119-27a

FINAL

119-27a

CONTROL TECHNOLOGY ASSESSMENT
FOR
COAL GASIFICATION AND LIQUEFACTION PROCESSES

Tennessee Valley Authority
National Fertilizer Development Center
Coal Gasification and Gas Purification Unit (CGGPU)
Muscle Shoals, Alabama

Report for the Site Visit of
September 1981

Contract No. 210-78-0084

April 1982

Submitted to:

Phillip A. Froehlich, Project Officer
National Institute for Occupational
Safety and Health
Division of Physical Sciences and Engineering
Robert A. Taft Laboratories
4676 Columbia Parkway
Cincinnati, Ohio 45226

Submitted by:

Donato R. Telesca, Manager,
Engineering Department
Dynamac Corporation
Enviro Control Division
11140 Rockville Pike
Rockville, Maryland 20852

FOREWORD

The Enviro Control Technology Assessment (CTA) team met with representatives of the Tennessee Valley Authority (TVA), National Fertilizer Development Center, Muscle Shoals, Alabama on September 1-2, 1981. Also in attendance at this meeting were representatives from the National Institute for Occupational Safety and Health (NIOSH), and from Texaco, Inc. At our initial meeting Donato Telesca of Enviro Control explained the purpose of our visit to the TVA Ammonia Plant and Coal Gasification and Gas Purification Unit (CGGPU) personnel and outlined the type of information Enviro wanted to collect. Based on this discussion Enviro was scheduled to interview appropriate TVA personnel over the next two days. Those attending this initial meeting were:

Tennessee Valley Authority

- Donald Waitzman, Project Manager
- Robert Lee, Assistant Project Manager
- David Nichols, Project Engineer
- Eugene Buggs, Chemical Engineer
- John McFeters, Industrial Hygienist
- Robert Jaynes, Industrial Hygienist

Texaco

- David Watts, Project Industrial Hygienist

Enviro Control, Inc.

- Donato Telesca, Project Manager
- Jan Scopel, Chemical Engineer
- Russell Tanita, Industrial Hygienist

NIOSH

- Phillip Froehlich, Chief, Chemical Industry Section of the Division of Physical Sciences and Engineering

This report was made possible by the excellent cooperation of the personnel at TVA.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

A. Background

The objective of the "Control Technology Assessment for Coal Gasification and Liquefaction Processes" program is to study the control technologies that are currently in use for preventing occupational exposure to hazardous agents in the various coal conversion plants. For the purposes of this study the term "control technology" has a very broad meaning. It includes equipment such as baghouses, dust collection hoods, and thermal oxidizers, whose specific function is the control of potentially harmful emissions. It also includes any equipment design or process design change that increases the reliability of the process. Fewer equipment failures result in less worker exposure due to accidental releases and less exposure of the maintenance personnel who must make the repairs. Controls in this category include better metallurgy and improved equipment designs. We also considered the plant's work practices and industrial hygiene program to be part of its control technology.

This report details the control technology and industrial hygiene information gathered at the Coal Gasification and Gas Purification Unit (CGGPU) of the Tennessee Valley Authority Ammonia-From-Coal Facility, National Fertilizer Development Center (NFDC), Muscle Shoals, Alabama.

Information concerning the ammonia synthesis section of the Ammonia-From-Coal plant is contained in a separate report [1].

B. Project History

The purpose of the TVA Ammonia from Coal Project is to develop design and operating data to assess the technological, economic, and environmental aspects of substituting gas derived from coal for natural gas in the manufacture of ammonia.

The interest in the study of ammonia from coal processes began at NFDC in the mid-1950's, after the early German processes were first placed in commercial operation in Europe. At that time natural gas feedstock was firmly established in the United States, but coal-based processes were of possible benefit to those developing countries lacking petroleum or gas feedstocks. Consequently TVA began surveying the literature pertaining to ammonia from coal processes.

TVA recognized the serious future threat to the U.S. nitrogen fertilizer industry because of the total reliance on natural gas as fuel and feedstock for ammonia production. As a result, in early 1974 TVA decided to step-up the study and evaluation of coal-based ammonia technology. Between January 1974 and August 1975, TVA contacted a number of Federal and State offices, American representatives of the German firms offering coal gasification technology, and retained an NFDC ammonia process consultant. Several Division of Chemical Development staff members were assigned to a more intensive literature review and to carry out conceptual design and cost studies of a 1000-ton-per-day ammonia plant based on one emerging and two existing gasification processes. The study was completed in July 1975. Although results of this cost study were not conclusive, it appeared that an emerging U.S. process had significant advantages over the existing German technology.

As a result of these studies, TVA chose to proceed with the design and construction of an 8 ton/hr coal gasification process and gas purification facility to produce synthesis gas for TVA's existing ammonia plant located at the National Fertilizer Development Center at Muscle Shoals, Alabama.

TVA chose the Texaco coal gasification process to produce the synthesis gas. The engineering, procurement, and erection of the coal gasification and gas purification facility was performed by Brown and Root Development, Inc. The air separation plant required to provide high-purity oxygen and nitrogen for the process was handled similarly by Air Products and Chemicals, Inc. Engineering, procurement, and construction of the coal handling and preparation area; interconnections to the existing ammonia plant; slag disposal; and services and utilities required for the plant were performed by TVA.

Start-up of the facility was scheduled for October 1980; however, the gasifier slag removal system had to be redesigned. TVA management stated that start-up of the facility is likely in spring, 1982.

C. Process Description

The following process areas comprise the TVA Coal Gasification and Gas Purification Unit (CGGPU): coal storage and crushing, coal grinding and slurry preparation, gasification, CO shift/COS hydrolysis, acid-gas removal, sulfur recovery, wastewater treatment, air separation and utilities. Figure 1 is a block diagram of these CGGPU processes.

Coal received by rail car is either crushed immediately or sent to a storage pile for later reclamation and crushing. Crushed coal is stored in a vibrating bin that feeds coal to a wet-grind mill. The slurry from the mill is discharged into a mix tank and adjusted to a solids concentration of greater than 60%. The slurry is then pumped to a feed tank and metered to the gasifier at approximately 8 tons of coal per hour.

The gasifier used at the CGGPU is an entrained bed slagging, oxygen-blown, high pressure partial oxidation reactor developed by Texaco. Oxygen from an air separation plant is fed to the gasifier along with the coal/water slurry. The gasifier operates at approximately 510 psig and in excess of 2,200 F (1204 C). At this temperature the ash becomes molten slag, which solidifies into a fritlike material when it is water quenched. The solidified slag is removed through a quench-water flooded lockhopper system, and screened. Over-size material is sent to disposal. Undersize material which contains unconverted carbon is recycled to slurry preparation.

The gas leaving the reactor is water quenched, and entrained particulates are removed by a scrubber. The raw gas is then sent to a carbon monoxide (CO) shift converter where the CO content is reduced from 22% to 2%. The adjusted gas is then sent to a COS (carbonyl sulfide) hydrolysis unit where all but 7 ppm is converted to hydrogen sulfide (H_2S).

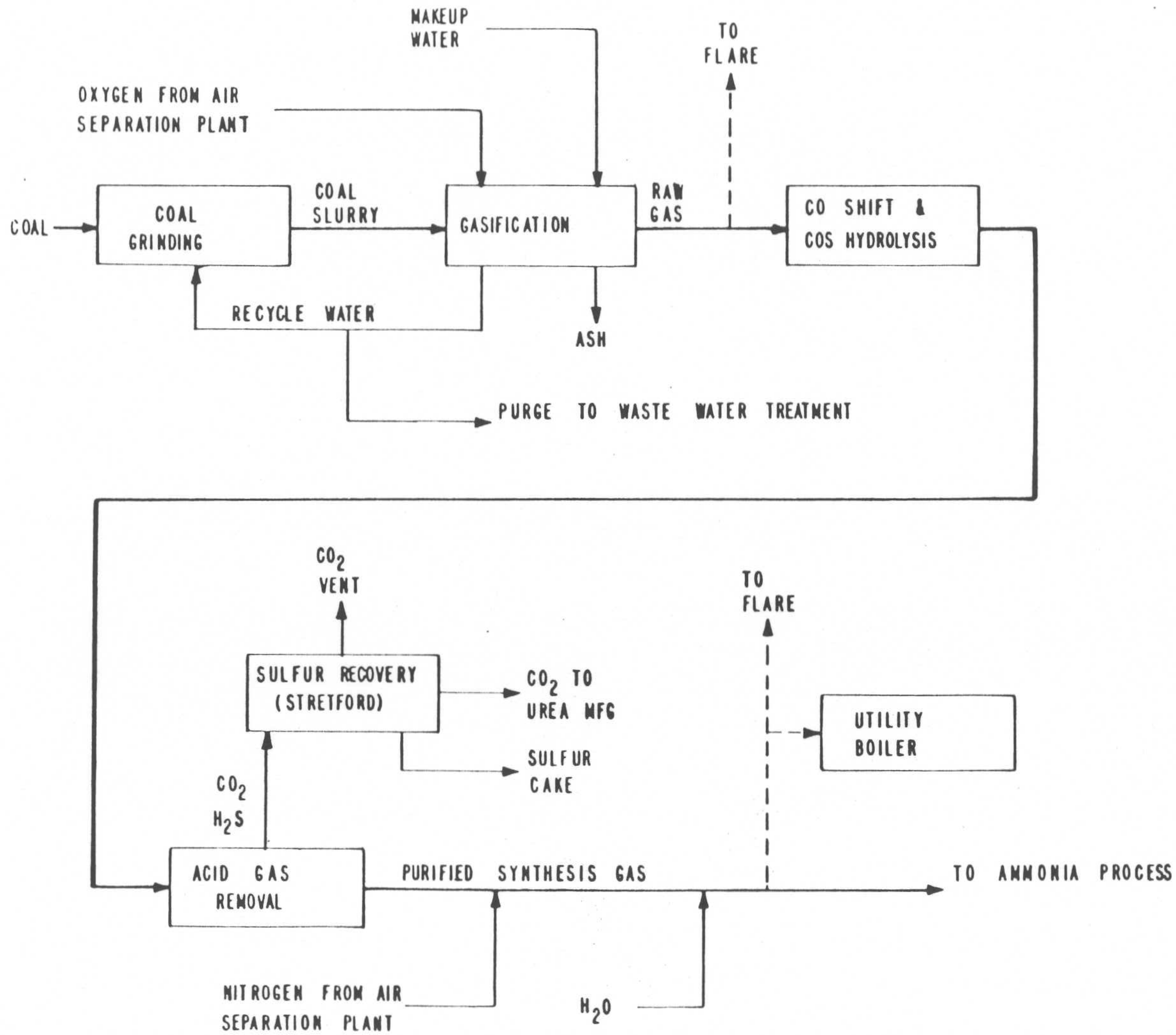

Figure 1. Block Flow Diagram of the CGGPU Facility[7]

The gas from the COS hydrolysis unit is sent to a Selexol acid gas removal (AGR) unit for removal of carbon dioxide (CO_2) and H_2S. Two CO_2 rich off-gas streams are produced in the Selexol unit. They are sent to two separate Holmes-Stretford Sulfur recovery systems, where elemental sulfur is recovered as a granular cake. The concentration of of reduced sulfur compounds (H_2S and COS) in the smaller of the two streams from the AGR unit is reduced from about 0.8 percent (8000 ppm) to 0.5 ppm H_2S and COS to meet urea manufacturing requirements. A bed of zinc oxide is used following the Holmes-Stretford process to achieve this low level of sulfur compounds.

The H_2S concentration of the larger CO_2 stream from the AGR unit is reduced from 4% (40,000 ppm) to 160 ppm. The CO_2 stream is then vented to the atmosphere under an emissions permit.

The product gas leaving the AGR system contains a maximum of 1 ppm total sulfur. Nitrogen from the air separation plant is added to the product gas to produce an H_2 to N_2 ratio of 3 to 1. The gas then flows through a zinc oxide sulfur guard bed to decrease the sulfur content to less than 0.1 ppm. Deaerated boiler feed water is added to bring the steam to dry gas ratio to 0.44 to 1. Prior to its entry into the ammonia plant, the gas is heated to about 600 F (316 C). The pressure of the gas is approximately 385 psig.

D. Layout of the Facility

Figure 2 is a layout of the integrated Ammonia-From-Coal facility showing the location of major equipment in the CGGPU. Table 1 is a list of the process areas that comprise the CGGPU.

Process equipment is either located on foundations at grade, or housed in open multilevel steel structures. The only enclosed process area is the shed where the coal cars are unloaded. All process areas are paved in concrete.

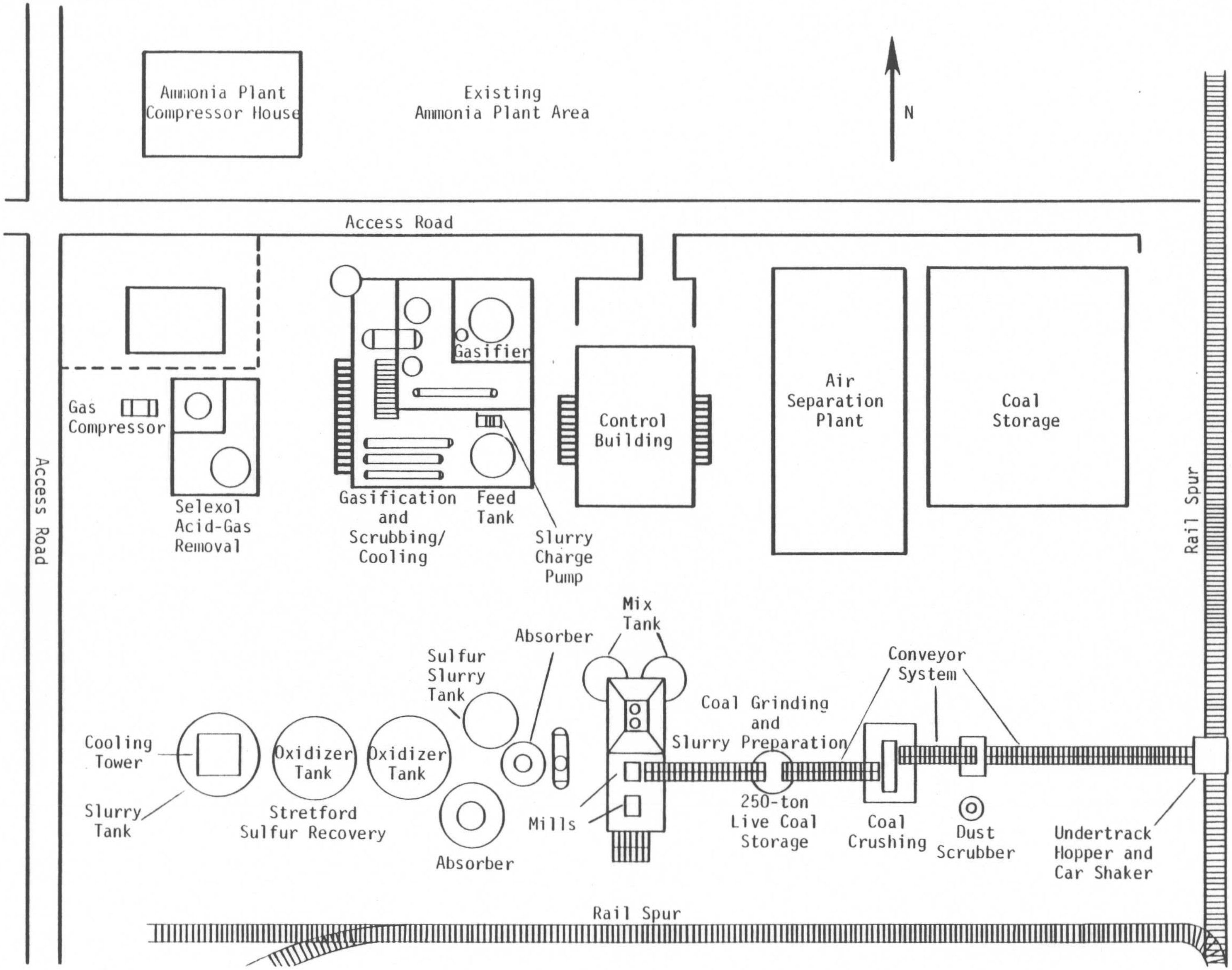

Figure 2. Layout of the Integrated Ammonia-From-Coal Plant

TABLE 1

CGGPU Process Area Designations

Process Area	Name Designation
100	Coal Grinding/Slurry Preparation
200	Coal Gasification
300	CO Shift/COS Hydrolysis
400	Wastewater Treatment
500	Selexol-Acid Gas Removal
600	Sulfur Removal - Holmes-Stretford
700	Utilities
xxx	Air Separation

E. Potential Hazards

Table 2 is a list of the possible hazardous agents associated with each process area in the Coal Gasification and Gas Purification Unit. These chemical and physical agents are listed because of their known or potential presence in each of the process areas. Additional operating experience will allow an assessment of the degree of danger posed by each hazard, as well as the identification of additional hazards.

TABLE 2

Potential Hazards by Process Area at the TVA CGGPU

Process Area	Potential Hazards
Coal Storage and Crushing	Respirable Coal Dust Fire/Explosion Noise
Coal Grinding and Slurry Preparation	Quench Water Contaminants Respirable Coal Dust Fire/Explosion Ammonia Noise
Gasification	High Temperature High Pressure Noise Heat Stress Carbon Monoxide (CO) Hydrogen Sulfide (H_2S) Carbonyl Sulfide (COS) Quench Water Contaminants Flammable/Explosive Gases Ammonia Polynuclear Aromatics Aromatic Amines
CO Shift/COS Hydrolysis	High Temperature High Pressure Carbon Monoxide Hydrogen Sulfide Carbonyl Sulfide Flammable/Explosive Gases Ammonia
Acid Gas Removal	Carbon Monoxide Hydrogen Sulfide High Temperature High Pressure Asphyxiation (CO_2) Flammable/Explosive Gases
Sulfur Recovery	Carbon Monoxide Hydrogen Sulfide Asphyxiation (CO_2) Noise
Waste Water Treatment	Ammonia Quench Water Contaminants

II. ENGINEERING CONTROL TECHNOLOGY

A. Introduction

A two part discussion of each process area in the Coal Gasification and Gas Purification Unit is presented. The first part consists of an area process description. The second part is a discussion of the potential hazards associated with that process area, and the engineering controls used to mitigate those hazards. The term engineering control means the use of hardware (e.g., ventilation systems, mechanical seals, or special metallurgy) to eliminate or reduce an occupational safety or health hazard. Work practices, protective equipment, monitoring programs and health and safety programs as a means of mitigating occupational safety and health hazards are discussed later in the report.

B. Coal Storage and Crushing

1. Process Description

The coals being used at the CGGPU are Illinois #6 and Kentucky #9. Coal is unloaded from hopper cars into an undertrack coal receiving bin. A car shaker is used to assist the discharge of coal. Coal from the bin drops onto a covered belt conveyor that is equipped with a tramp iron magnet. The coal is conveyed to either a 12,000 ton (60 day supply) coal storage pile or directly to a hammer mill where it is crushed to minus 1/2-inch. When coal is not being received at the plant, it is reclaimed from the coal pile with a front-end loader and fed to the crusher. From the crusher, coal is transported by conveyor to a 250-ton capacity coal storage bin. From the storage bin the coal is conveyed to a feed hopper within the wet-grinding area.

2. Control Technology

The potential hazards associated with the Coal Storage and Crushing operations are respirable coal dust emissions from coal crushing and conveying equipment, spontaneous combustion of stored coal, and coal dust explosions. The engineering controls used to mitigate these hazards are:

- State of Alabama coal dust emission permits have been obtained by TVA for this area. One covers coal receiving, unloading, conveying and storage. The other covers the primary coal crushing operation and conveying to the Coal Grinding and Slurry Preparation area. These permits require dust suppression equipment at all transfer points. In addition, the permits require a wet scrubber on the primary crusher. Scrubber water is sprayed on the coal storage pile for dust supression. As a result, respirators are not normally required.

- The coal storage areas are situated away from the remainder of the plant. This distance is provided so that the remainder of the plant will not be endangered by a fire in the coal storage area, and so that the area will be accessible to fire fighting equipment.

- A foam detergent is sprayed onto the coal as it is dumped from the railcar. This controls dust generation during this and subsequent operations.

- The storage pile is compacted to reduce void spaces in the coal which reduces the potential for spontaneous combustion.

C. Coal Grinding and Slurry Preparation

1. Process Description

Figure 3 is a diagram of the coal grinding and slurry preparation area. This is a batch-type operation and is controlled by operators in the area. A commercial plant would employ a continuous operation.

Crushed coal from the 250-ton storage bin is conveyed to a feed hopper on top of the operator-attended grinding/slurry preparation structure. The feed hopper delivers the coal to a weigh-belt feeder which then transfers the coal to a reversible belt conveyor. The reversible belt feeds one of two wet-grind mills. Make-up water from wastewater treatment, and carbon-containing slag and char recovered from the gasifier and product gas quench equipment, is added to the mill along with the crushed coal. The feed rate of make-up water is set to obtain a concentrated solids slurry.

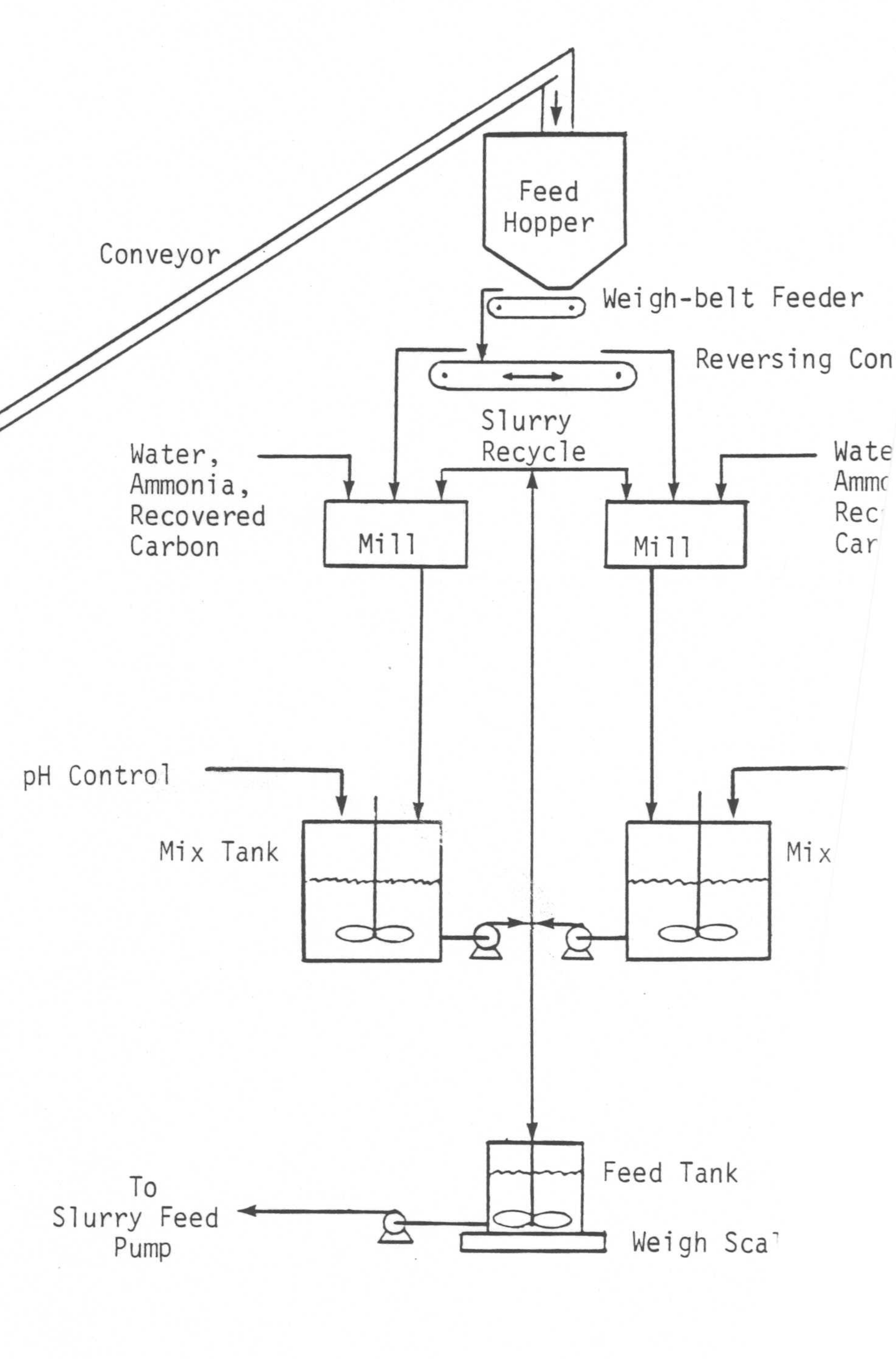

Figure 3. Flow Diagram of the Coal Grinding an
Slurry Preparation Area

The mills discharge to one of two 34,000 gallon agitated slurry mix tanks. Each mix tank holds 64 tons of coal which provides an 8-hour supply of coal feed to the gasifier. The slurry is tested for viscosity, pH, particulate size distribution and solids content. Every two hours, the operator checks for maximum screen-size. When the mills begin giving an improper screen size, the direction of the mill is reversed. The slurry in the mix tank can be recycled back to the mills to eliminate oversized particles.

Slurry is transported from the mix tanks to a 12-hour capacity (100 tons of coal, 60,000 gallon) "run" tank. The run tank sits on a weigh scale. The primary method of agitating the slurry in the run tank is by a mechanical mixer. Slurry from the run tank is transferred to the high pressure gasifier feed pump. The gasifier is fed at a rate of 40 gpm of slurry.

2. Control Technology

The potential hazards associated with the Coal Grinding and Slurry Preparation operations are respirable coal dust, coal dust explosions, noise, ammonia, and organic formates and cyanates.

The generation of coal dust is possible anywhere dry coal is handled. This includes the coal feed hopper, the weigh belt, the reversible belt conveyor, and all coal transfer points. High noise levels are generated by the mills and by the coal feed equipment above the mills. Organic formates and cyanates are dissolved in the make-up water from the wastewater treatment facility, and in the gasifier and particulate scrubber quench water used to recycle char and carbon containing slag to the mills. Leaks or spills of the wastewater, quench water, or coal slurry will release these materials into the workplace. Ammonia may be released from the slurry mix tank.

The engineering controls used to mitigate these hazards are discussed below.

- A dust collection hood is located over the transfer point from the coal feed hopper to the weigh belt feeder. The dust is vented to a bag filter, and the collected particulates are returned to the feed hopper.

- The coal feed hopper is vented to a wet scrubber.

- The reversible belt feeders are equipped with belt scrapers.

- The feed hopper and weigh belt are purged with nitrogen to prevent coal dust explosions. The slurry mix tank has provisions for nitrogen inerting, but thus far it has not been necessary to nitrogen blanket the mix tank.

- The mills grind the coal wet. Wet grinding eliminates the risk of coal dust explosions or fires. It also reduces the coal dust inhalation hazard.

- A pH control agent is added to the mix tank to neutralize the pH of the acidic coal slurry. This is done to reduce corrosion in the mix and run tanks and thus prevent equipment leaks and excessive maintenance.

- The mills are high maintenance items. Servicing the mills requires opening the mill, thus exposing the maintenance workers to potentially hazardous materials in the coal slurry.

- TVA is currently studying a metal-loss problem in the mix and run tanks. TVA says that lower pH accelerates erosion. Erosion of the tanks is most pronounced at the ends of the agitator blades.

- Spills in this process area are flushed into drains that go to the wastewater treatment facility. Fire water or service water is used for hosing down spills.

- The mix tank and run tank pumps are potentially high maintenance items because they pump an erosive slurry. These pumps have given good service thus far.

- The coal feed hopper outlet tends to plug. Air-pulse vibrators were used to aid coal flow but were extremely noisey. TVA has installed air cannons which are quieter than air-pulse vibrators. However, at times, both methods are required for proper coal flow. TVA has proposed installing a Vibra Screw live bottom on the feed hopper. TVA uses this equipment successfully, on the 250 ton coal storage bin.

- The mills are also noisey, however, no engineering controls have been implemented to reduce noise levels.

D. Gasification

1. Process Description

Figure 4 is a diagram of the gasification area. The gasification area includes slurry pressurization and feeding, gasification, ash-slag removal, product gas quenching and scrubbing, and quench water recirculation.

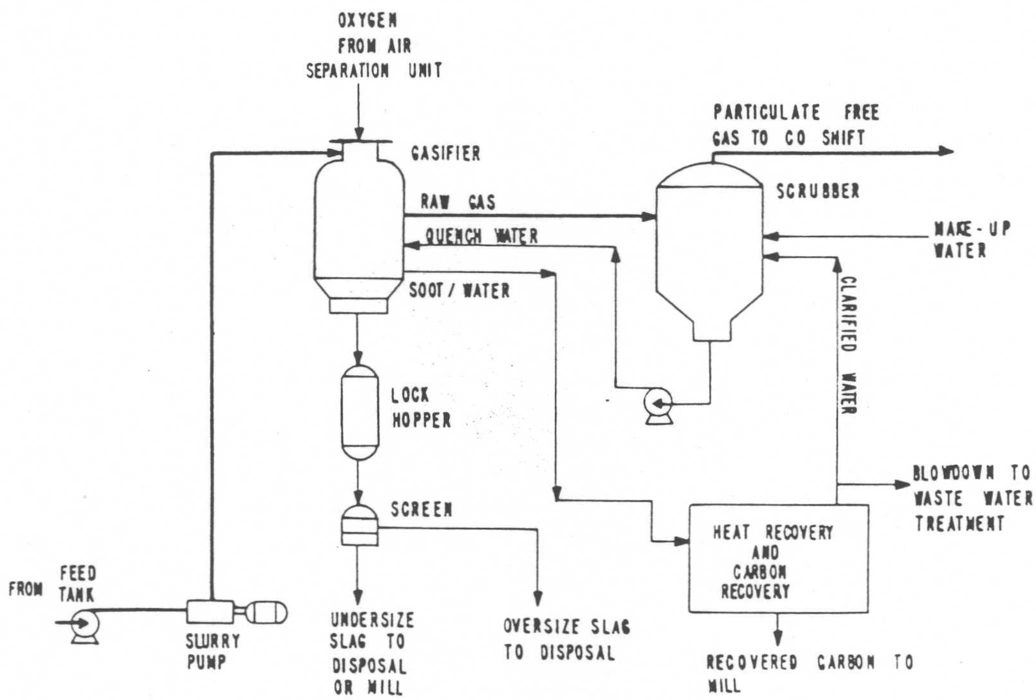

Figure 4. Flow Diagram of the Gasification Area

The slurry is pressurized to about 510 psig and pumped to the gasifier at 40 gpm. If a low-Btu coal is used, the slurry is heated before being fed to the gasifier.

The gasifier used at the CGGPU is an entrained-flow, slagging, oxygen-blown partial oxidation reactor developed by Texaco. The gasifier vessel consists of an upper reaction section which is refractory-lined steel and an unlined lower water-bath quench section. There are no internal moving parts.

Oxygen from the air separation plant is fed to the reactor at a rate of about 7.3 tons per hour at a pressure of 660 psig. Water in the slurry feed provides the steam for the partial oxidation, or gasification, reaction:

$$C + H_2O \longrightarrow CO + H_2$$

The oxygen burns a portion of the coal to provide heat for the endothermic partial oxidation reaction. The gasification reaction takes place in the reactor at a pressure of approximately 510 psig and a temperature in excess of 2200 F (1204 C). Sulfur compounds in the coal react in the reducing atmosphere of the gasifier to produce primarily hydrogen sulfide (H_2S) and some carbonyl sulfide (COS). Small quantities of other compounds such as ammonia and methane are also formed. At the high reactor temperature, no long-chain or aromatic hydrocarbons are formed. The operating temperature of the gasifier is high enough to cause the ash to slag, that is, become molten. The slagging ash droplets coat and flow down the gasifier refractory walls. The product gas and entrained molten slag pass into the quench. The quick-quench solidifies the slag into a pea-size frit-like material. The raw gas then flows into the wet scrubber for additional particulate removal.

The quenched slag is removed by a lockhopper system in the following manner. The quenched slag accumulates in the lockhopper. The valve between the gasifier quench tank and lockhopper is then closed and the discharge valve is opened. The contents of the lockhopper are emptied into a sump tank. The discharge valve is then closed and the upper valve is opened, thus completing the slag removal cycle.

Slag and water from the lockhopper are passed through a screen. About half of the slag is oversize and is moved to disposal. The undersized slag is screened again. If a significant carbon content is found, it can be recycled back to the mills, otherwise it is sent to disposal. Fine slag which is richer in carbon than course slag is recycled back to the mills. The system is designed so that, if desired, the fine slag can be disposed of with the course slag. The lockhopper water is collected in a sump. Excess water from the sump is sent to wastewater treatment. The gasifier quench water contains unconverted carbon. This quench water is withdrawn from the quench section of the gasifier to a heat recovery and carbon recovery system. Carbon is recovered in the form of sludge using a clarifier and is recycled back to the mills.

Clarified water is used as scrubbing water in the raw product gas wet scrubber. A blowdown stream is taken from the clarifier and pumped to the wastewater treatment facility. Particulate-laden scrubbing water from the scrubber reservoir contains unconverted carbon. This water is pumped to the gasifier for use as quench water. The raw gas is cooled and entrained particulates are removed in the wet scrubber. The scrubbing water then flows to a scrubbing water separator. The solids in the separater bottoms are sent to the gasifier. The clarified liquid is returned to the scrubber. The cooled gas leaving the scrubber is about 99.9% particulate free. The gas is then sent to the CO shift/COS hydrolysis section.

Table 3 presents the coal analysis used as the design basis for the CGGPU. Table 4 gives the temperature, pressure, composition and flowrate of product gas, slag and process wastewater blowdown from the gasifier.

2. Control Technology

The hazardous agents associated with the Gasification area include: carbon monoxide, hydrogen sulfide, carbonyl sulfide, organic formates and cyanides, flammable/explosive product gas, ammonia, high temperatures and pressures, noise and heat stress. Nickel carbonyl has not been detected at the Texaco pilot plant, however, an analysis of gasifier operating conditions by Texaco

TABLE 3

Coal Analysis

Proximate Analysis (Dry Basis)	Percent By Weight
Volatile Matter	37.3
Ash	13.3
Fixed Carbon	49.4
Moisture (as received)	7.8
Ultimate Analysis (Dry and Ash Free)	
Carbon	78.1
Hydrogen	5.5
Nitrogen	1.3
Oxygen	10.9
Chloride	0.1
Total Sulfur	4.3

Heating Value	BTU/LB
As received	11,480
Dry	12,375
Ash and Moisture-Free	14,279

ASH FUSION ANAYLSIS

Ash Fusion (In Reducing Atmosphere)	Temperature, ^{O}F
Initial Deformation	1980
Softening Point	2100
Fluid Point	2220

TABLE 4

Operating Conditions and Composition of Gasifier Streams

	Exit Gas from Gasifier to Venturi Scrubber	Slag Out	Blowdown to Wastewater Treatment
Temperature, ^{o}F	433	160	140
Pressure, psig	505	0	50
Flow, lbs/hr	83,350	4,230	24,045
Flow, SCFM*	10,957	--	--
WT.% Solids	--	50	0.5
Component	VOL.%		
Hydrogen	10.9		
Nitrogen	0.1		
Carbon Monoxide	14.6		
Carbon Dioxide	5.7		
Methane	0.1		
Argon	0.1		
Hydrogen Chloride	--		
Hydrogen Sulfide	0.4		
Water	68.1		
Carbonyl Sulfide	255 ppm		
Ash, Grains/SCF	--		
Slag	--		
Carbon	--		
Ammonia	--		
TOTAL	100.0		

* SCFM at $60^{o}F$ and 29.92 in Hg

predicts the formation of trace amounts.* The engineering controls used to reduce the potential for worker exposure to these agents is discussed below. Many of the controls discussed involve making the process more reliable in order to reduce the amount of maintenance required and thus reduce the potential for maintenance worker exposure to hazardous agents.

- The slurry transfer piping between the slurry feed tank and the gasifier is insulated and heat traced to prevent plugging in cold weather.

- Texaco recommends that the slurry transfer piping be flushed and filled with water during shutdowns to prevent the thixotropic slurry from plugging the line.

- The bearings failed in the pumps that circulate scrubber water back to the quench section of the gasifier. The failures are thought to be due to cavitation caused by plugged strainers on the pump suction.

- Operating conditions throughout the gasification area are outside the range of conditions which promote hydrogen embrittlement.

- The refractory lining in the gasifier was deteriorating. Texaco is working on a solution to this problem, however their work is proprietary.

- Because the thermocouple assemblies in the hot zone of the gasifier failed, gas leaks occurred. Texaco modified the thermocouple assemblies to solve the problem; however, information describing the modifications is proprietary.

- The thermocouple assemblies extend radially about 2 feet from the gasifier. This creates a safety problem for the plant operators. Each thermocouple was boxed in with 2 x 4 lumber.

- Flanges are checked for leaks during start-up operation. Each flange is taped and a pinhole is put in the tape. The pinhole is then checked with a portable CO monitor.

- Spiral wire thermoresistors are wrapped around the outside of the top section of the gasifier at various heights. These thermoresistors are used to detect a change in the skin temperature of the gasifier should the refractory lining fail. This will prevent a catastrophic failure of the gasifier pressure vessel shell.

- In order to heat-up the gasifier, a start-up burner is inserted through a flanged opening in the top of the gasifier. Replacing the start-up burner with the injector nozzle takes approximately 15 minutes, then the aspirator is shut-off.

---

*Texaco, Montibello, Trip Report, ECI, for NIOSH

- Flexitallic gaskets are used to prevent leaks at the flanged connections of the gasifier.

- Slag is granular, glassy material. As a result there is no dust problem associated with slag removal, storage, or disposal.

- The sump that the slag lockhopper discharges into is covered to prevent emissions of off-gases into the work area. The sump is vented to the Stretford sulfur recovery unit.

- The valves on the ash lockhopper are constructed of carbon steel with nickel-plated trim. The valves have leaked, requiring repair and replacement.

E. CO Shift/COS Hydrolysis

1. Process Description

The process gas from the wet scrubber flows through heat exchangers to a two stage carbon monoxide shift converter. The shift reactors are charged with a Haldor-Topsoe sulfur-tolerant shift catalyst. Gas flows, compositions, temperatures, and pressures in and out of the two stages of shift conversion are shown in Table 5.

The gas entering the converter is about 23 percent CO on a wet basis. After the shift, the CO content is about 2 percent, which matches the CO content of the gas entering the low-temperature shift converter in TVA's existing ammonia plant.

The carbonyl sulfide produced during the gasification is not removed by the sulfur recovery process. To decrease the quantity of COS, a hydrolysis unit containing activated alumina catalyst is provided to convert COS to H_2S by the reaction:

$$COS + H_2O \rightarrow CO_2 + H_2S.$$

Table 6 gives the flowrates, compositions, temperatures and pressures in and out of the hydrolysis unit. The effluent from the unit will contain less than 10 ppmv COS.

TABLE 5

CO Shift Conversion

	Shift 1 Inlet	Shift 1 Outlet	Shift 2 Inlet	Shift 2 Outlet
Temperature, °F	399	797	605	644
Pressure, psig	484	478	470	465
Flow, SCFM*	17,416	17,395		17,395
Components, Volume %				
Hydrogen	17.0	35.6		37.6
Carbon Monoxide	23.0	4.1		2.1
Carbon Dioxide	9.0	27.7		29.8
Hydrogen Sulfide	0.6	0.7		0.7
Carbonyl Sulfide	400ppm	58ppm		36ppm
Methane	0.1	0.2		0.2
Water Vapor	50.0	31.4		29.3
Nitrogen	0.2	0.2		0.2

*SCFM at 60°F and 29.92 in Hg (Source, Reference 2)

TABLE 6

COS Hydrolysis Unit

	Inlet	Outlet
Temperature, °F	401	401
Pressure, psig	462	458
Flow, SCFM*	17,395	17,395
Components, Volume %		
Hydrogen	37.6	37.6
Carbon Monoxide	2.1	2.1
Carbon Dioxide	29.8	29.8
Hydrogen Sulfide	0.7	0.7
Carbonyl Sulfide	36ppm	7ppm
Methane	0.2	0.2
Water Vapor	29.3	29.3

* SCFM at 60°F and 29.92 in Hg (Source, Reference 2)

2. Control Technology

The hazardous agents associated with the CO Shift/COS Hydrolysis area are: carbon monoxide, hydrogen sulfide, carbonyl sulfide, flammable/explosive gases, catalyst dust and high temperatures and pressures. Catalyst replacement may expose maintenance workers to catalyst dust. The life of the sulfur activated cobalt-molybdenum catalyst for the CO shift reactors is on the order of a few years, with a similar life for the COS hydrolysis catalyst. Therefore minimal exposure to catalyst dust is expected. During normal operations, emissions should be small, since these are commercially proven processes. Controls used to reduce emissions of hazardous materials include pressure during start-up, and leak inspection during operation.

F. Acid Gas Removal

1. Process Description

The process gas from the COS hydrolysis unit flows to the acid gas removal (AGR) system. The AGR system uses Allied Chemical's Selexol process (a physical absorbent system) to remove CO_2, H_2S, and the remaining COS from the process gas. Figure 5 is a diagram of the AGR process. Flow rates, compositions, temperatures and pressures in and out of the system are given in Table 7.

The system consists of a two-stage absorber, flash vessels where absorbed gases are flashed from the solution in stages, and a stripper where the spent solution is nitrogen stripped of last traces of sulfur. Regenerated solution is then returned to the absorber to remove CO_2 and sulfur gases (H_2S and COS) from the synthesis gas. The AGR system is capable of decreasing the total sulfur in the synthesis gas stream to less than 1 part per million by volume. Two reject acid gas streams are produced during regeneration of the Selexol solvent. One stream, containing up to 4 percent H_2S, is sent to a Holmes-Stretford sulfur recovery system and is then vented to the atmosphere. The second stream is relatively pure CO_2. This gas is sent to a separate Holmes-Stretford sulfur recovery unit and then to a zinc oxide sulfur guard reactor to meet sulfur purity requirements before being delivered to the urea manufacturing facility.

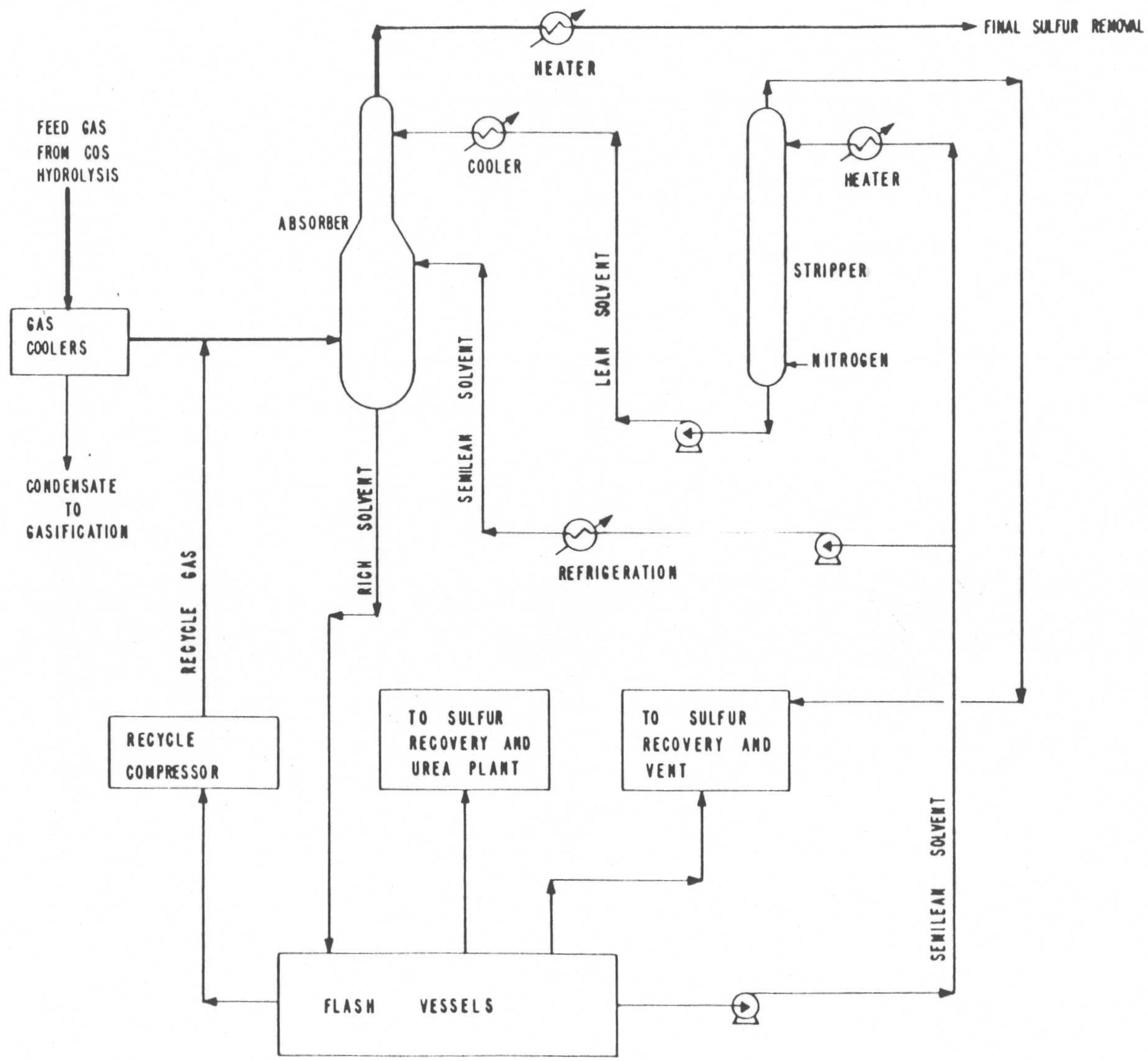

Figure 5. Flow Diagram of the Acid Gas Removal Area[7]

TABLE 7

Acid Gas Removal

	Product Gas		CO_2 to Holmes-Stretford	
	Inlet	Outlet	Vent	Urea Mfg.
Temperature, ^oF	289[a]	100	104	80
Pressure, psig	448	412	7	23
Flow, SCFM*	13,970	8,660	3,097	896
Components, Volume %				
Hydrogen	37.6	75.5	0.1	1.0
Carbon Monoxide	2.1	4.1	163 ppm	0.2
Carbon Dioxide	29.8	19.5	85.0	97.9
Hydrogen Sulfide	0.7		3.6	0.8
Carbonyl Sulfide	7ppm		29 ppm	14 ppm
Methane	0.2	0.3	61 ppm	0.1
Water Vapor	29.3	-	0.2	-

* SCFM at 60^oF and 29.92 in Hg

a Inlet to absorber is 55^o F

2. Control Technology

The hazardous agents associated with the Selexol acid gas removal system are: carbon monoxide, hydrogen sulfide, carbon dioxide, flammable/explosive gases, Selexol solvent (the dimethyl ether of polyethylene glycol-DMPEG) and high pressures. During normal operations, emissions from the process should be minor as this is a commercially proven process. Controls used to reduce emissions of hazardous materials include pressure testing equipment and piping during start-up, and leak inspection during operation.

G. Sulfur Recovery

1. Process Description

Two acid gas streams containing CO_2 and H_2S are withdrawn from the Selexol acid gas removal system and sent to separate absorption trains in the sulfur recovery system. This system uses a Holmes-Stretford process. A flow diagram of the process is shown in Figure 6. Flowrates and compositions in and out of the Stretford sytem are given in Table 8.

The Stretford system uses a proprietary solution containing an oxidized form of vanadium salts. The H_2S is oxidized in the solution to produce elemental sulfur according to the following reaction:

$$H_2S + 1/2\ O_2 \longrightarrow S + H_2O$$

The reduced metal salt is regenerated by blowing air through the solution. This operation also floats the elemental sulfur to the surface. The sulfur is skimmmed off and filtered to produce a wet granular cake.

One of the objectives of the ammonia from coal project is to demonstrate production of a CO_2 stream suitable for urea manufacture. For economy reasons, only 25% of the CO_2 removed from the process gas stream is treated in this manner. This stream from the AGR solution regeneration system contains about 0.8% H_2S and is processed in one of the two absorber trains in the sulfur recovery system. The CO_2 leaving the absorber

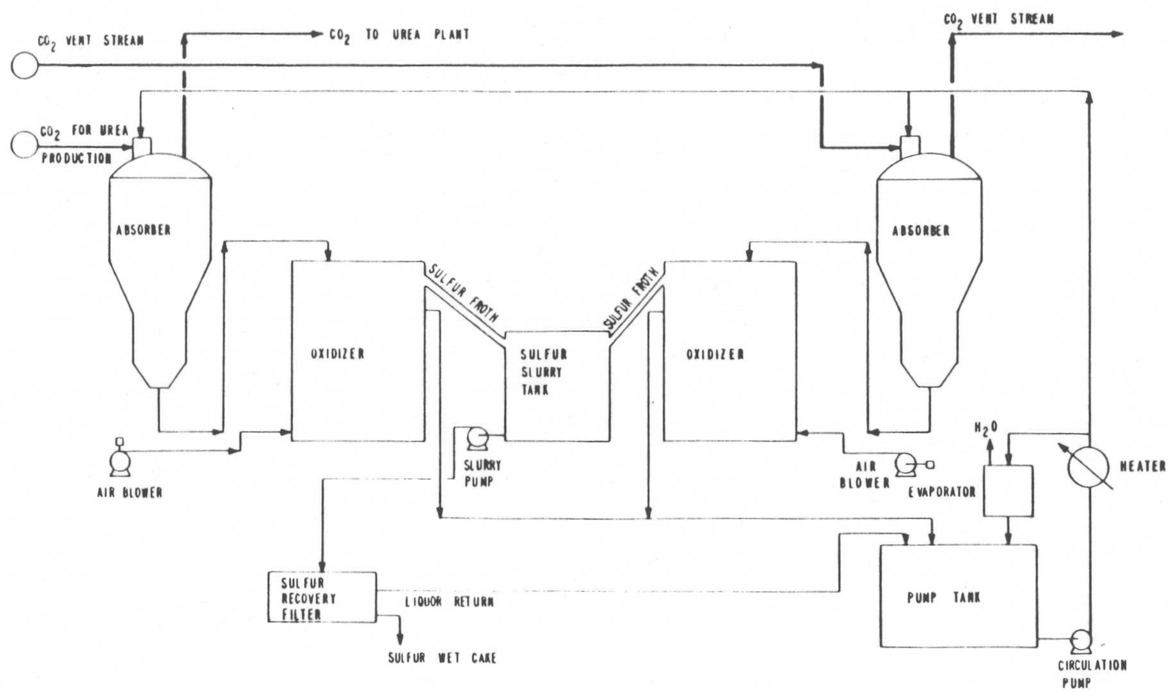

Figure 6. Flow Diagram of the Holmes-Stretford Sulfur Recovery Area

Table 8

Sulfur Recovery

	CO_2 to Urea		CO_2 to Vent	
	Inlet	Outlet	Inlet	Outlet
Temperature, °F	80	90	104	90
Pressure, psig	23	15	7	3
Flow, SCFM*	896	785	3,118	2,867
Components, Volume%				
Hydrogen	1.0	1.1	0.1	0.1
Carbon Monoxide	0.2	0.2	163 ppm	176 ppm
Carbon Dioxide	97.9	96.4	85.0	83.3
Hydrogen Sulfide	0.8		3.6	
Carbonyl Sulfide	14 ppm		29 ppm	
Nitrogen	71 ppm	80 ppm	11.1	12.7
Methane	0.1	0.1	61 ppm	66 ppm
Water Vapor	-	2.2	0.2	3.9

*SCFM at 60 F and 29.92 in Hg (Source, Reference 2) contains about 5 parts per million of H_2S and flows to a vessel containing zinc oxide to decrease the total sulfur content to less than 0.5 part per million to meet requirements for urea manufacture. This gas will be vented to the atmosphere when not being used by the urea plant.

The larger CO_2 stream from the AGR system contains up to 4% H_2S and is sent to the second absorber train in the sulfur recovery system. The tail gas from the absorber train contains about 160 parts per million by volume of H_2S, less than 30 parts per million by volume of COS, and less than 500 parts per million by volume of CO. The CGGPU plant has an emissions permit for this stream.

2. Control Technology

The hazardous agents associated with the Stretford Sulfur Recovery System are: hydrogen sulfide, carbon monoxide, carbonyl sulfide, carbon dioxide and noise from the oxidizer tank blowers.

Although noise levels around the oxidizer tanks is 90 dBA, workers are usually not in the area. Exposure to H_2S, CO, CO_2 and COS may occur due to leaking flanges and pump seals, and during maintenance of the sulfur recovery equipment. During normal operation, emissions from the process should be minor as this is a commercially proven process. Controls used to reduce emissions of hazardous materials include pressure testing equipment and piping systems during start-up and leak inspection during operation.

H. Wastewater Treatment

1. Process Description

Carbon-containing water from the gasifier quench section and wet scrubber, is sent to a clarifier to recover the carbon fines. Clarifier overflow is recycled to the scrubber and quench section of the gasifier. A blowdown stream is pumped to the wastewater treatment facility for chemical physical, and biological treatment. In the chemical treatment unit, the wastewater is first treated in a clarifier by addition of ferrous sulfate and hydrated lime to flocculate solids. The liquid fraction from the clarifier is steam-stripped to remove ammonia. The ammonia is recovered and routed to the coal slurry preparation area to neutralize the acidic slurry. The stripped aqueous material containing organic matter, primarily as formates, along with water from washdown operations is sent to an equalization-cooling basin for pH control, mixing, and cooling. After aeration the effluent from the equalization-cooling basin flows to the activated sludge unit for biological treatment. The overflow from the activated sludge unit is metered and sampled on its way to discharge. The sludge from biological treatment is combined with flocculated sludge from the clarifier and conditioned with ferric chloride to improve filtration. The conditioned sludge is then pumped to the filter press where the solids are removed for disposal. The filtrate is returned to the wastewater treatment system. Flowrates and compositions in and out of the wastewater treatment system are given in Table 9.

2. Control Technology

The hazardous agents associated with the Wastewater Treatment are ammonia and formates. Because of the limited amount of time this process unit has been onstream, the extent of the danger posed by these hazardous agents and the engineering controls that may have to be installed cannot be evaluated until more operating experience is gained.

Table 9

Wastewater Treatment

	Inlet	Outlet	Solids to Landfill
Flow, gal./min.	25*	29	-
Solids, lb./hr.	-	-	83
Total Suspended Solids, mg/l	330	30	-
Total Dissolved Solids, mg/l	1842	150	-
Ammonia - mg/l	1600	9	-
Sulfide - mg/l	100	1	-
Cyanide - mg/l	45	8	-
Formate - mg/l	350	150	-
Chloride - mg/l	1320	1140	-
Total Organic Carbon - mg/l	760	-	-
Total Inorganic Carbon - mg/l	104	-	-
BOD, ppm	-	30	-
COD, ppm	-	60	-

*Normal blowdown from gasification area. There will be additional flows from miscellaneous sumps.

III. WORK PRACTICES

A. Introduction

TVA states that the Texaco gasifier produces no heavy liquid by-products (coal tars) because of the high operating temperature of over 2200 F (1204 C). TVA also maintains that through their program of preventive maintenance, there will be minimal process leakage. Therefore, worker exposure should be a problem only during maintenance activities that require opening process lines and equipment. For these activities, work practices and procedures will be developed and modified as necessary to protect the worker's health and safety.

General practices have been developed for activities known or suspected of being hazardous. Such activities include start-up and shutdown, equipment maintenance and repair, and handling of spills. Workers handling chemical additives, and liquid and solid process wastes will use protective clothing and equipment if exposure, or the potential for exposure indicates the need for special protective measures. Process stream sampling, a major potential source of exposure in other facilities, is not expected to be performed at the TVA facility because of the use of on-line process stream monitoring.

B. Start-up

Process leaks are most likely to occur during start-up. Since the TVA gasifier operates at high pressure (510 psig) all systems are pressurized in incremental stages, with checks for leaks at each stage of pressurization. One method of checking for leaks is to tape certain flanged joints. If there is a leak, the tape will turn brown, providing an easy means of spotting flange leaks. In addition, the operators and industrial hygienists search for leaks, generally at the beginning of each shift, with hydrogen sulfide and carbon monoxide portable monitors. All leaks are repaired immediately, even if a shutdown is required.

C. Shutdown

During shutdown, either planned or emergency, the system is purged with an inert gas to clear the system of process gases and vapors. The oxygen feed line to the gasifier is blocked-off and purged with nitrogen. These steps are taken to purge the system of toxic and/or explosive gases before any repair work is performed during plant downtime.

Before working on process equipment, a safety and health hazard evaluation must be performed. If an inhalation hazard is believed to be present, a temporary exhaust system is used. Permanent ventilation systems are installed if work of a periodic nature is required. Hydrogen sulfide and carbon monoxide portable monitors are carried to provide a continuous readout of contaminant levels during the repair activity. Equipment is prepared for maintenance by being blocked-off; motors are locked-out and bleed-valves are opened to relieve any pressure in the system.

A vessel is prepared for entry by mechanically isolating it from all outside sources using blinds, caps, plugs, or valves. Isolating, or blanking-off a vessel consists of:

- closing the appropriate valves and depressurizing the vessel,
- removing a section of pipe between the valve and the vessel, and
- capping or plugging the valve.

If blanking-off is impractical, then the appropriate valves are closed, chained, and double-locked.

Once isolated, the vessel is drained and its contents disposed of or stored. The vessel is then purged with steam, or washed with chemical solvents followed by purging with an inert gas such as nitrogen. An alternative to the inert gas purge is to use fans to blow air through the vessel. This technique is prohibited if the exhaust gas will contaminate the area or create a fire hazard.

After purging with air, the vessel is opened and the vessel atmosphere is tested. The concentration of toxic gases, such as hydrogen sulfide and carbon monoxide, is measured with direct-reading instruments. The level of oxygen is measured and must be greater than or equal to 19% by volume. Respirators will be required if toxic gases are present in hazardous concentrations or if an oxygen-deficient atmosphere exists in the vessel. Supplied air respirators are used under these situations.

If the level of combustible gases exceeds 10% of the lower explosive limit, the vessel is purged again or reventilated to bring levels below 10%. Once testing criteria are met, the worker may enter the vessel. A buddy system is followed that allows only one person in the vessel at any given time.

D. Housekeeping

Time is allowed for each operator for cleanup of his assigned area. Liquid spills are cleaned by scooping up the material and adding an absorbent to the residue. The absorbent is removed and the area is scrubbed with a brush using a commercial detergent/water mixture. Flushing with only water is not permitted.

Dried spills are cleaned by one of two methods: either scrubbing with chlorinated hydrocarbon solvent or industrial detergent or by steam stripping. If steam stripping is employed, supplied-air respirators must be used.

Tools and equipment are decontaminated using commercial detergents and solvents. After cleaning, tools are examined in an ultraviolet dark box to ensure that all fluorescent contaminant has been removed.

Contaminated clothing is discarded. This is a precautionary measure followed because of the suspected carcinogenicity of PNAs. Showers are required at the end of the shift for those maintenance personnel who have entered contaminated vessels or who have otherwise come into contact with organic liquids.

E. Administrative Controls

Manually operated audible alarms located throughout the main process structure can be sounded to warn workers in the vicinity of major process upsets. Upon hearing the alarm, people are required to evacuate the structure.

A chain barrier has been placed around the gasifier to keep people away during operation. High maintenance equipment is installed at ground level whenever feasible to simplify maintenance requirements. A preventive maintenance program has been instituted following equipment manufacturer recommendations to reduce the number of equipment failures during plant operations.

IV. PROTECTIVE CLOTHING AND EQUIPMENT

TVA management and safety personnel consider the entrained-bed gasification system to be a relatively clean process. Additionally, because leaks and equipment failures are expected to be minimized by the plant's preventive maintenance program, the gasification facility is not expected to present any significant health concerns. Therefore, a simple protective clothing and equipment policy was adopted. This policy will be modified as needed once the plant achieves steady-state operation and worker exposure is characterized.

No special clothing regulation is enforced when the plant is not operating. During startup, operators are expected to wear disposable coveralls, boots, and hood. The operators who change burners wear mirror-finish fire suits during this operation. When the plant is operating, only disposable coveralls are required to prevent contact with any tars that may be formed. Exposure to tars is considered unlikely since an ultraviolet scan of coveralls after a 2-day run showed no fluorescence.

Workers engaged in maintenance activities are required to wear cotton coveralls, boots or shoe covers, hood, and gloves. Cotton gloves are generally used although other types such as rubber gloves are available. Cotton clothing or barrier creams are recommended when handling soda ash. Workers in the wastewater treatment area handle caustics and acids, and are therefore required to use goggles or face shield, rubber gloves, and rain coats.

Self-contained breathing appartus (SCBA) and supplied-air respirators are available for use at the facility. The SCBAs are used for emergency situations and have been placed in the main control room, coal preparation control room, and within the process area. Air outlets for the supplied-air respirators are located throughout the plant and are used mainly for entry into confined spaces, such as the gasifier, in order to perform maintenance work. The inspection and maintenance of these respirators are the responsibility of the Safety and Industrial Hygiene Branch.

V. INDUSTRIAL HYGIENE MONITORING

TVA personnel have had no prior experience with the gasification of coal and its associated health problems. Therefore, the industrial hygiene monitoring program proposed for this facility was based on information obtained from the literature and from discussions with people who have developed similar programs. TVA's monitoring program will be implemented once the plant reaches a steady-state mode of operation.

The program will consist of continuous area monitoring, compliance surveillance, and research monitoring. Continuous monitoring will record hydrogen sulfide, carbon monoxide, and combustible gas levels. Remote detection probes will be located throughout the main process area to monitor the concentration of these materials in the workplace. The combustible gases are of concern because of their flammable and explosive nature. Hydrogen sulfide and carbon monoxide pose an acute toxicity hazard because of their high concentration in the product gas stream.

Research monitoring is designed to characterize worker exposure to selected hazards and to insure that gasifier workers are not over exposed. The hazards selected include coal dust, simple aromatics such as benzene, coal tars, noise and heat. During the start-up of the facility a walk-through inspection and evaluation of the plant was conducted to determine:

- operational status of area monitors and engineering controls
- effectiveness of protective clothing and equipment program
- presence of any unsuspected potentially hazardous situations
- completeness of plant operations procedures with regard to health and safety.

Immediately following the attainment of steady-state conditions, area and personal samples will be collected to assess worker exposure to the selected contaminants. The results of this survey will be used to:

- determine which hazardous agents will be monitored periodically,
- maintain a record of employee exposure history and,
- assess protective clothing needs for plant personnel.

VI. HEALTH AND SAFETY PROGRAMS

A. Employee Education and Training

All workers now at the gasification facility have participated in a comprehensive 14-hour training program. This program is the same as that given to all TVA employees working on the Ammonia from Coal Project. The program uses a safety manual, slide presentation, demonstration, and worker participation to familiarize workers with the hazards present within their work environment and the protective measures available for reducing exposure to those hazards. Exams given at the end of selected segments of the program are used to evaluate worker comprehension of the TVA health and safety program.

Figure 7 is a typical training schedule. The entire program is given to new employees with different segments being emphasized on a periodic basis. New operators are on probation for a year and spend a portion of this time with a seasoned operator learning the correct and safe method of executing his duties.

B. Medical Program

The TVA medical program was developed based on information obtained from a review of the literature and from NIOSH. The program consists of a pre-employement and annual physical examination. The pre-employment physical is designed to detect pre-existing conditions that might be aggravated by working at the gasification unit. Emphasis of the examination is upon the condition of the skin, respiratory tract, and genitourinary tract. This examination was given to all workers in 1980, prior to the start-up of the gasifier.

The pre-employment and annual medical examinations are similar and include chest x-rays, audiograms, pulmonary function tests, and a skin examination. High quality color photographs are taken of exposed skin surfaces and any suspicious skin lesions or other skin problems. Sputum and urine cytology was discontinued because of the controversy involving the interpretation of results. The termination or transfer examination is expected to be the same as the pre-employmemt examination. Follow-up examinations of these workers will be voluntary.

Time	Tuesday	Wednesday	Thursday	Friday
8:00 - 8:55	Introduction Employee Rights and Responsibilities	ACP Chemical Hazards	Combustible Gas Testers	Heat and Cold Stress Solvent Usage
9:05 - 10:00	Compressed Gas and Cryogenic Safety	Air Contaminant, Noise Level, and Heat Stress Monitoring Equipment	Warning Signs, Colors, and Tags	Overview of Program
10:10 - 11:05	Noise Hazards	Respiratory Protection Equipment	Confined Space	
11:10 - 12:00	Back and Lifting Safety			

Figure 7. Training Schedule: Ammonia From Coal Project Safety and Health Orientation

VII. CONCLUSIONS AND RECOMMENDATIONS

The health and safety programs at the Ammonia from Coal Plant will not be completely defined until after the plant has achieved steady-state operation. The existing work practices and protective clothing requirements should provide adequate protection from any potential dermal contact with PNA-hearing material.

Barrier creams may be effective protection under mild working conditions such as handling weak acids and bases. However, impervious gloves of rubber or other suitable materials may be a better choice for handling strong acids and bases such as soda ash.

The respirator program can be more effective if other types of respirators are included. Escape-type respirators should be conveniently located through the process area to provide workers with a quick and reliable means of escape during process upsets. However, this type of respirator cannot be used for rescue purposes. SCBAs are not recommended for escape purposes because of the time required to don these respirators.

Air-purifying respirators may be used for certain vapors and under some conditions. Only fresh air suppled equipment is recommended for hydrogen sulfide and carbon monoxide. This is because of the poor warning qualities which these two gases exhibit.

Operating experience at the CGGPU has been extremely limited. It is probable that the need for additional engineering controls will be recognized once the plant has achieved steady-state operation.

REFERENCES

1. Tennessee Valley Authority, P.C. Williamson, D.A. Waitzman, Environmental Considerations for TVA's Ammonia from Coal Project: The Fertilizer Institute: Environmental Symposium '80 papers; April 7,8,9,10, 1980.

2. Tennessee Valley Authority, D.A. Waiteman (TVA), G.W. Alves (Brown & Root Development, Inc.), The TVA Ammonia From Coal Project- 1980 Update, Prepared for Coal Technology '80 3rd Internation Coal Utilization Conference and Exhibition; November 18-20, 1980.

3. Tennessee Valley Authority, R.D. Young and E.H. Brown. History of U.S. Facilities at Muscle Shoals, Alabama and Origins of TVA, Southeast Regional Meeting of American Chemical Society, October 29, 1976.

4. Eickmeyer & Associates, A.G. Eickmeyer and H.A. Gangriwala, The Role of Acid Gas Removal in Synfuels Production, Presented at the Symposium on Gas Purification at the AICHE 1981 Spring National Meeting and 11th Petrochemical Exposition Houston, Texas.

5. Eickmeyer & Associates, A.G. Eickmeyer, Saving Energy and Dollars With The CATA Processes, Presented at Petroenergy 80, Houston, Texas, September 17, 1980.

6. Catacarb CO_2 and H_2S Removal, Reprint from Hydrocarbon Processing, September 1974.

7. Tennessee Valley Authority, National Fertilizer Development Center, New Developments in Fertilizer Technology, 13th Demonstration; October 7-8, 1980.

8. Tennessee Valley Authority, National Fertilizer Development Center: Progress 80 - Annual Report.

9. Tennessee Valley Authority, Office of Agriculture and Chemical Development, Division of Chemical Development; Investigation Phase Report: Ammonia From Coal Project; October 1976.

10. Tennessee Valley Authority; Symposium: Ammonia From Coal; May 8-10, 1979.

11. National Institute for Occupational Safety and Health Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants; Enviro Control, Inc. January 1978; EPA-60017-78-007, DHEW (NIOSH) No. 78-120.

12. National Institute for Occupational Safety and Health Criteria for a Recommended Standard....Occupational Exposures in Coal Gasification Plants; September 1978, DHEW (NIOSH) No. 78-191.

13. Dravo Corporation, Chemical Plants Division, Handbook of Gasifiers and Gas Treatment Systems, February 1976, FE-1772-11, U.S. Energy Research and Development Administration.