NIOSH

CRITERIA FOR A RECOMMENDED STANDARD....

OCCUPATIONAL EXPOSURES IN

Coal Gasification Plants

U S DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

criteria for a recommended standard....

OCCUPATIONAL EXPOSURES
IN COAL GASIFICATION PLANTS

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

September 1978

DISCLAIMER

DHEW (NIOSH) Publication No. 78-191

PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and provide for the safety of workers occupationally exposed to an ever-increasing number of potential hazards. The National Institute for Occupational Safety and Health (NIOSH) has projected a formal system of research, with priorities determined on the basis of specified indices, to provide relevant data from which valid criteria for effective standards can be derived. Recommended standards for occupational exposure, which are the result of this work, are based on the effects of exposure on health. The Secretary of Labor will weigh these recommendations along with other considerations, such as feasibility and means of implementation, in developing regulatory standards.

Successive reports will be presented as research and epidemiologic studies are completed and as sampling and analytical methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of workers.

The contributions to this document on coal gasification by NIOSH staff members, the Review Consultants on Coal Gasification, the reviewers selected by the American Industrial Hygiene Association and the American Conference of Governmental Industrial Hygienists, and by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, are gratefully acknowledged.

The views expressed and conclusions reached in this document, together with the recommendations for a standard, are those of NIOSH. They are not necessarily those of the consultants, reviewers selected by professional societies or other Federal agencies that evaluated the document, or of the contractor. The comments from the Review Consultants and other reviewers have been considered carefully and, whether or not incorporated into the document, have been sent along with the criteria document to the Occupational Safety and Health Administration for its consideration in setting standards. A list of review consultants and a list of the Federal agencies to which the document was submitted are given on pages vi and vii.

Vernon E Rose
for J. Michael Lane, M.D.
Acting Director, National Institute
for Occupational Safety and Health

The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for the development of the criteria and recommended standard for coal gasification. Murray L. Cohen of this Division served as criteria manager and had program responsibility for this document. Enviro Control, Incorporated, developed the basic information for consideration by NIOSH staff and consultants under contract CDC-210-76-0171.

The Division review of this document was provided by Richard A. Rhoden, Ph.D. (Chairman), Jon R. May, Ph.D., and Frank L. Mitchell, D.O., with James H. Sterner, M.D., and Seymour D. Silver, Ph.D.

Funding of this project was provided by the Environmental Protection Agency under the Interagency Energy-Environment Research and Development Program.

REVIEW CONSULTANTS ON COAL GASIFICATION

Dennis I. Chamot, Ph.D.
Council of AFL-CIO Unions for Professional Employees
Washington, D.C. 20013

Cubia L. Clayton
Deputy Director
Health and Social Services Department
New Mexico Environmental Improvement Agency
Santa Fe, New Mexico 87503

Maury E. Goldman, M.D.
Medical Director
Exxon Research and Engineering Company
Linden, New Jersey 07036

Dale Hattis, Ph.D.
Center for Policy Alternatives
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

H. Ray Newsom
Director
Energy Conversion Development
Panhandle Eastern Pipeline Company
Houston, Texas 77001

Richard A. Wadden, Ph.D.
School of Public Health
University of Illinois at the Medical Center
Chicago, Illinois 60680

FEDERAL AGENCIES

Department of Defense

- Department of the Air Force
    - Office of the Surgeon General
    - Aerospace Medical Research Laboratory
    - Environmental Health Laboratories
- Department of the Army
    - Army Environmental Hygiene Agency
- Department of the Navy
    - Navy Environmental Health Center

Department of the Interior

- Bureau of Mines
- Fish and Wildlife Service
- Mining Enforcement and Safety Administration (now the Mine Safety and Health Administration, US Department of Labor)

Department of Energy

Environmental Protection Agency

National Aeronautics and Space Administration

Department of Health, Education, and Welfare

CRITERIA FOR A RECOMMENDED STANDARD...

OCCUPATIONAL EXPOSURES IN COAL GASIFICATION PLANTS

Contents

CRITERIA FOR A RECOMMENDED STANDARD...
OCCUPATIONAL EXPOSURES
IN
COAL GASIFICATION PLANTS

I. RECOMMENDATIONS FOR A COAL GASIFICATION STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to toxicants and hazardous conditions in coal gasification plants be controlled by adherence to the following sections. The recommended standard is designed to protect the health and provide for the safety of employees for up to a 10-hour workshift, 40-hour workweek, during a working lifetime. Compliance with all sections of the recommended standard should prevent or greatly reduce the adverse effects of toxicants or hazardous conditions on the health of employees and provide for their safety.

No attempt has been made in this document to develop permissible levels of exposure to toxic substances specific to coal gasification plants. It is recommended that where applicable existing Federal occupational exposure limits (29 CFR 1910, Subpart Z) be enforced, except where NIOSH has recommended a reduction in the existing Federal limit or where there is no existing Federal limit, in which cases the NIOSH recommendations should apply. Valid and reproducible techniques for measuring exposure are available to industry and government agencies. Furthermore, existing technology is adequate to permit compliance with the recommended standard. The criteria and recommended standard will be subject to review and revision as necessary.

These criteria and the recommended standard apply to the exposure of employees to toxicants and hazardous operating conditions in commercial coal gasification plants. As used herein, the term "commercial coal gasification plant" refers to any plant using coal to produce a gas that will be sold as a source of energy or otherwise utilized for commercial purposes. These criteria and the recommended standard pertain principally to the types of plants whose technology, construction, and utilization are anticipated around the year 1985. The term "toxicants" applies to all raw materials, products, and byproducts of coal gasification processes that may produce a toxic effect; toxicants include, but are not limited to, asphyxiants, irritants, nuisance particulates, poisons, and carcinogens. The following terms are used interchangeably with the term "toxicant(s)": "toxic compound(s)," "toxic material(s)," "toxic gas(es)," "hazardous material(s)," and "hazardous agent(s)." The term "hazardous operating conditions" refers to conditions that may impair the health of, or cause physical injury to, employees.

For all sections of the recommended standard except workplace monitoring, the terms "occupational exposure" and "employee exposure" are defined as any contact with any toxicant(s) in the work environment. For purposes of workplace monitoring, these terms are defined as in the existing Federal standards (29 CFR 1910) except where NIOSH has used different language, in which case the NIOSH definition applies.

Epidemiologic and toxicologic evidence from related processes has led NIOSH to conclude that employment in coal gasification plants may entail exposure to a number of chemical compounds that can increase the risk of cancer in exposed employees. Because of the large number of toxicants that may be present in a coal gasification plant, guidelines are presented for an indicator monitoring method to allow real-time detection of leakage in coal gasification plants. However, before it is adopted as a procedure for compliance with standards, this method should be compared with methods for the detection of specific hazardous compounds in terms of accuracy and sensitivity.

These criteria for a recommended standard encompass the entire coal gasification process and all of the attendant hazards. An engineering approach, separating coal gasification processes into unit operations, has been used to facilitate the orderly development of these criteria. Recommendations herein for the effective control of hazardous exposures are specific for the hazards associated with individual unit operations, although there are many recognized commonalities among the unit operations. These recommendations are not intended to replace existing general industry safety and engineering standards, although they do supplement such standards as necessary for coal gasification plants.

Each of three types of coal gasification processes is presented in a separate section of the recommended standard, distinguished not only by operating process and technology but also by the nature and extent of potential exposures: (1) high-BTU product coal gasification, (2) coal gasification (low- or medium-BTU product) utilizing bituminous coal or lower ranked feedstocks, and (3) coal gasification (low- or medium-BTU product) utilizing anthracite feedstock or very high temperatures. This allows the unique aspects of various processes to be discussed within a framework of principles and requirements that are common to all coal gasification processes.

Section 1 - High-BTU Coal Gasification

General Process Requirements

(a) Safety Procedures

During the design of a commercial coal gasification plant or during the design of a major modification of an operating plant, a thorough fault-tree systems analysis, failure-mode evaluation, or equivalent safety analysis shall incorporate a review of potential exposures to toxicants and physical agents as well as safety considerations. Process operating modes, including startup, shutdown, and emergency, shall be considered. Control options to protect employees during any identified failure mode shall be incorporated into the final plant design or into the standard operating and emergency procedures.

Automatically activated fire extinguishing equipment or its equivalent shall be installed in compressor areas, over lubricating oil consoles, over pumps containing material at or above its autoignition temperature, and over process vessels containing flammable liquids.

(b) Engineering Control Objectives

All lines or equipment containing toxic gases, vapors, or liquids shall be designed, constructed, and maintained to minimize leakage.

Collection systems draining to sealed sumps or equivalent shall be designed for the disposal or reuse of toxic materials which may leak from pumps, vessels, and other equipment.

Equipment and systems for handling or transferring tar and tar oil shall be enclosed to the extent feasible or shall otherwise be designed or controlled to prevent skin or eye contact and to minimize exposure to airborne particulates.

Drains and sumps from which flammable or toxic vapors may escape shall be engineered in such a manner as to prevent leakage or explosive mixtures.

Suspected leak points of equipment, vessels, or lines (eg, flanges, valves, pump shafts) containing toxic materials shall be individually monitored as appropriate for early leak detection.

Means shall be provided to shut down a process area safely in case of equipment failure.

Equipment shall be designed, located, controlled, or otherwise engineered to limit employee exposure to noise. The NIOSH recommended noise limit is 85 dBA for a continuous exposure of 8 hours. For other durations of exposure, see Chapter 14.

In areas of potentially high exposure, a procedure or an area shall be provided to protect the worker in the event of any dangerous emergency situation. Nonwork areas in which employees can eat or rest during breaks shall be designed to exclude contaminated air.

Where feasible, thermal barriers shall be installed around hot equipment or piping to protect employees from burns.

Flares used for disposal of gases shall be equipped with a pilot and an automatic alarm to signal pilot failure. Flare stacks shall be designed to minimize the emission of particulate matter or of uncombusted hydrocarbons.

(c) Work Practices

A preventive maintenance and inspection program shall be developed and implemented to maximize equipment reliability.

During maintenance, means shall be provided for the isolation of process components or integral units of equipment from the rest of the process. Before work in or on any tank, line, or equipment is commenced, provisions shall be made for the prevention of inadvertent entry of inert or toxic materials into the work area. Isolation blinds on valves shall be installed before employee entry. Where there are no valves, lines shall be disconnected or blinded. During startup, all flange bolts (on equipment, vessels, or lines) that had previously been opened shall be cold torqued and the flanges observed for leakage.

Process equipment and connecting lines handling toxic gases, vapors, or liquids shall be flushed, steamed, or otherwise purged before being opened. Liquids so flushed shall be safely disposed of by diversion to sealed drains, storage vessels, or other appropriate collecting devices. Toxic gases shall be safely disposed of by incineration, flaring, return to process, or by other effective means.

Tanks, process equipment, and lines shall be cleaned, maintained, and repaired only by properly trained employees under responsible supervision. When practical, such work shall be performed from outside the tank or equipment. Entry into confined spaces such as tanks, pits, and process vessels shall be controlled by a permit system. Such permits must be signed by an authorized representative of the employer and shall certify that preparation of the confined space, precautionary measures, and personal protective equipment are adequate and that prescribed procedures have been followed. No employee shall enter any tank or vessel that does not have an entrance large enough to allow free entry and exit to an employee equipped with safety harness, lifeline, and appropriate respiratory equipment. Employees entering contaminated tanks or vessels shall wear full-bodied protective clothing and appropriate safety equipment until inspection and testing have established that safe conditions exist. Confined spaces which have contained toxic gases shall be inspected and tested before and during entry for oxygen deficiency, presence of toxic gases, and flammable or explosive gas mixtures; shall be thoroughly ventilated, cleaned, neutralized, and washed, as necessary; shall be sealed off from adjacent spaces or vessels prior to entry by employees; and shall be mechanically ventilated during entry. Employees entering confined spaces where they may be exposed to toxic gases shall wear appropriate respiratory protective equipment if mechanical ventilation may not be adequate to maintain safe concentrations of released toxic gas. In confined spaces, supplied-air respirators shall be operated only in the positive pressure continuous-flow or pressure-demand mode and shall have an auxiliary self-contained air supply sufficient to permit escape.

When employees are working in confined spaces where hazardous conditions could develop, they shall also wear suitable harnesses with lifelines tended by an employee outside the confined space who shall also be equipped with the appropriate respiratory protective equipment. The two workers shall be in constant communication by an appropriate means and shall be under the surveillance of a third person equipped to take appropriate action to rescue them if necessary.

Confined spaces in which work is in progress shall be ventilated to keep the concentration of any toxic gases below their permissible exposure limits and to prevent oxygen deficiency.

The accumulation of hazardous material on work surfaces, equipment, and structures shall be minimized, and spills and leaks of hazardous materials shall be cleaned up as soon as possible. Employees engaged in cleanup operations shall wear suitable respiratory protective equipment and protective clothing. Cleanup operations shall be performed and directly supervised by employees instructed and trained in procedures for the safe decontamination or disposal of equipment, materials, and waste. All other persons shall be excluded from the area of the spill or leak until cleanup is complete and until safe conditions have been restored.

In any process area where there is a potential for the contamination of surfaces with tar or tar oil, such surfaces shall be pretreated to facilitate contaminant removal. After contaminant removal has been accomplished, the selected treatment shall be reapplied to the affected surface. Materials contaminated with tar or tar oil shall be treated or disposed of in such a manner that employees will not inhale, ingest, or otherwise come into contact with such materials, and water supplies will not be contaminated.

Employers shall designate as regulated areas all areas in which there is potential exposure to tar or tar oil. Only authorized personnel shall be allowed to enter such areas.

Facilities with adequate ventilation shall be provided for cleaning tools and equipment.

Procedures for sampling process lines or equipment containing toxic materials shall include the employment of local exhaust ventilation at sampling ports or the use of appropriate respiratory and full-body protective equipment, or other means to limit employee exposure to toxicants.

Washroom facilities, eyewash fountains, and emergency showers shall be provided at locations readily accessible from all areas where hazardous materials may contact the skin or eyes of employees. Employees shall be encouraged to wash their faces, necks, and hands as necessary during the workshift to remove contamination.

Contamination from process residues shall be prevented in eating areas. Before entering such areas, employees shall remove contaminated hardhats, gloves, and other protective equipment. Washing facilities shall be readily available.

Employers shall develop emergency plans and procedures, and take necessary steps to ensure that all employees are adequately trained in their effective implementation. Emergency procedures shall be reviewed periodically with employees, and written descriptions of the procedures shall be made available in work areas. Appropriate emergency equipment, including protective devices for rescue, shall be located adjacent to areas in which exposure to hazardous materials might occur. During emergencies, all employees shall be evacuated from the area except trained and properly equipped emergency personnel.

Each employee shall be instructed and trained in safe work practices and in the proper use of operational equipment and protective devices. Each employee shall participate in refresher sessions and drills, at least annually, in safe work practices and emergency procedures. Each employee shall be informed of the locations of all emergency and first-aid equipment and supplies in the work area and shall be informed of the requirement to report to responsible supervisory personnel any emergency, hazardous exposure, or injury.

(d) Workplace Monitoring

Existing Federal occupational exposure limits shall be enforced except where NIOSH has recommended a reduction in the existing Federal limit, or where there is no existing Federal limit, in which cases applicable NIOSH recommendations shall be complied with.

Area and personal monitoring for respirable particulates shall be conducted at least monthly in the following unit process areas: coal storage and preparation, coal feeding, and ash removal and disposal. The frequency of area and personal monitoring for respirable particulates may be reduced to a quarterly basis if six consecutive monthly determinations show that the concentrations of respirable particulates do not exceed the workplace exposure limit.

(e) Medical Surveillance

Medical surveillance shall be made available, as specified below, to all employees occupationally exposed in coal gasification plants. As applicable, NIOSH medical surveillance recommendations in criteria documents for workplace exposure to other hazardous substances shall also be considered.

Preplacement medical examinations shall include the following:

(1) Comprehensive medical and work histories, with special emphasis on the identification of preexisting disorders of the skin, respiratory tract, liver, and kidneys.

(2) A physical examination giving particular attention to the oral cavity, skin, and respiratory system. This shall include posteroanterior X-ray films (14 x 17 in) of all employees.

(3) Pulmonary function tests, including forced vital capacity (FVC) and forced expiratory volume at 1 second (FEV 1.0) shall be offered as part of the medical examination of employees who may be exposed. Other tests, such as sputum cytology, urinalysis, urine cytology, electrocardiogram, and multiple serum chemistry tests shall be performed as deemed necessary by the responsible physician. Audiometric examinations shall be given to all employees who may be exposed to noise.

(4) An evaluation of the employee's ability to use positive-pressure respirators shall be made.

(5) Employees or prospective employees with medical conditions that may be directly or indirectly aggravated by work in a coal gasification plant shall be counseled regarding the risks associated with employment in such plants.

Periodic examinations shall be made available at least annually. These examinations shall include interim medical and work histories and a physical examination, as outlined above.

On termination of employment, a physical examination following the same protocol as that of the periodic examination shall be made available if no such examination has been performed within the preceding calendar year.

Employee medical records should also include records of workplace exposures. Pertinent medical records shall be retained for 30 years after an employee's last occupational exposure in a coal gasification plant. These records shall be made available to the designated medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee or former employee.

(f) Personal Protective Clothing and Equipment

Employers shall provide, and shall instruct employees to wear, suitable clothing to prevent skin contact with tar and tar oil where the potential for exposure exists. These garments shall be made of materials resistant to penetration by tar and tar oil.

Gloves shall be used that are impervious to process residues. Nondisposable gloves shall be capable of withstanding cleaning.

Protective clothing for maintenance employees shall be selected for effectiveness in providing protection from the hazards associated with the specific work area involved. In all cases, documented work procedures shall designate the minimum protective clothing and equipment requirements for these employees.

Eye protection as required by 29 CFR 1910.133 shall be provided. Cup-type chemical safety goggles shall be worn by employees engaged in activities in which hazardous materials may come in contact with the eyes. In addition, full-length plastic face shields (8 inch minimum) shall be worn in areas where contact with tar or tar oil is likely, except when full-facepiece respirators are being worn.

Engineering controls shall be used when needed to keep the concentrations of airborne toxicants at or below the workplace exposure limits. Respirators may be used only during the time necessary to install or test the required engineering controls and for nonroutine operations or during emergencies when brief exposures at concentrations exceeding these limits may occur.

When use of respirators is permitted as stated above, such respirators shall be selected and used in accordance with the following requirements:

(1) Employers shall establish and enforce a respiratory protective program, according to the requirements of 29 CFR 1910.134.

(2) Based on the toxicants to be protected against, employers shall provide respirators and shall ensure that employees use the respirators properly when the concentrations of toxicants exceeds the workplace exposure limits. The respirators shall be those approved by NIOSH or the Mine Safety and Health Administration (MSHA). The standard for approval is specified in 30 CFR 11. Employers shall institute practices and procedures to ensure that respirators are properly fitted, cleaned, maintained, and stored when not in use.

(3) Emergency respirators for a given area shall be NIOSH- or MSHA-approved for specific protection against the process gases that may be present in that area. Emergency equipment shall be located at well-marked and clearly identified stations and shall be adequate to protect personnel during escape from the area or other emergency operations.

(4) Employers shall ensure that all protective equipment is regularly inspected and maintained and that damaged items are repaired or replaced.

(g) Sanitation

Employers shall provide clean change rooms equipped with storage facilities for street clothes and separate storage facilities for work garments, protective clothing, and protective equipment. "Clean" and "dirty" change rooms separated partially by a shower facility and partially by one-way doors should be installed in areas of high risk. Lockers should be provided on the "clean" side for each occupationally exposed employee. Facilities should be made available on the "dirty" side for storage of workboots, hardhats, and other safety equipment.

Employers shall ensure that, at the completion of a workshift, all protective clothing is removed only in the appropriate change rooms and that contaminated protective clothing that is to be drycleaned, laundered, or disposed of is placed in closed, labeled containers.

Protective clothing, respirators, goggles, and other personal protective gear that has been contaminated by hazardous substances shall be thoroughly cleaned before reuse. Persons who launder or dryclean contaminated protective clothing, or who clean contaminated protective equipment, shall be advised of the hazards associated with handling such clothing or equipment and of safe handling procedures. Contaminated shoes shall be decontaminated or discarded in a safe manner. Clothing which cannot be thoroughly decontaminated shall be discarded in a safe manner.

The presence, consumption, or dispensing (including vending machines) of food and beverages shall be discouraged in areas with a potential for exposure to tar and/or tar oil. The use of tobacco and chewing gum, and the application of cosmetics, shall also be discouraged in these areas.

Employees shall be instructed to wash their hands thoroughly with soap or mild detergent and water before using toilet facilities or eating.

To avoid enhanced dermal absorption of hazardous materials, employers shall instruct employees not to use chemical solvents for removing these materials from the skin.

Any employee whose clothing or person becomes contaminated with hazardous substances shall, as appropriate, wash, shower, shampoo, and/or change into clean work clothing promptly.

(h) Labeling and Posting

All signs and labels shall be kept clean and readily visible at all times.

All warning signs shall be printed both in English and in the predominant language of non-English-reading employees. All employees shall receive information regarding hazardous areas and shall be informed of the instructions printed on labels and signs.

During the performance of regulated functions such as maintenance, start-up, and shutdown, the immediate work area shall be secured and the following warning sign shall be posted at entrances:

CAUTION

RESTRICTED AREA

AUTHORIZED PERSONNEL ONLY

In all regulated areas the following sign shall be posted in readily visible locations at or near all entrances and on or near all equipment used for handling or containing these materials:

DANGER
CANCER HAZARD

AUTHORIZED PERSONNEL ONLY
WORK SURFACES MAY BE CONTAMINATED
PROTECTIVE CLOTHING REQUIRED
NO SMOKING, EATING OR DRINKING

In all areas where there is a potential for exposure to toxic gases, signs shall be posted in readily visible locations at or near all entrances. As a minimum, the signs shall contain the following information:

CAUTION

TOXIC GASES MAY BE PRESENT

AUTHORIZED PERSONNEL ONLY

In any area where emergency situations may arise from accidental skin, eye, or other exposures, the signs prescribed above shall be supplemented, where applicable, with additional information, such as emergency and first-aid instructions and procedures; the location of first-aid supplies and emergency equipment, including respirators; and the locations of emergency showers and eyewash fountains.

In areas where respiratory protection is required, the following statement shall be added to the signs prescribed above:

RESPIRATOR REQUIRED

Process vessels shall be labeled to warn employees that they contain toxic materials, as in the following:

CAUTION

(NAME OF CONTENTS)

CONTAINS TOXIC MATERIALS

All vessels, lines, or other equipment containing hazardous materials shall be identified by labeling, coding, or other effective means. Process samples and contaminated equipment intended for repair shall be identified, such as with colored tags.

(i) Informing Employees of Hazardss

At the beginning of employment or assignment for work, employers shall inform each employee of the potential hazards of such employment and of the possible adverse health effects resulting from such employment. Employees shall be instructed in the proper procedures for safe handling and use of raw materials, products, and by-products in coal gasification plants, in the operation and use of protective systems and devices, and in appropriate emergency procedures.

Employers shall institute a continuing education program, conducted by persons qualified by experience or special training, to ensure that all employees have current knowledge of job hazards, proper maintenance procedures, cleanup methods, and the correct use of personal protective equipment. The instructional program shall include a description of the medical and workplace surveillance procedures and the advantage of participating in these procedures.

(j) Recordkeeping

Records of workplace and personnel monitoring shall be retained for the duration of employment and for at least 30 years after the employee's last occupational exposure in a coal gasification plant. These records shall include the dates and times of measurements, job function and location within the workplace, methods of sampling and analysis used, types of respiratory protective devices in use at the time of sampling, concentrations of indicator or other hazardous substances found, and identification of exposed employees. Employees shall be allowed to obtain information on their own exposures. Workplace monitoring records and entry rosters shall be made available to designated representatives of the Secretary of Labor and of the Secretary of Health, Education and Welfare.

Signed work permits shall be kept on file for 1 year after the date of use.

Specific Unit Process Recommendations

(a) Coal Storage and Preparation

Coal storage piles shall be appropriately stacked to prevent oxidation and reduce the potential for ignition, and coal bins shall be designed to reduce coal oxidation and to prevent the accumulation of flammable gases.

Conveyor belts or elevators used for transporting coal shall be designed to minimize the dispersion of coal dust. Each transfer point shall be provided with an effective means of reducing dust emissions.

Coal bins directly attached to gasifiers shall be emptied before gasifiers or lockhoppers are taken out of service for extended periods.

An area emergency deluge system shall be located at points where high dust concentrations may result in fire or other hazardous conditions. Activation of the deluge system for an area shall automatically shut down equipment in that area.

Employees who may be exposed to coal dust should wear long-sleeved shirts, close fitting at the neck and cuffs, with trousers that overlap the top edge of the work boots. Employees shall be required to wear safety glasses, safety boots, gloves, and hardhats.

(b) Coal Feeding

A positive differential pressure shall be maintained between the coal-feed lockhopper and the gasifier in order to prevent the escape of gases from the gasifier through the lockhopper. Pressurizing gas not returned to the process shall be disposed of by flaring, incineration, or other appropriate means.

The section between the top of the coal-feed lockhopper and the coal feedbin shall be designed to minimize toxic gases and coal dust from entering the workplace.

An area emergency deluge system shall be located at points where high dust concentrations may result in fire or other hazardous conditions. Activation of the deluge system for an area shall automatically shut down equipment in that area.

(c) Coal Gasification

The start-up gas shall be flared, incinerated, or disposed of by an equivalent method.

During start-up, measures shall be taken to prevent the development of explosive mixtures in the gasifier or gasifier start-up vent during the first few minutes of operation with air. The same measures shall be repeated after switching to oxygen operation.

The gasifier shall be fitted with alarms and automatic equipment designed to facilitate safe shutdown in the event that any of the major operating parameters are exceeded.

Relief valves shall be designed and installed in such a manner that they will not become blocked.

(d) Ash Removal and Disposal

Ash-lockhopper systems shall be fitted with alarms and interlocking systems designed to allow operation only if operating parameters are within specified limits.

In any system in which dry ash dumping is necessary, employees shall wear respirators approved by NIOSH or MSHA for particulate matter, and appropriate protective equipment to prevent burns.

All potential leak points (flanges, valves, etc) shall be visually examined at least once per shift for evidence of water or steam leaks.

(e) Gas Quenching and Cooling

Piping or vessels with high erosion or corrosion rates shall be inspected at least annually and appropriate maintenance undertaken.

Whenever a failure occurs in the recycle system for the quench liquor, interlocking devices or equivalent means shall automatically activate a flush system. Whenever this system fails, the gasifier shall be taken off stream.

(f) Gas-Liquor Separation

Lines used for the removal of expansion gases shall be designed to prevent blockages.

Gas-liquor flow between the high- and low-pressure sections shall be effectively controlled in order to prevent gas breakthrough into the low-pressure section.

(g) Shift Conversion and Gas Cooling

Lines and vessels shall be monitored to indicate leakage due to hydrogen embrittlement, hydrogen blistering, corrosion, or erosion.

A dust-suppression system shall be available for use during catalyst loading and unloading procedures.

Gases resulting from the regeneration of catalysts shall be incinerated or safely disposed of in an appropriate manner.

(h) Gas Purification (Rectisol)

A system shall be provided to receive, transport, and store the methanol from all tanks, heat exchangers, pumps, and other equipment during emergencies and during maintenance operations.

(i) Methanation

Where nickel catalysts are used, an interlock system or its equivalent which is designed to safely dispose of any gas containing nickel carbonyl shall be incorporated.

Lines and vessels shall be monitored to indicate leakage due to hydrogen embrittlement or hydrogen blistering.

Start-up procedures for catalytic methanation units using nickel catalysts shall be designed to prevent the introduction of carbon monoxide into the unit before reactor temperatures exceed 260 C (500 F). During reactor shutdown procedures, all carbon monoxide shall be removed from the reactor before the temperature falls below 260 C.

Section 2 - Recommended Standard for Low- or Medium-BTU Gasification Utilizing Bituminous Coal or Lower Ranked Feedstocks

All general process requirements stated in Section 1, subparts (a)-(j), shall be met.

All specific unit process requirements stated in Section 1, subparts (a)-(f) shall also be met, as shall the following additional requirements:

(a) Coal Feeding

The sections between the top of the coal feed lockhopper and the coal feedbin and between the top of the coal feedbin and the coal storage bin shall be designed and constructed to prevent the escape of toxic gases and coal dust into the workplace.

(b) Coal Gasification

Pokeholes shall be designed to prevent the escape of toxic gases and vapors into the work area.

Section 3 - Recommended Standard for Low- or Medium-BTU Gasification Utilizing Anthracite Feedstock or Very High Temperatures

All general process requirements stated in Section 1, subparts (a)-(i), shall be met.

All specific unit process requirements stated in Section 2 shall be met with the exception that for processes which produce no tar and tar oil, those sections pertaining to tar and tar oil shall not apply.

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon that were prepared to meet the need for preventing occupational diseases and physical injuries arising from employment in commercial coal gasification plants. The criteria document fulfills the responsibility of the Secretary of Health, Education and Welfare, under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substances which will describe...exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

The National Institute for Occupational Safety and Health (NIOSH), after a review of data and consultation with others, formalized a system for the development of criteria upon which standards can be established to protect the health and provide for the safety of employees exposed to hazardous chemical and physical agents. The criteria for a recommended standard for the coal gasification industry should enable management and labor to develop better work practices and engineering and administrative controls that will result in a healthful work environment in this industry. This document is intended as a starting point for the development of superior controls, and simple compliance with the recommended standard should not be regarded as the final goal.

These criteria and the recommended standard for coal gasification plants are part of a continuing series of documents developed by NIOSH. The recommended standard for commercial coal gasification plants encompasses the entire coal gasification process, including all emissions from the primary gasification unit and from those auxiliary units that are unique to coal gasification processes. It is intended to (1) protect the health of, and prevent injury to, workers in coal gasification plants and (2) be attainable with existing technology.

The development of these criteria involved a worldwide literature survey and evaluation, visits to and evaluations of operational coal gasification facilities in the United States and abroad, and review of occupational safety and health practices and records in coal gasification plants. Data from operations and facilities with analogous exposures, such as coke ovens and coal liquefaction plants, were also considered in identifying potential hazards to workers in coal gasification plants. The health effects literature for specific regulated substances that might be present in coal gasification plants was not reevaluated. Permissible exposure limits cited in this report are either those already enforced by the Federal government or recommended previously by NIOSH.

To facilitate the development of the recommended standard, coal gasification processes were examined on the basis of unit operations, each of which is described herein as a separate entity. Specific exposure points, potential hazardous emissions, engineering controls, and specific safety procedures are discussed in relation to each unit operation. Control strategies were developed for each unit operation expected to exist in the commercial coal gasification plant.

The US Energy Research and Development Administration (now a part of the US Department of Energy) has estimated that by the year 2000 coal gasification products will be supplying 8.6 quadrillion BTU/year of our national energy needs [1], at which time the coal gasification industry may employ as many as 140,000 workers. Current coal gasification technology was developed largely before and during World War II. However, the Federal government and private industry are investigating various other approaches to coal gasification at the theoretical, bench-scale, and pilot-plant stages. It has been estimated that these "second generation" technologies will not be in commercial use before 1985 [2].

The scope of this document has been deliberately limited to commercial coal gasification technologies that will likely be operational in the US within ten years. On the basis of the nature and severity of potential occupational exposures these technolgies may be considered under the following categories:

1. High-BTU coal gasification;
2. Low- or medium-BTU coal gasification utilizing bituminous or lower ranked feedstock; and
3. Low- or medium-BTU coal gasification utilizing anthracite feedstock or very high temperatures.

In the course of the development of the recommended standard, several areas requiring further research were identified. Comprehensive, reliable industrial hygiene evaluations are needed to quantify worker exposures to hazardous agents in coal gasification plants. Control technology assessments and the development of effective engineering controls to prevent hazardous exposures should be accomplished simultaneously with the development of the coal gasification industry. Retrospective morbidity and mortality studies of workers who have left the coal treatment and coal conversion industries should be performed. The accuracy and utility of the indicator monitoring concept in identifying hazardous concentrations of airborne toxic chemicals in workplace air should be verified.

III. HAZARDS TO HEALTH AND SAFETY FROM EXPOSURES IN COAL GASIFICATION PLANTS

Potential Exposures

(a) High-BTU Coal Gasification

After the mid 1980's, the development of the second generation coal gasification processes (such as HYGAS, Bi-Gas, CO2 Acceptor, etc) should be sufficiently advanced for one or more of these processes to be commercialized and eventually replace the Lurgi gasifier in the United States. Until then, commercial high-BTU coal gasification plants built in the United states will follow the Lurgi design with minor modifications to suit local conditions [3-6]. Some of the statistics for four proposed high-BTU coal gasification plants are shown in Table III-1.

TABLE III-1

COAL GASIFICATION PLANT STATISTICS(a)

	Plant			
	A	B	C	D
Rated plant capacity(b)	275	ND	270	288
Capacity for 365 days per year operation(b)	250	250	246	266
Coal feed rate, Total tons/day	30,000	33,400	32,470	28,250
Number of gasifiers, total	34	ND	ND	28
Plant site, acres	1,070	1,440	ND	960
Area actually occupied, acres	300	640	334	ND
Personnel, plant only	612	ND	800	883

(a) Data for plants A-D adapted from references 3 through 6, respectively

(b) In millions of standard cubic feet per day (scfd)

Each of these proposed plants will require 600-1,000 employees. By 1985, 4,000 persons could be employed in high-BTU coal gasification plants. It is estimated that 40-90 of these facilities could be in operation by the year 2000 [2]. The principal product of these plants will be a pipeline-quality (high-BTU) gas with a heating value of approximately 1,000 BTU/standard cubic foot (scf). Byproducts may include coal tar, naphtha, phenolic compounds, sulfur, and ammonia.

The unit operations of the Lurgi process are: Coal handling and preparation, coal feeding, coal gasification, ash removal, quenching, shift conversion, gas cooling, gas purification (acid gas removal), methanation, sulfur removal, gas-liquor separation, phenol and ammonia recovery, and byproduct storage and cleanup. Brief discussions of these operations follow (more detailed information is presented in Chapter XI).

(1) Coal Handling and Preparation

Coal is delivered from the mine to the plant unloading hopper from which it is transferred by feeders and conveyors to primary and secondary mechanical crushers and is then stockpiled (Figure III-1). Later the coal is moved from the stockpile to sizing screens and to the coal-cleaning operation, for removal of fines which may present a dust and/or explosion hazard. The cleaned, sized coal is then used to produce gas and steam and, in some cases, power. Reject material can be returned to the mine for final disposal.

Occupational health hazards associated with the coal handling and preparation process include exposure to coal dust, noise, and fires from possible spontaneous combustion of coal in the storage areas, with the potential attendant inhalation of the products of combustion.

(2) Coal Feeding

After passage through the preparation operation, the coal is moved by conveyor either to intermediate storage or directly to the gasifier coal bunker (Figure III-2). Coal is then fed from this bunker to the coal lockhopper (Figure XI-2), the operation of which is cyclic, ie, the lockhopper is charged with coal, pressurized to gasifier pressure (with CO2, raw gas, etc), opened to discharge the coal to the gasifier, closed, depressurized, and then recharged with coal, the entire cycle taking 10-30 minutes. Each depressurization releases an estimated 280 cubic feet (cu ft) of pressurizing gas (which is incinerated or otherwise disposed of) [6]. It is conceivable that pressurizing gas or raw gas (see Table III-2) could be released into the coal bunker and result in exposure of operators.

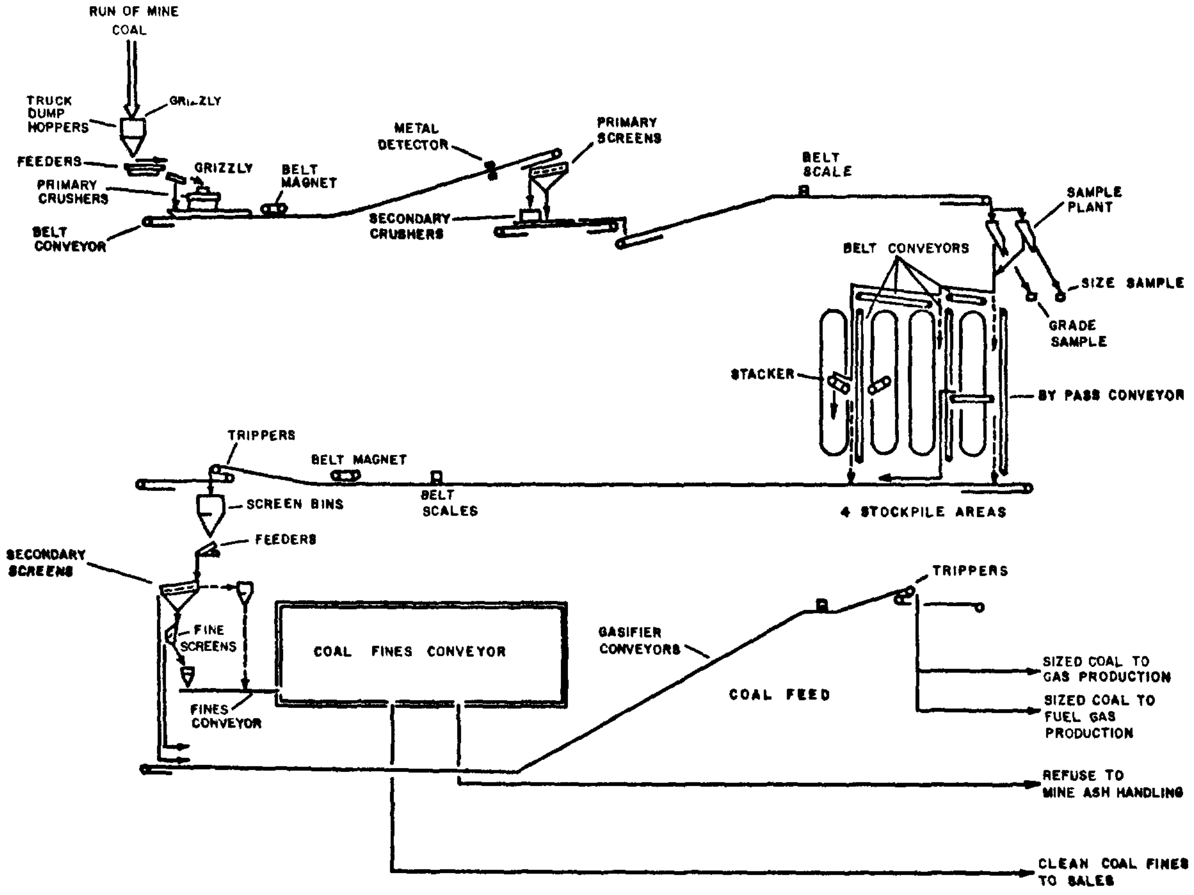
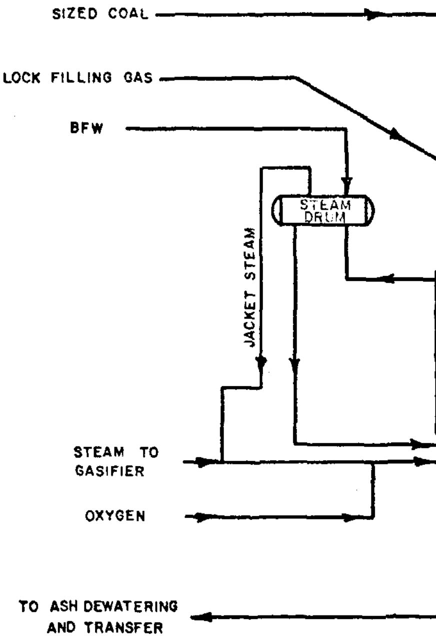


Figure III-1
Flow Scheme for Coal Handling and Preparation

Adapted from Reference 6



Adapted from Reference 6

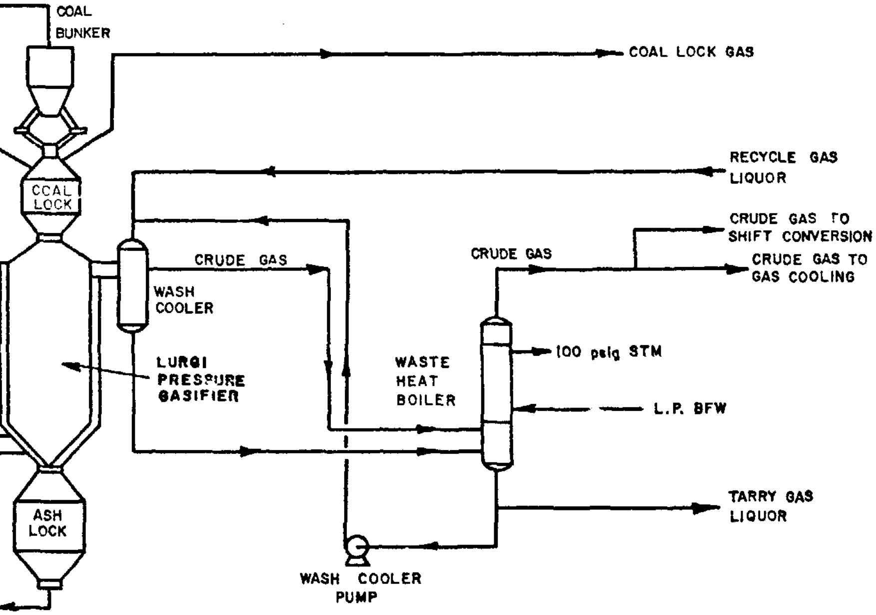


Figure III-2
Flow Scheme for Gas Production

Occupational health hazards associated with the coal-feeding process include exposure to coal dust, noise, and gaseous toxicants (Table III-2). There is also a potential for asphyxiation by inert gases used for lockhopper pressurization.

TABLE III-2

TYPICAL RAW GAS COMPOSITION (DRY)

Constituent	Concentration (vol %)
Carbon dioxide	28.4
Carbon monoxide	19.9
Ethane	0.6
Ethylene	0.1
Hydrogen	38.7
Hydrogen sulfide	0.5
Methane	10.3
Nitrogen and argon	0.3
Other hydrocarbons(a)	0.2

(a)"Other hydrocarbons" include propane, butane, benzene, toluene, xylene, napthalene, and phenols

Adapted from Reference 3

(3) Coal Gasification

High-BTU gasifiers operate at pressures of 350-450 pounds per square inch gauge (psig), and at temperatures of 870 C (1,598 F) in the combustion zone and 345 C (653 F) at the gas offtake. The feed streams to the gasifier are coal, steam, and oxygen [3].

Traveling by gravity, coal from the lockhopper encounters the hot gas rising to the top of the gasifier and is gradually heated to combustion temperature through successive, overlapping zones of preheat, devolatilization, gasification, and combustion. It is in the preheat and devolatilization zones, where temperatures range from 345 to 620 C (653 to 1,148 F), that the crude gas, tar, tar oil, naphtha, phenols, and other complex compounds are formed. Trace elements are volatilized from all parts of the bed. Steam and oxygen enter the gasifier near the bottom and are heated by the hot ash moving downward from the combustion zone.

Occupational health hazards associated with the gasifier operation include potential exposure to coal dust, high-pressure hot gases, trace elements, tar, fire, and noise.

(4) Ash Removal

Ash from the gasifier is continuously removed by a rotating grate and collected in a steam-pressurized lockhopper from which it is discharged. The ash is then dewatered and disposed of. The ash lockhopper pressurizing steam is condensed after passing through a cyclone for particulate removal and is vented to the atmosphere. Particulates collected in the cyclone are transferred to the ash disposal area. At the end of the ash discharge cycle, the ash lockhopper is repressurized [3,6].

The quantity of radioactive material in coal varies widely with geographic location and type of coal, but it is generally less than that in sedimentary rock [7]. At a gasification plant, any radioactivity would be found mainly in the product gas and the ash, neither of which should lead to significant worker exposure. There would also be furnace-stack emissions of gas and fly ash from any coal burned for steam generation. Fly ash removal by modern control methods, and elevated-stack emission of hot gases should result in negligible exposure. Even in the vicinity of a large (1,960 megawatt, electrical) electricity-generating plant with inefficient stack gas cleaning and short stacks, air samples have shown maximum lung and bone radiation dose rates of only about 1% of the maximum permissible rate recommended by the International Commission on Radiological Protection. It was also found that soil samples downwind from the plant showed no radioactivity above the natural background levels [8]. It is not possible at present to provide a more definitive assessment of potential radiation hazards.

Occupational health hazards associated with the ash removal process include potential exposure to heat, high-pressure steam, high-pressure oxygen, hot ash, and dust. Trace elements in coal, although averaging only 0.03% of the total weight, present a potential hazard for plant employees because of the large quantities of coal consumed.

(5) Quenching

The hot raw gas from the gasifier will contain tar oil and trace elements volatilized from the coal, excess steam, and solids (primarily coal fines entrained from the top of the gasifier). This gas is quenched (cooled) with recycled gas-liquor to 195 C (383 F) and passes to the wash cooler, located next to the gasifier. A major portion of the volatilized trace elements is also condensed and removed from the gas stream at this point. Excess heat is removed in the waste heat boiler. The condensate (gas-liquor), containing tar, tar oil, water, water-soluble compounds, and solids, is then recycled to the quench spray by a wash cooler pump.

Occupational health hazards associated with the quenching process include potential exposure to high-pressure, hot raw gas (see Table III-2), hot tar, hot tar oil, hot gas-liquor, fire, and noise.

(6) Carbon Monoxide Shift Conversion

Approximately half of the quenched and washed raw gas (which still contains light oil and phenols) is preheated and passed through the shift conversion unit (Figure III-3) and then to the gas cooling unit (see section 7 below); the other half is passed directly to the gas cooling unit (without shift conversion) [6].

The shift-conversion unit consists of a series of catalytic reactors in which carbon monoxide and steam are converted ("shifted") at 400 C (752 F) to hydrogen and carbon dioxide [9]. Operating conditions are chosen to permit conversion in the presence of tar oil. Other reactions that occur in the shift-conversion unit are desulfurization of sulfur-containing hydrocarbons and hydrogenation of organic compounds.

Occupational health hazards associated with the shift-conversion process include potential exposure to high-pressure hot raw gas (see Table III-2), high-pressure hot shifted gas, high-pressure steam, tar, tar oil (especially the naphtha fraction), hydrogen cyanide, fire, catalyst dust (during loading and unloading), fire, and heat.

(7) Gas Cooling

The gas cooling unit (Figure XI-5) cools the hot raw gas that bypasses the shift conversion unit and the shifted gases in two separate, but similar, trains. Condensate (gas-liquor) is transferred to the primary gas-liquor separator (see Section 11 below). The cooled gases are mixed and then transferred to the Rectisol unit (see Section 8 below) for purification [3,9].

Occupational health hazards associated with gas cooling include potential exposure to high-pressure hot raw gas, hot tar, hot tar oil, hot gas-liquor, fire, heat, and noise.

(8) Gas Purification (Acid-Gas Removal)

The Rectisol process (Figure XI-6) is a licensed gas purification process in which methanol is used to absorb acid gases such as carbon dioxide, hydrogen sulfide, carbonyl sulfide, and organic sulfur-containing compounds at cryogenic temperatures and at process pressure [9]. Methanol is regenerated by a combination of

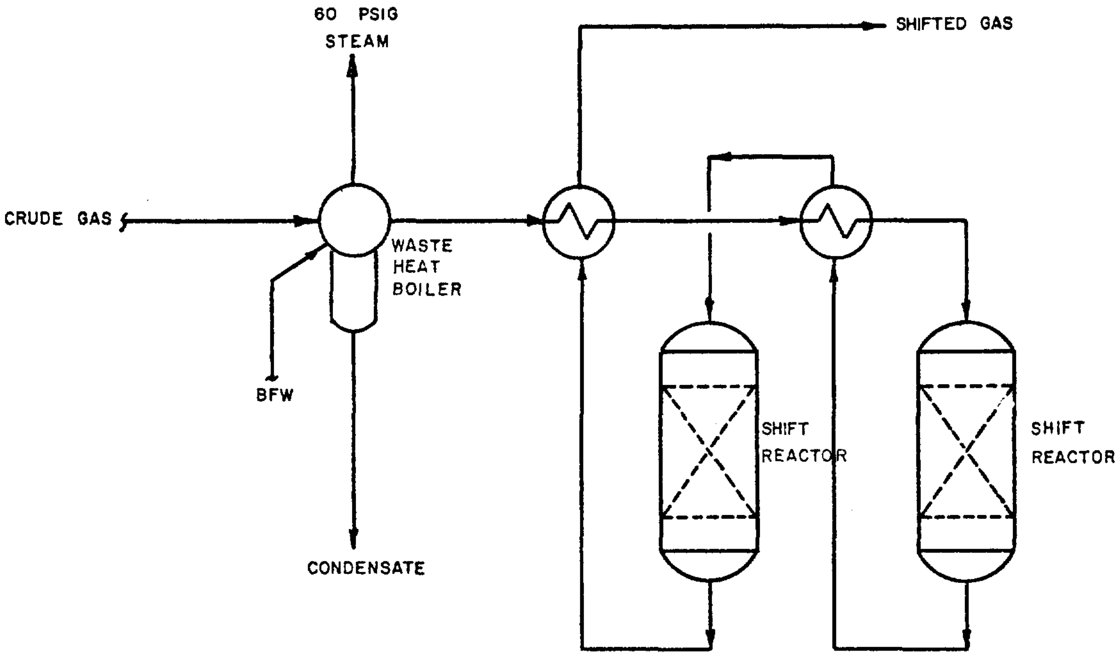


Figure III-3

Flow Scheme for the Shift Reaction Section

Adapted from Reference 6

flashing to atmospheric or subatmospheric pressure and heating to as high as 65 C (149 F). Naphtha (Table III-3) and residual heavy hydrocarbons are removed from the raw gas and recovered by extracting the methanol from the water at 75 C (167 F) [4].

TABLE III-3

NAPHTHA COMPOSITION

Major Constituents (>10% each)	Minor Constituents (<10% each)
Paraffins and olefins	Thiophenes
Benzene	Styrene
Toluene	Ethyl toluene
Xylenes and ethyl benzene	Indane
Trimethyl benzene	Indene
	Naphthalene
	Benzofuran

Adapted from reference 10

Two separate absorption steps are used to further purify the raw gas. These steps reduce the carbon dioxide content of the gas stream to about 8 vol %, and the concentration of hydrogen sulfide and other sulfides to a level of approximately 0.1 ppm as total sulfur.

Three offgas streams are produced in the Rectisol unit: (1) A 10% or higher hydrogen sulfide (rich) stream that is delivered to the Claus plant (see Section 10 below); (2) A 1% hydrogen sulfide (lean) stream that is directed to the Stretford plant (see Section 10 below); and (3) an expansion gas stream, containing approximately 30 ppm hydrogen sulfide, that is either incinerated [6] or recombined with the cooling section product upstream of the acid gas removal section [10]. Aqueous condensate is transferred to the water treatment area, and naphtha is delivered to storage for possible sale [10].

Occupational health hazards associated with the gas purification process include potential exposure to sulfur-containing gases, methanol, naphtha, cryogenic temperatures, high-pressure steam, refrigerant gases, and noise.

(9) Methanation

After purification, the gas is transferred to the methanation unit (Figure XI-7) where the catalytic reaction of carbon monoxide, carbon dioxide, and hydrogen takes place to produce methane and water. Synthesis equipment consists essentially of fixed-bed reactors charged with a form of pelleted nickel catalyst, and heat exchangers for heating incoming gas to reaction temperatures and for cooling the product gas either by heating incoming gas or by generating steam. (The incoming gas should be heated sufficiently to prevent nickel carbonyl formation [3].)

Gas from the methanation unit is returned to the Rectisol unit for final carbon dioxide and water removal. Dry product gas (Table III-4), which has an approximate heat content of 980 BTU/scf, is compressed to 1,000 psig before it is pumped into the pipeline.

TABLE III-4

TYPICAL PRODUCT GAS COMPOSITION
(DRY)

Constituent	Concentration (vol %)
Carbon dioxide	0.50
Carbon monoxide	0.06
Hydrogen	1.45
Methane	96.84
Nitrogen and argon	1.15
Hydrogen sulfide	<0.2 ppm

Adapted from reference 3

Occupational health hazards associated with the methanation process include potential exposure to high-pressure Rectisol product gas, high-pressure methanated gas (Table III-4), steam, nickel carbonyl, nickel catalyst dust, fire, and noise.

(10) Sulfur Removal Processes

In some plant designs, the hydrogen sulfide-rich offgas streams from the Rectisol process are treated in the Claus unit as shown in Table III-5.

TABLE III-5

CLAUS UNIT FEED AND PRODUCT GASES

Constituent	Feed Gas (wt %)	Product Gas (wt %)
Carbon dioxide	87.5	75.7
Carbon disulfide	0.005	ND
Carbon monoxide	Trace	ND
Carbonyl sulfide	0.1	0.03
Hydrogen sulfide	12.2	0.5
Naphtha	0.6	ND
Nitrogen and argon	ND	17.4
Sulfur	ND	0.1
Sulfur dioxide	ND	0.5
Water vapor	ND	5.5

Adapted from reference 10

ND = no data

The Claus unit utilizes a series of high-activity catalytic (bauxite) beds to decompose at least 85% of any carbonyl sulfide or carbon disulfide fed to them and to minimize sulfur dioxide entrainment. The offgas may be incinerated or fed to a Stretford unit (see below) for additional sulfur removal. It is estimated that the overall sulfur removal will be 99.5% [10].

The Stretford process treats the hydrogen sulfide-lean offgas from the phenol recovery unit (see Section 12 below) and the Rectisol process, as well as other gas streams containing low concentrations of hydrogen sulfide. The estimated compositions of the feed and product gases are shown in Table III-6.

TABLE III-6

STRETFORD FEED AND PRODUCT GASES

Constituent	Concentration Feed Gas (wt %)	 Product Gas (wt %)
Carbon dioxide	95.2	86.3
Carbon disulfide	trace	trace
Carbon monoxide	0.6	0.5
Carbonyl sulfide	0.02	0.01
Hydrogen	0.05	0.05
Hydrogen sulfide	0.9	0.001
Light oil	0.8	0.8
Nitrogen	0.9	8.6
Oxygen	ND	7.9
Water vapor	1.6	2.0

Adapted from reference 10

ND = no data

The Stretford process utilizes an aqueous solution of sodium and vanadium salts of anthraquinonedisulfonic acid (ADA) to precipitate elemental sulfur from the product stream. The Stretford offgas streams may be incinerated in the coal-fired boilers, or a thermal or catalytic incinerator, to eliminate the hydrocarbon content. These incinerated gases may be subsequently treated in the stack-gas treating unit [3].

The elemental sulfur may be stored on the ground within a retaining curb to prevent runoff [6] or in a heated sulfur pit [4].

Occupational health hazards associated with these unit processes include potential exposure to hydrogen sulfide, other sulfides, and sulfur oxides.

(11) Gas-Liquor Separation

In the gas-liquor separation process (Figure XI-9), absorbed ammonia, carbon dioxide, hydrogen sulfide, hydrogen cyanide, carbon monoxide, cyanide, tar, tar oil, and gas-liquor are separated by gravity in a series of atmospheric pressure, moderate temperature vessels. Feed to this unit includes overflow from raw-gas quenching, condensate from raw gas and from shifted-gas cooling, and perhaps condensate from gas purification.

At atmospheric pressure, the gases absorbed in liquids at the high operating pressures of the gas-processing units come out of solution. This expansion gas (approximately 96% carbon dioxide) may be either recompressed or incinerated [3,10]. The tar oil component is either fractionated for sale as refined products, or burned for its fuel value [3,6,9].

Tar containing up to 40% fines is withdrawn from the bottom of the separator and may be either returned to the top of the gasifier bed for further cracking, or used as a binder for briquetting coal fines [3,6].

Gas-liquor is processed to recover phenols and ammonia [3,6,10,11,12]. Analyses of tar oil, tar, and gas-liquor indicate that trace elements condensed from the crude gas tend to concentrate in the gas-liquor [11].

Occupational health hazards associated with the gas-liquor separation process include potential exposure to tar oil, tar, noise, and gas-liquor with high concentrations of phenols, ammonia, hydrogen cyanide, hydrogen sulfide, carbon dioxide, and trace elements.

(12) Phenol and Ammonia Recovery

The phenol recovery unit (Figure XI-10) utilizes an organic solvent such as isopropyl ether or n-butyl acetate to remove phenolic compounds from the recycled gas-liquor and clarified aqueous liquor streams [3,12]. Phenols are recovered from the solvent by steam-stripping and are either stored or further refined for subsequent sale.

The clean (dephenolized) gas-liquor is steam-stripped to remove acid gases, including hydrogen sulfide and carbon dioxide, which are recycled through the phenol recovery unit. The same liquor is then steam-stripped at a higher temperature to remove ammonia which is condensed for sale or further processed to produce pure anhydrous ammonia. Clean gas-liquor may be used for cooling-tower makeup [10] or transferred to a biological oxidation system before further use or disposal [3,12]. The ammonia may be stored, purified, or used to manufacture ammonium sulfate [3,10,12] for subsequent sale.

A second gas-liquor stream, about one-sixth the size of the clean gas-liquor stream from the gas-liquor separation process, is treated as described above in a parallel train. It is not subjected to acid-gas stripping or ammonia recovery because of process problems caused by its high solids content. Rather, it is transferred directly to the biotreatment system [3] or to the ash-dewatering system [11].

Occupational health hazards associated with the phenol and ammonia recovery processes include potential employee exposure to phenols, ammonia, acid gases, and gas-liquor. In addition, isopropyl ether is a fire hazard and may form explosive peroxide compounds when exposed to light or evaporated to dryness in the absence of inhibitors.

(13) Byproduct Storage, Handling, and Cleanup

The tar-oil or its byproducts may be stored in tanks [6]. If the liquid is to be used as fuel, it may be processed and/or burned.

Liquid byproducts, ammonia, and raw materials for the process may be shipped to and from the site by rail or truck. At one plant [11], 6.6 gallons of liquid byproduct were produced per ton of coal gasified. A coal feed rate of 22,000 tons/day would yield 145,000 gallons/day of liquid byproducts; tanks range in capacity from 21,000 to 1,680,000 gallons [6].

Occupational health hazards associated with byproduct storage, handling, and cleanup include potential exposure to tar, tar oil, phenols, ammonia, naphtha, methanol, and phenol recovery solvent. There is also a potential for fires in and around the storage tanks.

The wastewater treatment system for recovering the dephenolized gas-liquor may consist of oil-water separation for the bulk removal of suspended oils and solids, air flotation for the further removal of suspended oil and solids, biotreatment for the removal of residual phenols and other organics, and clarification and removal of activated sludge (ie, via microorganisms).

The various sludges produced in a high-BTU coal gasification plant are returned to the coal mining area for disposal, except for the calcium containing sludge, which is retained within a lined settling pond sized to have a 25-year life [3]. One company has applied for and received a state environmental permit for disposal in this manner [3].

Occupational exposures in both the water treatment and the disposal section of the plant should be low since there is little occasion for operators or maintenance personnel to be in the area. Those exposures which do occur will be to liquids or slurries, and primary potential exposure will be through skin contact.

(14) Summary

Table III-7 is a summary of the potential occupational exposures in high-BTU coal gasification as presented in the preceding sections.

TABLE III-7

POTENTIAL OCCUPATIONAL EXPOSURES IN HIGH-BTU COAL GASIFICATION

Unit Process	Potential Exposures
Coal handling and preparation	Coal dust, noise, fire
Coal feeding	Coal dust, noise, gaseous toxicants, and asphyxia
Gasifier operation	Coal dust, high-pressure hot raw gas, high-pressure oxygen, high-pressure steam, fire, noise
Ash removal	Heat stress, high-pressure steam, high-pressure oxygen under impact conditions, hot ash, and dust
Quenching	High-pressure hot raw gas, hot tar, hot tar oil, hot gas-liquor, fire, noise
Shift conversion	High-pressure hot raw gas, high-pressure hot shifted gas, high-pressure steam, tar, tar oil (naphtha), hydrogen cyanide, fire, catalyst dust, heat stress
Gas cooling	High-pressure hot raw gas, hot tar, hot tar oil, hot gas-liquor, fire, heat stress, noise
Gas purification	Sulfur-containing gases, methanol, naphtha, cryogenic temperatures, high-pressure steam, noise
Methanation	High-pressure Rectisol product gas, high-pressure methanated gas, steam, nickel carbonyl, nickel catalyst dust, fire, noise

Table III-7 cont'd

Unit Process	Potential Exposures
Sulfur removal	Hydrogen sulfide, other sulfides, and sulfur oxides
Gas-liquor separation	Tar oil, tar, gas-liquor with high concentrations of phenols, ammonia, hydrogen cyanide, hydrogen sulfide, carbon dioxide, trace elements, and noise
Phenol and ammonia recovery	Phenols, ammonia, acid gases, gas-liquor, ammonia recovery solvent, and fire
Byproduct storage	Tar, tar oil, phenols, ammonia, methanol, phenol recovery solvent, and fire

(b) Low- or Medium-BTU Coal Gasification Utilizing Bituminous or Lower Ranked Feedstocks

Estimates of the extent of low- or medium-BTU gasification technology range from 75 to 500 plants by the year 1985 [13]. By the year 2000, as many as 12,000 of these plants may be in operation [13]. The plants may vary from a single unit gasifying 75 tons of coal per day to multiple units gasifying several thousand tons per day. The estimated manpower requirement for these plants is one operator per shift per three gasifiers [14].

The products, byproducts, and uses of low-BTU gasifiers are similar to those of the high-BTU gasification units described above, except for differences resulting from the Lurgi gasifier operating at a pressure of 350-450 psig; most fixed-bed low-BTU gasification units can operate at approximately 15 psig or less. Unit processes include coal delivery and storage, coal preparation (in large facilities), coal feeding, and coal gasification.

In many cases the coal feeding operation consists of delivering coal into the gasifier through an unpressurized lockhopper or rotary valve. Air (or in the case of medium-BTU coal gasification, oxygen) is blown through the bottom of the bed, and in many cases steam is added by saturating the feed air with hot water vapor from the gasifier heating jacket.

A rotary grate is used to remove the ash from the bed at a controlled rate. The ash may fall into a water trough [15] or into a low-pressure lockhopper, where it may be wetted by water precipitated from the feed air or by other means [14,16]. In smaller plants, the ash may be dumped directly into a truck for disposal. Solids from the cyclone separator may be disposed of in a similar manner. Ash disposal methods for larger plants may be similar to those used in high-BTU coal gasification plants.

In the simplest design, low- or medium-BTU product gas at 240-400 C (464-752 F) passes through a cyclone separator for removal of entrained solids and is then used without further processing (Figure III-4) [16]. In more sophisticated designs (Figure III-5) downstream unit operations may include gas quenching and separation of tar and gas-liquor (cyclone or electrostatic precipitator). It may also be desirable to remove the acid gases [17,18] directly from the unsweetened gas [17-19]. Auxiliary operations include tar storage or disposal, gas-liquor treatment or disposal, and sulfur storage or disposal. For more detailed process information the reader should refer to Chapter 12.

Occupational health hazards associated with low- or medium-BTU gasification unit operations are similar to those of the high-BTU process. They include potential exposure to carbon monoxide, coal dust, ash dust, hot raw gases, tar and/or tar oil, gas-liquor (decanter water) containing high concentrations of phenolic compounds, nitrogen compounds including ammonia, sulfur compounds including hydrogen sulfide, trace elements and lesser concentrations of other toxic agents, heat stress, and noise.

(c) Low or Medium-BTU Gasification Utiling Anthracite Feedstocks or Very High Temperatures

(1) Anthracite Gasification

In comparison to lower ranked coals, anthracite has a very low volatile matter content, a low hydrogen to carbon ratio, and a low sulfur content [14,20]. A thorough investigation of the literature as well as discussions with those using US anthracite [14,20] indicate that the gasification of anthracite in a fixed-bed gasifier does not produce tar [21,22]. Examination of gasifier internal surfaces and piping downstream of operating units did not show the presence of tar deposits. Otherwise, from an occupational health and from a process viewpoint, the gasification of anthracite is similar to other low-BTU processes. Unit processes would include coal delivery and storage, coal feeding, gasification, ash removal, and product solids removal. Though not presently used, it is possible that downstream operations will include gas quenching, gas purification, and/or hydrogen sulfide removal. The latter may not be necessary because of the low sulfur content of most US anthracites.

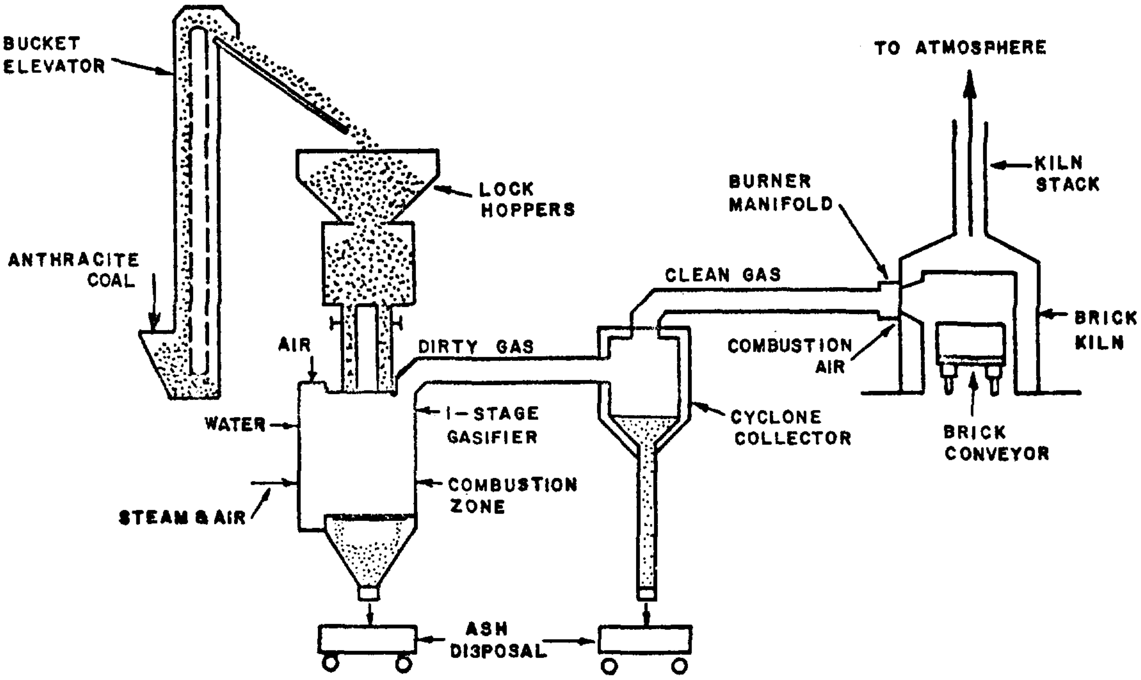


Figure III-4
Wellman-Galusha Gasifier, Single Stage

Adapted from Reference 102

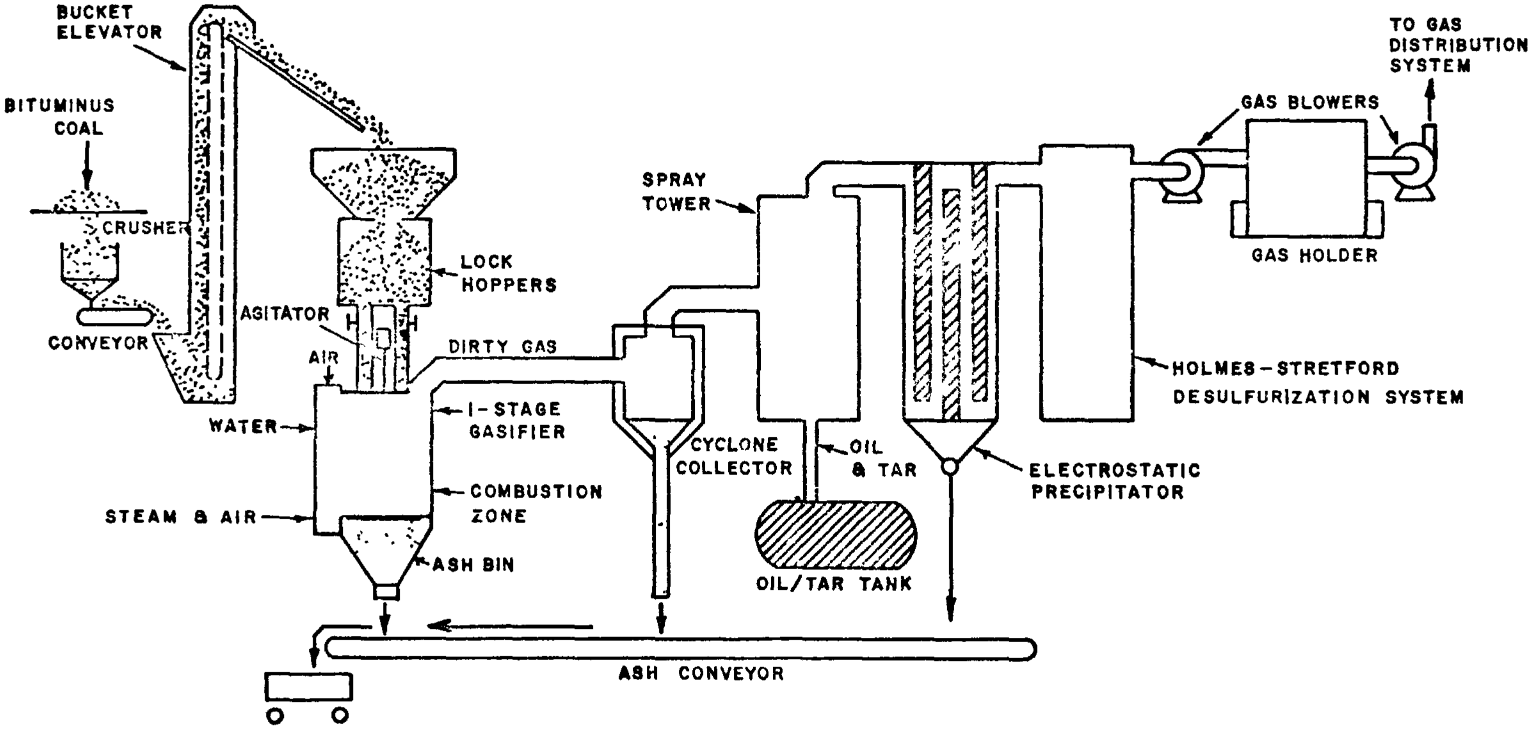


Figure III-5

Wellman Galusha Gasifier, Single Stage

Adapted from Reference 102

Occupational health hazards associated with these plants include potential exposure to carbon monoxide, coal dust, ash dust, hot raw gas, nitrogen compounds including ammonia, gas-liquor, trace elements, and sulfur compounds including hydrogen sulfide.

At present, 8 of 23 commercial low-BTU coal gasifiers in the United States use anthracite feedstock, and it is estimated that this ratio of anthracite to bituminous units will not diminish through 1985 [13] . The manpower requirement for these plants is approximately 2.8 man-hours per shift per operating gasifier for units using up to 75 tons/day of coal [14].

(2) Very-High-Temperature Coal Gasification

Very-high-temperature coal gasification may also eliminate tar production because tar molecules may be destroyed by heat in the reaction zone [18,19,23]. Coal feed (Fig III-6) is ground to 70-200 mesh and is conveyed with nitrogen.

The operating pressure of one high-temperature gasifier is less than one atmosphere[24]. Flame temperature is 1925 C (3497 F), and outlet temperature is approximately 1480 C (2696 F). The coal is fed into the gasifier by twin helical screws and then is fed through the burning nozzle with a combination of steam and oxygen. Some 40-80% of the ash is entrained in the product offgas. The remaining ash flows into the slag-quenching portion of the vessel. After passing through the steam superheater at the top of the gasifier, the product gas is quenched and the solids are removed by water scrubbing. The scrubbing should also eliminate the major portion of volatilized and entrained trace elements [18,24].

After scrubbing, the product gas may or may not be passed through a sulfur recovery unit, depending on its final use and the sulfur content of the coal. For more detailed process information, refer to Chapter XIII.

Occupational health hazards associated with operation of very-high-temperature gasification plants include potential exposures to ammonia, carbon dioxide, carbon monoxide, fire, high-pressure steam, hot raw gas, hydrogen sulfide, and trace elements, as well as coal dust and noise during maintenance. Upstream of the quenching unit, the concentrations of trace elements may be much higher than those in low-temperature processes.

Currently there are no very-high-temperature coal gasification plants in the United States. However, at least one such plant is being designed for installation in Kentucky [25]. It is estimated that by 1985 several such plants may be operating in the United States [13].

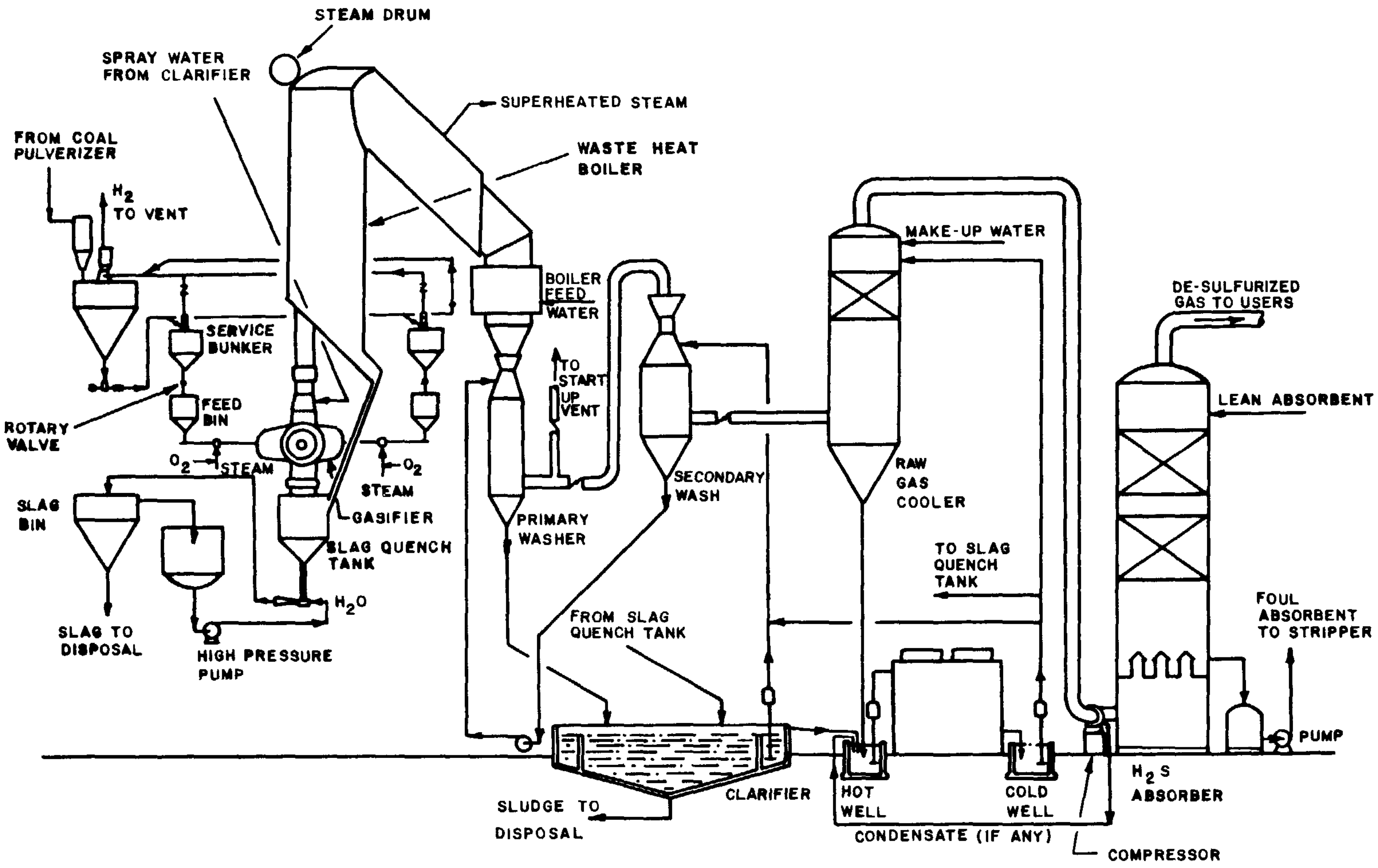


Figure III-6

K-T Gasification Process

Adapted from Reference 24

Biological Effects

(a) Introduction

Several factors complicate the analysis of the health hazards inherent in coal gasification processes. A large number of different toxicants are present in mixtures, varying with coal feedstock and with process type. Also, the effects of exposure may vary from transitory irritation, as in the case of ammonia, to death in a few minutes, as in the case of hydrogen sulfide, to cancer which may develop as the consequence of exposure to polycyclic aromatic hydrocarbons after up to 30 years. Some toxicants such as carbon monoxide are both acutely and chronically toxic.

In addition, exposure intensities may also vary enormously. A given worker may receive a relatively constant low-level exposure for many years plus intermittent high-level exposures. A single toxicant may be inhaled as aerosols and also absorbed through the skin, eg, polycyclic aromatic hydrocarbons.

Furthermore, the exposure received is only partly correlated with job classification. For example, ash-handlers may be performing similar duties both near the gasifiers (high exposure) and remote from the gasifiers (low exposure).

Effects of single chemicals are not discussed below. Though the potential hazards of exposure to such chemicals may be severe, there is very little information available that is specific to exposures in coal gasification plants. In addition, as shown in Table III-10, NIOSH has previously evaluated the biological information and thus assessed the hazard potential to workers of many of the chemicals potentially present in the environments of coal gasification plants. The workplace exposure limits recommended previously by NIOSH should be adhered to in coal gasification plants until such time as new data become available indicating the need for changes in the limits.

(b) Effects Observed in Humans and Experimental Animals

A medical study of health hazards at a coal liquefaction (hydrogenation) pilot plant in the United States was published in 1960 [26,27]. Except for follow-up of this study, no other reports of studies of hazards at coal gasification or liquefaction plants have been located within the United States or abroad. During the search for such data, representatives of NIOSH discussed with eyewitnesses occupational health programs that existed in some of the German facilities in the 1940's [28,29], and reviewed accident, fire, and explosion reports [30] from some of these facilities. The information so obtained was found to be of limited utility in developing recommended controls for future plants to be built in the United States.

(1) Coal Liquefaction Pilot Plant

Sexton [26] stated that at the time when a large West Virginia coal liquefaction pilot plant went into formal operation in 1952, its management realized that many toxic chemicals would be present, ie, over 200 individual chemicals had been identified in the process streams, including "at least one high boiling polycyclic aromatic chemical...known to be carcinogenic," and that toxicologic studies were therefore undertaken to ascertain "the existence of a problem."

Feedstock for the process included pulverized coal mixed with various carriers or "pasting oils," some of which consisted of blends of purchased coal tar and plant-produced materials, and others which consisted solely of plant-produced materials (see stream 3, below). The resulting pastes were preheated and reacted with hydrogen at high temperatures and pressures, after which unreacted solids were removed and the liquid products were separated in the "heavy products separation unit," into four major streams: (1) A "light oil" stream (boiling point 260 C) which, in turn, was separated, in the "light products separation unit," into four major crude fractions, ie, "stabilizer overhead," from which benzene and a number of other aromatic as well as aliphatic (C5-C7) compounds were refined, an acidic (phenolic) fraction containing phenol, cresols, etc, a basic (nitrogen bases) fraction containing aniline, etc, and a neutral fraction containing such aromatic and aliphatic compounds as toluenes and decane, as well as a phenolic pitch residue (boiling range = 260-380 C); (2) A "middle oil" stream (boiling range = 260-320 C) which was either sold as a semirefined product or recycled; (3) A "heavy oil" stream (boiling point 320 C) that was either recycled as pasting oil or distilled to obtain such polycyclic aromatic hydrocarbons as phenanthrene, chrysene, etc; (4) a "pitch" stream, ie, the nonvolatile residue, produced as a hot, molten material that solidified at 200 C, and which was either sold or diverted for further processing in the pitch polymerization unit.

The potential carcinogenic hazard associated with the process was demonstrated when samples from several process streams and residues were applied to the skins of mice [31]. It was observed that the light and heavy oil <u>products</u> were mildly tumorigenic; the light oil <u>stream</u> and its derivatives were not tumorigenic; and the higher boiling, ie, middle oil, light oil (phenolic pitch) residue, pasting oil (heavy oil stream), and pitch product materials were "highly" carcinogenic. The "degree of carcinogenicity" increased, and the length of the median latent periods decreased, with increasing boiling point. On the basis of these toxicologic findings, the plant medical director, in cooperation with plant safety and production personnel, initiated certain preventive measures.

Medical surveillance findings reported by Sexton [27] included the results of regular examinations of 359 workers over a 5-year period, during which 63 skin abnormalities were seen in 52 men, ie, despite the preventive measures. Of the 60 lesions excised, 55 tumors were examined microscopically by local pathologists, of which 11 were diagnosed as skin cancers, although later review of the sections confirmed only 5 of these as epitheliomas. Of 54 suspected "precancerous" lesions of the skin, 42 were verified as "precursors of skin cancer" by several pathologists.

The diagnoses supported by one or more microscopic evaluations showed 10 men with cutaneous cancer and 42 with precancerous lesions (see Table III-8). All lesions of significance were in men with less than 10 years of exposure, and one subject was found to have 2 skin cancers, one after only 9 months of exposure and one after 11 months of exposure.

TABLE III-8

PRECURSORS OF SKIN CANCER CASES (FINAL ANALYSIS)

Number of Cases	Mean Age (Years)	Length of Exposure (Months)	Diagnosis
3	30	10-74	Pitch acne(a)
1	39	41	Calcifying epithelioma malherbes
1	40	116	Keratoacanthoma
3	33	3.5-42	Chondrodermatitis helicis(a)
17	39	10-116	Keratoses(b)
8	44	17-96	Keratoses
9	40	4-108	Acanthoses and hyperkeratoses

(a) Clinical diagnosis only
(b) Diagnosis by a single pathologist only

Adapted from reference 27

An industrial hygiene study was undertaken [32] to ascertain the extent and nature of sources of airborne and other contamination, and to develop operational and engineering-related corrective measures. Because it seemed unreasonable to attempt analyses of their air samples for even a small fraction of the some 200 individual chemicals that had been isolated and identified in the process, the investigators decided to select for measurement a carcinogenic "tracer" material. They selected 3,4-benzpyrene (BaP) in that it was readily identifiable and quantifiable, and it was likely to be present in all of the middle and heavy oil fractions, ie, those fractions that had been found [31] to have the greatest carcinogenic potential.

Air samples (Hi-vol) were collected both on the plant premises and in surrounding community areas, and concentrations of BaP were found to range from a few micrograms per 100 cu m (typical of community air in several locales) in nearby residential areas to over 1,000 micrograms (ug) per cu m in the immediate vicinity of pitch treatment and solids removal operations.

The investigators also conducted "fallout" sampling, using horizontal plates to collect the large droplets of oily, fluorescent material that they had discovered upon the "otherwise clean" skins of certain plant employees. By integrating these results with those of the air sampling, they were able to locate a number of specific sources of airborne contamination, including windblown or otherwise disturbed piles of hydrogenation residue (pitch), solids removal equipment blowdown operations, liquid aeration operations, and the steam condensate from a vacuum system ejection jet discharge.

Many modifications were made in operations and in equipment at the plant as a result of this study, including installation of new or improved local exhaust ventilation systems and use of improved pump packing materials and methods. In addition, the use of protective clothing and encouragement of personal hygienic procedures were stressed. Employee preferences were taken into consideration in ordering protective clothing, and procedures were implemented for daily changes of underwear, outer clothing, and socks, plus daily inspections of each employee's hands, face and neck.

A follow-up of Sexton's medical study was reported by Coomes [33], who referred to a 1976 personal communication alleging that no systemic effects or additional cancers had been observed upon reexamination of "all workers who were employed in the early coal-synthetic fuel program" 15 years after their exposures. The number of workers reexamined was not reported; NIOSH followed up the personal communication reported by Coomes and could not determine the number of workers reexamined [34]

According to Weil [35] the skin cancer incidence in the plant was at least 20 times as high as the expected incidence ("normal" = 30-40/100,000/year). Weil also stated that since the end of December, 1958, the workers have been followed, and that, whereas at first there were 1-2 new cases of skin cancer every year, the incidence is now about 1 new case every 5 years, with no evidence of increases in systemic (including lung) cancers.

A follow-up mortality study was reported by NIOSH in 1977 [36] in which the records from the Sexton study were reviewed. An adjustment in numbers was found necessary because of previous double counting, giving 10 cutaneous cancer cases and 40 cases with skin cancer precursors. All but one of the 50 cases were followed up; their status as of 1977 is given in Table III-9.

TABLE III-9

FOLLOW-UP IN 1977 OF 50 WORKERS WITH SKIN CANCER OR SKIN-CANCER PRECURSORS REPORTED BY SEXTON IN 1960

	Deaths Other than Cancer	Retired	Still Working	Lost to Follow-up	Ill with Cancer	Total Cases
Confirmed Skin Cancer	2	1	5	1	1 (a)	10
Confirmed Precursor of Skin Cancer	3	13	23	0	1 (b)	40
Total	5	14	28	1	2	50

(a) Lung cancer: Age 60, lifetime heavy smoker
(b) Prostate cancer: Age 77

Adapted from reference 36

The five deaths were all reported as cardiac-related, two with pulmonary involvement; however, none had been autopsied. It was noted that, although the data had not undergone statistical analysis, the results suggested that the group was not at an increased risk of systemic cancer, which was the initial hypothesis that prompted this study.

A significant point that was not referred to in the report 36] is that 6 of the 10 cases of skin cancer were found in maintenance workers. (Job descriptions were not provided for the precursor cases.) It is conjectured that this finding is related to the fact that maintenance workers were likely to have worked in the pilot plant when it was not in operation and thus would have been at low or negligible risk of exposure to carcinogens by inhalation; however, they would have been at exceptionally high risk of exposure by direct skin contact. This group of workers would therefore not be expected to necessarily have exhibited a significantly increased incidence of systemic cancer. The most significant group of workers for follow-up for systemic cancer would appear to be those identifiable from the industrial hygiene survey [32] as having been exposed to the highest concentrations of airborne BaP. It cannot be determined from the follow-up reports whether any of these were included.

The finding that only skin cancers were observed, except for one heavy smoker who developed lung cancer [36], may have been due to the generally long induction period for lung and other systemic cancers and the lack of adequate follow-up either in the United States or abroad. This finding may be explained with equal plausibility by the possibility that the carcinogenic and tumorigenic fractions, ie, every stream and product except the light oil stream and its derivatives, had a boiling point above 260 C, meaning that their existence as vapors or in other air-suspended forms were probably quite short-lived. This hypothesis is supported by the BaP distribution pattern observed in the industrial hygiene study [32], which showed very high concentrations within about 200 feet of major sources of contamination but concentrations of only a few micrograms per 100 cu m in various plant areas and in surrounding community areas. Therefore, these materials tended not to volatilize, and must have been deposited near the sources of contamination.

No other report has been found of increased skin cancer incidence or other serious health effects in coal gasification or liquefaction plants, despite a thorough literature search and inquiries at coal gasification plants both in the United States and abroad [12,14-16,18-21,37-42]. There is, however, evidence of the presence of potential carcinogenic hazards, eg, a recent examination [42] of a pilot plant by ultraviolet light showed extensive surface contamination, visible by its bright fluorescence; the contaminant very likely included carcinogenic hydrocarbons.

(2) Other Related Industries

Gasworks, where coal is heated in retorts for the primary purpose of producing flammable gas, or coke ovens, where the coke is the primary product, have provided much more evidence of associated health effects than have coal gasification plants, and some of it is quantitative. It should be noted, however, that this evidence does not imply comparable degrees of hazard in coal gasification plants, gasworks, and coking plants. Gasworks and coking plants heat coal with minimal containment of the volatiles. Gasification plants typically operate at high pressure as well as high temperature, and therefore containment is essential under normal operating conditions.

Epidemiologic studies [43-46] of gasworkers and coke oven workers have provided evidence of work-associated cancers. The nature of the toxicants and their concentrations within the various process streams at future coal gasification plants are expected to be generally similar to those at gasworks and coke plants, although proper design and work practices can substantially reduce the quantitative aspects of exposures in coal gasification plants.

Mortality studies of gasworkers, coke-oven workers, and workers exposed to coal tar, coal tar pitch, creosote, and the emissions from coke ovens have been reviewed by NIOSH in preparation of the coke oven emissions and the coal tar products criteria documents [47,48]. The latter document also contains reviews of approximately 20 studies of morbidity, primarily of the skin and including eye effects, caused by coal tar products. From the epidemiologic and experimental toxicologic evidence on coke oven emissions, coal tar, coal tar pitch, and creosote, NIOSH concluded that coke oven emissions and these specific coal tar products are carcinogenic and can increase the risk of lung and skin cancer in workers, and perhaps cancer at other sites [48].

(c) Summary of Hazardous Agents

A tabular summary is presented in Table III-10 of the regulatory status of various hazardous agents that are potentially present in coal gasification plants, together with brief notes on significant health effects.

Most of Table III-10 is based on NIOSH criteria documents. For chemical substances not covered by NIOSH recommended standards, the current Federal occupational exposure standard is listed [49], and data on significant health effects have been derived from reference [50]. For substances covered by neither NIOSH recommendations nor OSHA standards, the table entry is limited to a notation on health effects based on information contained in Industrial Hygiene and Toxicology [51].

(d) Special Hazards

Exposure to several constituents of the coal gasification process and waste streams could cause severe acute effects if a plant malfunction or catastrophic accident resulted in massive leakage or if significant exposures were encountered on entering confined spaces. The specific toxicants of significance are hydrogen sulfide and carbon monoxide. In addition, there are simple asphyxiants, eg nitrogen, which can cause harm to exposed employees in confined spaces.

(1) Hydrogen Sulfide

Hydrogen sulfide is found in all process gas streams upstream of the gas purification systems. Process lines between the gas purification unit and the sulfur recovery systems and in the sulfur recovery systems themselves may contain up to 20% or more hydrogen sulfide. Hydrogen sulfide will also be absorbed in the gas-liquors or quench waters and may be evolved over a period of time after the gas-liquor is depressurized.

TABLE III-10

SUMMARY OF HEALTH EFFECTS OF AGENTS POTENTIALLY PRESENT IN COAL GASIFICATION PLANTS

Agent	Current Federal Occupational Exposure Standard(a)	NIOSH Recommendation for Permissible Exposure Limit(b)	Health Effects(b)	Reference
Ammonia	50 ppm (34.8 mg/cu m)	50 ppm ceiling (34.8 mg/cu m) (5 min)	Airway irritation	52
Arsenic, inorganic	0.5 mg/cu m	2 (u)g/cu m ceiling (15 min)	Dermatitis, lung and lymphatic cancer	53
Benzene	1 ppm (3.2 mg/cu m); 5 ppm maximum ceiling (15 min)	1 ppm ceiling (3.2 mg/cu m) (60 min)	Blood changes including leukemia	54
Beryllium	2 (u)g/cu m; 5 (u)g/cu m acceptable ceiling; 25 (u)g/cu m maximum ceiling (30 min)	0.5 (u)g/cu m (130 min)	Lung cancer; berylliosis	55
Cadmium	0.1 mg/cu m; fumes = 0.3 mg/cu m ceiling; (erroneously published as 3 mg/ cu m); 0.2 mg/cu m; dust = 0.6 mg/cu m ceiling	40 (u)g/cu m; 200 (u)g/cu m ceiling (15 min)	Lung and kidney	56
Carbon dioxide	5,000 ppm (9,000 mg/cu m)	10,000 ppm (18,000 mg/cu m); 30,000-ppm ceiling (54,000 mg/cu m) (10 min)	Respiratory	57
Carbon monoxide	50 ppm (55 mg/cu m)	35 ppm (40 mg/cu m); 200 ppm ceiling (229 mg/cu m)	Respiratory	58
Carbonyl sulfide	None	None	Similar to hydrogen sulfide, probably less hazardous	51
Chromium (VI)	100 (u)g/10 cu m ceiling	1 (u)g/cu m for carcinogenic Cr(VI); 25 (u)g/cu m for other chromium; 50 (u)g/cu m ceiling (15 min)	Lung cancer, skin ulcers, lung irritation	59
Coal dust	2.4 mg/cu m, if respirable dust fraction less than 5% SiO2; if respirable fraction is more than 5% SiO2, respirable mass formula is (10 mg/cu m)/(% SiO2 + 2)	None	Lung	50

Table III-10 cont'd

Agent	Current Federal Occupational Exposure Standard(a)
Coal tar products	0.2 mg/cu m (for benzene-soluble fraction of tar pitch volatiles)
Coke-oven emissions	150 (u) g/cu m
Cresol	5 ppm (22 mg/cu m) (skin)
Cyanide, hydrogen and cyanide salts	10 ppm (alkali cyanides); 5 mg CN/cu m (cyanides)
Fluorides, inorganic	2.5 mg/cu m
Hot environments	None
Hydrogen chloride	5 ppm (7 mg/cu m)
Hydrogen sulfide	20 ppm acceptable ceiling; 50-ppm maximum ceiling (10 min)
Isopropyl ether	500 ppm (2,100 mg/cu m)
Lead, inorganic	0.2 mg/cu m
Manganese	5 mg/cu m ceiling
Mercury, inorganic	0.1 mg/cu m ceiling
Methanol	200 ppm (260 mg/cu m)

NIOSH Recommendation for Permissible Exposure Limit(b)	Health Effects(b)	Reference
0.1 mg/cu m (cyclohexane-extractable fraction of coal tar, coal tar pitch, creosote or mixtures)	Lung and skin cancer	48
Work practices to minimize exposure to emissions	Lung cancer	47
10 mg/cu m	Skin, liver, kidney, and pancreas	60
5 mg CN/cu m ceiling (4.7 ppm) (10 min)	Thyroid, blood, respiratory	61
2.5 mg/cu m	Kidney and bone	62
Variable (sliding scale)	Heat stress	63
None	Corrosive to eyes, skin, and membranes. Respiratory irritant	50
15 mg/cu m ceiling (approximately 10 ppm) (10 min)	Irritation; severe acute nervous and respiratory systems	64
None	Anesthesia, irritation to skin and eyes	65
Less than 100 (u)g/cu m	Kidney, blood and nervous system	66
None	Deposited in liver, spleen, and certain nerve cells of the brain and spinal cord	59
0.05 mg/cu m	Central nervous system and behavioral	67
200 ppm (262 mg/cu m): 800 ppm (1,048 mg/cu m) ceiling (15 min)	Blindness; metabolic acidosis	68

Table III-10 cont'd

Agent	Current Federal Occupational Exposure Standard(a)	NIOSH Recommendation for Permissible Exposure Limit(b)	Health Effects(b)	Reference	
Nickel, inorganic, and compounds	1 mg/cu m (metal and soluble compounds as Ni)	15 (u)g Ni/cu m	Skin; lung and nasal cancer	69	
Nickel carbonyl	0.001 ppm (0.007 mg/cu m)	0.001 ppm (0.007 mg/cu m)	Lung, heart, liver and spleen carcinogen	70	
Nitrogen oxides	NO2: 5 ppm (9 mg/cu m)	NO2: 1 ppm (1.8 mg/cu m) ceiling (15 min);	Airway irritation	71	
	NO: 25 ppm (30 mg/cu m)	NO: 25 ppm (30 mg/cu m)	Blood		
Noise	90 dBA	85 dBA (8-hour TWA); 115 dBA ceiling	Hearing damage	72	dBA???
Phenol	5 ppm (skin)	20 mg/cu m (5.2 ppm); 60 mg/cu m (15.6 ppm) ceiling (15 min)	Skin, eye, central nervous system, liver, and kidney	73	
Selenium	0.2 mg/cu m compounds as Se	None	Irritation of the mucous membranes of the nose, eyes, and upper respiratory tract	50	
Silica, crystalline	(250)/(% SiO2 + 5) in mppcf, or (10 mg/cu m)/(% SiO2 + 2) respirable quartz	50 (u)g/cu m respirable free silica	Chronic lung disease (silicosis)	74	
Sulfur dioxide	5 ppm (13 mg/cu m)	0.5 ppm (1.3 mg/cu m)	Respiratory	75	
Toluene	200 ppm; 300 ppm acceptable ceiling; 500 ppm maximum peak above acceptable ceiling (10 min)	100 ppm (376 mg/cu m); 200 ppm (750 mg/cu m) ceiling (10 min)	Central nervous system depressant	76	
Vanadium	Vanadium pentoxide: dust = 0.5 mg/cu m ceiling; fume = 0.1 mg/cu m ceiling	Vanadium compounds: 0.05 mg/cu m ceiling (15 min)	Eye, skin, and lung	77	
Xylene	100 ppm (435 mg/cu m)	100 ppm (434 mg/ cu m); 200 ppm (868 mg/cu m) ceiling (10 min)	Central nervous system depressant; airway irritation	78	

(a) Adapted from reference 48; up to 8-hour time-weighted average unless otherwise noted

(b) Adapted from reference noted in final column of Table III-10; up to a 10-hour time-weighted average unless otherwise noted

Brief exposures to high concentrations of hydrogen sulfide may lead to rapid unconsciousness, respiratory paralysis, and death [64]. Exposure to hydrogen sulfide at concentrations above 140 mg/cu m rapidly abolishes the sense of smell, which thus cannot be relied on to warn against high concentrations [64]. In cases of hydrogen sulfide poisoning, immediate first aid can be lifesaving.

(2) Carbon Monoxide

The dry raw product gas from the gasifier contains as much as 20% carbon monoxide. Gas purification increases the carbon monoxide concentration in the gas stream by removing carbon dioxide and hydrogen sulfide. All gas streams except the final product stream contain potentially hazardous concentrations of carbon monoxide. Carbon monoxide may be absorbed in water or tar streams that come in contact with the process gas, and be released over a period of time when these liquors are depressurized to ambient pressure.

Acute carbon monoxide poisoning can result in dizziness, drowsiness and collapse [58]. Recommended first aid if breathing has stopped is artificial respiration, and the administration of oxygen. Behavioral impairment is a possible safety hazard at lower exposure levels [58]. In cases of carbon monoxide poisoning, immediate first aid can be lifesaving.

(3) Simple Asphyxiants

Each of the three gas-related deaths reported at coal gasification plants visited by NIOSH resulted from simple asphyxiation following the use of inert gas for vessel purging [12,18,20] . The simple asphyxiants that are present are usually nitrogen, carbon dioxide, and methane.

The oxygen plant is the largest source of nitrogen in high- and medium-BTU coal gasification plants. Nitrogen is used in the gasification process only as a purge gas. Relatively pure carbon dioxide is produced in the gas purification system; it may be piped directly to a stack, it may be used as a purge gas (eg, in coal lockhoppers), or it may be processed for commercial use (eg, as solid carbon dioxide). Methane and product gas are less often hazards as simple asphyxiants, partly because of the vigilance their other hazards (eg, fire, explosion) require.

(4) Burns

The presence of hot, pressurized gas and liquid streams creates a significant potential for burns in coal gasification plants. Employees should be trained in emergency aid procedures for burns.

(e) Conclusions

From a review of the available epidemiologic and toxicologic evidence, including that previously published, NIOSH concludes that there are insufficient data to support the development of new limits for occupational exposures to the variety of chemical and physical agents that are present in the environment of coal gasification plants. NIOSH recognizes the probability that exposures are likely to involve complex mixtures of toxicants. Currently, however, there is no reliable way of estimating overall response for given levels of exposure, because such exposures may or may not be simply additive and the extent of possible interactive effects is not predictable. To guard against possible synergistic effects, it is particularly important that exposures be minimized by application of the best available engineering control technology and work practices.

IV. WORKPLACE MONITORING

Employees of coal gasification plants may be exposed, at least occasionally, to the physical and chemical agents discussed in this document. Routine employee interaction with equipment during operation and maintenance may present exposure situations that are not readily defined. Real-time monitoring of all work areas for all anticipated hazards, though desirable, is not technologically feasible at present.

Methods for the sampling and analysis of a variety of these agents have been described in previous NIOSH criteria documents. These documents have discussed workplace monitoring specifically for the agent(s) of interest.

To measure worker exposure to potentially carcinogenic polycyclic aromatic hydrocarbons (PAH's) in coal gasification plants, a monitoring program is required. In addition, leak testing is necessary to locate sources of emissions. Methods are needed to analyze large numbers of samples rapidly at a reasonable cost. Such methods should have high sensitivity because the compounds are often present only in trace amounts. They should also be very selective because compounds that differ only slightly in chemical structure may vary considerably in the hazard they present [79].

The open nature of coal gasification plants presents problems in obtaining representative environmental samples. The difficulties are in choosing monitoring sites that will provide an accurate reflection of the hazard potential. Some aspects of this problem have been dealt with in a NIOSH document that presents recommended procedures for air-contaminant sampling [80].

The Indicator Monitoring Concept

The ideal program for worker protection would utilize continuous monitoring for all potentially hazardous chemical agents expected to be present in the coal gasification plant. Due to the large number of these agents, however, such monitoring would be extremely expensive and time-consuming. Additionally, technology is not currently available for such monitoring.

An indirect, theoretical method for real-time monitoring has been proposed by NIOSH specifically for coal gasification pilot plants [79] and is applicable to commercial-scale facilities as well. The proposed monitoring scheme uses a single indicator chemical as an index of exposure to an array of other chemicals present in the product streams of specific unit processes. Leading candidates for use as indicators are carbon monoxide (at the gasification, quenching, and shift conversion units), hydrogen sulfide (at the gas purification and sulfur removal units), and methane (at the methanation unit). Ideally, an indicator should (1) be easily monitored in real time by commercially available personal or remote samplers, (2) be suitable for analysis where resources and technical skills are limited, (3) not be present in ambient air at high or widely fluctuating concentrations, (4) be measurable without interference from other substances in the process stream or ambient air, and (5) be a regulated agent so that the measurements serve the two purposes of quantitative sampling for compliance purposes and indicator monitoring.

The rationale for adopting carbon monoxide, as an example, as an indicator gas for monitoring in designated confined areas, as a basis for an alarm mechanism in selected areas, and as a potential index of worker exposure to an array of toxic chemicals can be summarized as follows. Based on material-balance data for unit processes in a US coal gasification pilot plant [79], the concentration of carbon monoxide is higher than that of other toxic gases and vapors (eg, ammonia, hydrogen sulfide, coal tar volatiles, and trace metals) in the gas stream. Monitoring and alarm systems are currently available that can detect carbon monoxide at concentrations as low as 0.2 mg/cu m. It is assumed that the ratio of carbon monoxide to other constituents is the same for emissions as for the process stream; thus, the approximate concentrations of these constituents in any emissions can be calculated from measurements of the concentration of carbon monoxide. It is further assumed that all gases and vapors present in any fugitive emission will behave according to the ideal gas laws. (This is not the case for tar vapors and particulates. For these and other constituents whose behavior cannot reasonably be assumed to be ideal, specific analyses are required to verify the carbon monoxide indicator model.)

Taking into account these assumptions and inherent limitations, a procedure is proposed for determining the ratio of carbon monoxide to any other gas-stream component based on data from stream sample analysis or a materials balance for each unit process. To be reliable, the ratio of indicator to toxic substance must be determined empirically in each plant for each type of coal feedstock.

The following examples are based on data on gas stream composition [81,82]. Tables IV-1 and IV-2 present the concentration ratios of various components to carbon monoxide in the gas stream, in this instance at the gasifier outlet. The ratio of any stream component to the carbon monoxide indicator is calculated on a volume percent basis. Table IV-1 presents data for major stream components, and Table IV-2 presents data for trace stream components.

TABLE IV-1

RATIO OF STREAM COMPONENTS TO CARBON MONOXIDE

Stream Component	Concentration (vol %)	Ratio of Component to Carbon Monoxide
Ammonia	0.8	0.15
Carbon dioxide	18.9	3.63
Carbon monoxide	5.2	1.0
Ethane	0.4	0.08
Hydrogen	12.7	2.44
Hydrogen sulfide	0.4	0.08
Methane	12.4	2.39
Nitrogen	0.9	0.17
Heavy oil(a)	0.04	0.008
Light oil(a)	0.01	0.002
Middle oil(a)	0.05	0.010
Coal fines	(b)	(b)
Residue	(b)	(b)
Steam	48.2	9.0

(a) Estimated average molecular weights: Light oil, 150; middle oil, 190; heavy oil, 230.

(b) Remain as solids in the gasifier and are not used in volume calculations.

TABLE IV-2

RATIO OF TRACE COMPONENTS TO CARBON MONOXIDE

Stream Component (trace)	Concentration (ppm)	Ratio of Component to Carbon Monoxide
Carbon disulfide	10	0.0001
Carbon monoxide	79,000	1.0
Carbonyl sulfide	150	0.002
Dimethyl thiophene	10	0.0001
Methyl mercaptan	60	0.0008
Methyl thiophene	10	0.0001
Thiophene	31	0.0004
Arsenic	0.50	0.000006
Cadmium	0.03	0.0000004
Lead	0.13	0.000002
Mercury	0.01	0.0000001
Nickel	0.30	0.000004

Data from references 81,82

Table IV-3 illustrates the calculated carbon monoxide concentrations that, when detected by a workplace environmental sampler, would indicate the presence of various other gas-stream components at 50% of their permissible exposure limits. This indicates the "action level" [83] at which there is a need to initiate sampling for the specific gas-stream component. Following the table are explanations of the calculations and examples of how to use the table.

The "probable minimum detectable level" in Table IV-3 is calculated for each stream component by multiplying the "component to CO ratio" by the background level of CO. In Table IV-3, a background level of 5.7 mg/cu m (5 ppm) is used, as this is assumed to be the maximum average ambient carbon monoxide concentration due to nonplant sources. The "probable minimum detectable level" is also expressed as a percentage of the permissible exposure limit. This value gives the sensitivity of CO indicator monitoring for the specific component. For example, the margin of error for CO indicator monitoring for ammonia is 2.47% of the permissible exposure limit for ammonia. The margin of error for monitoring for

TABLE IV-3

CALCULATED CARBON MONOXIDE (CO) CONCENTRATIONS FOR

Stream Component	Permissible Exposure Limits (NIOSH Recommended Standard Unless Otherwise Noted) mg/cu m	Component to CO Ratio (from Tables IV-1 and IV-2)
Ammonia	34.8	0.15
Carbon dioxide	9,000(a)	3.63
Carbon disulfide	3.0	0.0001
Carbon monoxide	40	1.00
Carbonyl sulfide	None	0.002
Ethane	None	0.08
Hydrogen	None	2.44
Hydrogen sulfide	15	0.08
Methane	None	2.39
Dimethyl thiophene	None	0.0001
Methyl mercaptan	20(a)	0.0008
Methyl thiophene	None	0.0001
Thiophene	None	0.0004
Arsenic	0.002	0.000006
Cadmium	0.04	0.0000004
Lead	0.10	0.000002
Mercury	0.05	0.0000001
Nickel	0.015	0.000004
Heavy oil(b)	0.1	0.008
Light oil(c)	375.0	0.002

(a) Current Federal Occupational Standard.
(b) Calculated as cyclohexane-soluble fraction of total
(c) Calculated as toluene.

ACTION LEVELS OF STREAM COMPONENTS

Probable Minimum Detectable Level (Based on Background Concentrations of CO)		CO Level Required (Indicates Action Level of Stream Component)
mg/cu m	% PEL	mg/cu m
0.86	2.47	116
20.7	0.23	1,240
0.0006	0.002	15,000
5.7	14.2	20
0.01	None	None
0.46	None	None
13.9	None	None
0.46	3.07	94
13.6	None	None
0.0006	None	None
0.005	0.025	12,500
0.0006	None	None
0.002	None	None
0.000034	1.7	167
0.000002	0.005	50,000
0.000011	0.011	25,000
0.0000006	0.0012	250,000
0.000023	0.15	1,875
0.046	46.0	6.25
0.011	0.003	93,750

particulate matter, molecular weight 230.

heavy oil is 46% of the limit. Thus, the insensitivity of CO monitoring due to background levels of CO is of little consequence when indicating ammonia, but is severe enough to preclude indicator monitoring for heavy oil.

The "CO level required" in Table IV-3 is calculated for each stream component as follows: (permissible exposure limit) divided by (component to CO ratio) x (1/2). This gives the calculated carbon monoxide concentration that would indicate the concentration of stream components to be 50% of their permissible exposure limit. This indicates the "action level" at which there is a need to initiate sampling for the specific gas-stream component. For example, when a CO monitor at the location where these data were taken (gasifier outlet) reads 116 mg/cu m, the action level for ammonia has been reached.

In Table IV-3, the permissible exposure limit for the heavy oil fraction is assumed to be the same as the current NIOSH recommended standard for coal tar products, as determined by the cyclohexane-soluble fraction of the total particulate matter. Although this assumption overestimates the hazard by grouping all heavy oils into the same toxicity rating as coal tar products, it is used for the purposes of this example because no data are available on the amount of carcinogenic substances in the heavy oil fraction.

By using this method at each unit process, the concentration of any agent in the emission can be estimated from the carbon monoxide concentration.

A significant consideration is that as the quality of the gas improves from operation to operation, the carbon monoxide concentration decreases. This decrease is paralleled by a reduction in other toxic components, particularly PAH's [79]. The carbon monoxide indicator model is most sensitive in detecting gas-stream emissions at the unit processes where the hazard associated with leaks is most severe [79].

Real-time monitoring for carbon monoxide in enclosed areas or areas subject to leaks or emissions can serve, in theory, as an indicator for substances that cannot be readily analyzed in real time or are difficult or impossible to analyze at prevailing concentrations. The utility of carbon monoxide as an index of worker exposure or of plant performance in terms of toxic emissions remains to be determined. This model has been evaluated only in theory; actual evidence of reliability must await the results of ongoing and proposed studies in plants.

The following limitations should be noted with regard to the indicator monitoring concept:

- It is an unproven method that has yet to be validated in an operational facility.
- It cannot provide an absolute quantification of employee exposure to agents other than carbon monoxide.
- It provides a hazard index only for gas and vapor phase contaminants.
- It does not provide an index of exposure to particulates or toxic agents adsorbed on particulate matter.
- It consistently overestimates employee exposure to vapor- phase tars.
- It requires stable process-stream composition.

In summary, NIOSH does not propose that the indicator concept be used for compliance purposes. It is proposed as a tool to indicate possible noncompliance situations so that remedial action can be taken. Monitoring for a single substance should provide for more rapid identification of process leaks and noncompliance situations than would be possible by conventional monitoring procedures.

Once procedures are validated for continuous monitoring of the indicator substances, full-time monitoring for the entire array of chemical agents need not be initiated until the action level has been indicated.

Carbon monoxide has been presented as an example of an appropriate indicator. However, the choice of the indicator depends on the specific process and the specific coal. Other possible indicator substances, eg hydrogen sulfide and methane, may be appropriate for specific unit processes such as sulfur removal and methanation.

Polycyclic Aromatic Hydrocarbons (PAH's)

As noted above, one of the limitations of indicator monitoring is that it cannot provide an absolute quantification of exposure to specific agents other than the indicator substance. This is critical with respect to PAH exposures, which should not exceed the lowest concentration that can be reliably detected. The recommended methods for workplace monitoring for PAH's are described in Chapter XV.

Surface Contamination

If equipment and other surfaces are contaminated with condensed polycyclic hydrocarbons not visible to the unaided eye, examination of these surfaces with a hand-held UV lamp will render the residue visible by fluorescence. A UV scan of workers' clothing and equipment will indicate whether the risk of contact contamination is significant. This nonspecific test does not, however, indicate whether the compounds causing the fluorescence are carcinogenic nor whether nonfluorescent carcinogens are present. Nonetheless, the general rationale is that, since most PAH compounds fluoresce and since many members of the class are known carcinogens, this test gives an indication of the presence of suspect carcinogenic agents. A portable, battery-operated UV lamp (253.7 nm) could be used in a fabric-skirted box to permit surface viewing in a brightly lighted environment. Problems due to individual variations in dark adaptation and color sensitivity could be avoided by using a photovoltaic detector and meter or recorder.

V. ENGINEERING CONTROLS

General Engineering Control Objectives

Engineering control concepts that are generally applicable to all coal gasification processes, regardless of operating temperature and pressure, size, nature, and concentration of toxicants, etc, are discussed in this chapter.

Most health and safety hazards will arise during maintenance work or because of a failure in any one of a large number of pieces of equipment or process lines. Therefore, to reduce the potential for exposure, all possible failure modes during normal operation and during maintenance must be anticipated, examined, rated for risk factors (frequency and severity), and controlled to the greatest extent possible.

One way of approaching this formidable task is fault-tree system analysis and failure-mode evaluation. The requirement of a system safety analysis imposes a disciplined and inclusive approach to safety and health considerations. The analysis should include, but not be limited to, procedures for operational start-up, normal onstream operation, shutdown, and emergencies. This technique should be used before and during plant construction, throughout the life of the plant, and whenever changes in the process are contemplated. Fault-tree analysis has been used in coal gasification pilot plants [84] and is currently used by the world's oldest and largest plant to provide advice to engineers working on the design and construction of new facilities [12].

System safety analyses afford the opportunity for all responsible departments--including process engineering, mechanical engineering, safety engineering, maintenance, operations, and plant management--to become involved in decisions that will affect employee protection.

A very significant source of worker exposure in all coal gasification plants will likely be periodic, unpredictable leaks from process lines, vessels, flanges, valves, pumps, and other equipment. In pipes containing toxicants, welded joints should be used wherever possible. However, certain equipment must be readily accessible because maintenance is frequent, and flange connections are certainly necessary. Flat-face flanges have been reported to minimize leaks if the connections are maintained and inspected frequently and if the proper gasketing material is used [12,14]. Grooved, concentric, or other nonflat mating surfaces may reduce the frequency and severity of leaks by presenting a more circuitous and difficult path for gas escape. In some instances, increasing the number of flange bolts may improve performance. Retightening the flange bolts before and after the piping has reached operating temperature is another method of preventing leaks [9,85]. Periodic leak testing is necessary for all flange connections in pipes containing toxic materials.

It is important that leaks be located while small. This could be accomplished by banding the flanges, leaving only a small bleed connector to which the gas sampling apparatus could be attached. This allows small, otherwise nondetectable leaks to be located and repaired before the occurrence of workplace contamination. However, bleed connectors should be large enough to permit safe depressurization without blockage should a significant leak occur and go undetected. Thus, the connectors should be directed away from work areas or other equipment. In high-pressure gasification systems, leaks can usually be detected by the noise produced by the high-velocity escaping gas [12].

Proper selection of pump, compressor, and shaft seals should minimize worker exposure by reducing the frequency of leaks. Site visits and discussions with companies involved in coal gasification [9,12,18,37] have led NIOSH to the following conclusions that: (1) pressurized, double mechanical seals are not necessarily effective for gas streams containing entrained solids or liquids; and (2) the consequences of failure are more severe for pressurized double mechanical seals than for pressurized stuffing boxes. The increased severity would include both higher exposure to workers and relatively greater damage to equipment due to loss of pressurizing liquid and massive erosion. Thus, mechanical seals are not recommended for all conditions and process services. Process lines carrying liquids or gases should be designed to prevent erosion, leaks, and blockages. Design considerations should include adequate dimensions (both diameter and wall thickness), long-radius elbows, and minimization of stream velocities (above minimum transport velocities if the stream carries solids). Where blockages cannot be prevented by other means, mechanical means for line clearing should be installed. (Elbows that continue to experience erosion should be reinforced with welded metal sleeves with single-bleed nipples to allow early leak detection.)

Ultrasonic inspection of process lines is recommended. In most petrochemical or related facilities, including coal gasification plants, two types of leaks occur: those that disturb the process and those that do not. Recommended health standards should not need to address the former--process continuity should dictate prompt corrective action. It is the latter category, leaks that do not adversely affect plant operation, that is critically important in reducing workplace contamination (particularly in regard to chronic low-level employee exposure). The leak-detection program and other procedures specified in the recommended standard provide the means for locating low-level liquid or gaseous leaks. It is necessary to discourage the tolerance of small leaks of toxic materials, even though they do not affect plant operations. It is not reasonable to expect a plant to be shut down for the repair of a small leak from a pump or a valve. Conversely, considering the toxicity of many coal gasification products and the importance of maintaining employee health, it is not reasonable to allow leakage of toxic materials to continue for extended periods of time.

Conceivable solutions to the problem of leaks of toxic materials include the use of spared equipment, portable ventilation or ejector systems for small gas leaks, portable sumps (or eductors connected to closed sumps) for liquid leaks, and area isolation (restricted entry and provision of suitable protective equipment). To facilitate cleanup operations after a spill of toxic materials, adequate equipment and material (pumps, absorbent material, etc) should be readily available. To insure that process spills will be contained, process areas should be paved and appropriately curbed.

Process-area drains and sumps from which flammable or toxic vapors may be emitted should be covered and sealed to the extent possible to minimize employee exposure. Ventilation should be utilized to remove inflammable gases and vapors before explosive concentrations can build up in closed areas.

Process vessels containing toxic liquids should be designed to prevent overflow. Double block and bleed connections for process equipment to which access is needed are essential additions to line valves. Spectacle-type blanks, blinds, spool pieces, or the equivalent may be necessary to insure complete isolation before a vessel is breached and entered. Wherever possible, residual liquid in the isolated section should be drained into a closed treatment system. Gas lines must be thoroughly purged (also into a closed system and not directly to workplace air).

In closed process areas, adequate general ventilation should be provided to prevent hazardous buildups of toxic gases, vapors, or aerosols. The plant design should minimize recessed or low-lying areas in which toxic gases and vapors could accumulate. If such areas are unavoidable, they should be provided with adequate ventilation, even those that are open to the atmosphere.

Although the control measures discussed above should minimize persistent leaks, it may be determined in time that certain process points continue as sources of workplace contamination. If repeated efforts at process controls prove unsuccessful, local ventilation should be provided. An example of the applicability of local ventilation is an ejector system to exhaust the shrouded upper closure on the coal lockhoppers [9]. If the source of contamination is not continuous, it may be efficient to install a local ventilation system that can be dampered or "deadheaded" when not needed.

As in any large manufacturing facility handling large quantities of toxic, flammable, or explosive materials, sensitive process monitoring should be conducted to warn of any impending danger and to allow corrective action to be taken to prevent a process upset or, more importantly, to allow employees to evacuate anticipated dangerous areas.

Pressurized vessels and tanks containing volatile liquids should be equipped with safety relief valves to prevent dangerous pressure buildups. The relief valves should be so located or designed that they will not become blocked with tars or other viscous materials. Where blockage could be a problem, redundant safety systems should be installed (eg, a rupture disc, and a pressure relief valve). If the vessels contain toxic materials, the relief valves should be piped into some type of emergency vent and flared to prevent workplace contamination. Furthermore, storage tanks containing hazardous materials should be located in diked areas capable of holding the maximum volume of the tanks. All tanks and other equipment containing flammable materials should be electrically grounded.

All flares should have a pilot flame equipped with a failure alarm. This control will reduce the potential for workplace contamination with combustible gases and vapors.

Process equipment or lines hot enough to cause burns on contact or to cause heat stress should be isolated or insulated where necessary. An exception would be lines for which safety considerations, such as the need to identify hot spots, preclude the use of insulation. Such lines might be sufficiently isolated by expanded metal mesh guards, heat shielding, barriers, or increased air movement.

Control rooms, eating and rest areas, and process areas in which employees will spend significant amounts of time or may seek refuge during gas leaks or other emergencies should be designed to exclude contaminated air.

Noise can present significant chronic and acute health hazards to coal gasification workers unless adequate controls are integrated into plant design and unless such controls are satisfactorily maintained and strictly enforced.

It is necessary to control noise from compressors, pumps, and valves. It may be assumed that in any plant where steam is used there will also be steam leaks. Such leaks are significant sources of high levels of noise.

Process equipment that contributes to excessive noise exposures should be fitted with noise abatement controls and/or acoustically enclosed or isolated so that employee exposure does not exceed 85 dBA calculated as an 8-hour time-weighted average [72]. Expansion valves and ventilation blower inlets and outlets should be provided with appropriate mufflers. Steam lines (particularly high-pressure lines) must be designed to minimize leaks. Air compressors, particularly those in the oxygen plant, should be acoustically isolated in a separate area.

Specific Engineering Control Applications

(a) High-BTU Gasification

This section presents, on a unit-process basis, specific engineering control recommendations for high-BTU coal gasification plants. The specific hazards of each unit process are discussed in Chapter III. The recommended controls do not include all of the safety and health control measures necessary in such complex plants, and the recommendations may not be applicable to all unit processes. More efficient and effective control technologies very likely will become available as the commercial coal gasification industry develops in the United States. It should also be noted that not all unit processes are included in these discussions; in particular, ancillary operations that are not unique to coal gasification are omitted.

(1) Coal Storage and Transfer

The principal occupational hazards associated with coal handling (excluding mining) result from chronic dust inhalation, fire, and explosions. Although the degree and probability of these hazards vary in a coal-specific manner, control measures can be considered generally. Environmental problems such as leaching and water runoff can be significant but are beyond the scope of this document.

Coal may be stored in outdoor piles, closed bins, or silos. Surface fires and dust dispersion may be significant problems with outdoor piles. These potential hazards may be minimized by periodic surface wetting, compacting, and maintenance of the pile at a proper angle of repose. It has been suggested [9] that "dead" storage piles be compacted in 1-foot layers (compaction reduces contact with air and the resulting oxidation). The safest handling procedure, if consistent with other operational constraints, would be minimization of coal-storage retention time.

When such equipment as front-end loaders is used to handle coal before storage and preparation, significant amounts of dust will be generated. Unless the coal is kept thoroughly moistened (the only effective dust-control method), the cabs of all loading equipment, including continuous wheel excavator loaders and front-end loaders, should be enclosed and provided with filtered air supplies.

Occupational hazards in coal transfer operations are similar to those encountered in coal storage, including dust generation, fire, and explosions. Since a large amount of coal dust becomes airborne at conveyor transfer points, the number of transfer points should be minimized to the extent possible. Where transfer points cannot be avoided, water sprays and/or local ventilation should be used [9,12]. Two points deserve consideration: (1) a wet scrubbing system appears to be preferable for dust removal because of the potential for explosion in baghouse collectors and (2) the ventilation system must be designed for a transport velocity high enough to prevent settling of dust particles and resultant system blockage.

During coal transfer, dust particles may be dispersed by wind or other air disturbances. Partial or total enclosure of conveyors offers a simple solution.

To minimize fire hazards in coal conveyor systems, one US company plans to install water spray systems throughout the coal transfer network [9]. These systems will be designed for automatic activation controlled by temperature, temperature rise, and/or smoke monitors. (National Fire Protection Association Standard 15 provides design assistance and specifications.) Operation of the water spray system immediately shuts down the conveyor belt to confine the problem area for easier control.

(2) Coal Preparation

Coal preparation equipment consists of grinders, pulverizers, and screens. Occupational hazards are similar to those associated with coal storage and transfer, except that high levels of noise may be a serious problem. Often, only one or two employees are required in the coal preparation area, and they may spend much of their time in nonexposure areas such as a control room.

There are two critical requirements for a coal preparation area that is free from occupational health and safety hazards. First, frequent and thorough equipment maintenance is essential because the workplace environment can deteriorate rapidly should equipment, structures and seals develop leaks. Because such leaks will inevitably occur, liberal use of local ventilation is necessary. In addition, effective general ventilation should be provided. Second, dust explosions must be prevented. Despite the best housekeeping efforts, coal dust often accumulates on overhead rafters and other relatively inaccessible horizontal surfaces. These surfaces must be frequently cleaned (vacuum or equivalent) or hosed down. Good housekeeping in this area cannot be overemphasized because neglect can create secondary sources of airborne dust and increase the danger of serious dust explosions. Wet coal preparation techniques can reduce health, fire, and explosion hazards but because of the feed requirements these are not feasible in Lurgi gasification.

General safety precautions that apply to coal storage, preparation and transfer include use of explosion-proof electrical systems, properly grounded electrical connections, and adequate ventilation.

(3) Coal Feeding

Potential occupational hazards associated with the operation of coal lockhoppers include potential exposure to coal dust, crude gas, and high temperatures. The nature and extent of exposure depend on the kind of gas used to pressurize the lockhopper (carbon dioxide, crude gas, etc). Major sources of exposure include leakage from the upper lockhopper closure during pressurization, gas displacement through the upper lockhopper closure during charging, passage of crude gas upward through the lower closure when the gasifier is charged, and workplace reentry of gases vented during depressurization.

One proposed lockhopper design appears to offer effective worker protection [9]. The differential pressure between the lockhopper and the gasifier is constantly monitored. If the pressure in the gasifier approaches that in the lockhopper, the pressurizing gas injector automatically increases the lockhopper pressure, reducing the possibility of gasifier gases migrating into the lockhopper. During lockhopper depressurization, the lockhopper pressurizing gas is vented to a superheating stack. The remaining gas pressure in the lockhopper is reduced to atmospheric pressure with a nitrogen ejector, and any displaced gas is evacuated through a scrubber and vented to the atmosphere. Throughout the lockhopper charging sequence, a nitrogen ejector maintains a negative pressure in the upper closure shroud to prevent gas leakage into the workplace.

(4) Gasification

The most significant occupational hazards of Lurgi gasifiers will probably occur during start-up and shutdown operations. Start-up gas should be flared or equivalently disposed of in order to prevent the entry of crude gas into the workplace. Appropriate gas mixtures should be added to the gasifier and vent system during start-up to preclude the formation of explosive gas mixtures.

Without these precautions, explosive concentrations of crude gas could develop during the first few minutes of air operation and again after switching to oxygen operation.

Rapid shutdown will be necessary from time to time for process or safety considerations. A reliable, preferably redundant, system for immediately interrupting the steam and oxygen feeds to the gasifier is essential. Gas production ceases without this gas feed.

The crude-gas discharge line from the gasifier to the quench system is subject to blockage as a result of tar precipitation. This increases maintenance activities and undoubtedly subjects workers to dermal contact with carcinogenic tars. An automatic system for clearing the line of condensed tars is warranted. The Lurgi gasification system uses an automated ram to periodically clear the line [12,37]. The ram shaft assembly in the line has a significant leak potential due to the potential for extraordinary wear. Seal design must be given special attention and supplemental controls may be necessary. The crude gas discharge line and quench system are especially subject to both temperature and process stresses, including both erosion and corrosion. A means of monitoring the effects of these stresses should be included in system design.

To minimize the potential for burns, heat stress, materials-handling accidents, and other safety hazards during maintenance, the gasifier section must be designed with adequate clearances for operations and maintenance personnel.

(5) Ash Removal and Disposal

The most significant occupational health hazards associated with ash removal are heat stress, burns from hot lockhoppers and steam leaks, and dust exposure resulting from dumping lockhopper contents onto the ground. It is important that the lockhopper be well insulated, shielded, or isolated and that the system be designed to minimize steam leaks. Dust generation should be minimized by the use of wet handling methods. The ash lockhopper should be designed as part of a closed system, with the ash dumped into a liquid conveyor system, eg, a sluiceway [9,12]. Infrequently, the sluiceway water will be lost, and hot steaming ash will be dumped on the ground. Dust will be generated, and there is a significant burn hazard. However, this eventuality can be anticipated, and precautions such as isolation of the area and the use of personal protective equipment can be employed.

(6) Quenching

Except during maintenance operations, workers probably will spend little time in this process area. System design and operating efforts should be directed toward preventing leakage of crude gas, hot gas liquor, and tars, and toward minimizing the frequency of maintenance operations. The primary leak point will probably be at the recycle gas liquor pump. In the past mechanical seals for this pump have not been successful. One company has indicated that some of the new mechanical seals currently available may prove superior to stuffing boxes [9]. Because of the importance of preventing leaks from this pump, the best seals available at the time should be used. Two companies have indicated that they will use an interlock device to automatically activate a water-flush system should the gas temperature exceed a prescribed level [9,86]. The emergency flush system would be used either until repair of the recycle pump is accomplished or until the gasifier is taken offstream.

Another very effective method of exposure control is to reduce the frequency of maintenance operations. One company intends to design the waste-heat boiler to minimize both tar deposition on the cooling or boiler tubes and solids buildup at the bottom of the vessel [9]. All piping in this section should be heavy-walled, with long-radius elbows, and should be sized for minimum velocity. To prevent problems associated with thermal expansion of the piping network at high temperatures, the gas-liquor recycle pump could be suspended or the piping could be specially designed to minimize stress on the pump suction and offtake piping. The gas-quenching system should be designed to remove particulate matter elutriated from the gasifier or formed during quenching to minimize downstream problems associated with particles entrained in the gas stream.

(7) Gas-Liquor Separation

Occupational hazards in this process unit include potential exposure to escaping expansion gases, leaking tar separation equipment and pumps, and overflow of the tar separation vessel. Offgas lines should be properly sized to prevent plugging by entrained tar particles. Expansion gases should be scrubbed and incinerated [9], vented to the start-up vent line [86], or similarly disposed of in a safe manner.

Occupational exposure could occur should the gas-liquor separators overflow. This could result from a gas breakthrough at high pressure into the tar separation unit, causing raw gas liquor to overflow. The problem can be minimized by control of gas-liquor flow to the separation unit, using restrictive orifices, minimum orifice control valves, and fail-safe flow monitoring systems [9,12]. Emulsion formation in the tar separator can also cause overflow of raw gas-liquor. Methods of breaking and/or preventing these emulsions should be employed.

(8) Gas Purification (Rectisol)

Experience has shown that the potential occupational exposure from this process unit is low, except during sample collection, because the equipment is very reliable and leaks and/or maintenance requirements are likely to be minimal [9,12,86]. All pumps in the system should be designed for closed drainage into a separate "slop" system. Leaks also increase fire hazard; design should minimize both risk and potential consequences (eg, by ventilation).

(9) Phenol Recovery Unit

The phenol recovery unit may use either isopropyl ether or n-butyl acetate as the extraction medium. From a safety and health standpoint, the better of these is n-butyl acetate because of its relatively high 65 C (149 F) flashpoint and low toxicity. Isopropyl ether, on the other hand, is very volatile, with a flashpoint of -9.4 C (15 F) and a boiling point of 68 C (154.4 F), and can pose a severe fire hazard if not properly contained. Of greater concern is the fact that isopropyl ether forms potentially explosive peroxides when exposed to heat, light, and air (especially when evaporated to dryness). If this solvent is used, the system (including storage) must be completely tight. Leaked isopropyl ether must be contained and removed immediately. The formation of peroxides must be retarded by the addition of oxidation inhibitors such as diphenylamine, alpha-naphthol, beta-naphthol, or hydroquinone (approximately 0.05% addition) to the stored isopropyl ether. Water, at a concentration of 1% by weight, is also effective as an inhibitor [51].

(10) Oxygen Plants

Detailed safety procedures for oxygen plants are provided by the vendors of specific equipment. These should be followed carefully, and the hazards of accidental release of pure oxygen should be made familiar to all employees. Oxygen plants should be distant from areas where oils and tars are handled.

(b) Other Coal Gasification Processes

The general engineering control objectives discussed at the beginning of this chapter are applicable to all coal gasification processes. As with high-BTU processes, certain controls are unique to low- and medium-BTU coal gasification. These are discussed in this section. The controls described for high-BTU coal gasification are also applicable to Lurgi low- and medium-BTU processes.

In discussions of health and safety, the best classification of the various low- and medium-BTU processes is by (1) pressure and (2) tar and liquids production. Operating pressure affects not only the propensity for leakage but also, and possibly more importantly, the tolerance of personnel toward leaks. Obviously, in a high-pressure process leaks cannot be tolerated from an operational standpoint. Conversely, in a low pressure process, such as many low-BTU processes, small leaks do no great harm to operations, and thus there may be a tendency to tolerate leaks that may be significant from a health standpoint. The second factor of concern is the production of tar and potentially hazardous liquids. High-temperature gasification processes (eg, Koppers-Totzek) and processes using anthracite coal as feedstock do not produce these materials. In other processes, these materials are a substantial byproduct, and additional controls are necessary.

The methods of receiving and storing coal vary greatly in these processes, but the dust- and fire-control techniques discussed for high-BTU processes are basically applicable to all cases. However, the potential for dust and fire hazards is somewhat diminished because much smaller quantities of coal may be involved in low- and medium-BTU processes and because coal turnover is generally more rapid.

Some of these processes do not include coal preparation operations since coal sized to process specifications is delivered to the plant. The most notable exception is the Koppers-Totzek process, in which feed coal is ground very fine (90% less than 90 microns, 10% less than 7 microns) and which therefore has a high potential for dust generation. The enclosures and seals for coal pulverizing and transfer equipment must be very tight, and local exhaust ventilation may be necessary. In particular, the seals for the pumps that transfer the ground coal to a pneumatic conveyor system must be well designed, well constructed, and properly maintained. One company has indicated that leakage problems may be reduced by substituting stuffing boxes pressurized with nitrogen for the original mechanical seals [18]. In addition, stuffing-box wear was reduced by reducing pump speed. The coal preparation and handling areas of this plant, when observed in 1977 [18], were without significant traces of airborne or settled coal dust. Another exception is a process in which the coal is subjected to wet grinding and sizing [19]. There is little potential for dust generation since the coal is slurried.

Coal-feeding techniques for medium- and low-BTU processes vary greatly from those used in high-BTU processes. In low-pressure processes, there is no need for pressurized lockhoppers. Typically, there is a storage bin and a separate feed bin fitted with interlocked disc-type valves to control coal feed. The systems are generally manually operated, and the interlocks prevent the opening of the feed bin valve unless the storage bin valve is closed (and vice versa). As with a lockhopper system, some gas enters the feed bin when the gasifier is charged, either by simple displacement or by a small pressure differential between the two vessels. This gas can escape into the workplace through either of the disc valves or, more likely, up through the storage bin and into the coal bunker. Up to 500 ppm of carbon monoxide was measured in the coal bunkers of one such facility before ventilation was installed (carbon monoxide levels are now reported to be below the detectable level [14]). Methods should be devised to control this gas escape from the gasifier through the feed bin. At one facility, the coal bunker is connected to the gasifier through rotary barrel valves [15]. Emissions during gasifier charging are removed to the atmosphere via a discharge line above each valve [15]. Another installation minimizes gasifier pressure, applies general ventilation, and enforces restricted entry to the coal bunker area. An alternative method would be the use of local ventilation for the coal feed bin (conceivably by using the gasifier air blower). Any of these methods is acceptable if gas concentrations in the workplace are maintained at acceptable levels and if condensed tars are reduced to a minimum [15].

A temperature probe should be installed in the coal feed bin as a fire safety device [14].

There are other methods of coal feeding that require different types of controls. At one plant [18], fine coal from the service bin is fed to a feed bin where presssure-sensitive switches control the level of the coal. The system ensures a continuous feed of uniform density to the feed screw. The feed screws are designed to force the coal past a restricting plug inserted at the tip of the screw. This insert produces a large pressure drop across the front end of the screw, which keeps the screw filled at all times and helps to prevent the backflow of gas from the gasifier unit into the coal feed bunkers. The coal is picked up at the end of the screw feeder by oxygen and steam feed gas and is conveyed into the burner at a velocity of 300 ft/sec over the length of the 6-foot blowpipe. The high velocity prevents backflash into the conveying tube. At another gasifier that presently uses a lockhoppering feed system, a technique is being developed for extruding finely ground coal, bound with coal tar, into the gasifier [87]. This technique would provide a use for process tar, but special controls obviously would have to be used to minimize worker exposure to coal tar volatiles.

Another possible source of leakage from low-pressure gasifiers would be the rod-out ports where coal feed dip legs are used. When the ports are opened, producer gas can escape into the workplace. This exposure source should be controlled, particularly for tar producers, ideally by eliminating the necessity for the procedure. This should not be difficult in the case of new gasifiers, but process modifications (eg, larger dip legs, external vibrators, or local ventilation) may be necessary for existing facilities.

Most low-pressure gasifiers visited by NIOSH used metal pokers to prevent coal agglomeration in the gasifiers, to gauge ash height, and to locate the combustion zone [14-16]. Sealing methods for the "pokeholes" at the tops of the gasifiers ranged from iron balls loosely covering the holes to close-fitting covers tightened by dogs. Observation revealed the latter to provide superior sealing. At one such facility [14] the fire-bed depth is checked twice per shift. This operation is reported to require an average of 20 minutes, during which time the local carbon monoxide level rises to about 40 ppm [14]. In new plants, the gasifier should be designed to eliminate the use of "pokeholes." Consideration may also be given to purging steam or inert gas into the pokeholes during this operation to prevent the escape of gases. In existing plants, the holes should be tightly sealed during normal operation and provided with local exhaust ventilation when the pokers are inserted.

Gasifier pressures should be minimized to the extent possible, either by operating practices or external methods. The potential for leakage from the gasifier and surrounding lines is almost directly proportional to the internal pressure.

Another potential exposure source for low-pressure gasifiers is the gases vented during cold or hot start-up. For environmental reasons, these vent gases should be incinerated before release to the atmosphere. Vent flares should be designed to incinerate all materials vented. (One gas manufacturer [87] reported that tar condensation in the flare muffler resulted in tar droplets passing through the flame. The muffler was redesigned with a baffle plate, which ended the problem. During start-up operations, a technician is stationed at the flare to drain tar from the muffler.) Flares should be equipped with a pilot and a pilot alarm.

Other safety and health controls noted at low-pressure gasifiers include alarms in the producer gas stream to warn of excessive oxygen content, and directionally controlled blowout vents to minimize damage from an explosion in the gasifier area.

Ash removal and disposal do not appear to constitute a significant source of worker exposure in any of the low- and medium-BTU processes. At one facility [14], a slowly revolving grate removes ash to an ash hopper. Water is placed around the inside circumference at the top of the ash hopper to flush out the ash as a slurry (generally after a 24-hour accumulation). The ash is then taken to a landfill.

At one plant, approximately 80% of the ash is entrained in the product offgas, and the remaining 20% melts and flows downward as molten slag into a slag quench tank beneath the gasifier. At the top of the gasifier sufficient water is injected into the offgas to reduce the temperature, causing some of the ash to resolidify. Most of the remaining ash is removed from the gas in the water wash tower

[18]. For most coals, more than 50% of the ash flows down from the gasifier as molten slag and drains into the slag quench tank; the remainder of the ash leaves the gasifier as fine fly ash entrained in the exit gas. Approximately 90% of this fly ash is removed in the water wash tower. The remainder is removed in the electrostatic precipitators [24].

At one medium-BTU facility [18], the ash-laden quench water and slag discharge water are discharged to one of several long drag tanks. The ash settles to the bottom of the tank and is removed, while clean water overflows the tank and is sent to a cooling tower for subsequent recycle to the gasifier. Small quantities of hydrogen cyanide (6-17 ppm) in the gas stream are retained in the quench water. The plant [18] has reported an average hydrogen cyanide concentration of 10 ppm at the top of the cooling tower. Although workers probably would rarely spend much time in the cooling tower area, the exposure potential must be considered. In all cases where quench water is recirculated through cooling towers, the potential for exposure to toxicants (either from mist carryover or vaporization) must be evaluated and control measures taken. In this plant, the most persistent and serious area of potential employee exposure has been the compressor house, where the clean process gas is compressed to 30 atm. Even though the compressors are equipped with triple mechanical seals, leaks are common, and a 12-point automatic (sequential sampling) carbon monoxide monitoring system was installed. The sampling heads were installed on the compressors at areas of high leak potential. Problems with the mechanical seals evidently related to difficulty in balancing the nitrogen seal pressure between sections and maintaining adequate nitrogen pressure.

Basic control methods for toxic liquids in low- or medium-BTU plants using bituminous or lower ranking coals are similar to those discussed for high-BTU processes; equipment should be designed and maintained to contain the process liquids. Closed drains, separators, and sumps should be provided.

At one plant [15], tar and dust from the first water spray are collected in an open water seal. The heavy tar flows over a weir into a large open decanter. Float tar and solids are periodically raked from the surface of the water into a bucket or collector directly below the lip of the seal. The container is manually emptied into a chute leading to a dumpster, from which it is periodically taken to a landfill. Over the years, tar has grossly contaminated work surfaces in the area. New plants should be equipped with closed, automatic systems for removing the float tar and solids.

The decanter also collects contaminated water from the secondary and tertiary water sprays. The tar that settles at the bottom of the vessel is pumped to a steam plant for use as fuel. Excess water is recycled through a cooling tower for reuse as seal water, in scrubbers, and in the gas line. Controls to minimize drift carryover from the cooling tower should be considered (as well as the potential for escape of volatile liquids and gases), and an enclosed decanter system may be justified. One facility has developed [87] an effective method for controlling tar dispersion; gas is passed sequentially through a venturi contactor, a countercurrent gas cooler, and a washer. Condensed liquids are recycled through closed sump systems with underground storage. American Petroleum Institute (API) gravity separators are used to concentrate the tars for transfer to the extruder.

VI. WORK PRACTICES

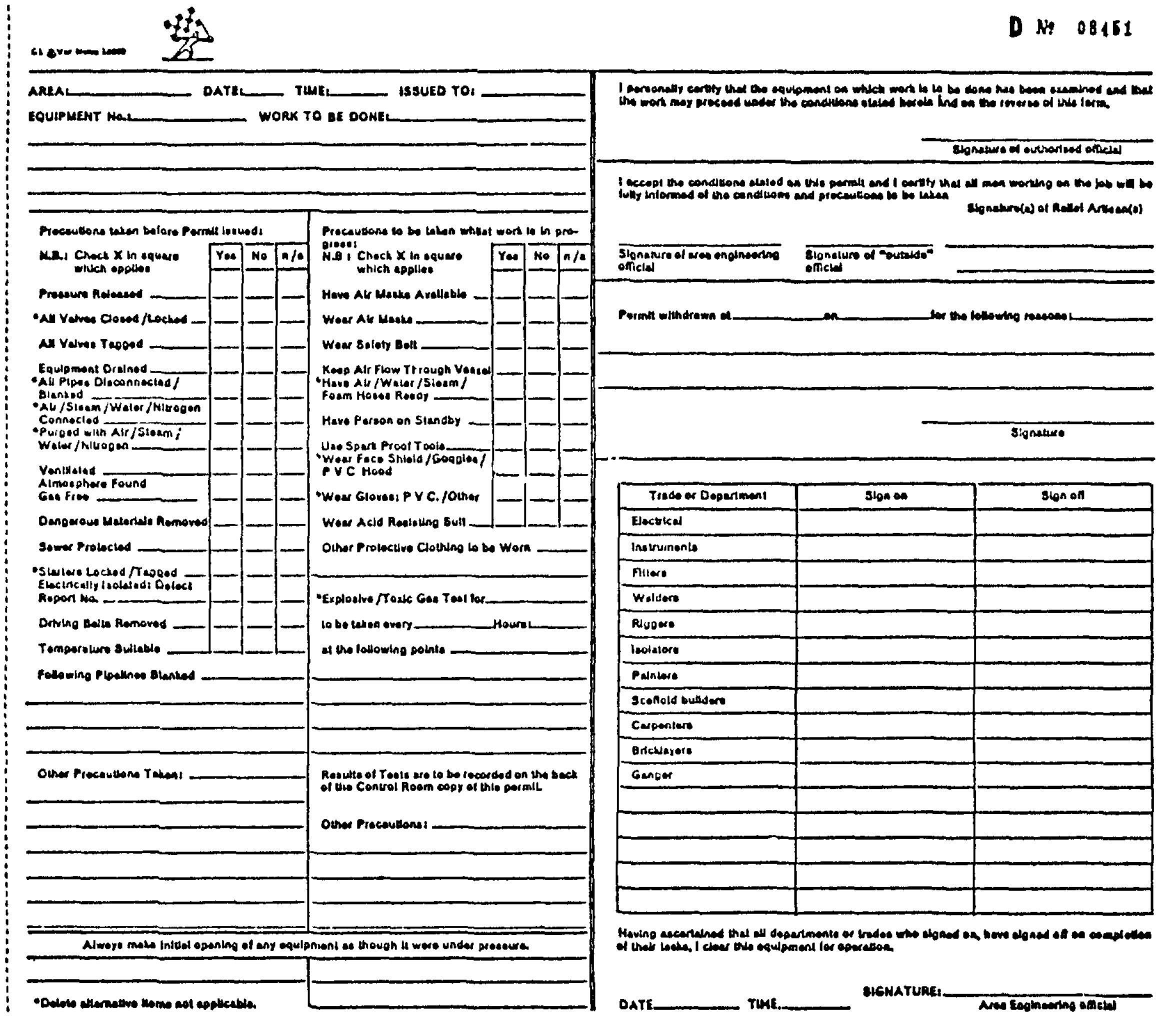
Good work practices, personal hygiene, and proper training all are essential to control the occupational hazards associated with coal gasification. Employees must be thoroughly trained in the use of all procedures and equipment required in their employment, and all appropriate emergency procedures and equipment. The effective use of good work practices and engineering controls depends on the knowledge and cooperation of employers and employees.

Written instructions informing employees of the particular hazards of specific substances, methods of handling the material, procedures for cleaning up spills, personal protective equipment requirements, and procedures for emergencies must be on file and readily available to employees. Employers must establish programs of instruction to familiarize all potentially exposed employees with these methods, procedures, and requirements.

An extensive preventive maintenance program is essential. Equipment in critical areas should be monitored for reconditioning or replacement at predetermined intervals based on the manufacturers' recommendations or, preferably, on operating experience. Equipment should be scheduled for thorough maintenance checks at appropriate intervals. High-maintenance equipment such as gasifiers must be taken off line periodically for complete cleaning and for the reconditioning or replacement of parts.

For each phase of routine and emergency maintenance or shutdown there should be developed a well-conceived and strictly enforced procedure, including the use of a safe work permit where appropriate (see Figures VI-1 and VI-2) [12]. The permit should include approvals for all facets of protection necessary to conduct the maintenance operation without danger to safety or health and to insure complete physical and electrical isolation of the maintenance area, which may require the use of a portable power supply. Before the start of any maintenance operation, a safety officer and/or shift or maintenance supervisor or the equivalent should complete the permit, detailing all necessary protective procedures. The permits should provide rigid requirements for personal protective equipment, respirators, lock-out and tag-out procedures, equipment isolation, air sampling, and emergency contingencies. A single, comprehensive safe work permit may be used for hot work, vessel or process-line entry, and routine maintenance; alternatively, separate permits may be developed and used for each of these operations.

At scheduled maintenance or inspection times, voluntary shutdown procedures are to be initiated, usually by first venting all process gases to a flare stack, purging the system twice with steam, and allowing the system to cool down. Voluntary shutdown is



D № 08451

AREA: ______ DATE: ______ TIME: ______ ISSUED TO: ______

EQUIPMENT No.: ______ WORK TO BE DONE: ______

Precautions taken before Permit issued:

N.B.: Check X in square which applies	Yes	No	n/a
Pressure Released			
*All Valves Closed/Locked			
All Valves Tagged			
Equipment Drained			
*All Pipes Disconnected/Blanked			
*Air/Steam/Water/Nitrogen Connected			
*Purged with Air/Steam/Water/Nitrogen			
Ventilated			
Atmosphere Found Gas Free			
Dangerous Materials Removed			
Sewer Protected			
*Starters Locked/Tagged Electrically Isolated: Defect Report No.			
Driving Belts Removed			
Temperature Suitable			

Following Pipelines Blanked ______

Other Precautions Taken: ______

Precautions to be taken whilst work is in progress:

N.B.: Check X in square which applies	Yes	No	n/a
Have Air Masks Available			
Wear Air Masks			
Wear Safety Belt			
Keep Air Flow Through Vessel			
*Have Air/Water/Steam/Foam Hoses Ready			
Have Person on Standby			
Use Spark Proof Tools			
*Wear Face Shield/Goggles/P V C Hood			
*Wear Gloves: P V C./Other			
Wear Acid Resisting Suit			

Other Protective Clothing to be Worn ______

*Explosive/Toxic Gas Test for ______

to be taken every ______ Hours: ______

at the following points ______

Results of Tests are to be recorded on the back of the Control Room copy of this permit.

Other Precautions: ______

Always make initial opening of any equipment as though it were under pressure.

*Delete alternative items not applicable.

I personally certify that the equipment on which work is to be done has been examined and that the work may proceed under the conditions stated herein and on the reverse of this form.

Signature of authorised official

I accept the conditions stated on this permit and I certify that all men working on the job will be fully informed of the conditions and precautions to be taken.

Signature(s) of Relief Artisan(s)

Signature of area engineering official

Signature of "outside" official

Permit withdrawn at ______ on ______ for the following reasons: ______

Signature

Trade or Department	Sign on	Sign off
Electrical		
Instruments		
Fitters		
Welders		
Riggers		
Isolators		
Painters		
Scaffold builders		
Carpenters		
Bricklayers		
Ganger		

Having ascertained that all departments or trades who signed on, have signed off on completion of their tasks, I clear this equipment for operation.

DATE ______ TIME ______

SIGNATURE: ______
Area Engineering official

Figure VI-1

Sample Permit to Do Hot Work, Weld or Burn

Adapted from Reference 12

CONTINUATION CERTIFICATE

Date	Time	Outgoing Production Foreman	Incoming Production Foreman	Authorised Official
	15h00			
	23h00			
	07h00			
	15h00			
	23h00			
	07h00			
	15h00			
	23h00			
	07h00			
	15h00			
	23h00			
	07h00			
	15h00			
	23h00			
	07h00			
	15h00			
	23h00			
	07h00			
	15h00			
	23h00			
	07h00			
	15h00			
	23h00			
	07h00			

GENERAL INSTRUCTIONS:

1. The conditions governing the issue and validity of this permit are described in Instruction No. 53, and any amendments thereof.
2. Work must cease and men must be withdrawn if any gas test is beyond the permissible limit.
3. Work must cease on the instructions of any person, pending confirmation by the Production Foreman or more senior official.
4. A ball-point or indelible pencil must be used to fill in the permit. The issuer must ensure that both copies are clearly legible.

GAS TESTS

DATE	TIME	LOCATION	TYPE OF TEST	RESULT	SIGNATURE
					TESTED BY:

Figure VI-2

Sample Safe Work Permit

Adapted from Reference 12

essentially a safe procedure, the principal safety hazard being incomplete purging of process gas before the flanges are "cracked." This hazard can be avoided by using two complete purges before cooldown, and by avoiding, in the original design, S-bends and blind piping, which are difficult to purge.

Comprehensive lock-out and tag-out procedures are essential. The principal single hazard that is characteristic of large multitrain high-BTU coal gasification plants is that individual process units (eg, gasifiers) are directly linked together and to a common utility main. In order to isolate one unit for maintenance, each of the many connections with other units and utilities must be blanked off. Failure to blank off even one of these points effectively may result in hazardous conditions in and around the unit [12].

To prevent asphyxiation of workers in enclosed areas, it is recommended that, wherever possible, steam be used for purging lines and vessels. Steam has very good warning properties (eg, visibility of condensate, increase in temperature), whereas carbon dioxide and nitrogen have none. Also, steam tends to be replaced by air after condensation. In addition, low-pressure steam probably will be readily available.

It must be emphasized that frequent air quality testings, both for the presence of carbon monoxide and for the presence of adequate oxygen, is required during vessel entry, since carbon monoxide and other gases adsorbed onto metal and refractory surfaces can be gradually released over a period of time. In addition to monitoring for carbon monoxide, at one plant a portable monitor is used to test for oxygen concentration before workers are allowed to enter a vessel [12]. At another plant, a portable oxygen detector equipped with an alarm remains in the vessel until the required maintenance work is completed [37]. Such continuous monitoring is recommended.

Employees entering confined spaces should wear suitable harnesses with lifelines tended by an employee outside the confined space who is also equipped with a self-contained breathing apparatus that operates in the pressure-demand mode (positive pressure) and has a full facepiece. The two workers should be in constant communication by some appropriate means and should be under the surveillance of a third person equipped to take appropriate rescue action if necessary [64].

Double-block-and-bleed connections, or the equivalent, are essential on both sides of all process equipment to which access is needed [79]. Spectacle-type blanks or spool pieces are effective in insuring complete isolation before a line is opened and the vessel entered [9]. Furthermore, all residual liquid in isolated sections of piping should be drained through closed systems and not directly to the workplace. Lines containing hazardous gases should be thoroughly purged (also through closed systems).

In high-pressure systems, leaks are major safety considerations in starting up the plant. Therefore, the entire system should be gradually pressurized to an appropriate intermediate pressure; at this point, the whole system should be checked for leaks, especially at valve outlets, blinds, and flange tie-ins, with particular attention to areas that have recently undergone maintenance or replacement. If no significant leaks are found, the system should be slowly brought up to operating pressure and temperature. The expansion of equipment at high temperature often serves to "tighten up" any pinpoint leaks. If leaks are found, appropriate maintenance should be performed.

Spills and leaks in process areas where toxic liquids are produced (eg, quenching, gas cooling, gas purification, gas-liquor separation, and Phenosolvan) must be cleaned up immediately, and employees engaged in cleanup must wear adequate personal protective clothing and NIOSH- or MSHA-approved respirators. The cleanup operation should be performed and directly supervised by employees instructed and trained in safe decontamination and disposal procedures.

When a significant leak or spill has been located, it must be contained as quickly as possible to minimize the area of contamination. Correction may be as simple as tightening a pump-seal packing gland or switching to spared equipment, or as drastic as initiating a process shutdown. Next, it is necessary to minimize the dispersion of the contamination by perimeter diking. In the case of small spills, a sorbent material may provide effective containment.

Every process area should have a suitable number of manually activated gas alarms for use during gas leaks. These alarms should serve to supplement any automatic gas monitoring systems. The number and placement of the manually activated alarms would vary in the individual work areas, but in the case of a serious leak a worker should have no difficulty reaching the alarm quickly and safely.

Process gas leaks due to the "freezing" of valves by intense process heat can be hazardous. Operators should first attempt to close manual backup valves upstream of the leak. If backup equipment also fails, operators should activate the alarm to initiate emergency shutdown procedures and should leave the area immediately. Emergency crews dressed in proper clothing should be dispatched to the area to begin wetting down structures or discharged solids [88].

Dried tar is difficult to remove from any surface, particularly from the inside of process vessels. Manual scraping and chipping, together with the use of chlorinated hydrocarbon solvents or commercial cleansers, are common methods of cleanup.

Contact of tars with the skin or eyes must be avoided. Where organic solvents are used for this purpose, special care is necessary to prevent employee exposures to solvent vapors. Cleaning solvents should be selected on the basis of low toxicity as well as effectiveness. Approved respirators should be worn while using such solvents. Steam stripping is also commonly used [12] and is effective, but it can cause significant inhalation exposures to airborne particulates, ie, lower-boiling-point residues may vaporize and high-boiling-point material may become entrained in induced air currents. Generally, steam stripping is not recommended because of the potential for the generation of airborne contaminants, but there may be instances (eg, small, confined surfaces) where it must be used. If steam stripping is to be used, it is recommended that NIOSH-approved supplied-air respirators be worn by all employees in the area and in adjacent areas.

The use of strippable paints or other effective surface coatings for plant surfaces where tar spillage can occur should be considered. Suitable coatings are impenetrable by tar and do not adhere well to surfaces. Thus any tar can be removed along with the coating, followed by repainting of the surface.

Hand tools and portable equipment frequently become contaminated and present an exposure hazard to employees who use them. Facilities with adequate ventilation should be provided for cleaning tools and equipment. Effective methods include vapor degreasing and ultrasonic cleaning. Before tools or equipment are returned to service, they should be examined in an ultraviolet darkbox for residual contamination. An ultraviolet scan of the affected areas after decontamination could be used to determine whether additional cleaning is necessary [48].

Process samples, contaminated tools, and equipment being moved out of process areas or going to repair shops should be identified with brightly colored tags [89] to warn employees that a potential hazard exists. Process equipment or areas containing tar, tar oil, or other hazardous materials should be identified by a brightly colored label, specific to the hazard.

Certain hazards are unique to specific gasification processes or unit operations within the process. One example is the potential formation of nickel carbonyl in the methanation units. The probability of this occurrence during steady-state operation of this unit is minimal so long as carbon monoxide does not contact the nickel catalyst at temperatures below 260 C (500 F), ie, lower temperatures should not occur during steady-state operation. To prevent the formation of nickel carbonyl while the methanation unit is being shut down, the partial pressure of the carbon monoxide in the gas stream must be kept low by means such as a hydrogen purge followed by a nitrogen purge. During start-up, this sequence should be reversed until the temperature exceeds 260 C (500 F).

Use of proper personal protective equipment and practice of good personal hygiene are particularly important for employees exposed to tar or tar oil. Employers should provide clothing that protects employees from the hazardous exposures anticipated in carrying out their duties. One effective garment is a jumpsuit type of cotton coverall with a fairly close weave designed to retard the penetration of contaminants yet permit the escape of body heat. The coveralls should be white or light in color so that contamination will be readily visible. Single-use disposable coveralls were tried in a low-BTU coal gasification plant [87], but they were found to be subject to tearing, provided no ventilation, were bulky, and were not well accepted by the employees. Another company reported favorable results with nylon coveralls [90]. In addition to being easily cleaned, these coveralls are reported to be heat resistant and capable of providing satisfactory protection against heat stress during emergency evacuation in the case of fire.

There is evidence that the type of clothing worn underneath the coveralls is very important to the reduction of skin contamination. In an experiment undertaken in 1957 at a coal hydrogenation pilot plant, it was observed that "pajamas," buttoned at the neck and with close-fitting arm and leg cuffs, worn under typical work clothes, were effective [32]. Apparently they prevented contaminants absorbed by the outer clothing from continually coming into contact with the skin. They also provided an additional barrier to vapors and aerosols. It probably would be beneficial if such clothing were worn under the coveralls. However, particularly in hot climates, this may contribute to heat stress, a hazard potentially more significant than the hazards avoided by the added skin protection.

It would be prudent to conduct laboratory tests with several types of protective clothing and fabrics prior to selecting and purchasing a large number of any one type. A decision should be made to determine the imperviousness of the exposed material by fluorescence testing of inner fabric surfaces.

Gloves are usually worn at coal gasification plants during cold weather, when heavy equipment is handled, or in areas where there is hot process equipment. Where gloves will not cause a significant safety hazard, they should be worn to protect the hands from process materials. Gloves made of absorbent materials should not be used because, once contaminated, they will remain a constant source of skin contamination until laundered. The ideal glove would be impervious to the absorption or passage of process residue and capable of withstanding daily laundering.

Outer clothing for use during cold or inclement weather must be selected carefully to insure that it provides adequate protection and can be laundered or drycleaned to eliminate contamination by process materials.

There should not be large quantities of liquid residue from the gasification processes on the floors, so that regular steel-toed work shoes should provide adequate protection. However, if problems involving footwear contamination do develop, loose, impervious overshoes should be considered. Rubber-soled overshoes are not recommended because the rubber may swell in contact with process oils.

Requirements for other types of protective clothing or devices should be based on the potential exposure as described in the safe work permit, eg, leather gloves and leather hoods with face shields for hot work, acid-resistant suits for use while handling acid.

Experience indicates that an effective method for removing coal-derived contamination from work clothes is drycleaning, followed by washing with soap or detergent and water [27,91,92].

Commercial drycleaning of gloves, socks, special clothing and coveralls of all workers exposed to tar and tar oil is employed by one company engaged in pilot-plant research [87]. The commercial drycleaning establishment receives the contaminated clothing in sealed plastic bags and is warned of the attendant hazard potential. Employees' personal clothing that has become contaminated is treated similarly.

The preceding discussion of protective clothing is pertinent only to gasification processes that produce tar and tar oil. General protective clothing requirements for workers in other plants will vary with the unit process or the job category.

If significant contamination of either exposed skin surfaces or outer clothing occurs, a prompt shower and change of clothing should be required. Because of the importance of this protective measure, supervisory employees must be responsible for insuring strict compliance with this requirement. Employees exposed to tar and tar oils should be required to shower at the end of each shift or at any time they become noticeably contaminated with tar or tar oil.

To promote good personal hygiene practices, to encourage adherence to the daily shower requirement, and to segregate contaminated clothing from street clothing, a double locker room separated partially by a shower facility and partially by one-way door(s) should be installed in such a way that passage from the "clean" to the "dirty" sides can occur only through the one-way door(s), while passage from the "dirty" to the "clean" sides can be accomplished only through the shower facility.

Storage space is necessary on the contaminated side to allow storage of work boots, hardhats, and other safety equipment. Soiled clothing removed after work should be segregated so that outer garments are not mixed with personal clothing that comes into direct contact with the skin. The indiscriminate collection of all clothing may cause the spreading of contamination from overalls, for example, to undergarments. Clothing so badly contaminated that it cannot be effectively laundered should be totally segregated from all other clothing and incinerated. A bin or other container with a tightly fitting lid should be available for the disposal of such clothing.

Many low-BTU gasification plants will be adjuncts to larger facilities and so small that probably only one or two workers may be potentially exposed to contaminants, and then only for several hours per shift. The construction of a double shower room for use by only one or two employees is probably not warranted. One company has reported the use of a specially designed shower trailer to serve the same purpose as the double shower [87]. If such a facility is not used, the minimum provision should be separate areas for clean and "dirty" work clothes for exposed employees.

An adequate number of washrooms should be provided throughout plants to encourage their frequent use by workers. In particular, a washroom facility should be located close to lunchrooms so that employees can wash thoroughly before eating. It is very important that lunchrooms remain uncontaminated to minimize the likelihood of ingesting tar or tar oil. It is necessary that the workers remove contaminated gloves, boots, coveralls, and hardhats before entering lunchrooms. Therefore, some type of interim storage facility should be provided.

Regular soap is recommended for use in showering; the use of organic solvents may facilitate the penetration of contaminants into the skin and thus hinder their removal. It is important also that workers thoroughly wash their hair during showers. Lanolin-based or equivalent nonaqueous hand cleansers should be provided in all washrooms in the plant and in the locker facility. All use of sanitary facilities should be preceded by a thorough cleansing of the hands.

Barrier creams have been suggested as an effective means of reducing skin contact with tar and tar oil, facilitating their removal should contamination occur. Proponents state that, if nothing more, barrier creams contribute to personal hygiene because they must be washed off and with them, presumably, contaminated material. It is further claimed that they provide additional protection for areas of the skin normally not covered by protective clothing (neck and face) and act as a sun screen. The major objection to their use is the unwarranted assumption that barrier creams alone provide adequate protection, which may encourage noncompliance with requirements for personal protective equipment and personal hygiene. Furthermore, it has been speculated that certain barrier creams may exacerbate the spread of tar and tar oils. The effectiveness of presently available barrier creams has not been established, and they are not recommended as a method of reducing skin contact with substances encountered in coal gasification plants. Since many questions regarding the use of barrier creams remain unanswered, research on the subject is recommended.

Respirators are to be considered a last-resort method of reducing employee exposure to airborne toxicants. Their use is acceptable only (1) after it is demonstrated that engineering, work practices, and administrative controls are not sufficient; (2) during periods before effective controls are implemented; (3) during the installation of new engineering controls; (4) during certain maintenance operations; and (5) during emergency shutdown, leaks, spills, and fires. A respiratory protection program meeting the requirements of 29 CFR 1910.134 must be established and enforced. Employees should be instructed in the proper use and leak-testing of respirators assigned to them.

Because of the complexity of potential exposures and the large number of possible toxicants in any given process area, the utility of cartridge or filter respirators will be limited. Any employee assigned to an operation requiring the use of a respirator should be examined to determine whether he is capable of performing the assigned task while using the device. It is the employer's responsibility to inform the employee of the necessity to use a protective device when the air concentration of hazardous substances cannot be kept at or below the permissible exposure limit. Respirators must be cleaned and inspected after each use. Cleanliness of respirators is particularly important because of the hazard associated with dermal exposure to tar and tar oil. Respirators restrict the wearer's field of vision and often his mobility as well. Since this may result in additional safety hazards, safety procedures appropriate to the job must be developed [93].

Supplied-air lines with a sufficient number of hookup locations could be provided in appropriate plant areas. Most plants will have an abundant supply of such air, but it must be cleaned and filtered for this purpose. The umbilicals and air-line masks could be used primarily during maintenance operations or for work in areas suspected of having high concentrations of toxicants.

Fault-tree analysis and failure-mode evaluation have been mentioned in Chapter V in relation to engineering control applications. Such systems safety techniques could be used to identify necessary work practices as well. References for these techniques are presented in Chapter XIV.

VII. DEVELOPMENT OF STANDARD

Basis for Previous Standards

A search was made for occupational health standards in those countries that are or have been actively engaged in the gasification of coal, including Great Britain, the Federal Republic of Germany, and the Republic of South Africa. None of these countries had occupational health standards specifically related to the gasification of coal. A state-by-state search in the United States also failed to uncover occupational health standards specifically related to coal gasification, although New Mexico has environmental regulations specific to high-BTU coal gasification.

In 1967, the American Conference of Governmental Industrial Hygienists (ACGIH) adopted a threshold limit value (TLV) of 0.2 mg/cu m for coal tar pitch volatiles (CTPV), described as a "benzene-soluble" fraction, and listed certain carcinogenic components of CTPV. The TLV was established to minimize exposure to the listed substances believed to be carcinogens, specifically, anthracene, benzo(a)pyrene, phenanthrene, acridine, chrysene, and pyrene [VII-5]. It was promulgated as a Federal standard under the Occupational Safety and Health Act of 1970 [49].

In 1973, NIOSH published _Criteria for a Recommended Standard...Occupational Exposure to Coke Oven Emissions_, recommending work practices to minimize the harmful effects of exposure to coke-oven emissions and the inhalation of CTPV. In 1974, the Occupational Safety and Health Administration (OSHA) established a Standards Advisory Committee on Coke Oven Emissions to study the problem of the exposure of coke-oven workers to CTPV and to prepare recommendations for an effective occupational health standard. In 1975, the Committee recommended a limit of 0.2 microgram/cu m for benzo(a)pyrene (Federal Register, 41:46741, October 22, 1976).

In 1976, OSHA promulgated a Federal standard for coke-oven emissions designed to reduce employee exposure to carcinogenic chemicals [93]. The standard was based on epidemiologic and animal-experimental evidence, indicating that the chemicals present in coke-oven emissions can produce skin, lung, bladder, and kidney cancer in humans and animals [48]. It was concluded that coke-oven emissions induced lung and genitourinary tract cancer in the exposed population. It was also concluded that coal tar products were carcinogenic to animal skin and were related to increased skin cancer morbidity in human populations similar to coke-oven workers. Thus, protective measures designed to reduce employee exposure to coke-oven emissions were deemed to be warranted. A standard for the benzene-soluble fraction of total particulate matter emitted during the destructive distillation or carbonization of coal was established; specific engineering controls and work practices designed to reduce exposure to coke-oven emissions were mandated [49].

In 1977, NIOSH published Criteria for a Recommended Standard... Occupational Exposure to Coal Tar Products, including coal tar, coal tar pitch, and creosote [48]. NIOSH concluded that these materials were carcinogenic and could increase the risk of lung and skin cancer in workers. These products often contain identifiable components which by themselves are carcinogenic, such as BaP, benzanthracene, chrysene, and phenanthrene. Other chemicals from coal tar products such as anthracene, carbazole, fluoranthrene, and pyrene may also cause cancer, but their causal relationships have not been adequately documented. The recommended standard included a permissible exposure limit of 0.1 mg/cu m based on the cyclohexane-extractable fraction of the sample (determined as a TWA concentration for up to a 10-hour workshift in a 40-hour workweek), methods for the sampling and analysis of coal tar products, and specific minimum requirements for medical surveillance, labeling and posting, personal protective equipment and clothing, informing employees of hazards, work practices, sanitation, and monitoring and recordkeeping designed to reduce the health and safety risks from exposure to coal tar products [48].

From 1972 to 1977, NIOSH published criteria for recommended standards for occupational exposure to a number of chemical and physical agents that may constitute occupational health hazards in coal gasification plants (see Table III-10).

Basis for the Recommended Standard

(a) Engineering Controls

Engineering control recommendations are discussed in Chapter V, with emphasis on process areas suspected or known to present potential occupational safety and health hazards. Examples of such areas are given and methods of controlling the hazards are suggested. Recognizing that the engineering design for commercial coal gasification plants is only now in the process of development, the emphasis is on design to prevent employee exposure. Because of the size and complexity of the process and the variable nature of hazardous emissions, unit-process-specific engineering controls are discussed, as well as those of more general applicability.

(b) Permissible Exposure Limits

Coal gasification plants should comply with permissible exposure limits recommended in NIOSH criteria documents which have not been acted upon by OSHA, and to all applicable Federal occupational standards. There are no reports of chronic disease resulting from occupational exposures in commercial coal gasification plants operated in foreign countries, and there is only one set of reports of health problems in a coal liquefaction pilot plant in the United States [26-27,31-32]. Thus, in the absence of data to support the development of permissible exposure limits specific for the environment of coal gasification plants, NIOSH concluded that in addition to compliance with applicable standards and permissible exposure limits, worker protection could best be achieved through adequate engineering controls, work practices, and medical surveillance.

(c) Sampling and Analysis

To determine compliance with recommended permissible exposure limits, NIOSH recommends use of the sampling and analytical methods presented in the criteria documents referenced in Chapter III (see Table III-10).

Guidelines are presented in Chapter IV for an indicator monitoring concept to allow real-time detection of leakage in coal gasification plants. However, before it is adopted as a procedure for compliance with standards, this method should be compared with methods for the detection of specific hazardous compounds in terms of accuracy and sensitivity.

(d) Medical Surveillance

It is recommendeded that a medical surveillance program be instituted for all occupationally exposed employees and that it include preplacement and interim medical histories supplemented with preplacement and periodic examination of the lungs, the upper respiratory tract, and the skin. Pulmonary function tests [FVC and FEV(1) at a minimum] should be performed, and posteroanterior (14 x 17 inch) chest X-ray films should be made to aid in detecting any existing or developing adverse effects on the lungs. Audiometric examinations should be given to all employees who may be exposed to noise. The skin of employees occupationally exposed to tar or tar oil should be routinely examined for any actinic effects or the presence of benign or premalignant lesions. Suspected malignant lesions should be removed or the employee should be referred to a dermatologist for examination and possible removal of the lesion.

Workers frequently exposed to tar or tar oil should be examined at least annually to permit early detection of adverse effects on the respiratory organs and of sensitization to these materials. In the case of workers potentially exposed to high concentrations of particulate matter, special attention should be given to the oral mucosa. A complete physical examination following the protocol of periodic examinations should be performed when workers terminate employment, if a complete examination has not been performed in the preceding year.

(e) Personal Protective Equipment and Clothing

Employers should provide clean work clothing, workshoes or shoe coverings, gloves, and protective equipment in certain plant areas, as described in Chapter VI.

(f) Informing Employees of Hazards

At the beginning of employment, all employees should be informed of the known occupational exposure hazards associated with coal gasification plants. Signs warning of potentially hazardous exposures must be posted in any work area with a potential for occupational exposure to toxic substances and hazardous conditions. The employer should develop and implement a continuing education program to insure that all employees have current knowledge of job hazards, signs and symptoms of overexposure, proper maintenance and emergency procedures, proper use of protective clothing and equipment, the advantages of good personal hygiene, and of participation in the medical surveillance program.

(g) Work Practices

Work practices are discussed in Chapter VI. They are directed to the prevention of hazardous exposures, fire, and explosion.

(h) Monitoring and Recordkeeping Requirements

Continuous monitors for carbon monoxide or other indicator substances should be used as described in Chapter IV. Performance criteria should be established to facilitate evaluation of progress toward protection objectives. The indicator monitoring concept, coupled with selected sampling and analysis for other toxicants, provides a reasonable vehicle for control performance assessment. The procedures are designed to enable rapid corrective action if a high carbon monoxide concentration is detected. The source of the leak must be found, generally by using a portable air sampler to trace the gas back to its source. Maintenance or other corrective action must then be accomplished. Records of these events, including frequency and severity of leaks by process area, provide an excellent means for comparing performance with objectives and for directing future efforts to problem areas. A further comparison of these records with data from periodic personal monitoring for specific toxicants affords additional performance evaluation.

To insure that sampling and analytical data and medical surveillance information are available for later reference and possible correlation with the health status of employees, employers should keep records of workplace monitoring and employee medical examinations for at least 30 years after the employment of occupationally exposed workers has ended. This will allow an analysis of the efficiency of engineering controls, of exposure potentials, and of the impact of process changes on the concentrations of airborne toxicants and on potential exposure of employees.

VIII. RESEARCH NEEDS

This chapter summarizes overall research recommendations in the areas of industrial hygiene, process design, process equipment, health effects, monitoring and analytical procedures, and safety.

The CO indicator monitoring concept should be verified at the earliest opportunity. Quantitative sampling and analysis should be accomplished for specific chemical substances in the work environment, and these findings should be compared for accuracy with the expected concentrations calculated in indicator monitoring procedures.

Comprehensive, reliable industrial hygiene evaluations of exposures to hazardous agents in coal gasification plants are needed.

The utility of presently known barrier creams to reduce skin contact with tar and other materials is unsettled, and more information on their effectiveness is needed.

The effectiveness of available cleansing materials for removal of tar from the skin should be investigated. More effective but safe materials are needed.

The effectiveness of ultraviolet (UV) radiation in detecting skin contamination should be thoroughly demonstrated. At the same time the possibility of tissue damage due to the use of UV surveillance should be examined. Alternative procedures for contamination detection should also be investigated.

A study of thermal oxidation processes including incineration should be undertaken to determine and verify the conditions under which complete oxidation of polynuclear aromatic hydrocarbons is effected.

Knowledge of the constituents of the gas stream at each point in the process is crucial in identifying the compounds to which employees may be exposed. The true distribution of trace metals and of sulfur and nitrogen decomposition products, for example, should be determined. At present, estimates of the total distribution are based primarily on calculations. The fate of the radioactive constituents of coal in coal gasification processes should be determined. The effects of shutdown on the deposition of carcinogenic products on surfaces that will be contacted by maintenance and/or production workers should be investigated.

It has generally been assumed that the coked or ashed solids from the reactor are essentially inert. Experimentation is needed to determine the actual hazard classification of these solids.

Under certain operating conditions nickel carbonyl may be formed in the methanator. The maintenance of temperatures above 260 C (500 F) while the synthesis gas is in contact with the catalyst will avoid this problem. However, in the event of an upset in the operating parameters or a "crash shutdown" of part of the process, the operating condition may no longer be safe. There is a need to determine the conditions under which nickel carbonyl is formed in the methanator and the concentrations at which it may occur.

The relative carcinogenicity of polycyclic aromatic hydrocarbons (PAH's) condensed on the exterior surfaces of equipment and structures should be determined by bioassay. PAH's are considered a source of contamination with a potential for skin cancer.

Retrospective morbidity and mortality studies of workers who have left the coal treatment and coal conversion industries should be performed.

Real-time monitoring is desirable, either for all polycyclic aromatic hydrocarbons (PAH's) or for a member of the group such as benzo(a)pyrene, which would serve as an indicator. The present method, measuring the amount of cyclohexane-soluble material in the total particulate matter, is relatively crude and is susceptible to various errors.

The techniques for collecting particulate matter containing PAH compounds should be studied to determine whether there are significant losses of PAH compounds by evaporation.

IX. REFERENCES

1. US Energy Research and Development Administration: A National Plan for Energy Research, Development, and Demonstration: Creating Energy Choices for the Future. US ERDA, 1976, vol 2, pp i-xi, 9-17

2. US Energy Research and Development Administration: A National Plan for Energy Research, Development, and Demonstration: Creating Energy Choices for the Future, US ERDA, 1976, vol 1, pp i-vi, 52-58

3. US Bureau of Reclamation: Final Environmental Statement: Proposed Western Gasification Company (WESCO) Coal Gasification Project and Expansion of Navajo Mine by Utah International, Inc, San Juan County, NM. US Dept of the Interior, 1976, pp 1/1-1/88, 8/47-8-74

4. North Dakota Gasification Project for ANG Coal Gasification Company. Bismarck, ND, Woodward-Clyde Consultants, 1975, vol III, pp 39-45

5. Sernco, Inc: Applicant's Environmental Assessment for a Proposed Coal Gasification Project in Campbell and Conserve Counties, Wyoming. Casper, WY, Wyoming Coal Gas Company and Rochelle Coal Company, 1974, pp III/1-III-40, E/37-E-48

6. US Bureau of Reclamation: El Paso Draft Environmental Statement. Before the Federal Power Commission, Docket No. CP 73-131, Application Z-Z, Suppl No. 2. El Paso, TX, US Bureau of Reclamation, 1976, vol III, Area 01-Area 19

7. Magee EM, Hall HJ, Varga GM Jr: Potential Pollutants in Fossil Fuels. NTIS-PB-225-039. Linden, NJ, Exxon Research and Engineering Company, 1973

8. Martin JE, Harward ED, Oakley DT, Smith JM, Bedrosian PH: Radioactivity from Fossil-Fuel and Nuclear Power Plants. IAEA-SM-146/19. Rockville, MD, DHEW, Bureau of Radiological Health, 1970

9. Report of visit to Fluor Engineers and Constructors, Inc, WESCO Project Group, Irvine, CA. Rockville, MD, Enviro Control, Inc, Nov 14-19, 1977 (submitted to NIOSH under contract No. 210-76-0171)

10. Sinor JE (ed): Evaluation of Background Data Relating to New Source Performance Standards for Lurgi Gasification, EPA-600/7-77-057. US Environmental Protection Agency, 1977

11. Janes TK, Rhodes WJ, Bertrand RR, Magee EE: Trip Report: Four Commercial Gasification Plants, November 6, 1974 to November 18, 1975. Research Triangle Park, NC, US Environmental Protection Agency, 1975, pp 1-37, Appendix C, Appendix D

12. Report of visit to South African Coal, Oil and Gas Corporation, Ltd (SASOL), Sasolburg, South Africa. Rockville, MD, Enviro Control, Inc, Dec 5-8, 1977 (submitted to NIOSH under contract No. 210-76-0171)

13. Evans JM: Estimate of Growth Potential for Low- and High-BTU Coal Gasification, unpublished first draft submitted to US Dept of Energy. Rockville, MD, Feb 1978, pp 1-2

14. Report of visits to Glen-Gery Corporation, Reading, PA and York, PA. Rockville, MD, Enviro Control, Inc, May 17, 1977, Dec 6, 1977, and Dec 21-22, 1977 (submitted to NIOSH under contract No. 210-76-0171)

15. Report of visit to Holston Army Ammunition Plant, Kingsport, TN. Rockville, MD, Enviro Control, Inc, Aug 24, 1977 (submitted to NIOSH under contract No. 210-76-0171)

16. Report of visit to National Lime and Stone Company, Carey, OH. Rockville, MD, Enviro Control, Inc, May 5, 1977 (submitted to NIOSH under contract No. 210-76-0171)

17. Ricketts TS: The operation of the Westfield Lurgi plant and the high-pressure grid system. In: Proceedings of the 100th Annual General Meeting, Institution of Gas Engineers, London, England, May 14-17, 1963

18. Report of visit to Modderfontein No. 4 Ammonia Plant, Johannesburg, South Africa. Rockville, MD, Enviro Control, Inc, Dec 7, 1977 (submitted to NIOSH under contract No. 210-76-0171)

19. Report of visit to Texaco Corporation, Wilmington, CA. Rockville, MD, Enviro Control, Inc, Nov 17, 1977 (submitted to NIOSH under contract No. 210-76-0171)

20. Report of visit to Morgantown Energy Research Center, Morgantown, WV. Rockville, MD, Enviro Control, Inc, Aug 5, 1977 (submitted to NIOSH under contract No. 210-76-0171)

21. Tenney RF, Clendenin JD, Sanner WS: Anthracite Gas-Producer Tests at a Brick Plant, Bureau of Mines report of investigations 5556. Washington, DC, US Dept of Interior, Bureau of Mines, 1960

22. Morgan RE, Eckerd JW, Ratway J, Baker AF: Lurgi-Gasifier Tests of Pennsylvania Anthracite, Bureau of Mines report of investigations 5420. Washington, DC, US Dept of Interior, Bureau of Mines, 1958

23. Evans JM: Memo, Conversation with Paul Musser, Department of Energy Project Officer for Combustion Engineering Entrained-Bed Low-BTU Coal Gasification Project. Unpublished paper submitted to NIOSH, Rockville, MD, Jun 1978

24. Report of visit to Koppers Company, Inc, Pittsburgh, PA. Rockville, MD, Enviro Control, Inc, Aug 1, 1977 (submitted to NIOSH under contract No. 210-76-0171)

25. Savage PR: New feeds and processes perk ammonia production. Chem Eng 84:79-82, 1977

26. Sexton RJ: The hazards to health in the hydrogenation of coal--I. An introductory statement on general information, process description, and a definition of the problem. Arch Environ Health 1:181-186, 1960

27. Sexton RJ: The hazards to health in the hydrogenation of coal--IV. The control program and the clinical effects. Arch Environ Health 1:208-231, 1960

28. Evans JM: Memo, Conversation with E Donath. Unpublished paper submitted to NIOSH, Rockville, MD, 1976

29. Herrman WA: The health hazards and the environmental impact of coal conversion plants. Unpublished report submitted to NIOSH by Enviro Control, Inc, Rockville, MD, Feb 1977, under contract No. 210-76-0171

30. US Bureau of Mines: Construction of Hydrogenation Stalls for Explosions, ln 558, May 3, 1943, TOM Reel 162, Frames 886-893. Accident Prevention, TOM Reel 130. Discussion of Two Accidents in Politz, T-121, Jul 17, 1942, TOM Reel 9. General Operating Instructions for Hydrogenation Plants and Special Instructions for High Pressure, T-136, Jun 1940, TOM Reel 78. Leuna Methods of Rapid Emptying and Pressure Release of Operating Equipment, Filled with Combustible Liquids and Gases, as Means of Prevention of Spreading of Fires, T-141, Leuna Dec 14, 1944, TOM Reel 70. Accidents and Damages in Hydro-Works, T-178, Nov 26, 1946, Ludwigshafen, 1942, TOM Reel 130. Experiences with Runaway Converters, etc

(Discussion held at Politz), T-239, Feb 11, 1947, Ludwigshafen, Aug 17, 1942. Safety Measures in the Construction of Hydrogenation Stalls, Based on Explosions at Politz, 1941, T-235, Feb 7, 1947. Clark WE: Letter to M L Cohen, Apr 24, 1978. Obtained from William E Clark, Abstracting Supervisor, Texas A&M University, Center for Energy and Mineral Resources, College Station, TX 77843

31. Weil CS, Condra NI: The hazards to health in the hydrogenation of coal--II. Carcinoginic effect of materials on the skin of mice. Arch Environ Health 1:187-193, 1960

32. Ketcham NH, Norton W: The hazards to health in the hydrogenation of coal--III. The industrial hygiene studies. Arch Environ Health 1:194-207, 1960

33. Coomes RM: Health effects of oil shale processing. Proceedings of the Oil Shale Symposium, Colorado School of Mines, Golden, Colo, Apr 29-30, 1976

34. Lane KS: Unpublished letter to James M Evans, Jun 21, 1978. Submitted to National Institute for Occupational Safety and Health, Rockville, MD, Jul 1978

35. Weil CS: Results of Exposure of Mice and Men to Coal Hydrogenation Products. In: Proceedings of the Eighth Annual Conference on Environmental Toxicology. Oct 4-6, 1977, Dayton, OH, 1977

36. National Institute for Occupational Safety and Health: Quick Response Evaluation of Energy Related Occupational Safety and Health Programs. Task Order 1: Mortality Study of 50 Workers Exposed to Coal Liquefaction Processes at a Union Carbide Plant, Institute, WV, Menlo Park, CA, Stanford Research Institute, 1977

37. Report of visit to Ruhrgas AG, Dorsten, Federal Republic of Germany. Rockville, MD, Enviro Control, Inc, Dec 13, 1977 (submitted to NIOSH under contract No. 210-76-0171)

38. Report of visit to Westfield Test Center, Cardendon, Scotland. Rockville, MD, Enviro Control, Inc, Dec 16, 1977 (submitted to NIOSH under contract No. 210-76-0171)

39. Report of visit to National Smokeless Fuels, Inc, London, England. Rockville, MD, Enviro Control, Inc, Dec 15, 1977 (submitted to NIOSH under contract No. 210-76-0171)

40. Report of visit to East Midland Gas Corporation, Westfield GAs Works, Leicester, England. Rockville, MD, Enviro Control, Inc, Dec 16, 1977 (submitted to NIOSH under contract No. 210-76-0171)

41. Report of visit to Pittsburgh Energy Research Center, Pittsburgh, PA. Rockville, MD, Enviro Control, Inc, Feb 24, 1977 (submitted to NIOSH under contract No. 210-76-0171)

42. Bolton NE: Industrial Hygiene Procedure: Polynuclear Aromatic Hydrocarbons. Oak Ridge, TN, Oak Ridge National Laboratory, 1975

43. Doll R, Fisher REW, Gammon EJ, Gunn W, Hughes GO, Tyrer FH, Wilson W: Mortality of gasworkers with special reference to cancers of the lung and bladder, chronic bronchitis and pneumoconiosis. Br J Ind Med 22:1-12, 1965

44. Doll R, Vessey MP, Beasley RWR, Buckley AR, Fear EC, Fisher REW, Gammon EJ, Gunn W, Hughes GO, Lee K, Norman-Smith B: Mortality of gasworkers--final report of a prospective study. Br J Ind Med 29:394-406, 1972

45. Redmond CK, Ciocci A, Lloyd JW, Rush HW: Long-term mortality of steelworkers--VI. Mortality from malignant neoplasms among coke oven workers. J Occup Med 14:621-629, 1972

46. Hammond EC, Selikoff IJ, Lawther PL, Seidman H: Inhalation of benzopyrene and cancer in man. Ann NY Acad Sci 271:116-124, 1976

47. National Institute for Occupational Safety and health: Criteria for a Recommended Standard...Occupational Exposure to Coke Oven Emissions. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1973

48. National Institute for Occupational Safety and health: Criteria for a Recommended Standard...Occupational Exposure to Coal Tar Products. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1978

49. Title 29 of the Code of Federal Regulations (CFR), Part 1910.1000, Subpart Z, 1976

50. Key MM, Henschel AF, Butler J, Ligo RN, Tabershaw IR (eds): Occupational Diseases: A Guide to Their Recognition. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1977, pp 114-115, 322-323, 368-370, 387-390

51. Patty FA (ed): Industrial Hygiene and Toxicology, ed 2. New York, Interscience Publishers, 1963, vol II, pp 911-936, 1991-1992

52. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Ammonia. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1974

53. National Institute for Occupational Safety and Health: New Criteria for a Revised Recommended Standard...Occupational Exposure to Inorganic Arsenic. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1975

54. National Institute for Occupational Safety and Health, Recommendation for Benzene Revised as a Part of NIOSH Testimony at OSHA Hearing, July 25, 1977. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1977

55. National Institute for Occupational Safety and Health, Recommendation for Beryllium Revised as a Part of NIOSH Testimony at OSHA Hearing Aug 19, 1977. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1977

56. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Cadmium. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1976

57. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Carbon Dioxide. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1976

58. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Carbon Monoxide. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1972

59. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Chromium (VI). Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1975

60. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Cresol. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1978

61. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Hydrogen Cyanide and Cyanide Salts. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1976

62. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Fluorides. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1975

63. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Hot Environments. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1972

64. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Hydrogen Sulfide. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1977

65. American Conference of Governmental Industrial Hygienists (ACGIH). Documentation of the Threshold Limit Values for Substances in Workroom Air. Cincinnati, OH, ACGIH, 1974

66. National Institute for Occupational Safety and Health, Revised Criteria for a Recommended Standard...Occupational Exposure to Inorganic Lead. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1975

67. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Inorganic Mercury. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1973

68. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Methyl Alcohol. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1976

69. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Inorganic Nickel Compounds. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1977

70. National Institute for Occupational Safety and Health: Special Occupational Hazard. Review and Control Recommendations for Nickel Carbonyl. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1977

71. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Oxides of Nitrogen. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1976

72. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Noise. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1972

73. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Phenol. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1976

74. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Silica. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1974

75. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Sulfur Dioxide. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1974

76. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Toluene. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1973

77. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Vanadium Compounds. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1977

78. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard...Occupational Exposure to Xylene. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1975

79. National Institute for Occupational Safety and Health: Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants. Rockville, MD, US Dept for Health, Education and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1978

80. Bar-Shalom Y, Budenaevs D, Schainke R, Segall A: Handbook of Statistical Tests for Evaluating Employee Exposure to Air Contaminants. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1975, pp I/1-I/18

81. Attari A: Fate of Trace Constituents of Coal During Gasification. NTIS PB-223-001. Chicago, IL, Institute of Gas Technology, 1973

82. Forney AJ, Haynes WP, Gasior SJ, Johnson GE, Strackey JP Jr: Analysis of Tars, Chars, Gases, and Water Found in Effluents from the Synthane Process. Technical Progress Report 76. Pittsburgh, PA, Pittsburgh Energy Research Center, 1975

83. Leidel NA, Busch KA, Lynch JR: Occupational Exposure Sampling Strategy Manual. Rockville, MD, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1977

84. Wilson AL: Interim Report, Safety Assurance Study of High-BTU Coal Gasification Pilot Plants. FE-2240-8. Alhambra, CA, C F Braun and Company, 1976, pp III/1-III/22

85. US Energy Research and Development Administration: Synthane Plant Test Program. Washington, DC, US Dept of Energy Research and Development Administration, 1976

86. Report of visit to ANG Coal Gasification Company, Detroit, Mich, Nov 18, 1977. Rockville, MD, Enviro Control, Inc, Nov 29, 1977 (submitted to NIOSH under contract No. 210-76-0171)

87. Report of visit to General Electric Company, Schenectady, NY. Rockville, MD, Enviro Control, Inc, Nov 29, 1977 (submitted to NIOSH under contract No. 210-76-0171)

88. Martin K: Text of recorded telephone conversation of Feb 25, 1977, between K Martin and R Rice. Unpublished transcript submitted to National Institute for Occupational Safety and Health, Rockville, MD, Feb 1977

89. Holt JP, Hendricks NV, Eckhardt RE, Stanton CL, Page RC: A cancer-control program for high-boiling catalytically cracked oils. Arch Ind Hyg Occup Med 2:325-334, 1951

90. Eckhardt RE: Hydrogenation of coal. Arch Environ Health 1: 232-233, 1960

91. Cheng RT: Industrial hygiene program and experience for a fifty ton per day solvent-refined coal pilot plant. In: Proceedings of the Second ORNL Workshop on Exposure to Polynuclear Aromatic Hydrocarbons in Coal Conversion Processes, CONF-770361. Oak Ridge, Tenn, Oak Ridge National Laboratory, 1977

92. Goldman ME: Response to external review questions concerning coal gasification criteria document by National Institute for Occupational Safety and Health. Unpublished letter submitted to the National Institute for Occupational Safety and Health, Rockville, MD, 1978

93. Title 29 of the Code of Federal Regulations (CFR), Part 1910.1029, Jul 1977

94. Evans MA: Coal Mining. In: Encyclopedia Britannica, 15th Edition: Coal. New York, NY, Helen Hemingway Benton, 1974

95. Western Gasification Company (WESCO): Coal Gasification: A Technical Description, Revised Jan 1, 1977. Farmington, New Mexico, WESCO, 1977

96. Casarett LJ, Doull J (eds): Toxicology, The Basic Science of Poisons. New York, NY, MacMillan Publishing Company, 1975, pp 214-217

97. Van Meter WP, Erickson RE: Environmental Effects from Leaching of Conversion Byproducts. Quarterly Report for the Period Jan-Mar 1977. FE-2019-7. Misspula, MT, University of Montana, 1977

98. Chu TJ, Ruane RJ, Steiner GR: Characteristics of waste water discharge from coal fired power plants. In: Proceedings of 31st Annual Purdue Industrial Waste Conference, May 4-6, 1976. West Lafayette, IN, Purdue University, 1976

99. Tisdale GC: Sasol operating experience in large scale pressure gasification. Presented at the Second Synthetic Pipeline Gas Symposium, November 1968, Pittsburgh, PA, American Gas Association, 1969

100. Western Coal Gasification Company (WESCO): WESCO application for permit and certification of registration. General Form for Sources Located Within the State of New Mexico. Farmington, NM, WESCO, 1973

101. Hoogendoorn JC: Gas from coal with Lurgi gasification at Sasol. Presented at the American Institute of Mining Engineers, June 1974. Dallas, TX, AIME, 1974

102. Bardos R: Gasifiers in Industry Program. Presented at the Fourth Annual International Conference on Coal Gasification, Liquefaction, and Conversion to Electricity, Aug 2-4, 1977. Pittsburgh, PA, University of Pittsburgh, 1977

103. South African Coal, Oil and Gas Corporation, Ltd: General Data on the Gas Production, Rectisol, Phenosolvan, and Effluent Streams of Sasol. Sasolburg, South Africa, Sasol, 1975

104. Lebowitz H, Tam S, Smithson G Jr, Nach H, Oxley J, Cavanaugh G, Borkin C, Dickerson J: Potentially Hazardous Emissions from the Extraction and Processing of Coal and Oil. NTIS PB-241-803. Columbus, OH, Radian Corporation and Battelle Columbus Laboratories, 1975, pp 4-9

105. Williams JE, Dressel JH: Coal Gasification: The New Energy Source. Can Min Metall Bull 66:72-77, 1973

106. US Bureau of Mines: Coal to Gas Prototype Pilot Plant. Lummus Job No. 6656, Process Flow Diagram, Coal Pressurization, Pretreatment, Gasification and Char Removal. Bruceton, PA, US Bureau of Mines, 1972

107. Nakles DV, Massey MJ, Forney AJ, Haynes WP: Influence of Synthane Gasifier Conditions on Effluent and Product Gas Production. PERC/RI-75/6, Bruceton, PA, Pittsburgh Energy Research Center, 1975

108. Massey MJ, Dunlap RW, McMichael FC, Nakles DV: A Report Concerning Environmental Analysis: Characterization of Effluents from the HYGAS Pilot Plant to the Institute of Gas Technology. Monroeville, PA

109. Lisauskis RA, Johnson SA: NO(x) Formation During Gas Combustion. Chem Eng Prog 72:76-77, 1976

110. Ruch RR, Gluskoter HJ, Shimp NF: Distribution of Trace Elements in Coal. Urbana, IL, Illinois State Geological Survey, 1974, p 18

111. Attari A, Mensinger M, Pau JC: Fate of Trace Constituents of Coal During Gasification, Part II. Proceedings of the American Chemical Society, Division of Fuel Chemistry. Washington, DC, ACS, 1975

112. Institute of Gas Technology: HYGAS Pilot Plant Process Flow Sheet, Project No. 8918, Drawing No. 2, Chicago, IL, IGT, 1973

113. Institute of Gas Technology: A Survey of R&D Projects Directed Toward the Conversion of Coal to Gaseous and Liquid Fuels. Chicago, IL, IGT, 1972, pp IF7-IF20, IF27, IG7-IG18

114. Moeller FW, Robert H, Britz B: Methanation of Coal Gas for SNG. Hydrocarbon Process 53:69-70, 1974

115. Huffstetler JK, Rickert LW: Conversion processes. In: Oak Ridge National Laboratory, ed. Environmental, Health and Control Aspects of Coal Conversion--An Information Overview. ORNL/EIS-94. Oak Ridge National Laboratory, Oak Ridge, TN, 1976

116. Mills GA, Steffgen FW: Catalytic Methanation. Catal Rev 8:159-210, 1973

117. Strakey JP, Forney AJ, Haynes WP: Methanation in Coal Gasification Processes. In: Proceedings of the 2nd Annual Symposium on Coal Gasification, Liquefaction and Utilization: Best Prospects for Commercialization, Pittsburgh, PA. US Energy Research and Development Administration, Pittsburgh, PA, 1975

118. Lowder WM: Radiological Impact of Coal Combustion in the Fixed-Bed Coal Gasification Process. (Letter dated March 10, 1978). Washington, DC, Physical and Technological Program, Division of Biomedical and Environmental Research, Department of Energy, 1978

119. Hoogendoorn JC: New applications of the Fischer-Tropsch process. In: Clean Fuels from Coal Symposium II, Chicago, IL, Institute for Gas Technology, 1975

120. Beers WD: Characterization of Claus Plant Emissions, NTIS PB-220-376, Process Research, Inc, Cincinnati, OH, 1973, pp 4-8

121. Maddox RN: Gas and Liquid Sweetening, ed. II. John M Campbell Publisher, Norman, OK, 1974, pp 98-115

122. Dailey NS: Process Effluents: Quantitites and Control Technologies. In: Oak Ridge National Laboratory, ed. Environmental, Health and Control Aspects of Coal Conversion--An Information Overview. ORNL/EIS 94. Oak Ridge National Laboratory, Oak Ridge, TN, 1976

123. Vasan S, Willett HP: Economics of Desulfurization of Coal Gas vs Flue Gas Desulfurization. In: Proceedings of the Third Symposium on Coal Utilization, Lexington, KY, NCA/BCR Coal Conference, Oct 1976, Bituminous Coal Research, Monroeville, PA, 1976

124. Report of visit to Woodall Duckham, Pittsburgh, PA. Rockville, MD, Enviro Control, Inc, Aug 1, 1977 (submitted to NIOSH under contract No. 210-76-0171)

X. GLOSSARY

ACID GAS	A gas which, when dissolved in an ionizing liquid such as water, produces hydrogen ions. Carbon dioxide, hydrogen sulfide, sulfur dioxide, and various nitrogen oxides are the typical acid gases produced in coal gasification.
ANTHRACITE	"Hard" coal containing 86 to 98 percent fixed carbon and small percentages of volatile material and ash.
ASH	Theoretically, the inorganic salts contained in coal; practically, the noncombustible residue from the combustion of dried coal.
ASPHYXIANT	A substance capable of producing a condition due to lack of oxygen in respired air, resulting in impending or actual cessation of life.
BINDERS	Carbon products, tars, etc., used to impart cohesion to the body to be formed; a coal- extract binder may be used to prepare formed-coke pellets from non-coking coals.
BITUMINOUS COAL	A broad class of coals containing 46 to 86 percent fixed carbon and 20 to 40 percent volatile matter.
BLOW DOWN	Periodic or continuous removal of water containing suspended solids and dissolved matter from a boiler or cooling tower to prevent accumulation of solids.
BTU	British thermal unit, the quantity of energy required to raise the temperature of one pound of water one degree Fahrenheit.
CAKING	The softening and agglomeration of coal as a result of the application of heat.

CARBON-STEAM REACTION (WATER-GAS REACTION)	The reaction in which steam is passed over incandescent carbon to form a low-BTU gas consisting of hydrogen, carbon monoxide and carbon dioxide.
CARBONIZATION	Destructive heating of carbonaceous substances with the production of a solid porous residue, or coke, and the evolution of a number of volatile products.
CAVITATION	The formation and collapse of vapor cavities in a flowing liquid where the local pressure on the liquid is reduced to the liquid vapor pressure at that temperature. Collapse of these cavities produces objectionable noises and erosion on the adjacent surfaces.
CHAR	The solid residue remaining after the removal of moisture and volatile matter from coal.
CLAUS PROCESS	An industrial method of obtaining elemental sulfur through the partial oxidation of gaseous hydrogen sulfide in air followed by catalytic conversion to molten sulfur.
COAL	A natural solid material consisting of amorphous elemental carbon with various amounts of organic and inorganic compounds.
COAL GAS	The gas that comes from retorts, mufflers, or coke ovens during the distillation of coal. Large quantities of coal gas are produced when coal is used to make coke, coal tar, benzene, toluene, ammonia, and other products.)
COAL GASIFICATION	The reaction of coal at high temperatures in an atmosphere (reducing) deficient in oxygen to produce a combustible gas.
COKE	Porous residue consisting of carbon and mineral ash formed when bituminous coal is heated in a limited air supply or in the absence of air. Coke may also be formed by thermal decomposition of petroleum residues.

COKE OVEN GAS	The gas secured from coke ovens during the production of coke. (The properties of this gas are identical to those of coal gas, and the two products are interchangeable. Coke is particularly useful in making iron and steel and as an industrial fuel.)
CRUDE GAS	The impure gas produced in a gasifier.
DEVOLATILIZATION	The removal of a portion of the volatile matter from medium- and high-volatile coals.
DOG	Any of various usually simple mechanical devices for holding, gripping, or fastening.
ECONOMIZER	Heat exchanging mechanism for recovering heat from flue gases.
ELUTRIATION	The preferential removal of the small constituents of a mixture of solid particles by a stream of high-velocity gas.
ENTRAIN	To draw in and transport (as solid particles or gas) by the flow of a fluid.
FINES	In general, the smallest particle of coal or mineral in any classification, process, or sample of material; especially those that are elutriated from the main body of material in the process.
FIXED BED	A bed in which the individual particles or granules of a solid are motionless and supported by contact with each other (in contrast with moving bed).
FLASH DISTILLATION (FLASHING)	A continuous equilibrium vaporization in which all the vapor formed remains in contact with the residual liquid during the vaporization process. It is usually accomplished by the sudden reduction of pressure in a hot liquid.

FLUE GAS (STACK GAS)	Synonymous terms for the gases resulting from combustion of a fuel.
FLY ASH	A fine ash from the pulverized coal burned in power station boilers, or entrained ash carried over from a gasifier.
GAS LIQUOR (SOUR WATER)	The aqueous acidic streams condensed from the coal conversion and processing areas by scrubbing and cooling of the crude gas stream.
GASIFIER	A vessel in which gasification occurs, usually utilizing fluidized-bed, fixed-bed, or entrained-bed units.
GASWORKS	Plants built during the 19th and early 20th centuries to produce gas. Coal was generally burned in reducing atmosphere with steam to form a low-BTU gas. The hot gas was passed through a brick checkerwork at atmospheric pressure to heat the brick. When the brick was hot, the gas was switched to a second checkerwork and oil was sprayed into the first. The gas produced from the thermally cracked oil was added to the coal gas to form a medium (500-BTU) gas.
HIGH-BTU GAS	Fuel gas having an energy content of 950-1035 BTU/scf.
HIGHER HEATING VALUE (HHV) (GROSS HEAT VALUE)	The heat liberated during a combustion process in which the product water vapor is condensed to a liquid and the heat of condensation is recovered.
LEACHING	The process of extracting a soluble component from a mixture by percolating a solvent, usually water, through the mixture, resulting in the solution and eventual separation of the soluble components.
LIGNITE	Brownish-black coal containing 65 to 72 percent carbon on a mineral-matter-free basis, with a rank between peat and sub-bituminous coal.
LOW-BTU GAS	A gas having a heating value of up to 125-175 BTU per standard cubic foot.

LOCKHOPPER	A mechanical device that permits the introduction of a solid into an environment at different pressure.
LOWER HEATING VALUE (NATURAL HEAT VALUE)	The heat liberated by a combustion process assuming that none of the water vapor resulting from the process is condensed, so that its latent heat is not available.
MEDIUM-BTU GAS	A gas having a heating value of 225-500 BTU per standard cubic foot.
METHANATION	The catalytic combination of carbon monoxide and hydrogen to produce methane and water.
MOVING BED	A body of solids in which the particles or granules of a solid remain in mutual contact, but in which the entire bed moves in piston- like fashion with respect to the containing walls (in contrast with fixed bed).
NATURAL GAS	Naturally occurring gas extracted from sedimentary structures, consisting mainly of methane and having a higher heating value of approximately 1,050 BTU per standard cubic foot.
NONCAKING GAS	A coal that does not form a cake under normal conditions.
ON-STREAM OPERATING TIME	The time during which the entire plant is actually working at preset conditions, as opposed to the time in which it is shut down for repairs, starting up, etc.
PILOT PLANT	A small-scale industrial process unit operated to test the application of a chemical or other manufacturing process under conditions that will yield information useful in design and operation of full-scale manufacturing equipment.
POKEHOLE	An opening in the cover of a process vessel through which steel rods are inserted, for the purpose of determining the fire bed depth and the ash bed depth in a gasifier.

PROCESS STREAM	Any material stream within the coal conversion processing area.
PRODUCT STREAM	Streams within the coal conversion plant that contain the material which the plant was built to produce.
QUENCHING	Cooling by immersion in oil, water bath, or water spray.
RANK	Those differences in the coals due to geological processes designated as metamorphic, whereby the carbonaceous materials change from peat through lignite and bituminous coal to anthracite or even to graphite; the degree of coal metamorphism.
RAW GAS	Impure gas produced in a gasifier.
REAL TIME	The actual time during which an event takes place with the reporting on or recording of the event simultaneously with its occurrence.
SLUDGE	A soft mud, slush, or mire, eg, the solid product of a filtration process before drying.
SOUR GAS	A gas containing acidic substances such as hydrogen sulfide or carbon dioxide.
SOUR WATER	See gas liquor.
SPARED EQUIPMENT	Standby, parallel equipment that is available for immediate use by switching power or process from on-stream equipment.
STUFFING BOX	A device that prevents leakage from an opening in an enclosed container through which a shaft is inserted.
SUB-BITUMINOUS COAL	Coal of intermediate rank (between lignite and bituminous); weathering and nonagglomerating coal having calorific values in the range of 8,300 to 11,000 BTU, calculated on a moist, mineral/matter-free basis.
SWEET GAS	Gas from which acidic constituents such as H2S have been removed.

SYNTHETIC NATURAL GAS (SNG)	Substitute natural gas; a manufactured gaseous fuel generally produced from naphtha or coal that contains 95% to 98% methane and has an energy content of 980 to 1,035 BTU/scf (about the same as that of natural gas).
SYNTHESIS GAS	A mixture of hydrogen and carbon monoxide which can be reacted to yield hydrocarbons.
TAIL GAS	A gas issuing from a gas-treatment unit which may be recycled to the process or exhausted.
TAR	A brown or black viscuous combustible liquor formed by the destructive distillation of coal. It condenses out of the raw gas stream as part of the gas liquor, has a specific gravity of approximately 1.1, and contains most of the fines which are carried over from the gasifier in the gas stream.
TAR OIL	The more volatile portion of the tar, with a specific gravity of approximately 0.9, a boiling range of approximately 185 to 300 C (365 to 660 F) depending on the coal feed and operation conditions. In addition, tar oil floats on the gas liquor.
TOXICANT	A substance that kills or injures an organism through chemical or physical action, or by altering the organism's environment.
TRACE ELEMENTS	The term "trace elements" is applied to elements that are present in the earth's crust in concentrations of 0.1% (1000 ppm) or less. Trace element concentrations are usually somewhat enriched in coal ash. Environmentally hazardous trace elements present in coal include: antimony, arsenic, beryllium, cadmium, mercury, lead, selenium, and zinc.
VENTING	Release of gases or vapors under pressure to the atmosphere.

XI. APPENDIX I

PROCESS DESCRIPTION: HIGH-BTU COAL GASIFICATION

Introduction

(a) Coal

Coal, as shown schematically in Figure XI-1, is derived from converted vegetable matter laid down in the swamps that covered large areas of the northern hemisphere during the lower Carboniferous (Mississippian) to Tertiary periods. The converted material (peat) was subjected to a variety of microbiologic, geophysical, and geochemical conditions to form coal. Because of the variety of conditions to which it was subjected, any quantitative statement concerning the composition, structure, and products of coal is subject to qualification, even for coal mined from the same general section of a specific coal seam.

Coal is "ranked" systematically according to volatile matter and heat content (BTU/lb), ie, from the low-rank lignite through subbituminous and bituminous coal to high-rank anthracite. In general, carbon content increases while oxygen content and volatile matter decrease with increasing rank [94].

Coal is composed of organic matter and up to 50% inorganic matter. The elements of organic matter include carbon, hydrogen, oxygen, nitrogen, and sulfur. The inorganic matter is associated partly with the coal (organometallic) but primarily with the ash, which ranges from 3 to 20 wt % in commercial coals and averages about 10 wt %. The ash content reflects the degree of care in both mining and cleaning as well as the intrinsic grade or quality of the coal itself. Coal is probably the most highly variable fuel used by man. The products of any given coal in any given reaction (combustion, pyrolysis, gasification, liquefaction, etc) may differ from those of another coal under identical circumstances. Despite its extreme variability, generalizations can be made about coal and its reactions, providing that the limitations are kept in mind.

(b) Coal Gasification

Coal gasification transforms a cumbersome, inconvenient, dirty solid fuel into a convenient, clean, gaseous fuel or into synthesis gas. Coal gasification entails the treatment of coal in a reducing atmosphere with air or oxygen, steam, carbon monoxide, hydrogen, or mixtures of these gases to yield a combustible product. The primary product of the reaction of coal carbon with the gasifying agent (eg, oxygen, steam, hydrogen) is usually a mixture of hydrogen, water, carbon monoxide, carbon dioxide, methane, inerts (eg, nitrogen), and minor amounts of hydrocarbons and other impurities.

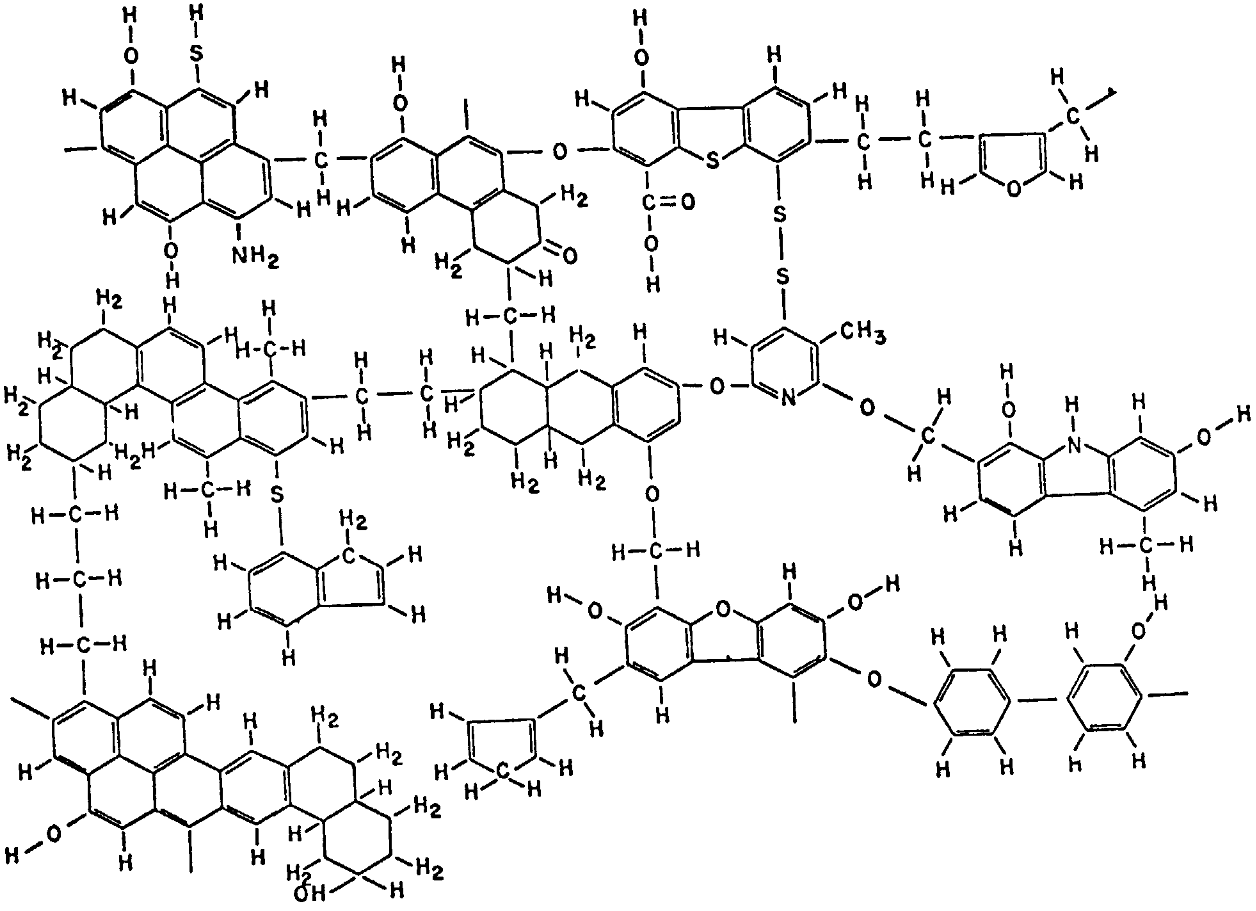


Figure XI-1

Representation of High-Volatile Bituminous Coal Structure

Adapted from Reference 79

If an air-steam mixture is used directly to gasify the coal, the product is called a low-BTU gas. This gas contains nitrogen as a major component. It will have a heat content of 125-175 BTU/scf (standard cubic foot). Low-BTU gas is suitable for use near the point of generation, but it is not economically attractive for long-distance transmission.

Medium-BTU gas, which contains only a minor amount of nitrogen and has a heat content of 225-500 BTU/scf, is obtained when oxygen-steam mixtures are used to gasify the coal. It can be used as an energy source or as a synthesis gas for the production of chemicals and synthetic liquid and gaseous fuels. It is economical to transport this gas up to approximately 100 miles.

Synthetic pipeline gas, which is indistinguishable from natural gas (950-1,035 BTU/scf, containing over 95% methane), is produced by further processing medium-BTU gas. The required processing includes removal of particulate matter and condensables, adjustment of gas composition by reacting some of the carbon monoxide with water to produce hydrogen and carbon dioxide (shift conversion), removal of hydrogen sulfide and carbon dioxide, and methanation of the resulting gas mixture.

Pyrolysis or devolatilization of coal occurs during the gasification of bituminous and lower ranking coals. The products of devolatilization range from low-boiling compounds such as methane or benzene through the very high boiling tars, which are normally solid at room temperature. These devolatilization products or tars are recovered as byproducts if the coal is heated slowly to gasification temperature, as in fixed-bed gasification, or if it is gasified at relatively low temperatures.

The gasification of devolatilized coal with carbon dioxide

$$C + CO2 \rightarrow 2CO$$

and the water-gas (hydrogasification) reaction

$$C + H2O \rightarrow CO + H2$$

are the heart of the gasification reaction and form synthesis gas. These two reactions are slow and are thermodynamically favored at temperatures above 732 C (1350 F), but are rarely at equilibrium at temperatures below 1093 C (2000 F). Heat is supplied by the combustion reactions

$$C + 1/2O2 \rightarrow CO$$

$$C + O2 \rightarrow CO2$$

$$H2 + 1/2O2 \rightarrow H2O$$

which are very rapid and proceed to completion, consuming the available oxygen.

The methanation of devolatilized coal

$$C + 2H_2 \longrightarrow CH_4$$

is highly exothermic and is thermodynamically favored at high pressures and at temperatures below 620 C (1150 F).

The shift reaction

$$CO + H_2O \longrightarrow CO_2 + H_2$$

is mildly exothermic and because it has a favorable equilibrium at temperatures below 732 C (1350 F), it is usually carried out outside the gasification reactor. The methanation reaction

$$CO + 3 H_2 \longrightarrow CH_4 + H_2O$$

is highly exothermic but is favored at low temperatures (approximately 550 F to 850 F) and elevated pressures. This reaction, necessary to the production of pipeline- quality gas, is generally catalytically augmented and is carried out outside the gasifier.

Because any incremental increase in methane production in the gasifier favors the economics of pipeline-gas production, most high-BTU gasification processes are high-pressure processes. For the same reason, several of the advanced or second generation coal gasification processes (processes not yet commercialized) use a hydrogen gas feed to augment or replace that produced by the water-gas shift reaction. Conversely, methane content is of no economic significance in low-BTU coal gasification, and these processes tend to favor low pressure.

(c) High-BTU Coal Gasification

At this time high-BTU coal gasfication plants in the US are in various stages of design. The only existing operation which approaches the US designed plant in both size and complexity is the South African Coal, Oil and Gas Corporation, Ltd (SASOL) plant, located in Sasolburg, South Africa. This plant, designed in the early 1950's using both German and US data, began production in 1955. Today this plant has thirteen oxygen-blown gasifiers and consumes approximately 9,000 tons of coal per day for steam, power, and gas production. Construction is currently underway to expand the operation to 14,000 tons of coal per day. As the plant has expanded during the past 23 years, SASOL engineers have continuously improved the original German (Lurgi) gasifier design. The latest SASOL improved Lurgi gasifier, the Mark IV, which is to be used in the expanded plant at SASOL II (a 40,000 ton per day plant currently under construction) and in the United States, is currently being tested [11,12].

SASOL owns over 40,000 acres, of which 480 acres are occupied by the plant. Approximately 25% of this plant is devoted to the gasification process while the remainder is occupied by the Fischer-Tropsch synthesis operation and chemical byproduct production. SASOL employs 5,600 people including a salaried staff of 500 (clinical staff, supervisors, foremen and administrators) and 1,100 operators. Of this total, 818 have been employed at SASOL for over 20 years and 2,620 have been employed for over 10 years [12]. (Coal mine employees are excluded from this count.) Because of South African employment policies, the plant is labor intensive by US standards.

Design for the US high-BTU coal gasification plants is heavily dependent on the gasification technology and experience demonstrated at SASOL. Statistics for four of the plants proposed for construction in the US are presented in Table XI-1.

A high-BTU coal gasification plant includes some combination of facilities for coal storage, coal preparation, coal feeding, gasification, gas quenching, shift conversion, gas purification, and methanation. Auxiliary facilities may include oxygen manufacture, gas-liquor separation, tar distillation, tar storage, dissolved hydrocarbon recovery, water purification, ash handling, steam generation, power generation or utilization, and general utilities.

The commercial high-BTU coal gasification plant will differ from low- or medium-BTU operations in two major respects. First, the medium-BTU gas produced in the gasifier must be upgraded to pipeline quality by a gas purification ("sweetening") process and by methanation. Second, the commercial high-BTU coal gasification plant must be large in order to take advantage of economies of scale and to produce sufficient gas to make pipeline transportation costs a reasonably small portion of the total cost of gas.

Coal Preparation

(a) Receiving

Coal preparation plants are described below for one plant [3]. This description may not be typical of other designs. Run-of-mine coal containing maximum-size lumps of 48 inches will be unloaded from bottom dump trucks (120-150 tons) into a double receiving hopper. The dumping operation will be carried out in an enclosure equipped to collect any dust released [3].

TABLE XI-1

PLANT STATISTICS

Plant Characteristics	Plant A	B	C	D
Plant size, mmscfd (rated)	275	288	137	270
(for 365-day/yr operation)	250	266	125	246
Coal feed rate, total, tons/day	28,688	28,250	22,848	32,470
Number of gasifiers	24	28	14	ND
Plant site, acres	1,070	960	1,100	ND
Area actually occupied, acres	300	ND	370	334
Personnel, plant only	612	883	577	800
Personnel distribution:				
Mine	400	ND	322	290
Plant management	101	ND	186	128
Plant operations	240	ND	160	400
Plant maintenance	271	ND	231	272
Coal composition:	LIG	SUB-B	LIG	LIG
Ash, Wt %	24.6	20.8	6.2	5.58
Sulfur, Wt %	0.8	0.7	0.77	0.32
Moisture, Wt %	12	17	34.3	28
Heating value, BTU/lb	8,584	8,320	7,272 (e)	8,448
Coal distribution, tons/day:				
Gasification	24,820	23,256	14,184	22,730
Steam and/or power	3,868	4,992	0 (f)	4,462
Export (coal fines)	ND	2,544	8,664 (g)	5,278
Reject	2,240	1,680	ND	ND

(a) Adapted from reference 3
(b) Adapted from reference 6
(c) Adapted from reference 4
(d) Adapted from reference 5
(e) "As received" basis
(f) Byproduct (tar, tar oil, etc) consumed in liquid boilers
(g) Based on coal usage by both coal gasification plant and local electric power plant

ND = no data
LIG = lignite
SUB-B = sub-bituminous

Reciprocating feeders will withdraw coal from the hoppers, discharging it to single-roll primary crushers that will reduce the coal to a size of 8 inches or less. These crushers are designed to be below grade under the coal dump hoppers, thus minimizing noise generation. The equipment is to be ventilated for proper control of coal dust, presumably using commercial separators and bag-type filters [3].

An enclosed 60-inch-wide conveyor will move the crushed coal to the secondary crushing house, where it will be discharged to a 120-ton surge bin. Four vibrating feeders will discharge coal from the bin to double-deck scalping screens for the removal of coal smaller than 1.5 inches. The oversize coal is to be discharged into two secondary crushers for reduction to less than 1.5 inches. These screens and secondary crushers are to be equipped with dust enclosures and bag filters to collect any dust that is formed [3].

The coal is to be recombined and conveyed by a 60-inch-wide conveyor that will pass through the primary sampling house where samples will be continuously taken to monitor coal properties. The sampling house is to be equipped with a controlled ventilation system for removing coal dust from the air being exhausted [3].

(b) Coal Storage

From the sampling house the coal will be carried by a series of 60-inch-wide belt conveyors to a traveling belt stacker, which will form piles of coal approximately 600 feet long, 120 feet wide at the base, and 44 feet high. In all there may be 6 to 10 of these piles. The electrically driven stacker will travel along these piles on tracks between the piles. The booms on the stacker will be automatically controlled to minimize the free fall of the coal onto the pile, thus minimizing coal dust release during stacking [3].

Coal will be reclaimed from storage piles by a bridge-type bucket- wheel reclaimer. This machine is a rail-mounted bridge that supports a rotating bucket-wheel and belt conveyor. The wheel moves across the face of the pile, making a vertical cut across the many layers of variable grades of coal. At the end of one cut, the reclaimer moves ahead a predetermined distance (inches). The wheel then makes another cut in the opposite direction. The excavated coal is carried by a reversible conveyor in the bridge and is transferred to the 60-inch stack reclaiming belt conveyor. Approximately 1.5 days will be required to reclaim one pile [3].

(c) Coal Cleaning

In one plant design, a series of 48-inch-wide conveyors will carry the coal to the product sizer [3]. This facility consists of an elevated surge bin, variable-rate vibrating feeders, vibrating double- and single-deck screens (for both dry and wet screening), and a dust collection system. The dry-screening process will produce 1-1/2 by 7/16-inch coal, which will be conveyed to the gasifiers. The minus 7/16-inch coal will be slurried with water and transported to a wet-screening circuit that removes the 7/16-inch x 4 mesh coal. This wet coal will be dewatered in centrifuges, combined with the plus 7/16-inch coal, and fed to the gasifiers [3].

In the wash plant, the slurried minus 4 mesh coal plus fines from bag collectors will be gravity fed to a series of gravity separation tables. Coal sized 4 x 48 mesh will be separated, dried in centrifuges, and fed to the steam plant [3].

Approximately 60% of the ash and 50% of the sulfur contained in the minus 4 mesh fines will be removed in the wash-plant cycle. (This ratio of total ash and sulfur in coal fines is not unusual and may well be applicable to other subbituminous coals, lignites, or bituminous coals.) These wastes will be slurried and piped to a water reclaiming circuit and concentrated. The reject slurry, consisting of 65 to 75% water and 25 to 35% solids, will be piped to an impoundment area. The reclaimed water will be recirculated to the wash plant [3].

Each impoundment area will be designed to receive 100-200 tons/hour of solids suspended in this slurry on a 24-hour/day, 6-day/week basis for the 25-year estimated life of the gasification plant. At the end of this period, the impoundment area will be stabilized by covering it with overburden from the mine and reseeding.

During the operation of the wash plant, the waste solids of the impoundment area will be covered with water and thus should present no dust problem. In the event that dry solids are exposed, they will be covered with suitable coarse material to prevent a dust problem [95]. (This discussion is specific to one plant design and does not apply to others which may not use wet screening or may screen at different sizes.)

(d) Workplace Hazards

In the coal preparation sections of the plant, there may be hazardous exposure problems due to coal dusting, fire, noise, and coal leaching.

Dusting may present an inhalation hazard with the potential for inducing pneumoconiosis (black lung). Respirable coal dust has been linked to pneumoconiosis [96]. Dusting from any equipment is possible, particularly if the equipment has to be maintained often and is not properly reassembled. (Elevators, rotating valves, augers, conveyors, and vibrating screens are common points for rapid wear and failure.) The greatest potential for dust generation will be when a truck is unloaded. (At many plants, this dust nuisance may be reduced by enclosing the bin on three sides). Coal dust can and will blow off the storage pile. However, the methods described above will definitely reduce this dusting. Dusting from conveyors is common but can be reduced by fully enclosing the conveyor as described above and by spraying water on the coal at the conveyor transfer points. (Explosions could occur at the air ventilation equipment should the dust loading become too high.)

Observation of existing coal gasification plants and pilot plants both during operation and when shut down indicates that the coal pile and conveyor dusting should normally be only a nuisance to coal plant operators and a housekeeping problem. In general, gasification workers do not appear to be at risk from coal dust. The possible exceptions are personnel assigned to unloading, front-end loader operation, or cleanup.

Lignite or subbituminous coals will ignite spontaneously when dried or exposed to air at ambient conditions. Resultant fires tend to be on the coal pile surface.

High-sulfur bituminous coals, especially coals containing fines, will ignite spontaneously after prolonged exposure to normal weather. Such fires are not uncommon after 2-6 months of exposure. Fires in these coals tend to be submerged in the piles. Small piles of "fines" (ie, high-sulfur bituminous coal dust), such as might be accumulated from dusting or equipment leakage, may ignite within 12 to 48 hours. [personal communication, December 2, 1976, from MA Evans, consultant, 620 Franklin Ave, Somerset, PA.]

At one plant, fires in the storage silos and bins do not normally occur, but only because a firm policy of as rapidly as possible feeding any coal that shows a temperature rise to the gasifier or to the boiler. When a temperature rise is observed in the coal silos, the silos are completely emptied [12].

All grinding and screening operations are inherently noisy. Wet screening operations tend to be less noisy than dry screening ones.

Coal exposed to weather will be subjected to leaching by rainwater. Water will also carry coal fines into the plant sewer system. Little is known at present about the effect of residence time, weather, pile size, and coal composition on the leachate from coal storage piles. Several long-term (5-year) studies are being considered by the US Bureau of Mines and the Illinois State Geological Survey. [Personal communication, February 1976, from HJ Gloskoter, Illinois State Geological Survey, Urbana, IL.] The University of Montana is also conducting a laboratory study under the auspices of the US Department of Energy [97]. Table XI-2 indicates runoff composition from two industrial coal piles [98]. The limited information in the literature indicates that the effect of dissolved materials in the leachate is little understood.

TABLE XI-2

ANALYSES OF DRAINAGE FROM TWO INDUSTRIAL COAL PILES

Constituent	Concentration (mg/liter) Coal Pile 1	Concentration (mg/liter) Coal Pile 2
Total acidity (as CaCO3)	1,700	270
Calcium	240	350
Chemical oxygen demand	9	ND
Chloride	0	ND
Conductance, mho/cm	2,400	2,100
Total dissolved solids	3,200	1,500
Hardness (as CaCO3)	600	980
Magnesium	1.2	0.023
pH	2.9	2.9
Potassium	ND	0.5
Silica (dissolved)	91	ND
Sodium	ND	4.1
Sulfate	2,600	ND
Total suspended solids	550	810
Turbidity (Jackson turbidity units)	300	ND
Aluminum	190	ND
Arsenic	0.01	0.009
Barium	ND	0.1
Beryllium	ND	<0.01
Cadmium	<0.001	<0.006
Chromium	<0.005	<0.005
Copper	0.56	0.18
Iron	510	830
Lead	<0.01	0.023
Manganese	27	110
Mercury	<0.0002	0.027
Nickel	1.7	0.32
Selenium	0.03	0.003
Titanium	<1	ND
Zinc	3.7	1.0

ND = No data

Adapted from reference 98

Each plant may handle stormwater runoff in a different manner; however, at one plant [95] all stormwater runoff from coal preparation and storage areas will be contained and used to supplement water supplies for the coal gasification plant. Coal storage areas will be paved with either clay or asphalt to prevent seepage. The areas will be inclined to allow surface runoff to stormwater catchments. Runoff will then be directed to a stormwater holding pond, along with surface runoff from the plant site. From the storage pond, water will be metered at a controlled rate and sent to the secondary treatment facilities. There it will be used for cooling or, after additional treatment, to supply primary gasification process streams. At a second plant, coal storage runoff water will be utilized in the coal preparation plant [6].

Gasifier Area Configuration

At one high-BTU plant [9] the gasifier area will have the following configuration: The structure housing the gasifiers will be in the shape of an H. Each of the long arms of the H will contain 12 gasifiers placed in a straight line. A traveling coal conveyor distribution system will be located at the top of the building above the coal bins. The coal bins will be located directly above the coal lockhoppers, which in turn will be located directly above each gasifier. The ash lockhopper will be located under each gasifier and just above the bottom floor. Present plans call for the ash disposal system to be located under the ground floor. The exterior side of each gasifier row will contain the operating components of the quench system, waste-heat boilers, and piping for the gasifiers of each row. These units are to be located in the open both for ease of access and to insure adequate ventilation. The center of the H-configuration will be used for maintenance work on the coal lockhoppers, ash lockhoppers, etc. The system is designed for maximum separation between operations and maintenance, and for maximum accessibility in maintenance work. Gathering systems for the product gas and gas-liquor for both sets of gasifiers will be funneled through the cross bar of the H to secondary and tertiary cooling and to tar separation. All liquid- and gas-carrying systems within this area will be designed for minimal flowrates and piping will contain maximum-radius elbows to reduce erosion [9].

Coal Feeding

(a) Coal Lockhoppers

Coal from the traveling conveyor belt will be fed into the bunker above the coal lockhopper. Coal from the bunker will be fed into the coal lockhopper by gravity when the coal lockhopper upper closure is open.

The coal lockhopper for one operating plant in South Africa [99] is operated as shown in Figure XI-2. It may be assumed that the general configuration of coal lockhoppers in the United States will be similar, although more highly automated. The internal top and bottom valves are operated through levers and shafts by external hydraulic cylinders. The coal valve below the superimposed bunker and the pressurizing and depressurizing valves are also hydraulically operated. The cycle of operation is performed by manually revolving a cam-shaft that controls the flow of hydraulic fluid through the operating cylinders in the correct sequence.

The coal-lockhopper operating sequence for a proposed United States plant [9] is as follows: The coal lockhopper, when empty, will be vented down from 435 psig to 5 psig, through the steam superheater stack. From 5 psig down to approximately 0.5 psig the lockhopper will be vented through a scrubber for removal of particulates. When the coal-lockhopper top closure is opened to admit coal, a small amount of gas can escape. Gas still in the coal lockhopper is displaced by the incoming coal. To prevent this gas from escaping up through the coal bin, a nitrogen ejector will operate to pull any gas from the lockhopper during filling and any gas from the shroud area through the scrubber to be discharged through a local vent above the gasifier. The nitrogen ejector will operate continuously during lockhopper filling [9,100]. When the lockhopper has been repressurized with carbon dioxide and opened once again into the gasifier, carbon dioxide will be fed continuously into the pressurized lockhopper to (1) make up for the removal of coal from the lockhopper and (2) prevent the upward migration of gasifier crude gas into the lockhopper. Pressure will always be positive on the carbon dioxide side [9].

The coal-lockhopper upper and bottom closures at one operating plant are very reliable and have an average life of 1 year [17,99]. When they do start leaking, it is initially a small amount of gas. The gasifier is then taken off line before hazardous amounts of gas can leak out. Leaks are easily detected during the pressurizing or depressuring cycle, which for US plants may utilize the following sequence: The upper valve will be closed and the lockhopper pressurized to 3 psig. If there is no change in pressure over a 30-second period, the lockhopper will be pressurized to reactor pressure. If a leak is detected, the cycle will be stopped, the lockhopper depressurized, the valve opened and reclosed, and the cycle repeated. The reverse is also true. When the lockhopper has been emptied, the bottom lockhopper valve will be sealed and the lockhopper depressurized from approximately 450 psig to approximately 340 psig. Pressure will be held for 30 seconds, and if no problems appear, depressurization will continue. Should a leak occur that is not observable on the guage, it will be noticed by the noise it makes on escaping from the coal-lockhopper valve [9,12].

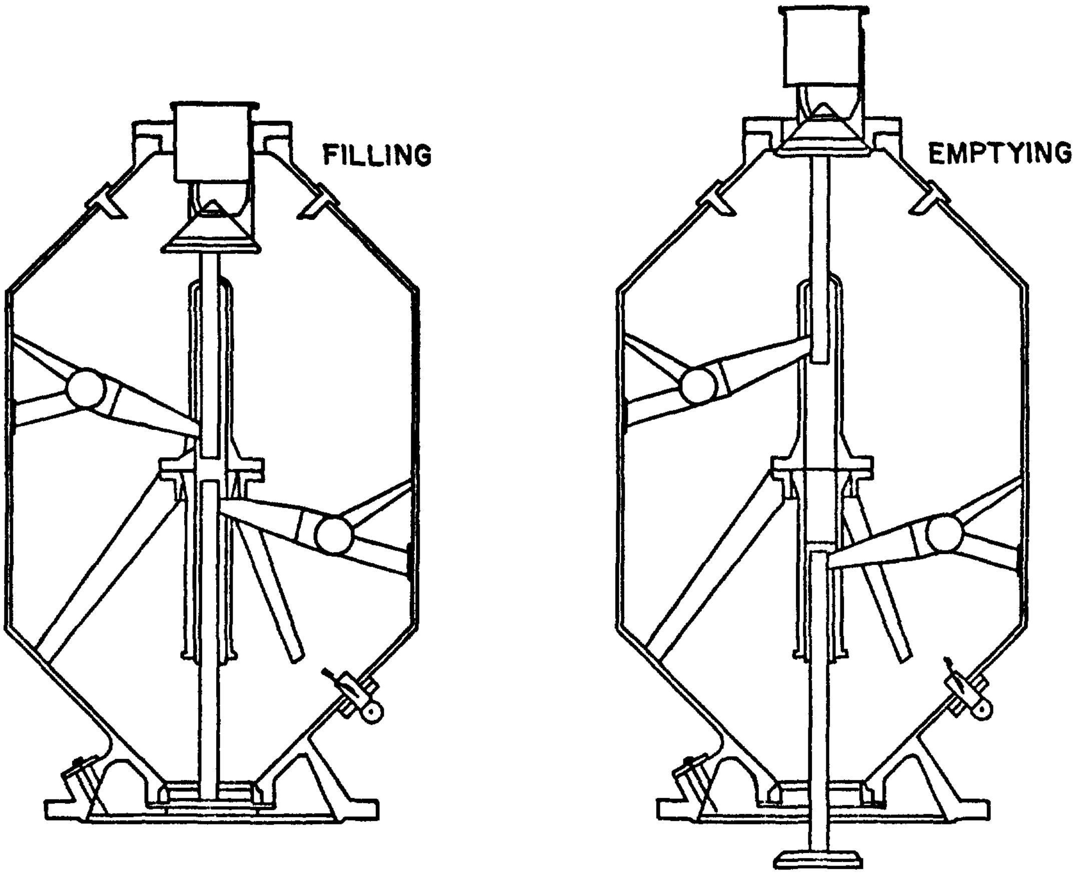


Figure XI-2
Coal Lock

Adapted from Reference 99

These coal locks have operated with very few difficulties. Proper shielding of the internal operating parts is necessary to prevent dust buildup, which may interfere with their operation [11]. One United States company anticipates a 6-month maintenance cycle for the coal lockhoppers [9,100].

(b) Lockhopper Pressurizing Gas

The composition of the coal-lockhopper pressurizing gas can be highly variable, depending upon the source utilized. Table XI-3 indicates the composition of the major part of the gas expected to be vented from the lockhoppers at two plants.

TABLE XI-3

COMPOSITION OF COAL-LOCKHOPPER PRESSURIZING GAS

	Concentration (vol %, dry)	
Constituent	Plant 1(a)	Plant 2
Carbon dioxide	77.53	28.03
Carbon monoxide	14.06	20.20
Ethane	0.47	0.61
Ethylene	0.29	0.40
Hydrogen	2.01	38.95
Hydrogen sulfide and carbonyl sulfide	0.76	0.37
Methane	4.6	11.13
Nitrogen	0.28	0.31

(a) In the environmental impact statements, the pressurizing-gas composition is given as dioxide, and the vent-gas composition is given as shown.

Adapted from reference 10

At another proposed United States plant, the coal lockhopper will be pressurized with product gas. Coal-lockhopper gas will be vented through the superheater for incineration and then discharged to the atmosphere through the 500-foot stack. Low-pressure lockhopper gas, plus gas escaping during filling, is to be exhausted together with excess air by coal-lockhopper ejectors to incineration [4].

At still another proposed United States plant, the coal lockhoppers will be pressurized by a slipstream from the raw product gas (see Table XI-5). This gas will then be sent to vent-gas recompression and added to the gas bypassing shift conversion [6].

(c) Workplace Hazards

The primary problem in this section of the plant is that the coal-lockhopper pressurizing gas may be either toxic or inert and would in either case be a potential hazard for operators in the area. In the plants operating today, this pressurizing gas may escape through the shroud into the operating area or percolate upward through the coal in the coal bunker. The engineering controls described in the recommended standard anticipate this problem, providing that the shroud is leaktight at the nominal pressures at which the upper valve of the coal lockhopper can be opened, and providing that the ejector nozzle is operating at all times.

It would be beneficial if the coal-lockhopper design were such that the feed and discharge valves were designed so that they could not be opened if a differential pressure existed across them. Thus, operator error would not cause the inadvertent dumping of large quantities of gas into the workplace.

Coal Gasification

(a) General Discussion

The gasifier is the heart of the coal gasification operation, although it comprises only about 20% of the cost of the system. For the purposes of this document, only the Lurgi coal gasifier is considered for high-BTU coal gasification (see Figure XI-3) [6]. The most advanced of the Lurgi gasifiers, the Mark IV gasifier with a diameter of 13.1 feet, is proposed for use in the United States [101]. In the older units the main gasifier consists of two shells; between the inner and outer shells is a space designed for cooling water [37]. There are many nozzles into the gasifier for feed, instruments, product, etc. Coal is fed from the top of the gasifier, and product is taken from the side of the gasifier near the top of the vessel. Ash is removed by a rotating grate at the bottom of the gasifier. The steam-oxygen mixture is fed through nozzles located in the ash grate. Originally the mixture was fed through three openings beneath different sections of the grate. Experiments have led to the inner opening being closed off altogether, most of the gas feed being distributed through the outer ring [99].

THE LURGI GASIFIER

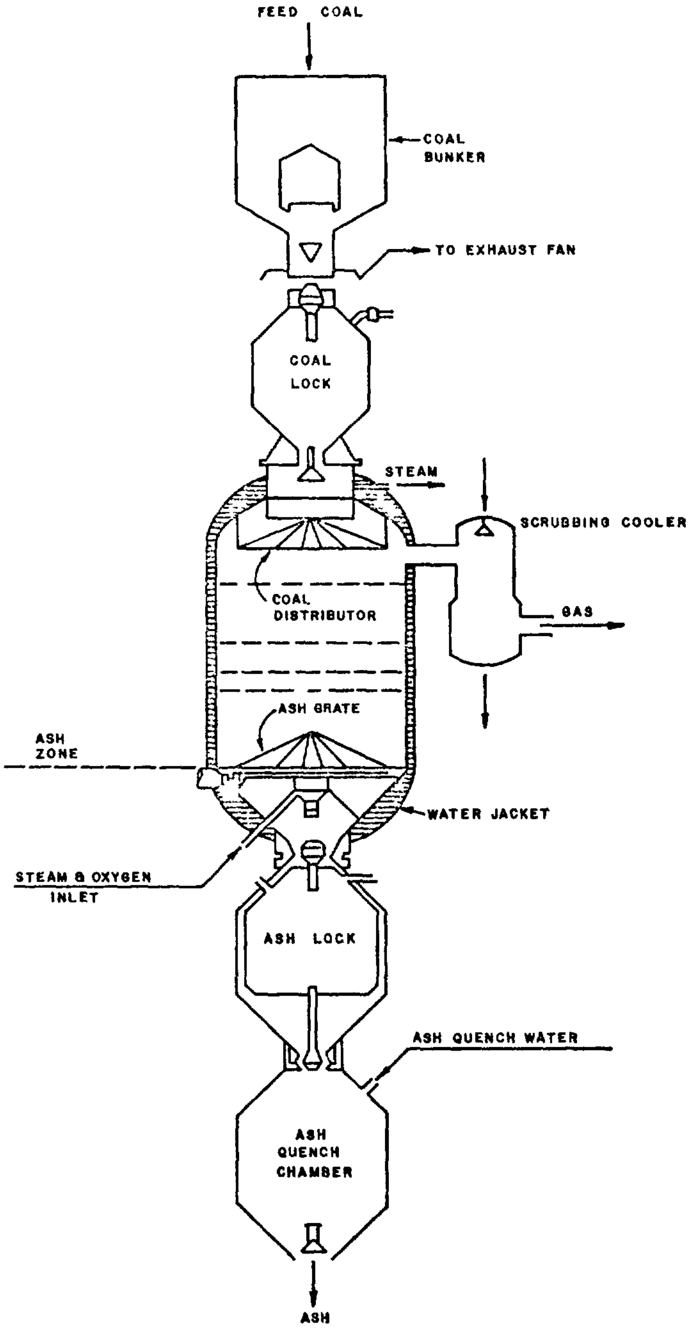


Figure XI-3
Gasifier Schematic with Exhaust Fan
Adapted from Reference 3

Wear of the grate surfaces has been greatly reduced by welding small strips of abrasion-resistant material radially to the surface of the grate. A layer of ash is held between the strips, protecting the grate itself and restricting the wear to the strips, which can be built up by welding from time to time. The shell is protected by wear plates at the floor of the gasifier below the grate. Corrosion or erosion of the inner shell of the water jacket has not been a problem [99].

Previously, feed water augmented by pump circulation from the water jacket was used to cool various parts of the reactor and the grate. The numerous flanges in the piping connecting the various parts were a source of frequent leakage. These flanges were eliminated and the piping connections are now welded [97,101].

(b) Process

When the coal lockhopper bottom closure is open, the coal falls by gravity onto the coal distributor located above the bed and above the product gas outlet. The coal flowing down through the gasifier represents a slowly moving bed of continuously changing chemical composition. The moving bed of coal, which occupies the volume between the coal distributor and the ash grate, has several distinct zones. These are, from top to bottom, drying, devolatilization, gasification, and combustion. The first zone preheats and dries the coal by contact with the rising hot crude gas. (Thus the moisture in the coal does not enter the water-gas reaction described below.) As the coal is heated, devolatilization and gasification commence in zones that overlap and have temperatures ranging between 620 C and 870 C (1.148 F and 1598 F). Coal devolatilization is accompanied by gasification of the resulting char.

This zone provides the overall heat for the gasification and devolatilization reactions, which are endothermic. About 86% of the moisture/ash-free (MAF) coal fed to the gasifier is gasified; the remaining 14%, which is mostly carbon, is burned in the combustion zone. Only a negligible amount of unburned carbon remains in the ash [3].

(c) Gasifier Feed

Oxygen and steam enter the gasifier near the bottom and are heated by the hot ash moving down from the combustion zone as they rise upward to the combustion zone (98% pure oxygen would be supplied to the gasifier). The steam-to-oxygen ratio determines the temperature in the combustion zone. This temperature must be below the ash melting point but high enough to insure complete gasification of the coal. Thus, the steam-to-oxygen ratio must be determined for each coal. The material balance for this proposed plant indicates that the coal gasifier feed will be as shown in Table XI-4.

TABLE XI-4

GASIFIER FEED

Component	Rate
Coal moisture, ton/hr	142
MAF coal, ton/hr	570
Coal ash, ton/hr	149
Steam, ton/hr	881
Oxygen, ton/hr	234
Steam/oxygen weight ratio	3.76
Steam/MAF coal weight ratio	1.55
Oxygen/MAF coal weight ratio	0.41

Adapted from reference 6

Of the total gas leaving the reactor, 37.3% is steam. The steam utilized/steam feed weight ratio is 0.57 [6].

(d) Feed Control

In an oxygen-blown gasification system, it is of the utmost importance to prevent the admission of oxygen with insufficient steam. The required ratio of steam to oxygen is normally maintained by ratio-linked flow controllers, but at one operating plant two additional safety devices have been installed. One of these trips a quick-closing valve in the main oxygen header if the steam supply pressure falls below that of the oxygen. The other, fitted to each gasifier, activates an alarm if the temperature of the oxygen-steam mixture varies by more than a few degrees above or below a preset temperature [11].

In addition to other instrumentation, including an alarm if the differential pressure between jacket and gasifier is exceeded, a device has been installed to trip both oxygen and steam-flow controllers if the gasifier pressure exceeds a certain figure. This latter precaution was considered necessary at SASOL after an incident in which a gasifier exceeded the relief valve set pressure without the relief valve opening. Investigation showed that, although the relief valve was installed in a short vertical nozzle, tarry vapors had condensed and hardened under the seat and plug, making the valve inoperative. The addition of a small steam-purge has served to prevent such occurrences, but even steam purges may inadvertently be shut off, and the additional trip device was considered necessary [99].

(e) Raw Product Gas

Coal feed, feed entry geometry, temperature, pressure, and reactor configuration all affect the reactor product. For this document, the situation is simplified because only the Lurgi gasifier is to be considered. However, the situation is complicated by the fact that a number of entirely different coals are being considered for gasification in the United States. Because the Lurgi gasifier is essentially a countercurrent plug-flow unit, there are significant differences in the gas-vapor composition at different levels within the reactor as the various dissociation, hydrogenation, polymerization, combustion, and reduction reactions occur, as described above. At the commercial plant level, the principal components of the product gas are of primary interest, as is the maximization of methane production and the relationship between carbon monoxide, carbon dioxide, and hydrogen. The other components, with the exception of hydrogen sulfide and ammonia, make up a minor fraction of the gasifier product.

Estimates of crude-gas composition are shown in Table XI-5. In addition to the components listed, the gasifier offgas may also contain steam, tar, oil, naphtha, phenols, fatty acids, ammonia, sulfur compounds, and small quantities of coal dust, all at 340-400 C (649-752 F).

(1) Oil and Tar

In addition to the components shown in Table XI-5, there are numerous minor constituents in the gas. A gross breakdown of these minor constituents would include light tar, heavy tar, sulfur compounds, nitrogen compounds, and volatilized metal compounds from the ash. The exact quantity of these constituents will depend on the coal, as will the specific compound composition. One company anticipates that it will have a total of 2,321 tons/day, or 4.26 wt % of its total output, as salable minor constituents (see Table XI-6) [3].

As US gasifiers will use tar recycle, it may be expected that most of the liquid hydrocarbons recovered will be in the tar-oil category and will be essentially 100% soluble in benzene whether the coal used is lignite, subbituminous, or bituminous. [Mass spectrometric analysis of a US pilot plant's benzene-soluble tar exemplifies the variation in structural type within a tar component

TABLE XI-5

RAW PRODUCT GAS COMPOSITION(a)

Constituent	Concentration (vol %)		
	(b)	(c)	(d)
Carbon dioxide	28.4	28.03	28.78
Hydrogen sulfide	0.5	0.37	(0.003) (e)
Carbon monoxide	19.9	20.20	20.20
Hydrogen	38.7	38.95	40.05
Nitrogen and argon	0.3	0.31	1.59
Methane	11.3	11.13	8.84
Ethylene	0.1	0.40	0.54
Ethane	0.6	0.61	0.54
Propane, Butene, and Butane	0.2	ND	ND

(a) Moisture/solids-free gas, estimated concentrations; no data available for ammonia, tar, pentanes and higher hydrocarbons.
(b) Data from reference 3
(c) Data from reference 6
(d) Data from reference 101
(e) Carbonyl sulfide < 10 ppm, ash = 20 ppm

ND = no data

TABLE XI-6

OIL AND TAR

Constituent	Tons/Day	Weight % Total Product
Sulfur	202	0.35
Naphtha	315	0.58
Ammonia	204	0.38
Phenols	102	0.19
Tar	743	1.37
Tar oil	755	1.39
TOTAL	2,321	

Adapted from reference 3

caused simply by the use of several different coals (see Table XI-7).] However, tar yields will increase with coal rank, varying from approximately 3 wt % for lignite to approximately 5 wt % for bituminous coals [104]. (This information was used in determining the concentration of the individually identified components in the reactor product gas, assuming a gas yield of 25 scf/lb of coal.)

(2) Sulfur Compounds

It has been reported that approximately 90% of the organic sulfur in coal can be converted to hydrogen sulfide during gasification [105]. While it is obvious that the total quantity of sulfur gasified will depend on reactor conditions, the distribution of sulfur compounds will depend upon the mode and temperature of operation, and the coal feed. Tables XI-8 and XI-9 illustrate the effects of different coal feed and process on the sulfur component distribution. Available data indicate that the gasified sulfur from the Lurgi gasifier may be distributed as shown in Table XI-8.

(3) Nitrogen

Nitrogen balances in pilot plants indicate that 78% of the nitrogen in the coal fed to the reactor (Synthane) is converted to ammonia [106]. Within the accuracy of bench-scale data, ammonia production in the Synthane process appears to vary from 15 to 20 lb/ton of MAF coal for lignite and to average approximately 20-22 lb/ton of MAF Illinois No.6 coal [107]. The characterization of the effluents of HYGAS by Massey et al [108] gives some indication of the distribution of nitrogen compounds that might be expected in Lurgi gasification (Table XI-10).

Because the gasifier atmosphere is reducing (contains excess hydrogen), no nitrogen oxides should be produced during gasification, whether air or oxygen is used. Furthermore, even though ammonia converts relatively easily to nitrogen oxides on combustion, tests with a low-BTU gasifier-combustor combination indicated that the overall conversion of coal nitrogen to nitrogen oxides in a gasification-combustion process is significantly less than that occurring in the direct burning of pulverized coal; the conversion was reduced by a factor of 2 [109].

(4) Trace Elements

The volatility of a substance depends on its own characteristics and those of the atmosphere concerned. A study of the volatility of the trace elements in a hypothetical coal was made by Ruch and Associates [110] under the reducing conditions of a gasifier (Table XI-11). This study was expanded by Attari [81] who examined the volatility of coal trace elements at several sequential temperatures. The trace element concentrations that might be expected in the make gas in various parts of Attari's gasifier system are listed in Table XI-12.

TABLE XI-7

MASS SPECTROMETRIC ANALYSES OF SYNTHANE(a) BENZENE-SOLUBLE TAR(b)

Structural Type	Boiling Point (deg C)	Illinois No.6 Coal Benzene Soluble Vol %	Illinois No.6 Coal Estimated Vol % Gas (c)	Lignite Benzene Soluble Vol %	Lignite Estimated Vol % Gas (c)	Montana Sub-bituminous Coal Benzene Soluble Vol %	Montana Sub-bituminous Coal Estimated Vol % Gas (c)	Pittsburgh Seam Coal Benzene Soluble Vol %	Pittsburgh Seam Coal Estimated Vol % Gas (c)
Benzenes	80.1	2.1	0.017	4.1	0.02	3.9	0.026	1.9	0.016
Indenes	182.4	8.6	0.048	1.5	0.005	2.6	0.012	6.1	0.034
Indanes	176.5	1.9	0.010	3.5	0.011	4.9	0.021	2.1	ND
Naphthalenes	217.9	11.6	0.058	19.0	0.059	15.3	0.061	16.5	0.083
Fluorenes	295	9.6	0.037	7.2	0.018	9.7	0.03	10.7	0.041
Acenaphthenes	277.5	13.5	0.056	12.0	0.030	11.1	0.037	15.8	0.066
Three-ring aromatics	354.5	13.8	0.05	10.5	0.023	9.0	0.026	14.8	0.053
Phenylnaphthalenes	325	9.8	0.031	3.5	0.0066	6.4	0.016	7.6	0.024
Four-ring pericondensed	ND	7.2	ND	3.5	ND	4.9	ND	7.6	ND
Four-ring catacondensed	ND	4.0	ND	1.4	ND	3.0	ND	4.1	ND
Phenols	182	2.8	0.019	13.7	0.056	5.5	0.03	3.0	0.020
Naphthols	288	ND	ND	9.7	0.026	9.6	0.034	ND	ND
Indanols	ND	0.9	0.0043	1.7	0.0049	1.5	0.0057	0.7	0.003
Acenaphthenols	ND	ND	ND	2.5	ND	4.6	ND	2.0	ND
Phenanthrols	168	2.7	0.0089	ND	ND	0.9	0.0023	ND	ND
Dibenzofurans	287	6.3	0.024	5.2	0.012	5.6	0.017	4.7	0.018
Dibenzothiophenes	332.3	3.5	0.012	1.0	0.002	1.5	0.004	2.4	0.0083
Benzonaphthothiophene	ND	1.7	ND	ND	ND	ND	ND	ND	ND

(a) Analyses derived from the 25-lb/hr coal feed laboratory-scale Synthane gasifier and may be representative of gases to be obtained from pilot plant and commercial operation of the Synthane process; there will be some differences due to both variation in temperature, steam-oxygen feed quantities, and coal [82].

(b) At the present time, most data concerning soluble coal material refer to benzene-solubles for most occupational health purposes; laboratory procedures for analysis of soluble coal material refer to cyclohexane-solubles. In this context, benzene is essentially equivalent to cyclohexane.

(c) Adapted from reference 79

ND = no data

TABLE XI-8

CONSTITUENTS OF SYNTHANE GASIFIER GAS (925-LB/HR COAL FEED, BENCH-SCALE GASIFIER)

Constituent	Boiling Point (deg C)	Illinois No.6 Coal ppm	Illinois No.6 Coal Vol %	Wyoming Subbituminous Coal ppm	Wyoming Subbituminous Coal Vol %	Western Kentucky Coal ppm	Western Kentucky Coal Vol %	North Dakota Lignite ppm	North Dakota Lignite Vol %	Pittsburgh Seam Coal ppm	Pittsburgh Seam Coal Vol %
Hydrogen sulfide	-60	9,800	0.9800	2,480	0.2480	2,530	0.2530	1,750	0.1750	860	0.08
Carbonyl sulfide	-50	150	0.0150	32	0.0032	119	0.0119	65	0.0065	11	0.0011
Thiophene	84	31	0.0031	10	0.0010	5	0.0005	13	0.0013	42	0.0042
Methyl thiophene	112-116	10	0.0010	ND	ND	ND	ND	ND	ND	7	0.0007
Dimethyl thiophene	137-141	10	0.0010	ND	ND	ND	ND	11	0.0011	6	0.0006
Benzene	80	340	0.0340	434	0.0434	100	0.0100	1,727	0.1727	1,050	0.1050
Toluene	111	94	0.0094	59	0.0059	22	0.0022	167	0.0167	185	0.0185
C9 Aromatics	ND	24	0.0024	27	0.0027	4	0.0004	73	0.0073	27	0.0027
Sulfur dioxide	-10	10	0.0010	6	0.0006	2	0.0002	10	0.0010	10	0.0010
Carbon disulfide	46	10	0.0010	ND	ND	ND	ND	ND	ND	ND	ND
Methyl mercaptan	6	60	0.0060	0.4	0.0004	33	0.0033	10	0.0010	8	0.0008

ND = no data

Adapted from reference 82

TABLE XI-9

VARIATION IN SULFUR DISTRIBUTION DUE TO DIFFERENCES IN FEED COAL OR PROCESS

	Synthane (vol %) (a)			Lurgi (vol %) (b)
Constituents	Illinois No.6 Bituminous	North Dakota Lignite	Pittsburgh Bituminous	
Hydrogen sulfide	97.2	94.2	91.1	95.0
Carbonyl sulfide	1.5	3.5	1.2	2.4
Thiophenes	0.5	1.3	5.8	0.3
Carbon disulfide	0.1	ND	ND	0.3
Mercaptans	0.6	0.5	0.8	2.0

(a) Bench-scale unit; adapted from reference 82

(b) Adapted from reference 105

ND = no data

TABLE XI-10

HYGAS PILOT-PLANT LIQUID-EFFLUENT CHARACTERISTICS, HYDROGASIFICATION OF MONTANA LIGNITE, RUN 37(a)

Constituent	Effluent Production of Nitrogen Compounds (lb/ton MAF Coal)(b)	Wt % of Nitrogen Effluent	Estimated Vol % of Reactor Gas Stream (Dry Basis)
Ammonia	12.8 to 13.4	83.97	0.47
Cyanide ion	0.000013 to 0.000044	0.0002	0.000067
Thiocyanate ion	2.3 to 2.7	16.02	0.03

(a) Reported data represent only lower bounds on actual plant effluent production rates. Not included in any steady-state data are effluents contained in oil-stripper water condensate, coal mill venturi-scrubber water, and condensate depressurization offgas. In addition, during steady-state period 1, effluents in product-gas cyclone slurry water and the oil-water-solids interface from the product-gas quench system were not measured.

(b) Adapted from reference 108

TABLE XI-11

ESTIMATED VOLATILITY OF TRACE ELEMENTS IN A COAL

Constituent	Hypothetical Coal(a) (ppm)	% Volatile
Chlorine	1,400	90+
Mercury	0.2	90+
Selenium	2.08	74
Arsenic	14	65
Lead	34.78	63
Cadmium	2.52	62
Antimony	1.26	33
Vanadium	32.7	30
Nickel	21.07	24
Beryllium	1.61	18
Chromium	13.75	Nil
Zinc	272.2	10(b)
Boron	102.2	10(b)
Fluorine	60.9	10(b)
Titanium	700	10(b)

(a) Volatility based mainly on gasification experiments [111]; data for chlorine from combustion tests

(b) Estimated at 10% for illustration in absence of data

Adapted from reference 110

TABLE XI-12

TRACE-ELEMENT CONCENTRATIONS IN A PITTSBURGH NO. 8 COAL AT VARIOUS TEMPERATURES FOR STAGEWISE HEATING(a)

				1000 C (1832 F) (b)					Trace-Element Concentration in Offgas (Vol %)		
Element	Raw Coal (ppm)	430 C (806 F) (ppm)	650 (C) (1200 F) (b) Loss (%)	ppm	Loss (%) After 430 C	ppm	Loss (%) After 650 C	Total Loss (%)	430 C (c)	650 C (d)	1000 C (e)
Mercury	0.27	0.19	30	0.06	68	0.01	19	96	0.00000071	0.0000012	0.0000016
Selenium	1.7	1.0	41	0.65	35	0.44	12	74	0.000016	0.0000094	0.000019
Arsenic	9.6	7.5	22	5.1	32	3.4	18	65	0.00005	0.000072	0.0001
Tellurium	0.11	0.07	36	0.05	29	0.04	9	64	0.00000057	0.00000031	0.00000067
Lead	5.9	4.4	25	3.3	25	2.2	19	63	0.000014	0.000013	0.000022
Cadmium	0.78	0.59	24	0.41	31	0.30	14	62	0.000003	0.0000034	0.0000052
Antimony	0.15	0.13	13	0.12	8	0.10	13	33	0.00000029	0.00000033	0.0000005
Vanadium	33	36	0	30	9	23	21	30	ND	0.00026	0.00024
Nickel	12	11	8	10	9	9.1	8	24	0.00003	0.000043	0.00006
Beryllium	0.92	1.0	0	0.94	0	0.75	18	18	ND	0.000037	0.000023
Chromium	15	17	0	16	0	15	0	0	ND	ND	ND

Adapted from reference 111

(a) Calculated on a raw-coal basis for Pittsburgh No.8 coal

(b) Maximum temperature

(c) Basis: Assume 21.2 scf total gas/lb coal, 0.038 lb make and feed water/lb coal, 0.0082 lb make oil/lb coal [112]

(d) Basis: Assume 28.7 scf total gas/lb coal, 0.43 lb make and feed water/lb coal, 0.038 lb make oil/lb coal [112]

(e) Basis: Assume 21 scf total gas/lb coal, 0.43 lb make and feed water/lb coal, 0.046 lb make oil/lb coal [112]

ND = no data

Table XI-13 data are forced averages of the distribution of trace elements found in the SASOL tar separator. These data indicate that, with the exception of boron and arsenic, more than half of each trace element remains with the ash. Large concentrations of the halides of antimony, arsenic, and mercury remain in the gas-liquor. In general, with the exception of arsenic, the concentration of trace elements in the tar oil is low.

TABLE XI-13

PERCENT DISTRIBUTION OF TRACE ELEMENTS PRESENT IN COAL AT THE SOUTH AFRICAN COAL OIL COMPANY

Element	Ash %	Gas-Liquor %	Tar %	Tar Oil %
Antimony	50	45.6	3.8	0.6
Arsenic	27.2	66.2	2.4	4.2
Beryllium	ND	ND	ND	ND
Boron	92.8	5.8	1.4	0.003
Bromine	10	88.6	1.4	ND
Cadmium	52	45	1.1	1.8
Cesium	99.9	0.1	0.003	<0.001
Chlorine	52.5	47.3	0.2	0.008
Fluorine	56.3	43.6	0.08	0.003
Lead	93.4	2.2	4.4	0.02
Manganese	99.7	0.3	0.007	<0.001
Mercury	50.6	40.4	8.3	0.7
Nickel	99.6	0.4	0.07	0.01
Vanadium	99.9	0.1	0.003	0.003

(a) Data forced to 100% balance, assuming that trace-element concentration in gas was negligible compared with trace-element concentration in these streams

ND = no data

Adapted from reference 103

Table XI-14 data are forced averages of the distribution of trace elements found in Rochelle coal and the products recovered from a test conducted at Westfield, Scotland (Wyoming Coal Gas Company) [5]. Despite their inconsistency, these data indicate that most of the trace elements remain with the ash or are removed in the quench operation.

TABLE XI-14

DISTRIBUTION OF TRACE ELEMENTS PRESENT IN ROCHELLE COAL AND ITS GASIFICATION PRODUCTS(a)

Element	Feed Coal (ppm)	% in Ash	% in Gas-Liquor
Antimony	0.08	100	25
Arsenic	0.57	100	7
Barium	87	100	0
Beryllium	0.71	33	92
Boron	32	100	49
Cadmium	0.31	66	95
Chlorine	220	6	93
Chromium	4.2	100	89
Cobalt	0.55	66	0
Copper	8.9	100	33
Fluorine	65	78	86
Lead	0.51	100	68
Lithium	3.6	100	76
Manganese	3.4	100	0
Mercury	0.17	2	96
Molybdenum	2.2	100	0
Nickel	1.7	100	88
Radium	(b)	ND	ND
Selenium	0.33	57	45
Silver	0.06	33	82
Tin	0.14	100	95
Uranium	0.88	100	45
Vanadium	14	55	53
Zinc	0.23	100	74

(a) Data forced on assumption that trace-element concentration in gas was negligible compared with trace-element concentration in these streams

(b) 0.0 (+/-) 0.2 pCi/g

ND = no data

Adapted from reference 5

(f) Workplace Hazards

Workplace hazards in the gasification system will most likely be plugged lines, hot spots, insulation problems, and leaks. Leaks may occur at any of the connections to the gasifier vessel, particularly at flanges and other connections such as valves, and instrument locations. The leaks will involve release into the workplace of toxic substances, including carbon monoxide, tar, sulfur compounds, nitrogen compounds, and trace elements. Leaks from the ash-lockhopper area, providing they are not catastrophic, will most likely be of steam and oxygen. Leaks in the area from the grate to above the combustion zone may contain steam, oxygen, carbon dioxide, carbon monoxide, hydrogen, and trace elements. Leaks above this point will contain increasing amounts of devolatilization products, but may contain lesser quantitites of trace elements.

Significant condensation in the reactor is unlikely unless the top of the reactor cools for unforeseen reasons. Condensation between the reactor and the quench system is possible, particularly when high-temperature tar is produced. Low-temperature devolatilization products should not condense before being quenched. (It should be noted that the high-temperature devolatilization products will condense in the reactor and in the reactor offgas line or any other line if the line temperature drops below the reactor temperature by as much as a few degrees.) Where condensation does occur, personnel will be exposed to the possibility of skin contact with condensed products on the interior vessel walls or on the interior of the lines, valves, or instruments when they are opened. In recognition of this fact, the Lurgi gasification system utilizes a ram to clean out the very short line (not more than 3 feet long) to prevent the accumulation of condensate in the line between the reactor and the water quench spray. This ram is activated once each shift. It is possible for material to condense on the cold ram shaft or to be forced through the packing and into the workplace. The mechanical seals at this point must be carefully installed and maintained to minimize leakage.

Gas Quench System

(a) Process

At one proposed plant [3], the 345 C (653 F) product gas will be led directly from the gasifier to the gas quench unit, a distance of approximately 3 feet. The hot gas is quenched to 195 C (383 F) by dumping recycled liquid quench water into the gas stream. The quenching operation itself deliberately creates emulsions that trap particulate matter elutriated from the gasifier. Quenched gas, steam, and liquor then go to the waste-heat boiler for cooling. The gas-liquor, tar, and solids are returned to a holding tank and from the holding tank to the centrifugal gas-liquor recycle pump for circulation to the quench tank. Excess condensate is level controlled to the tar separation system [3,9].

(b) Mechanical and Safety Considerations

Failure at any point in the high-pressure system may be observed by noise or by the odor of the gas leaking into the surrounding area. The gas line from the gasifier to the quench vessel and from the quench vessel to the waste-heat boiler may not be insulated, so that any system failures in the line can be spotted visually. (These lines will be protected from excessive expansion/contraction by line design or by metal bellows.) The liquid portion containing the recycle gas-liquor of the quench system will be designed for minimum erosion and will consist of heavy-wall pipe with long-radius elbows sized for minimum velocity [3]. Valve size will be limited to a 3-inch maximum opening, to prevent excessive velocity in the recycle liquor piping and to limit the flow to the tar separation units. The piping will be monitored for erosion with ultrasonic detectors [9].

The design of one proposed plant calls for the gas-liquor recycle pump to be hung so as to prevent the expansion and contraction of the feed and discharge pipes from affecting pump performance [9]. On this pump SASOL uses a stuffing-box seal that is cooled with cool gas-liquor [12]. Should the stuffing box fail, the gas-liquor is passed into the process from the flush system. Despite the erosive mixture of hot gas-liquor, emulsified tar, and solids elutriated from the gasifier, the total downtime for the entire gasifier system is low, and it may be inferred that recycle pump reliability is high. In one plant design, pump failure causes an interlock system to activate flushing by an emergency water injection system. This system can be used until the recycle pump is repaired or, in the case of serious damage, until the gasifier can be taken offstream [9].

(c) Workplace Hazards

Problem areas in the gas quench system primarily involve leaks of crude gas or hot gas-liquor into the working environment. The primary leak point is at the recycle gas-liquor pump. Should the seal of this pump leak, the work area could be contaminated with gas-liquor, unless a deliberate effort is made to drain off any potentially leaking material into a nearby sump (or the ash disposal system). This section is vulnerable to the loss of recycle water. Should this occur, the entire system would be heated to 345 C (650 F) by the producer gas. In addition, tar and solids would be deposited throughout the system, and dirty gas would be sent to the shift-conversion and gas cooling units. It is most likely that gas would also get into the tar separators, causing overflow.

Shift Conversion

(a) General Discussion

The shift-conversion unit consists of a series of catalytic reactors in which carbon monoxide and water are converted to hydrogen and carbon dioxide. The overall reaction is as follows:

$$CO + H_2O \longrightarrow CO_2 + H_2 + 16{,}538 \text{ BTU/lb-mole}$$

In the high-BTU coal gasification plant, approximately half of the raw gas will pass through the shift unit and half will go directly to the gas-cooling unit. The exact amount of gas passing through shift conversion will be determined by the ratio of hydrogen to carbon monoxide needed in the methanation feed gas to optimize the methanation step [3].

At one commercial plant [17], raw gas is passed through a guard bed to remove tar, water droplets, and dust; it is then passed through three stainless steel heat exchangers in series, where its temperature is raised by means of hot converted gas to approximately 400 C (752 F) before entry into the first catalyst vessel. After leaving the first catalyst vessel at a temperature of approximately 470 C (878 F), the gas passes through two of the stainless steel heat exchangers and enters the second catalyst vessel at a temperature of approximately 380 C (716 F). From the outlet of the second catalyst vessel, the gas passes at a temperature of approximately 400 C (752 F) into the third stainless steel heat exchanger and then successively through a gas-to-gas heat exchanger (where it meets the incoming unconverted gas stream) and two water-cooled heat exchangers. Raw gas leaves the final heat exchanger at a temperature of approximately 90 C (194 F) [17].

The operating conditions of the shift-conversion unit permit conversions to take place in the presence of tar oils and naphtha. In addition, desulfurization and hydrogenation of organic compounds occurs [3].

One US plant design calls for twin 42-inch lines to bring the crude gas into 4 parallel shift-conversion units [3]. These units are designed for low velocities so that a protective coating will develop on the pipe to protect it from erosive and corrosive effects. Because polymer formation on the catalyst bed is expected, periodic regeneration (at approximately 3 to 6-month intervals) with a steam-air mixture will be required. Gases from regeneration will go to an area collection header and will be sent to the boiler for incineration.

Most likely the shift-conversion catalyst will be a commercially available cobalt-molybdenum on an alumina base. It is anticipated that catalyst life will be several years. Once the catalyst is deactivated, it will probably be sent to the mine for disposal [86].

(b) Workplace Hazards

The high hydrogen content of the converted gas, the presence of hydrogen sulfide, and the elevated temperature and pressure will require suitable precautions in the design of various piping and vessels against hydrogen embrittlement, hydrogen blistering, and attack by hydrogen sulfide. At Westfield this was achieved by using 18-8 titanium-stabilized stainless steel for heat exhangers and pipework exposed to high temperatures; the catalyst vessels were constructed of 161 grade C silicon-killed carbon steel sprayed internally with aluminum and lined with 8.5 to 10.5 inches of refractory concrete [17].

During catalyst loading and unloading there may be a dust problem. During these periods, an ejector or blower may be used for dust control [9].

The main potential operator exposure in this section is to raw gas at high pressures and temperatures. There is the danger of combustion of a gas leak, especially at shift-conversion temperatures. It has been suggested that an operator will have to be available to inspect this section for leaks at least once per workshift. Should a leak be observed at any kind of bolted connection, the bolts should be torque tightened. If this is not effective, the unit should be put on standby or should be shut down until the leak can be eliminated [86] (see Figure XI-4).

Gas Cooling

(a) General Discussion

The gas-cooling unit is used to cool both the hot raw gas from gasification and the shifted gas before it is fed to the low-temperature purification process. Cooling will take place in three steps for reduction from 195 to 30 C (383 to 86 F). As much waste heat as possible will be recovered by generating steam. Cooling equipment will be arranged in two sections; one section for the gas from the shift conversion and one for the raw gas bypassing that process [6] (see Figure XI-5).

Crude gas that bypasses shift conversion will first be passed through a low-pressure steam generator. Air cooling followed by water cooling will complete the process [6].

On the raw-gas side, condensate (hot gas-liquor) and tar, which condense in the heat-exchanger steam generator, will be transferred to the primary gas-liquor separator mentioned below. The remaining condensates (the gas-liquor and tar oil-naphtha mixture) are to be processed in a second gas-liquor separator [6].

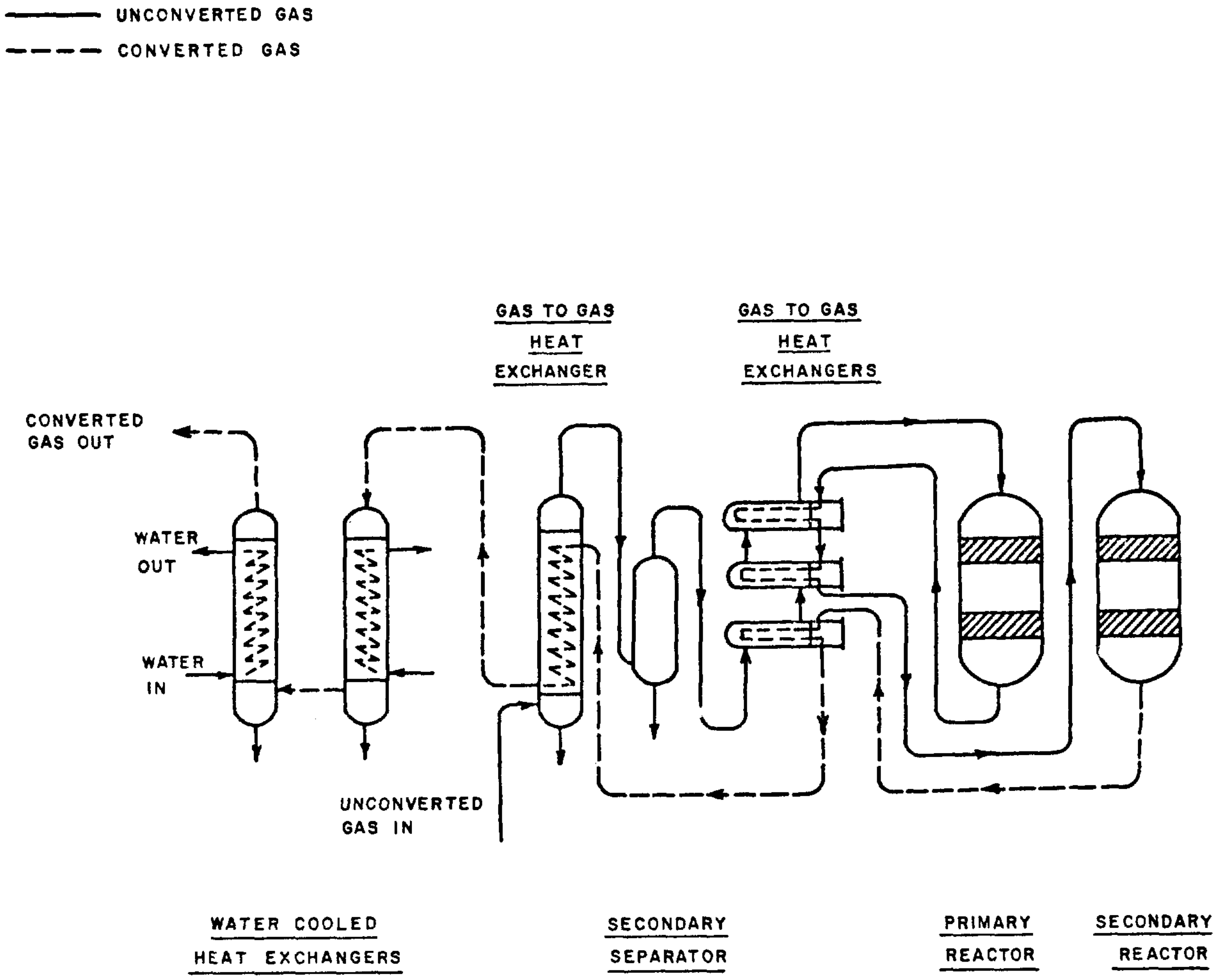


Figure XI-4

Simplified Flow Diagram of the Westfield Shift Conversion Plant

Adapted from Reference 17

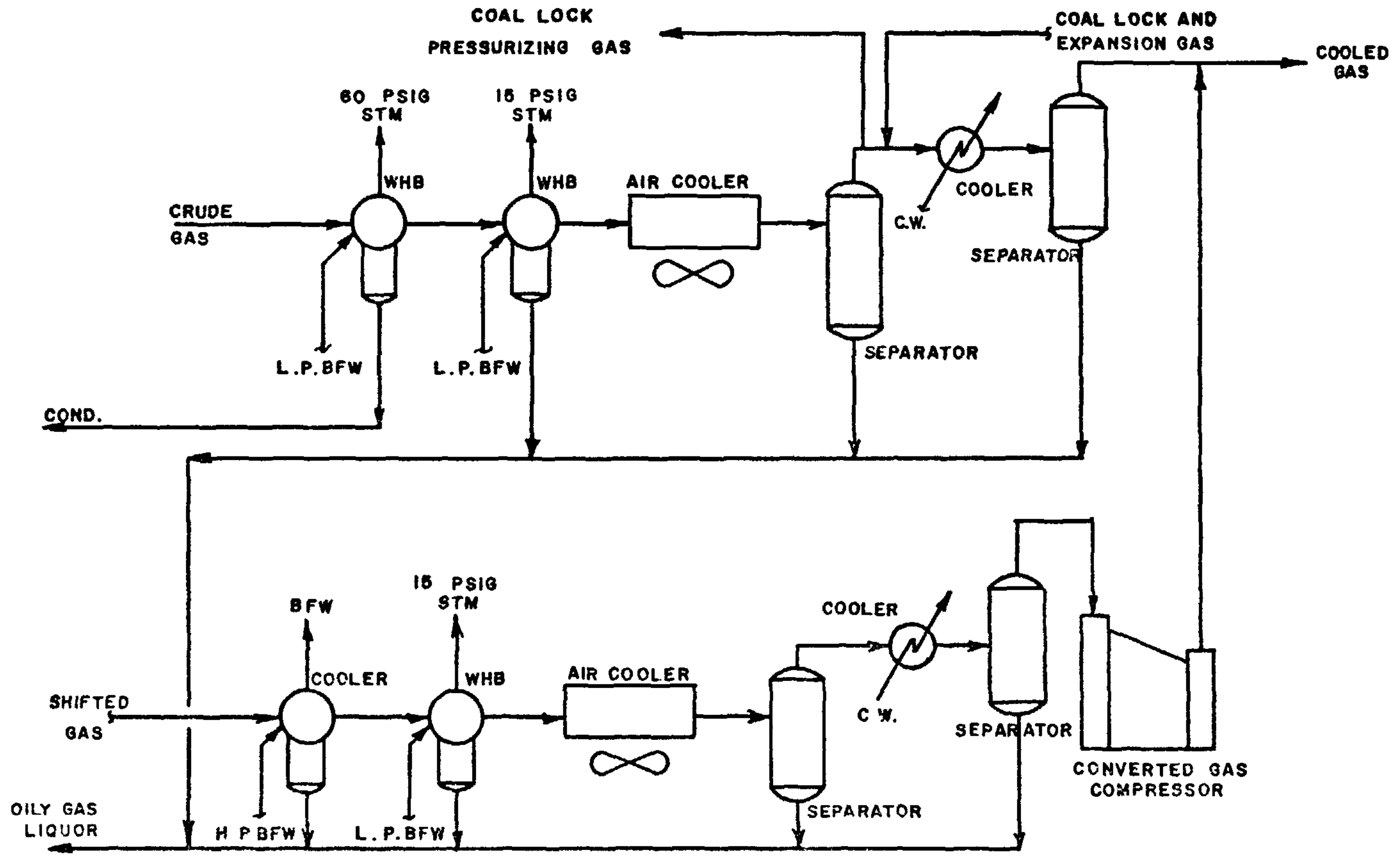


Figure XI-5

Flow Scheme for the Gas Cooling Section

Adapted from Reference 6

Shift-conversion gas will, for the most part, be cooled identically to the crude gas. It will be passed through a heat exchanger to preheat boiler feedwater. Air cooling and then water cooling are the final steps. Condensates will be cooled in heat exchangers and processed in the second gas-liquor separator with the gas-liquor and tar oil-naphtha mixture from the crude-gas cooling [6].

The cooled gases would be combined and sent to the Rectisol process for acid-gas removal [6].

(b) Workplace Hazards

Workplace hazards in this section include the potential for leaks from both the crude-gas and the cooled-gas equipment. There are also potential corrosion problems, particularly at points where water will condense.

Gas Purification

(a) General Discussion

Before the raw gas is upgraded to pipeline specifications by methanation, all sulfur compounds must be removed from the methanator feed gas or the methanation catalyst will be poisoned. Carbon dioxide must also be separated from the combustible product to achieve a heating value of approximately 1,000 BTU/scf.

A variety of processes are available for separating carbon dioxide and hydrogen sulfide from the product-gas stream. However, in the commercial high-BTU coal gasification plants now being considered, the Lurgi-licensed Rectisol process (Figure XI-6) will be used for gas purification. The original Lurgi Rectisol plant, the first of its kind to be built, was commissioned at SASOL in 1955. The SASOL Rectisol plants have a long-term reliability of 97% onstream time, which includes allowances for shutdowns, general overhaul, statutory inspections, etc. The onstream time is maximized by having the right standby equipment available for critical duties, preventive maintenance, fast cleaning procedures, and analytical control of stream compositions [101].

The Rectisol process is used to remove gases such as carbon dioxide, hydrogen sulfide, carbonyl sulfide, carbon disulfide, mercaptans, gas-naphtha vapor, water vapor, ammonia, hydrogen cyanide, and numerous other impurities present in minor quantities. As is the case with all acid-gas cleanup processes based on physical absorption, the Rectisol process operates more efficiently at high pressure, since the solubility of the acid gases in methanol increases with increasing pressure. Low temperatures [below -18 C (0 F)] also increase the solubility of acid gases in methanol. The solubilities of hydrogen sulfide, carbonyl sulfide, and carbon dioxide, the gases usually considered to be impurities, increase

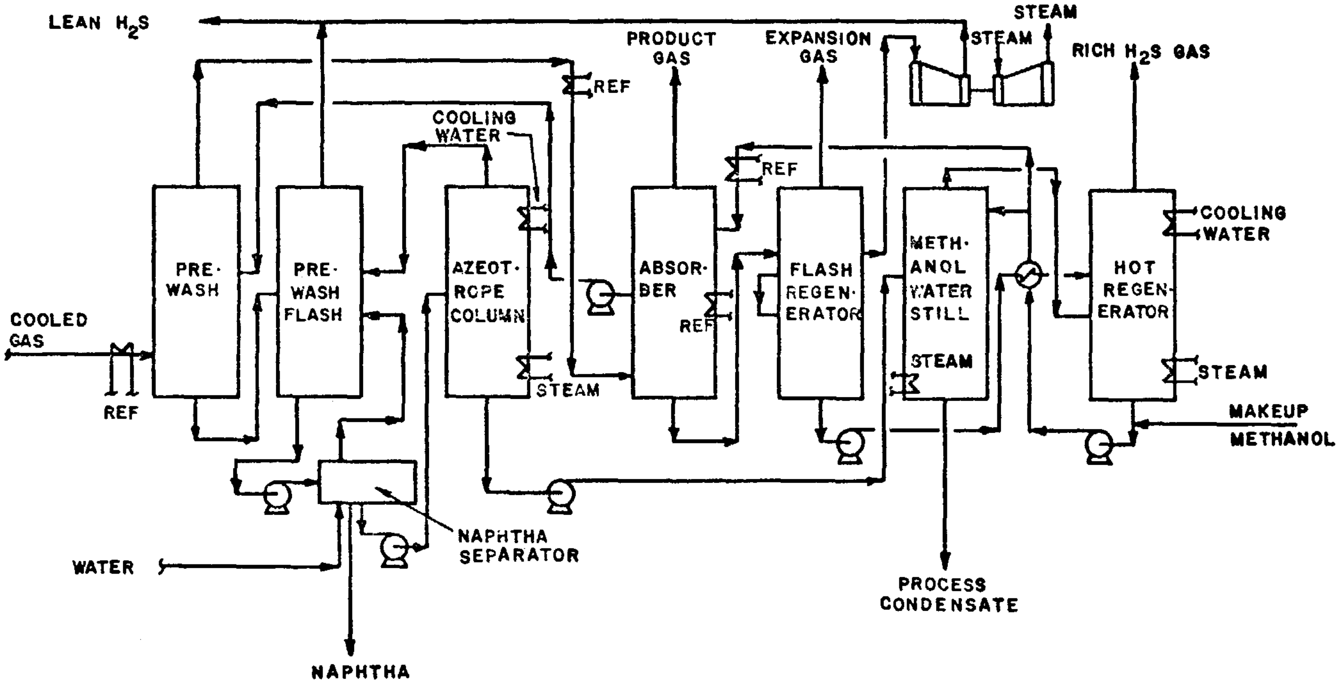


Figure XI-6

Flow Scheme for Gas Purification Section–Rectisol I Process

Adapted from Reference 6

with decreasing temperature. It should also be noted that the solubilities of carbon monoxide, methane, and hydrogen are not significantly affected by temperature; thus the Rectisol process is more efficiently operated at low temperatures, a condition that also minimizes solvent losses [10].

In one proposed US plant, the crude gas and the converted gas from the gas-cooling area will be combined into a single stream before entering the Rectisol unit [6]. The mixed gas will be chilled before entering the washtower, where water and naphtha will be removed by a cold methanol wash. Naphtha will be recovered from the methanol and water by means of the naphtha extractor. Naphtha recovery will be maximized by recycling the naphtha-methanol mixture through the azeotrope column. The methanol will be recovered by distillation in the methanol-water column [6]. The typical naphtha recovered at -35 C (-31 F) may include benzene, toluene, and xylene, as well as C6 through C10 hydrocarbons and hydrogen cyanide and hydrogen sulfide [103].

The denaphthized gas will enter the hydrogen sulfide absorber. Hydrogen sulfide and carbonyl sulfide levels in the sweetened product gas from the unit will be 0.1 ppm total sulfur; the carbon dioxide content will be 8 vol % [9]. Heat of absorption will be removed by refrigeration. Some of the absorbed acid gases will be removed from the methanol by multiflash distillation in the flash regenerator. The remaining acid gases will be stripped in the hot regenerator. One plant design calls for all of the acid-gas streams to be combined and delivered to the sulfur recovery plant [6]. A second plant is designed to give three different offgas streams from the Rectisol unit: (1) a 20% hydrogen sulfide content stream to the Claus plant, (2) a 1% hydrogen sulfide content stream for feed to the Stretford plant, and (3) a vent to the atmosphere containing approximately 30 ppm of sulfur dixoide. Aqueous condensates will be sent to the water treating area. Naphtha will be sent to storage and sold as a byproduct [3].

Typical compositions of the gases to and from the Rectisol unit and the composition of the flash gases from the flash and regenerating units are given in Tables XI-15 and XI-16, respectively.

After the recovery of refrigeration by countercurrent heat exchange with the feed gas, the sulfur-free gas (sweet gas) will leave the Rectisol unit for methanation. After methanation and first-stage compression, the methanation product gas will be returned to the Rectisol unit, where it will again be chilled, and will enter the carbon dioxide absorber, where the carbon dioxide concentration will be reduced to pipeline specifications. The dry purified high-BTU gas will be warmed and sent to the second-stage compression unit [6]. (Other plant designs do not use a Rectisol cleanup after methanation.)

TABLE XI-15

COMPOSITION AND PROPERTIES OF RECTISOL GAS

Constituent	Crude Gas to Rectisol (vol %)	Pure Gas from Rectisol (vol %)
Hydrogen	40.05	57.30
Carbon monoxide	20.20	28.40
Methane	8.84	11.38
Carbon dioxide	28.78	0.93
Nitrogen + argon	1.59	1.77
Nonmethane hydrocarbons	0.54	ND
Hydrogen sulfide	0.27	Not detectable
Carbonyl sulfide	<10 ppm	ND
Carbon disulfide	Not determined	ND
Mercaptans	20 ppm	ND
Total sulfur	ND	33 ppm
Temperature C (F)	30 (86)	15 (59)
Pressure, psig	365	330

ND = no data

Adapted from reference 103

TABLE XI-16

RECTISOL EXPANSION GASES

	Flash Gas (vol %)		
Constituent	High Pressure	Low Pressure	Atmospheric
Hydrogen	21.4	2.6	0.14
Carbon monoxide	18.2	4.8	0.0
Methane	11.4	7.2	0.9
Carbon dioxide	46.7	83.4	97.2
Nitrogen + argon	1.5	0.8	0.03
Nonmethane hydrocarbons	0.7	1.1	0.7
Hydrogen sulfide	0.30	0.46	0.83
Pressure, psig	180	55	1
Temperature C (F)	0 (32)	0 (32)	-5 (23)

Adapted from reference 103

(b) Manpower

Operating manpower for the Rectisol unit has been approximately 10 men per shift. Required maintenance was an average of 2.8 men per shift [103].

(c) Workplace Hazards

In the Rectisol unit there is a potential for exposure to naphtha, methanol, carbon monoxide, hydrogen sulfide, etc. Vapors evolved from naphtha are toxic because they contain hydrogen sulfide and hydrogen cyanide removed from the crude gas with the naphtha. Potential for exposure, apart from sample taking, is low because the equipment handling naphtha has proved to have a high service factor [12].

Vapor from the hot methanol is also toxic. In US plants, exposure potential should be low because methanol will be transferred from all tanks, heat exchangers, pumps, etc, into special slop tanks in cases of spills, leaks, or required maintenance. It is recommended that any vessel to be entered by personnel first be purged with steam [12].

Observations of three Rectisol units indicated that these plants are reliable and that there are few leaks [12,19,37]. In fact, exposed flanges were encased in a hard coating of ice that had formed from the moisture condensed from the air. This indicates the absence of leaks, as the leaking methanol or gas would have prevented ice formation.

Methanation

(a) General Discussion

The sweetened coal-derived synthesis gas contains a large quantity of carbon monoxide (low BTU value) and hydrogen (low BTU value per unit volume). For this gas to be enriched to pipeline-gas heating-value quality, the carbon monoxide and the hydrogen content must be reduced and the gas must be enriched in methane. Methane synthesis is accomplished by the following reactions:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O + 94{,}252 \text{ BTU}$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O + 77{,}714 \text{ BTU}$$

Both reactions are exothermic, liberating as much as 10% of the heating value of the total methane produced in the overall gasification process [113]. Other minor reactions taking place are the hydrogenation of ethylene to ethane and the hydrocracking of ethane to methane.

If the methanation reaction temperature is allowed to rise above 480 C (896 F), carbon will be deposited on the catalyst from the breakdown of either the carbon monoxide or the methane [114]. Furthermore, temperatures above 480 C will result in rapid catalyst deactivation.

The large amount of heat released is a major problem in methanation. This heat must be removed while the temperature is maintained between the limits of 260-480 C (500-896 F) at all points in the system. The various processes differ in the methods used to handle this problem [113].

Although the heats of reaction are not greatly influenced by temperature, the free energy and the equilibrium constants for methanation are quite sensitive to temperature. Thus, equilibrium methane yields are reduced critically at high temperatures, requiring that catalyst beds be operated at the lowest temperatures consistent with acceptable catalyst activity [115].

In the methanation section of the process, pressure does not appreciably affect methane yield. However, if the temperature exceeds 506 C (942 F), increasing pressure tends to decrease the minimum ratio of hydrogen to carbon monoxide required to prevent carbon deposition [116].

Considerable research has been done on catalyst materials. Only five--ruthenium, nickel, cobalt, iron, and molybdenum--have been identified as having commercial importance [117]. Ruthenium is very active but, because it is relatively rare, there is a question as to whether it would be available in the tonnages required for large-scale commercial use [115].

Nickel is inexpensive, very active, and highly selective in producing methane; it is therefore the catalyst of choice for most commercial operations. Cobalt is less active and less selective than nickel; iron is less active than cobalt and catalyzes carbon formation; molybdenum is less active than iron, fairly selective, and has the advantage of being resistant to sulfur [115].

Commercial nickel catalysts consist of 25-77 wt % nickel on a high-surface-area refractory support such as kieselguhr or alumina. Raney nickel is also a widely used catalyst. It is formed by the leaching of the aluminum with sodium hydroxide from an alloy composed of approximately 45 wt % nickel and 55 wt % aluminum. The result is a spongy catalyst that is very active in methanation [115].

Catalyst deactivation, a severe problem in catalytic methanation, can occur by any of several mechanisms [117].

1. $Ni + H_2S \longrightarrow NiS + H_2$
2. Ni (75 angstroms) --> Ni (1000 angstroms)
3. $2CO \longrightarrow C + CO_2$
   $CH_4 \longrightarrow C + 2H_2$
4. $3Ni + 2CO \longrightarrow Ni_3C + CO_2$
   $3Ni + CH_4 \longrightarrow Ni_3C + 2H_2$
5. $Ni + 4CO \longrightarrow Ni(CO)_4$
6. $Fe(CO)_5 \longrightarrow Fe + 5CO$

Reaction 1, the poisoning of the catalyst by sulfur, is common to all metallic catalysts except molybdenum. Strakey et al [117] tried to keep the sulfur concentration below 0.1 ppm to avoid irreversible contamination.

The sintering effect is represented by reaction 2. It is generally known that, at temperatures above 450 C (842 F), nickel crystallites grow in size, and the reduced surface area leads to reduced catalytic activity. Reaction 3 is the Boudouard reaction, in which elemental carbon is formed by the heterogeneous decomposition of carbon monoxide or methane during methane synthesis. Nickel carbide forms as a result of reaction 4. This reaction deactivates the catalyst material but is reversible; treatment with hydrogen at temperatures above 250 C (482 F) will reactivate a nickel carbide-deactivated catalyst [117]. A potentially serious reaction is the one that forms the volatile nickel carbonyl (reaction 5). Because this reaction occurs only at low temperatures, it is avoided by contacting the catalyst with synthesis gas at temperatures above 260 C (500 F) and maintaining that temperature until all carbon monoxide has been purged from the system [115].

The final reaction, reaction 6 above, is one that has its beginnings outside the reactor vessel. Iron carbonyl can form when carbon monoxide reacts, at high pressures and low temperatures (100 to 200 C), with carbon-steel piping. The iron carbonyl is carried into the reactor, where it decomposes and effectively deactivates the nickel catalyst by forming iron deposits. The use of less reactive piping material, such as stainless steel, will prevent the reaction [117].

(b) Process

One US plant design [6] requires two parallel trains of methanation equipment. Each train will be composed of two parallel lines of first-stage reactors and one line of second stage reactors. Feed gas entering the unit from gas purification will be heated by indirect heat exchange with the hot product-gas stream leaving the recycle loop. The hot feed gas will then be treated in a sulfur guard reactor before entering a synthesis loop consisting of a recycle methanation reactor, waste-heat recovery facilities, and a recycle compressor. The composition of feed gas for the recycle methanation reactor will be set by combining the fresh feed gas streams with the gas stream circulated by the recycle compressor. Since the reactor has excess catalyst, the reaction will proceed to near equilibrium. Thus, the temperature rise across the reactor can be controlled by adjusting the concentration of the reactants. Reaction heat from the recycle methanation reactor will be removed in the high- and low-pressure pressure waste-heat boilers [6].

Product gas from the recycle loop will be cooled in a feed/recycle product exchanger, and steam will be partially condensed in the recycle product cooler. The condensed water will be removed in a recycle product condensate separator. The gas stream leaving the separator will be reheated in a final-reactor feed/product heat exchanger before entering a final methanation reactor. Product gas leaving the reactor will first be cooled against the incoming feed and then cooled to near ambient temperature in a final product cooler. Condensed water will be separated in a final product condensate separator. Gas condensate from the two separators will be combined and returned to raw water treatment for reuse. (Table XI-17 and Fig XI-7).

(c) Workplace Hazards

The system described above may develop its own operating problems, including a plugged bed, plugged lines, leaking valves, or leaking pumps. Such leaks could release carbon monoxide, methane, and hydrogen into the workplace. However, the frequency and severity of such leaks should be far lower than in the upstream portion of the plant.

The formation of nickel carbonyl in the methanator reactor beds is of concern. However, if proper operating procedures are followed, few if any problems should develop. One startup procedure will include filling the methanation section with nitrogen before heating and then switching to hydrogen as the unit approaches operating temperature. Only after the unit is at operating temperature will the feed gas be introduced into the unit. During shutdown, the methanation unit will be flooded with hydrogen to eliminate carbon monoxide concentrations as the reactors cool down to the nickel carbonyl formation temperature range [9].

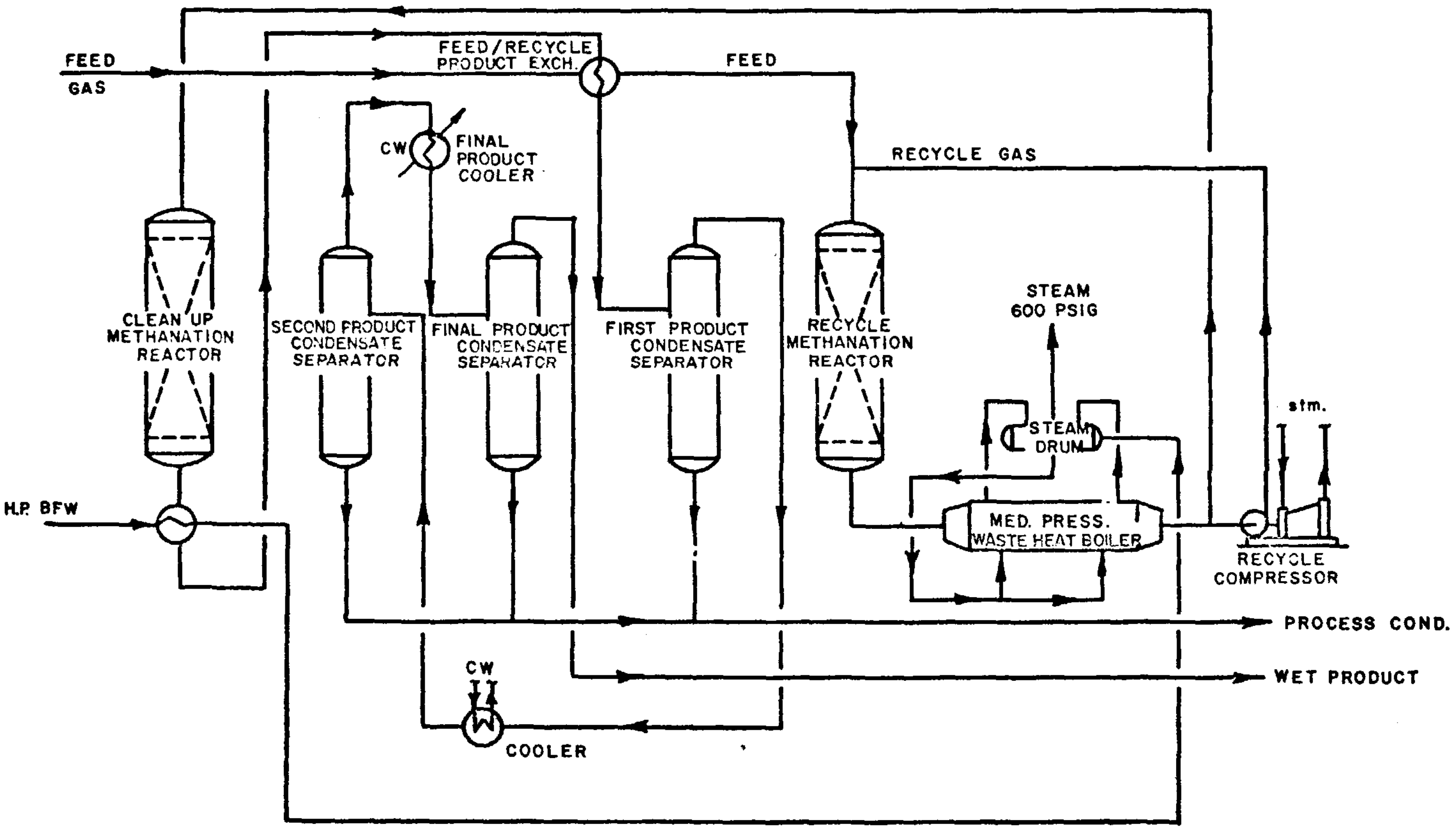


Figure XI-7

Flow Scheme for the Methanation Section

Adapted from Reference 6

TABLE XI-17

MATERIAL BALANCE FOR GASES IN THE METHANATION SECTION OF A GASIFICATION SYSTEM

Constituent	Feed Gas		Process Condensate	Wet Product Gas	
	scf/hr	Vol %	lb/hr	scf/hr	Vol %
Carbon dioxide	900,000	3.10	ND	206,000	1.81
Hydrogen sulfide	0.5	0.019 ppm	ND	ND	ND
Ethylene	130,000	0.44	ND	510	45 ppm
Carbon monoxide	4,907,000	16.92	ND	1150	101 ppm
Hydrogen	18,397,000	63.46	ND	474,000	4.15
Methane	4,331,000	14.94	ND	10,598,000	92.7
Ethane	200,000	0.69	ND	124,000	1.1
Nitrogen and argon	124,000	0.43	ND	26,000	0.23
Water vapor	ND	ND	ND	34	3 ppm
Propylene	290	10.0 ppm	ND	29	2.5 ppm
Propane	410	14.0 ppm	ND	ND	ND
Total sulfur	1.58	0.05 ppm	ND	ND	ND
Nitric oxide and nitrogen dioxide	3.12	0.11 ppm	ND	ND	ND
Ammonia	12.7	0.44 ppm	ND	ND	ND
Hydrogen cyanide	26.6	0.92 ppm	ND	5	0.44 ppm
Chlorine	0.60	0.02 ppm	ND	ND	ND
Oxygen	580	20.12 ppm	ND	ND	ND
Methanol	1190	40.9 ppm	ND	ND	ND

ND = no data

Adapted from reference 10

In all plans for commercial high-BTU plants discussed so far, the nickel catalyst from the methanation reactors will be returned to the manufacturer when it is deactivated, after the 2- to 3-year life expectancy. Loading and unloading of the nickel catalyst must be done either in the presence of water or in a reducing atmosphere to prevent excessive heating of the catalyst. Dusting must be prevented by the use of air ejectors [9,86].

Compression

Plans for one US plant call for methanated gas to be compressed from 225 to 500 pounds per square inch absolute (psia) and cooled to 32 C (90 F) in the first stage of a steam-turbine-driven centrifugal compressor before being sent to the second section of the Rectisol unit for final acid-gas removal and dehydration. This methanated gas is then to be returned to the second stage of the compressor, where it is to be boosted to pipeline pressure. The compressed gas is air cooled before delivery to the pipeline [6]. Other US plants will compress directly to pipeline pressure with no further acid gas removal required.

Ash

(a) General Discussion

The ash at the bottom of the gasifier directly above the grate has been cooled by incoming feed oxygen and steam to approximately 260 C (500 F) [10]. The rate of ash extraction is adjusted by varying the rate of rotation of the mechanical grate, which in turn is determined by the temperature of the ash leaving the base of the gasifier [17]. Since the ratio by weight of steam to oxygen in the feed to the gasifier is normally maintained between 2.5 and 3 to 1 and is determined by the analysis of the crude gas and the appearance of the ash when discharged, ash properties are important. For example, if the fusion temperature of the ash falls, it is necessary to alter the steam-to-oxygen ratio to avoid clinkering conditions within the gasifier [17]. (At a commercial plant, steam consumption was 36 lb/1000 scf of gas, while oxygen consumption was about 153 scf/1000 scf of crude gas [17].)

When the ash lockhopper is filled, the upper ash-lockhopper valve is closed and depressurization is begun by blowing the steam from the lockhopper first through a cyclone to remove solids and then through water to condense the steam. Any gases and vapors generated in this hopper pass through a cyclone for particulate and droplet removal and are vented to the atmosphere [3]. Solids from the cyclone and condensate from the water condenser are both discharged through the ash conveying system [9]. When the lockhopper is depressurized, the bottom valve is opened and the ash is discharged to a covered sluiceway [9], or the ash is water quenched and discharged to a conveyor [6]. The lockhopper is repressurized with steam in a sequence similar to that described for the coal lockhoppers. The ash is dewatered in settling tanks or by other means [3-6] and loaded into trucks for transportation to the mines, where it is disposed of in the original pit [3]. Excess liquid is sent to an ash-slurry thickener system [3-6]. Fine ash is sent to the mine [3,6] or to a settling pond for later recovery [5]. Water from the thickener is reused as quench water [6], evaporated [6], or sent to a clear-water pond before being returned to the gasifier sluiceways [6].

At one commercial plant [103], the gasifier ash is handled in a special type of hydraulic sluiceway. This sluiceway has a 6-inch water level and is enclosed. The gas exhausting above the sluice is mostly steam and is currently discharged to the atmosphere. The ash is carried by water to ash pumps and then pumped to a dewatering plant. The coarse ash is removed by screens and transported via a conveyor belt to a dump; classifiers and thickeners are used to settle the fine ash, after which the fine ash is also transported to disposal by conveyor belt. Power station ash is handled together with the gasifier ash. Disposal is above ground in an ash pile. The thickener overflow is further handled in slime dams [11,101].

The ash-handling step is part of water treatment, since the fine ash serves to absorb residual organics. Some of the water from the water-treatment facility is eventually returned for reuse in the ash sluiceway [11]; the remainder goes to a large lake.

The ash material, which is eventually collected for disposal, is used in part for various filling operations in road building. However, this represents only a small part of the total ash produced, and the remainder goes to the ash disposal facility [11].

(b) Workplace Hazards

(1) Ash Lockhoppers

The ash lockhopper is subjected to the most arduous duty of all equipment in a coal gasification plant. It is required to receive under high pressure hot and abrasive ash and clinker, and to store these until discharge at atmospheric pressure. It is similar to the coal lockhoppers, as can be seen in Figure XI-8 but is provided with a heat-protecting lining with steam cooling provided and the special depressurizing system described above. The ash lockhoppers are emptied approximately twice per hour and require 8 minutes for the emptying cycle [11].

The most troublesome part of the ash lockhopper is the top valve. This valve must close absolutely tight before the lockhopper is depressurized, as any leakage causes rapid erosion of the surfaces of the valve seat to the point where the rate of leakage becomes sufficient to prevent depressurization of the lockhopper. The lockhopper chamber must then be removed from the gasifier to renew the valve and seat. In one operating plant, the life of the top valves and seats was originally 2 months and has since been increased to 6 months. However, scheduled maintenance is performed once every 3 months. The maintenance procedures used on both top

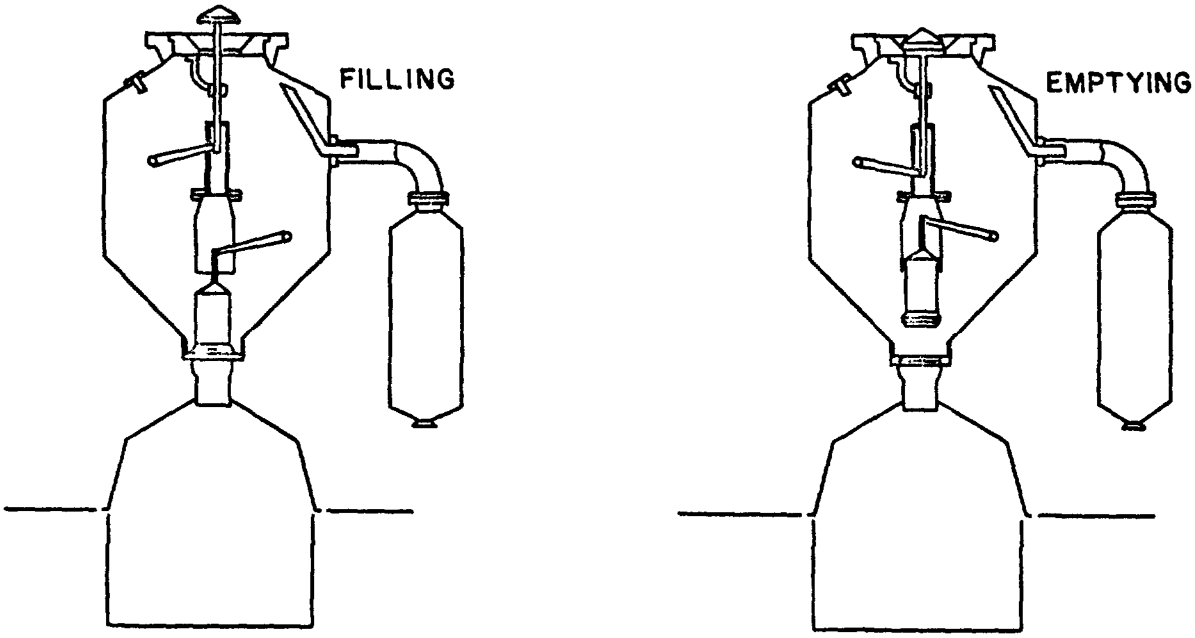


Figure XI-8

Ash Lock

Adapted from Reference 99

and bottom coal-lockhopper and ash-lockhopper valves involve building up the mating surfaces of the seats and discs with special hard-metal welding electrodes under controlled conditions to prevent crack formation. The redeveloped surfaces are then machined to close tolerances [11].

Many modifications have also been made to the depressurizing line leading from the interior of the ash lockhopper into the depressurizing vessel in order to reduce the rate of failure. Design and fabrication changes have now increased the life of this line to that of the top valve and seat [11].

(2) Leaks

The primary problem in the ash system is that of leaks in the lockhopper valves and/or the formation of plugs in the system. If the valves do leak, they will leak steam with dissolved oxygen into the workplace. A catastrophic failure would permit process gas to leak into the workplace.

(3) Hazardous Materials

The ash and char are essentially inert. However, because fine ash has a large surface area it may act as an oil or tar absorber if it is dumped into, or slurried with, water containing dissolved or suspended oil or tar. Similarly it may also concentrate dissolved trace elements from the recycled water. These hazardous materials, however, could be easily removed by leaching.

(4) Radioactivity

The mining, preparation, and combusion of coal can produce a radiological exposure in two ways. First, the destruction of the normal coal matrix results in a release to the atmosphere of a fraction of the radon-222 contained in it. Second, many radionuclides in the original coal become concentrated in the coal ash after combustion. Some of these can either (1) become airborne and be inhaled, (2) enter the human diet via deposition on plants or incorporation into drinking water. It is conceivable that the activity per unit mass of the ash can exceed normal values for these radionuclides in the local environment (ie, the radioactive material is concentrated) [118].

Certain coals in the Rocky Mountain region have been shown to contain uranium. Some of these coal deposits contain 0.0005 to 0.01% uranium, and deposits in local areas may contain higher percentages. Investigations by the US Geologic Survey showed that lignites may contain the most uranium and subbituminous coals the next largest concentrations. Uranium-bearing coal is present in Wyoming, Colorado, New Mexico, and southeastern Idaho. The higher ranked bituminous coals and anthracite of the central and eastern United States rarely contain more than 0.001% uranium [7]. Concentrations for Navajo coal are 0.000066% [3].

The impact of radionuclides contained in particulate matter that escapes from a gasification plant depends on a number of factors, including the effectiveness of particulate collection in the plant, population density and distribution, and the use of local biota for food. On the basis of a number of calculations in the literature on the analogous impact of particulate emissions from coal-fired power plants, this impact is expected to be exceedingly small. For example, it is estimated that the global dose commitment from 1 year's global production of electric energy by coal-fired power plants at the present installed capacity of 10 million MWe is equivalent to that arising from 30 minutes of exposure of the world population to natural radiation [118].

Measurements of gamma activity indicate that the content of radioactive elements in coal is generally less than that of sedimentary rocks [7]. Thus, assuming that there is reasonably efficient control of particulate emissions and that solids wastes are disposed of underground, no significant radiologic exposure in coal gasification plants is anticipated [118].

Tar and Gas-Liquor Separation

(a) General Discussion

The nomenclature currently used in the Lurgi-oriented high-BTU gasification industry defines three different types of liquids in the tar separation section. Tar oil is the hydrocarbon liquid that floats on the water; its specific gravity is less than 1.0. Gas liquor is water containing dissolved compounds that are primarily phenolic in nature. Tar is material that settles to the bottom of the separator, has a specific gravity greater than 1.0, and contains the solids. It is estimated that the tar will contain about 20% solids elutriated from the gasifier [12,17], although this will vary with coal size and gasifier operating conditions.

(b) Process

In commercial high-BTU coal gasification plants, condensate will be recovered from the reactor product gas in several different steps. First, the raw gas leaving the wash cooler will be cooled to about 190 C (374 F) in the waste-heat boilers to produce 112-psig steam. Some of the liquid condensed will be recycled to the wash cooler; the excess will be drawn off to the tar/gas-liquor separation unit. The gas-liquor will be let down to atmospheric pressure in an expansion vessel where gases dissolved at high pressure will be removed (Table XI-18). The tar will be settled out in a subsequent vessel.

The high-pressure raw gas leaving the waste heat boiler will be divided into two streams, half for shift conversion and half for shift-conversion bypass as discussed above. The bypass gas will first be cooled in a waste heat boiler generating steam at about 76 psig and then further cooled to generate 47 psig of steam. Gas-liquor and tar recovered from these cooling steps will be returned to the tar/gas-liquor separator. Crude gas will be further cooled, and gas-liquor and tar oil will be sent to a gas-liquor/tar-oil separator.

TABLE XI-18

TYPICAL COMPOSITION
OF GAS LIQUOR EXPANSION GAS

Constituent	Concentration (vol %)
Carbon dioxide	90
Carbon monoxide	4
Hydrogen	1
Hydrogen sulfide	1
Methane	4

Adapted from reference 10

The quantity of expansion gas is estimated to be 3.9 wt % of the gas-liquor [10]. At one commercial plant this expansion gas is water scrubbed to remove phenols, ammonia, cyanides, etc [119], before release to the atmosphere.

The converted gas from the shift-conversion process will pass through a parallel cooling section, from which all of the condensate will be sent to the gas-liquor/tar-oil separator. The tar oil-naphtha will be decanted and transported to storage or to distillation and fractionation. The gas-liquor will be pumped to the Phenosolvan unit for the recovery of phenol and ammonia. Gas-liquor decanted from the tar/gas-liquor separator will also be sent to the Phenosolvan unit. The tar containing solids elutriated from the gasifier will be sent to product storage or returned directly to the reactor. In plans for one US plant, expansion gas from the two gas-liquor separators and the coal lock vent gas will be recompressed and added back to the crude-gas stream going to the gas-cooling section [6].

At another US plant, all of the acid expansion-gas streams are to be sent to the boiler for incineration [3]. Figure XI-9 shows a schematic of the operation of the gas-liquor separation sections [17]. Table XI-19 shows the reported hydrocarbon recoveries from two very different coals. Table XI-20 lists the potential contaminants in the gas-liquor and Table XI-21 presents an analysis of the phenols found in the gas-liquor portion of the Westfield tar/gas-liquor separator and tar-oil/gas-liquor separator.

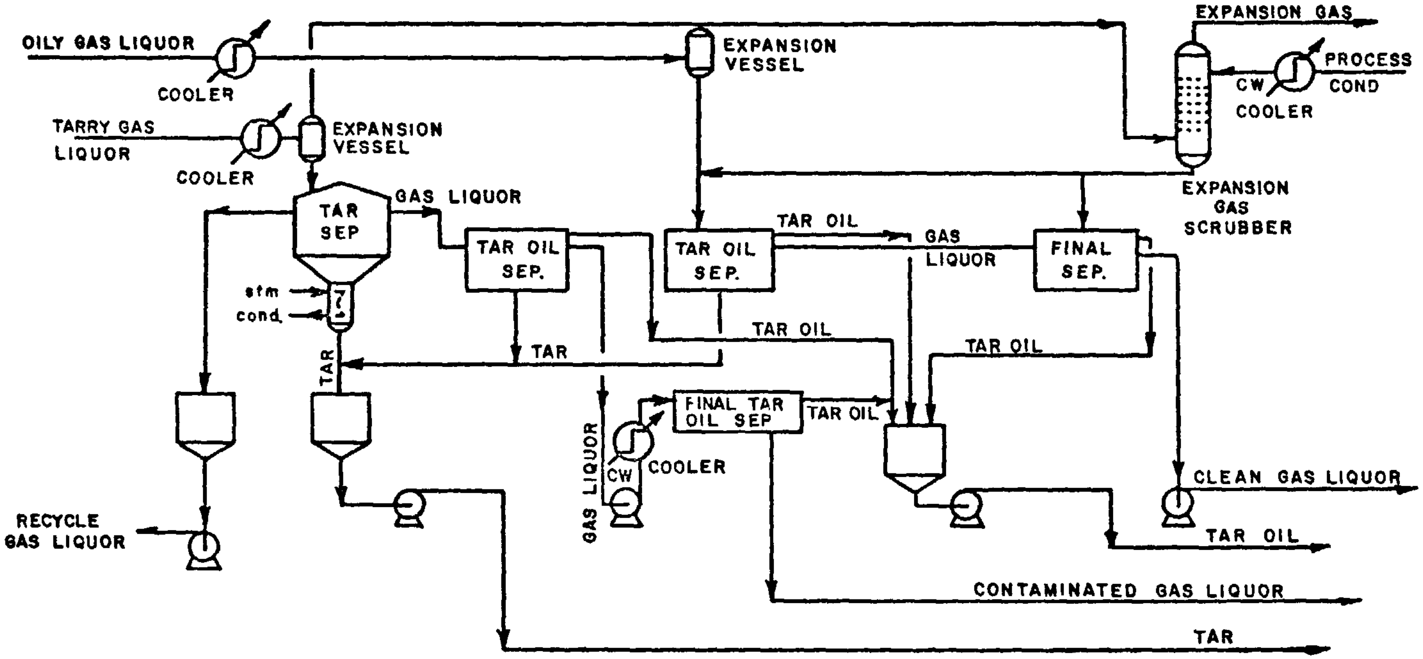


Figure XI-9
Flow Scheme for Gas Liquor Separation

Adapted from Reference 6

TABLE XI-19

REPORTED LIQUID HYDROCARBON RECOVERY FROM LURGI COAL GASIFICATION

Hydrocarbon	Westfield (a) (gal/ton coal)	SASOL (b) (gal/ton wet coal)
Tar	4.1	3.4
Oil	3.4	1.9
Benzene	3.0	1.3
Phenol	ND	1.0

(a) Adapted from reference 17
(b) Adapted from reference 103

ND = no data

TABLE XI-20

CONTAMINANTS FOUND IN AQUEOUS LAYERS OF GAS LIQUOR AT THE WESTFIELD WORKS

	Concentration (ppm)	
Constituent	Liquor Separated from Tar Phase	Liquor Separated from Oil Phase
Total ammonia (as NH_3)	1,795	9,597
Carbonate (as CO_3)	1,128	17,655
Sulfide as S	0.7	177
Thiosulfate (as S_2O_3)	9.0	15.8
Cyanide (as CN)	7.8	2.6
Thiocyanate (as CNS)	Nil	41.2
Ferrocyanide [as $Fe(CN)_6$]	4.2	10.5
Chloride (as Cl)	4.3	11.3
Sulfate (as SO_4)	90.6	74.1
Total iron (as Fe)	2.3	2.0
Fatty acids (as acetic acid)	696	228
Monohydric phenols	2,864	3,178
Dihydric phenols	2,917	1,869
Suspended solids	100	340
Fraction extractable by ether (tar, oil)	1,000-5,000	100-500
pH	9.4	8.0
Total alkalinity (as $CaCO_3$)	2500	5000
Calcium hardness (as $CaCO_3$)	Nil	Nil
Magnesium hardness (as $CaCO_3$)	Nil	Nil
Temperature, C (F)	71 (160)	27 (70)

Adapted from reference 17

TABLE XI-21

ANALYSIS OF PHENOLS IN AQUEOUS TAR LIQUOR AND TAR-OIL LIQUOR AT THE WESTFIELD WORKS, FEBRUARY 1962

Constituent	Concentration (ppm)	
	Tar Liquor	Oil Liquor
Phenols (total)	3,570	5,100
Monohydric phenols:	1,843	4,560
Phenol	1,260	3,100
o-Cresol	155	343
m-Cresol	170	422
p-Cresol	160	302
Total xylenols	100	393
Catechol	555	190
3-Methyl catechol	394	80
4-Methyl catechol	385	110
3,5-dimethyl catechol	Trace	Trace
3,6-dimethyl catechol	45	Trace
Resorcinol	272	176
5-Methyl resorcinol	40	64
4-Methyl resorcinol	36	ND
2,4-Dimethyl resorcinol	Trace	Trace

Adapted from reference 11

At one US plant, the tar from the tar/gas-liquor separator is to be used as binder to make briquettes from fine coal for feeding the gasifier [6]. At another US plant, it is planned to recycle the primary tar and dust into the top of the gasifier using a centrifugal tar-recycle pump and steam injection. The tar will be sufficiently viscous to require heating before being pumped. [3,9].

(c) Tar, Tar Oil, and Naphtha

As discussed above, tar from the gasifiers will be recovered in the gas-liquor separation unit and fed back to the gasifiers. A surge tank will be located within the separation area.

Tar oil condensed from the crude and the shifted gas in the gas-cooling section is to be recovered in two separate streams in the gas-liquor separation unit and stored in onsite tanks. These will be high- and low-sulfur tar oils. A portion of the low-sulfur oil (0.09 wt % sulfur) will be used for fuel in the steam superheater. The remaining low-sulfur oil will be blended with the high-sulfur oil and sold. The combined streams available for sale will have these approximate characteristics [3]:

Sulfur content, wt %	0.42-0.52
Heating value, BTU/lb (HHV)	17,250

The naphtha recovered in the Rectisol unit will be stored in tanks and sold. It will have the following characteristics [3]:

Sulfur content, Wt %	0.67
Heating value, BTU/lb (HHV)	18,580

(d) Workplace Hazards

As the tar and liquor condensed in the waste-heat boilers and precoolers are not only hot but also contain coal and ash dust, their letdown to atmospheric pressure results in high velocities and consequent severe erosion problems. At SASOL at one time, the level-control valves on the sumps of these vessels had a lifetime measured in days [99]. Today, the life has been improved by (1) depressurizing the liquid in stages through a series of expansion orifices, (2) improving the material of construction used for the valves, and (3) using a minimum-diameter control valve [12].

This process section may also be subject to surges, because of the potential loss of water at the wash cooler or because of plugging of the expansion-gas takeoff line. (While SASOL had considerable difficulty during the first years of operation with overflowing of separation tanks, the Ruhrgas plant in Dorsten reports very little difficulty. SASOL's new system has greatly reduced the severity of this problem [12,37,99].) Leaks in equipment may be expected in this area, especially in the high-pressure tar-recycle pump.

The designs for US plants call for a covered spill-collection system beneath the tar separation area. Liquids will probably be collected in a sump and pumped back into the tar separator [9,86].

Gas-Liquor Processing--Phenosolvan

(a) General Discussion

The gas-liquor treatment unit is designed to extract phenols and ammonia from contaminated water effluents from tar/gas-liquor separation, from tar-oil/gas-liquor separator, from gas purification, and, in one US design, from the fuel-gas production section [6]. In all cases currently on record in the United States, the proprietary Lurgi Phenosolvan process will be used. Two extraction solvents have been used commercially in this process. One plant uses normal butyl acetate [12], a chemical that in vapor form is an irritant, with a flashpoint of 70 C (158 F), and requiring a relatively low solvent-to-feed ratio. Designs for plants being considered in the United States call for the use of isopropyl ether, which is toxic, and has a flashpoint of -40 C (-40 F) [6,9,12].

(b) Process

In one US plant, the gas-liquor treatment area will be built in two parallel trains with a common liquor feed storage. This arrangement will permit uninterrupted coal gasifier operation during brief shutdowns of gas-liquor treating equipment [6].

Clean gas-liquor (ie, the gas-liquor from the tar-oil separator) and contaminated gas-liquor (ie, the gas-liquor from the tar/gas-liquor separator) are to be filtered in gravel (sand) filters to remove suspended matter [6]. Periodically this gravel will be backwashed with hot water, and the wash liquor will be returned to the gas-liquor separators. It is doubtful that it will be necessary to replace this filter material.

The filtered liquor will then be mixed with an organic solvent, ie, isopropyl ether, in the extractors. The phenols will dissolve in the solvent and the phenol-rich solvent extract will be collected for feed to the solvent distillation column, where crude phenol will be recovered as the bottoms product and the solvent as the overhead product. Recovered solvent will be separated from water by settling and then, with some makeup of fresh solvent, recycled to the extractors [6] (see Figure XI-10).

Before being heated and steam stripped, the lean liquor (raffinate) from the extractors will be stripped with fuel gas (or steam) to remove traces of solvent picked up in the extraction step. The resulting solvent-laden fuel gas will be scrubbed with crude phenol to recover the solvent (or the steam will be condensed). The phenol-solvent mixture will then be fractionated in the solvent-recovery stripper to produce crude phenol (see Table XI-22) and to collect the solvent for recycle to the extraction step [6].

TABLE XI-22

COMPOSITION OF CRUDE TAR ACIDS
RECOVERED FROM PHENOSOLVAN PROCESS

Constituent	Concentration (wt %)
Neutral oil	1
Pyridine bases	1-2
Phenol	38
_o_-Cresol	8
Mixed _m_- and _p_-cresols	14
Xylenols	13
Higher boiling tar acids	16
Pitch	8

Adapted from reference 119

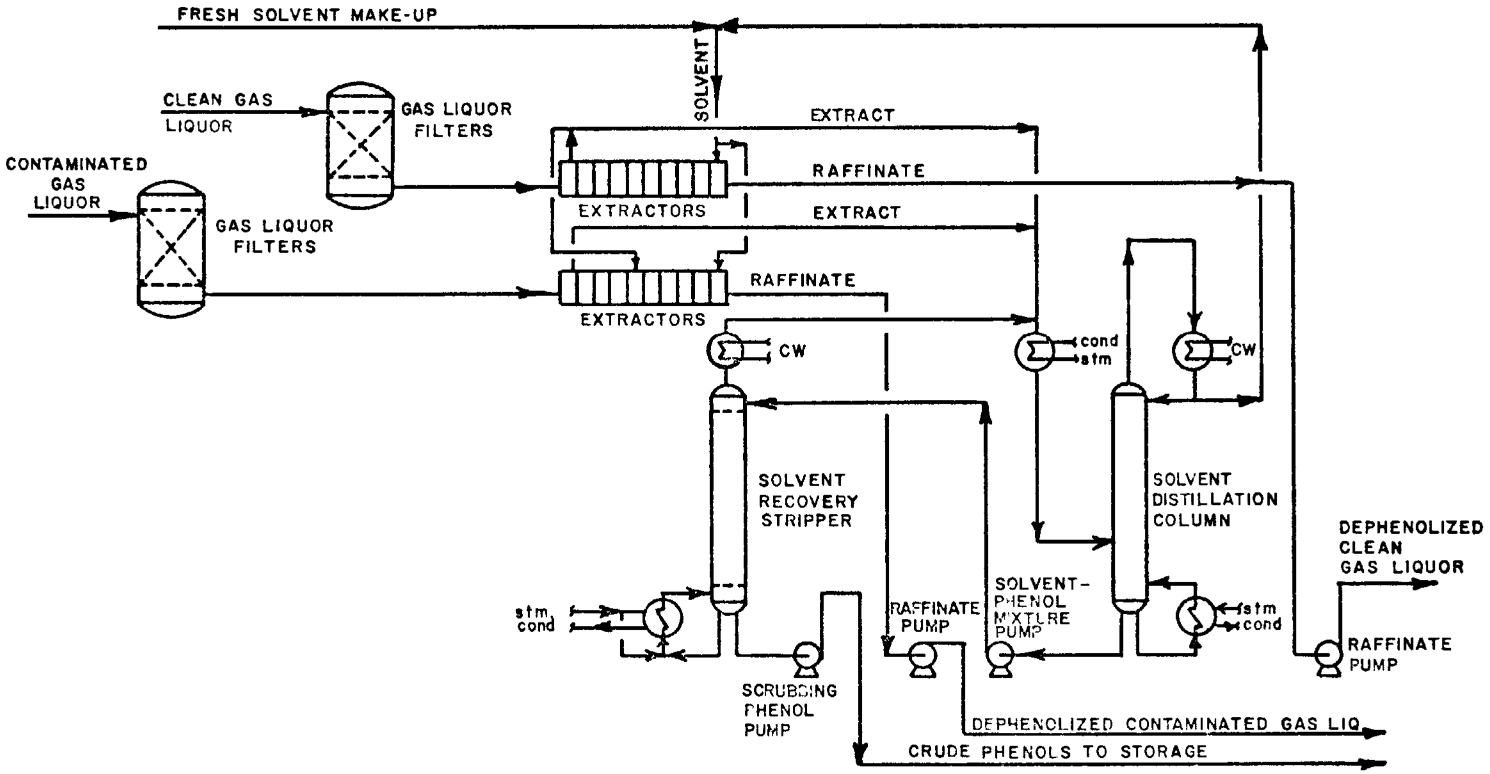


Figure XI-10

Flow Scheme for Phenol Extraction-Phenosolvan Process

Adapted from Reference 6

Solvent-free liquor will finally be heated and steam-stripped of carbon dioxide, hydrogen sulfide, and ammonia. The carbon dioxide and hydrogen sulfide will be removed separately from the ammonia and returned to the process for sulfur recovery [6]. At one US plant, the gas stream containing carbon dioxide and hydrogen sulfide is to be fed to the Stretford unit (see Sulfur Recovery section) for sulfur removal [3]. At another US plant, ammonia is to be stripped from the liquor and condensed as an aqueous solution of about 25 wt % ammonia [6]. If a market does not develop for this product, the ammonia vapor can be consumed as plant fuel [6]. (One plan calls for the production of anhydrous ammonia of 99.9% purity by a proprietary process [3].) Both sets of plans call for the treated effluent liquor from the ammonia stripper to be cooled and delivered to the biotreatment plant for further purification to render it suitable for cooling tower makeup [3,6]. Table XI-23 shows the performance of the Phenosolvan plant, giving both the input and the effluent concentrations [10,103].

(c) Manpower

Operating labor at one plant for the Phenosolvan unit averaged 3.1 men per shift on a 365-day/year operating basis. Maintenance manpower requirements, including calculated shutdown and cleanup, averaged 2.4 men per shift [103].

(d) Workplace Hazards

The Phenosolvan plant normally runs with few problems. However, as in any chemical operation, leaks can occur, especially in the vicinity of flanges, valves, and pumps. Isopropyl ether is toxic and flammable, and when exposed to light can form explosive peroxides. The phenolic materials can produce chemical burns, and they as well as the ammonia are toxic.

Cooling Water System

The cooling water system for one US plant will be based on water recirculation between process units and two evaporative cooling towers designed for minimum drift loss. The use of cooling water will be restricted to those heat-removal applications where air cooling would be impractical [3].

Each induced-draft cooling tower has a design circulation capacity of 32,000 gal/minute. Water returning from the process units will enter the tower at approximately 42 C (108 F). The warm water will be sprayed on the tower packing, and while the water flows downward, it is cooled to 21 C (70 F) by countercurrent airflow [3].

TABLE XI-23

PERFORMANCE OF THE PHENOSOLVAN PLANT (FOR COMBINED CLEAN AND CONTAMINATED GAS-LIQUOR STREAM)

Constituent	Concentration (ppm)
A. Input to Phenosolvan Process	
Phenols	3,250-4,000
Sodium	53
Ammonia (free)	600
Ammonia (fixed)	150-200
Suspended tar and oil	5,000
Cyanide ion	6
Total sulfide ion	228
Fatty acids (as acetic acid)	0.03%
Carbon dioxide	0.7%
B. Effluent (Feed to Biotreatment Plant)	
Phenols (steam volatile)	1
Phenols (bound)	60-160
Fatty acids (as acetic acid)	560
Ammonia (as N)	215
Hydrogen sulfide	12
Cyanide ion	1
Fluoride	56 mg/liter
Chloride	25
Calcium (as Ca)	18
Iron (as Fe)	1 mg/liter
Orthophosphate	2.5
Total dissolved solids	875
Suspended solids	21
COD (Chemical Oxygen Demand)	1,126
pH	8.4
Conductivity	1,000-1800 microSiemens/cm

Adapted from reference 103

Part of all of the required makeup water may be treated process water supplied from the biotreatment facility. Little corrosion is to be anticipated in such a system, as the ammonium salts will retard corrosion. The phenolic material will retard the growth of biologic contaminants.

Corrosion in the circulating cooling water system of one plant will be controlled by the injection of sulfuric acid to regulate the pH and inhibit corrosion. Algae growth will be controlled with chlorine. Continuous blowdown of the cooling tower will be used to control the solids concentration of the water. This blowdown will be directed to the holding pond for further reuse of the water [3].

Any oily process water, area drainage, and equipment drips will be collected separately from the Phenosolvan-processed water for processing in an oil separator and further treatment before reuse [3].

The reuse water system at one US plant will receive the de-oiled storm-basin effluent, demineralizer regeneration waste, treated sanitary waste effluent, biologically treated water in excess of that used for cooling makeup, utility water, cooling tower blowdown, and other minor streams [3].

Water retained in the holding pond will be reused for sulfur pelletizing, road wetting, ash sluiceway water, revegetation, and other mine uses. Because of the seasonal fluctuation of mine uses, such as irrigation, it will be necessary to supply additional water for peak use periods. The holding pond will have a volume of approximately 12.5 million cubic feet. It will be covered with an impervious synthetic membrane to prevent evaporation [3].

Steam and Power Generation

In one US plant, steam-generation facilities will consist of process-waste heat boilers and gas-fired power boilers. Generally, waste-heat boilers will provide heating and process reaction steam, while power boilers will provide motive-power steam. Power will be generated by an automatic extraction turbine on the power boilers. Air-cooled condensers will be used to minimize cooling water requirements. The gas-fired power boilers will normally use hot exhaust gas from the gas turbines for combustion air, but forced-draft fans will be provided to supply fresh air in the event the gas turbine is off line [6].

Three power boilers and electrical generators will each have a capacity of 50% of normal plant requirements. The 1500-psig, 510 C (950 F) steam from the power boilers will be used in an automatic extraction turbine driving electrical generators producing 57,000 kW. Exhaust steam will be condensed. Extraction steam at 500 psig will be used at various compressor drives throughout the plant [6].

One US company plans to provide a low-BTU fuel, gasified in airblown gasifiers operating at 285 psig [6]. Raw gas will be desulfurized by treatment in a hot potassium carbonate system. Quench, cooling, and tar/gas-liquor separation will follow the same schemes as described for the high-BTU plant. Product fuel gas will have a higher heating value of about 230 BTU/scf (dry). Flue gases from fuel-gas combustion will have 0.16 pound or less of sulfur dioxide per million BTU of fuel input. Ten gasifiers, nine operating and one spare, will be required for fuel-gas production [6].

Another US company plans to use high-pressure steam for the coal gasification plant, which is produced by coal-fired boilers burning coal fines [3]. The boilers will be fired with 3,868 tons/day of coal fines, to produce 3 million lb/hour of 1500-psig, 510 C (950 F) steam. The coal fed to the boilers will be screened and washed 4 x 48 mesh coal fines. Fly ash and compounds removed from the boiler flue gases will be collected in separate and independent systems. Exhaust gases from the boiler economizer will pass through a hot electrostatic precipitator to remove at least 99% of the fly ash and then through a scrubbing system to remove 90% of the sulfur compounds and virtually all of the remaining ash [3].

Oxygen Plant

The oxygen plant designs for two major US operations are similar. The first oxygen plant will produce 6,000 tons/day of 98% minimum purity vapor-phase oxygen while the second produces 99.8% minimum purity oxygen. At the first operation liquid storage and transfer pumping are planned and will be sized for 2,000 tons total (ie, 8-hour supply). A total of 633,000 actual cubic feet per minute (acfm) of atmospheric air will be filtered and compressed to 99 psi in three parallel low-BTU gas-turbine/steam-turbine centrifugal compressors of approximately 33,000 hp each [6].

The compressed air entering the cold box will be cooled to liquefaction temperature by a combination of heat exchange and expansion in a conventional air separation cycle. Once in the liquid state, oxygen and nitrogen will be separated by fractionation. The nitrogen (plus a small quantity of moisture, carbon dioxide, and oxygen) will be regasified in the heat-exchange process and its energy utilized before rejection to the atmosphere. The liquid oxygen will be taken first to provide liquid storage when required and then gasified to feed the six parallel-operating steam-turbine-driven oxygen compressors. These centrifugal units, each capable of compressing 12,000 tons/day, will raise the pressure level to 500 psig and deliver 5,620 tons/day of oxygen to the Lurgi coal gasifiers. The expansion process in the cold boxes will generate a total of about 500 kW each at full capacity [6].

Byproduct Storage

Typical byproduct storage provisions are presented in Table XI-24.

TABLE XI-24

TYPICAL STORAGE PROVISIONS

Constituent	Number of Tanks	Capacity Volume (barrels)	Time
Crude phenol	2	5,500	2 wk
Tar-oil naphtha	2	20,000	2 wk
Tar	2	40,000	2 wk
Naphtha product	2	12,000	2 wk
Ammonia solution	2	5,500	2 days
Sodium hydroxide	2	12-ft diameter x 50 ft (horizontal)	2 wk
Methanol	2	12-ft diameter x 50 ft (horizontal)	2 wk
Demineralized water	1	25,000	4 hr
Cold lime-treated water	2	25,000	12 hr
Condensate	2	25,000	6 hr
Liquid wastes	1	500	ND

ND = no data

Adapted from reference 6

Sulfur Recovery

(a) General Discussion

Each of the three commercial coal gasification processes most intensely studied in the development of this document has a distinct method for recovering the sulfur from the various process streams [3,4,6]. All three plants will use the Stretford process to recover sulfur from lean hydrogen sulfide-containing streams. Two of the designs will use the Claus process to recover sulfur from a concentrated sulfur stream. [3,4]. The third plant will utilize low-BTU coal gasification to produce clean fuel gas to eliminate the need for stack-gas scrubbing [6]; the other two plants will use variations of stack-gas scrubbing schemes to remove sulfur dioxide from tail gas and furnace effluent gas [3,4]. The Claus and Stretford units are discussed below.

(b) Process

(1) Claus Process

The Claus process is an essentially atmospheric pressure process operating in the following manner: The acid gas, containing 15-90 mole % hydrogen sulfide, is combined with sufficient air to burn one-third of the total hydrogen sulfide to sulfur dioxide and all of the hydrocarbons to carbon dioxide. (Alternatively, one-third of the total acid gas is burned and recombined with the unburned gas.) A part of the hot gas is cooled, and a portion bypasses the coolers so that the reactor temperatures can be maintained [120]. (Each reactor inlet temperature must be above the sulfur dewpoint, preferably 230 C [450 F], to avoid condensation of the liquid sulfur in the catalyst bed. Condensation could cause plugging and catalyst deactivation [121].)

In the reactor the sulfur dioxide and hydrogen sulfide react to form sulfur:

$$2H_2S + SO_2 \longrightarrow 1.5S_2 + 2H_2O$$

From the catalytic reactor the hot [370 - 400 C (698 - 752 F)] gases flow into the condenser, where they are cooled to 150 C (302 F) and the liquid sulfur is removed. Sulfur must be removed from the condenser in the 300 F range. [Because of a phase change at 160 C (320 F), the liquid sulfur increases rapidly in viscosity with increasing temperature and cannot be removed from the condenser.] Cooled gases can then be recombined with the second hot-gas bypass flow to balance temperatures at the entrance of the second reactor inlet. Product gas should contain only 0.5-10% of the hydrogen sulfide fed into the unit [121].

Claus process variations can accommodate the various concentrations of acid-gas feeds, with the optimum Claus process depending primarily on the hydrogen sulfide concentration in the feed [122].

One US plant's design and operating control features that contribute to maintaining high sulfur recovery include (1) the three converter configurations, (2) the small amount of hydrocarbons in the feed, (3) no water vapor in the feed, (4) high-temperature burner operation with two-thirds feed bypass, (5) computer control, (6) use of a high-activity catalyst bed to decompose at least 85% of any carbonyl sulfide and carbon disulfide formed, and (7) the minimization of sulfur mist entrainment. To insure constant availability of the Claus process for sulfur recovery, this gasification plant will include two complete 100% capacity units, one operating and one standby [3].

The Claus plant will treat the offgas streams from the Rectisol process. The composition of the combined gases from the naphtha extractor and the hydrocarbon removal unit that would be treated is shown in Table XI-25.

TABLE XI-25

ESTIMATED CLAUS PLANT FEED FROM THE RECTISOL PROCESS

Constituent	Concentration (vol %)
Carbon dioxide	34.2
Hydrogen sulfide	64.0
Hydrogen cyanide	0.2
Carbonyl sulfide	Trace
Hydrocarbons	1.6

Adapted from reference 3

Of the sulfur fed to the Claus unit, 95% will be recovered; 90% of the remaining sulfur in the Claus tail gas will be removed by the flue-gas desulfurization unit, for an overall sulfur removal of 99.5%. The elemental sulfur will be pelletized and stored on the ground within a retaining curb to prevent surface runoff or it may be stored in a lined, heated pit [4,6].

The types and amounts of hydrocarbons present in the acid gas entering the burner have an effect on the carbon content and hence the color of the sulfur product. Aromatics and olefins form carbon more readily than do paraffins. Also, the amount of carbonyl sulfide formed in the high-temperature region is believed to depend on the amounts of carbon dioxide and hydrocarbons in the burner feed. Some of the reactions that may occur are the following:

1. $CO_2 + H_2S \longrightarrow COS + H_2O$
2. $CO + 1/2S_2 \longrightarrow COS$
3. $2COS \longrightarrow CO_2 + CS_2$
4. $COS + H_2S \longrightarrow CS_2 + H_2O$
5. $2CO + S_2 \longrightarrow CO_2 + CS_2$
6. $C + S_2 \longrightarrow CS_2$
7. $2COS + 3O_2 \longrightarrow 2SO_2 + 2\ CO_2$
8. $2COS + O_2 \longrightarrow 2CO_2 + S_2$
9. $2COS + SO_2 \longrightarrow 3/2S_2 + 2CO_2$
10. $CS_2 + SO_2 \longrightarrow 3/2\ S_2 + CO_2$

Deactivation of Claus catalysts (bauxite) may be caused by carbonaceous deposits, sulfur condensation, sulfur vapor adsorption, thermal degradation, and sulfate formation. Unfortunately, bauxite contains both iron and silica compounds which facilitate catalyst deactivation. Porocel is an improved form of bauxite, which is made from high-grade activated bauxite and contains 88-92% alumina. Pure activated alumina is being proposed as a still better catalyst. In most cases a catalyst life of 2-5 years can be expected [10].

(2) Stretford Process

The Stretford process is capable of operating on acid gases containing only low concentrations of hydrogen sulfide. In this process, the 50 C (120 F) acid gas is washed countercurrently by the Stretford solution, which consists of sodium carbonate, sodium metavanadate, an anthraquinone disulfonate activator, citric acid, and traces of chelated iron; the pH is 8.5. The hydrogen sulfide in the acid gas reacts with the vanadate as follows:

$$4NaVO_3 + 2H_2S \longrightarrow Na_2V_4O_9 + 2S + 2NaOH + H_2O$$

The reduced vanadate is then oxidized by the anthraquinone disulfonate activator, which in turn is reoxidized by air sparging. The air also acts as a flotation agent in frothing out the fine-grained sulfur product. The slurry of solid sulfur is filtered, the filtrate is returned to the process, and the sulfur is collected in a molten-sulfur storage tank [10,113,121,123].

Unfortunately, carbonyl sulfide and carbon disulfide are not recovered by the Stretford process [3]. Effluent from the top of the Stretford absorber tower will be primarily carbon dioxide but will contain about 10 ppm by volume of hydrogen sulfide [6], and it has been estimated that it will contain 67 ppm carbonyl sulfide and a trace of carbon disulfide. The total hydrocarbon concentration is 9,400 ppm by volume (if methane and ethane are excluded, the concentration is 2,000 ppm by volume), and carbon monoxide emissions are 1,500 ppm by volume [10]. At one plant effluent gas streams will be incinerated in the coal-fine boilers to eliminate hydrocarbons. The gas will subsequently be treated in the stack-gas treating unit to increase the overall sulfur-removal efficiency to over 99.8% [3].

In the same plant design [3], the Stretford process will treat the offgases from the Phenosolvan and Rectisol processes. The composition of the gases to be treated is shown in Table XI-26.

In the Stretford unit, there is a small byproduct conversion of hydrogen sulfide to thiosulfate. Through proper design and the use of special additives, the conversion to thiosulfate can be kept down to the 1% to 2% level. Accumulated thiosulfate must be purged. A typical Stretford solution purge contains sodium salts of anthraquinone disulfonate, metavanadate, citrate, thiosulfate, and thiocyanate. At the one plant this purge stream will be sent to a recovery unit system in order to reuse the chemicals [10,86].

TABLE XI-26

ESTIMATED STRETFORD PLANT FEED

Constituent	From Phenosolvan (Vol %)	From Rectisol (Vol %)
Carbon dioxide	85.2	97.4
Hydrogen sulfide	1.2	0.9
Hydrogen cyanide	ND	Trace
Carbonyl sulfide	Trace	ND
Nitrous oxide	13.2	ND
Others	0.4	1.7

ND = no data

Adapted from reference 3

Tail Gases

In the Lurgi gasification process, which may include both a Claus and a Stretford unit for sulfur recovery, tail gases from these units will contain both hydrocarbons and sulfur compounds. There are a number of ways to treat these vent gases to obtain a final gas with an acceptable concentration of pollutants.

One way to destroy the hydrocarbons and recover the sulfur is incineration. The hydrocarbons are converted to carbon dioxide and water, and sulfur compounds are oxidized to sulfur dioxide, which is more easily recovered. However, incineration is expensive in terms of fuel cost because of the large volume of gas to be treated and the still larger volume of gas from which to recover the sulfur.

Another way would be to chemically remove the sulfur compounds from the gases to a point where the gases are no longer considered a health hazard or an air pollutant. Since the vent gases from a well-operated Stretford unit contain only about 10 ppm of hydrogen sulfide and somewhat larger amounts of carbonyl sulfide and carbon disulfide, a process in which the sulfur-rich gases are first treated in a Claus unit and then in a Stretford unit will reduce the sulfur in the vent gases to an acceptable limit [6]. Such a combined treatment will also reduce the volume of gases to be incinerated if the hydrocarbon content of the vent gases is considered objectionable.

Both the Beavon and the Scot processes chemically convert the sulfur compounds to hydrogen sulfide and then treat the gases to remove the hydrogen sulfide. In the Scot process, the hydrogen sulfide is absorbed in an alkanolamine solution and recycled to the Claus unit [37]. This process, however, requires the incineration of the tail gases from the Claus unit because of the high hydrogen sulfide content.

In the Beavon process, the sulfur compounds in the gases from the Claus unit are converted to hydrogen sulfide, which is recovered in the Stretford unit. Gases from the Beavon unit could add about 15% to the load on the Stretford unit.

Table XI-27 shows a material balance for the Claus-Beavon-Stretford process anticipated in the one US plant. The stream from the Rectisol unit, rich in hydrogen sulfide, is sent to a Claus unit along with a stoichiometric amount of air to convert one-third of the total sulfur to sulfur dioxide. Molten sulfur is the product of this operation. The offgases from the Claus unit are mixed with hydrogen and passed over a heated catalyst to convert all the sulfur to hydrogen sulfide in a Beavon reactor. The hydrogen sulfide is absorbed in a unit containing Stretford solution. The unabsorbed gases are vented to the atmosphere.

The hydrogen sulfide enriched Stretford solution from the Beavon reactor is sent to the Stretford unit where it becomes part of the Stretford liquor used to absorb the hydrogen sulfide in the lean hydrogen sulfide gases from the Rectisol unit and from the tar and ammonia recovery plant. The coal-lockhopper gases as well as other gases containing hydrogen sulfide are also treated in the Stretford unit. Elemental sulfur is recovered from the Stretford unit, and the offgases are vented.

From Table XI-27 it is apparent that the vent gases from the Beavon unit, with about 10 ppm by volume of hydrogen sulfide and about 150 ppm by volume of total sulfur with practically no hydrocarbons, poses little health hazard. Although the hydrogen sulfide and the total sulfur in the offgases from the Stretford unit are somewhat less than in the gases from the Beavon plant, this gas has an appreciable hydrocarbon content. The vented gases from the Stretford unit may have to be incinerated.

TABLE XI-27

MATERIAL BALANCE FOR THE CLAUS-BEAVON-STRETFORD
SULFUR RECOVERY PROCESS (LB/HR)

	CLAUS		BEAVON		STRETFORD	
Constituent	In from Rectisol II	Out to Beavon	In from Claus	Vented to atmosphere	In (a)	Vented to atmosphere
Carbon dioxide	75,064	75,275	75,275	75,489	657,507	757,507
Hydrogen sulfide	10,456	508	508	1	6,217 (b)	7
Carbonyl sulfide	112	343	343	21	110	110
Carbon disulfide	4	ND	ND	4	4	4
Ethylene	44	ND	ND	ND	1,347	1,347
Carbon monoxide	1	ND	ND	ND	4,055	4,055
Hydrogen	ND	ND	50 (c)	2	350	350
Methane	4	ND	ND	ND	1,957	1,957
Ethane	70	ND	ND	ND	2,164 (e)	2,164
Oxygen	5,261 (d)	ND	ND	ND	17,960 (e)	14,370
Nitrogen	17,310 (d)	17,310	17,310	17,310	65,480	65,480
Water vapor	ND	5,451	5,451	5,600	10,900	14,945
Methanol	ND	ND	ND	ND	ND	ND
Sulfur dioxide (f)	ND	528	3	ND	ND	ND

(a) Stretford solution from Beavon plus lean gas from Rectisol II, gas from coal lockhopper, and gases from tar and ammonia recovery

(b) Includes 1,035 lb/hr of hydrogen sulfide dissolved in Stretford solution from the Beavon unit

(c) Hydrogen added to gas stream

(d) Air added

(e) Air for catalyst regeneration

(f) Solid sulfur is recovered from gas stream at a rated 8,900 lb/hr from the Claus unit and 6,900 lb/hr from the Stretford unit

Adapted from reference 10

ND = no data

XII. APPENDIX II

PROCESS DESCRIPTION: LOW- OR MEDIUM-BTU COAL GASIFICATION UTILIZING BITUMINOUS COAL OR LOWER RANKED FEEDSTOCKS

The gasification of bituminous coal produces tars, which must be removed before the product gas can be utilized. The sulfur content ranges from 0.3 to over 5.5% by weight, and hence in many cases sulfur recovery units must be included for the treatment of the product gas. The analysis of a typical bituminous coal is shown in Table XII-1 [15].

TABLE XII-1

ANALYSIS OF A TYPICAL BITUMINOUS COAL

Constituent	Concentration (wt %)
Ash	3.6
Carbon	57.4
Moisture	3.1
Volatile matter	35.9
Heating Value	14,070 BTU/lb

Adapted from reference 15

Gas cleanup systems may vary from a simple cyclone to remove particulates when the product use can tolerate both tar and sulfur to the sophisticated system shown previously in Chapter III (Figure III-5) [102].

Low-BTU, low-pressure processes use an interlocking disc valve system or rotary barrel valve as part of the coal feed system. These feed systems result in the loss of only a small quantity of product gas to the atmosphere above the coal storage bin [15].

The raw product gas that comes off the top of the gasifier passes through a lined cyclone where elutriated coal dust is removed. The gas then passes through a water spray tower where the oils and tars are condensed and removed. The gas then passes through electrostatic precipitators where particulates and the remaining tar are removed. Sulfur is then removed from the gas by a Holmes-Stretford desulfurization system. In the system shown, the clean product gas (Table XII-2) is stored for future use [102].

TABLE XII-2

TYPICAL PRODUCT GAS ANALYSIS

Constituent	Concentration (vol %)
Carbon dioxide	4.2
Carbon monoxide	26.6
Ethane	0.3
Ethylene	0.2
Hydrogen	16.0
Methane	1.9
Nitrogen	50.9
Heating value	164 BTU/scf

Adapted from reference 15

Excess water from the water seal on the gas pipe in the primary, secondary, and high-pressure scrubbers is collected in a single decanter. A portion of the decanter water (gas-liquor) is sent to the cooling tower and then recycled to the tertiary high-pressure scrubber and used to maintain a gas temperature of 50 C (120 F). The decanter water is recycled from the decanter to all sprays, both in the primary and secondary scrubbers, the water seal, and the gas lines. Water condensed from steam used in gasifying the coal is collected in two 5,000-gallon tanks. When the water level becomes too high, steam coils are activated and the excess water is evaporated to the atmosphere [15]. In no case should any of the water in the process be sent to the sewer or otherwise discharged. Thus, the water should always contain an equilibrium quantity of contaminants including phenols and suspended tars and oils, and lesser amounts of ammonia, cyanide, phosphorus, nitrate, and trace metals [15]. It is assumed that any volatile contaminant in the water is discharged to the atmosphere with the evaporated water or, if above the saturation limits, is condensed into the tar at the bottom of the decanter. This tar is pumped to a nearby steam plant, where it is burned in a boiler.

Because of the products generated in the bituminous gasifier, the operator is exposed to hazardous substances when testing the bed through pokeholes (see Chapter XIII for detailed procedure). In one installation, a ring around the inside of the pokehole directs a steam jet downward into the gasifier and thus reduces emission through the pokehole [124].

The operation is generally run by one man per shift. The operator is located on the operating floor at the top of the gasifier but under the coal feed bins. Because the coal feed operation is automatic, the actual duration of direct exposure to producer gas is generally approximately 2-3 hours per shift [16].

XIII. APPENDIX III

PROCESS DESCRIPTION: COAL GASIFICATION (LOW- or MEDIUM- BTU) UTILIZING ANTHRACITE FEEDSTOCK OR VERY HIGH TEMPERATURES

Plants Utilizing Anthracite Coal Feedstock

A typical analysis of anthracite coal is shown in Table XIII-1 [14]. The low content of both sulfur and volatile matter significantly reduces the hazard of exposure to hydrogen sulfide, sulfur oxides, and tars in plants using anthracite feedstock as compared with exposures in plants using bituminous or lower ranked feedstocks.

TABLE XIII-1

ANALYSIS OF ANTHRACITE COAL--WASHED AND SIZED

Constituent	Content (Wt %)
Ash	12.00
Carbon	78.32
Moisture	5.44
Sulfur	0.47
Volatile matter	4.23
Heating value	12,190 BTU/lb

Adapted from reference 14

Figure XIII-1 is a diagram of the fixed-bed process at a plant [14] that uses anthracite feedstock. The gasifier has operated at levels varying from as low as 3 tons of coal per day, producing approximately 60,000 scf of natural gas equivalent, to as high as 24 tons of coal per day, producing 500,000 scf of natural gas equivalent [14].

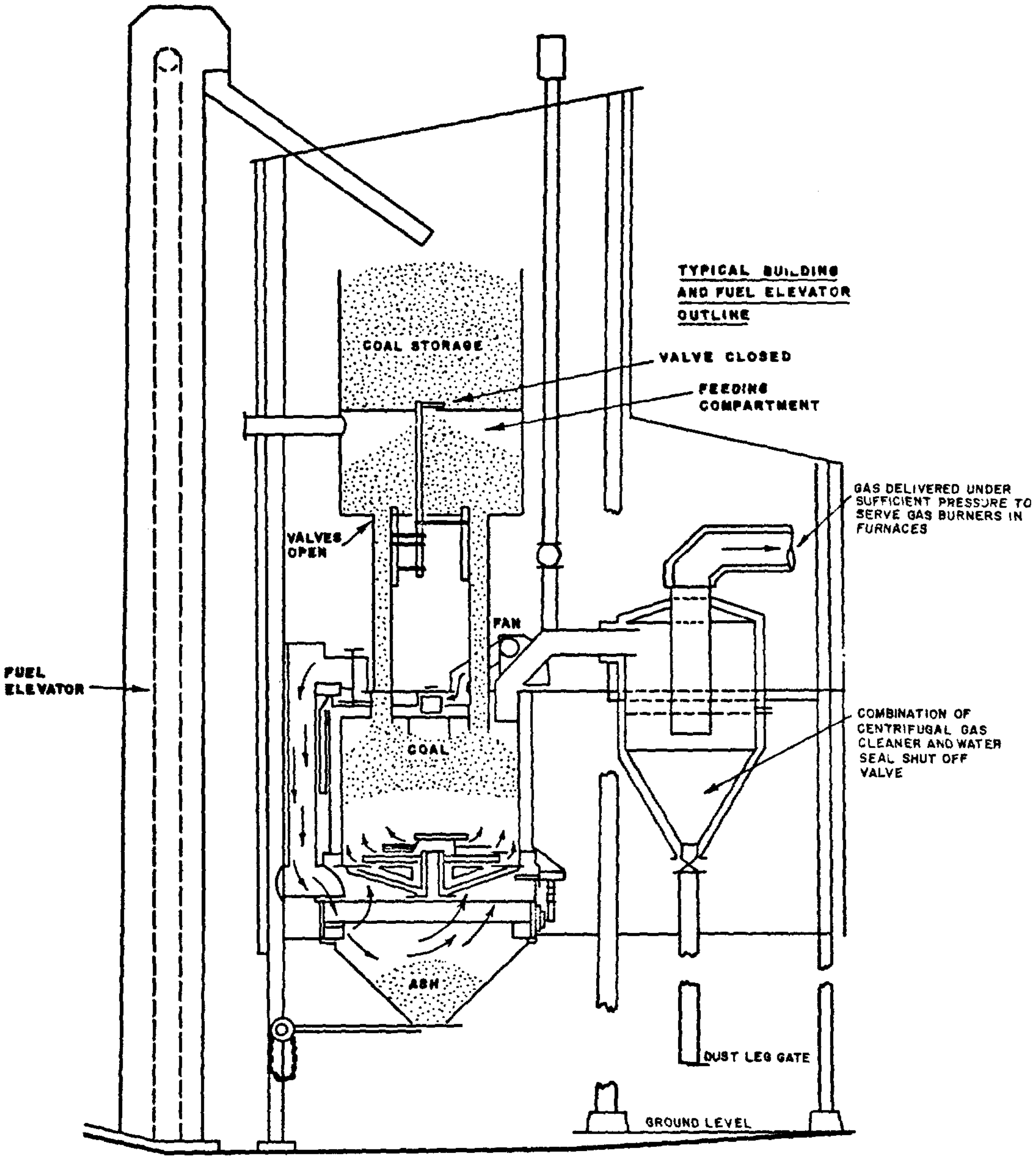


Figure XIII-1

Wellman-Galusha Standard Type Producer

Adapted from Reference 14

A fuel elevator is used to move the coal into the coal storage bin (capacity approximately 25 tons), which is the upper section of a two-compartment bin. The lower section, the feeding compartment (capacity approximately 5 tons), is separated from the coal storage bin by disc valves. Similar disc valves cover the openings to each of the heavy-steel feedpipes (approximately 1 foot in diameter and 12 feet long) connecting the feeding compartment to the gasifier. A simple interlocking mechanism prevents the opening of the upper valves unless all the lower valves are tightly closed, and vice versa.

The coal feed system is operated manually as needed. Coal fills the feeding compartment, the feed pipes and the gasifier via an automatic gravity feed system. To fill the coal feeding compartment, the disc valves between the coal storage bin and the feeding compartment are opened, and the disc valves between the feeding compartment and the gasifier are closed. To fill the feedpipes and the gasifier, the operator reverses the procedure, opening the disc valve between the feeding compartment and the gasifier, and closing the valves between the coal storage bin and the feeding compartment. The escape of product gas is minimized because of the coal in the feed system and the low operating pressure (5-7 inches water column) in the gasifier. The operating pressure decreases to 3 inches water column when a gas compressor is used.

The product gas fills the voids in the feed pipes. When the disc valves between the feeding compartment and the gasifier are opened, some of this gas escapes into the feeding compartment. When the disc valves between the feeding compartment and the coal storage bin are opened, some of the product gas escapes through the coal storage bin into the upper-floor work area.

The gas-making chamber is completely water jacketed. The inner wall is 1-inch-thick steel plate and requires no brick lining. Waste heat in the water jacket generates the process steam [actually water vapor at about 180 F (82 C)]. A direct-drive fan supplies the air required by the gasifier. On its way to the firebed, this air acquires moisture from the steaming water at the top of the jacket. Saturation is automatically controlled by regulating the rate of supply of jacketed water to maintain the desired saturation temperature of 140-150 F (60-66 C).

Startup can be performed with the gasifier either cold or hot. For cold startup, wicker boxes are located at various positions on the grate, and an ashbed is built on the grate and around the wicker boxes. An oil-saturated wick is inserted into the wicker boxes, so that it may be lighted from the ash bin. Oil-saturated charcoal is placed on the ashbed and on the wicker boxes. The gasifier is then loaded with anthracite. The blower is started, at a rate that produces a very low air flow through the bed. The ash-pit door is closed, the wicks are lighted, and the ashpit slide valve is closed. The air flowrate is set at a 1.0-inch water column for 1.5 hours and then increased to a 3.0-inch water column for 1 hour; the gasifier product is exhausted to the atmosphere [14]. After 3 hours, the exhaust is regulated to put pressure on the system. If the firebed is burning properly and the product gas meets specifications, the gas is fed to the distribution system.

For temporary shutdowns, the fire is banked by reducing the air flow, and the gasifier is vented to the atmosphere. To return the unit to full operation (hot startup), the air flow is increased, the exhaust valve is closed, and the gas flow is directed to the distribution system.

When the proper operating conditions have been established, the product gas is directed to the centrifugal gas cleaner to remove coal fines. The cleaned gas is delivered with sufficient pressure to serve the gas burners in the distribution system.

Slowly revolving grates remove the ash to an uninsulated hopper. Water from a 2-inch water line around the inside circumference at the top of this hopper is used to flush out a 24-hour accumulation of ash as a slurry. The ash is dumped into a truck, an operation that takes about 5 minutes, and removed to a landfill area. Gas production is not affected during this operation.

The product gas passes from the gasifier to a cyclone lined with refractory bricks and insulated on the outside. If the product-gas offtake line and the cyclone are not insulated, the operator would be potentially exposed to burns and to heat stress if required to work in the immediate area for long periods. The product gas (see Table XIII-2) leaves the cyclone at 315 C (600 F) [14].

TABLE XIII-2

TYPICAL PRODUCT-GAS ANALYSIS

Constituent	Concentration (Vol %)
Argon	0.52
Carbon dioxide	6.95
Carbon monoxide	24.03
Hydrogen	16.97
Methane	0.25
Nitrogen	51.12
Oxygen	0.16
Heating value	130/140 BTU/scf

Adapted from reference 14

The particulates collected in the cyclone, usually less than a wheelbarrow full, are removed once per week and sent to a landfill with the ash. The particulate material collected in the cyclone is 40-50% carbon [14].

Approximately every 4 hours, an operator checks the firebed depth by inserting a steel rod through pokeholes, which are normally closed by covers tightened by slide dogs. There are eight such holes over the outer grate, two over the inner grate, and one over the center. For the checking operation, the operator opens the pokehole and inserts a steel rod through the firebed and ashbed to the grate. This operation is repeated for all eight pokeholes, each with its own steel rod. The operator then sequentially closes and tightens the cover over each of the pokeholes after measuring and recording the ashbed and firebed depths (each rod remains in the gasifier between 3 and 5 minutes). The entire operation takes approximately 20 minutes. During the checking operation, small quantities of product gas escape into the operating area. On one occasion a carbon monoxide monitor located at the control station (approximately 10 feet away) registered a level of 40 ppm [14]. After the pokeholes were closed, the carbon monoxide level at the monitor decreased to a level of 1-2 ppm [14].

Both the gasifier and the coal feeding compartment are fitted with a direction-controlled blowout patch to minimize any danger that would result from the ignition of product gas. In 30 years of operation, there has been no reported incident of product gas igniting in any unit burning anthracite coal [14].

Normal maintenance, including lubrication, requires an average of 2 hours/week. During minor maintenance, the fire is banked. Major maintenance is done once a year and includes the following tasks [14]:

- The slide dogs and pokehole covers are resurfaced.
- The grates are refurbished.
- The insulation of the gasifier and the cyclone is repaired as needed.
- Any particulate matter that has accumulated at bends, dead ends, and at the end of the pipeline near the distribution system is raked out through cleanout ports.

The buildings housing the gasifiers are totally enclosed, with windows for ventilation. However, after experiencing levels of carbon monoxide as high as 500 ppm above the coal storage bin, one company installed push-out panels with controllable openings to increase the natural draft in the building [14]. At another plant [14], fans were installed on the top floor to increase air flow through the building and reduce the potential for carbon monoxide and product-gas accumulation. The level of carbon monoxide registered on the top floor was below 10 ppm.

Very High Temperature Coal Gasification

The operating temperature, at least 1816 C (3300 F), destroys most or all of the tars that would be produced in lower temperature processes, regardless of the coal feedstock used. This significantly reduces the hazard of exposure to tar and tar oil.

At one such plant [24], feedstock coal is dried to a moisture content of 2-8% and pulverized in a wind-swept closed system using a ball, rod, or roller mill until 70% of the coal can pass through a 200 mesh screen and 8-10% is smaller than 7 microns [24]. A classifier returns the oversized particles to the mill and allows the finer particles to continue to a cyclone. The properly sized coal is stored in a surge bunker, from which it is pneumatically conveyed with nitrogen to a service bin above the gasifier. Pressure switches control the feed to the service bin. The nitrogen is separated by a cyclone for reuse.

From the service bin the coal is fed to the feedbin. A control system using a screw feeder and metering head insures a continuous coal feed of uniform density.

At the mixing head, which is designed to prevent gas backflow and explosions, a mixture of steam and oxygen entrains the pulverized coal leaving the metering head, accelerates the coal particles, and projects them into the gasifier at velocities sufficiently high (approximately 300 ft/second) to prevent flashback.

The gasifier, shaped like two spheroidal cones joined at their bases, is of double-wall construction. The annulus between the inner and outer walls is water cooled and connected to a steam separator. The low-pressure steam generated is used as process steam and enters the gasifier through the mixing head.

Each gasifier cone contains two adjacent burners mounted in line with the opposing set. The sets of burners are designed to provide turbulence and to insure continuous ignition if one burner should become temporarily blocked.

The advantages of opposing burners are that particles passing through one flame region unburned are gasified in the opposing flame, and the problems associated with refractories at high temperature are minimized because the flame is directed into a gaseous medium.

The carbon in the entrained oxygen-steam stream is exothermically oxidized, producing a flame temperature of approximately 1925 C (3500 F). Steam production in the water jacket and endothermic reactions between the carbon and steam reduce the temperature to about 1650 C (3000 F). Theoretical equilibrium calculations show that essentially all hydrocarbons, phenols, tars, and ammonia are dissociated and oxidized [24]. In practice, the gas contains no complex hydrocarbon molecules and only small amounts of methane [24]; it is essentially carbon monoxide, hydrogen, and carbon dioxide, with relatively small quantities of nitrogen. Hydrogen sulfide, carbonyl sulfide, ammonia, and hydrogen cyanide concentrations depend on the sulfur and nitrogen content of the coal. There are only trace quantities of other compounds.

The gasifier is a completely enclosed unit and is monitored by 28 instruments [18]. If any parameter deviates from established limits, the gasifier automatically shuts down and is vented to the atmosphere.

Ash in the feedstock is liquefied in the high-temperature flame. Up to 50% of the ash flows down the walls as molten slag and draws into a slag quench tank; the remainder of the ash (50-80%) leaves the gasifier as fine fly ash entrained in the gas [18,24].

Molten particulates in the product gas, (1200 C, 2192 F) are solidified at the entry to the waste-heat boiler, which is usually a radiant-surface boiler, followed by a fintube boiler. The gas leaves the waste heat boiler at 205 C (400 F) and is washed and cooled in refractory-lined spray washers which remove approximately 90% of the heavy particulates. Subsequent cleaning is done downstream with disintegrators and electrostatic precipitators when the gas is to be compressed for subsequent use as a synthesis gas for chemical feedstock or pipeline gas.

After the clean product gas has been compressed, sulfur is removed by the Claus, Rectisol, Stretford, or other commercially available processes.

XIV. APPENDIX IV

SAFETY

The fault-tree analysis method of safety assurance is recommended as a useful technique in the design and operation of coal gasification plants. Fault-tree analyses tend to insure that all variables have been considered and provide a logical, systematic approach to identifying safety problems, assisting in their solution, and determining whether corrective action has been sufficient within the constraints of operation, time, and cost. This approach affords the opportunity to identify many accident situations that might be missed by less detailed investigations.

Several procedures for such analyses are currently available. The following are useful references:

- Chemical Industrial Safety and Health Council: Guide to Hazard and Operational Studies. London, England, Chemical Industries Association, Ltd
- Grose VL: System Safety in Rapid Rail Transit. Santa Barbara, California, Justin Institute of Technology
- Kolodner HJ: The Fault Tree Technique of System Safety Analysis as Applied to the Occupational Safety Situation, Monograph #1, Park Ridge, Illinois, American Society of Safety Engineers, 1971
- Lambert HE: Systems Safety Analysis and Fault Tree Analysis. Lawrence Livermore Laboratories, California, 1973

The Occupational Safety and Health Administration's Standards and Interpretations, 29 CFR 1910 [XIV-5], are the Federal regulations governing plant safety. These standards prescribe a useful minimum of safety practices in certain general plant situations, specifying adequate egress from plant areas (29 CFR 1910.37), provision of proper guards for machines (29 CFR 1910.219), positive electrical lockout of machinery during maintenance (29 CFR 1910.145), adequate fire extinguishing equipment (29 CFR 1910, Subpart L), and hearing protection in noisy areas (29 CFR 1910.95). Each state has safety laws and regulations applicable to large chemical plants; a compilation of these is available [129].

The applicable state and Federal standards are, however, of necessity very general and of minimal utility in designing a safe workplace in the coal gasification industry. They would be useful in implementing a "retrofit type" of safety program in existing unsafe work areas but fall short of providing sufficiently detailed technical data for insuring safety in the design of the very large and complex facilities foreseen for coal gasification at the commercial scale.

Handbooks and codes used by various industries can provide a greater degree of technical specificity for analyzing the hazards in coal gasification. Since these publications are generally applicable throughout industry, a detailed presentation is beyond the scope of this document on unique aspects of coal gasification. However, some of these documents are listed here and referenced. Of special interest is National Bureau of Standards Special Publication 329, An Index of US Voluntary Engineering Standards [129], which is a very comprehensive compilation of design standards used in industry. Other applicable standards are the following:

* American Standard Codes for Pressure Piping, ASA B31.1-1955 and B31.8-1958

* The American Society of Mechanical Engineers Boiler and Pressure Vessel Code, Section 8, "Unfired Pressure Vessels," New York, 1965

* Battelle-Northwest Laboratories: Battelle-Northwest Pressure Systems Manual, BNWL-MA-21. Richland, Washington

* Hanford Engineering Standards (HWS-10000, "Architectural- Civil Standards"; HWS-10001, "Mechanical Standards"; "Mechanical Standards"; HWS-10002, "Electrical Standards"; HWS-10003, "Guides," Vol 1, and HWS-10002, "Guides," Vol 2; HWS-10004, "Welding Standards"; HWS-10005, "Instrument Standards"; HWS-10006, "Standard Design Criteria"; and HWS 10007, "Protective Clothing Standards)"

* National Fire Codes, the National Fire Protection Association (Vol 1, "Flammable Liquids"; Vol 2, "Gases"; Vol 3, "Combustible Solids, Dust, and Explosives"; Vol 4, "Building Construction and Facilities"; Vol 5, "Electrical" (the National Electrical Code); Vol 6, "Sprinklers, Fire Pumps, and Water Tanks"; Vol 7, "Alarm and Special Extinguishing Systems"; Vol 8, "Portable and Manual Fire Control Equipment"; Vol 9, "Occupancy Standards and Process Hazards"; and Vol 10, "Transportation")

* United States of America Standards Institute: Safety Code for Cranes, Derricks, and Hoists, 1943, Reaffirmed, 1952. ASA B30.2, USA 51., 1952

* United States of America Standards Institute: Safety Code for Elevators, Dumbwaiters, and Moving Walks, 1965

* United States of America Standards Institute: Uniform Building Code, Vol 1. ASA A17.1, Pasadena, California, 1964

XV. APPENDIX V

SAMPLING AND ANALYSIS FOR POLYCYCLIC AROMATIC HYDROCARBONS

To determine the concentrations of polycyclic aromatic hydrocarbons in the occupational environment, samples should be collected on 0.8 micrometer pore size silver membrane filters (37 mm diameter) preceded by Gelman type A or equivalent glass fiber filters encased in 3-piece plastic (polystyrene) field monitor cassettes. The cassette face cap should be on and the plug removed.

Equipment

(a) Personal sampling pump suitable for exhausting at least 1.6 liters/minute
(b) Thermometer
(c) Manometer
(d) Stopwatch
(e) Tubing

Calibration

Since the accuracy of an analysis can be no greater than the accuracy with which the volume of air is measured, accurate calibration of sampling devices and flowmeters is essential. Frequency of calibration depends on the use, care, and handling of the sampling system. Pumps should be recalibrated if they have been abused or if they have just been repaired or received from the manufacturer. When sampling highly polluted or dusty environments, frequent cleaning and calibration may be necessary because the orifices of flowmeters and other equipment may become contaminated.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration depends on the type of instrument used as a reference. The choice of calibration procedure depends largely on where the calibration is to be performed. For laboratory testing, a 1-liter buret or wet-test meter is recommended, although other standard calibrating instruments, such as spirometer, Marriot bottle, or dry-gas meter, can be used. The actual setup will be similar for all calibration systems used. The calibration instrument should be connected to the sampling train, followed by the sampler pump. In this way, the calibration instrument will be at atmospheric pressure. Each personal sampling pump must be calibrated separately. If a buret is used for calibration, it should be set up so that the flow is toward the narrow end of the unit.

Assemble the calibration setup carefully to ensure that seals at the joints are airtight and that the length of connecting tubing is minimized. Calibration should be performed at the same conditions of pressure and temperature as those under which sampling will occur. A calibrated pump rotameter should be used to establish flow rate in the field.

Collection of Samples on a Glass Fiber Filter

Because of the large air volume to be sampled and the limited capacity of air movers available for personal monitoring, long sampling periods are required. Inspect the filter and air mover periodically and terminate sampling if either the filter or air mover are malfunctioning.

Submit the filters in the field monitors for analysis along with three blank filters from each lot.

Principal of the Analytical Method

The cyclohexane-soluble material in the particulates on the glass fiber filters is extracted ultrasonically. Blank filters are extracted along with, and in the same manner as, the samples. After extraction, the cyclohexane solution is filtered through a fritted glass funnel. The total material extracted is determined by weighing a dried aliquot of the extract.

Range and Sensitivity

When the electrobalance is set at 1 mg, this method can detect 75-2,000 (u)g/sample.

Precision and Accuracy

When nine aliquots of a benzene solution from a sample of aluminum-reduction plant emissions containing 1,350 (u)g/sample were analyzed, the standard deviation was 25 (u)g. Experimental verification of this method using cyclohexane is not yet complete.

Advantages and Disadvantages of the Method

(a) Advantages

This procedure is much faster and easier to run than the Soxhlet method.

(b) Disadvantages

If the whole sample is not used for cyclohexane-extraction analysis, small weighing errors make large errors in final results.

Apparatus

(a) Ultrasonic bath, 90 Kc, 60 watts, partially filled with water

(b) Ultrasonic generator, Series 200, 90 Kc, 60 watts

(c) Electrobalance capable of weighing to 1 (u)g

(d) Stoppered glass test tube, 150 x 16 mm

(e) Teflon weighing cups, 2 ml, approximate tare weight 60 mg

(f) Dispensing bottle, 5 ml

(g) Pipets, with 0.5 ml graduations

(h) Glass fiber filters, 37 mm diameter, Gelman Type A or equivalent

(i) Silver membrane filters, 37 mm diameter, 0.8 micrometer pore size

(j) Vacuum oven

(k) Tweezers

(l) Beaker, 50 ml

(m) Glassine paper, 3.5 x 4.5 inches

(n) Wood application sticks for manipulating filters

(o) Funnels, glass-fritted, 15 ml

(p) Graduated evaporative concentrator, 10 ml

Reagents

(a) Cyclohexane, ACS nanograde reagent

(b) Dichromic acid cleaning solution

(c) Acetone, ACS reagent grade

Procedure

(a) All extraction glassware is cleaned with dichromic acid cleaning solution, rinsed first with tap water, then with deionized water followed by acetone, and allowed to dry completely. The glassware is rinsed with nanograde cyclohexane before use. The Teflon cups are cleaned with cyclohexane, then with acetone.

(b) Preweigh the Teflon cups to one hundredth of a milligram (0.01 mg).

(c) Remove top of cassette and hold over glassine paper. Remove plug on bottom of cassette. Insert end of application stick through hole and gently raise filters to one side. Use tweezers to remove filters, and loosely roll filters around tweezers. Slide rolled filters into test tube and push them to bottom of tube with application stick. Add any particulates remaining in cassette and on glassine paper to test tube.

(d) Pipet 5 ml of cyclohexane into test tube from dispensing bottle.

(e) Put test tube into sonic bath so that water level in is above liquid level in test tube. Do not hold tube in hand while sonifying. A 50-ml beaker filled with water to level of cyclohexane in tube works well.

(f) Sonify sample for 5 minutes.

(g) Filter the extract in 15-ml medium glass-fritted funnels.

(h) Rinse test tube and filters with two 1.5-ml aliquots of cyclohexane and filter through the fritted-glass funnel.

(i) Collect the extract and two rinses in the 10-ml graduated evaporative concentrator.

(j) Evaporate down to 1 ml while rinsing the sides with cyclohexane.

(k) Pipet 0.5 ml of the extract to preweighed Teflon weighing cup. These cups can be reused after washing with acetone.

(l) Evaporate to dryness in a vacuum oven at 40 C for 3 hours.

(m) Weigh the Teflon cup. Use counterweighing techniques on electrobalance with full scale range of 1 mg to determine weight of aliquot to nearest microgram. The weight gain is due to the cyclohexane-soluble residue.

Calculations

The amount of cyclohexane-extractable fraction present in the sample (in mg) may be determined according to the following equation:

$$\text{mg/sample} = 2 \times [\text{wt sample aliquot (mg)} - \text{wt blank aliquot (mg)}]$$

The amount of cyclohexane-extractable fraction present in the air may then be determined according to the following equation:

$$\text{mg/cu m} = \frac{\text{mg/sample}}{\text{air volume collected (cu m)}}$$

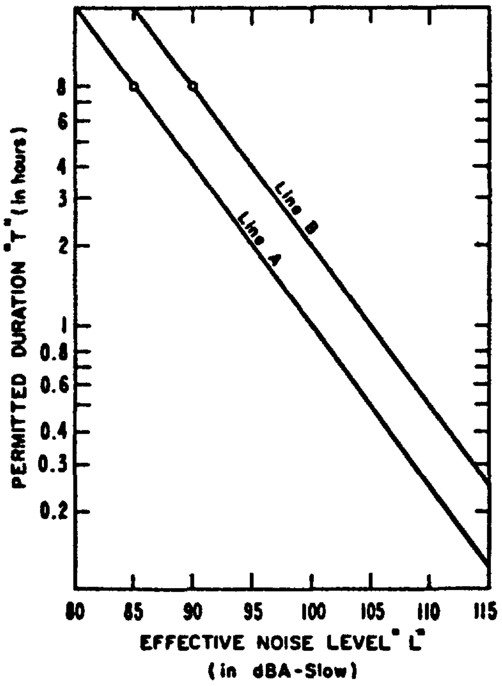
XVI. APPENDIX VI

NOISE TABLE

Occupational noise exposure shall be controlled so that no worker shall be exposed in excess of the limit described as line B in Figure XVI-1. New installations shall be designed with noise control so that the noise exposure does not exceed the limits described as line A in Figure XVI-1. For noise exposures consisting of two or more periods of exposure at different levels, the Daily Noise Dose, D, shall not exceed unity. Line A or line B, as applicable, shall be used in computing the Daily Noise Dose [72].

LINE A
FORMULA: $T = 16 \div 2^{(L-80)/5}$
RANGE: 80 to 115 dBA-Slow

LINE B
FORMULA: $T = 16 \div 2^{(L-85)/5}$
RANGE: 85 to 115 dBA-Slow



Adapted from Reference 72

Figure XVI-1

Permitted Duration vs Noise Level(a)

(a) The indicated duration limits which exceed 8 hours are to be used for purposes of computing Daily Noise Dose and are not to be regarded as defining noise exposure limits for work days which exceed 8 hours.

☆ U S GOVERNMENT PRINTING OFFICE 1978— 757-141/1841

DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
4676 COLUMBIA PARKWAY, CINCINNATI, OHIO 45226

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

U.S.MAIL

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF H.E.W.
HEW 396

DHEW (NIOSH) Publication No. 78-191