS	2,000-6,000	1,900	70,000	6,000
SULFIDE, S	100-500	16,000	30,000	12,000
AMMONIA, N	2,000-10,000	18,000	15,000	9,500
THIOCYANATE, SCN^-	20-200	—	—	10
CYANIDE, CN^-	0.1-10.0	—	4.0	4.0
TDS	1,000-5,000	15,000	—	—

FIGURE 1. COMPOSITION OF REPRESENTATIVE RAW CONDENSATE WATERS FOR "LOW TEMPERATURE" CONVERSION PROCESSES, PPM

WASTEWATER STREAM	SOURCE	QUANTITY Mgpd	MAJOR CONCERN
PROCESS CONDENSATE			
HIGHLY CONTAMINATED (LOW TEMPERATURE PROCESSES)	MOVING BED GASIFIERS DIRECT LIQUEFACTION	1.5-7.0 .06-1.0	ORGANICS
MODERATELY CONTAMINATED (HIGH TEMPERATURE PROCESSES)	ENTRAINED GASIFIERS	2.5-4.0	—
	FISCHER TROPSCH,* MOBIL-M*	1.0-3.0	ORGANICS
CLEAN	METHANATION STEP	0.2-1.0	—
BLOWDOWNS			
COOLING TOWER	COOLING TOWER SYSTEM	0.5	TDS
BOILER	ION EXCHANGE REGENERATION AND REVERSE OSMOSIS CONCENTRATE	0.1-1.0	
RAIN RUNOFF	RAIN FALL FROM IMPOUNDMENT	VARIABLE	MIXED
SANITARY WASTES	POTABLE WATER SYSTEM	75% POTABLE RATE	

*EXCLUSIVE OF GASIFICATION STEP

FIGURE 2. SUMMARY OF COAL CONVERSION PLANT WASTEWATER STREAMS (3×10^{11} Btu/d REF PLANT)

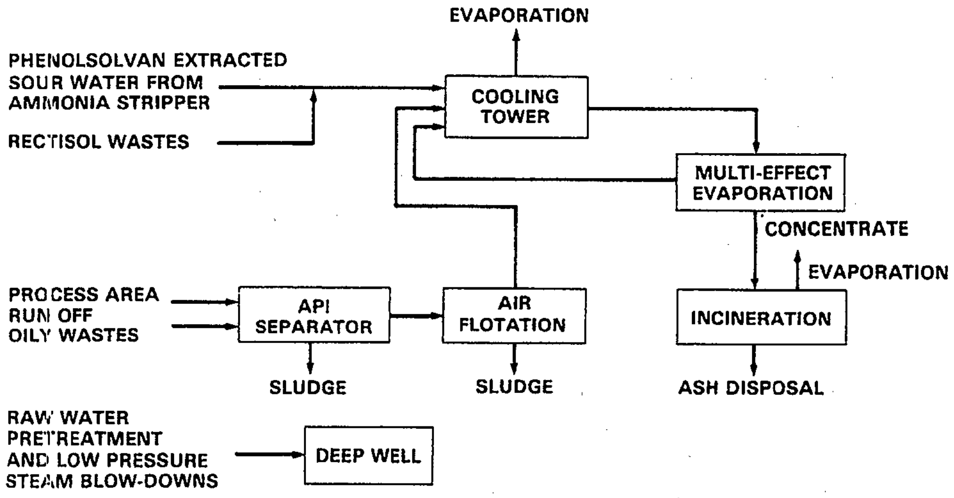

FIGURE 3. WASTEWATER TREATMENT SYSTEM ANG COAL GASIFICATION PLANT

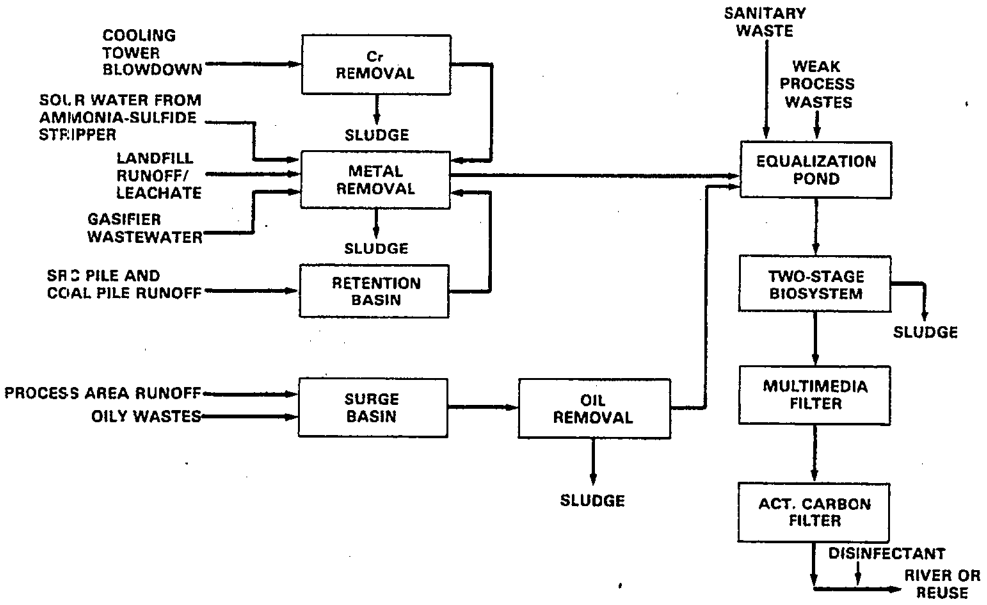

FIGURE 4. TENTATIVE WASTEWATER TREATMENT SYSTEM—
SRC-I DEMONSTRATION PLANT

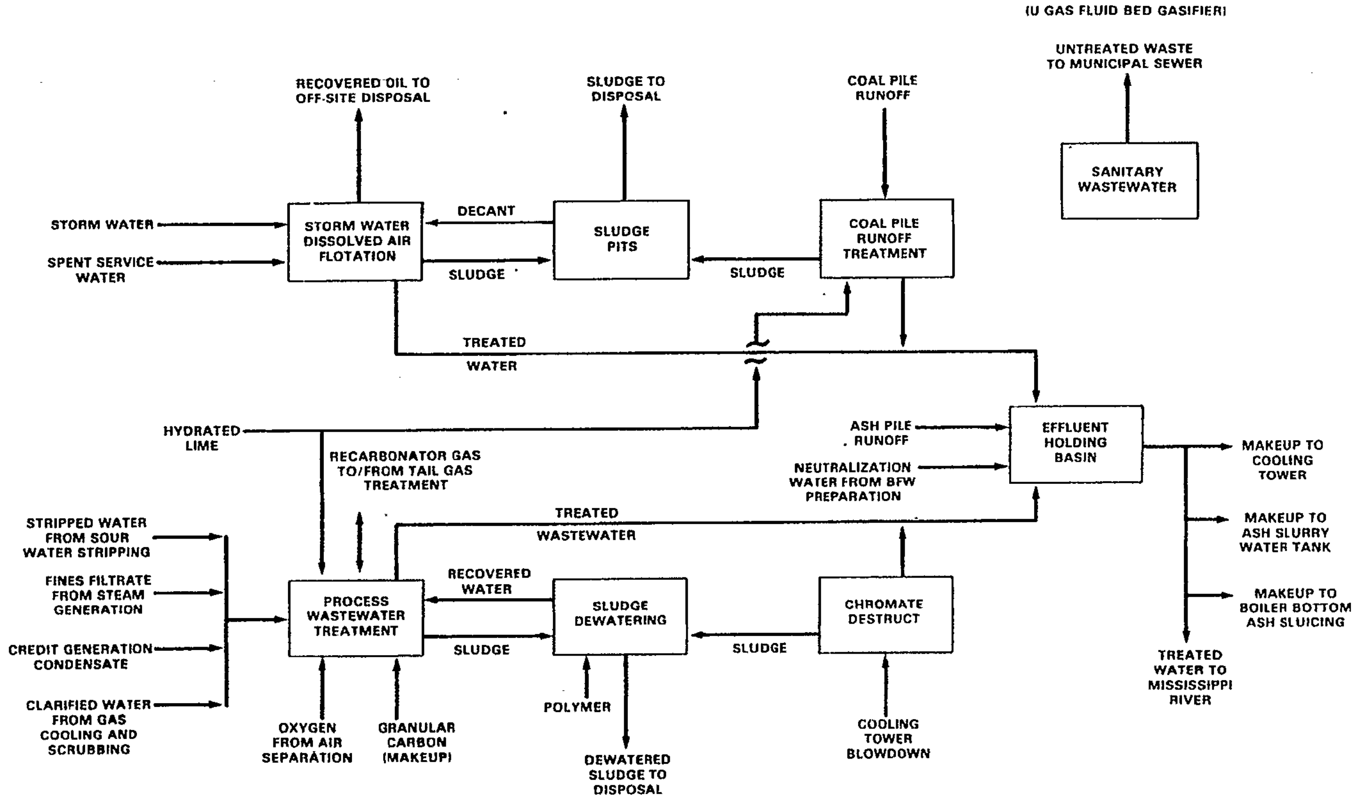

FIGURE 5. WASTEWATER TREATMENT SYSTEM — MEMPHIS INDUSTRIAL FUEL GAS PLANT

DESIGN BASIS FOR WASTEWATER TREATMENT TRAIN

While there are many options for the wastewater treatment/reuse systems, several criteria are overriding in determining the characteristics of the raw influent and the ultimate basis of design:

- geographical location of the plant (i.e., availability of water supply and nature of effluent acceptor);
- characteristics of conversion process; and
- environmental setting and/or controlling permits/standards.

These criteria are obviously interdependent. The geographical location also determines the coal type and influences the product/by-product mix as called for by the market place; this in turn dictates the configuration of the plant. The site specific environmental constraints also influence the process design--the type and nature of wastewater treatment system; the propensity for wastewater reuse and disposal options for wastewater sludges (both organic and inorganic).

GEOGRAPHIC SITING

Geographical water availability/discharge constraints strongly influence the design philosophy for water use integral to the plant. In the arid West, dry cooling and staged quenching may be considered to conserve water, while "zero discharge," coupled with evaporation ponding, is likely to be encouraged to preserve salt-taxed river basins. In the East a different situation prevails; while the use of effluent discharge is considered to provide an acceptable means of salt dispersion, the release of residual trace biorefactory material and trace elements into potential drinking water supplies even though highly diluted, causes anxiety. This is especially true for biological-activated-sludge treatment systems which may experience upsets and require extended periods (several weeks) to recover. During the recovery period, adequate contingency must be available (holding ponds, plant derating, activated carbon units, etc.) to allow the plant to continue to operate.

The large coal requirements and concomitant ash disposal needs for commercial synfuel facilities dictates that the plant be located at or near the mine. There are significant chemical and processing differences between the western and eastern coals. While it is recognized that there are large and overlapping variations in the composition and chemistry of different coal types and that pretreatments can modify the coal structure, decrease ash and reduce sulfur and nitrogen levels, some generalizations relative to plant siting and feed stock requirements for the process can be made:

> Western (lignite and sub-bituminous type coals) are geologically younger than the eastern bituminous coals. The lignites, in particular, contain high levels of moisture and inherently produce net water during conversion. In the East, the ready availability of water supplies and discharge acceptors makes once-through water use preferred, although ideally the conversion processes can be

designed to be a net water consumer. The bituminous coals have agglommerating properties that generally preclude their use in moving bed gasifiers without intensive pretreatment. As a consequence, the large scale gasification of eastern bituminous coal will likely rely on entrained and/or fluid-bed gasifiers with a concomitant improvement in the quality of process condensate waters. Condensate waters associated with direct liquefaction processes will contain gross organic contamination for all coal types.

The composition of the runoff from coal storage piles is likely to vary as function of coal pyrite content. The pyrite abets acid generation which enhances the mobility of metals and total dissolved solids (TDS). The higher pyritic coals are in the East, thus potentially aggrevating a concern in a region where "zero discharge" is not contemplated. Ferric iron tends to predominate the metal release (Figure 6). Conventional treatment practice is neutralization followed by settling.

PROCESS CHARACTERISTICS

The reaction conditions and coal type in the conversion process strongly affect the composition of the condensate water. The most important variable is the temperature-residence time regime to which the coal/reaction products are exposed. This is markedly illustrated by comparing condensate water qualities for an entrained gasifier (bench scale) and a slagging moving bed gasifier (pilot-scale) (Figure 7). While the residence time in entrained gasifiers is very short (on the order of 20 millisec in the Eyring unit), the very high temperatures obtained appear capable of precluding the formation of ring-structured compounds and ammonia during a rapid devolatization/pyrolysis step. At the onset, the extremely rapid exothermic carbon-oxygen reaction predominates the slower endothermic steam-carbon and carbon dioxide-carbon reactions (Figure 8, regions I and II, respectively). The residual char has been demonstrated to effectively scavenger for trace ring-structured compounds that may be formed--the condensate water has been found to be nearly devoid of organics. This is in marked contrast to the condensate waters associated with lower temperature processes such as direct liquefaction with residence times up to several hours, which can contain practically all the organic compounds found in the coal. Thus, from the standpoint of raw condensate water quality and subsequent amenability to treatment, the temperature of coal conversion processes represents a major variable and the condensate waters may be classified under low or high temperature regimes.

A major variable effecting the low-temperature processes is coal rank--the more easily pyrolyzed, more reactive lignite and sub-bituminous western coals generally produce more phenols, given similar process conditions (Figure 9).

Process configurations, quantity and recycle of product gas quench waters and/or staging also determines the quantity and quality of the condensate waste stream. General gross differences between gasification and liquefaction condensate waters are reflected in the sulfide and ammonia concentrations (Figure 1). With respect to organics, laboratory treatability testing of steam stripped waters indicates that biological substrate utilization rates for liquefaction condensates may be significantly (an order of magnitude or more) less than gasification. The incentive for staged quenching and concomitantly reducing water requirements have been found to reside mainly in the use of less expensive materials of construction (carbon steel instead of stainless) downstream of the initial quench which removes the strong acids. Coals with a halide content of 0.15% Cl or greater, generally eastern coals, are expected to benefit from such a configuration.

PARAMETER	MEAN, PPM	RANGE, PPM
pH	2.7	2.1-3.0
IRON	20,000	0.2-90,000
SULFATE	9,000	500-22,000
ZINC	3.6	1.6-23
COPPER	2.1	1.6-3.4
CHROMIUM	3.3	0-16
TDS	16,000	720-44,000

FIGURE 6. REPRESENTATIVE COMPOSITION COAL PILE RAIN RUNOFF, EASTERN COAL
(ANDERSON AND YOUNGSTROM, CORNELL UNIVERSITY)

	HIGH TEMPERATURE	LOW TEMPERATURE
PROCESS	ENTRAINED	SLAGGING-MOVING BED
COAL TYPE	BITUMINOUS	LIGNITE
ORGANIZATION	EYRING RESEARCH (MOUNTAIN FUEL)	GFETC
pH	—	8.6
BOD	NIL	26,000
TOC	NIL	11,000
COD	—	32,000
PHENOLS	NON-DETECTED (<5)	5,500
SULFIDE, S	1.5	100
AMMONIA, N	35 (FIXED)	6,000
THIOCYANATE	—	120
CYANIDE	.02 MAX	2
TDS	330	2400

*NOTE—ABSOLUTE CONCENTRATIONS ARE DEPENDENT ON QUENCH WATER CONTACT/RECYCLE ETC. WHICH DIFFER. RELATIVE PREDOMINANCE OF SPECIES IMPORTANT.

FIGURE 7. COMPARISON OF CONDENSATE WATER FROM "HIGH TEMPERATURE" AND "LOW TEMPERATURE" GASIFICATION PROCESSES, PPM*

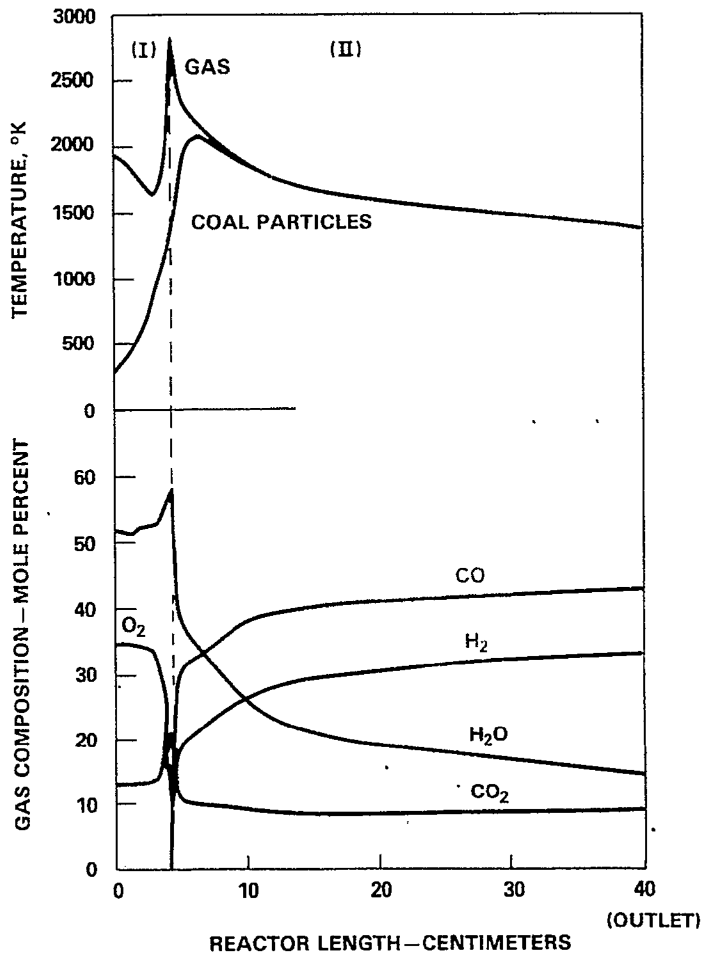

FIGURE 8. TEMPERATURE/COMPOSITION PROFILE ENTRAINED GASIFIER
(P. SMITH, BRIGHAM YOUNG UNIVERSITY)

PROCESS		PHENOL LEVEL, PPM*			
	COAL RANK*	LIGNITE	SUBBITUMINOUS	BITUMINOUS	
			MONTANA	ILLINOIS NO.6	PITTSBURGH NO. 8
LURGI/BRITISH GAS SLAGGING LURGI (WESTFIELD, SCOTLAND)		—	4,400	1,900	2,100
		NORTH DAKOTA	WYOMING		
PETC SYNTHANE (FLUID-BED)		6,600	6,000	2,600	1,700

*NOTE—ABSOLUTE CONCENTRATIONS ARE DEPENDENT ON QUENCH WATER CONTACT/RECYCLE ETC. WHICH DIFFER BETWEEN PROCESSES, TRENDS ARE IMPORTANT.

FIGURE 9. COMPARISON OF CONDENSATE WATER PHENOLIC CONTENT FROM DIFFERENT RANK COALS

Solid and semi-solid sludges and biosludges will result from wastewater treatment. The composition of these potentially biohazardous sludges will be variable. It is likely that the sludges will be rendered non-hazardous by oxidizing them at high temperatures by incineration (direct or fluid bed) or combining them with the coal feedstock or carbonaceous bottoms to be recycled to a high temperature gasifier. The role of wet-air oxidation to detoxify these sludges is under investigation.

ENVIRONMENTAL SETTING

Federal guidelines and standards along with state and local permitting authorities set the effluent specifications. Special site specific conditions and concerns can lead to stringent regulations which could conceivably dictate the degree of treatment and even the requirement for "zero discharge."

REPRESENTATIVE TREATMENT TRAIN

While a universal wastewater treatment train configuration does not exist, a inventory of unit operations are generally available to the different systems proposed for treating the condensate waters associated with low temperature coal conversion processes (Figure 10). Subsequent discussion will be confined to the treatment of low temperature condensate waters, representative of the most difficult to-treat waters, since coal pile runoff and sanitary wastes are susceptible to conventional treatment practice. The major unit operations are arranged with wastewater of intermediate compositions and/or dilution potential being interjected at various points along the treatment train. The sequence of the various steps, in particular, the extraction and stripping operations, may be interchanged:

Oil Separation

As a pretreatment to remove suspended oil, tar, grease and solids (includes settling ponds with skimmers, API separators, contrifuges, etc.). These pretreatments are not highly effective for emulsions, small particles, and substances which possess densities near that of the aqueous phase; thus dissolved air floatation which can remove these materials is sometimes employed as a follow-up pretreatment.

Steam Stripping

Removes volatile material, namely dissolved gases (NH_3, CO_2, H_2S, HCN and COS). Light, low boiling organics may also be removed. Steam requirements may vary from 0.05 to 0.2 lb. steam/lb. wastewater. Means must be provided to facilitate caustic addition to free fixed ammonia, because meeting free ammonia effluent limits in the final effluent is difficult with poorly stripped raw feeds. Process sewer streams typically require steam stripping prior to biotreatment.

Solvent Extraction

Removes gross organics, phenols and polyhydric aromatics, in particular.

Methyl isobutyl ketone (MIBK) and diisopropyl ether (DIPE) are preferred solvents, the MIBK having the broader selectivity for organic material. The requisite solvent recovery step generally involves stripping. When used in conjunction with biological systems solvent extraction tends to dampen fluctuations in organic loadings and potential toxic effects.

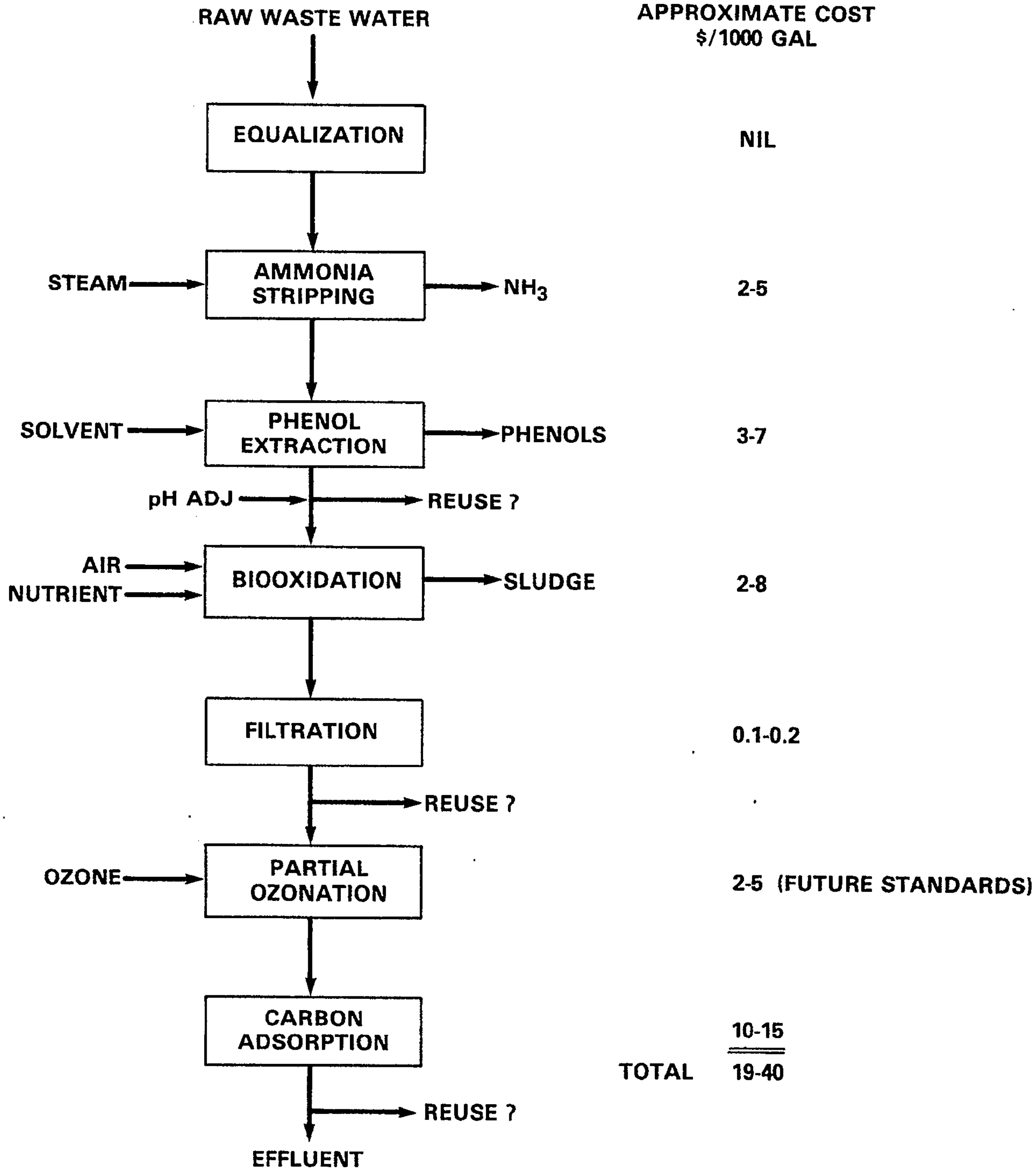

FIGURE 10. REPRESENTATIVE WASTEWATER TREATMENT TRAIN FOR COAL CONVERSION EFFLUENTS

Biological Treatment

Applicable where effluent discharge and/or reuse of a low biological oxygen demand (BOD) water is contemplated. Activated sludge treatment has a long and successful history of dealing with coking and petroleum refinery wastes which are similar in many respects to coal condensate waters. One of the principal advantages is the forgiving nature of the biological system in its ability to adapt to variable feed composition, provided abrupt changes are not encountered. It is capable of removing all the BOD (by definition) and approximately 75% of the chemical oxygen demand (COD) in the condensate waters. The susceptibility of the biological process to upsets and toxicity effects can be mitigated by introducing powder activated carbon (PAC) to the reactor. This also improves the settlability of the sludge. Polynuclear aromatics, some of which are refractory and collodial in nature, along with heavy metals, may be incorporated with the sludge and must be dealt with during disposal. The thiocynate content of the incoming feed can present difficulties, if a stringent free ammonia discharge standard must be met. The biological degradation of thiocynate releases NH_3 which may require subsequent air stripping and/or biological nitrification/denitrification. The latter step generally requires long residence times, e.g., holding ponds.

Carbon Adsorption

A polishing step to remove low level refractory organics and color bodies and may serve as a safeguard for process upsets. Prefiltration is normally required to preclude fouling of the bed. Pollutants may be leached from the bed immediately after carbon regeneration--recycle may be required.

While this touches on the more prominent conventional processes, there are a large inventory of treatment processes that may be brought to bear for special applications (Figure 11). The treatment of wastewater to discharge quality by such a train is not cheap by municipal standards. Costs are in the range of $20-35/1000 gals. This translates into an expense of 5-10% of projected synfuel selling costs--hardly a barrier to commercialization.

A recent study has shown that, if raw water and an acceptable discharge acceptor (large river or lake) is available to the plant site, e.g., an Eastern location, the most cost effective and preferred approach is to use a once-through water management plan based on PAC-biological treatment and regeneration of the PAC by wet air oxidation, as opposed to water recycle/reuse and/or "zero discharge" alternatives.

AREAS OF CONCERN AND FUTURE RESEARCH

The technology just discussed has assumed the availability of water and steady-state operation. If one considers "zero discharge" and the facility for handling process upsets, the representative treatment train needs some refinement or possible replacement. Before addressing the more stringent requirements imposed by "zero discharge" and unsteady operation, it appears useful to outline areas were perhaps the conventional technology could be improved or at least better understood.

						TREATMENT COST			
			APPLICABILITY				DEPENDENCE ON		
UNIT OPERATION	CONSTITUENT TREATED ORGANIC	 INORGANIC	GROSS REMOVAL	POLISHING	BY-PRODUCT RECOVERY	RANGE $/1000 GAL	EFFLUENT QUALITY	EFFLUENT QUANTITY	BASIS FOR RANGE
GRAVITY SEPARATION	✓	–	✓	–	–	0.10–0.20		✓	
STEAM STRIPPING	✓	✓	✓	–	✓	∿10		✓	
SOLVENT EXTRACTION	✓	–	✓	–	✓	∿5		✓	
BIOLOGICAL	✓	–	✓	–	–	10–20	✓		10,000ppm BOD
CARBON ADSORPTION	✓	–	–	✓	–	6–12	✓		{ 2,000ppm COD CARBON REGEN
OZONATION	✓	–	–	✓	–	5	✓		600ppm TOC
PRECIPITATION W/IRON	✓	✓	–	✓	–		✓		
WET-AIR OXIDATION	✓	–	✓	–	–	∿25	✓	✓	
ION EXCHANGE	–	✓	–	✓	✓	0.5–2	✓	✓	
DESALINATION PROCESSES	–	✓	✓	–	✓	5–10		✓	
INCINERATION/GASIFICATION	✓	✓	✓	✓	–		✓	✓	
DEEP-WELL INJECTION	✓	✓	–	–	–			✓	

FIGURE 11. SELECTED WASTEWATER TREATMENT OPTIONS

STATE-OF-THE-ART TREATMENT PROCESSES

Reviewing the characteristics and concerns associated with the major unit operations, several areas of research may be highlighted:

Oil Separation

The use of expendable/regenerable absorption media may be used to scavenge for neutrally bouyant entrained oleophillic materials. Absorbents such as coal, crushed slag, sand, etc., could be employed in a fluid-bed. Much of the multi-ring structured organic material is sparingly water soluble and is in the colloidal state; it appears that clarification and/or filtration enhanced with appropriate flocculation aids and polymer addition could significantly reduce the concentration of these materials.

Steam Stripping

Stripping is preferred for NH_3 concentrations $>$250 ppm. Subsequent, ammonia recovery is economical via the PHOSAM W or the Chevron process at NH_3 concentrations of 10,000 ppm and flows of 250-500 gpm. The preferred location of the steam stripping unit, before or after the extraction step, if extraction is employed, needs to be determined. Volatile organics are decreased if the stripper is located downstream of the extraction unit; however, residual dissolved solvent may enter the stripping system. The addition of lime to free fixed ammonia and reduce steam requirements also can be used to precipitate heavy metals. The addition of the lime, typically after the stripping of acid gases and free ammonia, increases softening requirements, if intensive reuse and/or concentration of waste brines is planned. A promising alternative under study is to use a liquid cation exchanger to selectively recover ammonia as a by-product and enhance stripping of the acid gases.

Solvent Extraction

As indicated, the preferred sequencing of the steam stripping and solvent extraction is not clearly established. High pH, characteristic of intensive ammonia stripping operations, causes appreciable ionization of phenols and correspondingly leads to lower distribution coefficients, the requirement of higher solvent to water ratios, and ultimately to a more costly process. The most difficult-to-extract component normally dictates the controlling solvent to water ratio. Extraction is capable of removing entrained organics such as polynuclear aromatic micelles. With the proper solvent or combination of solvents, extraction could also be effective at removing the more polar, hydrophillic organics which comprise that significant fraction of the TOC which is not extracted by commercial extraction processes, e.g., DIPE, MIBK, etc., nor by conventional analytical procedures, i.e., methylene chloride. For example, trioctyl phosphine oxide (TOPO), a stronger Lewis base than ketones, has been shown to remove 90% of the COD when used on a representative condensate water. TOPO is costly ($7-8/lb.) and solvent recovery is critical. Concomitant with the development of improved solvents and solvent systems, effective means of solvent regeneration/recovery need to be stressed.

Approximately 70% of the cost for extraction is equipment related, in contrast to stripping where a major portion of the cost is for steam. Extractor costs are nearly proportional to the number of stages. Thus there is incentive for better solvents, improved stage efficiency and an approach to true countercurrent operation. One might consider the use of ultrasonics, cavitation, etc., to obtain intimate contact between solvent and solute (especially when a low volume solvent to water ratio is used) and membranes to break the resultant emulsion. The potential role of membranes in solvent recovery may be worth exploring.

Biological Treatment

While biological treatment is effective, it is necessary to pretreat the feed or dilute it to bring the high BOD loadings (phenol in particular) to an acceptable level. With dilution, large volumes of bio-reactors are needed due to high (recycled) influent flows and residence times of several days. Solvent extraction becomes attractive for BOD levels of greater than 2000 ppm. It also reduces difficulties due to foaming. There is incentive for reducing the volume of the bioreactor systems. The use of oxygen enrichment (on-site generated oxygen is available at most coal conversion plants) should be considered to reduce volumes. The use of fluid bed bioreactors is being studied to greatly increase volumetric loadings of biosubstrate with a corresponding decrease in residence time requirements. Oxygen availability becomes controlling in such a system--coupled with enriched air, approximately an order of magnitude decrease in residence time can be achieved. While fluid bed systems require pumping power to recycle the wastewater and maintain the bed, the energy requirements are about one half those associated with aeration for air-activated sludge systems. Because of the reduced residence times, and availability of developed substrate to the process, it is anticipated that fluid bed reactors will be more accommodating to process variability and recover more quickly from process upsets. The potential role of PAC to help mitigate possible upsets in fluid bed biosystems should be investigated. Bioreactor staging can be considered as another means of increasing specific bioactivity and better accommodating process variability. In a single mixed reactor, concentrations are close to effluent concentrations; consequently, reaction rates are low. By approximating plug flow through staging, higher BOD loadings can be effected on the average, along with higher reaction rates. Appropriate real time instrumentation to anticipate toxic effects is desired, in lieu of monitoring completeness of thiocyanate degradation as a lead indicator.

It has been shown that the major fraction of TOC resistant to biological degradation has a molecular weight $>$30,000 and likely represents bio-organism wastes. Research at characterizing of and determining techniques for removing these materials is needed. It is quite likely that they are sparingly soluble and enhanced clarification/flocculation techniques could be applicable.

Carbon Adsorption

Because carbon consumption is related directly to the TOC of the water being treated, activated carbon is generally used as a polishing step. The performance of carbon with respect to the high molecular weight organics, touched on above, is uncertain. It has been found that ozonation prior to treatment improves the adsorption efficiency for multi-ring compounds from 50-60% to 90% or better. A major uncertainty exists with respect to carbon regenerability, especially in brackish waters. Acceptable carbon treatment costs are based on the premise of complete regeneration, with secondary loss and make-up of 5%. The actual capacity, effectiveness of regeneration and costs, for activated carbon when used in a polishing mode on condensate water needs to be better established.

PHYSICAL/CHEMICAL OPTIONS

Alternative treatment processes deserve consideration due to the relative high costs associated with the series of five or more process steps that comprise the typical state-of-the-art treatment train. An additional consideration is the concern over system reliability resulting from sequencing several unit operations, especially when a biological step, that is vulnerable to upsets, is in the train.

As previously indicated "zero discharge" considerations can impose an additional and overriding constraint. An end-of-the-pipe approach is to use desalting technology to control the salt content of the effluent to render it suitable for recycle/reuse at the front end of the process. The high quality of the effluent from the representative treatment train should insure the effluent is amenable to conventional desalting (distillation/reverse osmosis) and, depending on the hardness, some softening may be desirable to facilitate high product water recovery and reduce the quantity of brine that requires further concentration/disposal. Cooling towers have been universally used to cost-effectively reject process heat and perform the initial concentration of process wastewaters. Typically, filtered effluent from the activated sludge unit is used as make-up to the tower, although use of DIPE extracted, steam stripped condensate water is contemplated for the ANG dry-ash Lurgi plant at Beulah, North Dakota. Based on petroleum experience, it appears that cooling towers can handle BOD loadings up to 500 ppm in the make-up water. An area of concern, in addition to potential drift and odor difficulties, is the allowable concentration factor before biofouling and corrosion problems become a detriment to the heat exchanger loop. A study is underway to obtain a better handle on these limitations.

Ideally, one desires a single process step that can take the raw wastewater process stream and produce a moderate to good quality stream suitable for reuse and a small highly contaminated stream that can be treated intensively (Figure 12). Solvent extraction (previously discussed), distillation (vapor recompression, in particular), and membrane processes represent candidates for the major separation process, while wet-air oxidation, incineration, gasification, dirty steam generation, etc., could be used to deal with the resultant concentrate and render it acceptable for ultimate disposal. Distillation and membrane processes also can be used to retain the salts in the concentrated stream and, in this respect, are superior to solvent extraction which must be coupled with ion exchange or another desalination process to achieve this end. It should be noted that the product water may concentrate stream will have a very small volume, high unit processing costs can be tolerated. The limitations and tradeoffs associated with the distillation of poor quality wastewaters require better definition. The full integration of these processes with the conversion plant, proper, should be emphasized. Costs are estimated to be in the range of \$6-12/1000 gallons, thus there appears to be adequate leeway for system refinement and optimization to be competitive with a conventional treatment train.

Membranes

The potential application of membrane processes (ultrafiltration and reverse osmosis) to the concentration of raw coal condensate waters is relatively long range. Progress has been made in producing composite membranes from stable substrate polymers such as a porous polysulfone coated with an exceedingly thin film (~200Å) of salt rejecting membrane, for example a highly crosslinked polyurea. Polyurea membranes exhibit good stability at high and low pH's and in the presence of aromatic solvents. In general, membrane rejection for ammonia is poor and, as a consequence, any membrane concentration process will probably require steam stripping. The rejection of phenols is improved at high pH's (~11); as a consequence, the addition of lime to abet NH_3 stripping will also enhance rejection of ionizable organics. This is in contrast to solvent extraction processes.

The raw condensate water will likely undergo oil separation and filtration (essential, yet negligible cost pretreatments) prior to the reverse osmosis units. The physical configuration of the membrane unit has a bearing on the capability of handling a fouling/dirty feed--dead spots must be avoided to preclude the deposition of material and progressive pluging of the unit. Normally, tubular membranes are used (the influent flowing inside the tubes/tubule bundle) to assure positive flow. Membrane units of this configuration are in commercial applications on cheese whey and latex paints. In addition to the preferred membrane composition, open to question is the degree of concentration that can reliably be effected with a membrane unit--5 to 1 represents a conservative estimate, with 10 or 15 to 1 as probably an upper limit. Very preliminary estimates of membrane separation costs are \$4-8/1000 gallon; thus although the recovery may not be as high as vapor-recompression systems, the lower unit costs could more than compensate the larger volume of concentrate subject to subsequent treatment, e.g., wet-air oxidation. It would seem prudent to support a continuing research effort to advance the application of membranes to condensate waters and solvent recovery (previously mentioned).

Wet-Air Oxidation

Ideally wet-oxidation can convert pollutants to CO_2, N_2 and H_2O by reaction with oxygen at high temperature and pressure. Because of the large flows and expense for pressure vessels and heat exchangers, there is considerable incentive for optimizing and moderating reaction conditions. Only limited research is being directed at these tradeoffs. Costs are proportional to water throughput and advantage can be obtained from the combustion heat associated with high levels of organics. Costs are uncertain, but are expected to be in the range of \$20-30/1000 gallons. Wet-air oxidation require a polishing step to remove dissolved gases and/or hydrophillic organics (generally of a low molecular weight) that could interfere with the specific reuse application.

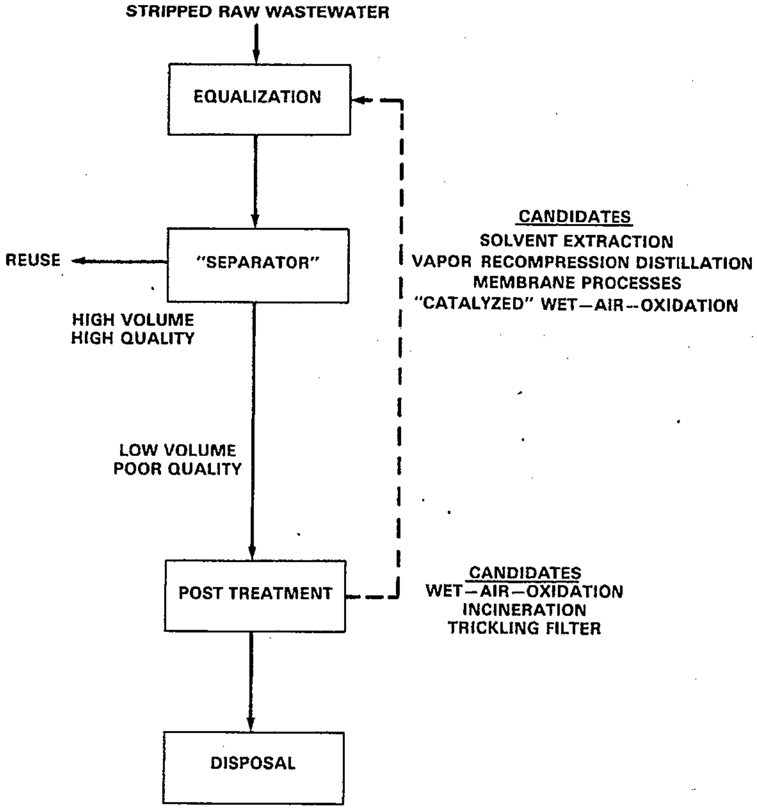

FIGURE 12. PHYSICAL/CHEMICAL OPTION

Distillation

The energy requirements for distillation processes can be greatly reduced by staging (multi-effect evaporators) and/or using vapor-recompression systems. The low quality heat, required for multi-stage evaporation, is readily available on-site and distillation processes might be expected to serve as an effective "bottoming cycle" to the conversion plant. High quality energy is required to run the fan compressor deployed in the vapor-recompression system; this, however, represents a small fraction (approximately 1/50) of the energy required for single stage distillation. Concentration factors as high as 25 have been achieved on raw condensate waters, with pretreatment involving the sequential addition of acid to remove temporary hardness and suppress carbonate scaling and caustic to ionize the phenolic compounds and hold them in the concentrate during the distillation. The distillate may require polishing (activated carbon treatment) for a high quality use such as boiler feed make-up. The concentrate will probably require wet-air oxidation or an equivalent treatment and evaporation to dryness. As the is deserving of continued attention to treat small flows of relatively concentrated streams.

REUSE

A number of water reuse options which avoid release to a surface acceptor are apparently evolving in commercial designs. As previously indicated, many processes are net water consumers; thus there is incentive for closing the "loop." The more prominent reuse options and their advantages and disadvantages are compared in Figure 13. Ideally it is economically desirable to use as poor a quality of water as the reuse application will permit. Many of the recycle systems are merely paper designs and it is not clear that special precaution has been taken to preclude the build-up of trace extractables including organics and corrosion products which may inadvertently react with or precipitate from the recycle loop, thereby impairing the operation and reliability of the system. Many times such difficulties are hard to anticipate. There appears to be room for more systems engineering, tradeoff and optimization at the "tail" of the water use cycle where the waste brine is typically concentrated for disposal. Innovation should be encouraged in this part of the cycle.

OPTION	POTENTIAL ADVANTAGES	POTENTIAL DISADVANTAGES	UNCERTAINTIES
REINJECTION INTO CONVERSION PROCESS	• "ZERO" DISCHARGE • DECREASES WATER USE • CAN CONSERVE SENSIBLE HEAT • LITTLE TREATMENT REQUIRED	• CONCENTRATION STEP MAY BE REQUIRED TO PRESERVE WATER BALANCE • PROCESS CHANGES MAY BE REQUIRED TO ACCOMMODATE	• RELIABILITY AND COST • SOME MATERIALS MAY FAVOR RECYCLE LOOP, MAKING PURGE NECESSARY • NATURE OF SOLID WASTES MAY BE MODIFIED
MAKE-UP FOR COOLING TOWERS	• "ZERO" DISCHARGE • DECREASES WATER USE	• SIGNIFICANT PRETREATMENT MAY BE REQUIRED • MAY NOT BE APPLICABLE ON YEAR-ROUND BASIS	• RELIABILITY AND COST • CONTAMINANTS IN DRIFT MAY PRESENT PROBLEM • CORROSIVE NATURE AND SPARINGLY SOLUBLE CONSTITUENTS MAY PRESENT DIFFICULTY
MAKE-UP FOR FLUE GAS DESULFURIZATION UNIT	• SAME AS ABOVE • COULD IMPROVE FORCED OXIDATION OF SLUDGE	• TRACE METAL PPT MAY ADVERSELY AFFECT LIME REACTIVITY	• TRACE ELEMENTS IN SLUDGE MAY PRESENT PROBLEM
WET-DOWN FOR DUST CONTROL AND IRRIGATION	• "ZERO" DISCHARGE • ASSISTS IN CONTROL OF FUGITIVE EMISSIONS • ABETS REVEGETATION EFFORT	• SIGNIFICANT PRE-TREATMENT REQUIRED • INTRUSION OF TRACE ELEMENTS AND REFRACTORY ORGANICS INTO ECOSYSTEM AND AQUIFERS	• EXTENT OF NATURAL "DETOXIFICATION" OF CONTAMINATED WASTES
BOILER FEEDWATER	• "ZERO" DISCHARGE	• SIGNIFICANT TREATMENT AND DEMINERALIZATION REQUIRED	• COST
FEED FOR SANITARY SYSTEM	• SAVE POTABLE WATER	• TREATMENT REQUIRED TO CONTROL COLOR AND ODOR. ADDITIVES MAY WORK	• COST BENEFIT • COLOR AND ODOR MAY CAUSE OBJECTIONS • EFFECT ON BIOTREATMENT PLANT

FIGURE 13. SELECTED WASTEWATER "REUSE" OPTIONS

CONCLUSION

While existing wastewater treatment technology, which is primarily based on biological oxidation, appears capable of meeting current discharge permit requirements, there is a need for confirmatory operating and performance data on large scale (low temperature) coal conversion facilities that produce and treat large volumes of highly contaminated condensate water. Considerable need and incentive exists for sustaining and expanding the ongoing R&D on state-of-the-art wastewater treatment trains, physical/chemical alternatives and sludge disposal options. The control and disposal of secondary pollutants which has not been addressed in this presentation should not be overlooked--the problem of salt disposal for "zero discharge systems" remains a concern. Greater emphasis should perhaps be given to system reliability, this aspect assuming greater import as plants get closer to being operative.

ACKNOWLEDGEMENT

The technical contribution of a number of individuals and their respective organizations which have worked for the Environmental Technology Division, Office of Environmental Programs, Assistant Secretary for Environmental Protection, Safety, and Emergency Preparedness, U.S. Department of Energy, is acknowledged. Special appreciation is expressed to J. King, University of California, for leading the recent wastewater workshop and providing insight into solvent extraction processes; J. Klein, ORNL, for initiating work on PNA control and the design and testing of an advanced treatment train; C. Drummond, PETC, for comparative treatability studies on gasification and liquefaction condensate waters; R. Luthy, Carnegie Mellon; and F. Castaldi, Engineering Science, Inc., for an assessment of water treatment options including solvent extraction and biological oxidation with PAC; and D. Goldstein, WPA, for a survey of reuse alternatives and recommendations for water management. Further details of these studies along with other Governmental and industrial research is contained in the workshop proceedings entitled "Processing Needs and Methodology for Wastewater from Coal, Oil Shale and Biomass Synfuel Processes-II" and will be made available upon request to the Division.

PB83-128280

CHARACTERIZATION OF COAL CONVERSION WASTEWATERS USING ON-SITE GC/MS †

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ABSTRACT

This paper discusses a study which was done to characterize a wastewater stream from a coal gasification facility using on-site extraction and GC/MS analysis. The objectives of this program were to:

- Characterize the wastewater organic components primarily for selected Priority Pollutants, Appendix C and Synfuels compounds,
- Investigate the stability of these compounds under refrigeration and ambient storage, and
- Evaluate the destruction of organics by wet oxidation.

Extractable material in the wastewater consisted primarily of phenols and alkylphenols. These compounds accounted for about 98 percent of the total organic mass identified. Several polynuclear aromatic (PNA) compounds were also identified. Deterioration in the composition of the sample was observed over a one month period. This was most evident in the concentration of dimethylphenols which dropped approximately 75 percent during two weeks of refrigerated storage. Ambient sample storage produced a greater decrease in the concentration of phenol but did not appear to affect the alkylphenols or the base/neutral compounds as much as phenol. It is expected that the observed changes in composition would hamper any off-site wastewater treatability studies with water of this type. Treatment of the wastewater by wet oxidation was also evaluated and found to remove greater than 90% of the extractable organics.

INTRODUCTION

The Chapman-Wilputte gasifier at the Holston Army Ammunitions plant in Kingsport, Tennessee, has been the site of several environmental assessment tests. This study deals with an effort to characterize more accurately the aqueous process condensate (separator liquor wastewater) at this facility. Previous studies have shown the Holston process condensate to be similar in composition to the Lurgi process condensate from the Kosovo plant* especially with respect to phenolic compounds.

Lurgi gasification facilities have been proposed for commercial plants in the United States but current operating facilities are not easily accessible. The Holston plant is located in the United States and provides a readily accessible source of coal gasification wastewater for characterization and treatment system development.

Successful treatment of wastewaters requires a good understanding of the composition of the wastewater and the chemistry involved in any decomposition. Previous characterization studies may have been conducted on samples that had deteriorated during shipment and cold storage. Analysis of a deteriorated sample can produce results which do not accurately reflect the composition of the water as it would be fed to a treatment system.

This study included immediate, on-site extractions which were performed in an attempt to minimize any sample deterioration. The on-site Hewlett-Packard Model 5993B gas chromatograph/mass spectrometer (GC/MS) provided immediate analysis of the sample extracts as well as the positive identification of any compound present. It could also identify and track the appearance and/or disappearance of compounds during decomposition.

The main objectives of this program were:

- to provide a more accurate characterization of the aqueous process condensate;
- to investigate sample stability during refrigerated and ambient storage; and
- to investigate the effects of wet oxidation on this wastewater.

PROCESS DESCRIPTION

The Chapman-Wilputte gasification process uses an air-blown, atmospheric pressure gasifier. It gasifies approximately one ton of bituminous coal an hour to produce a fuel gas with average heat content of 150 Btu/scf. The product gas is first quenched then cleaned via direct contact with the process water. The resulting liquor collects in a liquor separator. Here the aqueous layer is decanted from the oils and tars which were removed from the gas stream. The tar layer is recovered for use as a supplemental boiler fuel and the aqueous layer is recirculated through the gas quenching/scrubbing system.

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*Collins, R. V., K. W. Lee, and D. S. Lewis. Comparison of Coal Conversion Wastewaters. EPA 600/9-81-006. Contained in the Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology V, St. Louis, MO, (September, 1980). Radian Corporation, Austin, TX, January, 1981.

Excess water is blown down via an over flow weir to a holding sump. From there, the accumulated water is periodically pumped to a forced evaporator system for ultimate disposal. The brine and tar resulting from the evaporation is returned to the separator. There is no fresh water make up to the system and the net accumulation of water is minimized through the proper operation of the gasification and cleaning systems. Grab samples of the process condensate were collected from the aqueous layer in the separation tank at the point indicated in Figure 1.

PROCEDURES

SAMPLING

Grab samples of the aqueous process condensate were collected from the separator near the off take for the recirculating quench system. The water at this point contained a minimum amount of tar. The pH and temperature of the water were measured at the time of collection.

EXTRACTION

Samples were extracted using a base/neutral-acid extraction procedure. The separator liquor was first basified to pH$\geqslant$12 with NaOH and extracted with methylene chloride followed by diethyl ether to obtain the basic and polynuclear aromatic compounds. It was then acidified to pH $\leq$2 with HCl and extracted as before to obtain the phenolic compounds. The pH adjustment provided enhanced recovery of the basic and acidic compounds and the diethyl ether provided a polar medium for enhanced extraction of phenols. Extracts were concentrated by a factor of ten using a Kuderna-Danish apparatus. Further concentration was not possible due to the large amount of material present in the extracts.

ANALYSIS

Extracts were analyzed using EPA Priority Pollutant conditions* for acid, base/neutral and purgeable componds on a Hewlett-Packard 5993B gas chromatograph/mass spectrometer.

CHARACTERIZATION OF THE AQUEOUS PROCESS CONDENSATE

EXTRACTABLE COMPOUNDS

The base/neutral and acid extracts were analyzed for EPA base/neutral and acid extractable Appendix A Priority Pollutants as well as those compounds listed as Appendix C and Synfuels "priority pollutants". Additional compounds that might occur in coal conversion processes were included based

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*U. S. Environmental Protection Agency. Federal Register 44(233), 69464-69575, 1979.

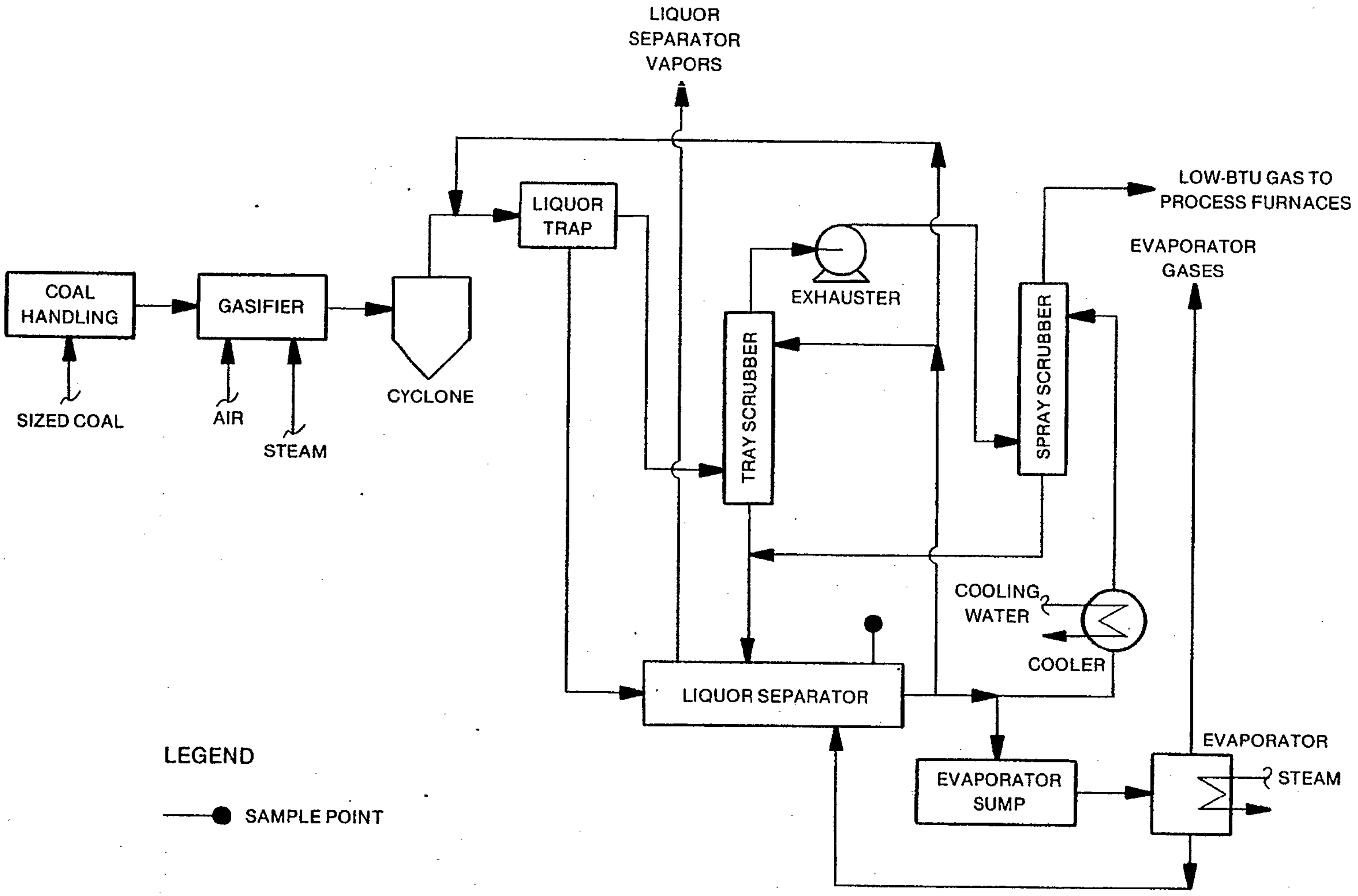

Figure 1. Location of water sampling point in process

on their documented behavior in biological oxidation systems* or their known or suspected carcinogenic activity.

Table 1 summarizes the results of the characterization study. The majority of the compounds identified were of a phenolic nature. Phenol, methylphenol, and dimethylphenol account for 98 percent of the total extractable organics. Significant levels of PNA's were also found. The values given represent the average concentration and the range of these values during the six days of monitoring.

The ranges of values indicate that significant variability exists in the data. In an effort to find the source of this variability, a followup study was done using Holston separator liquor which had been collected 24 hours prior to extraction and stored in amber bottles at 4°C since the time of collection. Determinations of instrument variability and extraction variability were made by replicate extractions and replicate analyses of the extracts. Values for representative compounds for instrument variability are given in Table 2. Values for representative compounds for overall (extraction and analysis) variability are listed in Table 3. The instrument variability for total chromatographable organics (TCO) is 1.7 percent while overall variability is 13 percent. This indicates that essentially all of the variability (12.9 percent) is due to extraction for chromatographable organics as a group. This same trend is also seen in the representative compounds presented in the tables except for naphthalene which is close to the detection limit. While the relative standard deviation (1σ) for the overall variability of phenol is only 16 percent, the cresols and naphthalene vary by 47 percent and 34 percent, respectively. These same trends were also observed in the samples which were extracted on-site.

Part of this variability may be due to the complexity of the wastewater sample matrix. The extraction procedure does not produce a clean separation between the base/neutrals (B/N) and the acids (A). . Much of the phenolics were extracted into the B/N fraction. The B/N extracts were also analyzed for phenols and the concentrations of phenols found in this fraction added to the values obtained in the acid fraction. The magnitude of this premature extraction is shown in Table 4. The concentrations of phenol show the greatest amount of variability in the base/neutral extract while the concentrations of phenol in the acid extract remain fairly constant. The dimethylphenols, some of the least acidic phenolic compounds identified, demonstrated the greatest amount of extraction into the B/N fraction.

VOLATILE ORGANICS

Volatile species (purgeable halocarbons and aromatics) were also determined in the raw water. These compounds, listed in Table 5, do not show

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*Singer, P. C., F. K. Pfander, J. Chinchilli, A. F. Maciorowski, J. C. Lamb III, and R. Goodman. Assessment of Coal Conversion Wastewaters: Characterization and Preliminary Biotreatability. EPA 600/7-78-181, PB-294 338. University of North Carolina, Department of Environmental Sciences and Engineering, Chapel Hill, NC, September, 1978.

TABLE 1. CHARACTERIZATION DATA FOR EXTRACTABLE SPECIES IN SEPARATOR LIQUOR

Identifications/Compound	Concentration in the Liquor (mg/L)	
	Average	Range
Acid Extractable Compounds		
† Phenol	2400	1900 - 3400
Methylphenols	3200*	1500 - 4700
+ Dimethylphenols (total)	1200	330 - 1900
†‡ 2,4-Dimethylphenol	420	98 - 820
Trimethylphenol	0.82	0.35 - 2.2
Indanol	1.7	< 0.07 - 3.2
1-Naphthol	5.0	3.3 - 8.5
2-Naphthol	6.7	5.4 - 9.2
Resorcinol/Catechol	30	3.6 - 65
Hydroxybenzaldehyde	5.7	< 0.18 - 19
Base/Neutral Extractable Compounds		
† Naphthalene	8.6	1.6 - 17
† Acenaphthylene	3.6	1.2 - < 6
† Fluorene	2.6	0.28 - < 6
† Phenanthrene/Anthracene	2.3	0.7 - < 6
† Fluoranthene	5.7	0.3 - < 9
† Pyrene	5.7	0.4 - < 9
† Bis(2-ethylhexyl)phthalate	12	1.2 - 32
✓ † Chrysene	0.12	
✓ Benzo(b)fluoranthene	0.10	
✓ † Benzo(a)pyrene	0.12	
✓ Pyridine	1.2	
2-Ethylpyridine	18	1.3 - 61
Quinoline	3.1	0.62 - 5.6
✓ 4-Methylquinoline	0.11	
1-Methylnaphthalene	2.3	0.43 - 4.3
2,3-Dimethylnaphthalene	2.3	0.65 - < 4.5
2,6-Dimethylnaphthalene	2.2	< 1.3 - < 3
Indole	12	8 - 14
2-Methylindole	12	2.2 - 16
3-Methylindole	2.4	0.58 - 3.6

† Appendix A Priority Pollutants

* One data point not included in the average was rejected due to extremely high value, but compound was identified 6 of 6 times.

\+ Includes 2,4-DMP.

‡ The portion of 2,4-DMP from the B/N fraction was estimated from the amount found in the acid fraction. The value presented here represents the sum of the acid and B/N fraction.

✓ Identified only in one of six samples.

TABLE 2. VARIABILITY IN ANALYSIS

	Average* (mg/L)	% Relative Std. Deviation ($\frac{\sigma}{x}$ x 100)
Phenol	2000 ± 190	9.5 %
Cresol	1200 ± 210	17.5 %
Naphthalene	3.2 ± 1.8**	56.0 %
Total Chromatographable Organics	4200 ± 70	1.7 %

* For three determinations.
**Close to detection limit.

TABLE 3. VARIABILITY IN EXTRACTION AND ANALYSIS

	Average* (mg/L)	% Relative Std. Deviation ($\frac{\sigma}{x}$ x 100)
Phenol	1700 ± 230	16 %
Cresol	800 ± 380	47 %
Naphthalene	3.5 ± 1.2**	34 %
Total Chromatographable Organics	3700 ± 480	13 %

* For three determinations of the combined variability (extraction and analysis).
**Close to detection limit.

TABLE 4. EXTRACTION OF PHENOLIC COMPOUNDS INTO BASE/NEUTRAL EXTRACT

Compound	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
Phenol (mg/L)						
Acid	1900	2200	1600	1800	1800	1800
B/N	370	590	1800	470	120	100
Total	2300	2800	3400	2300	1900	1900
B/N % of Total	16	21	53	20	6	5
Methylphenols (mg/L)						
Acid	1800	1500	690	1200	900	1100
B/N	2400	3200	30000	2900	580	430
Total	4200	4700	30700	4100	1500	1500
B/N % of Total	57	68	98	71	39	29
Dimethylphenols (mg/L)						
Acid	230	400	44	120	130	81
B/N	1300	1300	1900	1100	220	250
Total	1500	1700	1940	1200	350	330
B/N % of Total	87	76	98	92	63	76

TABLE 5. CHARACTERIZATION DATA FOR VOLATILE ORGANIC COMPOUNDS

	Average* (ug/L)	% Relative Std. Deviation ($\frac{\sigma}{x}$ x 100)
Benzene	630	12 %
Toluene	420	9 %
Ethylbenzene	48	69 %
Total Xylenes	280	25 %

*For six determinations.

the level of variability seen in the extractable compounds since the additional variability associated with extraction was not introduced.

INVESTIGATION OF SAMPLE STABILITY

The second objective of this program was to determine the effects of refrigeration and ambient storage of the wastewater on the stability of its composition. The refrigerated sample of water was stored in an amber bottle at 4°C for one month, while the ambient sample was stored in an amber bottle at ambient temperatures (up to approximately 35°C) for three weeks. These samples were then extracted and analyzed. The results were then compared to aliquots of the same sample which had been extracted immediately on-site. Figure 2 illustrates how the concentrations of representative compounds decreased with storage. The figure shows that the concentrations of most compounds appear to decrease more during ambient storage than when kept under refrigeration. However, a high relative error associated with the analysis may account for some of the differences observed in concentration between the ambient and refrigerated samples.

Physical changes were also observed in the sample stored under ambient conditions. These include a darkening of the color as well as an increase in the turbidity of the water.

WASTEWATER TREATABILITY BY WET OXIDATION

The third objective of this study was to evaluate the efficiency of removal of organics from process condensate by wet oxidation. The wet oxidation apparatus used to treat the wastewater is shown in Figure 3. Immediately after collection, approximately one liter of the water sample was placed in a stainless steel bomb, heated to 500°F and simultaneously pressurized to 1500 psig with zero air. The bomb remained under these conditions for about 30 minutes. After cooling and then depressurizing, an aliquot of the oxidized water was extracted, analyzed and compared to an aliquot of the unoxidized water sample which had been extracted immediately after sampling.

Table 6 compares the concentrations of each compound determined in the fresh aliquot to those determined in an aliquot of the same sample after wet oxidation. The amount of total extractable organic material is significantly reduced, from 8000 mg/L to approximately 600 mg/L or 8 percent of the original amount. The level of total phenols was reduced to approximately 10 percent of the original concentration. Phenol itself showed the least loss with an 85 percent reduction compared to methylphenols and dimethylphenols which exhibited about a 95 percent reduction in concentration. The less than values represent the detection limit of the instrument for each day of analysis.

Wet oxidation significantly reduced the high concentration of the phenol and alkylated phenols. Previous work by Singer, et al* shows that these

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Singer, P. C., 1978, (op. cit.).

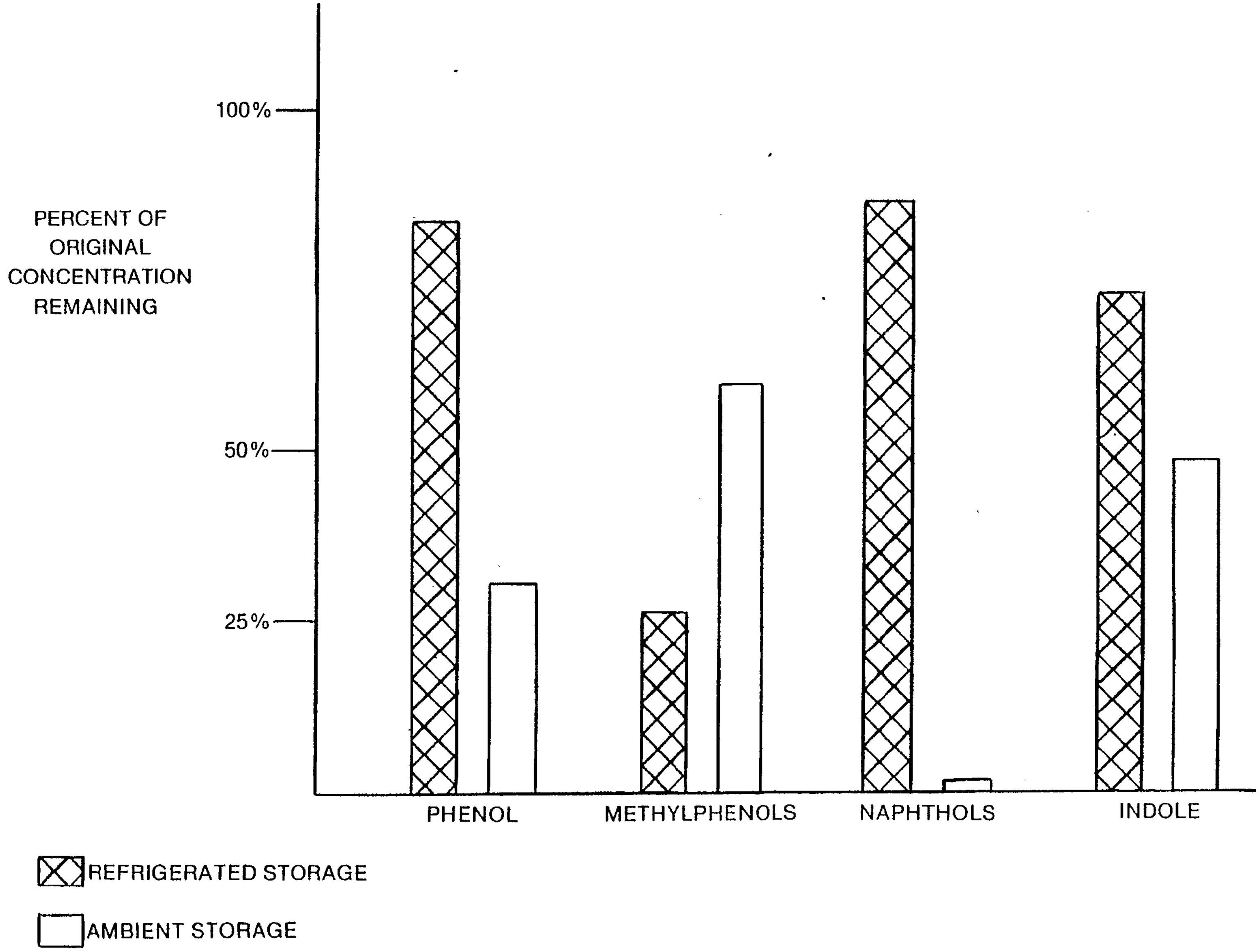

Figure 2. Results of the stability study

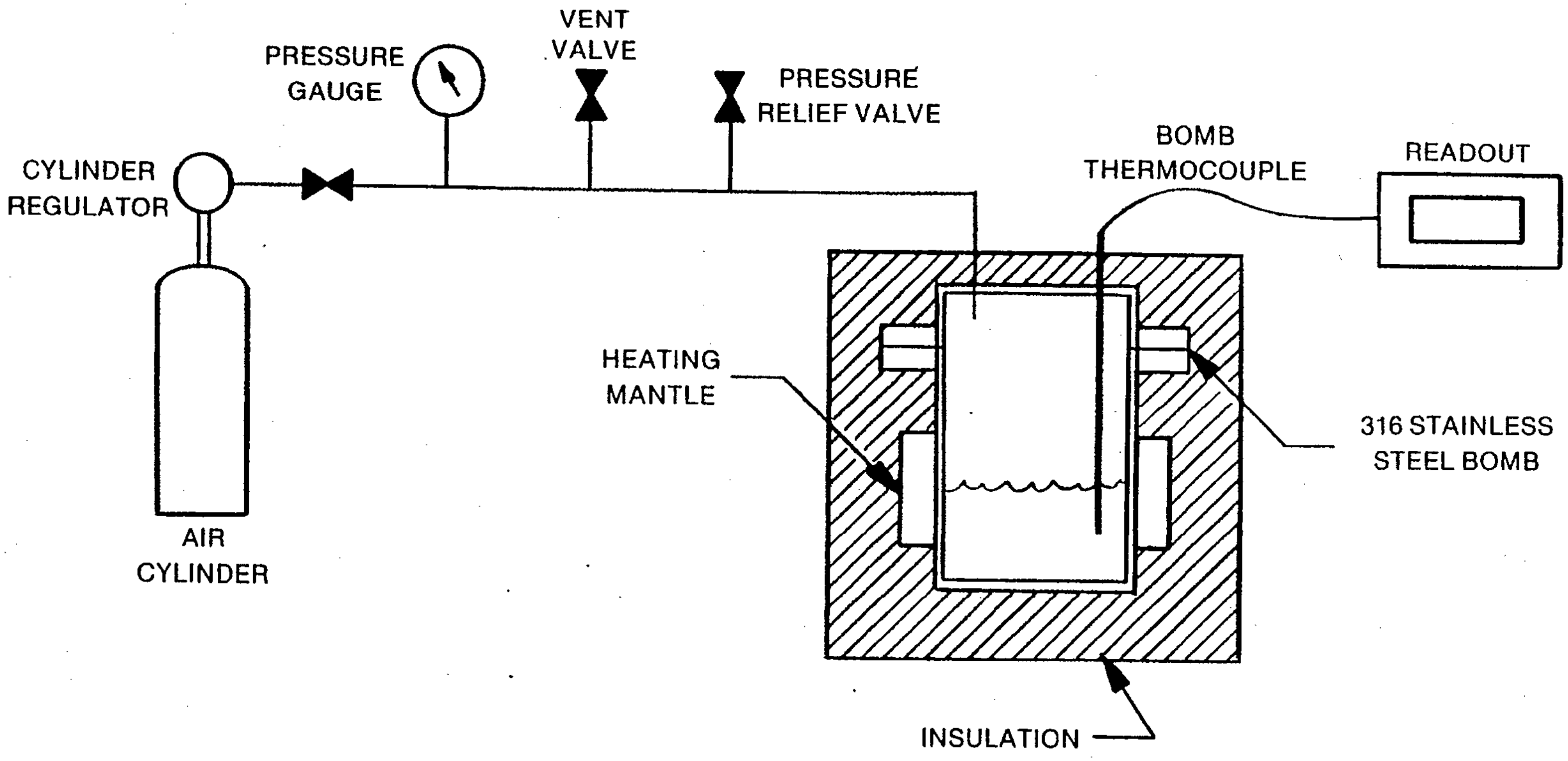

Figure 3. Schematic of the wet oxidation apparatus

TABLE 6. EFFICIENCY OF ORGANIC COMPOUND REMOVAL FROM SEPARATOR LIQUOR BY WET OXIDATION

Compound	Resistance to Bio-degradation†	Concentration (mg/L) Fresh Sample	After Wet Oxidation	% Removal Efficiency from Control Sample
Total Extractable Organics (as determined by the sum of the total chromatographable organics and the gravimetric residue after evaporation)		7900	600	92 %
Phenol	E	1900	280	85 %
Methylphenols	E	1500	80	95 %
Dimethylphenols	E/R	330	12	96 %
2,4-Dimethylphenol	NR	120	< 2.8	> 98 %
Trimethylphenol	M/R	2.2	< 0.63	> 71 %
Indanol	R	1.2	< 0.27	> 78 %
1-Naphthol	M	4.3	< 0.63	> 85 %
2-Naphthol	E	6.0	< 0.27	> 96 %
Resorcinol/Catechol	E	20	< 2.0	> 90 %
Hydroxybenzaldehyde	E/M	< 0.3	2.2	> 90 %
Naphthalene	E	1.6	< 1	> 38 %
Acenaphthylene	NR	1.5	1.0	33 %
Fluorene	NR	0.49	< 2	NA
Phenanthrene/Anthracene	NR	0.70	< 2	NA
Fluoranthene	NR	0.3	< 3	NA
Pyrene	NR	0.4	< 3	NA
Bis(2-ethylhexyl)phthalate	NR	1.4	0.34	76 %
Chrysene	NR	0.12	< 1	NA
Benzo(b)fluoranthene	NR	0.10	< 1.6	NA
Benzo(a)pyrene	NR	0.12	< 1	NA
Pyridine	R	1.2	< 1	NA
2-Ethylpyridine	R	1.3	< 1.7	NA
Quinoline	E	0.62	< 1.1	NA
4-Methylquinoline	R	0.11	< 1.1	NA
1-Methylnaphthalene	E	0.43	< 1.2	NA
2,3-Dimethylnaphthalene	R	0.65	< 1.6	NA
Indole	M	8.0	< 3.4	> 58 %
3-Methylindole	E	1.4	< 1	> 29 %

† = Reference 2
E = Easily Degraded
M = Moderately Degraded
R = Resistant to Degradation
NR = Biodegradation data not reported
NA = Not Applicable

compounds are also easily treated by bioxidation. However, wet oxidation also has the ability to reduce the levels of organic compounds which are not readily treated by biological systems. Figure 4 illustrates the efficiency of this reduction in the levels of a few representative compounds which are moderately biodegradable and/or resistant to biological treatment. The concentration of 1-naphthol, which is moderately resistant, was reduced by greater than 85 percent; trimethylphenol, which has both resistant and moderately resistant isomers, was reduced by 71 percent and the concentration of indanol, which is resistant to bioxidation, was reduced by greater than 78 percent. In all cases this reduction is greater than 70 percent. This value is outside the limits of the analytical variability discussed previously, indicating definite trends in the removal of organics. Table 6 also indicates the resistance to biodegradation (where available) for each of the other compounds not discussed in this section.

However, despite this efficiency, the overall feasibility of wet oxidation is limited. This is because 1) this technology is still in the developmental stages and 2) there are high costs associated with this process. To date, its usefulness is limited to a few specific applications where there is a need for treatment of highly toxic and/or small volume organic laden streams.

CONCLUSIONS

The following statements summarize the results of this study.

- A loss of sample integrity during sample handling and storage is indicated even when samples are refrigerated.
- Much variability is associated with the complex matrix of this aqueous process condensate. Better separation procedures are required before these samples can be more accurately quantified.
- It is possible to operate a GC/MS system under field conditions.
- About 95 percent (by mass) of the identified compounds are readily biodegradable.
- Wet oxidation reduced the levels of extractable organics by greater than 90 percent.
- Wet oxidation reduced the levels of some compounds which are not readily biodegradable.

RECOMMENDATIONS

The following recommendations, are presented in response to difficulties encountered during sample analysis and data reduction. Since a large source of variability seems to be associated with the extraction of phenols into the

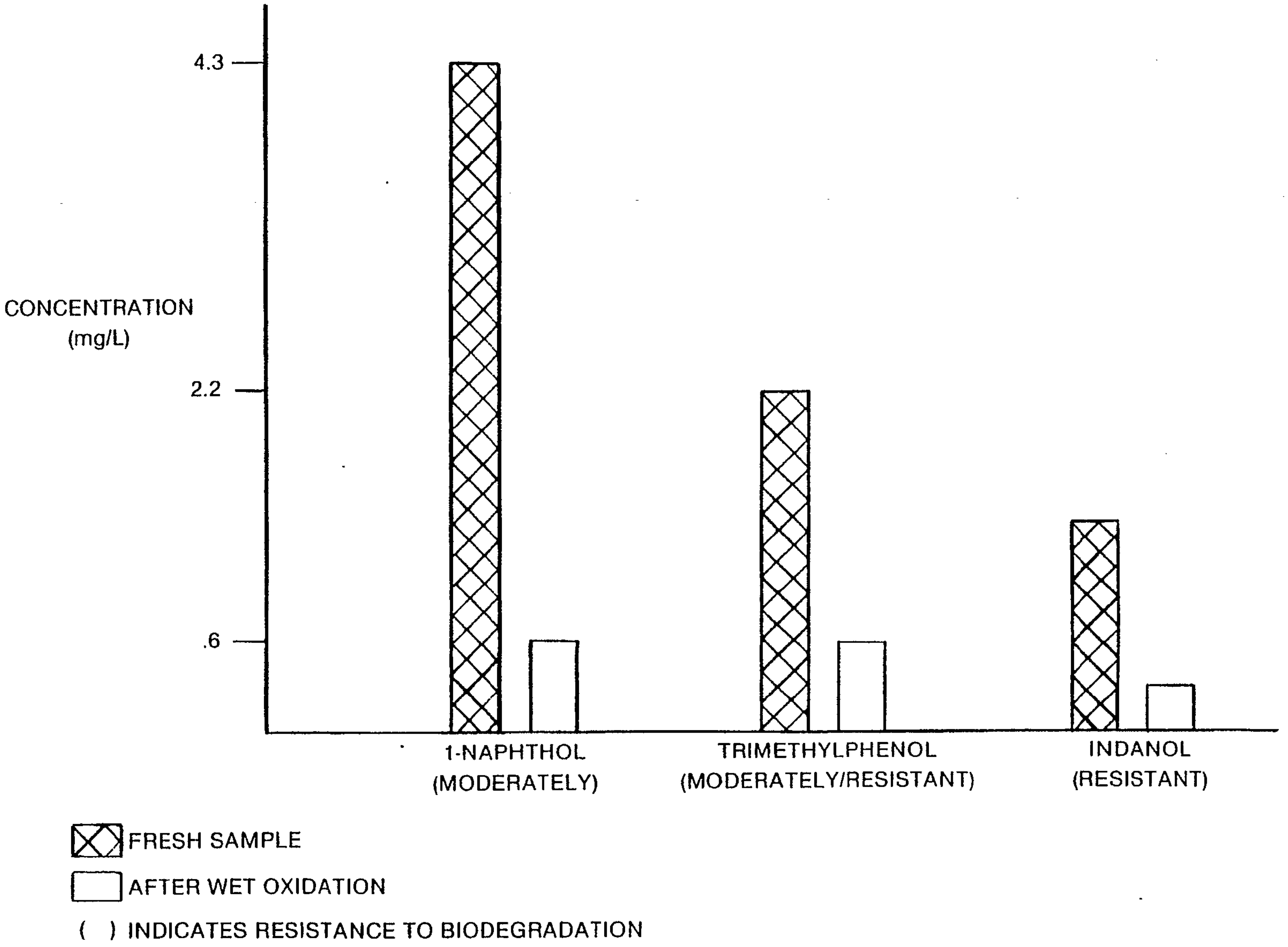

Figure 4. Wet oxidation results for compounds not easily biodegradable

base/neutral fraction, an extraction technique which provides good partitioning of acid and base/neutral compounds is required. This might be achieved by an acid/neutral followed by a basic extraction, then separation of the acid and neutral compounds by liquid chromatography or a less vigorous extraction of base/neutral compounds, using only methylene chloride for the base/neutral compounds, but continuing with a methylene chloride/diethyl ether extraction for the acidic compounds.

Sample analysis could also be facilitated by using a capillary column to provide better chromatographic separation in place of a packed column specified by EPA protocol. Use of the capillary column would allow better speciation of the compounds present.

The need for on-site extraction and GC/MS analysis has not been established. The possiblity of on-site extraction/off-site analysis should also be investigated. The stability of the extracted samples should be evaluated by analysis of the extract immediately after extraction and at predetermined intervals following the extraction to monitor any decrease in one or more compounds. If the stability of extracted samples is adequate to allow transport and storage, the expense of providing on-site analysis could be avoided.

PB83-128298

TREATMENT OF WASTEWATER FROM A FIXED-BED ATMOSPHERIC COAL GASIFIER†

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ABSTRACT

Previous studies using a simulated coal conversion wastewater have demonstrated the feasibility of treating this type of waste by an activated sludge process. Phenol concentrations were reduced to levels below 1 mg/l and the toxicity and mutagenicity of the simulated wastewater were reduced substantially by the biological treatment. This paper will present the results of an evaluation of the biological and subsequent physical-chemical treatability of a real coal conversion wastewater, along with a comparison of the results with those obtained using the simulated wastewater.

Coal gasification wastewater was obtained from a Chapman gasifier at the Holston Army Ammunition Plant in Kingsport, Tennessee. The wastewater was diluted to 25% of full-strength, supplemented with phosphate, and subjected to aerobic biological treatment in a 22.5-liter completely-mixed activated sludge reactor. The reactor was operated at a solids retention time of 20 days and a hydraulic detention time of 10 days. In addition to characterizing the quality of the effluent using various chemical and bioassay procedures, the effluent from the biological reactor was subjected to a series of physical-chemical treatment steps consisting of chemical coagulation, ammonia stripping, ozonation, and activated carbon adsorption. The chemical quality and bioassay characteristics of these various samples will be presented.

INTRODUCTION

Previous research at the University of North Carolina has dealt primarily with an assessment of the biological treatability of a simulated coal conversion wastewater (1,2,3). A 25% dilution of the simulated wastewater was fed to a series of completely-mixed activated sludge reactors, operated at several different solids retention times (sludge ages). The results indicated that TOC, COD, and BOD removal increase with increasing sludge age, and that phenol is essentially completely removed with a sludge age of 5 days. Cresols and xylenols required 10 and 20 days, respectively, for removal to levels below 1 mg/l. Bioassays of the raw and treated quarter-strength simulated wastewater showed that the acute toxicity of the wastewater to fish and to mammalian cells is reduced markedly as a result of the biological treatment and that the extent of the reduction in toxicity increases with increasing sludge age. Additionally, at the concentrations tested, biological treatment reduces the mutagenic activity associated with the raw simulated wastewater to undetectable levels.

BIOLOGICAL TREATMENT OF HOLSTON WASTEWATER

More recently, we were able to obtain a real coal gasification wastewater from the Holston Army Ammunition Plant in Kingsport, Tennessee. The Holston facility has a fixed-bed, atmospheric Chapman gasifier which produces a low Btu gas which is used as fuel for process heaters. The wastewater sample was collected by R. Collins of the Radian Corporation (4) from the separator liquor tank which receives process condensate and condensed tars and oils from the gas-quenching and scrubbing steps at the Holston facility. Separation of tars and oils was reasonably good as the aqueous wastewater sample was relatively free of particulate material. The wastewater was sealed in 55-gallon drums to preserve its chemical integrity and shipped to our laboratories in Chapel Hill. Upon receipt of the drums, a sample of the virgin wastewater was collected, under an argon atmosphere, for chemical analysis and for various aquatic and health effects bioassays. The remaining contents of the drum were re-sealed and stored under an argon atmosphere in order to avoid exposure of the wastewater to oxygen and to minimize the loss of volatile constituents of the wastewater.

Table 1 presents the chemical characteristics of the virgin Holston wastewater as it was received. Two different shipments were received, and the characteristics of each of the batches are shown. Batch 2, the second shipment, is stronger than Batch 1, particularly with respect to COD and ammonia. The composition of the simulated coal conversion wastewater used in our earlier studies (1, 2, 3) is shown for comparison. The concentrations of phenols, TOC, and COD in the simulated wastewater are comparable to those in Batch 1 of the Holston wastewater; the ammonia concentration is appreciably lower.

TABLE 1. CHARACTERISTICS OF VIRGIN HOLSTON WASTEWATER

Parameter	Concentration, mg/l* Batch 1	Batch 2	Simulated Coal Conversion Wastewater
TOC	5,450	7,090	4,640
COD	14,800	25,000	14,300
BOD_5	8,000	-	7,070
4-AAP Phenols	2,000	2,320	2,240
CN^-	4.1	21.7	-
SCN^-	600	950	-
NH_3, as N	3,770	7,260	1,000
pH	8.0	8.04	7.1

*Except pH

Batch 1 of the raw Holston wastewater was also analyzed for selected trace metals and polynuclear aromatic hydrocarbons (PAH). These analyses were performed on samples taken several weeks after the drum was first opened so that a significant amount of suspended material was found in the aged wastewater. Accordingly, both the aqueous and solid phases were analyzed. Table 2 shows the concentrations of these selected priority pollutants in the raw wastewater. With the exception of zinc which was present at a concentration of 1.3 mg/l, the trace metals were found at concentrations less than 0.2 mg/l. The concentrations of each of the PAH were less than 0.1 mg/l; the high value reported for pyrene is questionable.

TABLE 2. CONCENTRATIONS OF TRACE METALS AND POLYNUCLEAR AROMATIC HYDROCARBONS IN RAW HOLSTON WASTEWATER*

	Concentrations, mg/l		
	Dissolved	Suspended	Total
Metals			
Cr	0.032	0.016	0.048
Cu	0.056	0.144	0.200
Mn	0.020	0.104	0.124
Zn	0.828	0.496	1.324
Pb	0.080	0.056	0.136
PAH			
Naphthalene	0.024	<0.036	0.024-0.060
Fluorene	0.008	<0.016	0.008-0.024
Phenanthrene	<0.012	<0.048	< 0.060
Anthracene	0.048	<0.044	0.048-0.092
Pyrene	0.528**	<0.056	0.528-0.584**

* Batch 1

** Questionable

Table 3 shows the toxicity of Batch 1 of the virgin Holston wastewater to Daphnia, fathead minnows, and the Chinese hamster ovary (CHO) mammalian cell system. The toxicities are relatively comparable for each of the bioassay systems, with LC50s on the order of 0.1%, i.e. 0.1 ml of wastewater diluted in 100 ml of clean water will cause 50% lethality of each of the bioassay indicators. Again, for purposes of comparison, the toxicity of the full-strength simulated wastewater is also shown in Table 3. From a toxicity standpoint, the Holston wastewater is approximately four to five times stronger (more toxic) than the simulated wastewater with which we previously worked.

TABLE 3. TOXICITY OF VIRGIN HOLSTON WASTEWATER

A. Virgin Holston Wastewater*

	LC50, %			
Aquatic Toxicity	24-hr.	48-hr.	72-hr.	96-hr.
Daphnia	0.28	0.11	--	--
Fathead Minnow	0.11	0.10	0.09	0.09

Mammalian Cytotoxicity	LC50, %
CHO Monoclonal Assay	0.12

B. Simulated Coal Conversion Wastewater

	LC50, %			
Aquatic Toxicity	24-hr.	48-hr.	72-hr.	96-hr.
Daphnia	0.41	0.21	0.19	<0.11
Fathead Minnow	0.5	0.5	0.49	0.49

Mammalian Cytotoxicity	LC50, %
CHO Monoclonal Assay	0.48

*Batch 1

The wastewater was diluted to 25% of full-strength, supplemented with phosphate, and subjected to aerobic biological treatment in a 22.5-liter completely-mixed activated sludge reactor. The reactor was operated at a 20-day solids residence time and a 10-day hydraulic retention time. No other pre-treatment was provided. Table 4 shows the chemical quality of the reactor effluent compared to the diluted raw feed. Both batches of wastewater appear to be treated relatively effectively, with TOC removals of approximately 66% and 62% for batches 1 and 2, respectively, and COD removal averaging 63% and 62%, respectively. The average effluent TOCs and CODs are respectively 510 and 1650 mg/l for batch 1 and 629 and 2145 mg/l for batch 2. The differences presumably are due to the fact that batch 2 is appreciably stronger than batch 1.

In both cases, substantial removal of phenols (as measured by the 4-aminoantipyrene wet chemical procedure) occurred. The residual concentration of phenols was frequently below 1 mg/l. HPLC analysis showed that phenol itself was usually on the order of 0.1-0.2 mg/l in the reactor effluent.

TABLE 4. QUALITY OF BIOLOGICALLY-TREATED* HOLSTON WASTEWATER

	Concentration, mg/l**					
	Batch 1		Batch 2		Simulated Coal Conversion Wastewater*	
Parameter	Reactor Influent	Reactor Effluent	Reactor Influent	Reactor Effluent	Reactor Influent	Reactor Effluent
TOC	1510	510 (±81)	2000	629 (±67)	1410	204 (±51)
COD	4490	1650 (±209)	5580	2145 (±470)	3326	511 (±121)
BOD_5	1700	26	--	--	1770	22
4-AAP Phenols	526	1.2-3.3	498	0.2-3.6	560	0.14-2.6
CN^-	1.0	1.0	--	--	--	--
SCN^-	173	162-193	253	443-483	--	--
NH_3, as N	882	874	1810	1890	252	212
pH	7.48	7.45	7.0	7.0	7.1	6.9

*Activated sludge; 10-day HRT, 20-day SRT

**Except pH

No biological nitrification was observed, with effluent ammonia concentrations being similar to the influent ammonia concentration. No thiocyanate removal was apparent, although our results indicate an apparent increase in SCN^- for batch 2. Such a production of SCN^- has not been reported previously, yet we have measured this increase consistently, and have verified our analytical results using step addition procedures. Thiocyanate was measured using the spectrophotometric dithiocyanatopyridine chloroform extraction procedure (5).

Table 4 also shows the quality of the biologically-treated simulated coal conversion wastewater under parallel treatment conditions, i.e. diluted to 25% of full-strength and treated by an activated sludge system with a solids retention time of 20 days and a hydraulic retention time of 10 days. Treatment of the simulated wastewater was more effective, providing an 86% reduction in TOC and an 85% reduction in COD. The effluent TOC and COD concentrations are approximately 1/2 to 1/3 of those in the biologically-treated Holston effluent.

Table 5 shows the toxicity of the raw and biologically-treated Holston wastewater. The "raw" LC50s refer to the 25% diluted Holston wastewater corresponding to the influent to the biological reactors. It is apparent that there is a significant reduction in aquatic toxicity to the Daphnia and fathead minnows, and in the CHO mammalian cytotoxicity; 5 to 15-fold reductions in toxicity result from the biological treatment of the diluted Holston wastewater, using these assay systems. Because of the variability in effluent quality and in order to provide toxicity data for both batches of the raw wastewater, the bioassays were performed several times, as indicated by the dates in Table 5. (The reactor feed was switched from batch 1 to batch 2 in early April, 1980.) The LC50 values seem to be fairly consistent irrespective of this variability in gross chemical quality.

A comparison between the toxicity of the biologically-treated Holston wastewater and the biologically-treated simulated coal conversion wastewater (see Table 5) shows that the Holston effluent is appreciably more toxic to the three bioassay systems tested. Hence, despite the effectiveness of biological treatment in removing TOC and COD and in reducing the toxicity of the Holston wastewater, the biologically-treated effluent is still of unacceptable quality for discharge to the aquatic environment. The residual TOC and COD are still appreciable, as are the NH_3 and SCN^- concentrations. The toxicity of the effluent is also still substantial, suggesting that additional, i.e. post-biological, treatment is appropriate.

A 25% dilution of the virgin Holston wastewater was assayed for mutagenicity using the Ames test. Preliminary screening experiments showed that TA98 (a strain of Salmonella which tests for frameshift mutagenic activity) to be the most sensitive strain for this wastewater. With metabolic activation (the incorporation of the S-9 rat liver homogenate into the test system), TA98 gave a positive mutagenic response at all sample volumes tested up to 2.5 ml. The highest reversion ratio of 3.4 occurred for 1.5 ml of the wastewater sample.

TABLE 5. TOXICITY OF RAW* AND BIOLOGICALLY-TREATED** HOLSTON WASTEWATER

A. Holston Wastewater

AQUATIC TOXICITY

		LC50, %			
Daphnia	Date	24-hr.	48-hr.	72-hr.	96-hr.
Influent	8/26/80	1.12	0.44	--	--
Influent	6/23/81	1.8	0.76	0.53	0.49
Effluent	10/1/80	6.5	4.6	3.9	--
Effluent	10/27/80	4.5	4.1	3.9	--
Effluent	2/16/81	5.6	3.5	3.2	--
Effluent	6/29/81	4.8	3.3	2.5	--
Fathead Minnow					
Influent	8/12/80	0.44	0.40	0.38	0.38
Influent	5/15/81	1.1	1.0	1.0	1.0
Effluent	10/1/80	11	6.8	5.7	5.2
Effluent	10/15/80	9.6	5.9	4.9	--

MAMMALIAN CYTOTOXICITY

CHO Monoclonal Assay	Date	LC50, %
Influent	8/26/80	0.48
Influent	6/23/81	0.52
Effluent	9/26/80	4.90
Effluent	6/28/81	3.64
Effluent	7/14/81	7.01

B. Simulated Coal Conversion Wastewater

AQUATIC TOXICITY

	LC50, %			
Daphnia	24-hr.	48-hr.	72-hr.	96-hr.
Influent	1.65	0.85	0.7	<0.42
Effluent	57	49	38	--
Fathead Minnow				
Influent	2.0	2.0	2.0	1.9
Effluent	Ind.***	Ind.***	Ind.***	Ind.***

MAMMALIAN CYTOTOXICITY

CHO Monoclonal Assay	LC50, %
Influent	1.9
Effluent	15.7

---

*25% diluted Holston Wastewater

**10-day HRT, 20-day SRT activated sludge system

***Greater than 50% of the test organisms survived at concentrations up to 50% of the effluent.

Following biological treatment, no frameshift mutagenic activity, with or without metabolic activation, was found at sample volumes up to 2.0 ml using tester strains TA98 and TA1537. Additionally, no base-pair substitution mutagenic activity, using tester strain TA100 with or without metabolic activation, was found at sample volumes up to 2.0 ml of the treated wastewater. Apparently, mutagenic activity in the Holston wastewater was reduced to undetectable levels by biological treatment.

TABLE 6. MOLECULAR WEIGHT DISTRIBUTION OF RESIDUAL ORGANIC CARBON IN FILTERED ACTIVATED SLUDGE EFFLUENT

Molecular Weight		TOC, mg/l
<500		390
500 to 30,00		70
>30,000		200
	TOTAL	660

It is also worth noting that the filtered (0.45 μm) effluent following biological treatment contains a significant amount of high molecular weight organic material as shown in Table 6. The molecular weight distribution was measured by ultrafiltration techniques, using two different membranes with nominal molecular weight cut-offs of 500 and 30,000. Of the 660 mg/l of TOC, approximately 30% or 200 mg/l (on a carbon basis) consisted of organics with a molecular weight greater than 30,000. Sixty percent, or 390 mg/l, of the TOC consisted of organics of molecular weight less than 500. The remainder of the TOC consisted of compounds with a molecular weight in the 500-30,000 range. The fact that approximately 40% of the residual TOC following activated sludge biological treatment is comprised of compounds with a molecular weight greater than 500 implies that the residual TOC may cause problems if the biologically-treated effluent is to be recycled for use in a cooling tower. It is conceivable that these high molecular weight compounds will tend to adsorb to heat transfer surfaces in the tower, thereby fouling the tower and interfering with its operation. The amenability of this high molecular weight organic material to various post-biological treatment processes should be examined.

POST-TREATMENT OF BIOLOGICALLY-TREATED HOLSTON WASTEWATER

Filtered effluent from the biological reactors treating diluted Holston wastewater was subjected to a variety of physical-chemical treatment steps consisting of chemical coagulation and precipitation, ozonation, activated carbon adsorption, and ammonia stripping. The effectiveness of these post-biological treatment processes was assessed through measurements of TOC, COD, NH_3, SCN^-, and residual Daphnia and CHO toxicity.

Table 7 shows the results of coagulation and precipitation experiments on the filtered biologically-treated Holston wastewater. Alum (aluminum sulfate) and ferric chloride are standard water supply and wastewater treatment coagulants and have been shown (6) to effectively remove high molecular weight humic substances from water. Nevertheless, the application of these coagulants, even at extreme doses of up to 500 mg/1, resulted in no apparent floc formation. The chemicals were added to the wastewater, and the water was rapid-mixed to disperse the chemical, slow-mixed to allow for flocculation, and allowed to stand quiescently to provide for settling of any floc or precipitate. The fact that aluminum hydroxide or ferric hydroxide wasn't produced suggests that a substantial concentration of metal-complexing organics are still present in the biologically-treated wastewater.

TABLE 7. COAGULATION OF BIOLOGICALLY-TREATED* HOLSTON WASTEWATER

ALUM

0-500 mg/1 at pH 6.5 - no floc formed, no precipitation

FERRIC CHLORIDE

0-500 mg/1 at pH 6.0 and pH 8.0 - no floc formed, no precipitation

LIME

Dose, mg/1	pH	TOC, mg/1
0	7.0	640
720	8.5	475
2640	9.3	460
3360	9.6	455
5280	11.6	450

H_2SO_4

Dose, mg/1	pH	TOC, mg/1
0	6.9	600
6.5	3.0	570
10	2.5	480
25	2.0	425
60	1.5	420

BETZ 1190 CATIONIC POLYMER

Dose, mg/1	TOC, mg/1
0	640
200	460
400	410
1000	500
5000	1260

---

*Filtered activated sludge effluent, 10-day HRT, 20-day SRT

The addition of lime (CaO) raised the pH of the water and, after allowing for settling, resulted in the removal of some of the TOC. Approximately 25% of the TOC was removed by the addition of 720 mg/l of lime which raised the pH to 8.5. Little improvement was achieved with higher doses of lime.

Sulfuric acid caused precipitation of some of the residual organics by decreasing the pH of the wastewater. High molecular weight humic substances tend to precipitate under such acidic conditions. Approximately 30% of the TOC was removed when the pH was reduced to 2.0. Little precipitation of TOC was obtained until the pH of the water was decreased to below pH 3.

The addition of a cationic polyelectrolyte, BETZ 1190, a high charge density, relatively moderate molecular weight polymer, brought about some coagulation of TOC, but again at rather substantial doses. Edzwald (7) has shown that such cationic polymers are effective coagulants of high molecular weight humic substances. The optimal dosage range appeared to be between 200 and 1000 mg/l, with 35% removal of TOC occurring at a dose of 400 mg/l of the polymer. Apparently, little improvement in the quality of the wastewater can be obtained through coagulation or acid or base treatment, even at very high chemical doses.

Table 8 presents the results of an experiment in which the biologically-treated wastewater was treated further in an ozone contact column. A mixture of ozone and oxygen was bubbled through a sample of wastewater, and aliquots were removed at various times and analyzed. The pH decreased substantially during the course of ozonation, presumably due to the conversion of many of the organic impurities to organic acids and CO_2. Thiocyanate was oxidized almost completely by the ozone. Total organic carbon decreased as a result of ozonation, while the COD was decreased to an even greater degree. The relative decreases in TOC and COD suggest that many of the organic compounds were converted to organic acids and aldehydes in which the organic carbon is in a higher oxidation state than in the parent compound, while only a portion of the organic compounds were oxidized completely to CO_2. The ozone consumption, which was calculated by measuring the difference between the applied ozone in the feed gas and the ozone concentration in the off-gas, is relatively small compared to the change in COD and SCN^- concentrations, suggesting that some of the organics were removed by the application of ozone. The initial removal of NH_3 was probably through air-stripping; further ammonia removal was inhibited as a result of the acidic conditions (low pH) which were generated.

Table 9 shows the results of treating filtered biologically-treated Holston wastewater with activated carbon. Pulverized Nuchar WV-G (Westvaco Chemical Co) was used as the adsorbent. The studies were carried out as batch equilibrium experiments in which various doses of carbon were added to the wastewater, and the suspension was mixed for 4 hours to reach equilibrium. Upon equilibration, the activated carbon was removed by centrifugation and filtration, and the residual TOC was measured. Table 9 shows that the extent of TOC removal increased with increasing doses of

TABLE 8. OZONATION OF BIOLOGICALLY-TREATED* HOLSTON WASTEWATER

Ozonation Time min.	Applied Ozone Dose mg/1	Ozone Consumption mg/1	pH	TOC mg/1	COD mg/1	SCN⁻ mg/1	NH_3 mg/1
0	0	0	6.77	645	2777	428	2608
10	455	450	3.36	566	1801	106	1904
30	1365	910	2.65	520	1431	18	1890
60	2730	1140	2.59	491	1299	11	1820

*Activated sludge, 10-day HRT, 20-day SRT

TABLE 9. ADSORPTION OF BIOLOGICALLY-TREATED* HOLSTON WASTEWATER

Activated Carbon** Dose mg/1	TOC mg/1	COD mg/1	BOD mg/1	Daphnia Toxicity LC50, %		
				24-hr	48-hr	96-hr
0	662	1480	48	5.6	3.5	3.2
800	490	1030	10	-	-	-
1000	440	-	-	-	-	-
1800	380	-	-	-	-	-
2000	354	684	8	5.6	4.5	2.7
3500	283	-	-	-	-	-

*Filtered activated sludge effluent, 10-day HRT, 20-day SRT
**Powdered Westvaco Nuchar WV-G activated carbon

activated carbon and that approximately 50% of the TOC was removed with an activated carbon dose of 2000 mg/l. However, Table 9 also shows that despite the TOC and COD removals achieved by activated carbon adsorption, such treatment had little impact on the toxicity of the wastewater to Daphnia. The LC50s of the carbon-treated samples are essentially the same as those of the biologically-treated effluent with no carbon treatment. This may be a result of the high ammonia concentration of the samples, i.e. the toxicity of the treated wastewater may be due to the approximately 2000 mg/l of ammonia-nitrogen which is still in the wastewater even after the activated sludge and activated carbon treatment.

In order to test this hypothesis, samples of the biologically-treated Holston wastewater were treated with NaOH to raise their pH to approximately 11, air-stripped to release NH_3, neutralized to pH 7 with HCl, and subsequently treated with activated carbon as described above. Table 10 shows that while biological treatment of the diluted Holston wastewater reduced its toxicity to Daphnia and CHO cells by factors of approximately 3 and 13, respectively, reducing the ammonia concentration from 2000 to 110 mg/l (a 95% reduction) resulted in an additional 3- to 6-fold reduction in toxicity.

The reason for the apparent increase in TOC which accompanied the ammonia-stripping step is not known; it may have been due to (a) absorption of organics from the laboratory air that was used to strip the ammonia, although an activated carbon plug was used in the air line to trap any organic contaminants in the air, or (b) to the hydrolysis of some of the high molecular weight residual organics at the elevated pH which makes the organic carbon more amenable to detection by the analytical procedure used to measure TOC. The latter involves a high temperature (950°C) combustion of the organic carbon by oxygen, and measurement of the CO_2 released. Some of the high molecular weight organic carbon in the sample prior to ammonia-stripping may not have been oxidized completely to CO_2 and therefore may have escaped detection.

Table 10 shows that subsequent treatment of the ammonia-stripped biologically-treated Holston wastewater with 500 and 3600 mg/l of activated carbon reduced the TOC by 23% and 53%, respectively, but had no effect on the toxicity of the wastewater to Daphnia. However, the toxicity of the treated wastewater to the CHO cells was reduced to such a degree by activated carbon that more than 50% of the cells survived at all of the wastewater concentrations tested. While these activated carbon doses are relatively extreme, they do illustrate the impact of additional TOC removal on the toxicity of the wastewater.

In view of the reduction in toxicity resulting from ammonia stripping and the improvement in the gross chemical quality of the wastewater following ozonation (see Table 8), filtered biologically-treated wastewater was ammonia-stripped in the same manner as discussed above, and then subjected to ozonation. In this case, the ammonia-stripped wastewater was buffered with respect to pH in order to promote broad-based non-selective oxidation of the residual organics (8). Table 11 shows analytical results parallel to those shown in Table 8: substantial reduction of COD, some removal of TOC, essentially complete elimination of thiocyanate, and no oxidation of the residual ammonia. It appears, however, that cyanide is produced from the oxidation of thiocyanate and, while some of the cyanide is oxidized further by ozone, a significant concentration of cyanide remains in solution even after 60 minutes of ozonation. Correspondingly, the ozonated samples are more toxic to Daphnia and to the microbial seed used in the BOD measurements. In the former case, a quantitative determination of the 24-hr. LC-50 could not be made but it was observed that the 24-hr. LC-50 for the ozonated samples was less than 5% compared to a 24-hr. LC-50 of more than 15% for the ammonia-stripped, biologically-treated wastewater prior to ozonation. In the latter case, the BOD could not be measured using more than a 6% dilution of the wastewater; dilutions greater than 6% were toxic to the microbial seed. While some thiocyanate ozonation studies have already been conducted (9), additional studies are required to determine the relative oxidation kinetics of SCN^- and CN^- and to ascertain whether the observed increase in toxicity following ozonation is due to the generation of cyanide or to other toxic products of the ozonation reaction.

TABLE 10. ADSORPTION OF AMMONIA-STRIPPED BIOLOGICALLY-TREATED HOLSTON WASTEWATER

Sample	TOC mg/l	NH_3 mg/l as N	Daphnia Toxicity LC50, %				CHO Cyto-toxicity LC50, %
			24-hr	48-hr	72-hr	96-hr	
Holston Feed (25% strength)	1800	1970	1.8	0.76	0.53	0.49	0.52
Biologically-treated Effluent	600	1950	4.2	1.9	1.5	1.45	7.01
NH_3-stripped Effluent	705	110	17.3	11.8	8.3	8.3	19.4
Activated Carbon-treated NH_3-stripped Effluent							
500 mg/l AC*	540	110	18.8	11.3	10	7.7	Indet**
3600 mg/l AC*	330	110	23	11.8	8.4	7.5	Indet***

*Powdered Westvaco WV-G activated carbon

**Greater than 50% survival at concentrations up to 45%

***Greater than 50% survival at concentrations up to 75%

TABLE 11. RESULTS OF OZONATION STUDIES ON AMMONIA-STRIPPED, BIOLOGICALLY-TREATED HOLSTON WASTEWATER

Parameter	Time of Ozonation, min. 0	20	60
Ozone dose, mg/l	0	900	2700
Ozone consumption, mg/l	0	845	1505
pH	7.10	6.68	6.60
TOC, mg/l	803	744	676
COD, mg/l	2503	1798	1499
BOD, mg/l	115	45*	65*
NH_3, mg/l as N	146	147	153
NO_3^-, mg/l as N	8.0	4.6	10.0
SCN^-, mg/l	607	87	5
CN^-, mg/l	3.3	152	128
Daphnia Toxicity 24-hr LC50, %	>15	< 5	< 5

* Toxic at 6% concentration

SOLVENT-EXTRACTION OF HOLSTON WASTEWATER

In order to evaluate the impact of solvent-extraction of phenols on the biological treatability of the Holston wastewater, a large volume of the virgin Holston wastewater (i.e. a fresh sample from a newly-opened barrel of the wastewater) was extracted with n-butyl acetate. Three extractions, with a solvent-wastewater ratio of 1 to 10, were employed, and the residual butyl acetate in the aqueous phase was eliminated by air-stripping. The pH of the wastewater was raised to approximately 11 with NaOH and the sample was air-stripped to release NH_3. After re-adjustment of the pH to 7 with HCl, the wastewater was supplemented with phosphate and fed without any dilution to an activated sludge reactor operated at a 20-day sludge age and a 10-day hydraulic residence time.

Table 12 gives the results available to date. The solvent-extraction step reduced the concentration of phenols to 8.0 mg/l and resulted in TOC and COD removals of 68% and 67%, respectively. These removals were accompanied by a 6 to 7-fold reduction in Daphnia and CHO toxicity. Ammonia-stripping of the solvent-extracted wastewater to a level of 84 mg/l of ammonia resulted in an additional 6-fold reduction in toxicity to Daphnia. (Again, it should be noted that both TOC and COD appear to have increased as a result of pH adjustment and ammonia-stripping. Hydrolysis of high molecular weight organics or absorption of organics from the laboratory air are, again, possible explanations for this apparent increase.) The results of the biological treatment studies are not available at the time of this writing.

TABLE 12. RESULTS OF SOLVENT-EXTRACTION STUDIES

Parameter	Virgin Holston Wastewater*	Solvent-Extracted Holston Wastewater**	NH_3-stripped,*** Solvent-Extracted Wastewater
TOC, mg/l	7490	2390	2860
COD, mg/l	24,500	8200	10,100
Phenols, mg/l	2200	8.0	-
NH_3, mg/l as N	7290	7200	84
SCN^-, mg/l	445	-	-
Daphnia Toxicity			
24-hr LC50, %	0.076	0.44	2.6
48-hr LC50, %	0.050	0.24	1.55
96-hr LC50, %	0.038	0.23	1.38
CHO Cytotoxicity			
LC50, %	0.055	0.4	

*Batch 2, full-strength

**n-Butyl acetate; 1/10 solvent/water ratio, 3X; air-stripped to eliminate butyl acetate

***pH adjustment with NaOH, air-stripped to expel NH_3, pH re-adjustment with HCl

CONCLUSIONS

A comparison has been made between a real coal gasification wastewater from a fixed-bed atmospheric gasifier and a simulated coal conversion wastewater. The simulated wastewater was similar with respect to the concentrations of TOC, COD, and phenols, but the real wastewater had an appreciably higher ammonia content. In addition, the real wastewater was approximately 4 to 5 times more toxic than the simulated wastewater, based on Daphnia, fish, and CHO bioassays.

The real wastewater was biologically-treatable when diluted to quarter-strength. Treatment in an activated sludge reactor with a 20-day sludge age and a 10-day hydraulic residence time resulted in residual concentrations of phenols generally below 1 mg/l, TOC removals of approximately 65%, and COD removals of approximately 63%. The effluent TOC and COD concentrations, however, were approximately 2 to 3 times higher than those in the effluent from an activated sludge reactor treating the simulated coal conversion wastewater under parallel operating conditions. Additionally, while the toxicity of the real coal conversion wastewater to Daphnia, fish, and mammalian cells was reduced appreciably by biological treatment and the mutagenicity of the wastewater was reduced to undetectable levels, the effluent was significantly more toxic than the biologically-treated, simulated wastewater effluent.

A significant portion of the residual TOC (approximately 30%) in the filtered activated sludge effluent following treatment of the real wastewater consists of organic compounds with a molecular weight greater than 30,000. If the effluent is to be re-used and concentrated in a cooling tower, the presence of this relatively large amount of high molecular weight material may have an adverse impact on the operation of the cooling towers.

Post-biological treatment involving ammonia-stripping and activated carbon adsorption significantly alleviated the mammalian cytotoxicity of the real wastewater; such treatment had no effect on the toxicity of the wastewater to Daphnia. Ozonation improved the gross chemical quality of the wastewater, but had an adverse impact on Daphnia toxicity.

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REFERENCES

1. Singer, P. C. et al., "Evaluation of Coal Conversion Wastewater Treatability," in Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, IV, Report No. EPA-600/7-79-217, U.S. Environmental Protection Agency, Washington, D.C. (1979).

2. Singer, P. C. et al., Treatability and Assessment of Coal Conversion Wastewaters: Phase 1, Report No. EPA-600/7-79-248, U.S. Environmental Protection Agency, Washington, D.C. (1979).

3. Singer, P.C. et al., "Effect of Sludge Age on the Biological Treatability of a Synthetic Coal Conversion Wastewater," in Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, V, U.S. Environmental Protection Agency (in press).

4. Collins, R. V., K. W. Lee, and D. S. Lewis, "Comparison of Coal Conversion Wastewaters," in Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, V, U.S. Environmental Protection Agency (in press).

5. Luthy, R. G., Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters, DOE FE-2496-8 U.S. Dept. of Energy, (1977).

6. Babcock, D. B. and P. C. Singer, "Chlorination and Coagulation of Humic and Fulvic Acids," Journ. Amer. Water Works Assn., Vol. 71, no. 3, 149-152 (1979).

7. Edzwald, J. K., J. D. Haaf, and J. W. Boak, "Polymer Coagulation of Humic Acid Waters," Journ. Amer. Soc. Civil Eng., Env. Eng. Div., 103:EE6:989 (1977).

8. Hoigne, J. and H. Bader, "Ozone Initiated Oxidations of Solutes in Wastewater: A Reaction Kinetic Approach," Progress in Water Technology, Vol. 10, Nos. 5/6, p. 657-71, Pergamon Press (1978).

9. Kemker, G. H., S. J. Roadcap, and R. Sitchin, The Ozonolysis of Aqueous Solutions of Phenol and Thiocyanate, ORNL/MIT-318, Dept. of Energy (1980).