

XI. APPENDIX I

PROCESS DESCRIPTION: HIGH-BTU COAL GASIFICATION

Introduction

(a) Coal

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

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

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

(b) Coal Gasification

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

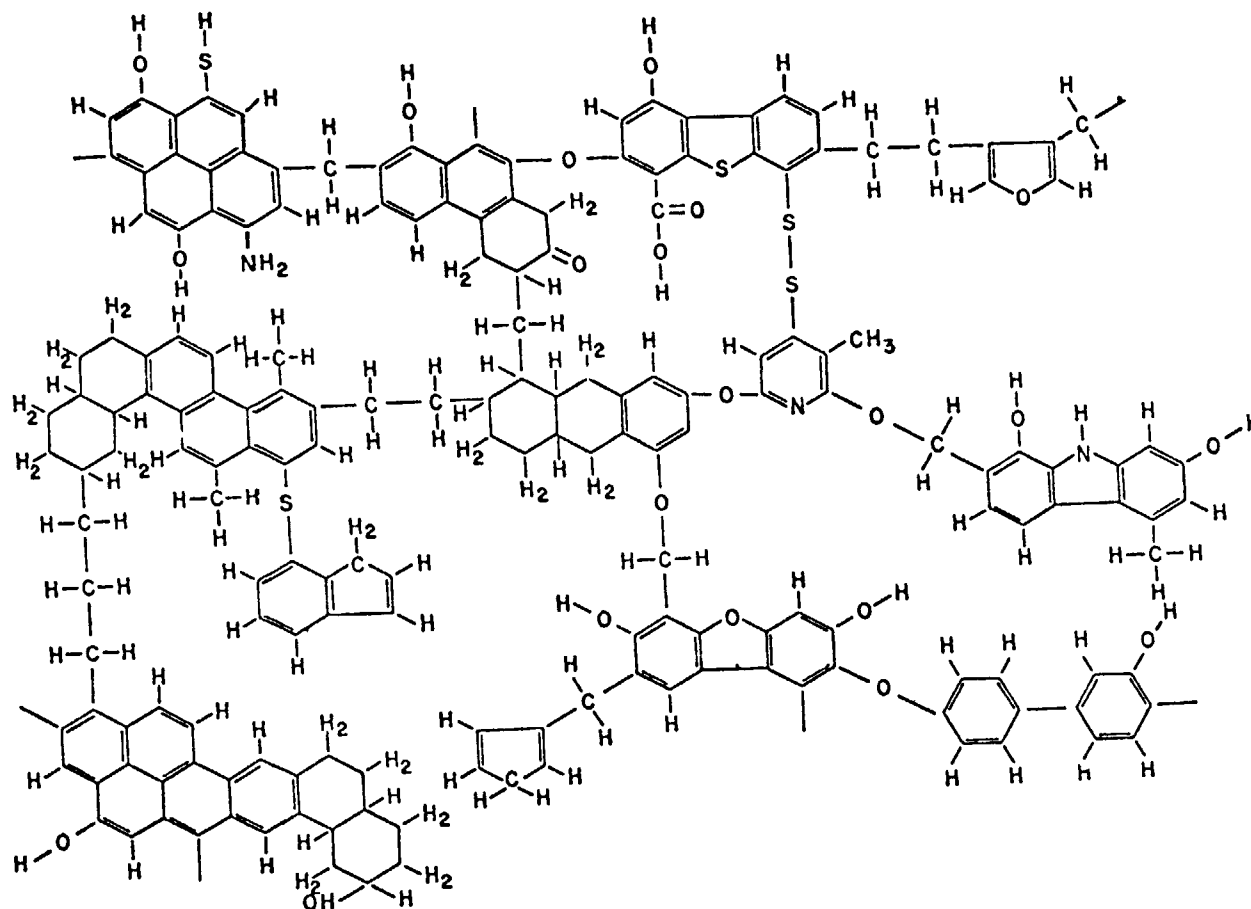


Figure XI-1

Representation of High-Volatile Bituminous Coal Structure

Adapted from Reference 79

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

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

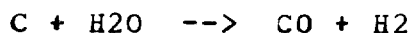
Synthetic pipeline gas, which is indistinguishable from natural gas (950-1,035 BTU/scf, containing over 95% methane), is produced by further processing medium-BTU gas. The required processing includes removal of particulate matter and condensables, adjustment of gas composition by reacting some of the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

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

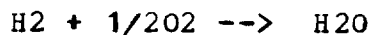
The gasification of devolatilized coal with carbon dioxide



and the water-gas (hydrogasification) reaction



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



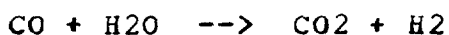
which are very rapid and proceed to completion, consuming the available oxygen.

The methanation of devolatilized coal

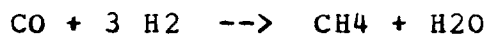


is highly exothermic and is thermodynamically favored at high pressures and at temperatures below 620 C (1150 F).

The shift reaction



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



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

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

(c) High-BTU Coal Gasification

At this time high-BTU coal gasification plants in the US are in various stages of design. The only existing operation which approaches the US designed plant in both size and complexity is the South African Coal, Oil and Gas Corporation, Ltd (SASOL) plant, located in Sasolburg, South Africa. This plant, designed in the early 1950's using both German and US data, began production in 1955. Today this plant has thirteen oxygen-blown gasifiers and consumes approximately 9,000 tons of coal per day for steam, power, and gas production. Construction is currently underway to expand the operation to 14,000 tons of coal per day. As the plant has expanded during the past 23 years, SASOL engineers have continuously

improved the original German (Lurgi) gasifier design. The latest SASOL improved Lurgi gasifier, the Mark IV, which is to be used in the expanded plant at SASOL II (a 40,000 ton per day plant currently under construction) and in the United States, is currently being tested [11,12].

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

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

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

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

Coal Preparation

(a) Receiving

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

TABLE XI-1
PLANT STATISTICS

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

(a) Adapted from reference 3

(b) Adapted from reference 6

(c) Adapted from reference 4

(d) Adapted from reference 5

(e) "As received" basis

(f) Byproduct (tar, tar oil, etc) consumed in liquid boilers

(g) Based on coal usage by both coal gasification plant and local electric power plant

ND = no data

LIG = lignite

SUB-B = sub-bituminous

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

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

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

(b) Coal Storage

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

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

(c) Coal Cleaning

In one plant design, a series of 48-inch-wide conveyors will carry the coal to the product sizer [3]. This facility consists of an elevated surge bin, variable-rate vibrating feeders, vibrating

double- and single-deck screens (for both dry and wet screening), and a dust collection system. The dry-screening process will produce 1-1/2 by 7/16-inch coal, which will be conveyed to the gasifiers. The minus 7/16-inch coal will be slurried with water and transported to a wet-screening circuit that removes the 7/16-inch x 4 mesh coal. This wet coal will be dewatered in centrifuges, combined with the plus 7/16-inch coal, and fed to the gasifiers [3].

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

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

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

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

(d) Workplace Hazards

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

Dusting may present an inhalation hazard with the potential for inducing pneumoconiosis (black lung). Respirable coal dust has been linked to pneumoconiosis [96]. Dusting from any equipment is possible, particularly if the equipment has to be maintained often and is not properly reassembled. (Elevators, rotating valves, augers, conveyors, and vibrating screens are common points for rapid

wear and failure.) The greatest potential for dust generation will be when a truck is unloaded. (At many plants, this dust nuisance may be reduced by enclosing the bin on three sides). Coal dust can and will blow off the storage pile. However, the methods described above will definitely reduce this dusting. Dusting from conveyors is common but can be reduced by fully enclosing the conveyor as described above and by spraying water on the coal at the conveyor transfer points. (Explosions could occur at the air ventilation equipment should the dust loading become too high.)

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

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

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

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

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

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

TABLE XI-2

ANALYSES OF DRAINAGE FROM TWO INDUSTRIAL COAL PILES

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

ND = No data

Adapted from reference 98

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

Gasifier Area Configuration

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

Coal Feeding

(a) Coal Lockhoppers

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

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

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

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

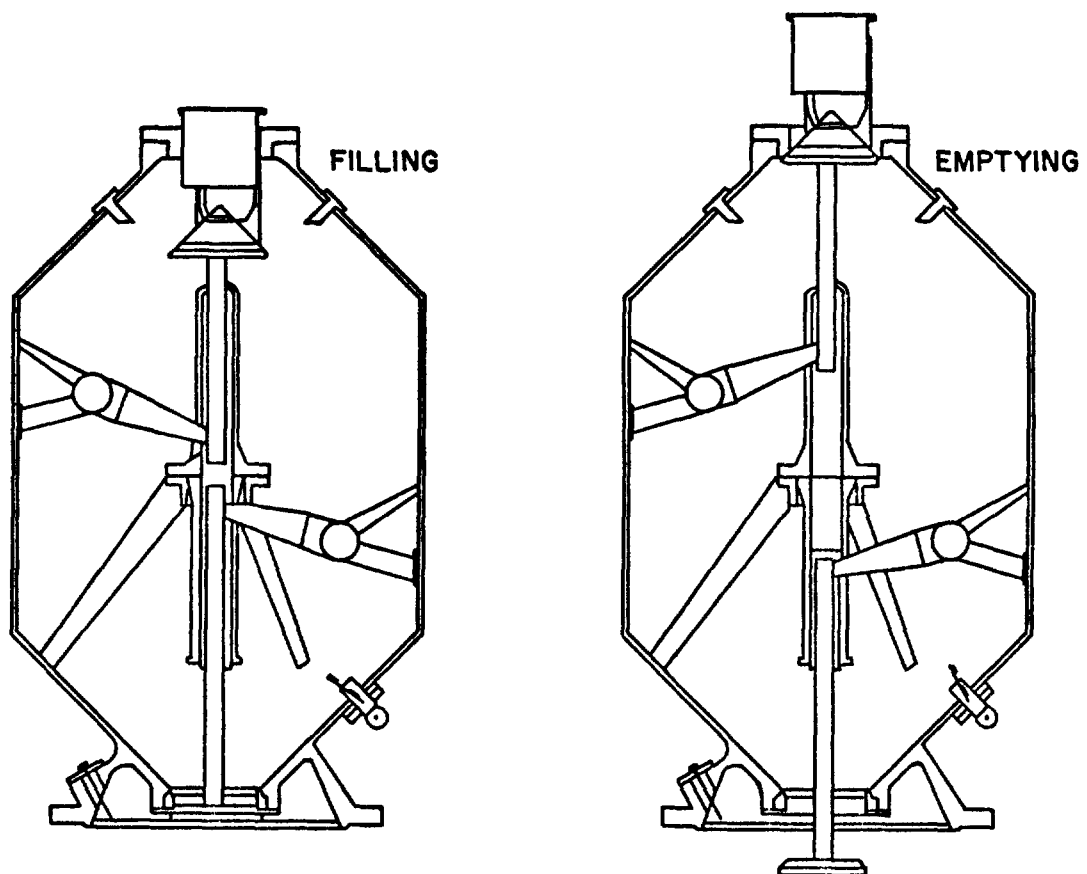


Figure XI-2
Coal Lock

Adapted from Reference 99

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

(b) Lockhopper Pressurizing Gas

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

TABLE XI-3

COMPOSITION OF COAL-LOCKHOPPER PRESSURIZING GAS

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

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

Adapted from reference 10

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

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

(c) Workplace Hazards

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

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

Coal Gasification

(a) General Discussion

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

THE LURGI GASIFIER

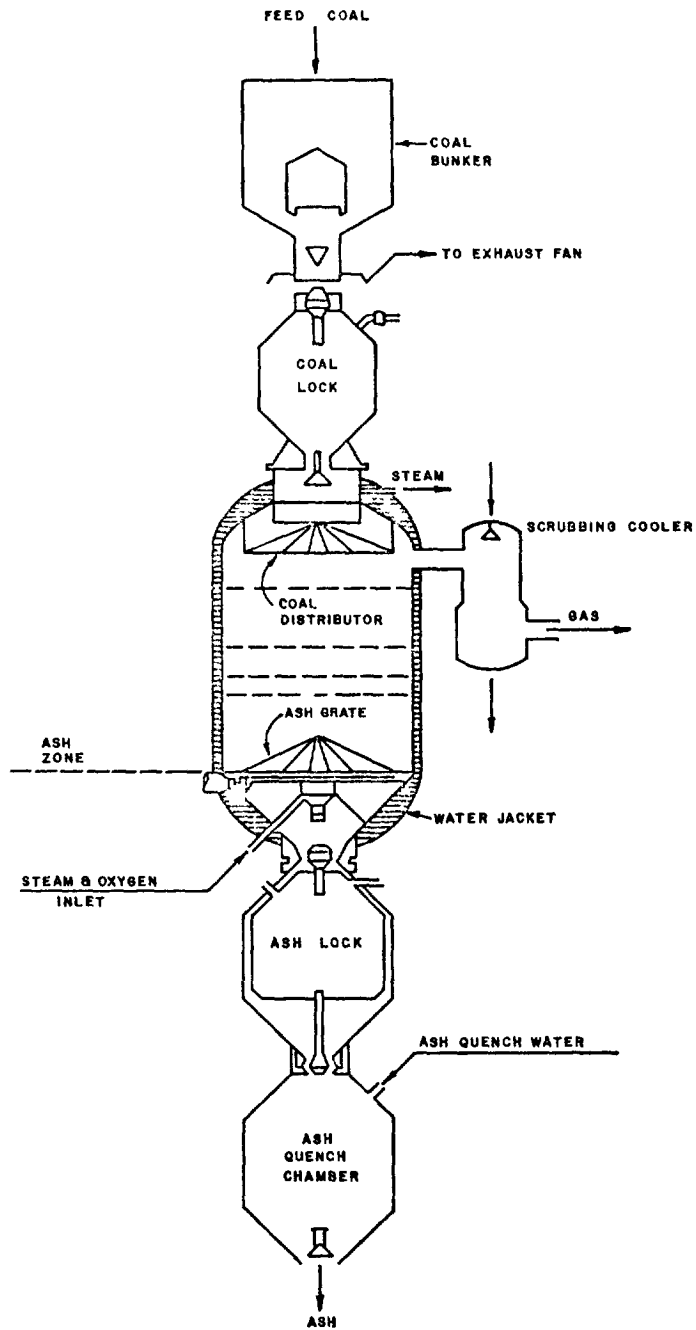


Figure XI-3

Gasifier Schematic with Exhaust Fan

Adapted from Reference 3

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

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

(b) Process

When the coal lockhopper bottom closure is open, the coal falls by gravity onto the coal distributor located above the bed and above the product gas outlet. The coal flowing down through the gasifier represents a slowly moving bed of continuously changing chemical composition. The moving bed of coal, which occupies the volume between the coal distributor and the ash grate, has several distinct zones. These are, from top to bottom, drying, devolatilization, gasification, and combustion. The first zone preheats and dries the coal by contact with the rising hot crude gas. (Thus the moisture in the coal does not enter the water-gas reaction described below.) As the coal is heated, devolatilization and gasification commence in zones that overlap and have temperatures ranging between 620 C and 870 C (1148 F and 1598 F). Coal devolatilization is accompanied by gasification of the resulting char.

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

(c) Gasifier Feed

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

TABLE XI-4
GASIFIER FEED

Component	Rate
Coal moisture, ton/hr	142
MAF coal, ton/hr	570
Coal ash, ton/hr	149
Steam, ton/hr	881
Oxygen, ton/hr	234
Steam/oxygen weight ratio	3.76
Steam/MAF coal weight ratio	1.55
<u>Oxygen/MAF coal weight ratio</u>	<u>0.41</u>
Adapted from reference 6	

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

(d) Feed Control

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

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

(e) Raw Product Gas

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

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

(1) Oil and Tar

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

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

TABLE XI-5

RAW PRODUCT GAS COMPOSITION (a)

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

(a) Moisture/solids-free gas, estimated concentrations; no data available for ammonia, tar, pentanes and higher hydrocarbons.

(b) Data from reference 3

(c) Data from reference 6

(d) Data from reference 101

(e) Carbonyl sulfide < 10 ppm, ash = 20 ppm

ND = no data

TABLE XI-6

OIL AND TAR

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

Adapted from reference 3

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

(2) Sulfur Compounds

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

(3) Nitrogen

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

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

(4) Trace Elements

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

TABLE XI-7

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

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

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

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

(c) Adapted from reference 79

ND = no data

TABLE XI-8
 CONSTITUENTS OF SYNTHANE GASIFIER GAS (925-LB/HR COAL FEED, BENCH-SCALE GASIFIER)

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

ND = no data

133

Adapted from reference 82

TABLE XI-9
 VARIATION IN SULFUR DISTRIBUTION DUE TO DIFFERENCES IN FEED COAL OR PROCESS

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

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

(b) Adapted from reference 105

ND = no data

TABLE XI-10

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

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

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

(b) Adapted from reference 108

TABLE XI-11

ESTIMATED VOLATILITY OF TRACE ELEMENTS IN A COAL

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

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

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

Adapted from reference 110

TABLE XI-12

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

Element	Raw Coal (ppm)	430 C (806 F) (ppm)	650 (C) (1200 F) (b) Loss (%)	1000 C (1832 F) (b)		Loss (%)		Total Loss (%)	Trace-Element Concentration in Offgas (Vol %)		
				ppm 430 C	Loss (%) After 430 C	ppm 650 C	Loss (%) After 650 C		430 C (c)	650 C (d)	1000 C (e)
Mercury	0.27	0.19	30	0.06	68	0.01	19	96	0.00000071	0.0000012	0.0000016
Selenium	1.7	1.0	41	0.65	35	0.44	12	74	0.000015	0.0000094	0.000019
Arsenic	9.6	7.5	22	5.1	32	3.4	18	65	0.00005	0.000072	0.0001
Tellurium	0.11	0.07	36	0.05	29	0.04	9	64	0.00000057	0.00000031	0.00000067
Lead	5.9	4.4	25	3.3	25	2.2	19	63	0.000014	0.000013	0.000022
Cadmium	0.78	0.59	24	0.41	31	0.30	14	62	0.000003	0.0000034	0.0000052
Antimony	0.15	0.13	13	0.12	8	0.10	13	33	0.00000029	0.00000033	0.0000005
Vanadium	33	36	0	30	9	23	21	30	ND	0.00026	0.00024
Nickel	12	11	8	10	9	9.1	8	24	0.00003	0.000043	0.00006
Beryllium	0.92	1.0	0	0.94	0	0.75	18	18	ND	0.000037	0.000023
Chromium	15	17	0	16	0	15	0	0	ND	ND	ND

Adapted from reference 111

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

(b) Maximum temperature

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

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

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

ND = no data

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

TABLE XI-13

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

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

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

ND = no data

Adapted from reference 103

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

TABLE XI-14

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

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

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

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

ND = no data

Adapted from reference 5

(f) Workplace Hazards

Workplace hazards in the gasification system will most likely be plugged lines, hot spots, insulation problems, and leaks. Leaks may occur at any of the connections to the gasifier vessel, particularly

at flanges and other connections such as valves, and instrument locations. The leaks will involve release into the workplace of toxic substances, including carbon monoxide, tar, sulfur compounds, nitrogen compounds, and trace elements. Leaks from the ash-lockhopper area, providing they are not catastrophic, will most likely be of steam and oxygen. Leaks in the area from the grate to above the combustion zone may contain steam, oxygen, carbon dioxide, carbon monoxide, hydrogen, and trace elements. Leaks above this point will contain increasing amounts of devolatilization products, but may contain lesser quantities of trace elements.

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

Gas Quench System

(a) Process

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

(b) Mechanical and Safety Considerations

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

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

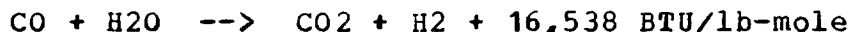
(c) Workplace Hazards

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

Shift Conversion

(a) General Discussion

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



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

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

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

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

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

(b) Workplace Hazards

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

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

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

Gas Cooling

(a) General Discussion

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

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

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

_____ UNCONVERTED GAS
 - - - - - CONVERTED GAS

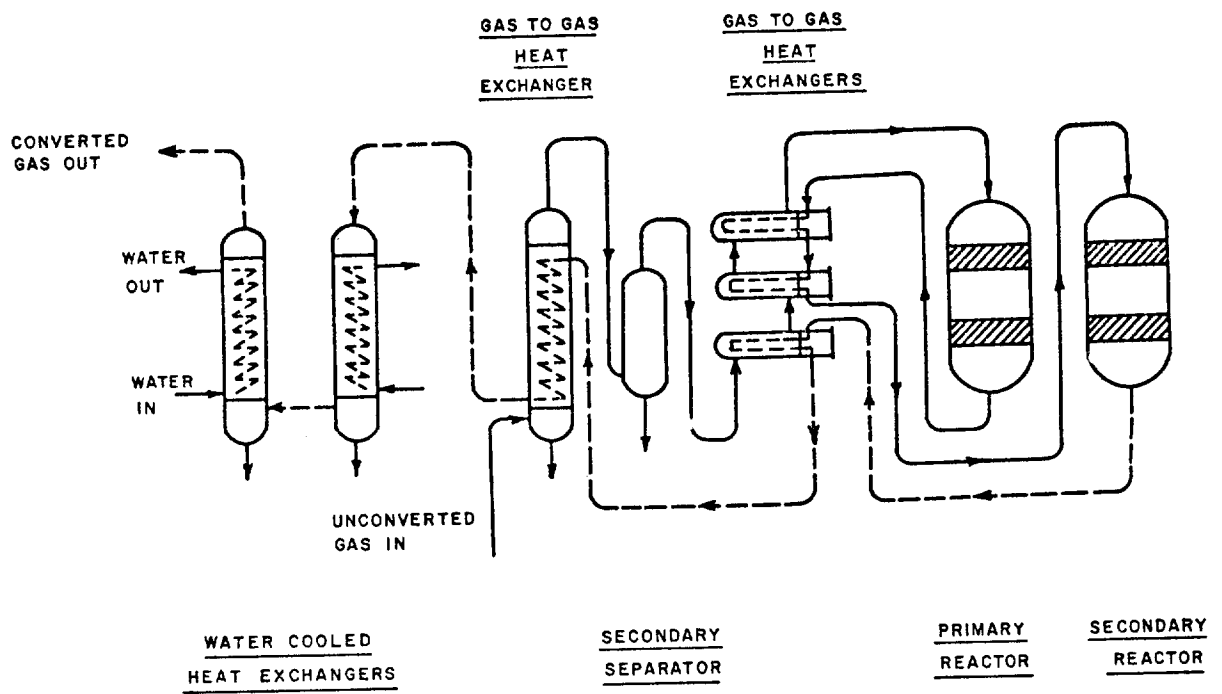


Figure XI-4

Simplified Flow Diagram of the Westfield Shift Conversion Plant

Adapted from Reference 17

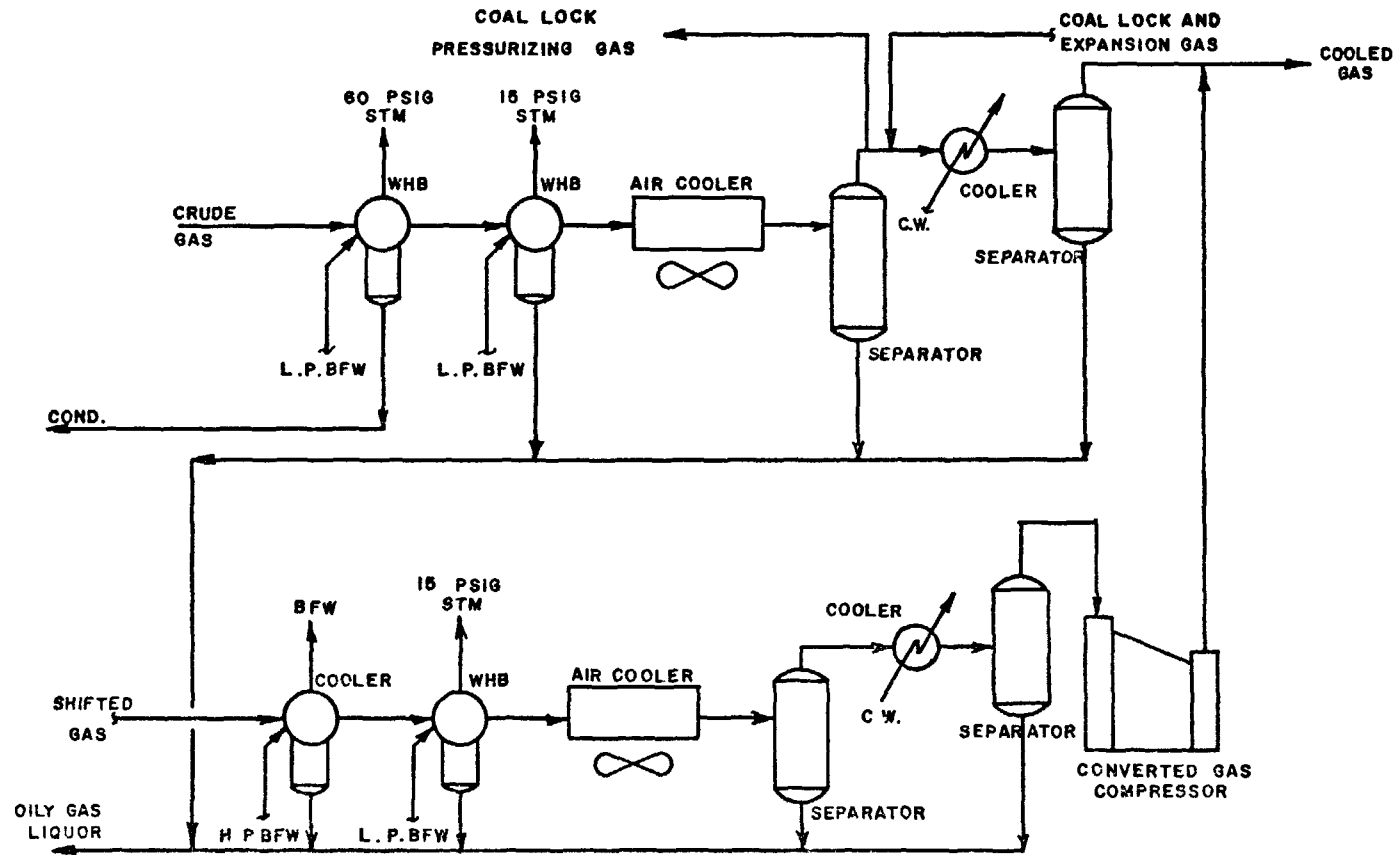


Figure XI-5

Flow Scheme for the Gas Cooling Section

Adapted from Reference 6

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

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

(b) Workplace Hazards

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

Gas Purification

(a) General Discussion

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

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

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

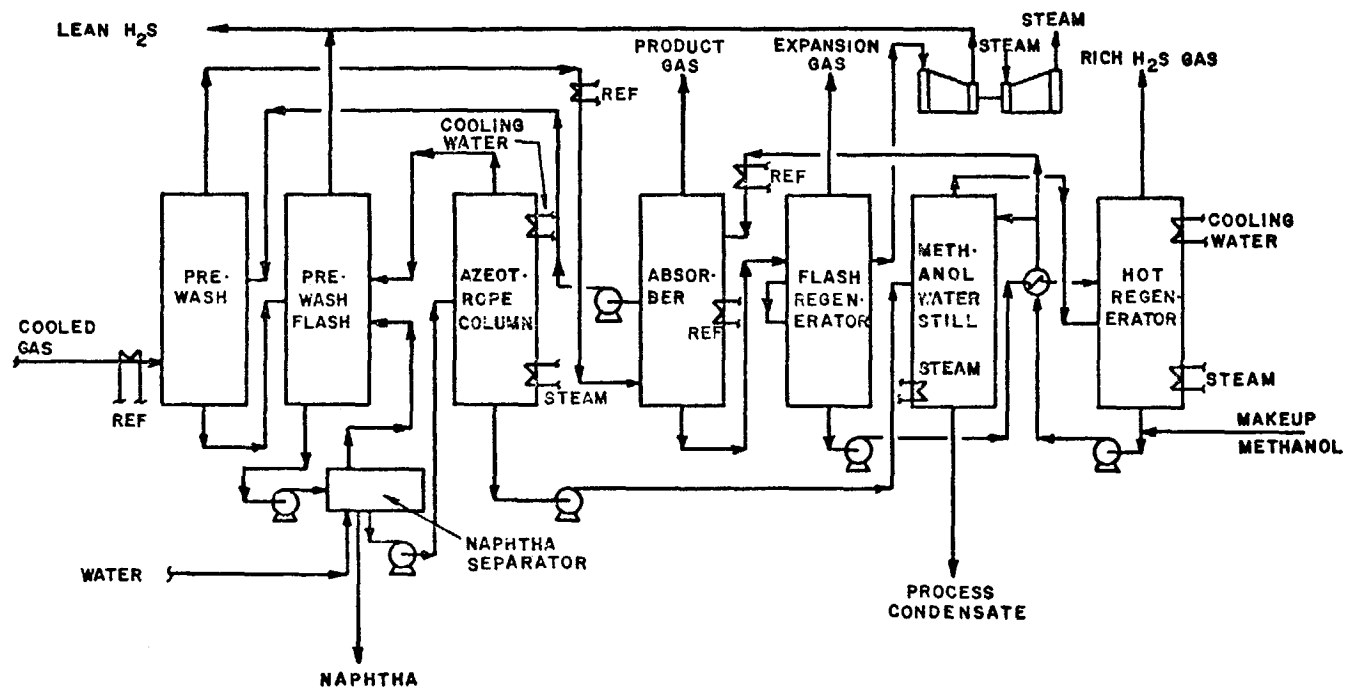


Figure XI-6
Flow Scheme for Gas Purification Section - Rectisol I Process

Adapted from Reference 6

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

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

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

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

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

TABLE XI-15

COMPOSITION AND PROPERTIES OF RECTISOL GAS

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

ND = no data

Adapted from reference 103

TABLE XI-16

RECTISOL EXPANSION GASES

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

Adapted from reference 103

(b) Manpower

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

(c) Workplace Hazards

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

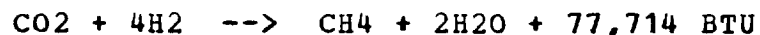
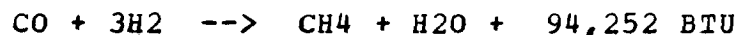
Vapor from the hot methanol is also toxic. In US plants, exposure potential should be low because methanol will be transferred from all tanks, heat exchangers, pumps, etc, into special slop tanks in cases of spills, leaks, or required maintenance. It is recommended that any vessel to be entered by personnel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

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

Methanation

(a) General Discussion

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



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

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

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

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

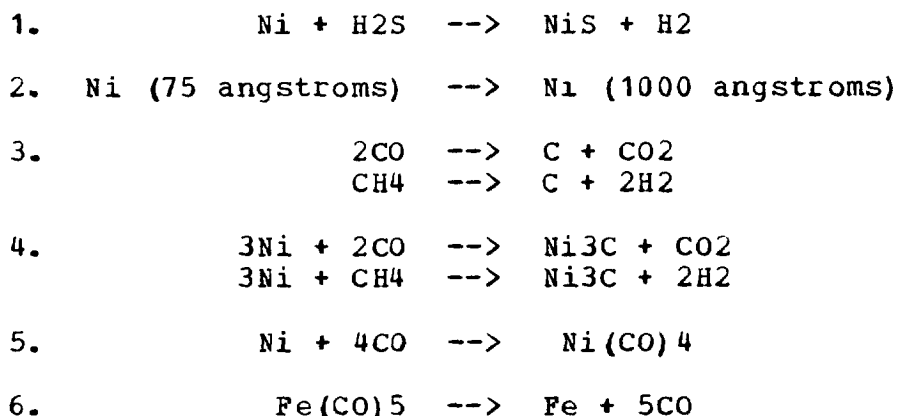
In the methanation section of the process, pressure does not appreciably affect methane yield. However, if the temperature exceeds 506 C (942 F), increasing pressure tends to decrease the minimum ratio of hydrogen to carbon monoxide required to prevent carbon deposition [116].

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

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

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

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



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

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

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

(b) Process

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

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

(c) Workplace Hazards

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

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

TABLE XI-17

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

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

ND = no data

Adapted from reference 10

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

Compression

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

Ash

(a) General Discussion

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

When the ash lockhopper is filled, the upper ash-lockhopper valve is closed and depressurization is begun by blowing the steam from the lockhopper first through a cyclone to remove solids and then through water to condense the steam. Any gases and vapors generated in this hopper pass through a cyclone for particulate and droplet removal and are vented to the atmosphere [3]. Solids from the cyclone and condensate from the water condenser are both discharged through the ash conveying system [9]. When the lockhopper is depressurized, the bottom valve is opened and the ash is discharged to a covered sluiceway [9], or the ash is water quenched and discharged to a conveyor [6]. The lockhopper is repressurized with steam in a sequence similar to that described for the coal lockhoppers. The ash is dewatered in settling tanks or by

other means [3-6] and loaded into trucks for transportation to the mines, where it is disposed of in the original pit [3]. Excess liquid is sent to an ash-slurry thickener system [3-6]. Fine ash is sent to the mine [3,6] or to a settling pond for later recovery [5]. Water from the thickener is reused as quench water [6], evaporated [6], or sent to a clear-water pond before being returned to the gasifier sluiceways [6].

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

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

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

(b) Workplace Hazards

(1) Ash Lockhoppers

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

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

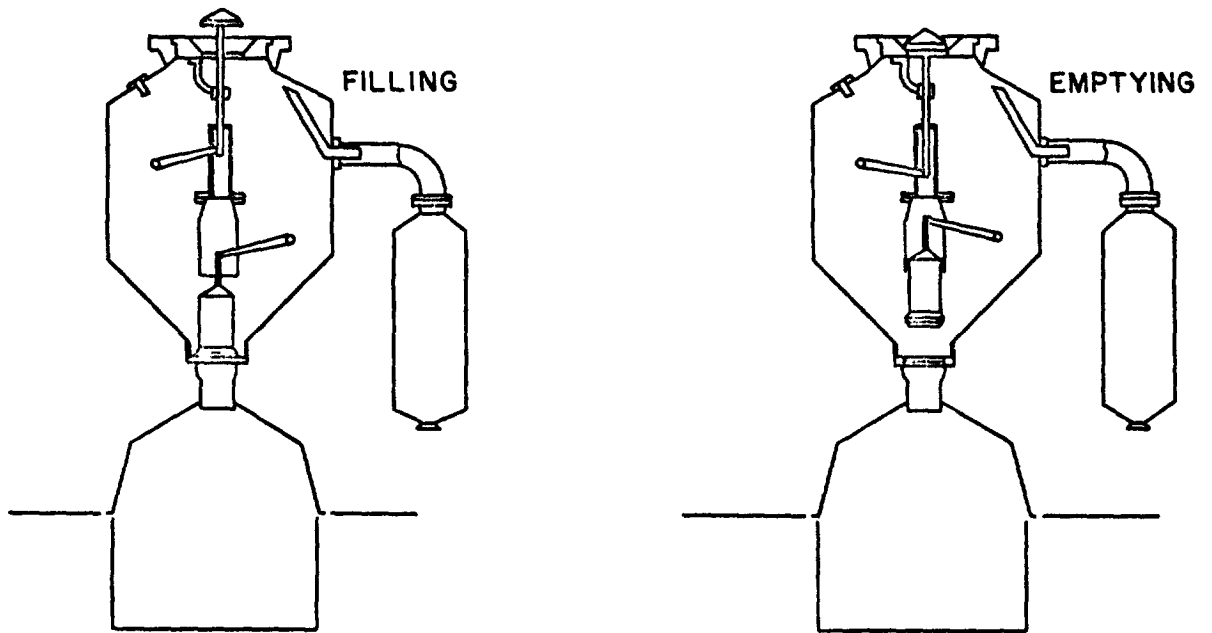


Figure XI-8
Ash Lock

Adapted from Reference 99

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

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

(2) Leaks

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

(3) Hazardous Materials

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

(4) Radioactivity

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

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

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

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

Tar and Gas-Liquor Separation

(a) General Discussion

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

(b) Process

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

The high-pressure raw gas leaving the waste heat boiler will be divided into two streams, half for shift conversion and half for shift-conversion bypass as discussed above. The bypass gas will

first be cooled in a waste heat boiler generating steam at about 76 psig and then further cooled to generate 47 psig of steam. Gas-liquor and tar recovered from these cooling steps will be returned to the tar/gas-liquor separator. Crude gas will be further cooled, and gas-liquor and tar oil will be sent to a gas-liquor/tar-oil separator.

TABLE XI-18
TYPICAL COMPOSITION
OF GAS LIQUOR EXPANSION GAS

<u>Constituent</u>	<u>Concentration (vol %)</u>
Carbon dioxide	90
Carbon monoxide	4
Hydrogen	1
Hydrogen sulfide	1
<u>Methane</u>	<u>4</u>

Adapted from reference 10

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

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

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

TABLE XI-19

REPORTED LIQUID HYDROCARBON RECOVERY
FROM LURGI COAL GASIFICATION

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

(a) Adapted from reference 17

(b) Adapted from reference 103

ND = no data

TABLE XI-20

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

Constituent	Concentration (ppm)	
	Liquor Separated from Tar Phase	Liquor Separated from Oil Phase
Total ammonia (as NH ₃)	1,795	9,597
Carbonate (as CO ₃)	1,128	17,655
Sulfide as S	0.7	177
Thiosulfate (as S ₂ O ₃)	9.0	15.8
Cyanide (as CN)	7.8	2.6
Thiocyanate (as CNS)	Nil	41.2
Ferrocyanide [as Fe(CN) ₆]	4.2	10.5
Chloride (as Cl)	4.3	11.3
Sulfate (as SO ₄)	90.6	74.1
Total iron (as Fe)	2.3	2.0
Fatty acids (as acetic acid)	696	228
Monohydric phenols	2,864	3,178
Dihydric phenols	2,917	1,869
Suspended solids	100	340
Fraction extractable by ether (tar, oil)	1,000-5,000	100-500
pH	9.4	8.0
Total alkalinity (as CaCO ₃)	2500	5000
Calcium hardness (as CaCO ₃)	Nil	Nil
Magnesium hardness (as CaCO ₃)	Nil	Nil
Temperature, C (F)	71 (160)	27 (70)

Adapted from reference 17

TABLE XI-21

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

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

Adapted from reference 11

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

(c) Tar, Tar Oil, and Naphtha

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

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

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

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

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

(d) Workplace Hazards

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

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

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

Gas-Liquor Processing--Phenosolvan

(a) General Discussion

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

(b) Process

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

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

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

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

TABLE XI-22

COMPOSITION OF CRUDE TAR ACIDS
RECOVERED FROM PHENOSOLVAN PROCESS

Constituent	Concentration (wt %)
Neutral oil	1
Pyridine bases	1-2
Phenol	38
<i>o</i> -Cresol	8
Mixed <i>m</i> - and <i>p</i> -cresols	14
Xylenols	13
Higher boiling tar acids	16
<u>Pitch</u>	<u>8</u>

Adapted from reference 119

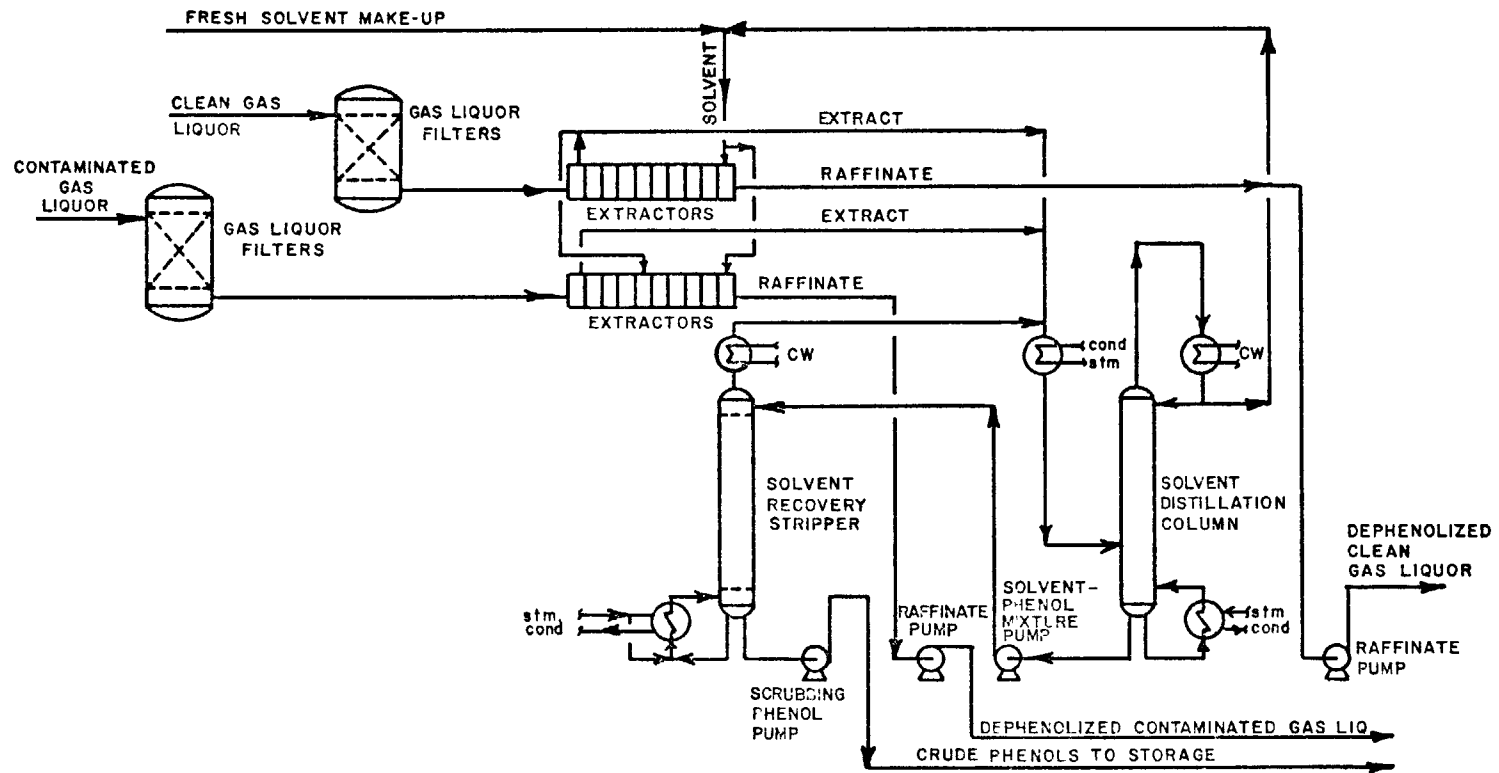


Figure XI-10

Flow Scheme for Phenol Extraction-Phenosolvan Process

Adapted from Reference 6

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

(c) Manpower

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

(d) Workplace Hazards

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

Cooling Water System

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

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

TABLE XI-23

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

<u>Constituent</u>	<u>Concentration (ppm)</u>
<u>A. Input to Phenosolvan Process</u>	
Phenols	3,250-4,000
Sodium	53
Ammonia (free)	600
Ammonia (fixed)	150-200
Suspended tar and oil	5,000
Cyanide ion	6
Total sulfide ion	228
Fatty acids (as acetic acid)	0.03%
Carbon dioxide	0.7%
<u>B. Effluent (Feed to Biotreatment Plant)</u>	
Phenols (steam volatile)	1
Phenols (bound)	60-160
Fatty acids (as acetic acid)	560
Ammonia (as N)	215
Hydrogen sulfide	12
Cyanide ion	1
Fluoride	56 mg/liter
Chloride	25
Calcium (as Ca)	18
Iron (as Fe)	1 mg/liter
Orthophosphate	2.5
Total dissolved solids	875
Suspended solids	21
COD (Chemical Oxygen Demand)	1,126
pH	8.4
<u>Conductivity</u>	<u>1,000-1800 microSiemens/cm</u>
Adapted from reference 103	

Part of all of the required makeup water may be treated process water supplied from the biotreatment facility. Little corrosion is to be anticipated in such a system, as the ammonium salts will retard corrosion. The phenolic material will retard the growth of biologic contaminants.

Corrosion in the circulating cooling water system of one plant will be controlled by the injection of sulfuric acid to regulate the pH and inhibit corrosion. Algae growth will be controlled with chlorine. Continuous blowdown of the cooling tower will be used to control the solids concentration of the water. This blowdown will be directed to the holding pond for further reuse of the water [3].

Any oily process water, area drainage, and equipment drips will be collected separately from the Phenosolvan-processed water for processing in an oil separator and further treatment before reuse [3].

The reuse water system at one US plant will receive the de-oiled storm-basin effluent, demineralizer regeneration waste, treated sanitary waste effluent, biologically treated water in excess of that used for cooling makeup, utility water, cooling tower blowdown, and other minor streams [3].

Water retained in the holding pond will be reused for sulfur pelletizing, road wetting, ash sluiceway water, revegetation, and other mine uses. Because of the seasonal fluctuation of mine uses, such as irrigation, it will be necessary to supply additional water for peak use periods. The holding pond will have a volume of approximately 12.5 million cubic feet. It will be covered with an impervious synthetic membrane to prevent evaporation [3].

Steam and Power Generation

In one US plant, steam-generation facilities will consist of process-waste heat boilers and gas-fired power boilers. Generally, waste-heat boilers will provide heating and process reaction steam, while power boilers will provide motive-power steam. Power will be generated by an automatic extraction turbine on the power boilers. Air-cooled condensers will be used to minimize cooling water requirements. The gas-fired power boilers will normally use hot exhaust gas from the gas turbines for combustion air, but forced-draft fans will be provided to supply fresh air in the event the gas turbine is off line [6].

Three power boilers and electrical generators will each have a capacity of 50% of normal plant requirements. The 1500-psig, 510 C (950 F) steam from the power boilers will be used in an automatic extraction turbine driving electrical generators producing 57,000 kW. Exhaust steam will be condensed. Extraction steam at 500 psig will be used at various compressor drives throughout the plant [6].

One US company plans to provide a low-BTU fuel, gasified in airblown gasifiers operating at 285 psig [6]. Raw gas will be desulfurized by treatment in a hot potassium carbonate system. Quench, cooling, and tar/gas-liquor separation will follow the same schemes as described for the high-BTU plant. Product fuel gas will have a higher heating value of about 230 BTU/scf (dry). Flue gases from fuel-gas combustion will have 0.16 pound or less of sulfur dioxide per million BTU of fuel input. Ten gasifiers, nine operating and one spare, will be required for fuel-gas production [6].

Another US company plans to use high-pressure steam for the coal gasification plant, which is produced by coal-fired boilers burning coal fines [3]. The boilers will be fired with 3,868 tons/day of coal fines, to produce 3 million lb/hour of 1500-psig, 510 C (950 F) steam. The coal fed to the boilers will be screened and washed 4 x 48 mesh coal fines. Fly ash and compounds removed from the boiler flue gases will be collected in separate and independent systems. Exhaust gases from the boiler economizer will pass through a hot electrostatic precipitator to remove at least 99% of the fly ash and then through a scrubbing system to remove 90% of the sulfur compounds and virtually all of the remaining ash [3].

Oxygen Plant

The oxygen plant designs for two major US operations are similar. The first oxygen plant will produce 6,000 tons/day of 98% minimum purity vapor-phase oxygen while the second produces 99.8% minimum purity oxygen. At the first operation liquid storage and transfer pumping are planned and will be sized for 2,000 tons total (ie, 8-hour supply). A total of 633,000 actual cubic feet per minute (acfm) of atmospheric air will be filtered and compressed to 99 psi in three parallel low-BTU gas-turbine/steam-turbine centrifugal compressors of approximately 33,000 hp each [6].

The compressed air entering the cold box will be cooled to liquefaction temperature by a combination of heat exchange and expansion in a conventional air separation cycle. Once in the liquid state, oxygen and nitrogen will be separated by fractionation. The nitrogen (plus a small quantity of moisture, carbon dioxide, and oxygen) will be regasified in the heat-exchange process and its energy utilized before rejection to the atmosphere. The liquid oxygen will be taken first to provide liquid storage when required and then gasified to feed the six parallel-operating steam-turbine-driven oxygen compressors. These centrifugal units, each capable of compressing 12,000 tons/day, will raise the pressure level to 500 psig and deliver 5,620 tons/day of oxygen to the Lurgi coal gasifiers. The expansion process in the cold boxes will generate a total of about 500 kW each at full capacity [6].

Byproduct Storage

Typical byproduct storage provisions are presented in Table XI-24.

TABLE XI-24
TYPICAL STORAGE PROVISIONS

Constituent	Number of Tanks	Capacity	
		Volume (barrels)	Time
Crude phenol	2	5,500	2 wk
Tar-oil naphtha	2	20,000	2 wk
Tar	2	40,000	2 wk
Naphtha product	2	12,000	2 wk
Ammonia solution	2	5,500	2 days
Sodium hydroxide	2	12-ft diameter x 50 ft (horizontal)	2 wk
Methanol	2	12-ft diameter x 50 ft (horizontal)	2 wk
Demineralized water	1	25,000	4 hr
Cold lime-treated water	2	25,000	12 hr
Condensate	2	25,000	6 hr
<u>Liquid wastes</u>	1	500	ND

ND = no data

Adapted from reference 6

Sulfur Recovery

(a) General Discussion

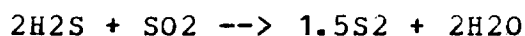
Each of the three commercial coal gasification processes most intensely studied in the development of this document has a distinct method for recovering the sulfur from the various process streams [3,4,6]. All three plants will use the Stretford process to recover sulfur from lean hydrogen sulfide-containing streams. Two of the designs will use the Claus process to recover sulfur from a concentrated sulfur stream. [3,4]. The third plant will utilize low-BTU coal gasification to produce clean fuel gas to eliminate the need for stack-gas scrubbing [6]; the other two plants will use variations of stack-gas scrubbing schemes to remove sulfur dioxide from tail gas and furnace effluent gas [3,4]. The Claus and Stretford units are discussed below.

(b) Process

(1) Claus Process

The Claus process is an essentially atmospheric pressure process operating in the following manner: The acid gas, containing 15-90 mole % hydrogen sulfide, is combined with sufficient air to burn one-third of the total hydrogen sulfide to sulfur dioxide and all of the hydrocarbons to carbon dioxide. (Alternatively, one-third of the total acid gas is burned and recombined with the unburned gas.) A part of the hot gas is cooled, and a portion bypasses the coolers so that the reactor temperatures can be maintained [120]. (Each reactor inlet temperature must be above the sulfur dewpoint, preferably 230 C [450 F], to avoid condensation of the liquid sulfur in the catalyst bed. Condensation could cause plugging and catalyst deactivation [121].)

In the reactor the sulfur dioxide and hydrogen sulfide react to form sulfur:



From the catalytic reactor the hot [370 - 400 C (698 - 752 F)] gases flow into the condenser, where they are cooled to 150 C (302 F) and the liquid sulfur is removed. Sulfur must be removed from the condenser in the 300 F range. [Because of a phase change at 160 C (320 F), the liquid sulfur increases rapidly in viscosity with increasing temperature and cannot be removed from the condenser.] Cooled gases can then be recombined with the second hot-gas bypass flow to balance temperatures at the entrance of the second reactor inlet. Product gas should contain only 0.5-10% of the hydrogen sulfide fed into the unit [121].

Claus process variations can accommodate the various concentrations of acid-gas feeds, with the optimum Claus process depending primarily on the hydrogen sulfide concentration in the feed [122].

One US plant's design and operating control features that contribute to maintaining high sulfur recovery include (1) the three converter configurations, (2) the small amount of hydrocarbons in the feed, (3) no water vapor in the feed, (4) high-temperature burner operation with two-thirds feed bypass, (5) computer control, (6) use of a high-activity catalyst bed to decompose at least 85% of any carbonyl sulfide and carbon disulfide formed, and (7) the minimization of sulfur mist entrainment. To insure constant availability of the Claus process for sulfur recovery, this gasification plant will include two complete 100% capacity units, one operating and one standby [3].

The Claus plant will treat the offgas streams from the Rectisol process. The composition of the combined gases from the naphtha extractor and the hydrocarbon removal unit that would be treated is shown in Table XI-25.

TABLE XI-25

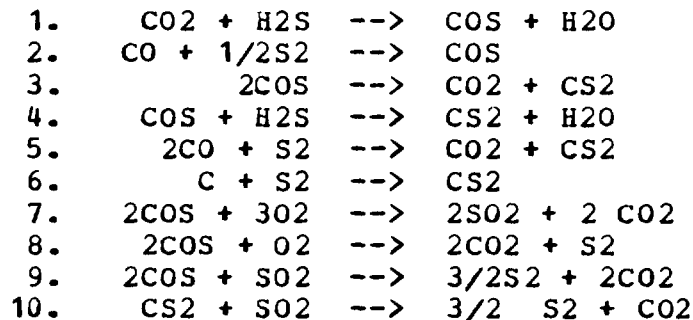
ESTIMATED CLAUS PLANT FEED FROM THE RECTISOL PROCESS

<u>Constituent</u>	<u>Concentration (vol %)</u>
Carbon dioxide	34.2
Hydrogen sulfide	64.0
Hydrogen cyanide	0.2
Carbonyl sulfide	Trace
<u>Hydrocarbons</u>	<u>1.6</u>

Adapted from reference 3

Of the sulfur fed to the Claus unit, 95% will be recovered; 90% of the remaining sulfur in the Claus tail gas will be removed by the flue-gas desulfurization unit, for an overall sulfur removal of 99.5%. The elemental sulfur will be pelletized and stored on the ground within a retaining curb to prevent surface runoff or it may be stored in a lined, heated pit [4,6].

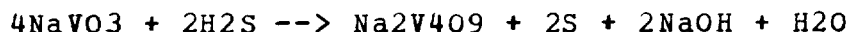
The types and amounts of hydrocarbons present in the acid gas entering the burner have an effect on the carbon content and hence the color of the sulfur product. Aromatics and olefins form carbon more readily than do paraffins. Also, the amount of carbonyl sulfide formed in the high-temperature region is believed to depend on the amounts of carbon dioxide and hydrocarbons in the burner feed. Some of the reactions that may occur are the following:



Deactivation of Claus catalysts (bauxite) may be caused by carbonaceous deposits, sulfur condensation, sulfur vapor adsorption, thermal degradation, and sulfate formation. Unfortunately, bauxite contains both iron and silica compounds which facilitate catalyst deactivation. Porocel is an improved form of bauxite, which is made from high-grade activated bauxite and contains 88-92% alumina. Pure activated alumina is being proposed as a still better catalyst. In most cases a catalyst life of 2-5 years can be expected [10].

(2) Stretford Process

The Stretford process is capable of operating on acid gases containing only low concentrations of hydrogen sulfide. In this process, the 50 C (120 F) acid gas is washed countercurrently by the Stretford solution, which consists of sodium carbonate, sodium metavanadate, an anthraquinone disulfonate activator, citric acid, and traces of chelated iron; the pH is 8.5. The hydrogen sulfide in the acid gas reacts with the vanadate as follows:



The reduced vanadate is then oxidized by the anthraquinone disulfonate activator, which in turn is reoxidized by air sparging. The air also acts as a flotation agent in frothing out the fine-grained sulfur product. The slurry of solid sulfur is filtered, the filtrate is returned to the process, and the sulfur is collected in a molten-sulfur storage tank [10,113,121,123].

Unfortunately, carbonyl sulfide and carbon disulfide are not recovered by the Stretford process [3]. Effluent from the top of the Stretford absorber tower will be primarily carbon dioxide but will contain about 10 ppm by volume of hydrogen sulfide [6], and it has been estimated that it will contain 67 ppm carbonyl sulfide and a trace of carbon disulfide. The total hydrocarbon concentration is 9,400 ppm by volume (if methane and ethane are excluded, the concentration is 2,000 ppm by volume), and carbon monoxide emissions are 1,500 ppm by volume [10]. At one plant effluent gas streams will be incinerated in the coal-fine boilers to eliminate hydrocarbons. The gas will subsequently be treated in the stack-gas treating unit to increase the overall sulfur-removal efficiency to over 99.8% [3].

In the same plant design [3], the Stretford process will treat the offgases from the Phenosolvan and Rectisol processes. The composition of the gases to be treated is shown in Table XI-26.

In the Stretford unit, there is a small byproduct conversion of hydrogen sulfide to thiosulfate. Through proper design and the use of special additives, the conversion to thiosulfate can be kept down to the 1% to 2% level. Accumulated thiosulfate must be purged. A typical Stretford solution purge contains sodium salts of anthraquinone disulfonate, metavanadate, citrate, thiosulfate, and thiocyanate. At the one plant this purge stream will be sent to a recovery unit system in order to reuse the chemicals [10,86].

TABLE XI-26

ESTIMATED STRETFORD PLANT FEED

Constituent	From Phenosolvan (Vol %)	From Rectisol (Vol %)
Carbon dioxide	85.2	97.4
Hydrogen sulfide	1.2	0.9
Hydrogen cyanide	ND	Trace
Carbonyl sulfide	Trace	ND
Nitrous oxide	13.2	ND
Others	0.4	1.7

ND = no data

Adapted from reference 3

Tail Gases

In the Lurgi gasification process, which may include both a Claus and a Stretford unit for sulfur recovery, tail gases from these units will contain both hydrocarbons and sulfur compounds. There are a number of ways to treat these vent gases to obtain a final gas with an acceptable concentration of pollutants.

One way to destroy the hydrocarbons and recover the sulfur is incineration. The hydrocarbons are converted to carbon dioxide and water, and sulfur compounds are oxidized to sulfur dioxide, which is more easily recovered. However, incineration is expensive in terms of fuel cost because of the large volume of gas to be treated and the still larger volume of gas from which to recover the sulfur.

Another way would be to chemically remove the sulfur compounds from the gases to a point where the gases are no longer considered a health hazard or an air pollutant. Since the vent gases from a well-operated Stretford unit contain only about 10 ppm of hydrogen sulfide and somewhat larger amounts of carbonyl sulfide and carbon disulfide, a process in which the sulfur-rich gases are first treated in a Claus unit and then in a Stretford unit will reduce the sulfur in the vent gases to an acceptable limit [6]. Such a combined treatment will also reduce the volume of gases to be incinerated if the hydrocarbon content of the vent gases is considered objectionable.

Both the Beavon and the Scot processes chemically convert the sulfur compounds to hydrogen sulfide and then treat the gases to remove the hydrogen sulfide. In the Scot process, the hydrogen sulfide is absorbed in an alkanolamine solution and recycled to the Claus unit [37]. This process, however, requires the incineration of the tail gases from the Claus unit because of the high hydrogen sulfide content.

In the Beavon process, the sulfur compounds in the gases from the Claus unit are converted to hydrogen sulfide, which is recovered in the Stretford unit. Gases from the Beavon unit could add about 15% to the load on the Stretford unit.

Table XI-27 shows a material balance for the Claus-Beavon-Stretford process anticipated in the one US plant. The stream from the Rectisol unit, rich in hydrogen sulfide, is sent to a Claus unit along with a stoichiometric amount of air to convert one-third of the total sulfur to sulfur dioxide. Molten sulfur is the product of this operation. The offgases from the Claus unit are mixed with hydrogen and passed over a heated catalyst to convert all the sulfur to hydrogen sulfide in a Beavon reactor. The hydrogen sulfide is absorbed in a unit containing Stretford solution. The unabsorbed gases are vented to the atmosphere.

The hydrogen sulfide enriched Stretford solution from the Beavon reactor is sent to the Stretford unit where it becomes part of the Stretford liquor used to absorb the hydrogen sulfide in the lean hydrogen sulfide gases from the Rectisol unit and from the tar and ammonia recovery plant. The coal-lockhopper gases as well as other gases containing hydrogen sulfide are also treated in the Stretford unit. Elemental sulfur is recovered from the Stretford unit, and the offgases are vented.

From Table XI-27 it is apparent that the vent gases from the Beavon unit, with about 10 ppm by volume of hydrogen sulfide and about 150 ppm by volume of total sulfur with practically no hydrocarbons, poses little health hazard. Although the hydrogen sulfide and the total sulfur in the offgases from the Stretford unit are somewhat less than in the gases from the Beavon plant, this gas has an appreciable hydrocarbon content. The vented gases from the Stretford unit may have to be incinerated.

TABLE XI-27

MATERIAL BALANCE FOR THE CLAUS-BEAVON-STRETTFORD
SULFUR RECOVERY PROCESS (LB/HR)

Constituent	CLAUS		BEAVON		STRETTFORD	
	In from Rectisol II	Out to Beavon	In from Claus	Vented to atmosphere	Ir. (a)	Vented to atmosphere
Carbon dioxide	75,064	75,275	75,275	75,489	657,507	757,507
Hydrogen sulfide	10,456	508	508	1	6,217 (b)	7
Carbonyl sulfide	112	343	343	21	110	110
Carbon disulfide	4	ND	ND	4	4	4
Ethylene	44	ND	ND	ND	1,347	1,347
Carbon monoxide	1	ND	ND	ND	4,055	4,055
Hydrogen	ND	ND	50 (c)	2	350	350
Methane	4	ND	ND	ND	1,957	1,957
Ethane	70	ND	ND	ND	2,164 (e)	2,164
Oxygen	5,261 (d)	ND	ND	ND	17,960 (e)	14,370
Nitrogen	17,310 (d)	17,310	17,310	17,310	65,480	65,480
Water vapor	ND	5,451	5,451	5,600	10,900	14,945
Methanol	ND	ND	ND	ND	ND	ND
Sulfur dioxide (f)	ND	528	3	ND	ND	ND

(a) Stretford solution from Beavon plus lean gas from Rectisol II, gas from coal lock-hopper, and gases from tar and ammonia recovery

(b) Includes 1,035 lb/hr of hydrogen sulfide dissolved in Stretford solution from the Beavon unit

(c) Hydrogen added to gas stream

(d) Air added

(e) Air for catalyst regeneration

(f) Solid sulfur is recovered from gas stream at a rated 8,900 lb/hr from the Claus unit and 6,900 lb/hr from the Stretford unit

Adapted from reference 10

ND = no data