NIOSH

OCCUPATIONAL HAZARD ASSESSMENT

COAL LIQUEFACTION,
Volume II - Assessment

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health

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PREFACE

The National Institute for Occupational Safety and Health (NIOSH) believes that coal liquefaction technology presents potential hazards to workers because of similarities with other coal-related processes that have shown high cancer risks. This occupational hazard assessment critically reviews the scientific and technical information available and discusses the occupational safety and health issues of coal liquefaction pilot plant operations. By addressing the hazards while the technology is in the developmental stage, the risk of potential adverse health effects can be substantially reduced in both experimental and commercial plants.

This occupational hazard assessment is intended for use by organized labor, industry, trade associations, government agencies, and scientific and technical investigators, as well as the interested public. The information and recommendations presented in this assessment should facilitate the development of specific procedures for hazard control in individual workplaces by those persons immediately responsible for health and safety. NIOSH will periodically update and evaluate new data and information as they become available and, at the appropriate time, will consider proposing recommendations for a standard to protect workers in commercial coal liquefaction facilities.

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CONTENTS

Page

PREFACE iii

REVIEW CONSULTANTS v

FEDERAL AGENCIES vii

I. EXECUTIVE SUMMARY 1

II. COAL LIQUEFACTION PROCESS TECHNOLOGY 4

Coal Conversion 4
Description of General Technology 7

III. POTENTIAL HAZARDS TO HEALTH AND SAFETY IN COAL LIQUEFACTION PLANTS 11

Extent of Exposure 12
Hazards of Coal Liquefaction 12
Carcinogenic, Mutagenic, and Other Effects 16
Reproductive Effects and Other Studies 34

IV. ENGINEERING CONTROLS 46

Introduction 46
Plant Layout and Design 46
Design Considerations 49
Systems Operations 54

V. WORK PRACTICES 61

Specific Work Procedures 61
Personal Protective Equipment and Clothing 65
Medical Surveillance and Exposure Monitoring 70
Emergency Plans and Procedures 78

VI. CONCLUSIONS AND RECOMMENDATIONS 80

Summary of Pilot Plant Hazards 81
Control of Pilot Plant Hazards 82

CONTENTS (CONTINUED)

Page

VII. RESEARCH NEEDS 93

Near-Term Studies 93
Far-Term Studies 96

VIII. REFERENCES 97

IX. APPENDIX I - Specific Coal Liquefaction Processes 115

X. APPENDIX II - Summary of Coal Liquefaction Processes Under Development in the United States 129

XI. APPENDIX III - Summary of Systems Applicability to Various Coal Liquefaction Technologies 132

XII. APPENDIX IV - Description of Equipment Used in Coal Liquefaction 134

XIII. APPENDIX V - Exposure Limits of Some Contaminants That May Be Present in Coal Liquefaction Processes 137

XIV. APPENDIX VI - Chemical Substances Potentially Associated with Coal Liquefaction Processes 142

XV. APPENDIX VII - System Safety References 150

XVI. APPENDIX VIII - Applicable Codes and Standards 151

XVII. APPENDIX IX - Ongoing NIOSH Contracts Related to Coal Liquefaction 153

XVIII. TABLE AND FIGURES 157

XIX. GLOSSARY 164

XX. ACRONYMS 170

I. EXECUTIVE SUMMARY

Coal liquefaction is one of the technologies now being developed in the United States to offset increasing energy demands. For commercial application of this technology, engineering design progresses through the stages of bench-scale units, process development units, pilot plants, and demonstration plants to commercial plants. Today, several coal liquefaction pilot plants, with varying capacities, are operating in the United States. Other pilot and demonstration plants that will have larger capacities are being constructed or designed [1].

This document reviews and evaluates potential occupational hazards to workers in coal liquefaction pilot plants. By addressing the hazard while direct coal liquefaction technology is still being developed, the risk of potentially adverse health effects can be substantially reduced. In this document recommendations are made for reducing the risks of these adverse health effects. Failure to take adequate precautionary measures may result in needless risks to worker health and safety.

Coal liquefaction is the conversion of coal to liquid hydrocarbon products. The major products of most coal liquefaction processes are condensed aromatic liquids; however, some gases and solids are also produced, depending on the type of coal, the process, and the operating conditions used [2].

Specific coal liquefaction processes differ in the methods and operating conditions used to break physical and chemical bonds, in the sources of hydrogen used to stabilize radical fragments, and in the physical and chemical characteristics of product liquids, gases, and solids. There are four categories of coal conversion processes: (1) pyrolysis, (2) solvent extraction, (3) direct hydrogenation, and (4) indirect liquefaction [3]. This assessment is concerned with direct liquefaction, ie, processes 1-3. Although equipment within a coal liquefaction plant varies according to the processes employed, there are many similarities. Some operations common to the plants include coal handling and preparation, liquefaction, physical separation, upgrading, product storage, and waste management.

Coal liquefaction materials contain potentially hazardous biologically active substances. Skin cancers were reported among workers in one coal hydrogenation pilot plant that is no longer operating [4]. Evidence from animal experiments indicates that local skin carcinomas may result when some coal liquefaction products remain on the skin for long periods of time [5-9]. Similarities exist between the toxic potential of coal liquefaction products and that of other materials derived from coal, such as coal tars, coal tar pitch, creosote, and coke oven emissions, which have been associated with a high cancer risk. Some compounds, such as benzo(a)pyrene, methyl chrysenes, aromatic amines, and certain other polycyclic aromatic hydrocarbons, that are known human carcinogens when they occur individually were found in pilot plant products and process streams [10-13]. The carcinogenic potential of these compounds when they occur in mixtures is unknown.

In addition to the carcinogenic potential of constituent chemicals in various coal liquefaction process streams, other long-term effects on nearly all major organ systems of the body have been attributed to them. Many of the aromatics and phenols irritate the skin or cause dermatitis. Silica dust and other components of the mineral residue may affect the respiratory system. Benzene, inorganic lead, and nitrogen oxides may affect the blood. Creosotes and coal tars affect the liver and kidneys, and toluene, xylene, hydrogen sulfide, and inorganic lead may affect the central nervous system (CNS). Evidence from recent animal studies [14,15] also indicates that coal liquefaction materials may have adverse effects on reproduction. The potential also exists for worker exposure to hazards that are an immediate threat to life, such as hydrogen sulfide, carbon monoxide, and fire and explosion.

The recommendations made in this document for worker protection include a combination of engineering controls, work practices, personal protective equipment, and medical surveillance. Additional recommendations for training, emergency procedures, and recordkeeping are made to support the engineering control and work practice recommendations. Although insufficient data are available at this time to support recommending environmental exposure limits for all materials found in coal liquefaction processes, some information is available from similar industries [16-18].

The primary objectives of engineering controls are to minimize the potential for worker exposure to hazardous materials and to reduce exposure levels. Design considerations should ensure the integrity of process containment; limit the need for worker exposure; provide for maximum equipment reliability; minimize the effects of erosion, corrosion, instrument failure, and seal and valve failure; and provide for equipment separation, redundancy, and fail-safe design.

The major objective of recommended work practices is to provide additional protection to the worker when engineering controls are not adequate or feasible. Most coal liquefaction pilot plants have written policies and procedures for various work practices, including breaking into pipelines, lockout of electrical equipment, tag-out of valves, fire and rescue brigades, safe work permits, vessel entry permits, wearing safety glasses and hardhats, housekeeping, safe storage of process materials, decontamination of equipment requiring maintenance, and other operational safety practices [1].

Personal protective equipment such as respirators and protective clothing may be necessary to prevent worker exposure to coal-derived materials. However, they should be used only when other methods of control are inadequate.

Because workers in coal liquefaction plants may be exposed to a wide variety of chemicals that can produce adverse health effects, medical surveillance is necessary to evaluate the ability of workers to perform their work and to monitor them for any changes or adverse effects. Particular attention should be paid to the skin, oral cavity, respiratory system, and CNS. NIOSH recommends that a surveillance program be instituted that includes preplacement, periodic, and termination physical examinations as well as preplacement and interim medical histories.

Sampling and analysis for air contaminants provide a way to assess the performance of engineering controls. Industrial hygiene monitoring can be used to determine employee exposure to chemical and physical hazards. The combination of data from exposure records, work histories, and medical histories provides a way to evaluate the effectiveness of engineering controls and work practices, and to identify causative agents for effects that may be revealed during medical monitoring. Thus, it is important that medical records and pertinent supporting documents be established and maintained for all workers and that copies of any applicable environmental exposure records be included.

At the beginning of employment, all workers should be informed of the occupational exposure hazards associated with coal liquefaction plants. As part of a continuing education program, training should be repeated periodically to ensure 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, and the advantages of good personal hygiene.

The data used in this occupational hazard assessment were obtained and evaluated through literature surveys and from visits to coal liquefaction pilot plants or related facilities. Data from industries in which workers have been exposed to materials similar to those found in coal liquefaction plants were also considered. Acronyms used in the document are listed in Chapter XX.

II. COAL LIQUEFACTION PROCESS TECHNOLOGY

Coal Conversion

(a) Background

Coal can be converted into synthetic fuels by coal gasification or liquefaction processes, mainly yielding a gas or liquid, respectively. However, both gaseous and liquid products and byproducts can be obtained from most gasification and liquefaction processes [3]. In addition, similar equipment, eg, gas purification systems and coal handling equipment, can be found in both types of processes. Where these similarities exist, NIOSH's previous recommendations in the criteria document on coal gasification plants are applicable [16].

Examples of equipment generally found in coal liquefaction plants, but not in gasification plants, include dissolvers, catalytic hydrogenation reactors, solid-liquid separation units, and solvent recovery units. Unlike coal gasification plants, coal liquefaction plants process coal-oil slurries at high pressures and temperatures. This operating environment presents the potential for erosion, corrosion, and seal failures, resulting in the release of flammable hydrocarbon liquids and/or other hazardous materials. Another problem in liquefaction is plugging associated with solidification of the coal solution when its temperature drops to less than the pour point of the mixture.

Coal gasification entails treatment of coal in a reducing atmosphere with air or oxygen, steam, carbon monoxide, hydrogen, or mixtures of these gases to yield a combustible material [16]. The primary product from gasification is a mixture of hydrogen, water, carbon monoxide, carbon dioxide, methane, inerts (eg, nitrogen), and minor amounts of hydrocarbons and other impurities [16]. Hydrogen and carbon monoxide are then catalytically treated to produce pipeline-quality gas and light oils. In a gasification process, liquid byproducts may be recycled to the reactor while gaseous products are cleaned, upgraded, and stored or shipped [3].

Coal liquefaction is the process that converts coal to liquid hydrocarbon products. Some gases and solids are also produced, depending on the type of coal, the process, and the operating conditions used. In general, the changes that occur in the liquefaction of coal include breaking weak van der Waal's forces and hydrogen bonds between layers in the coal structure, rupturing both aromatic-aromatic and aromatic-aliphatic chemical bonds, and stabilizing free radical fragments [2]. Although there are exceptions, the major products of most coal liquefaction processes are condensed aromatic liquids [2].

Although similarities in equipment exist, the hazards associated with each type of process were assessed independently [16]. Two important differences in health and safety hazards between the two processes are (1) the chemical composition of products and process streams, which may affect overall health risks; and (2) equipment configuration, which may affect the potential for release of process materials.

(b) Coal Liquefaction Processes

Specific coal liquefaction processes differ in the methods and operating conditions used to break physical and chemical bonds, in the sources of hydrogen used to stabilize radical fragments, and in the physical and chemical characteristics of product liquids, gases, and solids. Significant features of the four major categories of coal conversion processes are discussed below.

(1) Pyrolysis

Pyrolysis involves heating coal to a temperature between 400 and 550°C in the absence of air or oxygen, resulting in disruption of physical and chemical bonds, generation of radicals, and abstraction of hydrogen atoms by radicals for coal hydrogen-donors. During this process, some small radicals combine to form hydrogen-enriched volatile hydrocarbon components. Loss of donor-hydrogen from larger fragments produces char. Pyrolysis products include heavy oil, fuel oil, char, and hydrocarbon gases. Temperatures greater than 550°C promote cracking and high gas yields.

Pyrolysis in the presence of hydrogen, at or above atmospheric presure, is known as hydrocarbonization. Generally, hydrocarbonization products are similar to those obtained by simple pyrolysis, but are somewhat lower in char yield.

(2) Solvent Extraction

Solvent extraction processes are generally performed at high temperatures and pressures in the presence of hydrogen and a process-derived solvent that may or may not be hydrogenated. The solvent-refined coal (SRC) process produces either liquid or solid low-ash and low-sulfur fuels, depending on the amount of hydrogen introduced. The liquid is used as a boiler fuel. The Exxon donor-solvent (EDS) process produces gases and liquid fuels from a wide variety of coals.

(3) Direct Hydrogenation

Direct hydrogenation is a process in which a coal slurry is hydrogenated in contact with a catalyst under high temperatures and pressures. Process products are boiler fuels, synthetic crude, fuel oil, and some gases, depending on process conditions.

(4) Indirect Liquefaction

In indirect liquefaction, carbon monoxide and hydrogen produced by gasifying coal with steam and oxygen can be catalytically converted into liquid fuels. Another indirect catalytic liquefaction process produces methanol, which can be converted to gasoline.

(c) Process Development

Significant technical advances in coal liquefaction were made in Germany between 1915 and 1944 [19]. Germany developed and improved the Bergius coal liquefaction process, which consisted of hydrogenating finely ground coal by amalgamation with tar oils. Product oil was fractionated by distillation, and the heavy fraction provided the tar oil used to hydrogenate the finely ground coal. The light fraction was upgraded by using hydrogen-enriched steam to produce a liquid rich in aromatics [19]. During World War II, the Germans constructed 11 hydrogenation plants in addition to 7 existing plants. In 1944, the total output capacity of these 18 coal hydrogenation plants was 4 million metric tons (4 Tg) of oil a year. These plants supplied almost all of the fuel necessary for German aviation in 1944 [3].

Another coal liquefaction process was developed in the 1920's by Fischer and Tropsch [19]. This Fischer-Tropsch process uses synthesis gas, formed by passing steam over red-hot coke, to produce liquid hydrocarbons in a catalytic reaction. Currently, this process is being used on a commercial scale at the South African Coal, Oil, and Gas Corporation, Ltd (SASOL) plant in South Africa (SASOL I) [20,21]. In addition, South Africa is currently operating a second plant (SASOL II), and a third plant (SASOL III) is scheduled to be operating by 1984. The production capacity of the SASOL II plant is estimated to be 2.1 million metric tons (2.1 Tg) of marketable products per year [22]. Of this figure, SASOL estimates that motor fuels production will be 1.5 million metric tons (1.5 Tg) per year [3,22]. Currently, SASOL I total output is approximately 0.25 million metric tons (0.25 Tg) of petrochemicals per year, which includes 0.168 million metric tons (0.168 Tg) of gasoline [3].

Coal liquefaction experience in the United States [20] includes (1) synthetic oil research conducted at the Pittsburgh Energy Technology Center (PETC) (formerly Pittsburgh Energy Research Center) since the early 1950's, (2) a coal liquefaction demonstration plant using the Bergius process, which operated in the 1950's in Louisiana, Missouri, (3) a hydrogenation pilot plant operated by Union Carbide from 1952 to 1959 at Institute, West Virginia, (4) char-oil-energy development (COED) process development begun in 1962 by FMC Corporation, (5) Consolidation Coal Company development of Consol synthetic fuel (CSF) process begun in 1963, (6) Hydrocarbon Research, Inc, H-coal process begun in 1964, (7) SRC research initiated by the Office of Coal Research (OCR) in 1962, and (8) donor-solvent research started by Exxon in 1966 [3]. Congressional authorization bills for FY 76, 77, and 78 have provided approximately $100 million annually in Federal funding for coal liquefaction research and development [23]. More than $200 million annually has been authorized for FY 79, 80, and 81 [24,25].

Coal liquefaction operations in the United States have been limited to bench-scale units, process development units, and pilot plants capable of handling up to 600 tons of coal per day (545 Mg/d) [1]. However, a commercial plant that could process approximately 30,000 tons (27,000 Mg) of coal per day is envisioned for the late 1980's [26]. In addition to being larger than pilot plants, commercial plants will be designed and operated differently [1,26].

Pilot plants are used to assess the feasibility of process technology and operability of equipment such as pumps, seals, and solid-liquid separation units. They are also used to optimize operating conditions. To obtain the necessary data, production runs are of shorter duration than those in commercial plants, which are designed to operate continuously. Commercial plants are designed to economically produce marketable products. For this reason, commercial plants may recycle treated wastewater products and/or use char, mineral residue slurry, and sulfur byproducts [1,26,27], whereas most pilot plants currently do not. Equipment may differ based on the development of new technology, eg, new solid-liquid solvent de-ashing separation units currently being tested [1,28,29]. Some equipment used in pilot plants, eg, a rotating liquid/solid extractor or a mineral residue dryer, may not be feasible or necessary in commercial plants [1].

Although commercial plant design and equipment may differ from that of pilot plants, the engineering design considerations that may affect the potential for worker exposure may be similar. Both commercial and pilot plants will operate in an environment of high temperature and pressure, and in most cases, a coal slurry will also be used under these conditions [26,30]. The types of exposure resulting from leaks, spills, maintenance, handling, and accidents may be qualitatively similar for both commercial and pilot plants although frequency and duration of exposure may vary [1]. Specific control technology used to minimize worker exposure may differ in both types of plants. For example, due to the continuous operating mode of a commercial plant, a closed system may be used to handle solid wastes in order to minimize inhalation hazards. This system may not be economical for a pilot plant with batch operations, because portable local exhaust ventilation could be provided when needed [1]. Both of these systems are designed to minimize worker exposure to hazardous materials.

Description of General Technology

The Pott-Broche and Bergius processes were forerunners of two liquefaction processes under development in the United States [2,31]. These developmental processes, discussed at the beginning of the chapter, are categorized as solvent extraction and hydrogenation. Pyrolysis and indirect liquefaction are two additional processes currently used. Figure XVIII-1 illustrates the possible coal liquefaction routes. There is no clear distinction between the solvent extraction and hydrogenation categories [32]. Solvent extraction is generally grouped with noncatalytic hydrogenation [2,20,30,32], while in other studies catalytic and noncatalytic hydrogenation appear under one category, ie, hydrogenation [19,31,33,34]. The latter categorization is used in this assessment.

Coal liquefaction processes using solvent extraction, hydrogenation, pyrolysis/hydrocarbonization, and indirect liquefaction are discussed in Appendix I. Specific processes discussed are the CSF, SRC, H-coal, COED, and Fischer-Tropsch processes, respectively. Appendix II summarizes the major coal liquefaction systems under development in the United States. This assessment does not address the necessary controls and work practices for indirect liquefaction processes, eg, the SASOL technology, since they were previously evaluated by NIOSH [16]. Commercial plants using a process similar to the SASOL technology should follow the recommendations contained in the NIOSH coal gasification criteria document [16].

Although systems and components vary according to the process employed, there are similarities between most coal liquefaction plants. Systems common to coal liquefaction plants include coal handling and preparation, liquefaction, physical separation, upgrading, product storage, and waste management. Appendix III shows the applicability of these major systems to the various coal liquefaction processes summarized in Appendix II. Appendix IV lists the major equipment used in coal liquefaction and a description of its function.

Figure XVIII-2 is a schematic of the general systems used in coal liquefaction. Not all of the unit operations/unit processes shown are applicable to each coal liquefaction process.

(a) Coal Handling and Preparation

The purpose of the coal handling and preparation system is to receive run-of-mine (ROM) coal and prepare it for injection into the liquefaction system. This front-end process is basically the same in all liquefaction plants and produces pulverized coal and coal slurry. Dusts, coal fines, and solvents also may be present. ROM coal is received by rail or truck and is dumped into receiving hoppers. The coal is crushed and transferred to storage bins. When needed, the coal is retrieved from storage, pulverized and dried, and transferred to a blend tank where it is mixed with process solvent to form a coal slurry. At this point, the coal is pumped into the liquefaction system. The slurry blending step is essential for solvent extraction, and catalytic and noncatalytic hydrogenation processes. However, this step is omitted in pyrolysis processes, in which pulverized coal is fed directly into the reactor usually by means of lockhoppers.

(b) Liquefaction

The function of a liquefaction system is to transform coal into a liquid. Solvent extraction and catalytic and noncatalytic hydrogenation are three-phase systems that involve the use of significant quantities of hydrogen [2,35]. Pyrolysis is a two-phase, ie, solid-gas, system. If hydrogen is added during pyrolysis, the process is called hydrocarbonization. Temperatures in these systems range from 700 to 1,500°F (371 to 820°C); pyrolysis reactors generally operate in the upper range [2,35]. Materials found within the liquefaction system include hydrogen, recycled and makeup solvent, gases (hydrogen sulfide, carbon monoxide, methane), solids (unreacted coal, char, ash, catalyst), coal slurries, and organic liquid fractions of the product.

(c) Separation

The product stream from liquefaction contains a mixture of gases, vapors, liquids, and solids and is typically fed to a gas-liquid separator such as a flash drum. Here the pressure on the product stream is reduced, allowing the lower boiling chemicals to vaporize and gases to separate from the liquid. These vapors and gases are separated in a condensate system that removes the higher boiling components of the gas stream. The solids are separated from the liquids by such processes as filtration, centrifugation, distillation, or solvent de-ashing. Materials found in the separation systems include solvents, gases (carbon dioxide, hydrogen sulfide, hydrogen, methane), water, light oils, heavy oils, and solids (mineral residue, unreacted coal).

(d) Upgrading and Gas Purification

The upgrading and gas purification system refines and improves the gases and liquids obtained from the separation system. A gas desulfurization unit removes the sulfur from the gases. The hydrocarbon gases may be further upgraded by methanation to produce pipeline-quality gas or are sent to a hydrogen-methane separation unit where the resulting hydrogen could be used for hydrogenation [3]. The liquid stream may be upgraded by fractionation, distillation, hydrogenation, or a combination of these, resulting in products such as synthetic oils and solvent-refined coal.

(e) Product Storage

Gas products from the liquefaction plant can be stored onsite in tanks or can be piped directly offsite. If piped offsite, there could be reserve storage to allow for peak demands for the product. The liquid products can be stored in tanks, tank cars, or trucks or, as in the case of solvent-refined coal, can be solidified by using a prilling tower or a cooling belt. Depending on its biological and chemical properties, the solid product could be stored in open or closed storage piles.

(f) Waste Management

The waste management system includes gas scrubbers, settling ponds, and wastewater treatment facilities. Its function is to reduce pollutants in the waste streams in accordance with discharge regulations established by Federal, State, and local environmental protection agencies. Typical plant-produced wastes that must be treated and disposed of include solids such as coal particulate, ash, slag, mineral matter, sludges, char, and spent catalyst; wastewater containing suspended particles, phenols, tars, ammonia, chlorides, and oils; and gases such as carbon monoxide, hydrogen sulfide, and hydrocarbon vapors [31]. Waste treatment facilities are also designed to collect and treat process materials released by spills.

III. POTENTIAL HAZARDS TO HEALTH AND SAFETY IN COAL LIQUEFACTION PLANTS

Characterization of workplace hazards associated with coal liquefaction plants in the United States must rely on pilot plant data because currently there are no commercial plants. These pilot plants are experimental units that process up to 600 tons (545 Mg) of coal per day. Because pilot plant operations are experimental, operating parameters and equipment configurations are frequently changed; consequently, exposures may be more severe than might occur in a commercial production facility. On the other hand, because pilot plants have operated for a relatively short time (less than 10 years), exposure effects over a working lifetime cannot be documented.

Available data are sufficient to qualitatively define the hazards that may occur in future commercial coal liquefaction plants, but not to quantify the degree of risk associated with long-term, low-level exposures. Industrial hygiene studies conducted at several pilot plants provide some information about worker exposure [36-39]. In addition, the toxicity of some of the coal-derived materials produced in these plants has been assayed in animals, bacteria, and cell cultures [5-7,9,14,15,40-52]. Only one epidemiologic study [53] of coal liquefaction workers has been conducted in the United States, and the cohort of 50 workers examined was small.

The opportunity for epidemiologic studies has been restricted. In the United States, the longest exposure period for a worker for whom health effects have been reported is approximately 10 years [54]. One foreign plant has operated for more than 23 years [55], but epidemiologic studies of the work force have not been published.

Laboratory analysis of the toxic hazards inherent in coal liquefaction processes is complicated by at least four major factors. First, process streams contain a mixture of many different substances, and isolation of any one potential toxicant can be difficult. Second, the various toxicants can produce diverse effects, ranging from skin irritation to cancer. Third, depending on the physical state of an individual toxicant, different biologic systems can be affected. For example, as an aerosol, a substance may more readily produce respiratory or systemic effects; as a liquid or solid, dermal effects may be more likely. Finally, dose levels are difficult to establish because the composition of process streams can vary, partitioning of process stream components after aerosolization may alter the distribution of components, and weathering of fugitive liquid emissions may alter the toxicity of process materials.

Although occupational safety and health research specifically related to coal liquefaction is limited, studies have been conducted in other industries where exposure to some of the same materials may occur. For example, polycyclic aromatic hydrocarbons (PAH's), which are present in coal tar products, coke oven emissions, asphalt, and carbon black, are also present in coal liquefaction products [10,17,18,38,56,57]. Because some of these materials have reportedly caused severe long-term effects such as skin and lung cancer in workers in various industries [17,18], increased risk of cancer in coal liquefaction workers is possible. Other potential adverse health effects associated with constituent chemicals in coal liquefaction products include fatal poisoning from inhalation exposure [58,59], severe respiratory irritation [60], and chemical burns [61]. Fire and explosion are also significant hazards, because most systems in coal liquefaction operate at high temperatures and pressures and contain flammable materials.

Extent of Exposure

Coal liquefaction pilot plants currently operating in the United States (see Appendix II) employ approximately 100-330 workers and have production capacities of up to 600 tons (545 Mg) of coal per day [1].

In June 1980, the President called for a synthetic fuel production capacity equivalent of at least 2.0 million barrels of crude oil per day by 1992 [62,63]. Production of this amount of synthetic fuel by coal liquefaction processes would require approximately 12 plants, each of which would yield 50,000 barrels of fuel a day. Assuming that a commercial plant would employ at least 3 times as many workers as a large pilot plant, the projected 1995 work force would be approximately 12,000 workers [62,63].

Workers in pilot plants may be exposed to process liquids, solids, gases, aerosols, vapors, dusts, noise, and heat. Some of these potential hazards are summarized in Table III-1. Although coal liquefaction equipment is designed to operate as a closed system, it must still be opened for maintenance and repair operations, thereby exposing workers to potential hazards.

Processing of abrasive slurries, particularly at high operating temperatures and pressures, accelerates the erosion/corrosion effects on equipment such as piping, pressure vessels, seals, and valves in coal liquefaction plants. These effects increase the potential for worker exposure to process materials because leaks and fugitive emissions are more likely to occur [1]. Other sources of worker exposure to process materials include normal handling or inadvertent release of raw materials, products, and waste materials.

Hazards of Coal Liquefaction

According to a 1978 report [64], of an estimated 10,000 chemical compounds that may occur in coal, coal tar, and coal hydrogenation process and product streams, approximately 1,000 have been identified. For some of these chemicals, information is available on their potential hazard to workers. Appendix V summarizes the NIOSH-recommended limits and the current Federal

TABLE III-1

POTENTIAL OCCUPATIONAL HAZARDS IN COAL LIQUEFACTION PLANTS

System, Unit Operation, or Unit Process	Potential Hazards
Coal handling and preparation system	Coal dust, noise, fire, explosion, asphyxia (nitrogen and carbon monoxide gases), burns
Liquefaction system	Phenols, ammonia, tars, thiocyanates, PAH's, carbon monoxide, hydrogen sulfide, hydrocarbons, fires, explosions, burns, high pressures, noise, ash, slag, mineral residue, spent catalyst
Separation system	Oils, phenols, hydrogen cyanide, ammonia, hydrogen sulfide, burns, fires
Upgrading and gas purification	Light hydrocarbons, phenols, ammonia, hydrogen sulfide, carbon dioxide, carbon monoxide, burns, fire, explosion, high pressures
Shift conversion*	Tar, naphtha, hydrogen cyanide, fire, catalyst dust, burns, hot gases (carbon monoxide, hydrogen)
Methanation*	Carbon monoxide, methane, nickel carbonyl, spent catalyst dust, fire, burns
Waste treatment facilities	Hydrogen cyanide, phenols, ammonia, particulates, hydrocarbon vapors, sludges, spent catalyst, sulfur, thiocyanates

*Indirect liquefaction

Occupational Safety and Health Administration (OSHA) standards for various chemicals that have been identified in the process streams of coal liquefaction pilot plants.

Although exposure limits have been established for individual chemicals, in most cases the substances present in coal liquefaction plants will be complex mixtures of these and other compounds. Many of the chemicals listed in

Appendix V may be minor constituents in such mixtures. Other chemicals may be present that have no assessments of health effects. Some chemical constituents of coal liquids are presented in Appendix VI, grouped according to chemical structure.

Compounds that could present an acute hazard have been identified in pilot plant process and product streams [38]. These compounds include carbon monoxide and hydrogen cyanide, which are chemical asphyxiants, as well as hydrogen sulfide, which causes respiratory paralysis [58,65,66]. Workplace concentrations below NIOSH-recommended limits or OSHA standards for these compounds have been measured during normal pilot plant operations [38]. Plant malfunctions or catastrophic accidents could release lethal concentrations of these gases.

Liquefaction products generally include light and heavy oils, gases, tars, and char. Materials that may be used in the process in addition to coal vary according to the type of equipment used. These materials include hydrotreating catalysts, Claus catalysts, chemicals for wastewater treatment, heat exchange oils, such as phenylether-biphenyl mixtures, alkali carbonates from carbon dioxide removal, and filter-aid materials. Tetralin, anthracene oil, or other chemical mixtures may be used as recycle and/or startup solvents.

Numerous compounds are formed during various stages of liquefaction, upgrading, distillation, and waste treatment. Liquid streams consist of coal slurries and oils, which may be distilled into fractions having different boiling ranges. The liquids with higher boiling points are recycled in some processes. Solids are present in liquid and gas streams, filter residues, sludge from vacuum distillation units, spent catalysts, mineral residue from carbonizers, and sludge from wastewater treatment. Gas streams include hydrogen, nitrogen or inert gas, fuel gas, product gas, and stack gases. Occupational exposure to these materials is possible during maintenance and repair operations, or as the result of leaks, spills, or fugitive emissions.

Some of the compounds that have been identified in coal liquefaction process materials, eg, PAH's and aromatic amines, are known or suspect carcinogens. Kubota et al [10] analyzed PAH's in coal liquefaction-derived products and intermediates, including benzo(a)pyrene (40 $\mu g/g$ of liquid) and benz(a)anthracene (20 $\mu g/g$ of liquid). Industrial hygiene surveys at three direct liquefaction pilot plants [3,37,38] confirmed the presence of these and other PAH's in the workplace environment. Ketcham and Norton [37] measured benzo(a)pyrene levels at various locations in the coal liquefaction pilot plant at Institute, West Virginia, for durations varying from approximately 10 minutes to 2 days. Benzo(a)pyrene concentrations ranged from <0.01 to approximately 19 $\mu g/m^3$. Measurements of benzo(a)pyrene taken by personnel at the Fort Lewis, Washington, SRC pilot plant [38] ranged from 0.04 to 1.2 $\mu g/m^3$, and total PAH's ranged from <0.04 to 26 $\mu g/m^3$. Concentration ranges reported for both of these plants are based on high volume area sampling rather than personal breathing zone sampling.

A more recent industrial hygiene survey [13] reported potential worker inhalation exposure levels for PAH's, aromatic amines, and other compounds as 8-hour time-weighted averages (TWA's) in two coal liquefaction pilot plants: the SRC plant in Fort Lewis, Washington, and the CSF plant at Cresap, West Virginia. Workers at the Fort Lewis pilot plant were exposed to PAH concentrations (reported as the sum of 29 PAH's) ranging from 1 to 260 $\mu g/m^3$, with an average of 68 $\mu g/m^3$; exposures to PAH's in the CSF plant ranged from 0.02 to 0.5 $\mu g/m^3$, with an average of 0.2 $\mu g/m^3$. The higher exposure levels at the Fort Lewis pilot plant may be a result of it having processed more coal over a longer period of time than the CSF plant. This suggests that a greater deposition of process stream material may have occurred in the workplace through leaks, spills, and maintenance activities. Volatilization of these materials may have contributed to increased worker exposure.

Seven aromatic amines including aniline, o-toluidine, and o- and p-anisidine were also measured in the survey [13]. Exposure to these aromatic amines was of the same order of magnitude at both pilot plants. Concentrations measured were less than 0.1 ppm. The degree of risk of such exposures cannot be determined because toxicologic data for evaluation of effects at low exposure levels are unavailable.

Fluorescence is a property of benzo(a)pyrene and numerous other aromatic chemicals. Fluorescence has been used to observe droplets of material on the skin of workers under ultraviolet (UV) light [1,37]. This indicates that skin contact with airborne coal liquefaction materials or with contaminated equipment surfaces is also a potential route of exposure. There is, however, concern about the risk of skin sensitization and promotion of carcinogenic effects from excessive use of UV light. UV examination for skin contamination should only be conducted under medical supervision for demonstration purposes, preferably by a hand-held lamp.

Koralek and Patel [31] reviewed process designs at 14 plants and predicted the most likely sources of potential process emissions. According to their report, coal dust may escape from vents and exhausts used for coal sizing, drying, pulverizing, and slurrying operations. Hydrocarbon emissions from evaporation and gas liberation may occur in the liquefaction, physical separation, hydrotreatment, acid gas removal, product storage, wastewater treatment, and solid-waste treatment operations. Other potential air emissions included carbon monoxide, nitrogen oxides, hydrogen sulfide, sulfur dioxide, ammonia, and ash particulates. Potential solid waste materials included reaction wastes (particulate coal, ash, slag, and mineral residue), spent catalysts, spent acid-gas removal absorbents, water treatment sludges, spent water-treatment regenerants, tank bottoms for product storage tanks, and sulfur from the Claus unit. Wastewater could contain phenols, tars, ammonia, thiocyanates, sulfides, chlorides, and oils. Wastewater sources identified were quench water, process condensate, cooling water, gas scrubbers, and water from washdown of spills [31]. The potential for worker exposure to toxic materials is also significant for activities such as equipment repairs requiring vessel entry or line breaking, removal of waste materials, collection of process samples, and analysis of samples in a quality control laboratory.

Because some equipment and operations are similar, the nature and circumstances of injuries experienced in petroleum refining may approximate safety hazards that may exist in coal liquefaction plants. In 1977, the occupational injury and illness incidence rate, as reported to OSHA, for petroleum refining industries was 6.71 for the total number of cases and 1.38 for fatalities and lost workday cases [67]. For the entire petroleum industry, which includes areas such as exploration, drilling, refining, marketing, research and development, and engineering services, these figures were 4.52 and 1.56, respectively. The 1976 figures for all private sector industry were 9.2 and 3.5, respectively [68]. Incidence rates were calculated as:

$$\text{Incidence Rate} = \frac{\text{Number of Injuries and/or Illnesses} \times 200{,}000}{\text{Total Hours Worked During the Year}}$$

These results indicate that the total injury and illness incidence rate is greater for petroleum refining than for the entire petroleum industry. The fatality incidence rate in petroleum refining, however, is less than that of the petroleum industry as a whole. From May 1974 to April 1978, 58 deaths in the petroleum refining industry were reported to OSHA [69]. Contributing environmental factors in approximately half of these fatalities were gas, vapor, mist, fume, smoke, dust, or flammable liquid exposure [69]. About 33% of these deaths resulted from thermal burns or scalding injuries, and 16% from chemical burns. The primary source of injury was contact with or exposure to petroleum products, which accounted for approximately 28% of the total number of deaths. Fire and smoke accounted for approximately 17% of total deaths [69].

Carcinogenic, Mutagenic, and Other Effects

(a) Epidemiologic Evidence in Coal Liquefaction Plants

Epidemiologic data on coal liquefaction employees are scarce, primarily because of the early stage of development of this technology. Data that are available come from medical surveillance programs conducted for employees of pilot plants. These programs were instituted because of toxic effects known for some chemicals in the coal liquefaction processes.

Between 1952 and 1959 a coal liquefaction hydrogenation pilot plant operated at Institute, West Virginia. Many changes and repairs of equipment were necessary in the early phases of the operation. According to a report by Sexton [4] about the medical surveillance program, "These early and intermittent start-ups resulted in excessive exposure to some employees, the extent of which is not known and much of which was not recorded in the medical files." Operating pressures in this plant were much higher (5000-10,000 psi or 350-690 MPa) [70] than expected for other processes and may have increased potential for release of air contaminants and escape of some oil, which would contaminate equipment surfaces. Extensive protective measures were not implemented until 1955.

During the plant's 7 years of operation, the 359 male employees regularly assigned to the coal liquefaction operation were given annual physical examinations and, after 1955, quarterly skin examinations. The author [4] reported that this medical surveillance revealed 63 skin abnormalities in 52 men (later corrected by Palmer to be 50 men [53]). Diagnostic criteria were not specifically defined; nevertheless, diagnoses of cutaneous cancer were reported for 10 men and precancerous lesions for 42 men. The expected number of cases was not reported. Duration of exposure to coal tar, pitch, high boiling aromatic polycyclic compounds, and other compounds for the 359 men, including prior exposures, ranged from several months to 23 years. All cancerous and precancerous lesions were in men with less than 10 years of exposure, however. One worker was found to have two skin cancers, one occurring after only 9 months and the other after 11 months of exposure.

The author [4] acknowledged some doubt that 9 months of exposure to the process could have resulted in a carcinoma of the skin; other risk factors and sources of exposure must be analyzed before a causal relationship can be suggested for this case. According to the author, the age-adjusted skin cancer incidence rate for this population of workers was 16 times greater than the incidence rate for US white males as reported by Dorn and Cutler [71] and 22 times greater than the "normal" incidence as reported by Eckardt [72]. Sexton [4] concluded that an increased incidence of skin cancer was found in workers exposed 9 months or more to coal hydrogenation chemicals.

It was stated [4] that these workers were also exposed to UV radiation to demonstrate that their skin was not always clean after normal showering. Although skin cancer has been reported in workers exposed to the UV radiation of sunlight [73], it is questionable that a brief exposure to UV radiation in this pilot plant could have substantially contributed to the excess risk observed. The excess risk may have been overestimated, however; the incidence in a carefully surveyed cohort was compared with that in the general population (where underreporting of skin cancer was believed to be common) [74]. Taking this underreporting into account would reduce the observed to expected incidence ratio but not eliminate the excess risk. Several other features of the medical surveillance study also hindered accurate quantification of excess risk [4]. Prior occupational exposures of these workers were inadequately assessed in this paper and could have contributed somewhat to observed risk. In addition, specific exposure data were not ascertained. Because specific diagnostic criteria were not established, diagnoses conflicted among the consulting physicians in the study. In spite of these flaws, an excess risk to skin cancer is suggested, and better control of the worker exposure to the chemicals identified in the coal liquefaction process is therefore warranted.

A followup mortality study on the 52 employees with skin lesions was undertaken to determine whether or not these men were at an increased risk for systemic cancer mortality [53]. A review of the records revealed previous double counting; the number of affected employees with cancerous skin lesions was 10 and with precancerous skin lesions was 40. All but 1 of the 50 cases were followed up, and, after an 18- to 20-year latency period, 5 deaths had occurred. The five deaths were reported as cardiac-related, two with pulmonary involvement. No autopsies were performed on them. The expected number of deaths in this population was not reported. The author [53] stated that the results did not indicate an increased risk for systemic cancer mortality for the group. Since most occupationally associated cancers occur 20 or more years after initial exposure [73], the followup period in this study would not be expected to reveal an increased risk to systemic cancer mortality in this small and select cohort (the workers who developed skin lesions). A better risk estimate would have been derived if (1) the disposition of all the 359 men who had worked in the pilot plant was ascertained and (2) if the followup period had been longer than 20 years. The fact that all five deaths were cardiac-related may deserve special attention. It may be an early indication of adverse heart changes similar to the decreased functional capabilities of the cardiovascular and respiratory systems observed among carbon black workers [56].

Findings from the medical surveillance program at the SRC plant in Fort Lewis, Washington, were reported by Moxley and Schmalzer [75]. No discernible changes were revealed by comparing the exposed employees' medical records prior to and following the initiation of coal liquefaction production. The only known occupational health problems encountered at the SRC pilot plant were eye irritation and mild transient dermatitides from skin contact with coal-derived materials; eye irritation was the most common medical problem. Neither the number of exposed workers nor the length of time the medical surveillance program was operative was stated. However, the pilot plant had been operating for only 5 years at the time of the report. In this short time the surveillance program could not possibly have detected chronic effects having long latency periods.

The medical surveillance program for approximately 150 full-time workers at another pilot plant revealed 25-30 cases of contact dermatitis per year and 150-200 cases of thermal burns per year [1].

Preceding reports demonstrate that the available epidemiological data on exposed coal liquefaction workers concentrate on the acute hazards of exposure (dermatitis, eye irritation, and thermal burns). Preliminary evidence suggests the presence of a potential carcinogenic hazard, as illustrated by an apparent excess incidence of skin cancer [4]. However, no conclusive statement on the full potential of cancer or other diseases of long latency from occupational exposure to the coal liquefaction process can be made on the basis of current epidemiologic data. Nevertheless, the known carcinogenic and noncarcinogenic properties of the many chemicals in the liquefaction process mandate every possible precautionary measure be taken to protect workers.

Although this assessment is primarily concerned with the direct coal liquefaction process, the possibility of obtaining epidemiologic data from plants utilizing the indirect process should not be overlooked. The medical facilities of SASOL I commonly see cases of burns (steam, tar, and thermal) and eye irritations [18,21]. No epidemiologic study has been published, however, on the SASOL facility.

(b) Other Related Industries

PAH's in coal liquefaction products have also been identified in coke oven emissions, coal tar products, carbon black, asphalt fumes, and coal gasification tars. NIOSH has previously reviewed the health effects data for a variety of these materials in different industrial environments [16-18,56,76].

In the coal tar products criteria document [17], NIOSH concluded that coal tar, coal tar pitch, and creosote could increase the risk of lung and skin cancer in exposed workers. This conclusion was based on considerable evidence, including the identification of product components that by themselves are carcinogenic (benzo(a)pyrene, benz(a)anthracene, chrysene, and phenanthrene), the results of animal experiments, and the incidence of cancer in the worker populations studied.

In the carbon black criteria document [56], NIOSH concluded that carbon black may cause adverse pulmonary and heart changes. Investigations of the adsorption of PAH's on carbon black, retention of these materials in the lung, and the elution of PAH's from carbon black by human blood plasma were reviewed. The reports suggest a potential risk of cancer from PAH's adsorbed on carbon black, which workers should be protected from. Other health effects associated with carbon black exposure were lung diseases (pneumoconiosis and pulmonary fibrosis), dermatoses, and myocardial dystrophy. Although carbon black workers are exposed primarily to dusts and coal liquefaction workers to process liquids and vapors, similarities in substances such as PAH's could result in the same adverse health effects, including cancer.

In the criteria document on asphalt fumes [76], NIOSH concluded that available evidence did not clearly demonstrate that a direct carcinogenic hazard is associated with asphalt fumes. Three studies were cited that quantified PAH's in asphalts and coal tar pitches. Benzo(a)pyrene and benz(a)anthracene concentrations in eight asphalts ranged from "not detected" to 35 ppm; benzo(a)pyrene and benz(a)anthracene concentrations in two coal tar pitches were in the range of 0.84-1.25% by weight. NIOSH is concerned that future investigations may suggest a greater occupational hazard from asphalt fumes than is currently documented [76].

(c) Animal Studies

During the 1950's, Hueper [5,6,8] tested the carcinogenic potential of oils produced in the experimental and large-scale production plants using the Bergius and Fischer-Tropsch processes. Tests were performed on mice, rabbits, and rats by cutaneous and intramuscular (im) administration.

(1) Cutaneous Administration

Hueper [8] examined the carcinogenic effects of various fractions of Bergius oil or Fischer-Tropsch oil when applied to the skin of mice. Three Bergius oils (heavy, light, and centrifuge residue) obtained from the experimental operation at Bruceton, Pennsylvania, were tested in two different strains of mice. Three groups of 100 strain A mice were exposed to a 50% solution of each oil fraction once a week for 15 months. Two groups of 25 strain C57 black mice were exposed to the heavy oil or the centrifuge residue in concentrations of 100, 25, and 10% once a week for 14 months. Ethyl ether was used as a diluent in all cases, but only the study involving C57 black mice had a control group.

Post-mortem examinations were performed on all mice that died or were killed, with the exception of those that were cannibalized. Histopathologic examinations of the skin, the thigh tissues, and the organs of the chest and abdomen were made [8].

Skin papillomas and carcinomas were observed in both strains of mice with all fractions of oil. In strain A mice, three adenomas occurred (one animal from each treatment group), and four mice had leukemia. The author's observations, as shown in Table III-2, indicate that the carcinogenic potency of the centrifuge residue extract and the heavy oil fraction was greater than that of the light oil. The number of lesions observed in this study decreased with the progressive dilution of the oils [8].

In the same study, Hueper [8] tested light and heavy oils and reaction water, ie, the "liquor" containing the water-soluble products, of Fischer-Tropsch oils in each of three strains of mice: strains A, C, and C57 black. Each experimental group consisted of 125 mice. Fractions were applied with a micropipette to the skin of the mice once a week for a maximum of 18 months. The heavy oil was diluted with ethyl ether at a ratio of 1:2 by weight; the light oil was undiluted; the reaction water was diluted with water at a ratio of 1:4 to reduce its toxicity. No diluent or untreated controls were used, and the source of the diluent water was not mentioned.

Repeated applications of Fischer-Tropsch heavy oil, light oil, and reaction water to mice resulted in neoplastic reactions. Five lesions occurred in male strain C mice treated with light oil: one intestinal cancer, one breast cancer, two lung adenomas, and one incidence of leukemia. The only lesion that occurred in female strain C mice treated with heavy oil was one breast

TABLE III-2

INCIDENCE OF SKIN CARCINOMA IN MICE AFTER
REPEATED CUTANEOUS APPLICATION OF
BERGIUS OILS

		Incidence in Mice Examined (%)		
Concentration	Strain	Centrifuge Extract	Heavy Oil	Light Oil
50%	A	4 of 78 (5)	4 of 64 (6)	1 of 82 (1)
100%	C57	5 of 22 (23)	6 of 17 (35)	-
25%	C57	2 of 12 (17)	3 of 22 (14)	-
10%	C57	3 of 21 (14)	-	-

Adapted from reference 8

cancer. In strain A mice four lesions were observed following treatment in reaction water; three were lung adenomas and one was a breast cancer [8]. In strain A mice treated with heavy oil, five males had lesions; four were hepatomas, and the fifth a breast cancer. One male strain C57 mouse had a skin papilloma following treatment with reaction water.

The author [8] dismissed the neoplasms of the breasts, lungs, and hematopoietic tissues as spontaneous tumors, although no control animal data were presented. In addition, he dismissed the single skin papilloma and the intestinal adenocarcinoma because they were the only ones that occurred. However, the author attributed the hepatomas to the application of heavy oil because most of the livers observed had extensive necrotic changes. Cirrhotic lesions associated with local bile duct proliferations were also seen in one case. Because no diluent or untreated control groups were used and the same number, strain, and sex of mice were not tested with each fraction, the validity of this study is reduced.

Hueper [6] carried out a followup study on product samples obtained from the US Bureau of Mines (BOM) Synthetic Fuels Demonstration Plant in Louisiana, Missouri, which used the Fischer-Tropsch process. He applied five fractions of these oils, each with a different boiling point, by dropper to the nape of the neck of 25 male and 25 female 6-week-old strain C57 black mice twice a week for life. The use of control animals or a diluent control group was not mentioned. The five fractions used were (1) thin synthesis condensate, corresponding to a one- to four-part mixture of diesel oil with gasoline, (2) cracking stock, (3) diesel oil, (4) raw gasoline, and (5) used coolant oil diluted with xylene. The only skin lesions observed were one small papilloma in each of two mice painted with Fraction 4. At necropsy, one mouse (sex unspecified) had a liver sarcoma. The specific times when these lesions appeared and when the animals died were not mentioned. According to the author [6], the effects revealed at necropsy of mice that died in the latter part of the study were not uncommon in untreated mice of the same strain. These effects included nephritis and amyloid (starchlike) lesions of the spleen, liver, kidneys, and adrenal glands.

Certain factors that would affect the author's conclusions were not addressed. These include the use of both untreated and diluent-treated control animals, the maintenance of the fraction at the site of application, the prevention of absorption due to animals licking the site, and the amount of hair remaining at the site following scissoring rather than shaving or clipping, which would interfere with absorption of the material. In addition, no criteria for the necropsies or microscopic evaluations were presented, nor was it mentioned whether the xylene used as a diluent was assayed for benzene contamination.

In the same report [6], Hueper discussed the effects of applying these same five fractions of Fischer-Tropsch oils twice a week to the skin of five 3-month-old Dutch rabbits. Neither the sex of the rabbits nor the concentrations of the fractions were reported. The skin sites included the dorsal surfaces of the ears and three areas on the back. Applications were continued for up to 25 months and followed a rotation scheme that allowed each fraction to be tested on all areas. Several fractions, however, were applied to the same rabbit at different sites. As with the mice, the hair at each site was first cut with scissors. None of the rabbits developed any neoplastic lesions.

Interpretation of this lack of neoplastic lesions is hindered by three considerations: (1) the number of animals used was small, (2) the adherence of the fractions to the site of application was not verified, and (3) the amount of the fraction absorbed was indeterminate. No evidence of cutaneous absorption was given. Painting the same rabbit with different fractions invalidates the results because if tumors were found away from the site of application there would be no way to identify which fraction was responsible. In addition, no control groups were used, and necropsy and microscopic examination criteria were lacking.

In one of two studies with Bergius oil, Hueper [5] tested nine different fractions of Bergius coal hydrogenation products obtained in a large-scale production process operated by the US BOM at its Synthetic Fuels Demonstration Plant at Louisiana, Missouri. These fractions ranged from pitch to finished gasoline and had different boiling points and physiochemical properties. Each fraction was applied by dropper twice a week to the nape of the neck of 25 male and 25 female 6-week-old strain C57 black mice. Applications continued throughout life, except that supplies of Fraction 9 ran out after about 6 months. Post-mortem examinations were performed on all animals used. Histologic examinations of the various tissues and organs were made whenever any significant pathologic changes were found at necropsy.

Papillomas were found at the primary contact site in mice treated with Fractions 1, 2, and 3. Ten squamatous carcinomas occurred with all fractions except Fractions 1, 2, and 8. In addition to these, leukemic or lymphomatous conditions were noted in one mouse treated with Fraction 1, in two mice treated with Fraction 3, and three mice treated with Fraction 7. The author [5] was unsure about the relation of these reactions to the cutaneously applied oils. However, he attributed the fact that none of the mice survived more than 16 months to the high toxicity of the Bergius products. He also concluded that with the exception of finished gasoline, Bergius products possess carcinogenic properties for mice.

Hueper [5] also reported on the application of the same nine Bergius fractions to the skin of ten 3-month-old Dutch rabbits twice a week for 22 months. However, four or five of the fractions were applied to each rabbit at different sites, ie, the dorsal surfaces of ears and back, so that an additional 10 rabbits were used for the study. The skin preparation and mode of application were the same as for the mice. Applications continued for up to 22 months, except that Fraction 9 was discontinued after 6 months because supplies ran out. Hueper [5] performed necropsies on all of the rabbits and histologic examinations on 19. He found 10 carcinomas and 18 papillomas at the primary contact site. In addition, he observed extensive mononuclear leukemic infiltrations in the liver, abdominal lymph nodes, and pancreas in one rabbit treated with Fractions 5 to 9.

Table III-3 shows the distribution by the different oil fractions of benign and malignant tumors at the site of primary contact in mice and rabbits. The author [5] suggested that the greater number of skin tumors in rabbits may have been caused by a greater susceptibility in rabbits than in mice. He did not report the use of untreated or diluent control mice or rabbits, the doses applied to the skin, the steps taken to ensure that the substance remained on the skin, or observations of any tumors at the application sites.

In a series of three separate experiments, Holland et al [9] tested the carcinogenicity of synthetic and natural petroleums when applied to the skin. In these studies SPF male and C3H/fBd female mice were exposed to test materials at various concentrations. The number of animals varied from 20 to 50 per dose group. The effects of coal liquid A, produced by the Synthoil catalytic hydrogenation process, and coal liquid B, produced by the pyrolytic COED process using Western Kentucky coal, were compared with the carcinogenicity of a pure reference carcinogen, benzo(a)pyrene, tested in in vitro tissue

TABLE III-3

INCIDENCE OF CARCINOMAS AND PAPILLOMAS IN MICE AND RABBITS TREATED WITH BERGIUS OIL FRACTIONS

Fraction No.	Product	Carcinomas		Papillomas	
		Mice	Rabbits	Mice	Rabbits
1	Centrifuge residue	0	2	3	4
2	Heavy oil let-down	0	3	1	5
3	Light oil bottoms	1	2	1	2
4	Middle oil	2	3	1	2
5	Cold catchpot liquid	1	0	0	3
6	Cold catchpot vapor	1	0	0	0
7	Raw gasoline	1	0	0	2
8	Finished gasoline	0	0	0	0
9	Pitch flash distillation residue	4	0	0	0

Adapted from reference 5

culture studies. In the same series of studies, three other fossil liquids were also tested: crude shale oil, single-source natural petroleum, and a blend of six natural petroleums. All fractions were analyzed for PAH content by acid-base solvent partition. Three regimens were followed, and in each, the animals were given pasturized feed and hyperchlorinated-acidified water. The test materials were dissolved by sonication or dispersed in a solvent of 30% acetone and 70% cyclohexane, by volume [9]. Fifty microliters of each test material were applied to the dorsal skin of the mice.

In the first of the three treatment regimens, four groups of 15 male and 15 female mice were treated with 25 mg of four of five test materials, which were applied three times a week for 22 weeks [9]. (Single-source petroleum was not tested.) A 22-week observation period followed. With coal liquid A treatment, 20 animals had died by the end of the study, and the final percentage of carcinomas (squamous epidermal tumors) was 63%; for coal liquid B, these figures were 3 and 37%, respectively; and for shale oil, 37 and 47%. No carcinomas or deaths occurred in the animals treated with blended petroleum. The average latency period in animals treated with coal liquid A was 149 days (standard error: 8); in animals treated with coal liquid B, 191 days (14); and in animals treated with crude shale oil, 154 days (9).

In the second regimen, groups of 20 mice (10 male and 10 female) each were tested with one of four materials: coal liquid A, coal liquid B, shale oil, and single-source petroleum, at one of four dose levels: 25, 12, 6, and 3 mg. The applications were administered twice a week for 30 weeks, followed by a 20-week observation period. No skin lesions and no deaths were seen in animals treated with single-source petroleum at any dose level, with crude shale oil and coal liquid B at the 6- or 3-mg levels, or with coal liquid A at the 3-mg level. Other results of this study are presented in Table III-4.

As indicated in the table, all of the syncrudes tested were capable of causing malignant squamous epidermal tumors. Dose-response was observed for the syncrudes. Coal liquid A also appeared to be a tumorigenic agent at the reduced dose level as compared with coal liquid B and shale oil.

In the third regimen, the doses were considerably reduced per application although the frequency of applications was increased from two to three times a week for 24 months [9]. The length of time that the applications were allowed to remain on the skin was also increased. The doses per application for each material were 1.0, 0.3, 0.2, and 0.04 mg for coal liquid A; 0.8, 0.3, 0.17, and 0.03 mg for coal liquid B; 2.5, 0.5, 0.3, and 0.1 mg for shale oil; and 2.0, 0.4, 0.3, and 0.08 mg for composite petroleum. The number of mice used in this regimen was also increased to 50 (25 of each sex) per dose level.

In general, the results of this regimen were similar to those of the second regimen with the higher dose and shorter application time. However, this longer exposure at lower doses allowed time for carcinoma induction and expression in the blended petroleum group. This result was not seen in the previous regimen. The design of the study, ie, using several dose levels, produced evidence that a sufficient amount of fraction was being applied to produce effects. In each case, no effects or a weak effect (0-4% carcinoma) was produced at the lowest doses and a much stronger effect was produced at the highest doses (up to 92%). The results of this regimen are shown in Table III-5.

The authors [9] compared the data from the third regimen with results obtained by applying benzo(a)pyrene in the same solvent three times weekly to the same strain of mice. Fifty mice (25 of each sex per dose level) were tested with 0.05, 0.01, and 0.002 mg of benzo(a)pyrene. At the two highest doses, the percentage of skin carcinomas observed was 100%, with an average latency of 139 days at the 0.05-mg level and 206 days at the 0.01-mg level.

TABLE III-4

CARCINOGENICITY OF SYNCRUDES APPLIED TO MICE TWICE A WEEK FOR 30 WEEKS

Material	Dose/Application (mg)	Final Percentage of Carcinomas
Coal liquid A	25	80
	12	35
	6	10
Coal liquid B	25	10
	12	5
Crude shale oil	25	35
	12	5

Adapted from reference 9

TABLE III-5

CARCINOGENICITY OF SYNCRUDES APPLIED TO MICE THREE TIMES A WEEK FOR 24 MONTHS

Material	Dose/Application (mg)	Final Percentage of Carcinomas
Coal liquid A	1.0	92
	0.3	26
	0.2	8
	0.04	4
Coal liquid B	0.8	8
	0.3	4
	0.17	2
	0.03	2
Shale oil	2.5	90
	0.5	2
	0.5	2
	0.3	0
Composite petroleum	2.0	8
	0.4	0
	0.3	0
	0.08	0
Vehicle (30% acetone + 70% cyclohelane)	--	0

Adapted from reference 9

At the lowest dose (0.002 mg) the percentage of skin carcinomas observed was 90%, with an average latency of 533 days. At 24 months, 58% mortality was observed. The dose that most closely approximated the carcinogenicity of the syncrudes was the 0.05-mg dose. The authors indicated that this amount was one five-hundredth of the amount of coal liquid A that would be required to elicit a comparable skin tumor incidence.

In addition to the study discussed above, the same authors [9] analyzed the percentages of PAH's and benzo(a)pyrene in each sample. The PAH content did not correlate with the carcinogenicity of the materials, but the benzo(a)pyrene concentration did agree with the potency of each mixture. The percentages of PAH's by weight for coal liquid A, coal liquid B, shale oil, and blended petroleum were 5.1, 6.0, 2.0, and 2.6, respectively. Single-source petroleum was not analyzed. The micrograms of benzo(a)pyrene per gram for coal liquid A, coal liquid B, shale oil, blended petroleum, and single-source petroleum were 79, 12, 30, approximately 1, and 1, respectively.

In a study of 15 coal hydrogenation materials, Weil and Condra [7] applied samples from streams and residues to the skin of 15 groups of 30 male mice, three times a week for 51 weeks. Two species of mice were tested, Rockland All-Purpose (20% of animals) and C3H (80%). The authors compared the results with positive (0.2% methyl cholanthrene in benzene) and negative (benzene and water) control agents, and concluded that the light and heavy oil products were "mildly" tumorigenic, ie, predominantly produced papillomas. A high incidence of carcinogenicity was seen for middle oil stream, light oil stream residue, pasting oil, and pitch product (Table III-6). The specific types and numbers of papillomas and carcinomas were not reported. In general, the incidence of carcinogenicity increased as the boiling points of the fractions rose.

Renne et al [51] recently published results of studies of skin carcinogenesis in mice. The materials tested were heavy and light distillates from solvent-refined coal, shale oil, and crude petroleum. Also tested were reference carcinogens benzo(a)pyrene and 2-aminoanthracene. A mixture of 50 ml of the test materials in acetone was applied 3 times per week to the dorsal surface of C3Hf/HeBd mice of both sexes.

After 465 days of exposure, the mice showed high incidences of skin tumors with heavy distillate, shale oil, and benzo(a)pyrene. Petroleum crude (Wilmington) and light distillate showed less tumorigenic activity. The two groups of mice treated with the highest doses of heavy distillate (22.8 and 2.3 mg per application), shale oil (21.2 and 2.1 mg per application) and benzo(a)pyrene (0.05 and 0.005 mg per application) showed almost 100% tumor incidence. In contrast, only one mouse in each of the high (20 mg per application) and medium (2.0 mg per application) dose groups exposed to light distillate developed skin tumors. The latency period for tumors was shortest (56 days at the highest concentration) for mice exposed to heavy distillate. All tumors were malignant squamous cell carcinomas, regardless of the treatment group. Untreated and vehicle-treated (acetone) control mice did not

TABLE III-6

PERCENTAGE OF TUMORS AND CANCERS PRODUCED BY COAL PROCESS MATERIALS IN MICE*

Coal Process Material	Boiling Point °C	Percentage of Tumors	Percentage of Cancers
Heavy oil product	--	30	0
Light oil product	--	27	4
Light oil stream	260	0	0
Middle oil stream	260-320	46	15
Light oil stream residue**	260-380	66 87	38 39
Pasting oil**	320-450	78 100	56 100
Pitch product**	>450	54 77	12 63
Stabilizer overhead	35-100	0	0
Crude nitrogen bases	195-260	0	0
Neutral light oil	115-260	0	0
Crude naphthalene	200-230	0	0
High boiling hydrocarbons	230-260	0	0
Low boiling phenols	180-230	0	0
High boiling phenols	230-260	0	0
Phenolic pitch	260+	0	0

*Eighty percent of the experimental mice were of the C3H strain. The remaining mice were identified as Rockland All-Purpose from Rockland Farms. No tumors or cancers were observed in control mice.

**Two different samples were tested.

Adapted from reference 7

develop any tumors. Tumor incidence in the 2-aminoanthracene positive control group was 25/32 and 0/49 at dose levels of 0.05 and 0.005 mg, respectively [51].

(2) Intramuscular Injections

In addition to the dermal studies using mice and rabbits, Hueper [5] also conducted injection studies using rats. Each of the nine fractions of Bergius oils previously described were injected im into the right thighs of groups of ten 3-month-old Wistar rats once a week for 3 successive weeks. This regimen was repeated with rats surviving after 6 months. Each fraction was diluted at a ratio of 1.1 g oil to 16.5 cc tricaprylin. An individual 0.3-cc dose of this mixture contained 0.02 g of oil. Fraction 3 was administered to 20 additional rats because of high mortality early in the experiment (weeks 5-6). The time when these extra animals were added to the study was not mentioned.

The controls consisted of two groups of 30 rats each. One control group was injected in the marrow cavity of the right femurs with 0.1 cc of a 2% gelatin solution in physiologic saline. The same amount of solution was injected into the nasal sinuses of the other control group through a hole drilled in the frontal bone. The purpose of this second control was not reported. After a 2-year observation period, all surviving animals were killed and histologic examinations of selected tissues and organs were made in cases where pathologic changes were observed. No diluent (tricaprylin) control animals were studied.

Rats died throughout the study period, with the highest incidences per group (5-9 deaths) between weeks 7 and 10 for all fractions except Fraction 3. For Fraction 3, 28 deaths were reported, 23 of which occurred during weeks 5 and 6. A total of 13 tumors away from the site of injection were observed in the 100 treated animals. Of these, 11 tumors were malignant [5].

Rats treated with Fractions 3, 4, 6, 7, 8 (three cases), and 9 showed large round-cell sarcomas. Ovarian fibromas were also observed in one rat in each of the groups injected with Fractions 1 and 9; an ovarian adenocarcinoma was observed in one rat given Fraction 3. A retroperitoneal fibrosarcoma was found in a rat treated with Fraction 7, and a small squamous-cell lung carcinoma was found in one rat treated with Fraction 9. In addition, a fibrosarcoma was found at the injection site in each of two rats. Nine malignant and two benign tumors were observed in the 60 rats used as controls; these tumors included four round-cell abdominal lymph node sarcomas, five spindle-cell liver sarcomas, one squamous-cell papilloma of the forestomach, and one breast adenofibroma. The author [5] concluded that one of the spindle-cell liver sarcomas was due to the presence of a parasitic infection and originated from the wall of a cyst. Tumors were not observed at the site of gelatin injection in either treated or control animals.

Several factors detract from the conclusiveness of Hueper's findings [5]. For example, neither the time of appearance of these lesions nor the time of necropsy were reported. In addition, the incidence of lesions occurring away from the injection site was reported to be 13 lesions in 100 rats, but this total does not agree with the total number of deaths and necropsies (110) reported for the treated animals. This discrepancy may be a result of the author not including the original 10 rats tested with Fraction 3 in his reports. Additional discrepancies were: 11 deaths and necropsies were reported for rats treated with Fraction 7 although only 10 animals were studied; 9 deaths were reported for rats treated with Fraction 9 but no mention was made of the 10th animal in that group; and 9 malignant tumors were observed in the 60 control animals, but the author did not indicate in which of the two control groups these lesions were seen.

Hueper [6] also conducted one study consisting of three series of im injections of the five Fischer-Tropsch oil fractions using Wistar rats. There was a 2-month interval between the first and second series and a 4-month interval between the second and third series. Two injections were given in each series, and there was an interval of 1 week between the injections. Each of the five treatment groups consisted of 15 Wistar rats of both sexes. At the end of a 2-year observation period, all surviving rats were killed for histopathologic examination. Pathologic studies were done on 41 rats.

This study revealed that Fischer-Tropsch products showed definite carcinogenic properties for rats when administered by im injections. Fischer-Tropsch products are species and tissue specific. The carcinogenic effects of these oils may not be restricted to the tissues in which these materials are deposited. The histopathologic results showed that lesions occurring at the site of injection varied. For Fraction 1, necrosis and multicystic fat tissue were observed; for Fractions 2 and 5, granulomas were seen; and for Fraction 3, fibrosis occurred. Fraction 4 produced no lesions. A total of 19 tumors in 75 rats was observed. Two tumors, a breast adenofibroma and an adrenal hemangioma, were benign, and the 17 others were malignant. These were spindle-cell sarcomas or fibrosarcomas of the right thigh, spindle-cell abdominal lymph node sarcomas, round-cell abdominal sarcomas, kidney adenocarcinomas, and squamous-cell lung carcinomas. The spindle-cell and round-cell sarcomas produced had metastasized to other organs such as the spleen, liver, kidney, and lung. The tumors that resulted from each of the five oil fractions injected im into rats are listed in Table III-7.

According to Hueper [6], the proximity of the spindle-cell thigh sarcomas to the injection site implicated the injected materials (Fractions 2, 4, and 5). The types of cancer observed indicated that Fraction 5 seemed to be the most carcinogenic and Fractions 2 and 4 followed in degree of carcinogenicity, while the carcinogenic potency for Fractions 1 and 3 was uncertain. Hueper did not explain the relationship of the other cancers to the materials tested except to say that the materials may have been transported through the lymph nodes to the remote sites. This study did not include any untreated or diluent control animals.

TABLE III-7

MALIGNANT TUMORS IN RATS INTRAMUSCULARLY INJECTED WITH FISCHER-TROPSCH OILS

Fraction No.	Fraction Name	No. of Tumors	Types of Tumors
1	Synthesis condensate	1	Spindle-cell abdominal sarcoma
2	Cracking stock	5	2 Spindle-cell abdominal sarcomas 2 Spindle-cell thigh sarcomas 1 Lung carcinoma
3	Diesel oil	4	1 Spindle-cell abdominal sarcoma 3 Round-cell abdominal sarcomas
4	Raw gasoline	3	1 Spindle-cell thigh sarcoma 1 Round-cell abdominal sarcoma 1 Kidney carcinoma
5	Coolant oil	4	4 Spindle-cell thigh sarcomas

Adapted from reference 6

These studies show that the fractionation products obtained through the hydrogenation of coal are, in general, carcinogenic in at least one animal species; that the incidence of carcinogenicity seems to decrease as the boiling points of the fractionation products decrease; and that carcinogenicity may not be restricted to the tissues into which the material was originally administered. Although treatment schedules were not the same as possible daily industrial exposures, and the numbers of animals tested were small (5-100) or not reported at all, the results of these studies indicate that certain coal liquefaction products contain carcinogenic chemicals.

(d) Mutagenicity Studies

Mutagenicity studies have been conducted using strains of the bacterium *Salmonella typhimurium* that require histidine for growth [40-45,50]. Two of these strains (TA 100 and 1535) are used to detect base-pair mutations, and others (TA 98, 1536, 1537, and 1538) are used to detect frameshift mutations. Rubin et al [42] tested 14 fractions of syncrude from the COED process using *S typhimurium* strains TA 1535, 1536, 1537, and 1538. An unspecified number of control plates was used for spontaneous reversion and sterility checks. The results showed an increase in the number of revertants (1,000 colonies over background) with four fractions when the system was metabolically activated. These fractions were benzene/ether (TA 1536, 1537, and 1538), hexane/benzene (TA 1537 and 1538), and hexane (TA 1537 and 1538), and one ether-soluble fraction (TA 1537 and 1538).

Using chemicals supplied by the manufacturers, Teranishi et al [41] reported results of mutagenicity tests on PAH's found in coal liquefaction processes by observing metabolic activation in *S typhimurium* strains TA 1535, 1536, 1537, and 1538. In at least one strain, the authors found at least a doubling of the number of revertants above those shown in the dimethylsulfoxide controls. Using this criterion, benzo(a)pyrene, benz(a)anthracene, 7,12-dimethyl-benz(a)anthracene, and dibenzo(a,i)pyrene were mutagenic. Anthracene, benzo(e)pyrene, dibenzo(a,c)pyrene, and dibenz(a,h)anthracene did not produce a doubling of the number of revertants above that of the controls.

Shults [40] reported on preliminary studies with 17 fractions of COED syncrude tested at Oak Ridge National Laboratory (ORNL) using four *S typhimurium* strains (TA 1535, 1536, 1537, and 1538). Mutagenicity was recorded for 8 of 17 fractions: hydrochloric acid insolubles, ether soluble bases and weak acids, first and second cyclohexane extracts, phenanthrene-benz(a)anthracene, benz(a)anthracene, and benzo(a)pyrene. Fractions that did not induce mutagenicity included ether-soluble strong acids, neutrals, polar compounds in water, dimethylsulfoxide residuals, phenanthrene, insoluble weak and strong acids, insoluble bases, and insoluble sodium hydroxide. No mention was made of whether or not metabolic activation was incorporated.

Epler and coworkers [44] tested fractions of Synfuels A and B for mutagenic activity in *S typhimurium* strains TA 98 and 100 using metabolic activation. The results indicated mutagenicity from both Synfuel A (1, 2, and 3) and Synfuel B, although the insoluble base fraction (a) showed a greater increase in the number of revertant colonies than did the neutral fraction, the insoluble sodium hydroxide fraction, or the diethyl ether-soluble fraction. Fractions producing little or no increase in revertant colonies over that of the control product, composite crude oil, included the insoluble weak and strong acids, the water-soluble strong acids, the water-soluble bases,and the insoluble base fraction (b).

In the same laboratory, Rao et al [45] tested four fractions of Synfuel A-3. He detected an increase in the number of revertant colonies after metabolic activation of the test materials in the tester strains (TA 100 and 1535) designated to detect mutagenicity by base-pair substitution. Strains TA 98, 1537, and 1538, designated to detect frameshift mutations, proved to be more sensitive to metabolically activated fractions, with strains TA 98 and 1538 exhibiting a 20- to 75-fold increase over the incidence of spontaneous reversion.

Using selected fractions of Synfuels A and B that provided a large number of revertant colonies in the *S typhimurium* assay, Epler and coworkers [43] compared their results by using other systems. Comparative systems included forward and reverse mutation assays in *Escherichia coli* and *Saccharomyces cerevisiae*, chromatid aberrations in human leukocytes, and gene mutation in *Drosophila*. The results of the *E coli* 343/113 (K-12, *gal RS* 18, *arg 56*, *nad 113*) assay supported the results obtained with *S typhimurium*. Results with *S cerevisiae* strain XA4-8Cρ^-, *his1-7*, with forward mutants to canavanine resistance (*CAN*-*can*) and revertants to histidine prototrophy indicated antagonistic effects with metabolic activates. In this assay, $1.2x10^8$ cells in an unspecified amount of buffer were used. Treatment of the human leukocytes with the fractions did not produce chromatid aberrations; however, metabolic activation was not attempted, and in the *Drosophila* sex-linked recessive lethal test, no fraction gave a significant increase over the spontaneous level. The genus and number of *Drosophila* used and the number of chromosomal preparations from human peripheral leukocytes were not specified.

Pelroy et al [50] recently published the results of studies that used the *S typhimurium* test system to evaluate the mutagenicities of light, middle, and heavy distillates from the SRC-II process, raw shale oil, crude petroleums, and some SRC-I process materials. Tests were performed in both the presence and absence of mammalian liver microsomal enzymes (S9) in several strains of *S typhimurium*. Significant mutagenic activity was seen with high boiling point materials from the SRC-II (heavy distillate) and the SRC-I (process solvent) processes. In strain TA 98, 90.0±23 and 12.3±1.9 revertants per mg of heavy distillate (SRC-II) and process solvent (SRC-I), respectively, were observed. The light and middle distillates showed no mutagenic activity. Raw shale oil (Paraho-16, Paraho-504, and Livermore L01) had very low mutagenic activity. Crude petroleum (Prudhoe Bay and Wilmington) showed less than 0.1 revertants per mg of material. When the mutagenic activities of the coal liquefaction materials were compared with those of the pure reference carcinogens benzo(a)pyrene and 2-aminoanthracene in strain TA 98, benzo(a)pyrene was 3 times more active than the heavy distillate, while 2-aminoanthracene was 100 times more active.

The materials encountered in coal liquefaction processes are generally complex organic mixtures, so identification of the biologically active components is essential. This was accomplished by chemical and physical fractionation of the mutagenically active products, followed by additional mutagenicity testing. Fractionation of heavy distillate by a solvent-extraction procedure yielded acidic, basic, and neutral fractions, as well as basic and neutral tar fractions. When these fractions were tested for mutagenicity by the Ames system, the basic fraction showed the highest number of revertants per mg of material. The basic and neutral tar fractions were 0.125 and 0.5 as active as the basic fraction. The acidic and neutral fractions were nonmutagenic. Basic fractions from shale oil and other materials also showed high specific activity. These results suggested that the polar nitrogen-containing components might be responsible for the mutagenic activity of the heavy distillate and other oils. Separation of mutagenic compounds from the heavy distillate and the process solvent was followed by gas chromatographic/mass spectral (GC/MS) analyses of the specific components. The results indicated that 3- and 4-ring primary aromatic amines were responsible for a large fraction of the mutagenic activity of the heavy distillate and the process solvent. The 2-ring aminonapthalenes contributed little to the mutagenic activity of these products.

Indications that the aromatic amines were responsible for mutagenic activity were further confirmed by mutagenicity testing of materials eluted by thin-layer chromatography (TLC) of the basic fraction of heavy distillate. Testing was conducted in strain TA 98 S typhimurium, utilizing mixed-fraction amine oxidase (MFAO) or a mixture of hepatic enzymes (S9). MFAO is specific for the metabolic transformation of primary aromatic amines to mutagenically active compounds; it is inactive with PAH's. The mutagenic responses obtained with the TLC components of heavy distillate using both MFAO and S9 were comparable, yielding direct evidence of the presence of aromatic amines in heavy distillate. Additional evidence of the mutagenicity of the aromatic amines was provided when the mutagenic activity of the heavy distillate, the process solvent, and their basic and tar fractions was reduced by 90% after nitrosation.

In all of these studies, the PAH's, the ether-soluble bases and weak acids of COED syncrude and Synfuels A and B, and the insoluble bases and neutral portions of Synfuels A and B are mutagenic when tested in S typhimurium, but studies in higher organisms (human leukocytes and Drosophila) indicate negative results. Both SRC-II heavy distillate and SRC-I process solvents are mutagenic in S typhimurium. Further testing indicates that this activity is caused by their aromatic amine components.

Reproductive Effects and Other Studies

Andrew and Mahlum [14,15] also evaluated reproductive effects by exposing pregnant rats to SRC-I light oil, wash solvent, and process solvent [47,52]. These substances were given either undiluted or in corn oil by gavage once daily for either days 7-11 or 12-16 of gestation. Corn oil alone was administered to vehicle control groups, and 2.5% Aroclor 1254 in corn oil was used for positive control groups. Rats were killed at 21 days of gestation for evaluation of embryotoxicity or were permitted to deliver offspring for postnatal monitoring of growth, physical maturation, and reflex ontogeny.

Maternal lethality and embryolethality of $\geq 50\%$ were seen in groups dosed on days 7-11 of gestation with light oil, wash solvent, or process solvent at 3.0, 1.4, or 0.7 g/kg/d, respectively. Similar results were seen after the same dosing on days 12-16 of gestation. Malformations, consisting of cleft palate and brachydactyly, and low fetal weights were seen after light oil dosing at 3.0 g/kg/d on days 7-11 of gestation or after process solvent dosing at 0.7 g/kg/d on days 12-16. No effects on postnatal maturation were seen.

Andrew and Mahlum [15] reported the results of studies on reproductive effects of SRC-II light, medium, and heavy distillates. Pregnant rats were administered unspecified doses once daily for 5 consecutive days during the gestation periods of either 7-11 days (early period of organogenesis) or 12-16 days (late period of organogenesis). Embryolethality, malformations, and fetal weights were determined after killing the rats at 21 days of gestation. Fetal growth and survival were decreased by all three materials administered during either period. Fetal effects for all three materials were more severe at 12-16 days of gestation than at 7-11 days of gestation. None of the materials increased the incidence of malformation over that in controls at 7-11 days of gestation. Increased incidence of malformations, principally cleft palate, diaphragmatic hernia, and hypoplastic lungs, was produced by the heavy distillate when administered at 12-16 days of gestation. In most cases, doses of materials that produced prenatal toxicity also produced some indications of maternal toxicity.

In 1978, MacFarland [46] reported the results of several short-term toxicity studies in rats and rabbits exposed to dry mineral residue (DMR) and to solvent-refined coal products. The lethal dose for 50% survival of group (LD_{50}) for both materials tested was >15,380 mg/kg in short-term oral studies on rats. The short-term dermal LD_{50} for both compounds in rabbits was >10,250 mg/kg. For short-term vapor inhalation in rats, lethal concentration for 50% survival of group (LC_{50}'s) were determined for the process solvent (>1.69 mg/liter), coal slurry (>0.44 mg/liter), heated filter feed (>1.14 mg/liter), wet mineral residue (3.94 mg/liter), light oil (>71.6 mg/liter), and wash solvent (>7.91 mg/liter). The adult rats that received lethal doses of light oil or wash solvent showed signs of distress within 30 minutes, including convulsions and twitching of extremities. Because of their low volatility, the process solvent and wash solvent were tested as aerosols in short-term inhalation studies using rats, and the LC_{50}'s were determined to be >7.6 and 16.7 mg/liter, respectively. Tests for acute eye irritation in rabbits identified light oil and wash solvent to be severely irritating, wet mineral residue extremely irritating, coal slurry and filter feed moderately irritating, process solvent mildly irritating, and dry mineral residue and solvent-refined coal minimally irritating [46]. The three materials identified to be severely or extremely irritating were tested in 14-day eye irritation studies. Only with light oil was there a noticeable improvement after 14 days. Indications of fetotoxicity were reported in rats and rabbits in pilot teratogenic testing with filter feed and wet mineral residue applied dermally [46]. However, no additional data were included. In addition, the number of animals used in the short-term studies was not mentioned, except for the statement that a small number of animals was used.

Mahlum and Andrew [47,58] observed short-term toxicities in fasted adult, female Wistar rats following administration of SRC-I and SRC-II liquids by gavage. Ten to 25 rats per dose per material in two to four replicates were used. Adult LD_{50}'s were determined for SRC-I light oil, wash solvent, and process solvent and for SRC-II light, medium, and heavy distillates. The process solvent was also tested in newborn and weanling rats. Acute adult LD_{50}'s of 0.57, 2.9, and 2.8 g/kg were obtained for undiluted wash solvent, light oil, and process solvent, respectively. Dilution in corn oil increased the LD_{50} for wash solvent to 1.7 g/kg but did not alter values for light oil and process solvent. LD_{50} values for light and heavy distillates (2.3 and 3.0 g/kg, respectively) were similar to those for light oil and process solvent, while the value for distillates of 3.7 g/kg was five times the value for wash solvent. The lethal dose (LD) of process solvent for weanling and adult rats was similar but about twice as high as that for newborn rats. Subchronic LD_{50}'s for light oil, wash solvent, and process solvent diluted in corn oil were 2.4, 1.5, and 1.0 g/kg/d, respectively. Subchronic toxicity data for light, middle, and heavy distillates were 0.96, 1.48, and 1.19 g/kg/d, respectively. All materials were administered once a day for 5 consecutive days. For all materials except light oil and wash solvent, the subchronic values were significantly lower than the acute values. These results indicate that the cumulative effects are low for light oil and wash solvent, but significant for process solvent and light, middle, and heavy distillates.

Frazier and coworkers [77,78] examined the in vitro cytotoxicity of materials from the SRC-I and SRC-II processes and compared the results with those from studies with other fossil fuel products. The clonal growth assay and Syrian hamster embryo (SHE) cell transformation assay were used. The SRC-I process solvent, the shale oil, and the SRC-II heavy distillate caused a 50% reduction in the relative plating efficiency (RPE_{50}) of Vero African green monkey kidney cells at concentrations between 30 and 50 µg/ml. Other materials, including other SRC byproducts, diesel oil, and several crude oils, were slightly less toxic and produced RPE_{50}'s at concentrations between 50 and 500 µg/ml.

Transformation studies were also performed in SHE cells in the presence and absence of S9 [77,78]. Cells that were preincubated for 16-24 hours were treated with the test materials. The results of the transformation assays were in general agreement with those of the microbial mutagenesis studies. Heavy distillate and process solvent produced 6.8 and 10% transformed colonies, respectively, compared with 0.2-0.4% for petroleum crudes and 3% for shale oil. Basic fractions were more active than the unfractionated crudes. Transformation frequency was higher for all the materials when they were metabolically activated. Petroleum crudes and shale oil exhibited low levels of activity in the cell transformation assays.

The authors concluded that these data demonstrate that certain fossil fuel components are toxic and are capable of transforming mammalian cells. However, the authors also stressed that considerable variability in these assays, due to solubility differences, may arise, and therefore these data represent only potential results and should not be used to establish the carcinogenic potential of these compounds [77,78].

In the same series of tests, Burton and Schirmer [79,80] examined by gas chromatography (GC) the tissue distribution of SRC process solvent components in two rats administered 90% process solvent in corn oil (1 ml/300 g) by gavage. The rats died within 2 days. Small, unspecified amounts of process solvent were found in the kidneys, liver, lungs, and fat; larger amounts were found in the gut and gut contents, and in the stomach and stomach contents. Total amounts recovered were 10-40% of the administered dose.

A second group of 10 rats was administered 0.5 ml of process solvent by gavage. The animals were killed 2, 4, 8, 24, and 48 hours after the dose, and tissues, urine, and feces were collected. In addition, blood samples were taken at 0.5, 1, 1.5, and 16 hours as well as after the animals were killed. Significant levels of phenanthrene (17 μg/g), biphenyl (3 μg/g); and 2-methylnaphthalene (7 μg/g) were found in the livers within 1 hour. Significant levels were also found in red blood cells (RBC's) after 1 hour. Concentrations were highest during the first 8 hours and significantly lower through 48 hours.

In the same series of experiments, the pulmonary resistance, dynamic pulmonary compliance, respiratory rate, tidal volume, and minute volume were also determined in guinea pigs that inhaled 100 mg/m^3 light oil from solvent-refined coal [49]. Preexposure values were recorded for 15 minutes prior to exposing the animals. Animals were then exposed either to air or to light oil for 30 minutes, followed by a 15-minute recovery period. No effects were noted, indicating that inhalation of 100 mg/m^3 of light oil did not affect pulmonary resistance, dynamic compliance, or breathing patterns in guinea pigs.

By measuring fluorescence intensity, Holland et al [9,81] developed an assay system to determine the time-integrated dose of material that interacts with epidermal deoxyribonucleic acid (DNA) after topical application in vivo. Although a relationship between fluorescence intensity and carcinogenicity exists for certain materials, with the exception of coal liquid A, the synthetic petroleums actually exhibited lower specific fluorescence than did the reference blend of natural petroleum, thus exhibiting little or no correlation with carcinogenicity. The authors also compared in vitro and in vivo fluorescence intensity with carcinogenicity for coal liquid A, coal liquid B, shale oil, and composite crude. A positive correlation between tissue fluorescence and carcinogenicity was observed for both of the coal liquids but not for shale oil. Nonfluorescing constituents of shale oil may have been responsible for these differences, which indicate limitations in using this technique for complex organic mixtures.

Data on the effects of exposing animals to coal liquefaction materials are summarized in Table III-8.

TABLE III-8

SUMMARY OF TOXICITY STUDIES

Animal Organism (Number)	Exposed to	Maximum Dose and Route	Effects (Incidence)	Reference (Year)
Mice (225 male and 225 female)	Bergius oil fractions: Centrifuge residue* Heavy oil let-down Light oil bottoms Middle oil Cold catchpot liquid Cold catchpot vapor Raw gasoline Finished gasoline Pitch flash distillation residue*	Undiluted, 2x/wk/lifetime, cutaneous	Carcinoma (10), papilloma (6), leukemia (6)	5 (1956)
(450)	Bergius oils: Heavy oil Light oil Centrifuge residue	Progressive dilutions, lx/wk/15 mo, cutaneous	Carcinoma (28), papilloma (45), leukemia (4), lung adenoma (3)	8 (1953)
(375)	Fischer-Tropsch oil: Light oil (undiluted) Heavy oil (diluted 1:2) Reaction water (diluted 1:4)	lx/wk/18 mo, cutaneous	Papilloma (1), carcinoma (5), adenoma (4), leukemia (1), hepatoma (4)	8 (1953)
(25 male and 25 female)	Fischer-Tropsch oil: Synthesis condensate Cracking stock Diesel oil Raw gasoline Coolant oil	Undiluted, 2x/wk/lifetime, cutaneous	Papilloma (2), sarcoma (1)	6 (1956)
(450)	15 coal hydrogenation chemicals	Varying dilutions, 3x/wk/1 yr, cutaneous	Carcinogenic**, tumorigenic**	7 (1960)
(120)	Product oils: Synthoil COED Shale oil Composite petroleum	25 mg 3x/wk/22 wk, cutaneous	Carcinoma (44)	9 (1979)

TABLE III-8 (CONTINUED)

SUMMARY OF TOXICITY STUDIES

Animal Organism (Number)	Exposed to	Maximum Dose and Route	Effects (Incidence)	Reference (Year)
Mice (continued)				
(320)	Product oils: Synthoil COED Shale oil Single source petroleum	25 mg 2x/wk/30 wk, cutaneous	Carcinoma (36)	9 (1979)
(800)	Product oils: Synthoil COED Shale oil Composite petroleum	2.5 mg 3x/wk/24 mo, cutaneous	Carcinoma (124)	9 (1979)
Guinea Pigs	Light oil from solvent-refined coal	100 mg/m^3 for 30 min, inhalation	No pulmonary effects	49 (1979)
Rats (100)	Bergius oil fractions: Centrifugation residue Heavy oil let-down Light oil bottoms Middle oil Cold catchpot liquid Cold catchpot vapor Raw gasoline Finished gasoline Pitch flash distillation residue	0.02 g for 1x/wk/3 wk, then 1x/wk/3 wk after 6 mo, im	Sarcoma (7), carcinoma (2), fibroma (1)	5 (1956)
(75)	Fischer-Tropsch oil: Synthesis consensate Cracking stock Diesel oil Raw gasoline Coolant oil	Dose unknown, 6 doses in 7 mo, im	Sarcoma (15), carcinoma (2)	6 (1956)
	Dry mineral residue Solvent-refined coal	LD_{50} > 15.4 g/kg, oral		46 (1978)

TABLE III-8 (CONTINUED)

SUMMARY OF TOXICITY STUDIES

Animal Organism (Number)	Exposed to	Maximum Dose and Route	Effects (Incidence)	Reference (Year)
Rats (continued)				
	Process solvent	LC_{50} >7.6 mg/liter		46 (1978)
	Wash solvent	LC_{50} >16.7 mg/liter, inhalation		
		LC_{50}'s, vapor inhalation:		46 (1978)
	Process solvent	>1.69 mg/liter		
	Coal slurry	>0.44 mg/liter		
	Heated filter feed	>1.14 mg/liter		
	Wet mineral residue	3.94 mg/liter		
	Light oil	>71.6 mg/liter		
	Wash solvent	>7.91 mg/liter		
	SRC-I light oil	Acute LD_{50}, = 2.9 g/kg		47 (1979)
	Wash solvent	oral = 0.7 g/kg		
	Process solvent	= 2.8 g/kg		
	"	0.7, 1.4, and 3.0 g/kg to pregnant rats, oral	Fetal malformations, low fetal weights	14 (1979)
	SRC-I light oil	Subchronic = 2.4 g/kg/d		52 (1979)
	Wash solvent	LD_{50}, oral = 1.5 g/kg/d		
	Process solvent	= 1.0 g/kg/d		
	SRC-II light distillate	Acute LD_{50}, = 2.3 g/kg		52 (1979)
	Middle distillate	oral = 3.7 g/kg		
	Heavy distillate	= 3.0 g/kg		
	SRC-II light distillate	Subchronic = 0.96 g/kg/d		52 (1979)
	Middle distillate	LD_{50}, oral = 1.48 g/kg/d		
	Heavy distillate	= 1.19 g/kg/d		

TABLE III-8 (CONTINUED)

SUMMARY OF TOXICITY STUDIES

Animal Organism (Number)	Exposed to	Maximum Dose and Route	Effects (Incidence)	Reference (Year)
Rabbits (5)	Fischer-Tropsch Fractions: Synthesis condensate Cracking stock Diesel oil Raw gasoline Used coolant oil	2x/wk/25 mo, cutaneous	Noncarcinogenic effects	6 (1956)
	Bergius oil fractions: Centrifuge residue Heavy oil let-down Light oil bottoms Middle oil Cold catchpot liquid Cold catchpot vapor Raw gasoline Finished gasoline Pitch flash distillation residue	2x/wk/22 mo, cutaneous	Carcinoma (10), papilloma (18), leukemia (1)	5 (1956)
	Dry mineral residue Solvent-refined coal	LD$_{50}$ >10.3 g/kg, cutaneous		46 (1978)
S typhimurium	Fractions of Synfuels A and B:	Unspecified		44 (1978)
	Sodium hydroxide, insoluble		Mutagenic	
	Weak acids, diethyl ether-soluble		"	
	Bases, insoluble (a)		"	
	Bases, diethyl ether-soluble		"	
	Neutral		"	
	Weak acids, insoluble		Nonmutagenic	
	Strong acids, insoluble		"	
	Strong acids, water-soluble		"	
	Bases, insoluble (b)		"	

TABLE III-8 (CONTINUED)

SUMMARY OF TOXICITY STUDIES

Animal Organism (Number)	Exposed to	Maximum Dose and Route	Effects (Incidence)	Reference (Year)
S typhimurium (continued)				
	Fractions of Synthoil and COED process:	Unspecified		40 (1976)
	Hydrogen chloride, insoluble		Mutagenic	
	Bases, ether-soluble		"	
	Weak acids, ether-soluble	"		
	First cyclohexane extract (neutrals)		"	
	Second cyclohexane extract	"		
	Phenanthrene-BaA		"	
	BaA		"	
	BaP		"	
	Sodium hydroxide, insoluble		Nonmutagenic	
	Weak acids, insoluble		"	
	Strong acids, insoluble		"	
	Bases, insoluble		"	
	Strong acids, ether-soluble		"	
	Neutrals		"	
	Polar compounds in water			
	Dimethyl sulfoxide residuals		"	
	Phenanthrene		"	
	Fractions of Syncrude from COED process:	Unspecified		42 (1976)
	Sodium hydroxide, insoluble		Nonmutagenic**	
	Weak acids, insoluble		"	
	Weak acids, diethyl ether-soluble		"	
	Strong acids, insoluble		"	
	Strong acids, diethyl ether-soluble		"	
	Strong acids, water-soluble		Mutagenic**	
	Bases, insoluble (a)		Nonmutagenic	

TABLE III-8 (CONTINUED)

SUMMARY OF TOXICITY STUDIES

Animal Organism (Number)	Exposed to	Maximum Dose and Route	Effects (Incidence)	Reference (Year)
S typhimurium (continued)				
	Bases, insoluble (b)		Nonmutagenic	
	Bases, diethyl ether-soluble		Mutagenic	
	Bases, water-soluble		Nonmutagenic	
	Hexane		Mutagenic	
	Hexane/benzene		"	
	Hexane/ether		"	
	Methanol		Nonmutagenic	
	Polyaromatic hydrocarbons:	50 μg/plate		41 (1975)
	Anthracene		Nonmutagenic	
	Benzo(a)pyrene		Mutagenic	
	Benzo(a)anthracene		"	
	Benzo(e)pyrene		Nonmutagenic	
	7,12 Dimethyl-benz-(a)anthracene		Mutagenic	
	Dibenzo(a,i)pyrene		"	
	Dibenzo(a,c)pyrene		Nonmutagenic	
	Dibenz(a,b)anthracene		"	
	Light oil		Mutagenic	50 (1979)
	Wash solvent		"	
	Process solvent		"	
	Light distillate		"	
	Medium distillate		"	
	Heavy distillate		"	
	Paraho 16 shale oil		"	
	Paraho 504 shale oil		"	
	Livermore L01 shale oil		"	
	Fractions of Synfuel A-3	Unspecified	Mutagenic	45 (1978)
	Fractions of Synfuels A and B	"	"	43 (1977)
E coli	"	"	"	43 (1977)

TABLE III-8 (CONTINUED)

SUMMARY OF TOXICITY STUDIES

Animal Organism (Number)	Exposed to	Maximum Dose and Route	Effects (Incidence)	Reference (Year)
Saccharomyces	Synfuel A	Unspecified	Mutagenic	43 (1977)
Human leukocyte	Synfuel B	"	Nonmutagenic	43 (1977)
Drosophila	"	"	Weakly mutagenic	43 (1977)

*Applied in diluted form

**Incidence not reported

IV. ENGINEERING CONTROLS

Introduction

Engineering controls combined with good work practices will minimize worker exposure in coal liquefaction plants. Such controls pertain to erosion, seal and instrument failures, maintainability, reliability, and sample withdrawal systems. Additional engineering controls for specific equipment or systems are also identified in the following paragraphs.

Engineering controls to protect worker health and safety include (1) modification of design layout and specifications, (2) modification of operating conditions, or (3) add-on control devices to contain liquids, gases, or solids produced in the process and/or to minimize physical hazards. Modifying operating conditions or adding control devices may require retrofitting equipment or components after plant startup. Such modifications may necessitate system or plant shutdown.

Throughout this chapter, modification of plant design and specifications is emphasized. Engineering controls based on this methodology may minimize maintenance and retrofitting requirements. Engineering controls involving design include system safety analyses, containment integrity, equipment segregation, redundancy of safety controls, and fail-safe design. The application of these engineering controls, as discussed in the following sections, will minimize the need to modify operating conditions or to add control devices.

Plant Layout and Design

Plant layout and design features to ensure a safe work environment include system safety programs and analyses, pressure vessel codes, control room location and design, equipment layout, insulation of hot surfaces, noise abatement, instrumentation, emergency power supplies, redundancy, and fail-safe features.

(a) System Safety

Identification of hazards and necessary controls is important in the design of a safe operating plant. Hazards and controls should be determined during the design phases of the plant and whenever a change in process design occurs. For example, after recognizing the hazards associated with high-pressure vessels, one plant installed protective barriers around its bench-scale coal liquefaction process [1]. An explosion did occur in this system, but because of the barriers no workers were injured. Incidents in other industries have resulted in fatalities when initial design and/or design changes were inadequately reviewed for potential safety problems [82-84].

Review and analysis of design, identification of hazards and potential accidents, and specification of controls for minimizing accidents and their consequences should be performed during plant design, construction, and operation. Review and analysis should include, but not be limited to, procedures for startup, normal operations, shutdown, maintenance, and emergencies. This review process should be performed by knowledgeable health and safety personnel working with the engineering, maintenance, and management staff who are cognizant of the initial design and/or process design changes. To provide this interaction, a formal program should be developed and documented. At a minimum, it should include review and analysis requirements, assignment of responsibilities, methods of analyses to be performed, and necessary documentation and certification requirements. All of these elements are necessary in order to review the design, identify hazards, and specify solutions, and would be included in a well-documented, formalized system safety program.

The system safety concept has been used in the aerospace and nuclear industries [85] to control hazards associated with systems or products, from initial design to final operation. This concept is also being applied in other industries, eg, the chemical industry [82].

Fault-tree analysis is one method of system safety evaluation that has been applied in coal gasification pilot plants [86], and it is used in the world's oldest and largest coal liquefaction plant to help engineers with the design and construction of new facilities [21]. In the coal gasification criteria document [16], NIOSH recommended that fault-tree systems analysis, failure-mode evaluation, or equivalent safety analysis be performed during the design of coal gasification plants or during the design of major modifications of existing plants.

A system safety program that incorporates design reviews, hazard identification and control, organization, and fault-tree analysis should also be used during the design of coal liquefaction plants and during any design modifications of operating plants. This program would provide a disciplined approach to involving all responsible departments in design decisions that will affect employee protection. Appendix VII lists several references on system safety.

(b) Pressure Vessels

Because most liquefaction plants operate at high pressures ranging from 400 to 4,000 psi (2.8 to 28 MPa) and at temperatures ranging from 800 to 932°F (427 to 500°C) [33], it is essential that pressure vessels be properly designed. Rupture of a pressure vessel containing flammable solvent or other flammable materials could be catastrophic [87]. Pressure vessels at existing plants are designed in accordance with the applicable American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Codes to ensure vessel design adequacy [1,88]. Quality control measures should be formulated and performed to ensure the necessary reliability of the vessel integrity [1]. A quality assurance (QA) program should be established prior to plant and equipment design. The program should document formalized quality control measures for design, construction, and operation. It should also document the requirements of functions such as audits, inspections, and tests. The program should be modeled after the ASME QA programs and the American National Standards Institute (ANSI) QA standards.

Pressure safety and relief valves should be installed where appropriate, as determined by well-established engineering practice [1,88]. If the discharge of these valves is a toxic or potentially dangerous material, it should be collected and treated in an acceptable manner. Flaring should be restricted to gaseous discharges; any liquid discharges should be contained by appropriate knockout drums. Pressure safety valves on steam drums and other vessels that do not contain toxic or dangerous materials should be vented in accordance with standard safety practices. These valves should be designed or located so that they will not become plugged with condensed coal products.

(c) Control Room Design

The control room for plant operation should be designed to provide a safe environment for operating personnel and to remain functional in the event of an accident and/or the release of hazardous materials within the plant. For example, at one site, reinforced concrete walls were provided between the liquefaction system and the operating control room to protect the operating personnel from possible explosions [1]. An explosion did occur, but control room personnel were not injured, and control equipment was not damaged. As a result, the operators were able to shut down the operation to prevent additional occurrences, such as intense fire resulting from the uncontrolled flow of hydrogen. The control room was structurally designed to withstand the forces generated by anticipated accidents.

Air supplied to the control room should not be contaminated with hazardous materials. In the event of an accident or the release of hazardous materials (such as hydrogen sulfide) within the plant, operators must be able to respond effectively.

(d) Separation of Systems or Equipment

System safety analyses can identify those systems, unit processes, and unit operations that should be separated from one another by design or location. In one coal liquefaction pilot plant, a fire resulting from a pump seal failure contacted an adjacent pump and caused it to fail [1].

Experience with hydrocrackers used in petroleum refineries for producing gasoline from heavier hydrocarbons has led the Oil Insurance Association to recommend that these units be remotely located within the plant perimeter [89]. Hydrocrackers operate at pressures of up to 3,200 psi (22 MPa) and at temperatures of up to 1,800°F (980°C) [89], similar to the hydrotreatment units used in coal liquefaction. When a hydrocracker fails, flammable material is released over a larger area than with lower-pressure units. Based on experience with hydrocrackers [89], the hydrotreater unit should also be remotely located within the plant to minimize the impact that its failure might have on other equipment. A systems safety analysis can identify the types of multiple failures that could occur in a specific plant design. Unit processes and operations should be designed or located to prevent a single failure from initiating subsequent failures.

(e) Location of Relief Valves

Relief valves discharging directly to the atmosphere should be located so that operating personnel are not exposed to releases. These valves should not be located near stairways or below walking platforms [1].

Design Considerations

The systems in coal liquefaction plants are closed because flammable and other hazardous materials are handled at high pressures and temperatures. However, workers can be exposed to the process materials when these systems are opened. The opening of the system may be intentional, as is the case during maintenance. On the other hand, poor connections, seal failures, or line failures due to erosion or corrosion can result in leaks that may release process materials into the work environment. Minimizing maintenance activities, limiting the amount of process material present during maintenance, and preventing leaks will reduce the potential for worker exposure. Design factors requiring engineering controls for systems, unit operations, and unit processes include maintainability, seals, erosion/corrosion in systems handling fluids that contain solids, hot surfaces, noise, instrumentation, emergency power, redundancy of controls, fail-safe design, and sampling.

(a) Maintainability

Maintenance activities are the most frequent cause of worker exposure to the process materials in coal liquefaction plants. Coal liquefaction plants should be designed to ensure that systems, unit processes, and unit operations handling hazardous materials can be maintained with minimum employee exposure. Prior to maintenance, the equipment should be isolated from the process stream by blinds and isolation valves [1,90,91]. The equipment should also be depressurized if necessary, flushed, and then purged, where practicable, with steam or an inert gas (nitrogen or carbon dioxide). Cleaning solvent, water, or other suitable material may be used for flushing equipment that handles liquids and solids. Flushing and purging are necessary to minimize residual process materials in equipment requiring maintenance or removal.

Decontamination of equipment in place requires appropriate systems with adequate flush and purge capacity as well as adequate storage capacity for the materials flushed out of the system. The contaminated flushing material should be contained, treated, and disposed of properly if it is not recycled [1,92]. At one plant, the inert gas purge is sent to a flare header system and then to a flare stack [88]. Decontamination at another plant is performed after the equipment has been removed from the process system and prior to maintenance activities [1]. In other cases, equipment is removed first, decontaminated, and checked for contamination using a UV light prior to any maintenance [1]. However, UV light was ineffective in fluorescing thick layers of coal-derived materials [1]. Decontamination of equipment after removal from the system increases the potential for worker exposure to residual material in the equipment. However, if the equipment is decontaminated prior to removal from the system, the amount of residual material would be minimal.

Employee exposure during maintenance should be minimized by providing redundant equipment. If an entire system must be shut down to repair one piece of equipment, workers will sometimes be instructed to postpone maintenance and continue operating with marginal equipment until extensive maintenance is necessary. Redundant equipment permits maintenance activities to be performed without interrupting normal operations [88]. Isolation and decontamination capabilities should also be available for equipment requiring frequent maintenance.

Maintenance activities may result in process material spills. All spills should be contained and collected to control the release of the material. Dikes with chemical sewer drains are sometimes used to contain and collect spills [1]. For example, one plant was built on a diked concrete pad that drained into a chemical sewer arrangement [1]. Adequate ventilation should be provided where flammable liquids are collected to reduce the flammable vapor concentration to less than its lower explosive limit.

(b) Systems Handling Fluids Containing Solids

Minimizing leaks will reduce employee exposures. Good engineering practices should minimize leakage from loose flange bolts, connections, or improper welds.

(1) Seals

In systems that handle fluids containing solids, abrasive particles may enter the seal cavity and cause rapid seal failure, resulting in the release of hazardous materials [1,88,93-95]. To reduce the frequency of leaks and minimize personnel exposure, pumps, compressors, and other equipment with rotating shafts should be designed so that seals are compatible with the fluid environment.

(2) Erosion/Corrosion

Where erosion occurs in a corrosive environment, base metals are more susceptible to corrosion. The term "erosion/corrosion" is used throughout this document to indicate erosion, corrosion, or a combination of both. Erosion/corrosion often causes leakage problems in systems, unit processes, and unit operations that handle gases with entrained solids and slurries. Where practicable, slurry transport pipes should be designed to minimize sharp elbows and turbulent flows, which increase the severity of erosion [1,93,96-98]. Severe erosion has also been observed where there is poor alignment at flanged joints on piping and at slip joints of inner tubes inserted to minimize erosion. Erosion is enhanced by the flow turbulence at these discontinuities [98].

Periodic ultrasonic tests may be performed to indicate locations of excessive erosion [1,88]. Other methods that have been used include dye-checking for cracks, special metallographic examinations, and X-rays to identify affected areas [88]. The location and frequency of monitoring for erosion/corrosion should be established prior to plant operation and revised as necessary.

Valve internals should also be designed to minimize erosion/corrosion. Considerable erosion/corrosion has been observed in high-pressure letdown valves in coal liquefaction plants [88,93,96,99,100]. However, improved designs and materials, such as multiple letdown valves in series and tungsten carbide trim, have minimized erosion effects [88,94,96]. Other valves used in slurry service have also shown signs of erosion/corrosion [96,100]. Considerable research has been and is being conducted on methods to minimize valve erosion/corrosion [32,88,96,98,101]. A hard surface metal to be applied to the valve internals is currently being developed [1,94]. However, a major problem to date has been effecting an adequate bond between the protective coating metal and the base metal [1,94]. In addition, extra care needs to be exercised during construction and maintenance to avoid chipping any protective coatings [94]. Valves used in systems handling fluids that contain solids should also be designed to close properly, because problems have occurred when suspended solids have prevented proper valve closure [1]. Where these valves are needed for control purposes, redundant valves should be included in the plant design.

Pump casings, particularly centrifugal pumps, should also be designed to minimize erosion. Centrifugal pumps have been designed with hard coatings to provide abrasion resistance in slurry service [94], and pumps operating at temperatures below 150°F (66°C) were relatively successful. However, poor coating adherence to the base metal was noted with pumps that handle slurries at temperatures above 150°F (66°C).

Although one plant experienced erosion problems in its centrifugal pumps [94], another plant had favorable experience using Ni-Hard casings for its centrifugal pumps [88].

Other material problems in coal liquefaction systems include hydrogen embrittlement, particularly in hydrogenation processes and hydrotreater units, and stress-corrosion cracking, particularly around welds. These problems have been investigated [32,88,96,98,101], and research is being conducted in an effort to solve or minimize them [102,103].

Erosion/corrosion is also a problem in pyrolysis and hydrocarbonization processes. Erosion in these processes is due to entrained solids in gas and vapor streams at high velocities. These problems are analogous to those experienced in coal gasification processes where solids become entrained in gas and vapor streams.

(c) Hot Surfaces

Equipment operated at elevated temperatures should be designed to minimize personnel burn potential and heat stress. One method for accomplishing this is to insulate all hot surfaces. However, experience has shown that there is a fire potential if the process solvent contacts and reacts with certain insulation materials. One example of this occurred in a small development unit when hot process materials came into contact with porous magnesium oxide insulation, causing a minor fire [1,88]. Therefore, insulation used to protect personnel from hot surfaces should be nonreactive with the material being handled.

(d) Noise

Noise abatement should be considered during facility design. Noise exposures occur in the coal handling and preparation system, around pumps and compressors, and near systems with high-velocity flow lines [38]. Where practical, noise levels in the plant should be minimized by means of equipment selection, isolation, or acoustic barriers. The noise levels to which employees may be exposed should not exceed the NIOSH-recommended 85 dBA level, calculated as an 8-hour TWA, or equivalent dose levels for shorter periods [104].

(e) Instrumentation

Instrumentation necessary to ensure the safe operation of the coal liquefaction plant should be designed to remain functional in the most severe operating environment. Instrument lines can become plugged with materials in the process stream [1] and should be purged where needed with a suitable material to prevent plugging. For process liquid streams, instrument lines are normally purged with clean process solvent [1], while instrument lines in gas systems are usually purged with inert gases such as nitrogen or carbon dioxide [1]. The purge material selected should be compatible with the process stream. Because of small flowrates used in pilot plant operations, the purge material may dilute the process stream.

Radioactive sources and detectors are used in some coal liquefaction plants to monitor the liquid level inside vessels and, in some cases, to perform density analyses by neutron activation [1]. Sufficient shielding is needed to minimize the radiation levels to which workers are exposed in areas in and around the radioactive source location. The use of radioactive materials also requires comprehensive health physics procedures and monitoring, particularly when maintenance is to be performed on equipment in which radioactive materials are normally present. Anyone using radioactive materials must comply with the regulations in 29 CFR 1910.96. Combining engineering controls and work practices should prevent radiation exposures in excess of those specified.

(f) Emergency Power Supplies

Instrumentation and plant equipment that must remain functional to ensure safe operation and shutdown of the plant should have emergency power supplies. For example, pumps used for emptying equipment such as catalytic reactors of all material that might coke or solidify and inert gas purge systems necessary for shutdown need an emergency power supply. Without an inert gas purge or blanket during shutdown, the potential for a fire or an explosion increases [1]. Emergency power supplies should be remote from areas in which accidents identified in the system safety analysis are likely to occur.

(g) Redundancy of Controls Needed for Safety

Throughout the coal liquefaction plant, equipment, instruments, and systems needed to perform a safety function should be identified by the system safety analysis. These safety functions should be redundant. For example, pressure relief valves are provided to prevent overpressurization and vessel rupture. Where necesary, parallel relief valves, rupture disks, or safety valves should be provided for an added degree of safety so that in the event that one fails to function when needed, another is present. Redundant pressure relief systems are used in the petroleum industry [91] and in coal liquefaction operations [1].

(h) Fail-Safe Design

The failure of any safety component identified in the system safety analysis should always result in a safe or nonhazardous situation [1,105]. For example, fail-safe features include spring returns to safe positions on electrical relays, which deenergize the system [106]. All pneumatically actuated valves should fail into a safe or nonhazardous position upon the loss of the pneumatic system [105]. The safe position, open or closed, of a valve depends on the valve function.

(i) Process Sampling

A common source of worker exposure to hazardous materials in the petroleum industry is process stream sampling [107]. This source of exposure also exists in coal liquefaction plants. In addition, process streams containing flammable liquids or gases present fire and explosion hazards [1]. To minimize the potential for fires, explosions, or personnel exposures, sampling systems should be designed to remove flammable or toxic material from the lines by flushing and purging prior to removal of the sampling bomb. Flushing and purging also minimize the potential for some process materials to solidify in the lines if allowed to cool to near-ambient temperatures [1,88,95]. A number of sampling systems have been developed and are shown in Figure XVIII-3. The system shown as "best" in this figure does not permit removal of the material between the isolation valves prior to removal of the bomb. The sampling system shown in Figure XVIII-4 allows removal of material contained between the two isolation valves on each side of the bomb [1]. When the operator removes the bomb, the potential for fire, explosion, or worker exposure to residual process material is minimized. Further protection from exposure would be afforded if a flush and purge system were provided to remove the material from the sampling lines but not from the bomb. The flush and purge system could also be used to enhance depressurization of high-pressure sampling systems. For gas sampling systems, the bleed lines should discharge to a gas collection system for cleanup and disposal.

Systems Operations

Another safety aspect in plant design involves evaluating systems, their hazards and engineering problems, and the necessary engineering controls.

(a) Coal Preparation and Handling

The coal preparation and handling system receives, crushes, grinds, sizes, dries, and mixes the pulverized coal with process solvent, and preheats the coal slurry. Slurry mixing and preheating may not be required for the pyrolysis and hydrocarbonization processes, but the other operations are needed for all coal liquefaction processes. Instead of slurry pumps, pyrolysis and hydrocarbonization processes generally have lockhoppers, which provide a gravity feed of the coal into the liquefaction reactor [70]. NIOSH's coal gasification criteria document [16] discussed and recommended standards for lockhopper design.

Noise, coal dust, hot solvents, flammable materials, and inert gas purging are factors that contribute to potential health and safety hazards. For example, coal dust presents inhalation, fire, and explosion hazards. Inhalation hazards should be minimized by using enclosed systems for transporting the coal fines, by using an inert gas stream [1,88], or by using proper work practices [1]. Vacuum and water spray systems have been suggested as methods for cleaning up coal dust resulting from fugitive emissions [92]. To minimize the fire and explosion potential, standards should be applied such as the National Fire Protection Association (NFPA) Standard 653, "Prevention of Dust Explosions in Coal Preparation Plants"; NFPA Standard 91, "Blower and Exhaust

Systems, Dust, Stock, and Vapor Removal or Conveying"; NFPA Standard 85F, "Pulverized Fuel Systems"; NFPA Standard 85E, "Prevention of Furnace Explosions in Pulverized Coal-Fired Multiple Burner Boiler-Furnaces"; and NFPA Standard 69, "Explosion Prevention Systems." Pressure relief valves are used to prevent overpressurization and equipment failure resulting from fires in the coal handling system [1]. Equipment in the coal handling and preparation system has been identified as a major noise source [38]. This equipment includes the pulverizer (90-95 dBA), preheater charge pump (95-100 dBA), gravimetric feeder (90-95 dBA), and vibrator (110 dBA) [38]. When selecting such equipment, priority should be given to equipment designed to attain noise levels that are within the NIOSH-recommended limits [104]. If this equipment design is impractical, acoustical barriers and personal protective equipment (see Chapter V) should be used.

Certain operations, such as coal pulverizing and drying, should be performed in a relatively oxygen-free atmosphere to minimize the potential for fires or explosions. At various plants, the oxygen concentration level during startup, shutdown, and routine and emergency operations is maintained at <5% by volume using nitrogen as the inert purge gas [1,106,108]. At one plant, the baghouse used to collect coal dust and the coal storage bins are blanketed with an inert gas, ie, nitrogen [1,108]. At one bench-scale hydrocarbonization unit [106], nitrogen purge is used to remove hydrogen during shutdown. The oxygen concentration level, which minimizes or eliminates the fire and explosion potential, varies with the type of purge and blanketing gas and the type of coal being used [109]. If carbon dioxide is used as the inert gas, the oxygen concentration should be less than 15-17% by volume, depending on the type of coal used, to prevent ignition of coal dust clouds [109]. When the inert gas is nitrogen, the oxygen concentration should be lower [109]. The maximum oxygen concentration in the coal preparation and handling system should be determined by the type of inert gas and the type of coal used. Oxygen levels should be continuously monitored during plant operations [1,106,108]. In addition, redundancy in oxygen monitoring should be provided because the oxygen concentration is an important parameter in assuring a safe system operation.

Purge and vent gases for all systems handling coal-derived materials in a coal liquefaction plant should be collected, treated, recycled, or flared [1,92]. An emergency backup purge system (storage of carbon dioxide or nitrogen) with sufficient capacity should be provided for emergency shutdown and extended purging periods. Inert gas purging presents an asphyxiation hazard if it accumulates in areas where worker entry is required. Plant designs that include enclosed or low-lying areas should be avoided to minimize the potential for such accumulation. Where carbon dioxide generators are used, monitoring should be performed to detect increases in carbon monoxide concentrations resulting from incomplete combustion [38].

Coking and solidification of the process stream can occur in the preheater tubes and in the piping to the liquefaction system [1,88,108]. One factor that contributes to coking is improper heating of the slurry. To minimize coking and subsequent maintenance, controls and instrumentation should be provided to ensure the proper heating of the slurry. If the tubes cannot be decoked in place by combustion with steam and air, they must be removed and decoked by mechanical means such as chipping [108]. Worker exposure to process materials, particulates, vapors, and trapped gases should be minimized during the decoking of the lines. Where practicable, prior to the performance of maintenance activities, the material that has not coked should be removed. Worker exposure can be minimized if adequate ventilation and/or personal protective equipment such as respirators are provided (see Chapter V). However, adequate ventilation may not always be possible because of difficulties in obtaining capture velocities in outdoor locations where there are high winds, and difficulties in locating the exhaust on portable ventilation units so as not to discharge vapors into another worker's area. Where adequate ventilation is not possible, work practices and personal protective equipment should be relied upon to minimize worker exposure during decoking activities.

The process stream can also solidify and plug the preheater tubes and the transfer lines beyond the preheater if the slurry temperature approaches ambient temperature [1,88,108]. At one plant, the pour point of the process solvent used for slurrying ranged from 25 to 45°F (-4 to 7°C) [108]; the process solvent was semisolid at room temperature [1]. Until the pour point of the material is lowered by hydrocracking to a temperature less than the anticipated ambient temperatures, the potential exists for the material to solidify or become too viscous for transporting. Solidification in the lines is possible from the preheater to the liquefaction system in all coal liquefaction processes except pyrolysis and hydrocarbonization. Plugging can be minimized by heat-tracing the lines to maintain the necessary temperature during startup, routine operations, shutdown, and emergency operations [1]. Plugging due to the settling of solids can be minimized by avoiding dead-leg piping configurations and by connecting into the top of process piping [1].

Even when pipes are heat-traced and properly designed, there will be occasions when plugging occurs and maintenance is required [1]. Lines must be removed from the system if the obstruction cannot be flushed out under pressure [1]. Where practicable, prior to removal of the plugged lines or equipment, residual, nonsolidified process material should be removed to avoid worker exposures. If the material has completely solidified, the line or equipment may be cleared by hydroblasting [1], which is a method of dislodging solids using a low-volume, high-pressure (10,000 psi or 70 MPa), high-velocity stream of water [1]. During the hydroblasting process, workers may be exposed to particulates, aerosols, and process materials, but this exposure has been reported to be low [1]. Portable local exhaust ventilation should be used, wherever possible, to control inhalation exposures. The exhaust from portable ventilation should be directed to areas that are not routinely occupied. Water contaminated with process material should be collected, treated, and recycled, or disposed of. If the material plugging the line is semisolid, the line can be cleared using mechanical means, eg, a scraper or rod [1]. During the removal of semisolids, generation of particulates is minimal. However, hydrocarbon vapors or gases may be present [1], and local exhaust ventilation, if practical, should be used to minimize worker inhalation of these materials. Where local exhaust ventilation is not practical, personal protective equipment should be provided.

(b) Liquefaction

In pyrolysis/hydrocarbonization processes, solid coal from the coal preparation and handling system is transferred to the liquefaction system. In the hydrogenation and solvent extraction processes, the coal is first slurried with a solvent, and erosion/corrosion and seal failure may occur because of solid particles suspended in the slurry [1,88]. Erosion can also occur in pyrolysis/hydrocarbonization processes because of solids entrained in the gas-vapor stream leaving the reactor. Pressure letdown valves in the liquefaction system are another area where considerable erosion occurs [1,88,99,108]. Erosion/corrosion and seal failure problems can result in releases of process material into the worker environment, and these releases may present a fire hazard [1].

Plugging caused by solidification of the process material can occur in the hydrogenation and solvent extraction liquefaction systems, particularly in transfer lines [1,88]. Major problems with agglomeration may be encountered in pyrolysis reactors when strongly caking coals are used [2]. If agglomeration occurs, maintenance must be performed to unplug the equipment or lines. Unplugging may expose workers to aerosols, particulates, toxic and/or flammable vapors, and residual process material.

During the startup of a coal liquefaction plant, inspections should be performed to detect potential leaks at welds, flanges, and seals. Leaks, when found, should be repaired as soon as is practicable. Systems throughout the plant should be pressure tested prior to startup using materials such as demineralized water and nitrogen [88] to locate and eliminate leaks, thereby reducing the potential for worker exposure.

The liquefaction system of all coal liquefaction processes should be flushed and purged when the plant shuts down to minimize process material solidification and/or plugging due to solids settling. A flush and purge capacity equal to or greater than the capacity of the liquefaction system should be available. Storage vessel capacity should be equal to the flush capacity so that all materials flushed from the system can be collected and contained. During shutdown, as well as during startup, the purge material (carbon dioxide, nitrogen, etc) may contain flammable hydrocarbon vapors and should be collected, cleaned, and recycled, or collected and sent to a flare system to be incinerated.

Other health and safety hazards associated with the liquefaction system for all liquefaction processes are thermal burns and exposure to hazardous liquids, vapors, and gases during operation and maintenance.

(c) Separation

The separation system separates the mixtures of materials produced in the liquefaction system. Table XVIII-1 lists the separation methods used for coal liquefaction processes. Materials found in separation systems include solvents, unreacted coal, minerals, water containing compounds such as ammonia, tars, and phenols, and vapors containing compounds such as hydrocarbons, hydrogen sulfide, ammonia, and particulates [31]. Workers may be exposed to these materials during maintenance activities and when releases occur because of leaks, erosion/corrosion, and seal failures. Steam is sometimes used to clean equipment that has been used to separate solids from hot oil fractions [31]. Steam discharges from blowdown systems and ejection jets on vacuum systems have been identified as sources of airborne materials that fluoresce under UV lighting [31]. Engineering controls should be provided to minimize these discharges. Steam should be discharged into a collection system where it is condensed, treated, and/or recycled.

Plugging and coking may be a problem in separation systems for all coal liquefaction processes. For instance, plugging has occurred in the nozzles inside the filtration unit [88]. Material remaining in the nozzle may react chemically and solidify at the filter temperature. Coking in the wash solvent heaters also produces solids that plug the nozzles downstream. Nozzles should be cleaned during each filter outage and should be aimed downward when not in use to permit adequate drainage of material. Coking has also occurred in the mineral residue dryer downstream from the filter [88]. However, the use of mineral residue dryers has been observed at only one plant [1]. These dryers may not be used in larger plants where the solids from the separation unit may be sent to a gasifier [26,27]. The dry mineral residue itself presents problems because of its pyrophoric nature [100].

The separation methods discussed are those currently used in coal liquefaction pilot plants. As new separation technology is developed, the present separation systems and their related problems may no longer be relevant. For example, solvent de-ashing processes have been developed and will be tested at two coal liquefaction pilot plants [1,28,29,110]. Data on these new units are limited because of proprietary information [1,110]. As new technology is developed, the health and safety hazards associated with the new units should be identified, and controls should be specified to minimize risks to worker health and safety. A system safety program would perform this function by reviewing hazards and determining necessary control modifications.

(d) Upgrading

The upgrading system receives the liquid products from the separation system. Upgrading is achieved by using methods such as distillation and hydrogenation. Process solvents, filtered coal solution, catalysts, hydrocarbon vapors, hydrogen, and other gases may be present in the fractionator and the hydrotreater. Maintenance activities present a significant potential for worker exposure to these materials. Plugging resulting from solidification of the process stream is a problem in solvent extraction and noncatalytic and catalytic hydrogenation processes [1].

Severe corrosion has occurred in the distillation system at one plant, particularly in the wash solvent column [88,111]. The design of the distillation system and of all systems susceptible to corrosion should minimize corrosive effects. This may be accomplished by developing and/or using more suitable construction materials (eg, 316 Stainless Steel and alloys such as Incoloy 825 [88]).

The hydrotreater presents a significant potential for fire or explosion hazards because of high pressure, high temperature, and the presence of hydrogen and flammable liquids and vapors. Vessel integrity should be ensured to reduce this potential. Proper metallurgy should be used in hydrotreater design to minimize hydrogen attack and other corrosion problems [1].

(e) Gas Purification and Upgrading

The process gases are purified using an acid-gas removal system to remove hydrogen sulfide and carbon monoxide from the hydrogen and hydrocarbon gases such as methane. Methanation may be used to upgrade the hydrogen with carbon monoxide to form pipeline quality gas, or the hydrogen may be recycled within the plant for hydrogenation.

Potential safety and health hazards to workers in this system include hot surfaces and exposure to hazardous materials during maintenance. NIOSH has previously made recommendations [16] on engineering controls for nickel carbonyl formation, hydrogen embrittlement monitoring, catalyst regeneration gases, and other safety and health hazards associated with this system.

Nickel carbonyl formation in the methanation unit is a major hazard associated with this system. As the methanation unit cools during shutdown, carbon monoxide reacts with the nickel catalyst to form highly toxic nickel carbonyl. In the coal gasification criteria document [16], NIOSH recommended that an interlock system, or its equivalent, be used to dispose of any gas containing nickel carbonyl where nickel catalysts are used. Formation of nickel carbonyl can be eliminated during startup and shutdown of methanation units if carbon monoxide is not permitted to contact the catalyst once the catalyst temperature is below 260°C (500°F) [1,16].

(f) Product Storage and Handling

Pilot plants operate in batch modes, and batch operations require personnel to handle products frequently. Product storage and handling equipment should be designed to minimize, to the extent possible, employee exposure to coal-derived liquids, vapors, and solids during routine and maintenance operations.

Specific engineering controls should be developed as problems are identified. For example, dust in the solid product handling system at one plant presented an inhalation hazard [88]. A baghouse and collection system were installed to minimize this hazard. A dust collection and filter system should be provided for product storage and handling areas in all coal liquefaction plants where an inhalation hazard is found to be present.

Liquid and gas are stored in closed systems, thus minimizing the potential for worker exposure under normal conditions. However, workers may be exposed to these materials during maintenance. Exposures can be minimized by emptying the equipment prior to maintenance. During filling operations, vapors inside tanks will be displaced. Vapors and gases from liquid and gas storage should be collected and recycled, or flared.

(g) Waste Treatment Facilities, Storage, and Disposal

Waste treatment facilities concentrate waste products that may contain potentially hazardous materials. Because of the presence of concentrated waste materials, ventilation systems and/or personal protective equipment should be provided during waste treatment equipment maintenance. Similar precautions need to be taken during the handling and disposing of wastes such as spent carbon, ash, contaminated sludge from ponds, and contaminated catalysts. Where possible, waste products should be contained when handled or transported, using appropriate methods. One method could involve packaging and sealing contaminated wastes in drums under controlled conditions prior to handling or transporting.

Where provisions are made for pumping or spraying liquids into liquid retention ponds, engineering controls such as louvered windbreaks should be provided to limit the dispersal of water droplets from the spray. An industrial hygiene study at a Charleston, West Virginia, pilot plant revealed that the airborne water droplets originating in the aeration pond contained material that was fluorescent under UV lighting. A louvered windbreak was installed adjacent to the pond in an attempt to confine the water droplets [37]. Whenever possible, liquids should be pumped into the bottom of the pond to minimize the generation and dispersal of contaminated sprays.

V. WORK PRACTICES

Occupational health hazards associated with coal liquefaction can also be minimized or reduced by the use of work practices, defined here as all aspects of an industrial safety and health program not covered under engineering controls (discussed in Chapter IV). Work practices cover areas such as personal protective equipment and clothing, specific work procedures, emergency procedures, medical surveillance, and exposure monitoring.

Specific Work Procedures

Workplace safety programs have been developed in coal liquefaction pilot plants to address risks of fire, explosion, and exposure to toxic chemicals [1]. These programs are patterned after similar programs in petroleum refineries and the chemical industry. Most coal liquefaction pilot plants have written policies and procedures that govern work practices in the plant. These include procedures for lockout of electrical equipment, tag-out of valves, fire and rescue brigades, safe work permits, vessel entry permits, wearing safety glasses and hardhats, housekeeping, and other operational safety practices [1].

Personnel responsible for the development of occupational health and safety programs for coal liquefaction plants should refer to general industry standards (29 CFR 1910) to identify mandatory requirements. In addition, they should use voluntary guidelines of similar industries, recommendations of equipment manufacturers, and their own operating experience and professional judgment to match programs with specific plant operations. Reiteration here of all appropriate requirements would detract from recommendations for work practices needed in coal liquefaction, but unlikely to be applied in other industries. This section describes special work practices to minimize the risk of accidents or adverse chronic health effects to workers in coal liquefaction plants.

(a) Training

The effective use of good work practices and engineering controls depends on the knowledge and cooperation of employers and employees. Verbal instructions, supplemented by written and audiovisual materials, should be used to inform employees of the particular hazards of specific substances, methods for handling materials, procedures for cleaning up spills, personal protective equipment requirements, and procedures for emergencies. A continuing employee training program is also necessary to keep workers abreast of the latest procedures and requirements for worker safety and health in the plant. Additionally, experience at coal liquefaction pilot plants indicates that provisions are needed to evaluate employee comprehension of safety and health information [1].

(b) Operating Procedures

It is common practice in industry to develop detailed procedures for each phase of operation, including startup, normal operation, routine maintenance, normal shutdown, emergency shutdown, and shutdown for extended periods. In developing these procedures, consideration should be given to provisions for safely storing process materials, for preventing solidification of dissolved coal, for cleaning up spills, and for decontaminating equipment that requires maintenance. In high-pressure systems, leaks are major safety considerations during plant startup. 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. Particular attention should be given to areas that have been recently repaired, maintained, or replaced. If no significant leaks are found, the system should be slowly brought up to operating pressure and temperature. If leaks are found, appropriate maintenance should be performed [16].

Equipment such as the hydrotreater, which operates at high pressures, should be inspected routinely at predetermined intervals to determine maintenance needs. Because of the limited operations of pilot-plant and bench-scale coal liquefaction processes, the inspection or monitoring intervals and the equipment replacement intervals cannot be specified. These intervals should be based on actual operating experience. A similar approach should be used to develop monitoring and replacement intervals for equipment susceptible to erosion and corrosion, eg, slurry pumps and acid-gas removal units. Monitoring requirements, schedules, and replacement intervals should be part of the QA program for coal liquefaction plants.

(c) Confined Space Entry

In several plants, a permit system controls worker entry into confined spaces that might contain explosive or toxic gases or oxygen-deficient atmospheres [1,112,113]. Previously, NIOSH discussed the need for frequent air quality testing during vessel entry [16]. Procedures for vessel entry were also described, including recommendations for respiratory protection, and lifelines. Surveillance by a third person, equipped to take appropriate rescue action, has been recommended where hydrogen sulfide is present [65]. Safety rules developed at one coal liquefaction facility [1] recommended: (1) disconnecting the lines containing process materials rather than using double-block-and-bleed valves and (2) providing ventilation sufficient for air changeover six times per hour in the vessel during entry. This recommended procedure may not be feasible in all circumstances, but should be adopted where possible; disconnecting piping from vessels would provide greater protection to workers than would closing double-block-and-bleed connections.

(d) Restricted Areas

Access in coal liquefaction plants should be controlled to prevent entry of persons unfamiliar with the hazards, precautions, and emergency procedures of the plant. Access at one hydrocarbonization unit is controlled by using warning signs, red lights, and physical barriers such as doors in areas subject to potential PAH contamination [106]. Due to the small scale of this operation, the use of doors is feasible for access control. Different mechanisms, such as fences and gates, would serve similar functions in larger facilities. At other plants, access controls include visitor registration with the security guard, visitor escorts in process areas, and fences around the plant [1]. Because of the variety of potential hazards (including highly toxic chemicals, fire, and explosion), process areas should be separated from other parts of the plant by physical barriers. Access to the plant area should be controlled by registration of those requiring entry. Visitors should be informed of the potential hazards, the necessary precautionary measures, and the necessary actions to take in an emergency. An entry log should be kept of workers entering restricted areas. This will facilitate medical followup of high-risk groups in the event of occupational illness among workers. In addition, the visitors' log would help account for people at the plant if there were an accident or emergency.

(e) Decontamination of Spills

Spills and leaks from equipment containing toxic liquids should be cleaned up at the earliest safe opportunity. Cleanup operations should be performed and directly supervised by employees instructed and trained in safe decontamination and disposal procedures [16]. Correction may be as simple as tightening a pump-seal packing gland or switching to spare equipment, or as drastic as initiating a process shutdown. Small spills may be effectively contained by a sorbent material [16]. Used sorbent material should be disposed of properly.

Safety rules have been developed for the removal of solidified coal from equipment and plugged lines [1]. Whenever possible, hydroblasting should be used to remove the solidified coal extract rather than forcing the blockage out with high pressure. When high-pressure water is used, the pressure limits of the piping and equipment should not be exceeded. Access of plant personnel to the work area should be restricted while hydroblasting is in progress or while equipment is under pressure [1].

Dried tar is difficult to remove from any surface, particularly from the inside of process vessels. Manual scraping and chipping and the use of chlorinated hydrocarbon solvents or commercial cleansers are common methods of cleanup [16]. Where organic solvents are used for this purpose, special care is necessary to prevent employee exposure to solvent vapors. Cleaning solvents should be selected on the basis of low toxicity and low volatility, as well as for effectiveness. If necessary, approved respirators should be worn while using such solvents. Steam stripping is also commonly used and is effective, but it can cause significant inhalation exposures to airborne particulates (low-boiling-point residues may vaporize and high-boiling-point materials may become entrained in induced air currents). Generally, steam stripping is not recommended because it may generate airborne contaminants. There may be instances, however, where it must be used, eg, on small, confined surfaces. If it is used, emissions should be contained and treated.

The use of strippable paints or other effective coatings should be considered for plant surfaces where tar can spill. Suitable coatings are impenetrable by tar and do not adhere well to surfaces. Thus, any tar can be removed along with the coating, and the surface repainted [16].

Hand tools and portable equipment frequently become contaminated and present an exposure hazard to employees who use them. Contaminated tools and equipment can be steam-cleaned in an adequately ventilated facility [1] or cleaned by vapor degreasing and ultrasonic agitation [16].

(f) Personal Hygiene

Good personal hygiene practices are important in controlling exposure to coal-derived products. Instructions related to personal hygiene have been developed in facilities that use coal-derived products. Employees are advised to: (1) avoid touching their faces or reproductive organs without first washing their hands [1,114], (2) report to the medical department all suspicious lesions, eg, improperly healing sores, dead skin, and changes in warts or moles [114], (3) wash skin with soap and water after direct contact with coal-derived products [1,114], and (4) wash their hands, forearms, face, and neck after completion of each operation involving known or suspected carcinogens [1,114].

Showers are commonly required at the end of each shift in facilities where potential carcinogens are handled [1,113-115]. To segregate contaminated clothing from street clothing, employers should provide a shower facility with a double locker room. Figures XVIII-5 and XVIII-6 give examples of floor plans for shower and clothes change facilities [116].

If either exposed skin or outer clothing is significantly contaminated, the employee should wash the affected areas and change into clean work clothing at the earliest safe opportunity. Because of the importance of this protective measure, supervisory employees must be responsible for ensuring strict compliance with this requirement.

An adequate number of washrooms should be provided throughout each plant to encourage frequent use by workers. In particular, washrooms should be located near lunchrooms, so that employees can wash thoroughly before eating. It is very important that lunchrooms remain uncontaminated, minimizing the likelihood of workers inhaling or ingesting materials such as hydrocarbon vapors, particulates, or coal-derived oils. It is necessary that workers remove contaminated gloves, boots, and hardhats before entering lunchrooms. Therefore, some type of interim storage facility should be provided [16].

Cheng [115] reported that experience at one SRC pilot plant indicated that the following skin care products were useful for and accepted by workers: waterless hand and face cleaners, emollient cream, granulated or powdered soap for cleansing the hands, and bar soap for use in showers. NIOSH recommends providing bar soap in showers and lanolin-based or equivalent waterless hand cleaners in all plant washrooms and in the locker facility. The use of organic solvents such as benzene, carbon tetrachloride, and gasoline for removing contamination from skin should be discouraged for two reasons. First, solvents may facilitate skin penetration of contaminants and thus hinder their removal [16]. Second, many of these solvents are themselves hazardous and suspected carcinogens. Workers should thoroughly wash their hair during showers [1,16], and should pay particular attention to cleaning skin creases, fingernails, and hairlines. All use of sanitary facilities should be preceded by a thorough hand cleansing [16].

In summary, good personal hygiene practices are needed to ensure prompt removal of any potentially carcinogenic materials that may be absorbed by the skin. These practices include frequent washing of exposed skin surfaces, showering daily, and observing and reporting any lesions that develop. To encourage good personal hygiene practices, employers should provide adequate washing and showering facilities in readily accessible locations.

Personal Protective Equipment and Clothing

The proper use of protective equipment and clothing helps to reduce the adverse health effects of worker exposure to coal liquefaction materials that may be hazardous. Many types of equipment and clothing are available, and selection often depends on the type of exposure anticipated.

(a) Respiratory Protection

Respirators should be considered as a last means of reducing employee exposure to airborne toxicants. Their use is acceptable only (1) after engineering controls and work practices have proven insufficient, (2) 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 [16].

When engineering controls are not feasible, respiratory protective devices should reduce worker inhalation or ingestion of airborne contaminants and provide life support in oxygen-deficient atmospheres. Although respirators are useful for reducing employee exposure to hazardous materials, they have certain undesirable usage aspects. Some problems associated with respirator usage include (1) poor communication and hearing, (2) reduced field of vision, (3) increased fatigue and reduced worker efficiency, (4) strain on heart and lungs, (5) skin irritation or dermatitis caused by perspiration or facial contact with the respirator, and (6) discomfort [117,118]. Facial fit is crucial to effective use of most air-purifying respirators; if leaks occur, air contaminants will bypass a respirator's removal mechanisms. Facial hair, eg, beards or long sideburns, and facial movements can prevent good respirator fit [117,118]. For this reason, at least one coal liquefaction plant [1] prohibits beards, and mustaches extending below the lip.

Selection of appropriate respirators is an important issue in environments where a large number of chemicals may be present in mixtures. In general, factors to consider for respirator selection include the nature and severity of the hazard, contaminant type and concentration, period of exposure, distance from available respirable air, physical activity of the wearer, and characteristics and limitations of the available respiratory equipment [59].

Where permissible exposure limits (PEL's) for contaminants have been established by Federal standards, NIOSH and OSHA guidelines for respirator selection should be followed. In addition to exposure limits, the NIOSH guidelines examine skin absorption or irritation, warning properties of the substance, eye irritation, lower flammable limits, vapor pressures, and concentrations immediately dangerous to life or health [119]. Situations where PEL's cannot be used to determine respirator selection require individual evaluation. Such conditions are likely in coal liquefaction plants, especially during maintenance that requires line breaking or vessel entry, or during emergencies.

Training workers to properly use, handle, and maintain respirators helps to achieve maximum effectiveness in respirator protection. Minimum requirements for training of workers and supervisors have been established by OSHA in 29 CFR 1910.134. These requirements include handling the respirator, proper fitting, testing facepiece-to-face seal, and wearing it in uncontaminated workplaces during a long trial period. This training should enable employees to determine whether respirators are operating properly by checking them for cleanliness, leaks, proper fit, and exhausted cartridges or filters. The employer should impress upon workers that protection is necessary and should train and encourage them to wear and maintain respirators properly [119]. One way to do this is to explain the reasons for wearing a respirator. According to ANSI Standard Z88.2, Section 7.4 [120], the following points should be included in an acceptable respirator training program: (1) information on the nature of the hazard, and what may happen if the respirator is not used, (2) explanation of why more positive control is not immediately feasible, (3) discussion of why this is the proper type of respirator for the particular purpose, (4) discussion of the respirator's capabilities and limitations, (5) instruction and training in actual respirator use, especially with an emergency-use respirator, and close and frequent supervision to ensure proper use, (6) classroom and field training in recognizing and coping with emergency situations, and (7) other special training as needed. At least one major coal liquefaction research center has adopted these points for inclusion in its safety manual [121].

Respirator facepieces need to be cleaned regularly, both to remove any contamination and to help slow the aging of rubber parts. Employers should consult the manufacturers' recommendations on cleaning methods, taking care not to use solvent materials that may deteriorate rubber parts.

(b) Gloves

Gloves are usually worn at coal liquefaction plants in cold weather, when heavy equipment is handled, or in areas where hot process equipment is present. Where gloves will not cause a significant safety hazard, they should be worn to protect the hands from process materials. Gloves made of several types of materials have been used in coal liquefaction plants, including cotton mill gloves, vinyl-coated heavy rubber gloves, and neoprene rubber-lined cotton gloves [1,115]. After using many types of gloves, the safety staff at the PETC did not find any that satisfactorily withstood both heat and penetration by process solvents [1].

Sansone and Tewari [122,123] studied the permeability of glove materials. They tested natural rubber, neoprene, a mixture of natural rubber and neoprene, polyvinyl chloride, polyvinyl alcohol, and nitrile rubber against penetration by several suspected carcinogens. The glove materials were placed in a test apparatus, separating equal volumes of the permeant solution and another liquid miscible with the permeant. Samples were extracted periodically and analyzed by GC. For one substance tested, dibromochloropropane, the concentration that penetrated neoprene after 4 hours was approximately 10,000 times greater than the concentration that penetrated butyl rubber of the same thickness; polyvinyl alcohol, polyethylene, and nitrile rubber were less permeable than neoprene [122]. Measurable penetrant concentrations, ie, greater than 10^{-6} volume percent, were reported after 5 minutes for most glove materials tested against dibromochloropropane, acrylonitrile, and ethylene dibromide [122]. Readily measurable amounts of nitrosamines penetrated glove materials within 30 minutes [123]. Although the chemicals tested are not present in coal liquefaction processes, the test results suggest that the protection afforded by gloves can vary markedly with the chemical composition of the materials being handled.

In another study related to the selection of gloves, Coletta et al [124] investigated the performance of various materials used in protective clothing. They surveyed published test methods for relevance in evaluating protective clothing used against carcinogenic liquids, but no specific methods were found for testing permeation resistance, thermal resistance, or decontamination. More than 50 permeation tests were conducted in an apparatus similar to the one used by Sansone and Tewari, with the protective material serving as a barrier between the permeant and distilled water. Nine elastomers were evaluated for resistance to permeation by one or more of nine carcinogenic liquids. Of particular importance are the tests conducted with coal tar creosote and benzene, because benzene and some constituents of creosote, eg, phenols and benzo(a)pyrene, have been identified in coal liquefaction materials. Neoprene resisted penetration by creosote for 270 minutes, and benzene for 25 minutes [124]. Butyl rubber and Viton were more resistant to both creosote and benzene than was neoprene. Other elastomers were not tested for resistance to creosote, but were inferior against benzene. In general, a wide variation in permeability was observed for different combinations of barrier and penetrant. These data demonstrate the need to quantitatively evaluate the resistance of protective clothing materials against coal liquefaction products before making recommendations for suitable protective clothing.

NIOSH recently reported on an investigation at the Los Alamos National Laboratory and on a research project to develop a permeation testing protocol. It was demonstrated that some materials of garments made to protect workers may be ineffective when used for more than a short time. Design criteria are being developed for the degree of impermeability of protective material and for the specific materials to use against various chemicals.

No quantitative data on glove penetration by coal liquefaction materials have been reported. In the absence of such data, it is prudent to assume that gloves and other protective clothing do not provide complete protection against skin contact. Because penetration by toxic chemicals may occur in a relatively short time, gloves should be discarded following noticeable contamination.

(c) Work Clothing

Proper work clothing can effectively reduce exposure to health hazards from coal liquefaction processes, especially exposure to heavy oils. Work clothing should be supplied by the employer. The clothing program at one coal liquefaction pilot plant provides each process area worker with 15 sets of shirts, slacks, tee-shirts, underpants, and cotton socks; 3 jackets; and 1 rubber raincoat [115]. Thermal underwear for use in cold weather is also provided at this plant [1]. Work clothing should be changed at the end of every workshift, or as soon as possible when contaminated.

Cotton clothing with a fairly close weave retards the penetration of many contaminants, yet permits the escape of body heat. Nylon coveralls used at one coal liquefaction plant proved to be easier to clean than cotton coveralls (ME Goldman, written communication, February 1978). However, most synthetic fibers melt when exposed to flame. For comparison, Nylon 6,6 sticks at 445°F (229°C) and melts at about 500°F (260°C), while cotton deteriorates at 475°F (246°C) [125].

There is evidence that clothing worn under the coveralls aids in reducing skin contamination. In a 1957 experiment at a coal hydrogenation pilot plant [37], "pajamas" (buttoned at the neck with close-fitting arm and leg cuffs) worn under typical work clothes prevented contaminants absorbed by the outer clothing from coming into contact with the skin. They also provided an additional barrier to vapors and aerosols. However, in some instances, particularly in hot climates, this practice may contribute to heat stress, which is a potentially more significant hazard [16].

All work clothing and footwear should be left at the plant at the end of each workshift, and the employer should be responsible for proper cleaning of the clothing. Because of the volume of laundry involved, in-plant laundry facilities would be convenient. Any commercial laundering establishment that cleans work clothing should receive oral and written warning of potential hazards that might result from handling contaminated clothing. Operators of coal liquefaction plants should require written acknowledgment from laundering establishments that proper work procedures will be adopted.

In one study [37], experiments showed that drycleaning followed by a soap and water laundering removed all but a very slight stain from work clothing. One industry representative suggested that using the above procedures required periodic replacement of the drycleaning solvent to prevent buildup of PAH's (ME Goldman, written communication, February 1978).

Outer clothing for use during cold or inclement weather should be selected carefully to ensure that it provides adequate protection and that it can be laundered or drycleaned to eliminate process-material contamination [16].

(d) Barrier Creams

Barrier creams have been used in an attempt to reduce skin contact with tar and tar oil and to facilitate their removal should contamination occur [1]. Using patches of pig skin, the PETC tested several commercially available barrier creams for effectiveness in preventing penetration of fluorescent material [1]. The barrier cream found to be most effective is no longer manufactured. Weil and Condra [7] showed that barrier creams applied before exposure to pasting oil and various methods of washing after the oil had reached the skin only slightly delayed tumor induction in mice. Simple soap and water wash appeared to be as efficient as any treatment [7]. This study indicated that barrier creams were insufficient protection against skin contamination by coal liquefaction products and that they should not be used in place of other means of protection.

(e) Hearing Protection

Exposure to noise levels in excess of the NIOSH-recommended standard of 85 dBA for an 8-hour exposure may occur in some areas of a coal liquefaction plant. Engineering controls should be used to limit the noise to acceptable levels. However, this is not always possible, and it may be necessary to provide workers with protective hearing devices.

There are two basic types of ear protectors available: earmuffs that fit over the ear, and earplugs that are inserted into the ear. Workers should choose the type of ear protector they want to wear. Some may find earplugs uncomfortable, and others may not be able to wear earmuffs with their glasses, hardhats, or respirators.

A hearing conservation program should be established. As part of this program, workers should be instructed in the care and use of ear protectors. This program should also evaluate the need for protection against noise in various areas of the coal liquefaction plant and should provide workers with a choice of ear protectors suitable for those areas. Workers should be cautioned not to use earplugs contaminated with coal liquefaction materials.

(f) Other Protective Equipment and Clothing

Specialized protective equipment and clothing, including safety shoes, hardhats, safety glasses, and faceshields, may be required where the potential for other hazards exists. One company requires rubber gloves with long cuffs, plastic goggles, and a rubber apron for the handling of coal tar liquid wastes, and a thermal leather apron, thermal leather gloves, full-face visor shield, and thermal leather sleeves for the handling of hot solids samples [126]. Requirements for other types of protective clothing and equipment should be determined in specific instances based on the potential exposure.

Steel-toed workshoes should provide adequate protection under most circumstances. However, workers involved in the cleanup of spills or in other operations involving possible contamination of footwear should be provided with impervious overshoes. Rubber-soled overshoes are not recommended, because the rubber may swell after contact with process oils [16].

Medical Surveillance and Exposure Monitoring

(a) Medical Surveillance

Medical monitoring is essential to protect workers in coal liquefaction plants from adverse health effects. To be effective, medical surveillance must be both well timed and thorough. Thoroughness is necessary because of the many chemicals to which a worker may be exposed (see Appendix VI). In addition, worker exposure is not predictable; it can occur whenever any closed process system accidentally leaks, vents, or ruptures. Not all adverse effects of exposure to the chemicals are known, but most major organs may be affected, including the liver [127], kidneys [128], lungs [129], heart [58], and skin [130].

A medical surveillance schedule includes preplacement, periodic, and postemployment examinations. The preplacement examination provides an opportunity to set a baseline for the employee's general health and for specific tests such as audiometry. During the examinations, the worker's physical job-performing capability can be assessed, including his ability to use respirators. Finally, the examination can detect any predisposing condition that may be aggravated by, or make the employee more vulnerable to, the effects of chemicals associated with coal liquefaction. If such a condition is found, the employer should be notified, and the employee should be fully counseled on the potential effects.

Periodic examinations allow monitoring of worker health to assess changes caused by exposure to coal chemicals. The examinations should be performed at least annually to detect biologic changes before adverse health effects occur. Physical examinations should also be offered to workers before termination of employment in order to provide complete information to the worker and the medical surveillance program.

A comprehensive medical examination includes medical histories, physical examinations, and special tests. History-taking should include both medical and occupational backgrounds. Work histories should focus on past exposures that may have already caused some effect, such as silicosis [129], or that may have sensitized the worker, as may be the case with many coal-derived chemicals [17]. Physical examinations should be thorough, and medical histories should focus on predisposing conditions and preexisting disorders. Some clinical tests may be useful as general screening measures.

A thorough medical history and physical examination will permit an examining physician to determine the presence of many pathologic processes. However, laboratory studies are necessary for early determination of dysfunction or disease in organs that are relatively inaccessible and that have a high degree of functional reserve. In the screening aspect of a medical program, worker acceptance of each recommended laboratory test must be weighed against the information that the test will yield. Consideration should be given to test sensitivity, the seriousness of the disorder, and the probability that the disorder could be associated with exposure to coal liquefaction materials. Furthermore, wherever possible, tests are chosen for simplicity of sample collection, processing, and analysis. In many instances, tests are recommended because they are easy to perform and are sensitive, although they are not necessarily specific. If the results are positive, another more specific test would be requested. The choice of tests should be governed by the particular chemical(s) to which a worker is exposed. Appropriate laboratory tests and elements of the physical examination to be stressed are described in the following paragraphs, according to target organ systems.

(1) Skin

NIOSH has studied some chemicals or mixtures that are similar to those found in coal liquefaction processes and that are known to affect the skin. For example, the NIOSH criteria document on coal tar products [17] cited cases of keratitis resulting from creosote exposure and cases of skin cancer produced from contact with crude naphtha, creosote, and residual pitch. In addition, there is the possibility of developing inflamed hair follicles or sebaceous glands. In the NIOSH criteria document on cresol [127], skin contact was shown to produce a burning sensation, erythema, localized anesthesia, and a brown discoloration of the skin. Other relevant NIOSH criteria documents that list skin effects as major concerns include those on carbon black [56], refined petroleum solvents [130], coke oven emissions [18], and phenols [61].

Skin sensitization may occur after skin contact with, or inhalation of, any of these chemicals. Patch testing can be used as a diagnostic aid after a worker has developed symptoms of skin sensitization. However, patch tests should not be used as a preplacement or screening technique, because they may cause sensitization in the employee. Skin sensitization potential is best determined by medical history and physical examination.

Written and photographic records of skin lesions are one method of monitoring potential development of skin carcinomas [1]. When comparison of these records indicates any changes in appearance of the skin lesions, the worker should be referred to a qualified dermatologist for expert opinion. A clinical diagnosis of cancer or a "precancerous" condition should be substantiated by histologic examination.

(2) Liver

The NIOSH criteria document on cresol [127] indicated that liver damage may result from occupational exposures to this chemical. Medical surveillance with emphasis on preexisting liver disorders has been recommended by NIOSH in criteria documents on coal gasification [16] and phenols [61].

Because of the vast reserve functional capacity of the liver, only acute hepatotoxicity or severe cumulative chronic damage will produce recognizable symptoms such as nausea, vomiting, diarrhea, weakness, general malaise, and jaundice. Numerous blood chemistry analyses are available to screen for early liver dysfunction. The tests most frequently employed in screening for liver disease are serum bilirubin, serum glutamic oxaloacetic transaminase (SGOT), serum glutamic pyruvic transaminase (SGPT), gamma glutamyl transpeptidase (GGTP), and isocitric dehydrogenase.

(3) Kidney

Impaired renal function has been indicated by NIOSH criteria documents on cresol [127], carbon disulfide [128], coke oven emissions [18], and coal tar products [17]. Kidney function can be screened by urinalysis followed up with more specific tests.

(4) Respiratory

Inhalation of chemicals associated with coal liquefaction may be toxic to the respiratory system. For example, sulfur dioxide and ammonia are respiratory tract irritants [60,131]. Substantial exposures to ammonia can produce symptoms of chronic bronchitis, laryngitis, tracheitis, bronchopneumonia, and pulmonary edema [60]. Asphyxia and severe chemical bronchopneumonia have resulted from exposures to high concentrations of sulfur dioxide in confined spaces [131]. Evidence that lung cancer is associated with inhalation of coke oven emissions and coal tar products has also been presented in NIOSH criteria documents [17,18]. Silicosis, a pulmonary fibrosis, is caused by inhalation and pulmonary deposition of free silica [129].

In the absence of respiratory symptoms, physical examination alone may not detect early pulmonary illnesses in workers. Therefore, screening tests are recommended. These should include a chest X-ray examination performed initially and thereafter at the physician's discretion and pulmonary function tests, ie, forced vital capacity (FVC) and forced expiratory volume in 1 second (FEV_1).

(5) Blood

On the basis of evidence that benzene is leukemogenic, NIOSH [132] recommended that benzene should be considered carcinogenic in man. For workers exposed to benzene, a complete blood count (CBC) is recommended as a screening test for blood disorders. This includes determination of hemoglobin (Hb) concentration, hematocrit, red blood cell (RBC) count, reticulocyte count, white blood cell (WBC) count, and WBC differential count.

(6) Central Nervous System

CNS damage can be caused by carbon disulfide, carbon monoxide, cresol, and lead, as indicated by NIOSH criteria documents on those chemicals [58,127,128,133]. Following a substantial exposure to any CNS toxicant, or if signs or symptoms of CNS effects occur or are suspected, a complete neurologic examination should be performed.

(7) Cardiovascular

Carbon disulfide has been suggested to have an effect on the cardiovascular system [128]. Recommended medical surveillance emphasizes cardiovascular evaluation, including an electrocardiogram (ECG) [128]. Deleterious myocardial alterations such as restricted coronary blood flow may occur in workers with chronic heart disease who are exposed to carbon monoxide [58].

The medical history will help to identify workers with a family history of heart problems.

(b) Exposure Monitoring

Industrial hygiene monitoring is used to determine whether employee exposure to chemical and physical hazards is within the limits set by OSHA or recommended by NIOSH (see Appendix V) and to indicate where corrective measures are needed if exposure exceeds those limits. There are no established exposure limits for many substances that may contaminate the workplace air in coal liquefaction plants. In these circumstances, exposure monitoring can still serve two purposes. First, failures in engineering controls and work practices can be detected. Second, data can be developed to help identify causative agents for effects that may be revealed during medical monitoring. It is not possible at this time to predict which individual chemicals may have the greatest toxic effect. Furthermore, the possible interaction of individual chemicals must be considered.

NIOSH has published an Occupational Exposure Sampling Strategy Manual [134] to provide employers and industrial hygienists with information that can help them determine the need for exposure measurements, devise sampling plans, and evaluate exposure measurement data. Although this manual was specifically developed to define exposure monitoring programs for compliance with proposed regulations, the information on statistical sampling strategies can be used in coal liquefaction plants. Guidelines are also provided for selecting employees to be sampled, based on identification of maximum risk employees from estimated exposure levels or on random sampling when a maximum risk worker cannot be selected.

The manual [134] suggests that a workplace material survey be conducted to tabulate all workplace materials that may be released into the atmosphere or contaminate the skin. All processes and work operations using materials known to be toxic or hazardous should be evaluated.

Many of the materials present in coal liquefaction plants are complex mixtures of hydrocarbons, which may occur as vapors, aerosols, or particulates. It would be impractical to routinely quantitate every component of these materials. For many materials, measuring the cyclohexane-soluble fraction of total particulate samples would yield useful data for evaluating worker exposure. Chemical analysis procedures developed for coal tar pitch volatiles can be readily applied to coal liquefaction materials, and comparison of data from other industries would be possible. However, this does not imply that the PEL of 0.15 mg/m^3 of benzene-soluble coal tar pitch volatiles established for coke oven emissions is a safe level for coal liquefaction materials. Instead, monitoring results should be interpreted with toxicologic data on specific coal liquefaction materials, including products, intermediate process streams, and emissions.

Several additional exposure monitoring techniques have been suggested for consideration in specific plants.

(1) Indicator Substance

The use of an indicator substance for monitoring exposures has been suggested by several sources [16,37,135]. An indicator is a chemical chosen to represent all or most of the chemicals that may be present. Ideally, an indicator should be (1) easily monitored in real time by commercially available personal or remote samplers, (2) suitable for analysis where resources and technical skills are limited, (3) absent in ambient air at high or widely fluctuating concentrations, (4) measurable without interference from other substances in the process stream or ambient air, and (5) a regulated agent so that the measurements serve the purposes of quantitative sampling for compliance and of indicator monitoring [16]. Indicators mentioned in the literature include carbon monoxide [16], benzo(a)pyrene [37,136], PAH's [136], 2-methylnaphthalene [1], and hydrogen sulfide [16].

Although indicator substances may be useful in coal gasification plants [16], this monitoring method is not recommended for coal liquefaction because interpretation of results may be misleading. Exposures to complex mixtures of aerosols, gases, and particulates may occur in coal liquefaction, but when indicator substances are used, quantification of employee exposure to agents other than the indicator cannot be determined. For example, in one plant [38], chemical analysis of nearly 200 particulate samples for benzene-soluble material did not reveal any consistency in the ratio of the mass of benzene-soluble constituents to the total mass concentration. An additional drawback is that this method provides a hazard index only for contaminants in the same physical state as the indicator substance. For example, carbon monoxide acts as an indicator only for other gases and vapors, not for particulates. An indicator substance approach may be useful for planning a more comprehensive exposure monitoring program and for identifying emission sources of coal-derived materials, but not for evaluating employee exposure.

(2) Alarms for Acutely Toxic Hazards

White [135] suggested monitoring substances or hazards that could immediately threaten life and health, such as hydrogen sulfide, carbon monoxide, nitrogen oxides, oxygen deficiency, and explosive hazards. Recommendations for hydrogen sulfide alarms have been published by NIOSH [65] and should be adopted where the possibility exists for high concentrations of hydrogen sulfide to be released.

(3) Ultraviolet Fluorescence

Based on the toxic effects described in Chapter III, skin contamination must be considered an important route of entry for exposure to toxic substances. Skin contamination can occur by direct contact with a chemical or by contact with contaminated work surfaces. Studies are currently being conducted [1,137] to develop instrumentation to quantitate specific PAH constituents in surface contamination using a sensor that detects fluorescence at specific wavelengths. Existing methods are based on fluorescence when illuminated by broad-spectrum UV lamps. Methods based on fluorescence have been recommended for monitoring PAH's in surface contamination [138,139]. However, this test is insensitive to specific chemical compounds that may be carcinogenic. Possibly harmless fluorescent materials are detected, while nonfluorescing carcinogens are not.

Although UV light has been used in several plants to detect skin contamination [1], there is concern about the risk of skin sensitization and promotion of carcinogenic effects. In the criteria document on coal tar products, the potential for photosensitive reactions in individuals exposed concurrently to UV radiation and coal tar pitch was discussed. UV radiation at 330-440 nm, but not at 280-320 nm, in combination with exposure to coal tar pitch was found to induce a photosensitive reaction evidenced by erythema and wheal formation [17].

In one plant, a booth to detect skin contamination has been constructed for use by employees [1]. This booth operates at 320-400 nm with an approximate exposure time of 15-30 seconds. A person standing inside the booth under UV light can observe fluorescent material on the body by looking into mirrors on all four walls [1]. This enables the worker to detect contamination that might otherwise go unnoticed. Contamination may occur from sitting or leaning on contaminated surfaces or from not washing hands before using sanitary facilities. When the booth is used, eye protection is required, and employees are instructed to keep exposure time to a minimum [1]. Because of the possible risk associated with excessive use of a UV booth, UV examination for skin contamination should only be conducted under medical supervision for demonstration purposes, preferably with hand-held lamps.

At present, no suitable method for quantitative measurement of surface contamination has been developed. Skin contamination was recorded by the medical personnel in one plant [1] who used contour marking charts and rated fluorescent intensity on a subjective numeric scale. This method of estimating and recording skin contamination could provide a useful indication of such exposure. Some preliminary work [39] has been completed to develop a method for analyzing skin wipe samples from contaminated skin. Analysis of contaminants extracted from 5-cm gauze pads wetted with 70% isopropyl alcohol showed that benzene-soluble materials can be recovered from the skin surface; wipe samples of contaminated skin contained 10 times more benzene solubles than did wipe samples from apparently clean skin [39].

(4) Baseline Monitoring

One company has developed a system of baseline monitoring for coal-derived materials in its coal conversion plants [140]. In this system, detailed comprehensive area and personal monitoring is conducted. The baseline data obtained are used to select a representative group of area sites and people (by job classification) to be monitored periodically. Changes can be noted by comparing the results over time. Baseline monitoring should be repeated quarterly [140]. When this technique is used, chemicals representative of the process should be chosen and monitored in places where they are likely to be emitted.

(c) Recordkeeping

In previous sections of this chapter, monitoring of worker health and the working environment is recommended as an essential part of an occupational health program. These measures are required to characterize the workplace and the exposures that occur there and to detect any adverse health effects resulting from exposure. The ability to detect potential occupational health problems is particularly critical with a developing technology such as coal liquefaction, where exposures to sulfur compounds, toxic trace elements, coal dust, PAH's, and other organic compounds result in an occupational environment that is most difficult to characterize. Actions taken by the industry to protect its workers and by government agencies to develop regulations must be based on data that define and quantify hazards. Because coal conversion is a developing technology, it is also particularly appropriate to recommend that certain types of occupational health information be collected and recorded in a manner that facilitates comprehensive analysis.

This need for a recordkeeping system that collects and analyzes occupational health data has resulted in a proliferation of methods being adopted, usually on a company-by-company basis [141,142]. There is a need for standardized recordkeeping systems for use by all coal liquefaction plants that will permit comparisons of data from several sources [143]. Accordingly, those engaged in coal liquefaction should implement a recordkeeping system encompassing the following elements:

(1) Employment History

Each employee should be covered by a work history detailing his job classifications, plant location codes, and to the extent practical, the time spent on each job. In addition, compensation claim reports and death certificates should be included.

(2) Medical History

Each employee's medical history, including personal health history and records of medical examinations and reported illnesses or injuries, should be maintained.

(3) Industrial Hygiene Data

All results of personal and area samples should be recorded and maintained in a manner that states monitoring results, notes whether personal protective equipment was used, and identifies the worker(s) monitored or the plant location code where the sampling was performed. An estimate of the frequency and extent of skin contamination by coal-derived liquids should be recorded annually for each employee.

Emergency Plans and Procedures

(a) Identification of Emergency Situations

The key to developing meaningful and adequate emergency plans and procedures is identification of hazardous situations that require immediate emergency actions to mitigate the consequences. In most chemical industries, hazards such as fires, explosions, and release of and exposure to possibly toxic chemicals have been identified, and adequate safety, health, and emergency procedures have been developed [1,112,113,144,145]. In addition, chemical and physical characteristics of materials processed in coal liquefaction plants present additional health and safety hazards, as discussed in Chapter III. These hazards should be formally addressed in the development of emergency plans and procedures. Some failure mechanisms could result in situations requiring emergency actions, eg, rupture of high-pressure lines due to thinning by erosion and corrosion, and rupture of lines during the use of high-pressure water to clear blockage resulting from the solidification and plugging of coal solutions. System safety analyses can be used to identify possible failures or hazards expected during plant operation.

(b) Emergency Plans and Procedures for Fires and Explosions

Prior to plant operation, emergency plans and procedures for fires, explosions, and rescue should be developed, documented, and provided to all appropriate personnel. The plans should formally establish the organization and responsibilities of a fire and rescue brigade, identify all emergency personnel and their locations, establish training requirements, and establish guidelines for the development of the needed emergency procedures. They should follow the guidelines in 29 CFR 1910, Subpart L, Fire Protection, Means of Egress, Hazardous Materials. Regulations contained in the Energy Research and Development Administration (ERDA) Manual, Chapter 0601, "Emergency Planning Preparedness and Response Program, 1977," [146] should also be used as guidelines for developing the emergency plan.

Training of emergency personnel should also follow the guidelines in 29 CFR 1910, Subpart L, with special attention given to systems handling coal-derived materials and any special procedures associated with these systems. Special firefighting and rescue procedures, protective clothing requirements, and breathing apparatus needs should be specified for areas where materials might be released from the process equipment during a fire or explosion. These procedures should be documented and incorporated into standard operating procedures, and copies of these documents should be provided to all emergency personnel.

Emergency services should be adequate to control such situations until community-provided emergency services arrive. Where a large fire department is staffed with permanent, professionally trained employees and has developed adequate training programs, it would be appropriate for a plant manager to rely more on the emergency services of that department. When local community services are relied upon for emergency situations, the emergency plan discussed above should include provisions for close coordination with these services, frequent exercises with them, and adequate training in the potential hazards associated with the various systems in the plant.

(c) Emergency Medical Treatment

It is important to identify the hazardous materials associated with coal liquefaction and the medical treatment necessary. In their operating and safety procedures, plants have documented recognized and established first-aid and medical treatment for various chemical exposures [1,112,113,144,145]. The first-aid program should comply with the requirements in 29 CFR 1910.151.

Emergency medical personnel, such as nurses or those with first-aid training, should be at the plant at all times. Immediate response is needed when life would be endangered if treatment were delayed, eg, the inhalation of toxic gases such as hydrogen sulfide or carbon monoxide, and asphyxiation due to oxygen displacement by inert gases such as nitrogen.

Each coal liquefaction plant should develop fire, rescue, and medical plans and procedures addressing all hazards associated with the handling of coal liquefaction materials. Fire, rescue, and medical services should be provided that are capable of handling and controlling emergencies until additional community emergency services can arrive at the plant site. The emergency personnel at the plant should direct all emergency actions performed by outside services.

VI. CONCLUSIONS AND RECOMMENDATIONS

NIOSH recognizes that there are many differences between a pilot plant and a commercial plant. First, commercial plants are designed for economical operation, whereas pilot plants are designed to obtain engineering data to optimize operating conditions. For example, commercial plants may reuse wastewater after treatment or process byproducts, such as char, mineral residue slurry, and sulfur, that are not used in pilot plants. Recycling of materials may result in higher concentrations of some toxic compounds in process streams. Second, because commercial plants operate longer between shutdowns than pilot plants, there may be significant differences in employee exposure to process materials. Third, the chemical composition of materials in commercial plants, the equipment configuration, and operating conditions may differ from those in pilot plants. New technology may be developed that could alter process equipment or the chemical composition of products or process streams. Such differences in chemical composition have been described for Fischer-Tropsch and Bergius oils [2]. Solvent de-ashing units are currently being investigated for solid-liquid separation [1]. Differences in equipment selection resulting from new technology or process improvements may affect the type of emission sources and extent of worker exposure.

Although the design of a commercial plant and the equipment used may be different than for a pilot plant, the engineering design considerations, which may affect the potential for worker exposure, and the recommended controls and work practices should be similar. Both commercial and pilot plant processes will operate in a high-temperature, high-pressure environment, and in most cases, a coal slurry will be used. Although the equipment may differ, the sources of exposure, such as leaks, spills, maintenance, handling, and accidents, will be similar. In addition, specific technology used to minimize or control worker exposure may be different for the two plant types. For example, commercial plants operate continuously and may use a closed system to handle solid wastes and to minimize inhalation hazards. This system may not be suitable for a pilot plant, which generally operates in a batch mode and where a portable local exhaust ventilation system could be provided when needed [1]. The systems differ, but both are designed to minimize worker exposure to hazardous materials.

Potential worker exposure to hazardous materials identified in pilot plants (see Appendix VI) warrants engineering controls and work practices as well as a comprehensive program of personal hygiene, medical surveillance, and training to minimize exposure in both pilot and commercial plants. If additional hazardous materials are identified in commercial plants, further precautions should be taken. If new process technology were to reduce potential hazards, a less vigorous control program might be warranted, but evidence of this is unavailable. When new data on these hazards become available, it will be appropriate to review and revise these recommendations.

Summary of Pilot Plant Hazards

An apparent excess incidence of cancerous and precancerous lesions was reported among workers in a West Virginia coal liquefaction plant that is no longer operating [4,53]. Although excess risk may have been overestimated because of design limitations, the excess observed to expected incidence would not be expected to be eliminated. Fifteen years after the initial study, a followup mortality study was conducted on the 50 plant workers who had cancerous and precancerous skin lesions. This followup study did not indicate an increased risk of systemic cancer. However, a better estimate of risk of systemic cancer mortality would have been derived if the entire original work force in the pilot plant had been followed up for more than 20 years.

Two other reports [1,75] demonstrated that the most common medical problems at pilot plants have been dermatitis, eye irritation, and thermal burns. From the available epidemiologic evidence, it is possible to identify several acute problems associated with occupational exposure to the coal liquefaction process. The full potential of cancer or other diseases of long latency possibly related to coal liquefaction, however, has not been established because of inadequate epidemiologic data.

There are numerous hazardous chemicals potentially in coal liquefaction plants for which health effects have been identified, dose-response relationships defined, and exposure limits established. Additional hazardous chemicals are present about which less is known. Furthermore, the combined effects of these chemicals in mixtures may differ from their independent effects.

Results of recent studies [14,15] using rats show that SRC-I and SRC-II process materials can cause adverse reproductive effects, including embryolethality, fetotoxicity, and fetal malformations. These effects are observed when materials are administered during both mid- and late gestation at dose levels high enough to cause >50% maternal lethality.

Long-term effects on nearly all major organ systems of the body have been attributed to constituent chemicals in various coal liquefaction process streams. Many of the aromatics and phenols irritate the skin or cause dermatitis. Silica dust and other components of the mineral residue may affect the respiratory system. Benzene, inorganic lead, and nitrogen oxides may affect the blood. Creosotes and coal tars affect the liver and kidneys, and toluene, xylene, hydrogen sulfide, and inorganic lead may affect the CNS.

Operating conditions in coal liquefaction plants (such as high temperature and pressure, and erosion/corrosion associated with slurry handling) increase the potential for leaks in process equipment. These conditions also increase the potential for acute, possibly fatal exposures to carbon monoxide, hydrogen sulfide, and hydrocarbon emissions. Furthermore, there is the potential for explosions when combustible material is released from processes operating at temperatures above the autoignition temperature of the materials being contained.

Because of the new technology involved, it is not possible to accurately predict the operational longevity of individual equipment components used in a plant. Often, frequent maintenance is required for some components, involving disassembling normally closed system components and, in some cases, requiring worker entry into confined spaces.

Control of Pilot Plant Hazards

Because sufficient data are not available to support exposure limits for all coal liquefaction materials, recommendations are made for worker protection through the combined implementation of engineering controls, work practices, medical surveillance, exposure monitoring, education and training, and use of personal protective equipment. In many cases, it is not possible to specify a single course of action that is correct for every situation. The information presented in this document is intended to assist those persons responsible for evaluating hazards and recommending controls in coal liquefaction pilot plants. By applying these recommendations to individual situations, it may be possible to reduce or eliminate potential workplace hazards.

(a) Medical Surveillance

Workers in coal liquefaction plants may be exposed to a wide variety of chemicals that can produce adverse health effects in many organs of the body. Medical surveillance is therefore necessary to assess the ability of employees to perform their work and to monitor them for any changes or adverse effects of exposure. Particular attention should be paid to the skin, oral cavity, respiratory system, and CNS. Effects on the skin may range from discoloration to cancer [17]. In addition to local effects on the respiratory tract mucosa [60,61], there is the potential for disabling lung impairment from cancer [17,18].

NIOSH recommends that a medical surveillance program be instituted for all potentially exposed employees in coal liquefaction plants and that it include preplacement and interim medical histories supplemented with preplacement and periodic examinations emphasizing the lungs, the upper respiratory tract, and the skin. Workers frequently exposed to coal-derived materials should be examined at least annually to permit early detection of adverse effects. In addition, a complete physical examination following the protocol of periodic examinations should be performed when employment is terminated.

Pulmonary function tests (FVC and FEV_1) should be performed annually. Chest X-ray films should also be made annually to aid in detecting any existing or developing adverse effects on the lungs. Annual audiometric examinations should be given to all employees who work in areas where noise levels exceed 85 dBA for an 8-hour daily exposure. The skin of employees who are occupationally exposed to coal-derived liquids should be thoroughly examined periodically for any actinic and other effects or the presence of benign or premalignant lesions. Employees with suspected lesions should be referred to a dermatologist for evaluation.

Other specific tests that should be included in the medical examination are routine urinalysis, CBC, and tests to screen liver function. Additional tests, such as sputum cytology, urine cytology, and ECG, may be performed if deemed necessary by the responsible physician.

Information about specific occupational health hazards and plant conditions should be provided to the physician who performs, or is responsible for, the medical surveillance program. This information should include an estimate of the employee's actual and potential exposure to the physical and chemical agents generated, including any available workplace sampling results, a description of any protective devices or equipment the employee is required to use, and the toxic properties of coal liquefaction materials.

Employees or prospective employees with medical conditions that may be directly or indirectly aggravated by work in a coal liquefaction plant should be counseled by the examining physician regarding the increased risk of health impairment associated with such employment.

Emergency first-aid services should be established under the direction of the responsible physician to provide care to any worker poisoned by materials such as hydrogen sulfide, carbon monoxide, and liquid phenols. Medical services and equipment should be available for emergencies such as severe burns and asphyxiation.

Pertinent medical records should be maintained for all employees for at least 30 years after the last occupational exposure in a coal liquefaction plant.

(b) Engineering Controls

In coal liquefaction plants, coal liquids are contained in equipment that is not open to the atmosphere. Standards, codes, and regulations for maintaining the integrity of that equipment are currently being applied. The use of engineering controls to minimize the release of contaminants into the workplace environment will lessen dependence on respirators for protection. In addition, lower contaminant concentration levels resulting from the application of engineering controls will reduce the instances where respirators are required, make possible the use of less confining, easier-to-use respirators when they are required, and provide added protection for workers whose respirators are not properly fitted or conscientiously worn.

Principles of engineering control of workplace hazards in coal liquefaction plants can be applied to both pilot and commercial plants, and to all types of liquefaction processes. Recognizing that engineering design for both demonstration and commercial coal liquefaction plants is only currently being developed, emphasis should be placed on design to prevent employee exposure, ie, to ensure integrity of process containment, limit the need for worker exposure during maintenance, and provide for maximum equipment reliability. These design considerations include minimizing the effects of erosion, corrosion, instrument failure, and seal and valve failure, and providing for equipment separation, redundancy, and fail-safe design. Additional techniques for limiting worker exposure, such as designing process sampling equipment to minimize the release of process material, are also appropriate. A system safety program that will identify control strategies and the risks of accidental release of process materials is needed for evaluating plant design and operating procedures.

The primary objectives of engineering controls are to minimize the potential for worker exposure to hazardous materials and to reduce the exposure level to within acceptable limits. Many of the engineering design considerations discussed throughout this assessment are addressed in existing standards, codes, and regulations such as the ASME Boiler and Pressure Vessel Code and the NFPA standards. These provide the engineering design specifications necessary for ensuring the integrity and reliability of equipment used to handle hazardous materials, the degree of redundancy and fail-safe design, and the safety of plant layout and operation. Although these regulations address design considerations that may affect worker safety and health, several engineering design considerations are not specifically addressed. These include the need for a system safety program, equipment maintainability, improved sampling systems, and reducing the likelihood of coal slurry coking or solidifying.

Because coal liquefaction plants are large and involve many unit operations and unit processes, a mechanism is needed to ensure that engineering designs are reviewed and supported by the appropriate safety and health professionals. This review would provide for early recognition and resolution of safety and health problems. A formal system safety program should be formulated and instituted for this review and analysis of design, identification of hazards and potential accidents, and specification of safety controls and procedures. Review and analysis should be conducted during both initial plant design and process design modifications using methods such as fault-tree analysis, failure-mode evaluation, or other safety analysis techniques. Process operating modes such as startup, normal production, shutdown, emergency, and maintenance should be considered in the hazards review process. At a minimum, the system safety program should include:

(1) A schedule stating when reviews and analyses are required.

(2) Assignment of employee responsibilities to ensure that these reviews are performed.

(3) Methods of analyses that should be used.

(4) Documentation and safety certification requirements.

(5) Documented review procedures for ensuring that knowledgeable health and safety personnel, as well as the engineering, maintenance, or management staff review designs and design changes.

Coal liquefaction plants should be designed to ensure that systems, unit operations, and unit processes handling hazardous and coal-derived materials can be maintained or repaired with minimal employee exposure. Prior to removal or maintenance activities, such equipment should, at a minimum, be:

(1) Isolated from the process stream.

(2) Flushed and purged, where practicable, to remove residual materials.

The flush, purge, and residual process materials should be contained, treated, and disposed of properly if they are not recycled. Gas purges should be disposed of by incineration in a flare system or by other effective methods. Areas into which flammable materials are collected should have adequate ventilation to reduce the flammable vapor concentration to less than its lower explosive limit. When employees must enter these areas, adequate ventilation should be provided to reduce the toxic vapor concentration to whatever NIOSH recommends as the lower exposure limit.

During process stream sampling, the potential for worker exposure to the material being sampled can be significant. Sampling techniques observed during plant visits have ranged from employees holding a small can and directing the material into it using a nozzle, to closed-loop systems using a sampling bomb. Reducing employee exposure during sampling is essential. Where practicable, process stream sampling systems should use a closed-loop system designed to remove flammable or toxic material from the sampling lines by flushing and purging before removing the sampling bomb. Discharges from the flushing and purging of sampling lines should be collected and disposed of properly.

The chemical and physical characteristics of the coal slurry handled in coal liquefaction plants may necessitate frequent maintenance, increasing the possibility of worker exposure to potentially hazardous materials. If heated improperly, the coal slurry can coke and plug lines and equipment. In addition, the pour point of the coal slurry is high, and lines and equipment will become plugged if the temperature of the slurry falls below this point.

Instrumentation and controls should be provided to maintain proper heating of the coal slurry, thus minimizing its coking potential. When coking does occur, local ventilation and/or respirators should be provided to limit worker exposure to hazardous materials during decoking activities. The potential for solidification of the coal slurry in lines and equipment during startup, routine and emergency operations, and shutdown should be minimized by heat-tracing equipment and lines to maintain temperatures greater than the pour point of the material.

Where practicable, equipment used to handle fluids that contain solids should be flushed and purged during shutdown to minimize the potential for coal slurry solidification or settling of solids.

When lines become plugged, one method for removing the plug is hydroblasting. During hydroblasting activities, adequate ventilation or respiratory protection should be provided. Water that is contaminated by process materials should be collected, treated, and recycled, or disposed of.

These design considerations and controls are necessary to protect worker safety and health by minimizing exposures to potentially hazardous materials. During the design and operation of coal liquefaction plants, every effort should be made to use engineering controls as much as possible. When available engineering controls are not sufficient or practical, work practices and personal protective equipment should be used as a supplementary protective measure.

(c) Work Practices

The major objective in the use of work practices is to provide additional protection to the worker when engineering controls are not adequate or feasible. Workplace safety programs have been developed in coal liquefaction pilot plants to address risks of fire, explosion, and toxic chemical exposure. These programs are patterned after similar ones in the petroleum refining and chemical industries. Most coal liquefaction pilot plants have written policies and procedures for various work practices, eg, procedures for breaking into pipelines, lockout of electrical equipment, tag-out of valves, fire and rescue brigades, safe work permits, vessel entry permits, wearing safety glasses and hardhats, housekeeping, and other operational safety practices [1]. Personnel responsible for the development of safety programs for coal liquefaction plants can draw upon general industry standards, voluntary guidelines of similar industries, equipment manufacturers' recommendations, operating experience, and common sense to develop similar programs tailored to their own operations. Appendix VIII contains some of the codes and standards applicable to both the development of safety programs for, and the design of, coal liquefaction plants.

It is common practice in industry to develop detailed operating procedures for each phase of operation, including startup, normal operation, routine maintenance, normal shutdown, emergency shutdown, and shutdown for extended periods. In developing these procedures, consideration should be given to provisions for safe storage of process materials, and for decontamination of equipment requiring maintenance.

Emergency fire and medical services are recommended. At a minimum, these services should be capable of handling minor emergencies and controlling serious ones until additional help can arrive. Prior to operation, local fire and medical service personnel should be made aware of the various hazardous chemicals used and any special emergency procedures necessary. This step will help to ensure that, when summoned, these local services know the hazards and required actions. In addition, emergency medical services are needed at the plant at all times to provide treatment necessary in life or death situations such as asphyxiation.

The potential for occupational exposure to hazardous materials increases during maintenance operations. For this reason, provisions should be made for preventing inadvertent entry of inert or toxic materials into the work area before work begins in or on any tank, line, or equipment. Where practicable, process equipment and connecting lines handling toxic gases, vapors, or liquids should be flushed, steamed, or otherwise purged before being opened. Flushed liquids should be safely disposed of by diverting them to sealed drains, storage vessels, or other appropriate collecting devices. Toxic gases should be incinerated, flared, recycled, or otherwise disposed of in a safe manner.

Tanks, process equipment, and lines should be cleaned, maintained, and repaired only by properly trained employees under responsible supervision. When practical, such work should be performed from outside the tank or equipment.

To avoid skin contamination, the accumulation of hazardous materials on work surfaces, equipment, and structures should be minimized, and spills and leaks of hazardous materials should be cleaned up as soon as possible. Employees engaged in cleanup operations should wear suitable respiratory protective equipment and protective clothing. Employees should also be aware of the possible permeation risk of some protective equipment and protective clothing, and should take care to change such equipment or clothing whenever skin contact with hazardous materials occurs. Cleanup operations should be performed and directly supervised by employees instructed and trained in procedures for safe decontamination or disposal of equipment, materials, and waste. All other persons should be excluded from the area of the spill or leak until cleanup is complete and safe conditions have been restored.

A set of procedures covering fire, explosion, asphyxiation, and any other foreseeable emergencies that might arise in coal liquefaction plants should be formulated. All potentially affected employees should be thoroughly instructed in the implementation of these procedures and reinstructed at least annually.

These procedures should include emergency medical care provisions and prearranged plans for transportation of injured employees. Where outside emergency services are used, prearranged plans should be developed and provided to all essential parties. Outside emergency services personnel should be informed orally and in writing of the potential hazards associated with coal liquefaction plants. Fire and emergency rescue drills should be conducted at least semiannually to ensure that employees and all outside emergency services personnel are familiar with the plant layout and the emergency plans and procedures. Necessary emergency equipment, including appropriate respirators and other personal protective equipment, should be stored in readily accessible locations.

Access to process areas should be restricted to prevent inadvertent entry of unauthorized persons who are unfamiliar with the hazards, precautions, and emergency procedures associated with the process. When these persons are permitted to enter a restricted area, they should be informed of the potential hazards and of the necessary actions to take in an emergency.

(d) Informing Employees of Hazards

At the beginning of employment, all employees should be informed of the known occupational exposure hazards associated with coal liquefaction plants. The following information could be included as part of a training program:

(1) Identification of toxic raw materials and coal liquefaction products and byproducts.

(2) Toxic effects, including the possible increased risk of developing cancer.

(3) Signs and symptoms of overexposure to hydrogen sulfide, carbon monoxide, other toxic gases, and aerosols.

(4) Fire and explosion hazards.

(5) Oxygen deficiency hazards.

(6) Emergency first-aid treatment for overexposure.

(7) Plant layout and emergency evacuation procedures.

(8) The use, limits of use, storage, and maintenance of all personal protective clothing and equipment that may be used.

(9) Hazards that may arise during materials handling, process sampling, housekeeping, waste disposal, and maintenance.

(10) The reasons for and the practice of personal hygiene.

(11) A description of the general nature of environmental and medical surveillance procedures and the advantages to the employee in cooperating with such procedures.

Training should be repeated periodically as part of a continuing education program to ensure 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, and the advantages of good personal hygiene. Retraining should be conducted at least annually or whenever necessitated by changes in equipment, processes, materials, or employee work assignments.

Because employees of vendors who service coal liquefaction pilot plants may also come into contact with contaminated materials, similar information should be provided to them. This can be accomplished more readily if operators of coal liquefaction plants obtain written acknowledgements from contractors receiving waste products, contaminated clothing, or equipment that these employers will inform their employees of the potential hazards that might arise from occupational exposure to coal liquefaction materials.

Another means of informing employees of hazards is to post warning signs and labels. All warning signs should be printed both in English and in the predominant language of non-English-reading employees. Employees reading languages other than those used on labels and posted signs should receive information regarding hazardous areas and should be informed of the instructions printed on labels and signs. All labels and signs should be readily visible at all times.

It is recommended that the following sign be posted at or near systems handling or containing coal-derived liquids:

DANGER
CANCER-SUSPECT AGENTS

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

In all areas in which there is a potential for exposure to toxic gases such as hydrogen sulfide and carbon monoxide, signs should be posted at or near all entrances. At a minimum, these signs should contain the following information:

CAUTION
TOXIC GASES MAY BE PRESENT
AUTHORIZED PERSONNEL ONLY

When respiratory protection is required, the following statement should be posted or added to the warning signs:

RESPIRATOR REQUIRED

The locations of first-aid supplies and emergency equipment, including respirators, and the locations of emergency showers and eyewash basins should be clearly marked.

Based on the potential for serious exposure or injury, the employer should determine additional areas that should be posted or items that should be labeled with appropriate warnings.

(e) Sanitation and Personal Hygiene

Good personal hygiene practices are needed to ensure prompt removal of any coal liquefaction materials that may be absorbed through the skin. These practices include frequent washing of exposed skin surfaces, daily showers, and self-observation and reporting of any lesions that develop. To encourage good personal hygiene practices, adequate facilities for washing and showering should be provided in readily accessible locations.

Change rooms should be provided that are equipped with storage facilities for street clothes and separate storage facilities for work garments, protective clothing, work boots, hardhats, and other safety equipment. Employees working in process areas should be encouraged to shower and shampoo at the end of each workshift. A separate change area for removal and disposal of contaminated clothing, with an exit to showers, should be provided. The exit from the shower area should open into a clean change area. Employers should instruct employees working in process areas to wear clean work clothing daily and to remove all protective clothing at the completion of the workshift. Closed, labeled containers should be provided for contaminated clothing that is to be drycleaned, laundered, or discarded.

Lunchroom facilities should have a positive-pressure filtered air supply and should be readily accessible to employees working in process areas. Employees should be instructed to remove contaminated hardhats, boots, gloves, and other protective equipment before entering lunchrooms, and handwashing facilities should be provided near lunchroom entrances.

The employer should discourage the following activities in process areas: carrying, consuming, or dispensing food and beverages; using tobacco products and chewing gum; and applying cosmetics. This does not apply to lunchrooms or clean change rooms.

Washroom facilities, eyewash fountains, and emergency showers should be readily accessible from all areas where hazardous materials may contact the skin or eyes. Employees should be encouraged to wash their hands before eating, drinking, smoking, or using toilet facilities, and as necessary during the workshift to remove contamination. Employers should instruct employees not to use organic solvents such as carbon tetrachloride, benzene, or gasoline for removing contamination from the skin, because these chemicals may enhance dermal absorption of hazardous materials and are themselves hazardous. Instead, the use of waterless hand cleansers should be encouraged.

If gross contamination of work clothing occurs during the workshift, the employee should wash the affected areas and change into clean work clothing at the earliest safe opportunity. The employee should then contact his immediate supervisor, who should document the incident and provide the data for inclusion in the medical and exposure records.

Techniques using UV radiation to check for skin contamination have been tested [1]. However, the correlation between contamination and fluorescence is imperfect, and there are also possible synergistic effects of using UV radiation with some of the chemicals. For these reasons, the use of UV radiation for checking skin contamination should only be allowed under medical supervision.

(f) Personal Protective Equipment and Clothing

Employers should provide clean work clothing, respiratory protection, hearing protection, workshoes or shoe coverings, and gloves, subject to limitations described in Chapter V. Respirators may be necessary to prevent workers from inhaling or ingesting coal-derived materials. However, because respirators are not effective in all cases--for reasons including improper fit, inadequate maintenance, and worker avoidance--they should be used only when other methods of control are inadequate. Selection of the proper respirator for specific operations depends on the type of contaminant, its concentration, and the location of work operations. Selection of respirators and other protective equipment can be controlled through the use of safe work permits.

Protective clothing should be selected for effectiveness in providing protection from the hazards associated with the specific work area or operation involved. The employer should ensure that protective clothing is inspected and maintained to preserve its effectiveness.

(g) Monitoring and Recordkeeping Requirements

Performance criteria should be established to help employers evaluate the progress made toward achieving their worker protection objectives. Sampling and analysis for air contaminants provide a reasonable means for control performance assessment. Records of disruptions in plant operation by process area, including the frequency and severity of leaks, provide an excellent means for comparing performance with objectives and for directing future efforts to problem areas. A comparison of these records with data from periodic personal monitoring for specific toxicants affords additional performance evaluation.

Where appropriate, industrial hygiene monitoring should be used to determine whether employee exposure to chemical and physical hazards is within the limits set by OSHA or those recommended by NIOSH and to indicate where corrective measures are needed if such exposure exceeds those limits. To determine compliance with recommended PEL's, NIOSH recommends the use of the sampling and analytical methods contained in the NIOSH Manual of Analytical Methods [147-149].

Because of the numerous chemicals involved in coal liquefaction processes, it is impractical to routinely monitor for every substance to which exposure might occur. Therefore, an exposure monitoring program based on the results of an initial survey of potential exposures is recommended. The cyclohexane-soluble fraction (cyclohexane extractable) of the sampled airborne particulate, which has been recommended in criteria documents [17,18,76] as an indicator of the quantity of PAH compounds present, should be used. Additional compounds for which worker exposure may exceed established limits should be selected for inclusion in the monitoring program based on results of the initial survey. Exposure monitoring should be repeated quarterly, and the number of employees selected should be large enough to allow estimation of the exposure of all employees assigned to work in process areas.

The combination of data from exposure records, work histories, and medical histories, including histories of personal habits such as smoking and diet, will provide a means of evaluating the effectiveness of engineering controls and work practices, and of identifying causative agents for effects that may be revealed during medical monitoring. The ability to detect potential occupational health problems early is particularly critical in a developing technology such as coal liquefaction. Such identification is needed because exposures to numerous aromatic hydrocarbons, aliphatic hydrocarbons, sulfur compounds, toxic trace elements, and coal dusts result in an occupational environment for which anticipation of all potential health effects is difficult.

It is important that medical records and pertinent supporting documents be established and maintained for all employees, and that copies be included of any environmental exposure records applicable to the employee. To ensure that these records will be available for future reference and correlation, they should be maintained for the duration of employment plus 30 years. Copies of these medical records should be made available to the employee, former employee, or to his or her designated representative. In addition, the designated representatives of the Secretary of Health and Human Services and of the Secretary of Labor may have access to the records or copies of them.

VII. RESEARCH NEEDS

Information obtained from coal liquefaction pilot plants can be used to qualitatively assess the hazards in commercial plants in the future. Differences in operating conditions between pilot and commercial plants, however, do not currently allow these risks to be quantified. Once commercial plants begin operating, data can be collected for quantification. Studies currently being conducted by NIOSH are listed in Appendix IX. Additional research topics, divided into near- and far-term needs, are discussed here. Most of the research necessary can be based on pilot plant operations (near-term studies) and then carried over into commercial operations. However, certain research will not be possible until commercial plants are in operation (far-term studies). Research should not only be directed at recognition and evaluation of the risks but at future quantification and control of them.

Near-Term Studies

Additional research needed to identify and assess the toxicity of materials in coal liquefaction plants can be based on the materials in pilot plants. Included in this research should be industrial hygiene studies, animal toxicity studies, personal hygiene studies, prospective epidemiology studies of pilot plant workers, and studies on the carcinogenic, mutagenic, teratogenic, and reproductive effects of these coal liquefaction materials.

Near-term industrial hygiene studies are necessary because the risks cannot be assessed unless the hazards can be detected and measured. To account for changes that occur, these studies should be expanded concurrently with development of the technology. Detailed chemical analyses of all liquid and gaseous process streams, as well as surface contaminants, should be conducted to provide additional information on potential hazards. These analyses will be complicated by the fact that process stream composition will vary over a wide range depending on the reactivity and type of coal, rate of heating, liquefaction temperature, catalysts, pressure, and contact time [2]. Therefore, as many combinations of coal types and operating conditions as possible should be studied in order to characterize these changes. Studies should also be conducted to determine the extent to which PAH compounds and aromatic amines are absorbed on the surface of mineral residues and to determine whether PAH's or aromatic amines are lost through evaporation during aerosol sample collection. Studies to correlate fluorescence of surface contamination with biologically active constituents may lead to useful methods for measuring surface contamination. Instruments that measure PAH's and aromatic amines in real time are desirable.

The significance of both PAH's and aromatic amines as inhalation hazards should be determined. Existing sampling and analytical methods for determining PAH concentrations in the workplace air, based on the cyclohexane-soluble material in particulate samples, require refinement to improve accuracy, sensitivity, and precision. The current sampling method does not capture vapor-phase organic compounds, and some loss of the more volatile compounds from the airborne particulate may occur during sampling. Mutagenicity tests with various fractions of coal liquefaction materials containing 3- and 4-ring primary aromatic amines are important mutagens [150]. Further chemical analyses of these fractions should be done to identify the specific compounds present. As individual aromatic amines are identified, sampling and analytical methods need to be developed to measure them. Studies are also needed to determine how long samples remain stable prior to analysis. If necessary, handling methods that prevent sample deterioration and loss should be developed.

Animal studies to determine the toxicities of distillation fractions are required in order to investigate the potential effects of long-term exposure to coal liquids, vapors, and aerosols, particularly at low concentrations, and effects of the distillation fractions of the liquids on various physiologic systems. As the individual components of these fractions are determined, animal toxicity studies should be done for them as well. Previous studies [5-8] have only used dermal and im routes of administration. Well-planned inhalation studies in several animal species are needed to determine the exposure effects of aerosols and volatiles from synthetic coal liquids. Comparative animal studies using products from different processes could provide information that would help to further identify chemical constituents contributing to the toxic effects.

Toxicologic investigations [5-9,51] of carcinogenic effects in animals have illustrated that liquefaction products can induce cancerous lesions in some animal species, although not all materials produced similar results in all of the species tested. Additional tests of mutagenic, carcinogenic, teratogenic, and reproductive effects should be performed to augment available information on various process streams and products from different coal liquefaction processes. Less is known about the toxicity of products from pyrolysis and solvent extraction processes than about products from catalytic and noncatalytic hydrogenation and indirect liquefaction processes. Another area that requires further investigation is the potential for co-carcinogenesis and inhibition or promotion of carcinogenic effects by various constituents of coal liquefaction materials. Tests for teratogenic and reproductive effects have only been performed for one type of coal liquefaction process, ie, noncatalytic hydrogenation. Additional tests should be performed for coal liquefaction materials from other processes, particularly those selected for commercial development.

Microbial studies [40,42,44,45,50,150] have indicated mutagenic potential in various coal liquefaction products and their distillation fractions. However, these effects have not been replicated in cell cultures of human leukocytes [43]. The potential mutagenic effects should be systematically investigated in greater detail both in human cell cultures and in animals. Additional studies with mutagenic test systems would be useful for identifying the active constituents in fractions from different process streams.

While much research can be done to learn more about the hazards of exposure to process materials, research should also be carried out to improve the safety of work with materials already known or suspected to be toxic. Some contamination of workers' skin and clothing will occur regardless of the engineering controls implemented and work practices used. Therefore, personal hygiene studies should be conducted to determine the best cleaning methods for skin areas, including wounds and burns, and to develop ways to determine that cleansing has been effectively accomplished. UV radiation has been used to detect skin contamination [1]; however, further investigations are needed on the synergistic effects of UV radiation and coal liquefaction materials, particularly at wavelengths above 360 nm. The application of image enhancement devices to allow the use of low UV radiation intensities should be considered. Alternative methods for measuring or detecting skin contamination should also be considered.

Methods are also needed to test and evaluate the effectiveness of personal protective clothing against coal liquefaction materials. Decontamination procedures need to be developed for items such as safety glasses and footwear. In addition, the adequacy of laundering procedures should be evaluated.

The development of a simple noninvasive method for biologic monitoring of significant exposure to coal liquefaction products would be useful, because it is difficult to determine the extent of exposure from skin contamination. A urine test that would signal such an exposure is desirable.

Many pilot plant workers will be involved in commercial plant operation in the future. If these workers are included in future epidemiologic studies of commercial plant workers, it will be important to know their previous history of exposure in pilot plants. Therefore, prospective epidemiologic studies of these workers should begin now. In addition, it would be desirable to conduct a followup study of all employees of the Institute, West Virginia, plant, including 309 workers who were not followed up in Palmer's study [53]. It is possible that workers other than those who developed lesions were exposed to process materials. A followup study may reveal the occurrence of adverse health effects in these workers.

Solid waste generated during coal liquefaction processes includes ash, spent catalysts, and sludge. Trace levels of contaminants, eg, heavy metals, that are present in raw materials will be concentrated in this waste. Therefore, studies should be done to characterize solid waste composition and to assess worker exposure to hazardous waste components.

Far-Term Studies

Unless epidemiologic studies are undertaken independently outside the United States, there will be no opportunity to gather meaningful epidemiologic data on commercial plants until they are operating in this country. Once these commercial operations begin, detailed, long-term prospective epidemiologic studies of worker populations should be conducted to assess the effects of occupational exposure to coal liquefaction materials and to quantify the risks associated with these effects. Because the purpose of these epidemiologic studies is to correlate the health effects with exposure, they must include, at a minimum, detailed industrial hygiene surveys and comprehensive medical and work histories.

Detailed industrial hygiene surveys, including measurements of materials such as PAH's, aromatic amines, total particulates, trace metals, and volatile hydrocarbons, are necessary on a continuous or frequent basis so that worker exposure can be characterized over time. In addition, these surveys will identify any problems associated with the engineering controls or work practices. Comprehensive work and medical histories, including smoking or other tobacco use, and eating and drinking habits, are important for detecting confounding variables that may affect the potential risk to workers. Morbidity and mortality data from worker populations in coal liquefaction plants should be compared with those of properly selected control populations; eg, persons exposed to coal conversion products should be compared with those working in crude petroleum refinery plants.

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IX. APPENDIX I

SPECIFIC COAL LIQUEFACTION PROCESSES

Coal Liquefaction Processes

Specific coal liquefaction process designs are discussed below for solvent extraction, noncatalytic hydrogenation, catalytic hydrogenation, pyrolysis, and indirect liquefaction. These designs include the Consol synthetic fuel (CSF), solvent-refined coal (SRC), H-coal, char-oil-energy development (COED), and Fischer-Tropsch processes, respectively.

Solvent Extraction

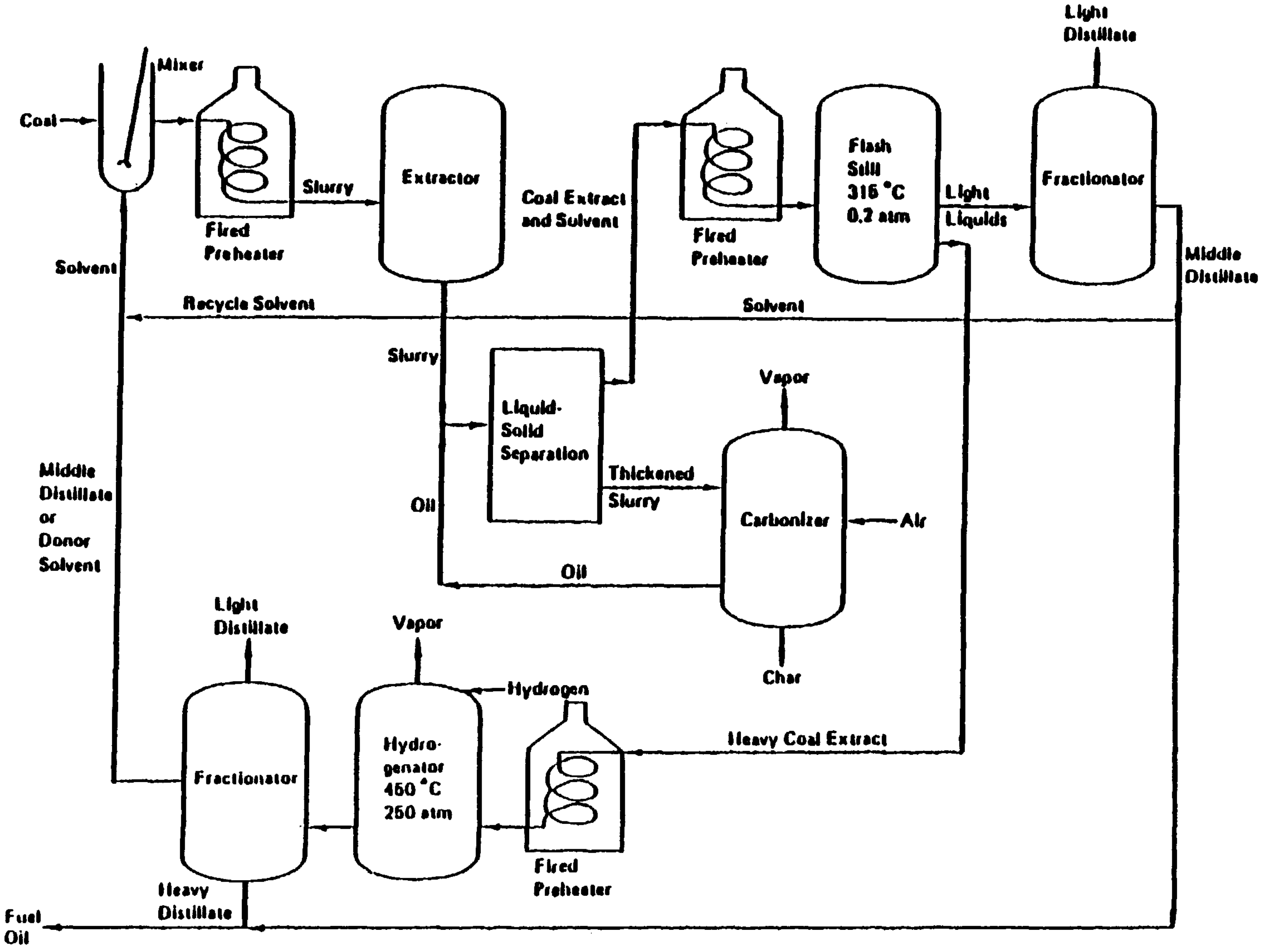
The solvent extraction process begins with a slurry of pulverized coal and a hydrogen-donor solvent. When the slurry is heated, chemical bonds in the coal structure are broken, and the donor solvent transfers hydrogen atoms to the reactive fragments that are formed. This transfer helps prevent repolymerization by decreasing free radical lifetime. Approximately 75% of the coal is liquefied due to this hydrogen transfer [2].

The CSF solvent extraction process, based upon pilot plant operations, is shown schematically in Figures IX-1 and IX-2. In this process, coal is crushed, dried, and stored under an inert gas atmosphere. The coal is then mixed with hydrogenated process solvent to form a slurry. The slurry is preheated and transferred to the stirred extraction vessel operated at about 400°C and 11-30 atm (1.1-3.0 MPa) [2].

Unreacted coal, minerals, and liquefied coal are contained in the slurry leaving the extractor vessel. The slurry passes on to the liquid-solid separation system where the unreacted coal and minerals are separated from the liquid product. The liquid product is then passed through a flash still to obtain light liquids and a heavy coal extract. Heavy coal extract is further processed in a catalytic hydrotreater (hydrogenator) where a heavy distillate product (fuel oil) and donor solvent are produced. Fractionation of the hydrotreater product stream produces light, middle (donor-solvent), and heavy distillates.

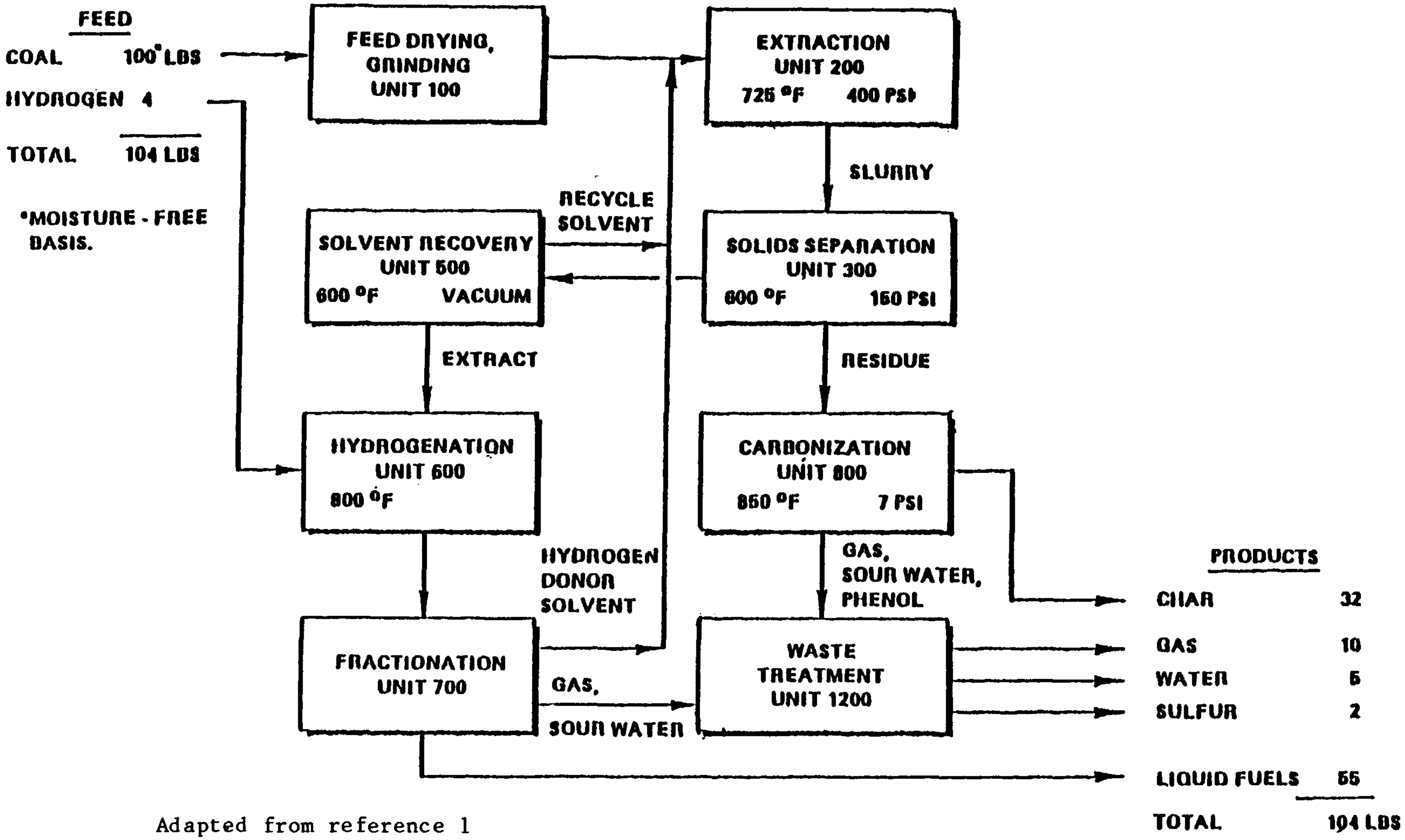
The light liquids from the flash still are fractionated and separated into light and middle distillates. The latter is used as recycle solvent and as fuel oil.

The solids-rich stream from the separation system is pyrolyzed in a fluid bed of char at about 925°F (496°C) [19] and 7 psi (48 kPa), known as the low-temperature carbonizer [1].



Adapted from reference 2

FIGURE IX-1. SCHEMATIC OF THE CSF PROCESS



Adapted from reference 1

FIGURE IX-2. FLOW DIAGRAM OF THE CSF PROCESS

The vapors from the unit operations and processes are collected. Most of these vapors then pass through gas-liquid separators where sour gas, sour water, and other liquids are separated. The remaining vapors are normally sent to a desulfurization unit and then to a flare system. The sour gas and sour water are transferred to treatment facilities to remove waste materials, such as hydrogen sulfide, ammonia, and phenols.

Hydrogenation

(a) Noncatalytic Hydrogenation

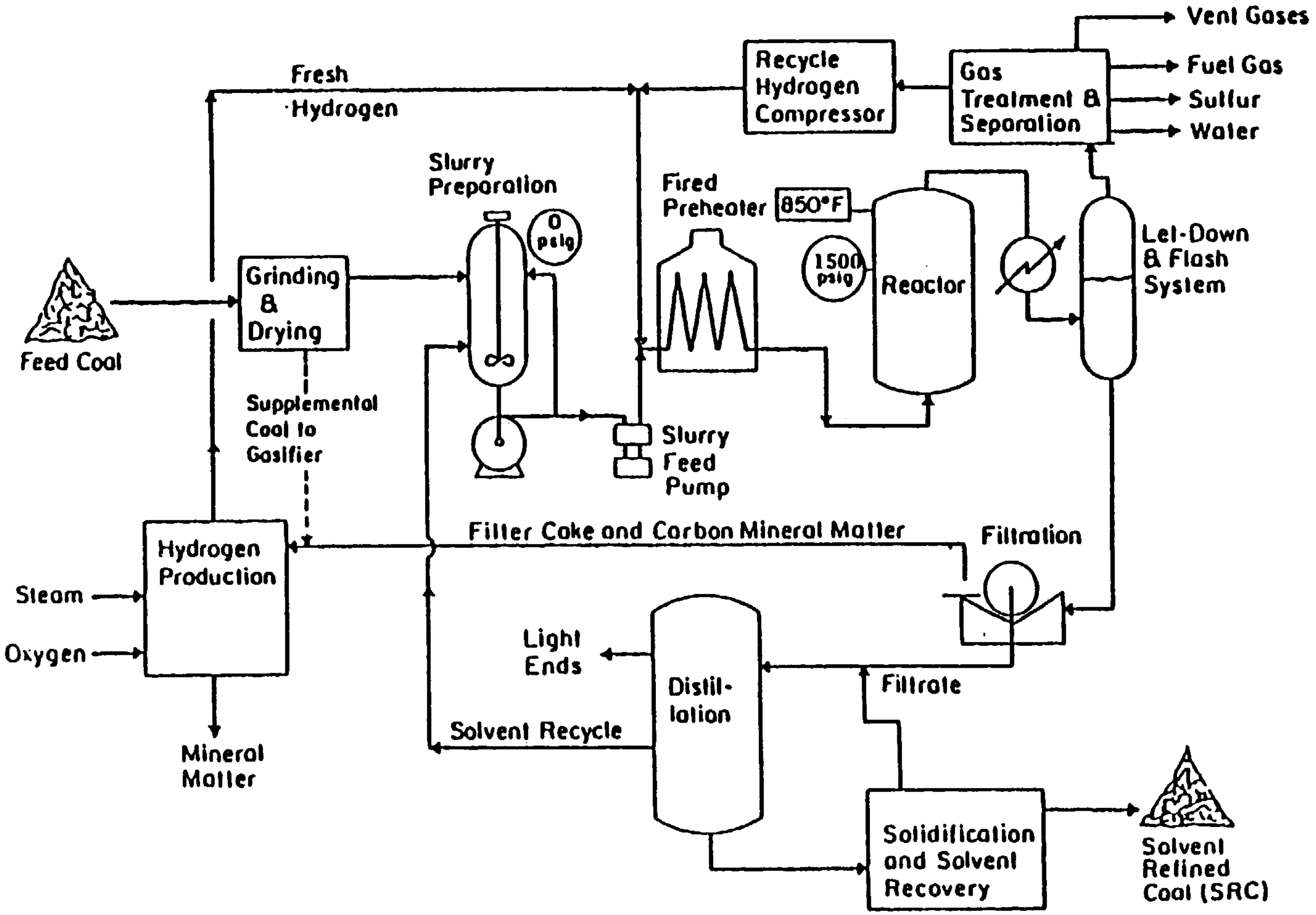
In noncatalytic hydrogenation, prepared coal, hydrogen, and a hydrogenated or nonhydrogenated solvent are combined in a pressure vessel to form hydrogenated coal products. The SRC processes, I and II, are examples of the noncatalytic hydrogenation process. However, the minerals in the recycled stream may act as a natural catalyst.

(1) SRC-I Process

A schematic of the SRC-I process is shown in Figure IX-3. In the coal preparation area, raw coal is received, unloaded, crushed, and then stored in bins. The coal is sized, pulverized, and mixed with a hydrocarbon solvent having a boiling range of 550-800°F (290-430°C). Initially, a blend of petroleum-derived carbon black feedstock and a coal tar distillate is used as a startup solvent. Ultimately, coal-derived liquids replace the startup blend as the process solvent. Solvent-to-coal ratios vary from as low as 2:1 to as high as 4:1 [108].

The resulting coal-solvent slurry is pumped from the coal preparation area to the preheater. Hydrogen or synthesis gas and water are added to the slurry as it enters the preheater. The slurry and hydrogen are pumped through a natural gas-fired preheater to a reactor. The remaining undissolved material consists primarily of inorganic mineral matter and undissolved coal. The preheater and dissolver are designed to operate between 775 and 925°F (413 and 496°C) at pressures from 500 to 2,000 psi (3 to 14 MPa) [108]. The current operating temperature is 850°F (454°C) [1].

The excess hydrogen and gases, eg, hydrogen sulfide, carbon monoxide, carbon dioxide, methane, and light hydrocarbon gases, produced in the reaction are separated from the slurry. The hydrogen sulfide and carbon dioxide (acid gases) are removed using a diethanolamine (DEA) absorption system. A Stretford sulfur recovery unit is then used to convert the hydrogen sulfide to elemental sulfur. The clean hydrogen-hydrocarbon gas stream from the DEA absorber is partly vented to flare and partly recycled to the process. Such streams will probably be used for fuel gases in a demonstration and/or commercial facility [152]. Fresh hydrogen is added to the recycle stream to maintain hydrogen partial pressure in the circulating gas [108].



Adapted from reference 151

FIGURE IX-3. SCHEMATIC OF THE SRC-I PROCESS

The slurry from the gas-liquid separator goes to mineral separation where the solids may be separated from the coal solution using rotary pressure precoat filters. These filters consist of a rotating drum inside a pressure vessel. Diatomaceous earth is used as the filtering aid with process solvent as the precoat slurry medium. Hot inert gas is circulated through the filters and filtrate receivers to maintain filtration pressure at approximately 150 psi (1 MPa) and temperature at approximately 350-650°F (180-340°C) [108]. This process also uses solvent de-ashing separation in place of filtration [1].

Filter cake, consisting of the undissolved solids and diatomaceous earth, is dried using an indirect, natural gas-fired, rotary kiln. The drying process removes the wash solvent, which is pumped to the solvent recovery area for fractionation. The dry mineral residue from the dryer is cooled with water and stored in a silo [108].

The filtered coal solution goes to solvent recovery for solvent removal by vacuum distillation. The vacuum flash overhead is fractionated into a light oil fraction, a wash solvent fraction, and the process solvent for recycle to slurry blending in the coal preparation system [108].

The vacuum bottoms stream is the principal product of the SRC-I process. This stream is the solvent-refined coal and may be solidified using a water-cooled, stainless steel cooling belt or a prilling tower. The solidified product is then sent to product storage [108].

The SRC-I process involves reacting most of the coal in a donor solvent derived from the process, separating undissolved coal solids, obtaining original process solvent by distillation, and recovering dissolved coal as a low-ash, low-sulfur, friable, black-crystalline material with glossy fractured surfaces, known as solvent-refined coal. The SRC-II process dissolves and hydrocracks the coal into liquid and gaseous products. This process does not require the filtration or solvent de-ashing step used in SRC-I for solid-liquid separation. An ashless distillate fuel oil is produced containing substantially less sulfur than the solid solvent-refined coal [26]. The current SRC-II process is a modification of the SRC-I process.

(2) SRC-II Process

SRC-II is a coal liquefaction process in which coal is mixed with a recycled slurry and hydrocracked to form liquid and gaseous products. The primary product of the SRC-II process is a distillate fuel oil [26].

A flow diagram of the SRC-II process design is shown in Figure IX-4. In the coal preparation area, coal is pulverized, dried, and mixed with hot recycle slurry solvent, from the process. The coal-recycle slurry mixture and hydrogen are pumped through a fired preheater to a hydrocracking reactor [26].

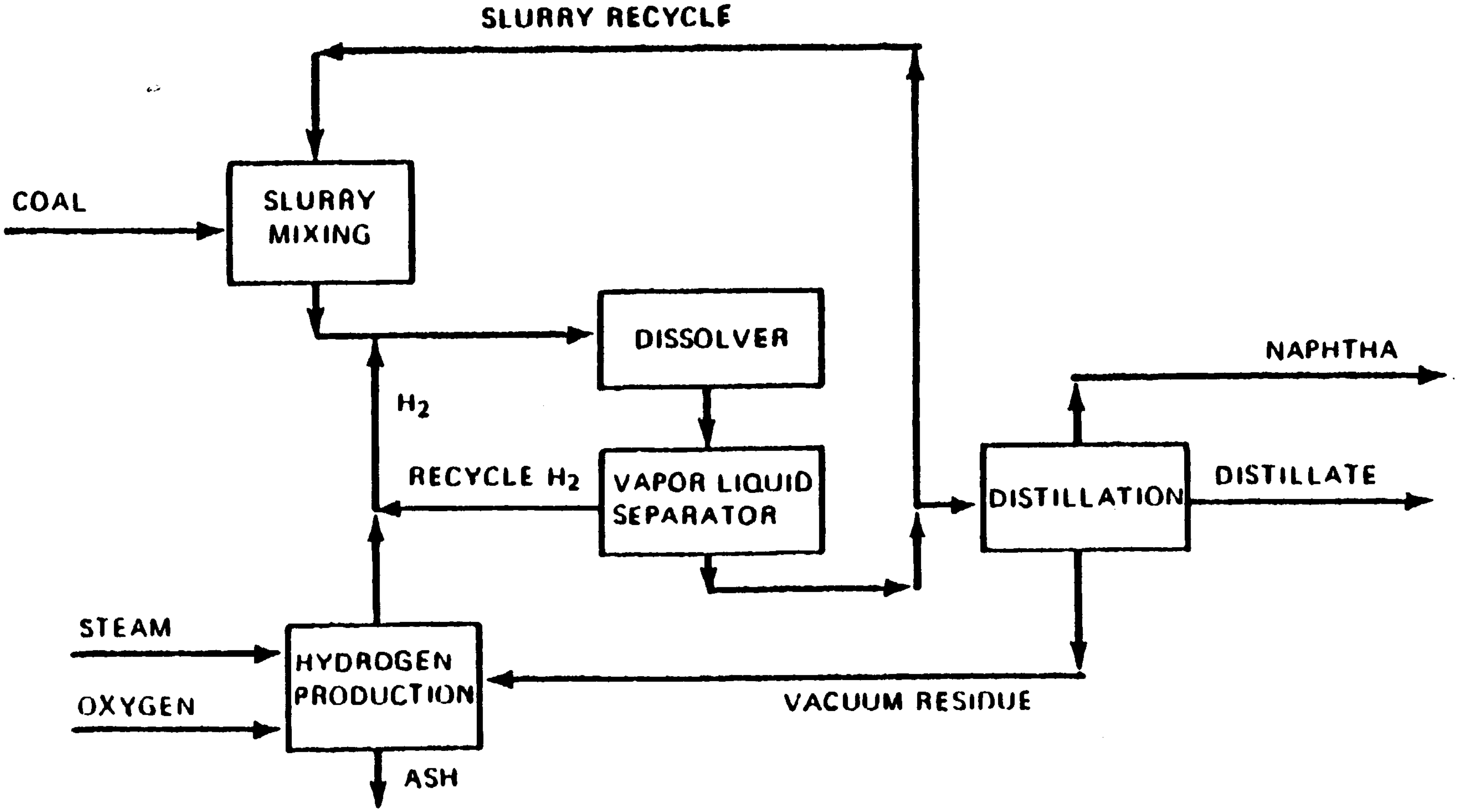


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FIGURE IX-4. FLOW DIAGRAM OF THE SRC-II PROCESS

The temperature at the outlet of the preheater is about 700-750°F (370-400°C). While in the preheater, the coal begins to dissolve in the recycle slurry solvent. The heat generated by the exothermic reactions of hydrogenation and hydrocracking raises the temperature of the reactor to 820-870°F (440-470°C). Cold hydrogen is used as a quench to control the temperature in the reactor [26].

Material leaving the reactor goes to a hot, high-pressure separator. The hot overhead vapor stream from the separator is cooled to provide vapor-liquid separation by condensation. Condensed liquid from these separators is fractionated. Noncondensed gas, consisting of unreacted hydrogen, methane and other light hydrocarbons, and acid gases, is treated to remove hydrogen sulfide and carbon dioxide. A portion of the gases is passed through a naphtha absorber to remove much of the methane and other light hydrocarbons [154]. The excess gas is sent to a flare system. The recovered hydrogen is used with additional hydrogen as feed to the process [154].

The raw distillate from the vapor-liquid separation system is distilled at atmospheric pressure. A naphtha overhead stream and a bottoms stream are separated in this fractionator. The heavier slurry from the hot, high-pressure separator flashes to a lower pressure where it splits into two major streams. One stream comprises the recycle solvent for the process. Fuel oil is separated from the other stream in a vacuum flash tower. The major fuel oil product of the SRC-II process is a mixture of the atmospheric bottoms stream and the vacuum flash tower overhead [26].

In a pilot plant, the vacuum tower bottoms are normally packaged into drums and either stored onsite or disposed of offsite. However, in a commercial plant, the vacuum tower bottoms, consisting of all of the undissolved mineral residue and the vacuum residue portion of the dissolved coal, may be used in an oxygen-blown gasifier to form synthesis gas. Synthesis gas can be converted to hydrogen and carbon dioxide using a shift converter. These product gases would then undergo an acid gas removal step to remove carbon dioxide and hydrogen sulfide. The hydrogen from the shift conversion step would comprise the principal source for the hydrogen requirements of the process. Any excess synthesis gas produced in the gasifier would be treated in an acid-gas removal unit to remove hydrogen sulfide and carbon dioxide, and burned as plant fuel. The excess synthesis gas can be separated into hydrogen and carbon monoxide, and the carbon monoxide can be used as plant fuel [26].

(b) Catalytic Hydrogenation

In catalytic hydrogenation, coal is suspended in a recycle solvent, mixed with hydrogen, and contacted with a catalyst in a reactor to form a coal-derived liquid product [2]. The catalytic hydrogenation process described in this document is the H-coal process.

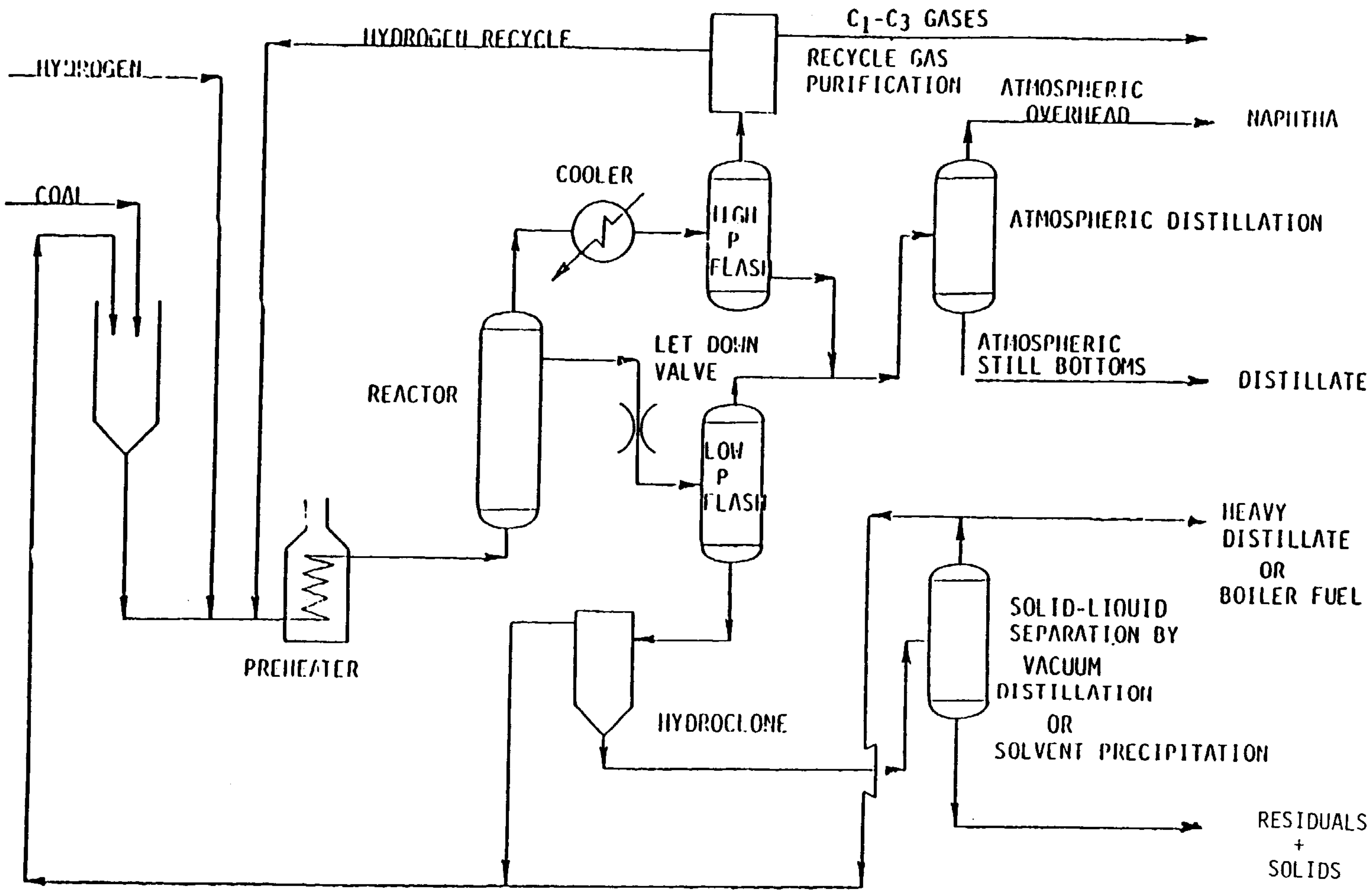
A schematic of the H-coal process development unit is shown in Figure IX-5. Pulverized coal is dried using hot nitrogen gas and then stored in a vessel under a nitrogen blanket. The prepared coal is slurried with a process-derived oil, eg, refined hydroclone products, atmospheric still bottoms, and vacuum tower overhead. Hydrogen is added to the coal slurry prior to preheating. The slurry and hydrogen mixture is then fed to a catalytic ebullated-bed reactor, which operates at an approximate temperature of 850°F (454°C) and a pressure of approximately 3,000 psig (21 MPa). Cobalt/molybdenum is the catalyst. Preheated high-pressure recycled hydrogen is also introduced into the reactor. The catalyst size is such that it remains suspended while ash particles and some unreacted coal leave the reactor in the liquid stream. Small amounts of catalyst fines may be carried over in the liquid stream, which is let down at essentially reactor tempeature to atmospheric pressure. At this stage, a portion of the lighter hydrocarbon liquids is flash vaporized and fed to an atmospheric distillation tower. The products from this tower are naphtha and atmospheric still bottoms. The naphtha is sent to storage, and the bottoms are used as a slurry oil. Excess bottoms are stored in drums [1].

The slurry remaining in the flash drum is fed to hydroclones for partial solid separation. The refined hydroclone product is used as a slurry oil and/or stored in drums. The hydroclone bottoms are sent to either a vacuum distillation tower (syncrude mode) or a solvent precipitation unit (fuel oil mode). In the syncrude mode, the vacuum overhead, which is a heavy distillate, may be partially recycled to the slurry mix tank. The vacuum bottoms are stored in drums as a solid. All gases are scrubbed to remove light hydrocarbons, ammonia, and hydrogen sulfide. Hydrogen gas of approximately 80% purity is recompressed and recycled to the process. The remaining off-gases are sent to a flare system [1].

Pyrolysis/Hydrocarbonization

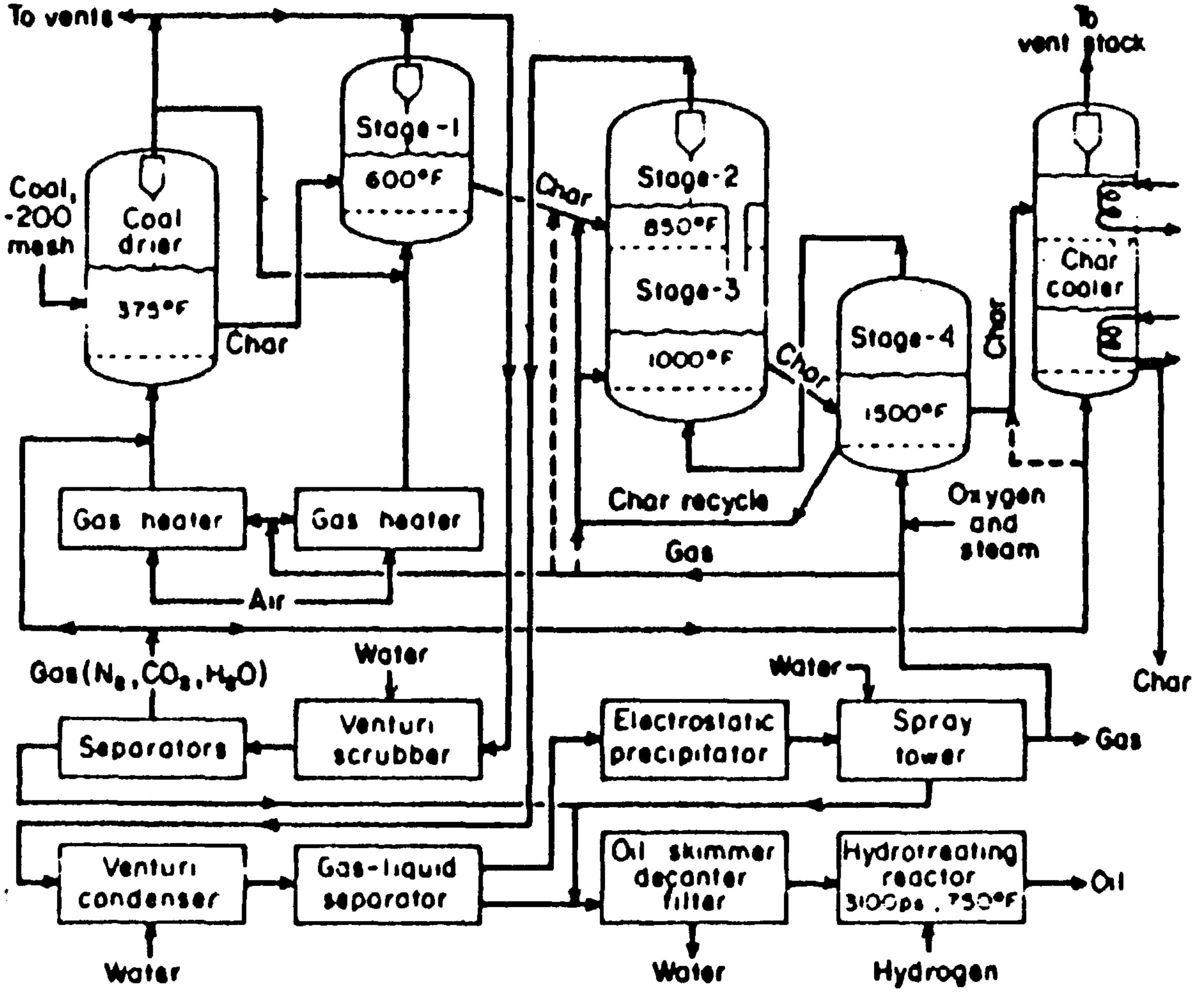
Pyrolysis is the thermal decomposition and recombination of coal with coal-derived or donor hydrogen that occurs in the absence of oxygen. If thermal decomposition occurs with added hydrogen, the process is known as hydrocarbonization. Oils, gases, and char are produced in the pyrolysis reactor. Char may be burned to produce heat needed for the endothermic pyrolysis process [19].

The COED process is an example of how a coal liquefaction plant uses a pyrolysis process (Figure IX-6). In the COED process, coal is crushed, dried, and heated to successively higher temperatures (350-1,550°F or 177-843°C) in a series of fluidized-bed reactors operated at low pressures (1-2 atm or 100-200 kPa) [31,34,155]. After the coal is partially devolatilized in one reactor stage, it is heated further in the next stage. The temperature of each bed is just below the temperature at which the coal would agglomerate and plug the bed. The dryer and the four process stages typically operate at the



Adapted from reference 1

FIGURE IX-5. SCHEMATIC OF THE H-COAL PROCESS DEVELOPMENT UNIT



Adapted from reference 3
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FIGURE IX-6. COED PROCESS SCHEMATIC

following approximate temperatures, in the order of the stages through which the coal passes: 350°F (180°C), 550°F (290°C), 850°F (450°C), 1,000°F (540°C), and 1,550°F (843°C) [34,155].

The close arrangement and descending elevation of these stages permit gravity flow of the char from one stage to the next and minimize heat losses and pressure drops. In commercial plants, heat for the process may be generated using the char from the last stage. The char is burned with a steam-oxygen mixture forming hot gases and high-pressure steam. These hot gases act as the fluidizing gases and heat sources for the previous stages [31,34,155]. In pilot plants, gas heaters are used [3].

Solids are separated from the exit gases in each stage. The solids separation is accomplished by an internal particulate separation system. The volatiles stream from the second stage passes through an external particulate separation system to remove solids that would otherwise collect in and plug subsequent processing steps. The gases containing oil vapors are passed through an absorption system; hydrogen sulfide and carbon dioxide are removed, leaving a product gas [31,34,155].

Oil and water from the pyrolysis gas/vapor stream are separated into an oil fraction heavier than water, an oil fraction lighter than water, and an aqueous fraction. The two oil fractions are dehydrated and filtered [31,34,155].

Oil from the product recovery system contains some char particles that are removed by filtration. Hot filter cake consisting of char, oil, and a filter aid is discharged from filtration to char storage. The filtered oil contains small amounts of impurities such as sulfur, nitrogen, and oxygen. In the hydrotreating area, a catalytic (nickel-molybdenum) reactor operates at 750°F (400°C) and 2,000 psi (14 MPa) [155,156] to convert the oil impurities into hydrogen sulfide, ammonia, and water; these are then separated from the product oil to improve oil quality [31,34,155].

Indirect Liquefaction

In indirect liquefaction, coal is converted into a synthesis gas by the use of a gasifier. This gas, containing carbon monoxide and hydrogen, is then passed over a catalyst to form liquid products [19]. The Fisher-Tropsch synthesis process is an example of an indirect liquefaction process. Considerable experience has been obtained using this process. The South African Coal, Oil, and Gas Corporation, Ltd (SASOL) plant in Sasolburg, South Africa, uses the Fischer-Tropsch synthesis process to produce liquid products, such as motor fuels, on a commercial scale [19,31,34].

A schematic of the Fischer-Tropsch synthesis process used at SASOL is shown in Figure IX-7. Coal is crushed, ground, and then mixed with steam and

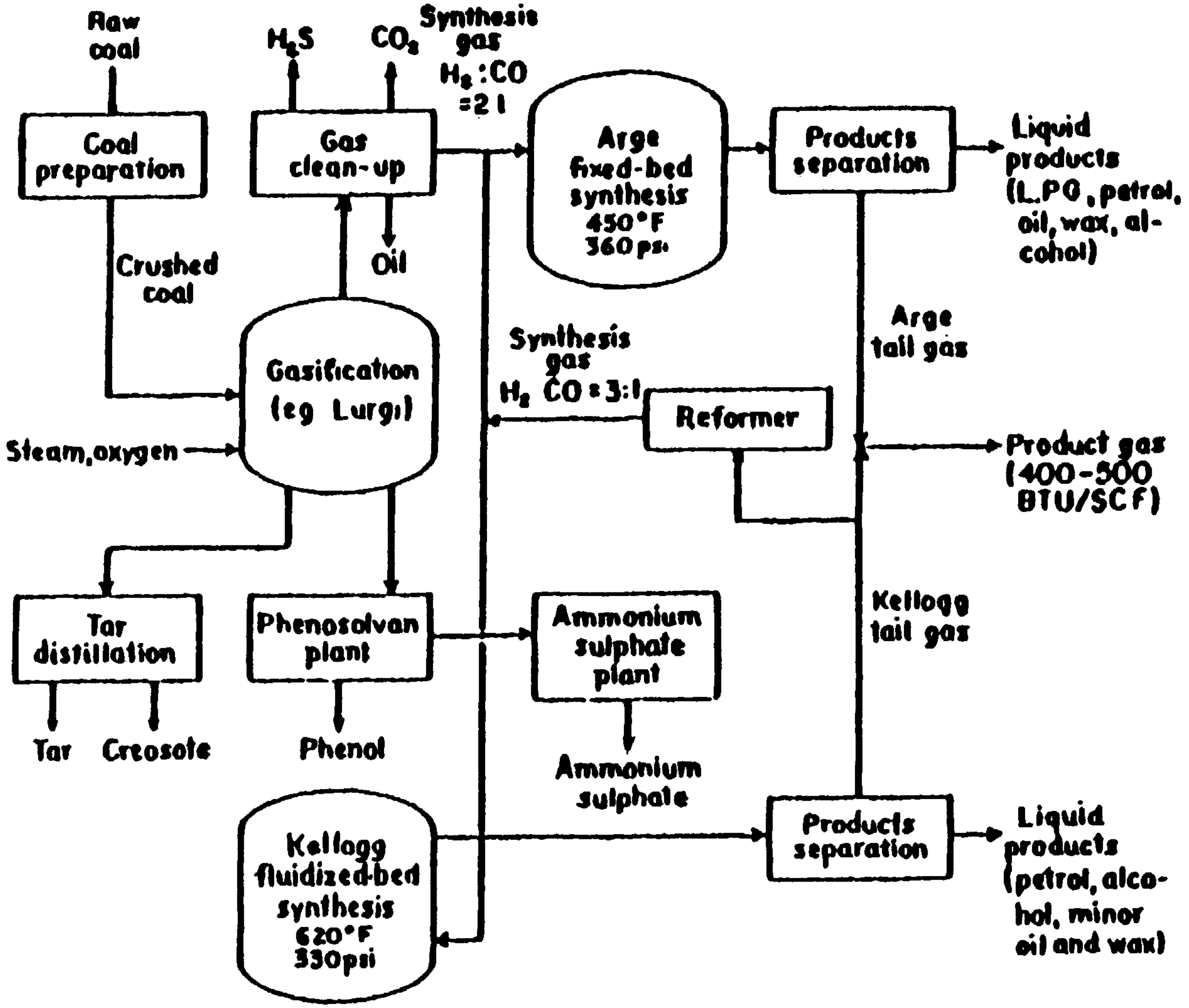

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FIGURE IX-7. FISCHER-TROPSCH SYNTHESIS SCHEMATIC oxygen in the gasifier. Synthesis gas is produced in a Lurgi gasifier by burning coal in the presence of steam and oxygen. The operating pressure and temperature of a Lurgi gasification reactor are 350-450 psi (2.4-3.1 MPa) and 1,140-1,400°F (616-760°C), respectively [3]. Synthesis gas from the reactor contains impurities such as ammonia, phenols, carbon dioxide, hydrogen sulfide, naphtha, water, cyanide, and various tar and oil components [31]. These impurities are removed by using gas-purification units, such as a quenching system, or by methanol scrubbing. The cleaned synthesis gas is then passed to an Arge fixed-bed synthesis reactor and a Kellogg fluidized-bed synthesis reactor parallel with one another, where a mixture of gases, vapors, and liquids are formed. Each of these reactors contains a catalyst needed for the synthesis step. The catalysts are iron/cobalt and iron, respectively [3]. The liquids produced are sent to refinery operations for separation into products such as fuel gas, propane, butane, gasoline, light furnace oil, waxy oil, methanol, ethanol, propanol, acetone, naphtha, diesel oil, creosote, ammonium sulfate, butanol, pentanol, benzol, and toluol [31].

X. APPENDIX II

SUMMARY OF COAL LIQUEFACTION PROCESSES UNDER DEVELOPMENT IN THE UNITED STATES

Category	Process	Developer	Coal	Reactor Type	Reaction Temp[a] °F (°C)	Reaction Pressure[a] atm abs (MPa)	Status of Development[b]
Pyrolysis and hydrocarbonization processes	Char-oil-energy development (COED)	FMC Corp	Illinois No. 6	Multiple fluidized beds	550-1,500 (290-820)	1.4-1.7 (.14-.17)	Operated 36 ton/d (33 Mg/d) pilot plant
	Occidental coal pyrolysis	Occidental	Western Kentucky	Entrained flow	1,100 (579)	1 (.1)	Results based upon 1-in (2.54-cm) diameter reactor; process to be tested in an available 3.6 ton/d (3.3 Mg/d) pilot plant
	Toscoal	The Oil Shale Corporation (Tosco)	Subbituminous and bituminous	Kiln-type retort vessel	797-1,000 (425-540)	1 (.1)	25 ton/d (23 Mg/d) coal test; operated 1,000 ton/d (900 Mg/d) plant for oil shale
	Clean coke	US Steel Corp	Illinois No. 6	Fluidized bed	1,200-1,400 (650-750)	6.5-11 (.66-1.1)	A 0.25-0.5 ton/d (0.230-0.450 Mg/d) process development unit under development; 100 ton/d (90 Mg/d) pilot plant under design
	Union Carbide Corp	Union Carbide Corp	Lake de Smet	"	1,050 (566)	69 (7)	Successfully operated 18 ton/d (16 Mg/d) pilot plant on noncaking coals
	Flash hydropyrolysis process (FHP)[c]	Brookhaven National Laboratory	Lignite	Entrained tubular flow	1,382-1,472 (750-800)	136-170 (13.79-17.24)	2 lb/hr (908 g/hr) experimental unit operated

APPENDIX II (CONTINUED)

Category	Process	Developer	Coal	Reactor Type	Reaction Temp[a] °F (°C)	Reaction Pressure[a] atm abs (MPa)	Status of Development[b]
Solvent extraction and noncatalytic hydrogenation processes	Consol synthetic fuel (CSF)	Conoco Coal Development Co	Lignite and sub-bituminous	Stirred-tank extractor; ebullated-bed catalytic hydrotreater	750 (400)	10-30 extractor; (1-3); 205 hydro-treater (21)	20 ton/d (18 Mg/d) plant operated at Cresap, WV, until 1970; revamped plant in operation
Solvent extraction and noncatalytic hydrogenation processes	Solvent-refined coal (SRC)	Pittsburg and Midway Coal Mining Co	Subbituminous and bituminous	Vertical tubular plug flow	840 (450)	69-103 (7-10)	6 ton/d (5 Mg/d) plant operating at Wilsonville, AL; 50 ton/d (45 Mg/d) plant at Fort Lewis, WA
	Solvent-refined lignite (SRL)	Univ of North Dakota	Lignite	Tubular plug flow	700-900 (370-480)	69-205 (7-21)	0.5 ton/d (0.45 Mg/d) pilot plant in startup stage
	Costeam	US BOM	Lignite and sub-bituminous	Stirred tank	707-840 (375-450)	137-275 (13.9-27.9)	Bench-scale continuous flow unit
	Exxon donor-solvent (EDS)	Exxon Research and Engineering Co	Subbituminous and bituminous	Tubular plug flow	797-900 (425-480)	100-140 (10-14)	Operated 1 ton/d (0.910 Mg/d) automated pilot plant; 250 ton/d (230 Mg/d) plant designed
Catalytic hydrogenation processes	H-Coal[a]	Hydrocarbon Research	Lignite, subbituminous, and bituminous	Ebullated bed	840 (450)	150-205 (15.2-20.8)	Successfully tested in 3 ton/d (3 Mg/d) plant, Kentucky site construction of 600 ton/d (500 Mg/d) demonstration plant

APPENDIX II (CONTINUED)

Category	Process	Developer	Coal	Reactor Type	Reaction Temp[a] °F (°C)	Reaction Pressure[a] atm abs (MPa)	Status of Development[b]
	Synthoil[d]	ERDA--Pittsburgh Energy Research Center	"	Fixed bed	840 (450)	135-275 (13.7-27.9)	1/4 ton/d (0.23 Mg/d) pilot plant with 1.0 bbl/d (.2 m^3/d) oil output in operation, 8 ton/d (7 Mg/d) pilot plant is in design and engineering stages
	Catalytic coal liquefaction (CCL)	Gulf Oil Corp	Lignite and subbituminous and bituminous	Fixed bed	>750 (>400)	135+ (13.7)	1 ton/d (0.91 Mg/d) pilot unit started up January 1975
	Clean fuel from coal (CFFC)	CE Lummus	Lignite and subbituminous	Expanded bed	750-810 (400-430)	68+ (6.9)	Small pilot plant scale tests, Lummus holds patents on solvent separation technique
Catalytic hydrogenation processes	Liquid-phase zinc chloride	Continental Oil Company	Bituminous and subbituminous	--	680-752 (360-400)	100-240 (10.1-24.3)	Small bench-scale unit; a 1.2 ton/d (1.1 Mg/d) unit to be built; funding by Conoco, Shell Development Corporation, and ERDA

NOTE: It is difficult to compare results of the processes because of the various conditions and different coals used.

[a] Exact operating conditions will depend on the coal processed and the products desired.

[b] Status as of December 1977

[c] Taken from reference 152 [1977], status as of June 1979

[d] Synthoil yields include gas and liquids obtained from pyrolysis of solids residue for Western Kentucky coal.

Adapted from reference 2

XI. APPENDIX III

SUMMARY OF SYSTEMS APPLICABILITY TO VARIOUS COAL LIQUEFACTION TECHNOLOGIES

Specific Process	System/Unit Operation/Unit Process									
	Coal Preparation	Hydrogenation	Pyrolysis/ Hydrocarbonization	Hydrotreating	Catalytic Synthesis	Phase Separation	Fractionation	Gas Cleaning	Hydrogen/ Synthesis Gas Generation	Auxiliaries
Synthoil	+	+	-	-	+	+	-	+	+	+
H-coal	+	+	-	-	+	+	+	+	+	+
Bergius	+	+	-	-	+	+	+	+	+	+
SRC-I	+	+	-	-	-	+	+	+	+	+
SRC-II	+	+	-	-	-	+	+	+	+	+
Costeam	+	+	-	-	-	+	-	+	+	+
COED	+	-	+	+	-	+	+	+	+	+
Supercritical Gas Extraction (SGE)	+	-	-	+	-	+	+	+	-	+
Coalcon	+	-	+	-	-	+	+	+	+	+
Clean coke	+	+	+	+	-	+	+	+	+	+
Toscoal	+	-	+	-	-	+	-	+	-	+
Occidental Research Corporation (ORC)	+	-	+	+	-	+	-	+	-	+
Fischer-Tropsch synthesis	+	+	-	-	+	+	+	+	+	+

APPENDIX III (CONTINUED)

Specific Process	System/Unit Operation/Unit Process									
	Coal Preparation	Hydrogenation	Pyrolysis/ Hydrocarbonization	Hydrotreating	Catalytic Synthesis	Phase Separation	Fractionation	Gas Cleaning	Hydrogen/ Synthesis Gas Generation	Auxiliaries
Donor solvent	+	+	-	+	-	+	+	+	+	+
Methanol synthesis	+	+	-	-	+	+	+	+	+	+

+ Module or process is in the system.
- Module or process is not in the system.

Adapted from reference 12

XII. APPENDIX IV

DESCRIPTION OF EQUIPMENT USED IN COAL LIQUEFACTION

The items below are listed in the order they normally appear in a coal liquefaction plant when following the process from receiving coal to storing the end product.

Item	Description
Storage bins	Usually cylindric steel storage bins with a storage capacity of >1,000 tons (907 kg); closed facilities reduce weathering effects and combustion hazards, and require less land area for storage.
Surge hopper	Stores coal intermittently in the process. Coal is sent to process equipment, ie, preheater or gasifier, through a surge hopper.
Lift pipe	Part of coal preparation/pretreatment sector of the processing plant; conveys pulverized coal from lower to higher elevations. Usually, the conveying medium is inert gas.
Pulverizer	Term used for size-reduction equipment. Depending on the desired size of prepared coal, a ball mill or roller mill can be used to pulverize coal.
Screw conveyor, bucket conveyor	Convey coal from one piece of equipment to another. Bucket conveyors usually carry coal to elevated equipment.
Screens	Used in coal preparation section of the plant to size coal; may be stationary or moving. Oversized coal is returned to a pulverizer for further size reduction. Desired size of coal is sent to the processing unit.

Item	Description
Slurry mix tank	Part of coal prepartion section of the plant. Generally, coal and oil are mixed in this piece of equipment to form a slurry.
Slurry pumps	Part of coal slurry feed system; generally reciprocating or centrifugal pumps.
Fired preheater	Preheats the coal-oil slurry before it goes to a dissolver or coal liquefaction reactor.
Pyrolysis reactor	Heats coal in the absence of oxygen.
Dissolver	Dissolves or liquefies coal in a solvent in processes such as solvent-refined coal and Exxon donor-solvent (solvent-extraction processes).
Catalytic hydrogenation reactor	Used for direct liquefaction of coal; may be fixed bed (Synthoil) or ebullated bed (H-coal).
Hydrocarbonization reactor	Heats coal in the presence of hydrogen.
Filtration unit	Used for solid-liquid separation. Generally separates ash and unreacted or undissolved coal from dissolver or liquefaction reactor.
Gas Purification System Equipment:	
Cyclone separator	Separates char ash and other solid particulates from gaseous stream.
Quench towers and venturi scrubbers	Used to remove particulates and droplets (oil, tar, liquor, etc) from the product gas.
Quench water separator	Usually separates oil, tar, and char particulates from gases.
Absorber	Absorbs acid gas (H_2S, CO_2, etc) from product gas.

Item	Description
Desorber or stripper	Desorbs gases from absorbent and cleans gas.
Solvent (coal) recovery unit	Recovers solvent from coal solution or coal liquids; recycles it back to prepare slurry from process-derived solvent.
Hydroclone	Device used extensively for classification and/or removal of fluid from slurries; generally used to separate ash and unreacted coal from coal solutions or coal liquids.
Centrifuge	Developed for solid-liquid separation, particularly when solids are very small (<200 mesh).
Fractionator or distillation column	Distills liquid product to separate the various components.
Hydrotreater	Pressure vessel in which the quality of liquid hydrocarbon streams is improved by subjecting them to mild or severe conditions of hydrogen pressure in the presence of a catalyst.
Atmospheric tanks	Any tank that is designed to be used within a few psi of atmospheric pressure. Syncrudes produced by coal liquefaction processes may be stored in American Petroleum Institute (API) standard 12A tanks.

XIII. APPENDIX V

EXPOSURE LIMITS OF SOME CONTAMINANTS THAT MAY BE PRESENT IN COAL LIQUEFACTION PROCESSES

Compound	OSHA Standard^{a,b}		NIOSH-Recommended Exposure Limit^{b}		Area Affected and/or Health Effects	Reference^{d}
	ppm^{c}	mg/m^{3,c}	ppm^{c}	mg/m^{3,c}		
Acetic acid	10	25				
Acetone	1,000	2,400				
Alkanes			(varies)	350	Skin and nervous system	157
Ammonia	50	35	(50)	(34.8)	Airway irritation	60
Aniline--skin	5	19				
Antimony		0.5				
Arsenic		0.5		(0.002)	Dermatitis; lung and lymphatic cancer	158
Arsine		0.2				
Barium		0.5				
Benzene	10 (50)		(1)	(3.2)	Blood changes, including leukemia	132
Beryllium		0.002		0.002 (0.025)	Lung cancer	159
Boron oxide		15				
1,3-Butadiene	1,000	2,200				
Cadmium dust		0.2 (0.6)		0.04 (0.2)	Lungs and kidneys	160
Cadmium fume		0.1 (0.3)				

APPENDIX V (CONTINUED)

Compound	OSHA Standard[a,b]		NIOSH-Recommended Exposure Limit[b]		Area Affected and/or Health Effects	Reference[d]
	ppm[c]	mg/m^3[c]	ppm[c]	mg/m^3[c]		
Carbon dioxide	5,000	9,000	10,000 (30,000)	18,000 (54,000)	Respiratory system	161
Carbon disulfide	20 (100)		1 (10)	3 (30)	Heart; nervous and reproductive systems	128
Carbon monoxide	50	55	35 (200)	40 (229)	Heart	58
Chromium					Lung cancer; skin ulcers; lung irritation	
Soluble salts		0.5		0.001		162
Insoluble salts		1		0.025 (0.05)		162
Coal tar pitch volatiles		0.15		0.1	Lung and skin cancer	17
Cobalt		0.1				
Copper fumes		0.1				
Dusts and mists		1				
Creosote				0.1	Lung and skin cancer	17
Cresol--skin	5	22	2.3	10	Skin, liver, kidneys, and pancreas	127
Cyanides (HCN)--skin		5	(4.7)	(5)	Thyroid, blood, and respiratory system	66
Ethyl mercaptan						
Free silica				0.050	Chronic lung disease (silicosis)	129

APPENDIX V (CONTINUED)

Compound	OSHA Standard^{a,b}		NIOSH-Recommended Exposure Limit^{b}		Area Affected and/or Health Effects	Reference^{d}
	ppm^{c}	mg/m^{3} ^{c}	ppm^{c}	mg/m^{3} ^{c}		
Hydrogen chloride	(5)	(7)				
Hydrogen fluoride	3		6 (12)	2.5 (50)	Skin, eyes, airway irritation; bone	163
Hydrogen sulfide	ceiling limit only		(10)	(15)	Eye irritation; severe acute effects on nervous and respiratory systems	65
Hydroquinone		2		(2)	Eyes and skin	164
Iron oxide (fume)		10				
Lead fumes and dusts		0.05		0.10	Kidneys, blood, and nervous system	133
Manganese		(5)				
Mercury					CNS and behavior	165
Alkyl						
Nonalkyl				0.05		
Methyl ethyl ketone	200	590				
Methyl mercaptan						
Naphtha (coal tar)	100	400				
Naphthalene	10	50				
β-Naphthylamine	(See 29 CFR 1910.1009)					
Nickel		1		0.015	Skin; lung and nasal cancer	166

APPENDIX V (CONTINUED)

Compound	OSHA Standard[a,b]		NIOSH-Recommended Exposure Limit[b]		Area Affected and/or Health Effects	Reference[d]
	ppm[c]	mg/m³[c]	ppm[c]	mg/m³[c]		
Nickel carbonyl	0.001	0.007	0.001	0.007	Lung and nasal cancer	167
Nitric oxide	25	30	25	30	Blood	168
Nitrogen dioxide	5	9	(1)	(1.8)	Airway irritation	168
Ozone	0.1	0.2				
Phenol--skin	5	19	5.2 (15.6)	20 (60)	Skin, eyes, CNS, liver, and kidneys	61
Propane	1,000	1,800				
Pyridine	5	15				
Refined petroleum solvent	500	2,950		350	Eye, skin, nose, and throat irritation; nervous system	130
Resorcinol						
Selenium		0.2				
Sulfur dioxide	5	13	2	5	Respiratory system	131
Thallium		0.1				
Tin--						
Organic compounds		0.1				
Inorganic compounds (except oxides)		2				
Toluene--skin	200 (500)		100 (200)	375 (750)	CNS depressant	169

APPENDIX V (CONTINUED)

Compound	OSHA Standard[a,b]		NIOSH-Recommended Exposure Limit[b]		Area Affected and/or Health Effects	Reference[d]
	ppm[c]	mg/m^3[c]	ppm[c]	mg/m^3[c]		
Vanadium					Eyes, skin, and lungs	170
V_2O_5 dust		(0.5)		0.05		
V_2O_5 fume		(0.1)		0.05		
Xylene	100	435	100 (200)	434 (868)	CNS depressant; airway irritation	171
Zinc oxide fume		5		5 (15)	Metal fume fever	172

NOTE: Parentheses indicate a ceiling value.

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[a] See 29 CFR 1910.1000

[b] For some of these substances, ceiling limits have been established that vary with duration of exposure, and these can be found in the original reference.

[c] 8-hour time-weighted average

[d] Only for NIOSH exposure limits and health effects data

XIV. APPENDIX VI

CHEMICAL SUBSTANCES POTENTIALLY ASSOCIATED WITH COAL LIQUEFACTION PROCESSES

Category	Where Found	Ref
Aliphatic Hydrocarbons		
n-Butane, isopentane, n-pentane, n-paraffins, i-paraffins, monocycloparaffins, dicycloparaffins, tricycloparaffins, unsaturated mono-, di-, and tricycloparaffins, olefins, diolefins	Liquid products from H-coal conversion processes	12
Various hydrocarbons	Vents and exhausts of coal pretreatment equipment; some wastewater streams of coal liquefaction operation	31
Ethylene, propylene	Major products of the clean coke process	11
Cyclohexane, methylcyclohexane, dimethylcyclohexane, dihydroxylene, hexahydromesitylene	Major constituents of neutral oil from liquid-phase hydrogenation of coal	173
Alcohols		
Methyl alcohol, ethyl alcohol	Identified from the carbonization of coal	173
Epoxides		
Diphenylene oxide	Gasworks tar	174
2-Hydroxybiphenylene oxide	Identified from the carbonization of coal	173
Aldehydes		
Acetaldehyde, paraldehyde	"	173

APPENDIX VI (CONTINUED)

Category	Where Found	Ref
Ketones		
Acetone, methyl ethyl ketone	Identified from the carbonization of coal	173
Methyl heptyl ketone	"	
Acetophenone	"	
Methyl tolyl ketone	"	
Carboxylic Acids and Derivatives		
Ethyl propionate, formic acid, acetic acid, propionic acid	"	173
n-Valeric acid, oxalic acid	"	
Nitriles		
Cyanogen	"	173
Acetonitrile	"	
Benzonitrile	"	
1- and 2-Naphthonitrile	"	
Amines		
Aminobenzenes, naphthylamines, aminobiphenyls	Coal tars	12
Toluidines	Low-temperature tar from coal carbonization	174
Aniline	Product of the clean coke process; product of a coal liquefaction plant	11
Diethylamine, triethylamine	Identified from the carbonization of coal	173
Aniline	"	
o- and p-Toluidine	"	
2,3-Xylidine	"	

APPENDIX VI (CONTINUED)

Category	Where Found	Ref
Mercaptans, Sulfides, and Disulfides		
Methylmercaptan, ethylmercaptan, dimethylsulfide, diethylsulfide	Identified from the carbonization of coal	173
Tolylmercaptan	"	
Diphenylene sulfide	"	
Benzene and Substituted Benzene Hydrocarbons		
C_6-C_{12} alkyl benzenes	Liquid products from H-coal conversion processes	12
Biphenyls	"	175
Biphenyl, triphenylbenzene	Coal liquefaction products	10
Benzene	Significant commercial product of a coal liquefaction plant	11
Benzene, toluene, xylene, polyalkylbenzenes	Significant constituents of neutral oil liquid-phase hydrogenation of coal	173
Ethylbenzene, styrene, cumene, ethylbenzene, propylbenzene, o-, m-, and p-ethyltoluene, mesitylene, hemimellitene, cymene, 3,4-dimethylethylbenzene	"	
Phenols		
Phenols (components only defined by 108, 122, 136, and 150 mol wt)	Liquid products from H-coal conversion process	12
Phenols (undefined components)	Liquid products from Synthoil conversion processes	175
Phenols (undefined components)	Some wastewater streams of coal liquefaction operation	31
Phenol, cresols, xylenols, pyrocatechin	Low temperature (below 450-500°C) tar from coal carbonization	174

APPENDIX VI (CONTINUED)

Category	Where Found	Ref
Phenols (continued)		
α- and β-Naphthol	Gasworks tar	174
Phenol, o-cresol, m- and p-cresols, xylenols	Products of the clean-coke process	11
Phenol, cresols, mixed xylenols	Products of a coal liquefaction plant	11
m-, p-, and o-Ethylphenols, 2,3-, 3,5-, 2,4-, 2,5-, and 2,6-xylenols	Identified from the carbonization of coal	173
Isohomocatechol	"	173
Paraphenylphenol	"	173
Tertramethylbiphenol	"	173
Resorcinol	"	173
Phenol, cresols, xylenols, undefined phenols	Heavy oil from Synthoil process	12
Fused Aromatic Hydrocarbons and Derivatives		
Naphthalenes, phenanthrenes, chrysenes, 1,2-benzanthracenes, 3,4-benzophenanthrenes, pyrenes, 5-ring compounds	Liquid products from H-coal conversion products	12
Anthracenes, phenanthrenes, phenylnaphthalenes, 4- and 5-ring aromatics (both peri- and cata-condensed), peri-condensed 6-ring compounds	Liquid products from Synthoil conversion products	175
Naphthalene, 2-methylnaphthalene, 7-methylnaphthalene, azulene, 2,6-dimethylnaphthalene, 1,3-dimethylnaphthalene, 1,5- and/or 2,3-dimethylnaphthalene, acenaphthalene, acenaphthene, phenanthrene and/or 1,3,6-trimethylnaphthalene, 2-methylphenanthrene, 1-methylphenanthrene, 2-phenylnaphthalene, 9-methylanthracene, 1,2-dihydropyrene, fluoranthene, pyrene, 1,2-benzofluorene, 4-methylpyrene, 1-methylpyrene, 1,2-benzanthracene, chrysene and/or triphenylene	Coal liquefaction products	10

APPENDIX VI (CONTINUED)

Category	Where Found	Ref
Fused Aromatic Hydrocarbons and Derivatives (continued)		
Chrysene, 2-methylchrysene, 3-methylchrysene, 5-methylchrysene, 6-methylchrysene	Coal liquefaction products	176
1,2- and 4,5-Benzopyrene, crackene, benzerythrene, perylene, picene, triphenylene	Identified from the carbonization of coal	173
Fused Nonalternant Polycyclic Hydrocarbons		
Indans, indenes, acenaphthylenes, (C_nH_{2n-14} and C_nH_{2n-16})	Liquid products from H-coal conversion processes	12
Indans, indenes, acenaphthylenes	Liquid products from Synthoil conversion processes	175
Octahydroanthracene, 9,10-dihydrophenanthrene, fluorene, 9-methylfluorene	Coal liquefaction products	10
Naphthalene	Significant product of a coal liquefaction plant	11
Heterocyclic Nitrogen Compounds		
Carbazole, phenyl p-naphthylcarbazole, acridine, a-dimethylquinoline	Gasworks tar	174
Pyridine, α-picoline	Products of the clean-coke process	11
Pyridine, pyrrole	Products of a coal liquefaction plant	11
Quinoline	Identified from the carbonization of coal	173
Acridine, carbazole, 2- and 3-methylcarbazole	"	
Heterocyclic Oxygen Compounds		
β-Naphthofuran	Gasworks tar	174
3-, 4-, and 5-Methylcoumarone	Identified from the carbonization of coal	173
1,9-Benzoxanthene	"	

APPENDIX VI (CONTINUED)

Category	Where Found	Ref
Heterocyclic Sulfur Compounds		
Benzothiophene, methylbenzothiophene, dimethylbenzothiophene, methylthiophene	Light oil product of coal hydrogenation	175
Benzylthiophene, tetrahydrobenzothiophene, dibenzothiophene, methyldibenzothiophene, benzo(d,e,f)dibenzothiophene, naphthobenzothiophene, methylnaphthobenzothiophene, dinaphthothiophene	Heavy oil product of coal hydrogenation	175
Diphenylene sulfide	Gasworks tar	174
Dimethylthiophene	Identified from the carbonization of coal	173
Thionaphthene	"	173
Dibenzothionaphthene	"	173
Organometallics		
Metal porphyrins	Coal	177
Iron, nickel, and cobalt carbonyls	Gas phase after conversion	177
Iron, nickel, chromium, vanadium, tantalum, molybdenum, and tungsten metallocenes	Potentially in coal liquids	177
Arene carbonyls	"	177
Metal chelates	Potentially in aqueous process streams	177
Inorganic Elements		
Aluminum, antimony, arsenic, barium, beryllium, boron, bromine, cadmium, calcium, cesium, chlorine, chromium, cobalt, copper, europium, fluorine, gallium, germanium, hafnium, iodine, iron, lanthanum, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, phosphorus,	Coal	12

APPENDIX VI (CONTINUED)

Category	Where Found	Ref
Inorganic Elements (continued)		
potassium, rubidium, scandium, selenium, silicon, sodium, strontium, sulfur, tantalum, thorium, tin, titanium, uranium, vanadium, yttrium, zinc, zirconium, cerium, dysprosium, gold, indium, lutetium, samarium, silver, tellurium, terbium, thallium, tungsten, ytterbium		
Inorganic Oxides		
SiO_2, Al_2O_3, Fe_2O_3, TiO_2, P_2O_5, CaO, MgO, Na_2O, K_2O, SO_3	Ash, Illinois No. 6 Coal	12
TiO_2	Spent catalyst of H-coal liquefaction plant	178
Inorganic Chemicals (General)		
Ammonia, hydrogen sulfide	Gas phase of coal hydrogenation reactions	12
Carbon monoxide, nitrogen oxides	Vents and exhausts of coal pretreatment equipment and from gas leaks during coal liquefaction	12
Sulfur dioxide, other sulfur oxides, ammonia, hydrogen sulfide	Separation operations, auxiliary processes, purification and upgrading operations	12
Ammonia, thiocyanates, sulfides, chlorides	Some wastewater streams of coal liquefaction operation	12
Boron, sulfur, molybdenum, and cobalt compounds	Spent catalyst of H-coal liquefaction plant	178
Hydrogen sulfide	Concentrated in gas stream from acid gas removal operation of H-coal liquefaction plant	178

APPENDIX VI (CONTINUED)

Category	Where Found	Ref
Inorganic Chemicals (General) (continued)		
Sulfur, ammonia	Marketable byproducts of the clean coke process	11
Hydrogen chloride, ammonium cyanate, carbon disulfide, ammonium sulfide	Identified from the carbonization of coal	173

XV. APPENDIX VII

SYSTEM SAFETY REFERENCES

Several sources concerning system safety are currently available. Useful references concerning fault-tree analysis and system safety analysis were recommended by NIOSH in Appendix IV of the coal gasification criteria document [16]. Other useful references are listed below.

(1) Johnson WG: The Management Oversight and Risk Tree-MORT--Including Systems Developed by the Idaho Operations Office and Aerojet Nuclear Company (SAN 821-2). US Government Printing Office, 1974 (GPO-052-010-00-329-1)

(2) Knox NW, Eicher RW: MORT User's Manual--For Use with the Management Oversight and Risk Tree Analytical Logic Diagram/ERDA-76-45-4/SSDC-4. Idaho Falls, Aerojet Nuclear Company, 1976 (Submitted to ERDA under Contract No. E(10-11)-1375)

(3) Nertney RJ, Bullock MG: Human Factors in Design/ERDA-76-45/SSDC-2. Idaho Falls, Aerojet Nuclear Company, 1976 (Submitted to ERDA under Contract No. E(10-11)-1375)

(4) Nertney RJ, Clark JH, Eicher RW: Occupancy-Use Readiness Manual--Safety Considerations/ERDA-76-45-1/SSDC-1. Idaho Falls, Aerojet Nuclear Company, 2nd printing, 1976 (Submitted to ERDA under Contract No. E(10-11)-1375)

(5) Rodgers P: Introduction to System Safety Engineering. New York, John Wiley and Sons, Inc, 1971

XVI. APPENDIX VIII

APPLICABLE CODES AND STANDARDS

There are several handbooks, codes, and standards used by various industries that may apply to the design and operation of coal liquefaction plants. Since these publications are generally applicable throughout industry, a detailed presentation of codes and standards relevant to coal liquefaction is beyond the scope of this document. However, a few of the codes and standards that may be applicable are listed here. This list does not in any way imply a comprehensive compilation of codes and standards for coal liquefaction plants.

(1) American Standard Codes for Pressure Piping, ASA B31.1-1955 and B31.8-1958

(2) The American Society of Mechanical Engineers Boiler and Pressure Vessel Code, Section VIII, "Unfired Pressure Vessels," New York, 1965

(3) Chemical Plant and Petroleum Refinery Piping, American National Standards Institute (ANSI) B31.3-1976

(4) 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"

(5) Prevention of Dust Explosions in Coal Preparation Plants, ANSI/NFPA No. 653-1959 [ANSI Z12.7]

(6) Safety Guide for Respiratory Protection Against Coal Mine Dust, ANSI Z88.4-1972

(7) Liquid Petroleum Transportation Piping Systems, ANSI B31.4-1974, Addenda ANSI B31.4a-1975

(8) Method of Sampling Petroleum and Petroleum Products, ANSI/ASTM D270-65 (1975)/API 2546-1965 [ANSI Z11.33]

(9) Safety Standard for Liquid-Level Gauges and Indicators for Petroleum Products, ANSI/UL 180-January 1975 [ANSI B158.1]

(10) Flame Arresters for Use on Vents of Storage Tanks for Petroleum Oil and Gasoline, ANSI/UL525-September 1973 [ANSI Z222.1]

(11) Flammable and Combustible Liquids Code, ANSI/NFPA No. 30-1973 [ANSI Z288.1]

(12) Safety Standard for Pipe Connectors for Flammable Liquids and LP-Gas, ANSI/UL567-August 1972 [ANSI B148.1]

(13) Gaseous Hydrogen Systems at Consumer Sites, ANSI/NFPA No. 50A-1973 [ANSI Z292.2]

(14) Liquefied Hydrogen Systems, ANSI/NFPA No. 50B-1973 [ANSI Z292.3]

XVII. APPENDIX IX

ONGOING NIOSH CONTRACTS RELATED TO COAL LIQUEFACTION

ISSUING OFFICE: National Institute for Occupational
Safety and Health
Procurement and Grants Management Branch
5600 Fishers Lane, Room 8-29
Rockville, Maryland 20857

CONTRACT NUMBER: 210-78-0040

Contract Title: Industrial Hygiene Characterization of Coal Gasification Plants

Contract Period: July 18, 1978 to July 17, 1980

Contractor: Enviro Control, Inc.
One Central Plaza
11300 Rockville Pike
Rockville, Maryland 20852

Sponsor: Division of Respiratory Disease Studies

Contract Objective: Perform comprehensive research for industrial hygiene characterization of worker environments, including the development of a catalog of worker exposure through estimations from area sampling and time-motion studies, or through personal sampling in two coal gasification plants; determine the composition of process streams, product and byproduct streams, effluents, and fugitive emissions; identify potential exposure locations, such as waste removal, spent catalyst handling, and other transfer points, and determine whether carcinogens are being concentrated in any process area; conduct a thorough technical characterization of coal gasification on a unit process basis as an integral portion of the overall characterization study; and, based on the technical and industrial hygiene findings, make specific recommendations identifying areas where control technology assessment studies are necessary.

CONTRACT NUMBER: 210-78-0082

Contract Title: Industrial Hygiene Characterization of Petroleum Refineries

Contract Period: September 28, 1978 to May 12, 1979

Contractor: Enviro Control, Inc.
One Central Plaza
11300 Rockville Pike
Rockville, Maryland 20852

Sponsor: Division of Surveillance Hazard Evaluations and Field Studies

Contract Objective: Perform an in-depth industrial hygiene characterization of worker environments in nine selected petroleum refineries, at selected unit operations, and/or within selected job classifications.

CONTRACT NUMBER: 210-78-0084

Contract Title: Control Technology Assessment for the Coal Gasification and Liquefaction Processes

Contract Period: September 27, 1978 to December 26, 1980

Contractor: Enviro Control, Inc.
One Central Plaza
11300 Rockville Pike
Rockville, Maryland 20852

Sponsor: Division of Physical Sciences and Engineering

Contract Objective: Conduct a study of the control technology available to prevent occupational exposure to hazardous agents in coal conversion plants. Where possible, the study will be performed on a unit operations basis and will include consideration of existing gasification and liquefaction pilot plants, existing or planned demonstration and commercial plants, and similar industrial processes such as coke ovens or petroleum refining, where appropriate.

CONTRACT NUMBER: 210-78-0085

Contract Title: Evaluation of Respiratory Protection in Coal Preparation Plants

Contract Period: September 29, 1978 to September 28, 1979

Contractor: Enviro Control, Inc.
One Central Plaza
11300 Rockville Pike
Rockville, Maryland 20852

Sponsor: Division of Physical Science and Engineering

Contract Objective: Perform an evaluation of coal mine surface operations to determine the nature of respirable dust and chemical vapor hazards and the use and effectiveness of respirator protective equipment provided to workers against hazardous atmospheres occurring in and around coal mining surface operations such as coal preparation plants, drilling, augering, loading, transporting, and dumping.

CONTRACT NUMBER: 210-78-0101

Contract Title: Study of Coal Liquefaction Processes

Contract Period: February 23, 1971 to February 22, 1980

Contractor: Enviro Control, Inc.
One Central Plaza
11300 Rockville Pike
Rockville, Maryland 20852

Sponsor: Appalachian Laboratory for Occupational Safety and Health

Contract Objective: Conduct comprehensive, original research for industrial hygiene characterization of worker environments in four coal liquefaction plants to determine the composition of process streams, product and byproduct streams, effluents, and fugitive emissions. For purposes of this contract, a plant is defined as either a pilot plant, process demonstration unit (PDU), or a commercial plant. This effort will include the identification of potential exposure locations, such as waste removals, spent catalyst handling, and other transfer points, and a determination of whether carcinogens are being concentrated in some process areas. Based on the technical and industrial hygiene findings, specific recommendations will be made identifying areas where control technology assessment studies are necessary.

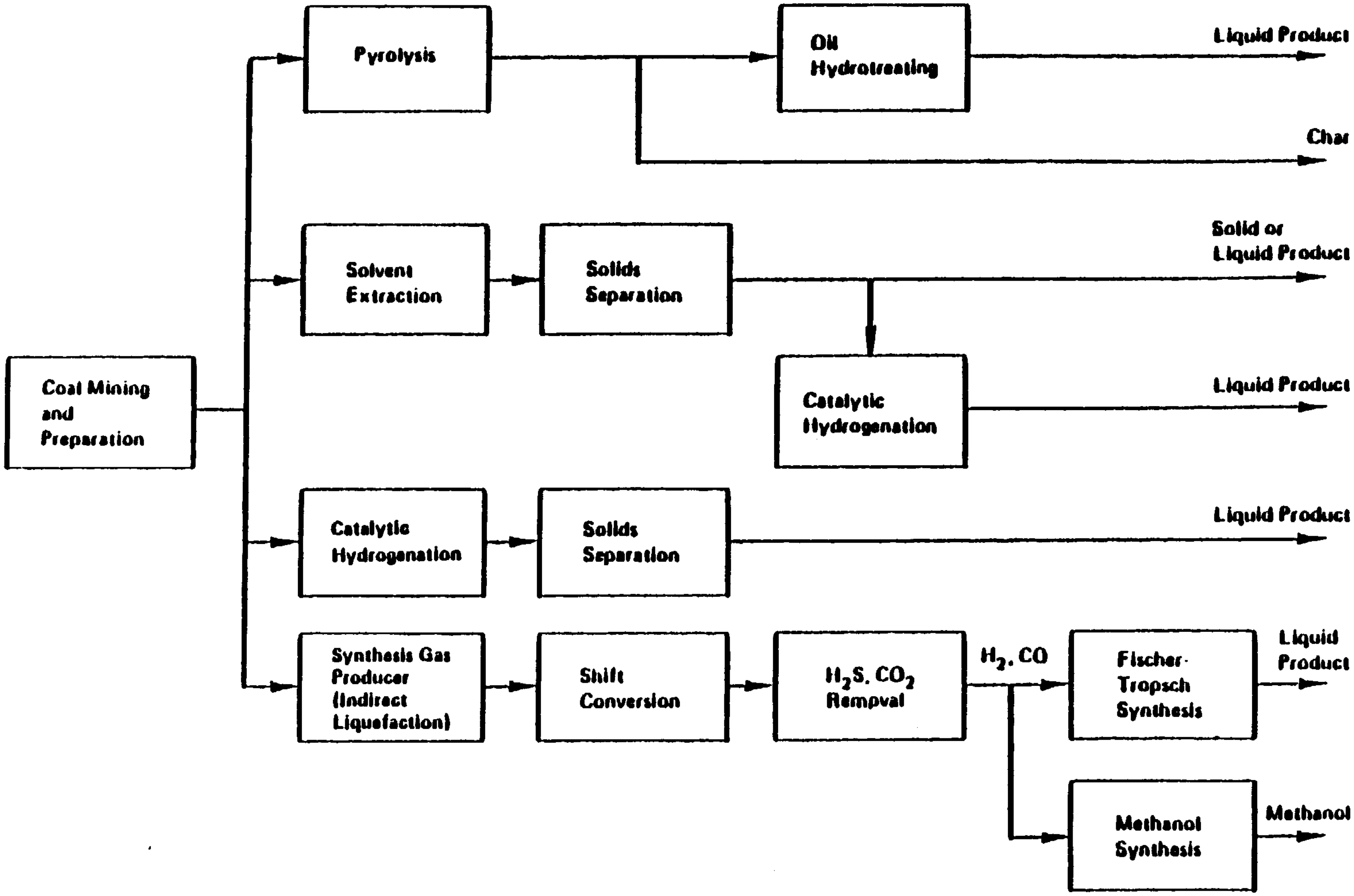
XVIII. TABLE AND FIGURES

TABLE XVIII-1

COAL LIQUEFACTION SEPARATION METHODS

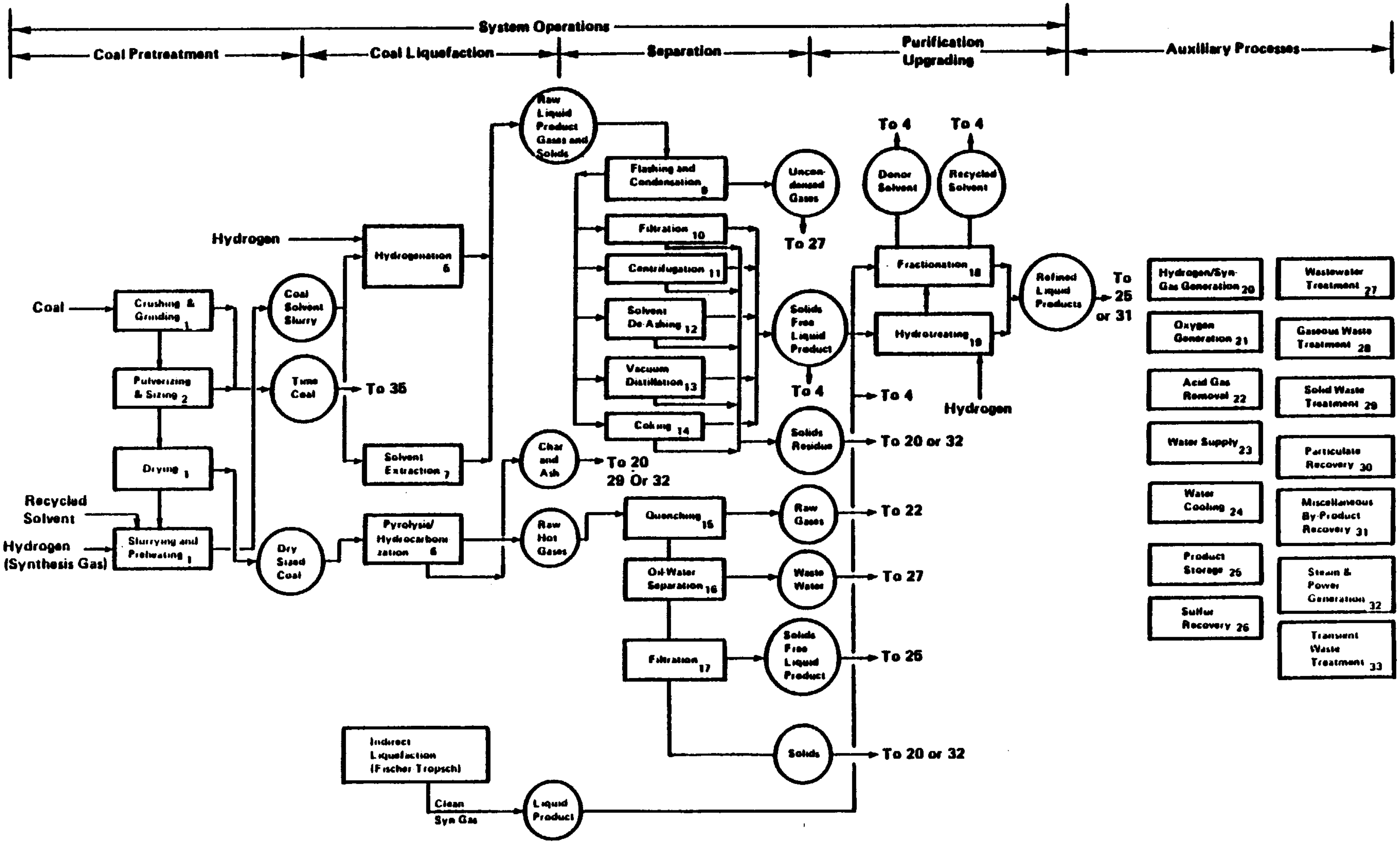
Name	Feed	Separating Agent	Products	Principle of Separation
Equilibration Separation Methods				
Flash expansion	Liquid (slurry)	Pressure reduction	Liquid + vapor	Difference in volatiles (vapor pressure)
Vacuum/flash distillation	Liquid (slurry) and/or vapor	Heat	"	Difference in volatiles
Stripping	Liquid (slurry)	Noncondensate gas	"	"
Solvent de-ashing	Liquid + solid	Solvent	"	Precipitation by increasing particle size (by agglomeration)
Condensation	Liquid and/or vapor	Cooling	"	Difference in volatiles
Mechanical Separation Methods				
Filtration	Liquid + solid	Pressure reduction (energy), filter medium	Liquid + solid	Size of solid greater than pore size of filter medium
Centrifuge (filtration type)	"	Centrifugal force	"	Size of solid greater than pore size of filter medium Density difference
Cyclone	Gas + solid or liquid	Flow inertia	Gas + solid or liquid	Density difference

Adapted from reference 31



Adapted from reference 2

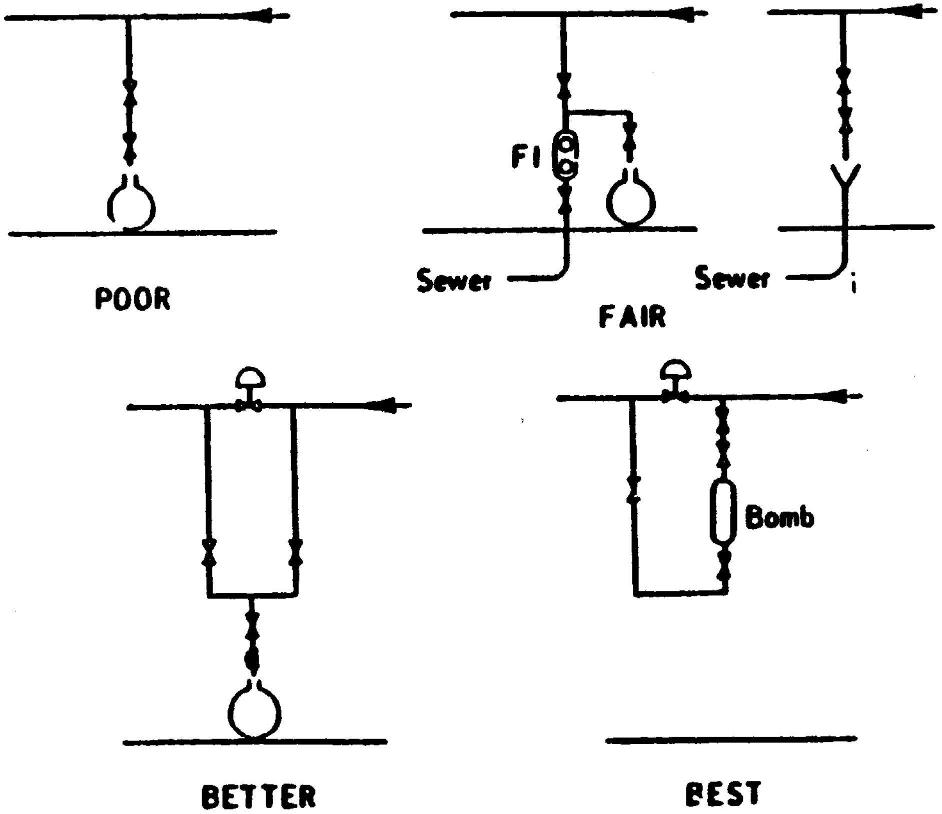
FIGURE XVIII-1. COAL LIQUEFACTION ROUTES (ONLY MAJOR PRODUCTS ARE SHOWN)



NOTE: The numbers indicate where the process stream goes with in the plant.

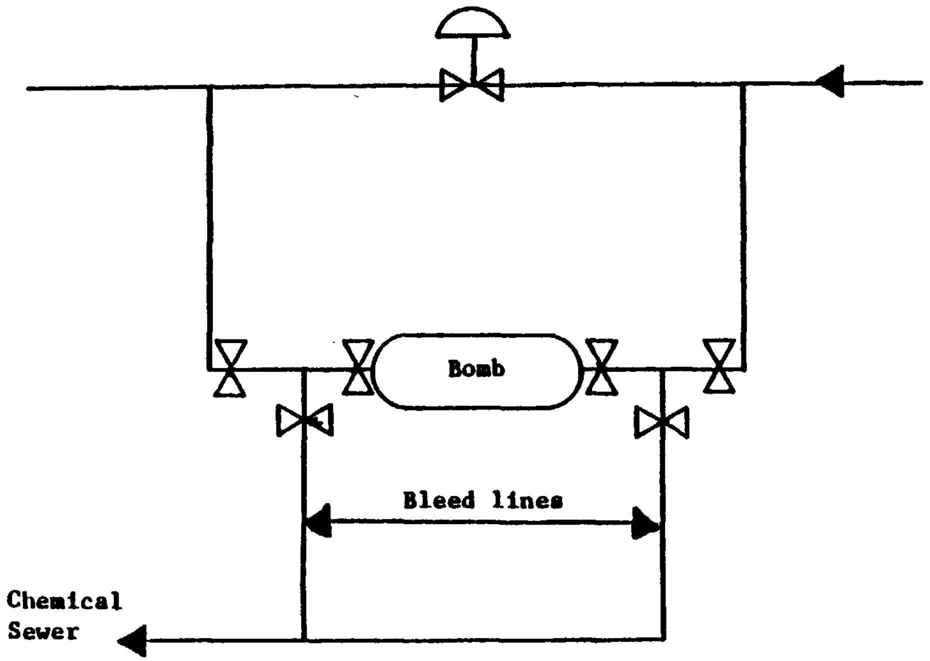
Adapted from reference 31

FIGURE XVIII-2. SCHEMATIC OF GENERAL SYSTEMS USED FOR COAL LIQUEFACTION PROCESSES



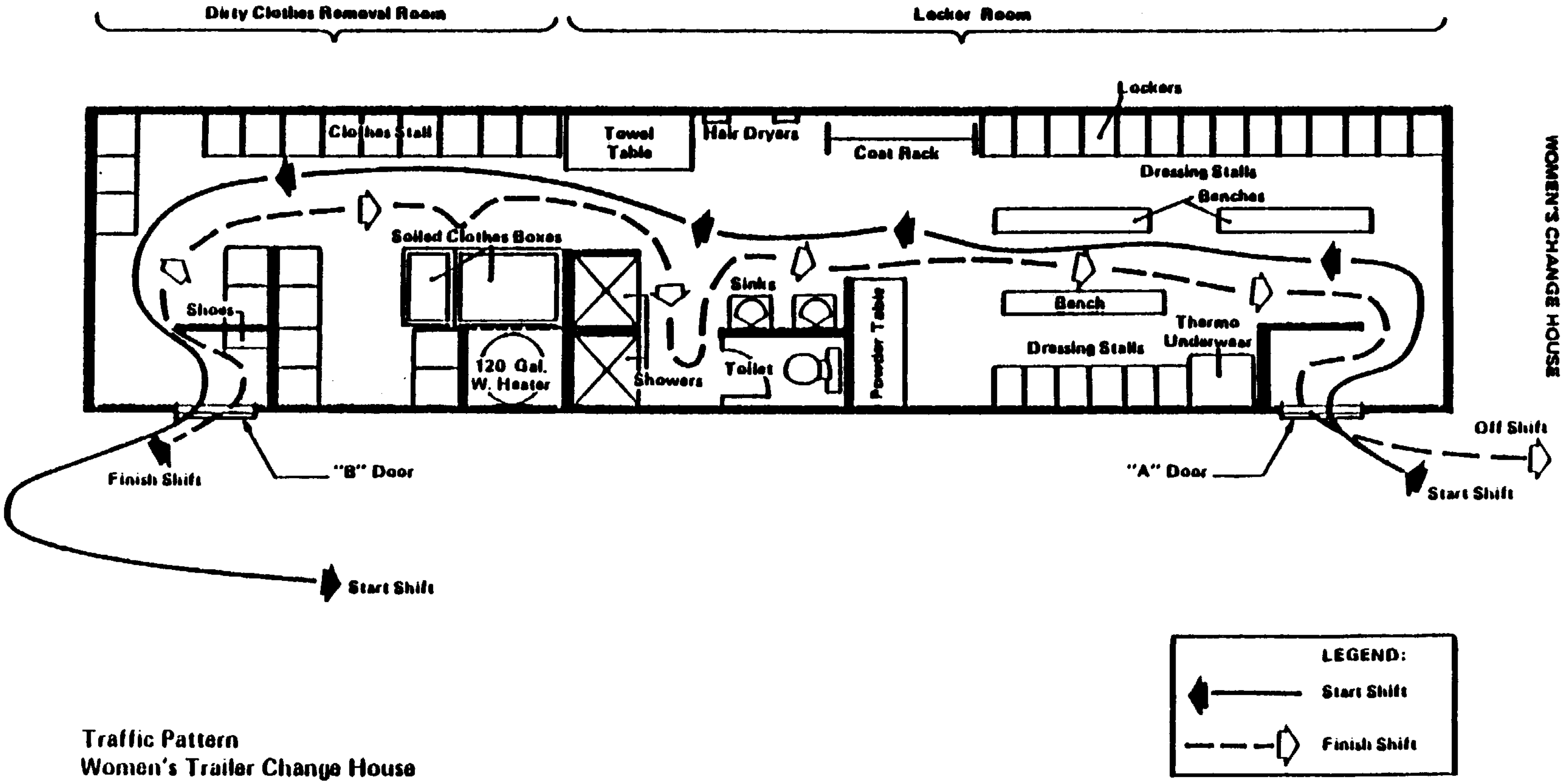
Adapted from reference 107

FIGURE XVIII-3. SAMPLING SYSTEMS



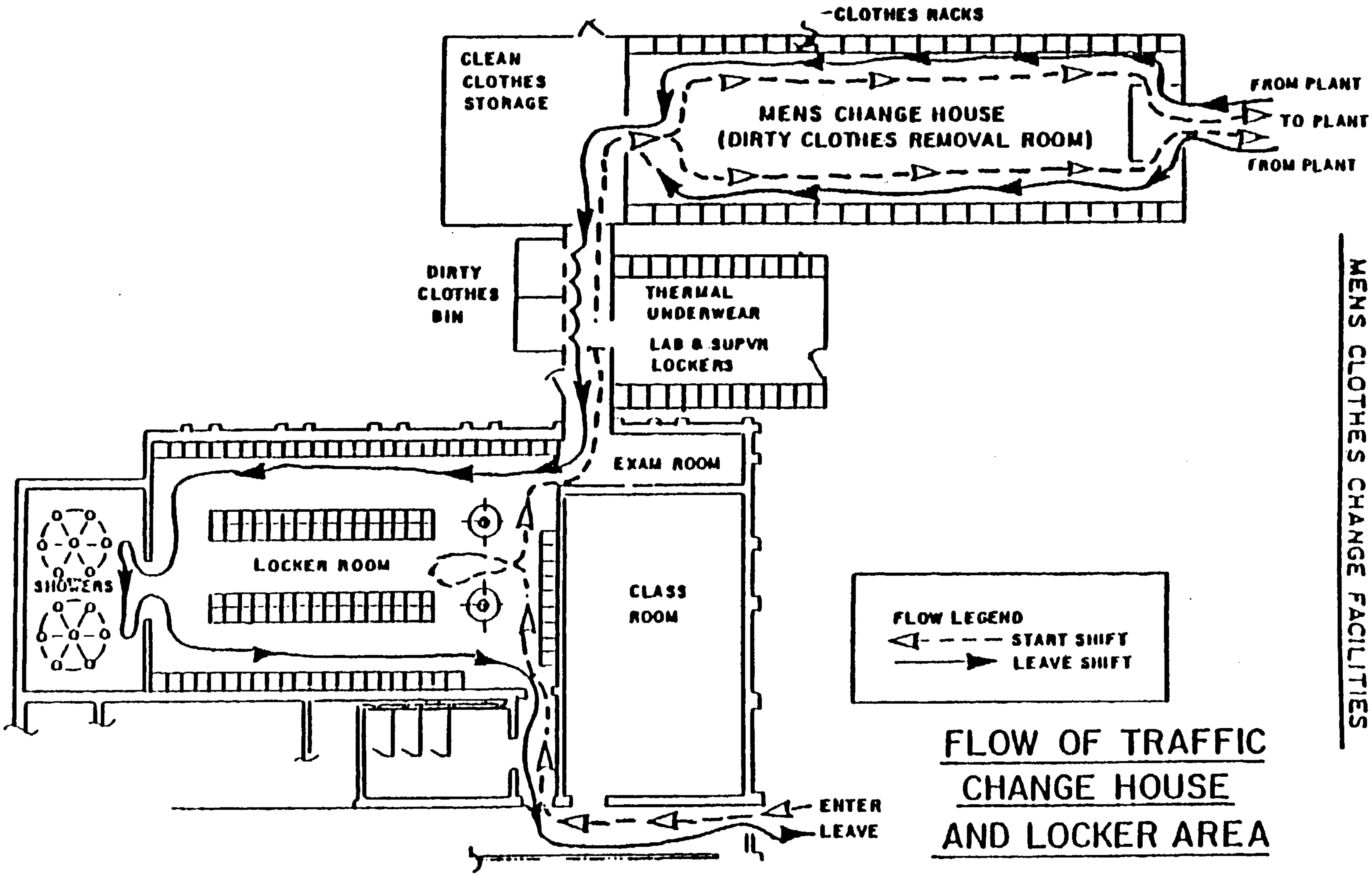
Adapted from reference 1

FIGURE XVIII-4. IMPROVED SAMPLING SYSTEM DESIGN



Adapted from reference 116

FIGURE XVIII-5. FLOOR PLAN FOR WOMEN'S CLOTHES CHANGE FACILITIES



Adapted from reference 116

FIGURE XVIII-6. FLOOR PLAN FOR MEN'S CLOTHES CHANGE FACILITIES

XIX. GLOSSARY

ACID GAS. A gas that, when dissolved in an ionizing liquid such as water, produces hydrogen ions. Carbon dioxide, hydrogen sulfide, sulfur dioxide, and various nitrogen oxides are typical acid gases produced in coal gasification.

ANTHRACITE. A "hard" coal containing 86-98% 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 that causes unconsciousness or death due to lack of oxygen.

BENCH-SCALE UNIT. A small-scale laboratory unit for testing process concepts and operating parameters as a first step in the evaluation of a process.

BITUMINOUS COAL. A broad class of coals containing 46-86% fixed carbon and 20-40% 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, or the quantity of energy required to raise the temperature of 1 lb (.454 kg) of water 1°F (.556°C).

BTX. Benzene, toluene, xylene; aromatic hydrocarbons.

CAKING. The softening and agglomerating of coal as a result of heat.

CARBONIZATION. Destructive heating of carbonaceous substances that produces a solid porous residue, or coke, and a number of volatile products. For coal, there are two principal classes of carbonization: high-temperature coking (about 900°C) and low-temperature carbonization (about 700°C).

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 readily combustible rock containing >50-weight % and 70-volume % of carbonaceous material and inherent moisture, respectively, formed from compaction and induration of variously altered plant remains.

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.

COKING. Process whereby the coal solution changes to coke.

CRACKING. The partial decomposition of high-molecular-weight organic compounds into lower-molecular-weight compounds, generally as a result of high temperatures.

DEVOLATILIZATION. The removal of a portion of the volatile matter from medium- and high-volatile coals.

DISSOLUTION. The taking up of a substance by a liquid, forming a homogeneous solution.

DOG. Any of various, usually simple, mechanical devices for holding, gripping, or fastening.

EBULLATED BED. A condition in which gas containing a relatively small proportion of suspended solids bubbles through a higher-density fluidized phase so that the system takes on the appearance of a boiling liquid.

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.

FAULT-TREE ANALYSIS. An all-inclusive, versatile, mathematic tool for analyzing complex systems. An undesired event is established at the top of a "tree." System faults or subsequent component failures that could cause or contribute to the top event are identified on branches of the tree, working downward.

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 (vs a moving bed) and supported by contact with each other.

FLASH CARBONIZATION. A carbonization process characterized by short residence times of coal in the reactor to optimize tar yields.

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.

FLUIDIZATION (DENSE PHASE). The turbulent motion of solid particles in a fluid stream; the particles are close enough to interact and give the appearance of a boiling liquid.

FLUIDIZATION (ENTRAINED). Gas-solid contacting process in which a bed of finely divided solid particles is lifted and agitated by a rising stream of gas.

FLUIDIZED BED. Assemblage of small solid particles maintained in balanced suspension against gravity by the upward motion of a gas.

GAS LIQUOR (SOUR WATER). The aqueous acidic streams condensed from coal conversion and processing areas by scrubbing and cooling the crude gas stream.

GASIFIER. A vessel in which gasification occurs, often using fluidized-bed, fixed-bed, or entrained-bed units.

HYDROBLASTING. A method of dislodging solids using a low-volume, high-pressure (10,000 psi or 70 MPa), high-velocity stream of water.

HYDROCLONE. A cyclone extractor that removes suspended solids from a flowing liquid by means of the centrifugal forces that exist when the liquid flows through a tight conic vortex.

HYDROCRACKING. The combination of cracking and hydrogenation of organic compounds.

HYDROGENATION. Chemical process involving the addition of gaseous hydrogen to a substance in the presence of a catalyst under high temperatures and pressures.

HYDROGEN DONOR SOLVENT. Solvent, such as anthracene oil, tetralin (tetrahydronaphthalene), or decalin, that transfers hydrogen to coal constituents causing depolymerization and consequent conversion to lower-boiling liquid products, which are then dissolved by the solvent.

LIGNITE. Brownish-black coal containing 65-72% carbon on a mineral-matter-free basis, with a rank between peat and subbituminous coal.

LIQUEFACTION. Conversion of a solid to a liquid; with coal, this appears to involve the thermal fracture of carbon-carbon and carbon-oxygen bonds, forming free radicals. Adding hydrogen to these radicals yields low-molecular-weight gaseous and condensed aromatic liquids.

LOCKHOPPER. A mechanical device that permits the introduction of a solid into an environment at different pressure.

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 (vs a fixed bed) in piston-like fashion with respect to the containing walls.

PILOT PLANT. A small-scale industrial process facility operated to test a chemical or other manufacturing process under conditions that yield information about the design and operation of full-scale manufacturing equipment.

POUR POINT. The lowest temperature at which a material can be poured.

PRILLING TOWER. A tower that produces small solid agglomerates by spraying a liquid solution in the top and blowing air from the bottom.

PROCESS DEVELOPMENT UNIT. A system used to study the effects of process variables on performance, between a bench-scale unit and a pilot plant in size.

PROCESS STREAM. Any material stream within the coal conversion processing area.

PRODUCT STREAM. A stream within a coal conversion plant that contains the material the plant was built to produce.

PYROLYSIS. Thermal decomposition of organic compounds in the absence of oxygen.

QUENCHING. Cooling by immersion in oil, water bath, or water spray.

RANK. Differences in coals due to geologic processes designated as metamorphic, whereby carbonaceous materials change from peat through lignite and bituminous coal to anthracite or even to graphite; the degree of coal metamorphism.

REGENERANT. A substance used to restore a material to its original condition after it has undergone chemical modification necessary for industrial purposes.

SHIFT CONVERSION. Process for the production of gas with a desired carbon monoxide content from crude gases derived from coal gasification. Carbon monoxide-rich gas is saturated with steam and passed through a catalytic reactor where the carbon monoxide reacts with steam to produce hydrogen and carbon dioxide, the latter being subsequently removed in a scrubber by a suitable sorbent.

SLAG. Molten coal ash composed primarily of silica, alumina, and iron, calcium, and magnesium oxides.

SLUDGE. A soft mud, slush, or mire, eg, the solid product of a filtration process before drying.

SLURRY. A suspension of pulverized solid in a liquid.

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.

STACK GAS. See flue gas.

STUFFING BOX. A device that prevents leakage from an opening in an enclosed container through which a shaft is inserted.

SUBBITUMINOUS COAL. Coal of intermediate rank (between lignite and bituminous); weathering and nonagglomerating coal having calorific values in the range of 8,300-11,000 BTU (8,756,500-11,605,000 J), calculated on a moist, mineral-matter-free basis.

SWEET GAS. Gas from which acidic constituents such as hydrogen sulfide have been removed.

SYNTHETIC NATURAL GAS (SNG). Substitute for natural gas; a manufactured gaseous fuel, generally produced from naphtha or coal, that contains 95-98% methane and has an energy content of 980-1,035 BTU/ft^3 (36.5-38.6 MJ/m^3), or about the same as that of natural gas.

SYNTHESIS GAS. A mixture of hydrogen and carbon monoxide that can be reacted to yield hydrocarbons.

SYSTEM. A collection of unit operations and unit processes that together perform a certain function. For example, the coal handling and preparation system consists of the following unit operations: crusher, pulverizer, and dryer.

TAR (COAL). A dark brown or black, viscous, combustible liquor formed by the destructive distillation of coal.

TAR OIL. The more volatile portion of the tar, with a specific gravity of approximately 0.9 and a boiling range of approximately 185-300°C, depending on the coal feed and operation conditions. In addition, tar oil floats on the gas liquor.

TOXICANT. A substance that injures or kills an organism through chemical or physical action, or by alteration of the organism's environment.

TRACE ELEMENTS. A term applied to elements that are present in the earth's crust in concentrations of $\leq$0.1% (1,000 ppm). Concentrations are usually somewhat enriched in coal ash. Environmentally hazardous trace elements in coal include antimony, arsenic, beryllium, cadmium, lead, mercury, selenium, and zinc.

VENTING. Release to the atmosphere of gases or vapors under pressure.

UNIT OPERATIONS. Equipment application resulting in physical changes of the material, eg, pulverizers, crushers, and filters.

UNIT PROCESSES. Equipment application resulting in chemical changes or reactions of the material, eg, hydrotreater, gasifier, and pyrolysis reactor.

XX. ACRONYMS

ANSI	American National Standards Institute
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
BOM	Bureau of Mines
CBC	complete blood count
CCL	catalytic coal liquefaction
CFFC	clean fuel from coal
CNS	central nervous system
COED	char-oil-energy development
CSF	Consol synthetic fuel
DEA	diethanolamine
DMR	dry mineral residue
DMSO	dimethyl sulfoxide
ECG	electrocardiogram
EDS	Exxon donor-solvent
ERDA	Energy Research and Development Administration
FEV_1	forced expiratory volume in 1 second
FHP	flash hydropyrolysis process
FVC	forced vital capacity
GC	gas chromatography
GGPT	gamma glutamyl transpeptidase
Hb	hemoglobin
LC_{50}	lethal concentration for 50% survival of group
LD_{50}	lethal dose for 50% survival of group
LD	lethal dose
MFAO	mixed-fraction amine oxidase
MS	mass spectrometry
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
OCR	Office of Coal Research
ORC	Occidental Research Corporation
ORNL	Oak Ridge National Laboratory

PAH	polycyclic aromatic hydrocarbon
PDU	process demonstration unit
PEL	permissible exposure limit
PETC	Pittsburgh Energy Technology Center
QA	quality assurance
RBC	red blood cell
ROM	run-of-mine
RPE_{50}	relative plating efficiency
SASOL	South African Coal, Oil, and Gas Corporation, Ltd
SGE	supercritical gas extraction
SGOT	serum glutamic oxaloacetic transaminase
SGPT	serum glutamic pyruvic transaminase
SHE	Syrian hamster embryo
SRC	solvent-refined coal
SRL	solvent-refined lignite
TLC	thin-layer chromatography
TWA	time-weighted average
UV	ultraviolet
WBC	white blood cell

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