LIQUEFACTION ENVIRONMENTAL ASSESSMENT

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Abstract

Part of Hittman Associates environmental assessment of coal liquefaction processes has been the development of functionally discrete unit modules, composed of an aggregation of unit process operations. This paper presents an overview of the current liquefaction process technology and applicable control technology based on the unit module approach. Eleven unit modules are developed including: Coal Preparation, Hydrogenation, Pyrolysis/Hydrocarbonization, Hydrotreating, Catalytic Synthesis, Supercritical Gas Extraction, Phase Separation, Fractionation, Acid Gas Removal, Hydrogen/Synthesis Gas Generation, and Auxiliaries/Utilities.

INTRODUCTION

With the entry into an era of declining petroleum reserves, reduced discoveries, escalation of prices, and real or induced shortages, coal liquefaction technology has once more assumed a major role as a potential solution to liquid fuel problems. Currently some twenty-odd processes are in various stages of development by industry and federal agencies.

All liquefaction processes achieve the objective of producing liquids by yielding a material having higher hydrogen content than coal. Hydrogen is present in coal at a level of about 5 percent. In high-Btu gas it is roughly 25 percent. Fuel oils contain 9 to 11 percent hydrogen and gasoline about 14 percent. Whether the required hydrogen increase is obtained by adding hydrogen to the coal components or by stripping the hydrogen-rich components from the coal depends upon the particular process. It also affects the yield of liquid from the process.

Environmental Assessment Definition

In their efforts to assist in the development of an environmental assessment methodology protocol, the EPA IERL-RTP supported contractors have used the term environmental assessment to mean a continuing iterative study aimed at:

(1) determining the comprehensive multimedia environmental loadings and environmental control costs, from the application of the existing and best future definable sets of control/disposal options, to a particular set of sources, processes, or industries; and

(2) comparing the nature of these loadings with existing standards, estimated multimedia environmental goals, and bioassay specifications as a basis for prioritization of problems/control needs and for judgement of environmental effectiveness.

Included in Hittman Associates' liquefaction environmental assessment program are six basic components. They are: (1) Current Process Technology Background, (2) Environmental Data Acquisition, (3) Current Environmental Background, (4) Environmental Objectives Development, (5) Control Technology Assessment, and (6) Environmental Alternatives Analysis. This paper presents an overview of the modular approach used during Hittman's initial efforts at current process technology description and control technology assessment.

UNIT MODULES

Although significant technical differences exist between the liquefaction processes, many individual unit and process operations are common to two or more processes. Further, at the present stage of development, most published process designs are only conceptual, and significant differences between the current design and future commercial plants are certain to arise.

To avoid the redundancy of studying each unit operation in each process, and the hazards associated with conceptual designs, unit operations were grouped within a series of functional modules. Each module was structured to perform a specific function, for example, hydrotreating, to remove S, N and O from liquid hydrocarbons.

Each module is composed of one or more individual unit operations or unit processes. Because of the functional orientation, the streams entering and leaving a module will be essentially the same, even though the individual components of the module may be slightly different for different processes.

Process streams are defined as any stream entering a module and any stream leaving a module having as its destination another module. Waste streams are defined as those streams leaving a module having as destinations either a control system or the environment. Eleven modules were developed to characterize the unit operations contained in coal liquefaction processes.

Coal Preparation Module

Operations which are performed in the coal preparation module include crushing, grinding, pulverizing, screening, drying, slurry preparation, and preheating. In general, crushing, grinding, drying, and screening will be included in the module for all processes. Pulverizing is included as well for several processes, and all of the hydrogenation processes which use a solvent will use slurry preparation and preheating.

Process streams leaving this module are either prepared coal or heated coal/oil slurry. Waste streams include particulates from mechanical operations and stack gas from drying. Processes which slurry and preheat the coal will have an additional stack gas stream as well as potential venting of gases.

Hydrogenation Module

In this module hydrogen is added to the "coal molecule." Portions of the coal which can be converted to soluble compounds dissolve leaving an insoluble carbon residue and mineral matter in suspension.

Variations include catalytic, non-catalytic, and donor solvent systems. Since these operations are usually carried out at high pressure, a pressure reducing operation may be included. The crude liquid/solid leaving the reactor may be cooled using waste heat boilers or heat exchangers.

There are only two process streams leaving the module. These are the crude coal liquid and, in some processes, a gas stream. No waste streams are generated continuously, but occasional venting may occur, and periodic replacement of the catalyst will be necessary.

Pyrolysis/Hydrocarbonization Module

High temperature gases are used to strip volatiles from and/or to chemically add hydrogen to coal in this module. Pyrolysis requires introduction of steam and oxygen to react with the coal while hydrocarbonization uses heated hydrogen.

Vapor leaving the pyrolysis or hydrocarbonization reactor is cooled by quenching with either water or oil. Non-condensibles are used elsewhere in the process. Waste heat recovery may precede the quench. The condensed liquid may contain an aqueous phase as well as particulates, and a separation step may be included in the module.

Process streams leaving the module are the crude quenched liquid, noncondensible gas, and the char. Waste streams may include water used to cool the char and excess quench water.

Hydrotreating Module

The purposes of hydrotreating are to remove sulfur, nitrogen, and oxygen compounds via conversion into hydrogen sulfide, ammonia, and water and to further hydrogenate the crude oil.

Hydrotreating is a high pressure and high temperature process. Heat is supplied by plant fuel gas to preheat the crude and the reaction itself is exothermic. The reactor product is depressurized and cooled. An oil and an aqueous phase are formed. The oil is stripped to remove hydrogen sulfide and ammonia.

Process streams leaving the section are a sour gas stream from depressurization, the sour stripping stream, and the purified oil. Waste streams include stack gas, sour water, intermittent vents, and periodic catalyst disposal or regeneration.

Catalytic Synthesis Module

This module catalytically converts synthesis gas into liquid hydrocarbons or methanol.

Operations are heating and pressurizing the feedstock, catalytic conversion, cooling the raw product, and separating byproduct gases and water from the raw product. A sulfur guard reactor may be used to protect the catalyst.

Process streams are liquid hydrocarbons and hydrocarbon gases. Waste streams are water, spent catalyst, spent sulfur guard absorbent, and stack gas.

Supercritical Gas Extraction Module

This module performs a function similar to the hydrogenation module via a completely different route.

A solvent, above its critical temperature and pressure, is used to extract soluble and fusible components from coal. Operations required are compression and heating of the solvent, separation of the solvent/solute mixture from remaining coal material, reduction of mixture pressure, and finally, separation of the extract and solvent.

Phase Separation Module

Solids, liquids and gases are separated in numerous different unit operations. In coal liquefaction processes, situations arise involving two, three, and four phases. The phase separations are gas/solid, gas/liquid, liquid/solid, liquid/liquid, gas/liquid/solid, and gas/liquid/liquid/solid.

Operations include cycloning, filtering, centrifuging, decanting, settling, and depressurizing.

Depending upon where in the process the module is located, process streams and waste streams may be solids, liquids, and gases. Process streams generally will be oils, carbon containing residues, and fuel gases. In general, waste streams will be water, ash or slag, and tars or other heavy residuals. Phase separation modules may be incorporated as an operation in other modules. Under that circumstance, they are not treated as a separate module.

Fractionation Module

The fractionation module separates crude feedstock into product and byproduct components.

Primary operations used may be distillation, vacuum flashing, and stripping. In addition, heat must be supplied, depressurization may be necessary, and cooling is required.

Process streams are: product and byproduct to further processing or storage, recycle process solvent, fuel gases, and solvents. Waste streams may include water and gases, and in rare instances liquid hydrocarbons and solid or semisolid residues.

Acid Gas Removal Module

This module separates hydrogen sulfide from hydrocarbon gas streams. In some instances, carbon dioxide may be separated also.

Operations in the primary section consist of one or more gas/liquid or gas/solid contacts, appropriate temperature and pressure adjustment, and demisting, when necessary. Supporting operations are absorbent regeneration and make up.

Product gas, free of acidic constituents is the main process stream in this module. The primary waste stream is regenerator off gas, hydrogen sulfide, carbon dioxide, or both. Depending upon the system used, spent solid absorbent or solution will also be a waste stream.

Hydrogen/Synthesis Gas Generation Module

The purpose of this module is to produce a reducing gas composed of hydrogen and carbon monoxide. In the case of Fischer-Tropsch and methanol synthesis, the gas is used in catalytic synthesis to produce liquid hydrocarbons. In the other liquefaction processes, the gas is used for either hydrogenation and/or hydrotreating.

Coal gasification, particulate removal, CO-shift, and gas cleanup are the major operations in this module. In addition, there are quenching, cooling, and drying operations. Waste heat recovery is included.

The only process stream leaving the module is the synthesis gas. Because of the numerous operations included in this module, waste streams predominate. Ash, slag, or char will be discharged from the gasifier. Water streams originate in the quench and cooling operations. Particulates are removed from the gas and tars, oils, and other organics are present. A carbon dioxide/hydrogen sulfide stream exits the gas cleanup operation. Spent catalyst will be periodically removed.

Process operations involved in hydrogen generation are the same as those in synthesis gas generation except in two respects: carbon residue or char, supplemental with coal, is used instead of coal alone; and the CO-shift reaction is controlled to produce a much higher hydrogen content. All equipment, operations, process streams, and waste streams are the same as in synthesis gas generation.

Auxiliaries and Utilities Modules

These include the oxygen generation module, where nitrogen is the only waste stream; the make up water module in which waste streams include sludges, brines, and spent regenerant solutions; the cooling water module where waste streams are cooling tower blowdown, evaporation and drift; the stream power generation module where waste streams include stack gas, boiler blowdown and ash; the the product storage module in which the waste streams are intermittent and fugitive losses of vapors, liquids, and particulate during loading and storage periods.

Unit Modules Summary

Table 1 presents a summary of the modules and module components contained in nineteen coal liquefaction processes. Some modules are present in all liquefaction processes. Other modules are specific for particular liquefaction processes, such as catalytic synthesis and supercritical gas extraction.

CONTROL TECHNOLOGIES

Liquefaction processes produce a range of airborne, waterborne, solid, and transient wastes. The data acquisition phases of our environmental assessment program are being structured to provide a more quantified picture of liquefaction related pollutant constituents than that presently available. The modular approach will provide the framework upon which pollutant control technologies can be comparatively assessed.

Air Emissions

The predicted sources and characteristics of air emissions within each process module are specified in Table 2. Flue gas emissions include carbon monoxide, nitric oxides, sulfides, ammonia, and unburned hydrocarbons. The preparation of the coal for further treating can produce particulates and possibly hydrocarbon vapors. Cataly.t removal and replacement may be a source of particulates, ammonia, and hydrogen sulfide. In fractionation, uncondensed gases such as H_2S and CO_2 may be emitted. Cooling tower drift and blowdown contains biocides, anti-corrosive agents, and other solids found in the circulating cooling water. Combustion of fuels may produce air emissions such as NO_x, SO_x, hydrocarbons, particulate, and fly ash, depending upon the fuel type used. Hydrocarbons, sulfides, sulfur dioxides, ammonia, and particulates all may be found in the vapors emitted from flash drums used in the phase separation module. From acid gas removal, CO_2 gases are emitted. These gases may include some CO, hydrocarbons and sulfides.

There is a variety of equipment available to control different types of emissions. Table 3 indicates some of the more common technologies. Control of air emissions may result in increased water pollution or solid waste. Particulates containing hydrocarbons, organic and inorganic sulfur compounds, heavy metals, cyanides, etc., must be disposed of. Scrubber wastes include sludges and water containing similar contaminants.

Water Emissions

Almost all modules reject a wastewater stream. The volume and characteristics of water from each module is process specific, but similarities exist among constituents of wastewater from a particular module for all processes utilizing the module. Water requirements for coal liquefaction processes vary

TABLE 1

MODULE COMPONENTS CONTAINED IN MAJOR LIQUEFACTION PROCESSES

LIQUEFACTION PROCESS

MODULE/ MODULE COMPONENT \ LIQUEFACTION PROCESS	SRC I	SRC II	H-COAL	EXXON	SYNTHOIL	COED	CSF	COSTEAM	CLEAN COKE	FISCHER-TROPSCH	GARRETT	COALCON	METHANOL	TOSCOAL	ADL	GAS EXTRACTION	BERGIUS	SOLID PHASE HYDROGENATION	LIQUI-COAL
1. COAL PREPARATION	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
A. Crushing	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
B. Drying	+	+	+	+	+	+	+	o	+	+	+	+	+	+	+	+	+	+	+
C. Pulverizing	+	+	+	+	+	o	+	+	+	+	o	+	+	o	+	+	+	+	+
D. Slurry Preparation	+	+	+	+	+	o	+	+	+	o	o	o	o	o	+	+	+	o	+
E. Preheating	+	+	+	+	+	o	+	+	+	o	o	+	+	o	+	+	+	o	+
2. HYDROGENATION	●	●	●	●	●	X	●	●	●	X	X	X	X	X	●	X	●	●	●
A. Catalytic	o	o	+	o	+	o	o	o	o	o	o	o	o	o	o	o	+	o	o
B. Non-catalytic	+	+	o	+	o	o	+	+	+	o	o	o	o	o	+	o	o	+	+
3. PYROLYSIS	X	X	X	X	X	●	X	X	●	X	●	●	X	●	X	X	X	X	X
A. Direct	o	o	o	o	o	+	o	o	o	o	+	o	o	+	o	o	o	o	o
B. Hydrocarbonization	o	o	o	o	o	o	o	o	+	o	o	+	o	o	o	o	o	o	o
C. Cooling	o	o	o	o	o	+	o	o	+	o	+	+	o	o	o	o	o	o	o
D. Quenching	o	o	o	o	o	+	o	o	+	o	+	+	o	o	o	o	o	o	o
4. HYDROGEN/SYNTHESIS GAS-GENERATION	●	●	●	●	●	●	●	●	●	●	●	●	●	X	●	X	●	●	●
A. Coal Gasification	+	+	+	+	+	o	+	+	o	+	o	Y	+	o	+	o	+	+	+
B. Char Gasification	+	+	o	o	o	+	o	o	+	o	+	+	o	o	o	o	o	o	o
C. Particulate Removal/ Quenching	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	o	+	+	+
D. Shifting	+	+	+	+	+	+	+	Y	+	+	+	+	+	o	+	o	+	+	+
5. CATALYTIC SYNTHESIS	X	X	X	X	X	X	X	X	X	●	X	X	●	X	X	X	X	X	X
A. Trace Sulfur Removal	o	o	o	o	o	o	o	o	o	+	o	o	+	o	o	o	o	o	o
B. Synthesis Reaction	o	o	o	o	o	o	o	o	o	+	o	o	+	o	o	o	o	o	o
C. Cooling	o	o	o	o	o	o	o	o	o	+	o	o	+	o	o	o	o	o	o
6. PHASE SEPARATIONS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
A. Vapor & Gas Separation	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o
B. Solids Removal	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
7. HYDROTREATING	X	X	X	●	X	●	●	X	X	X	●	X	X	X	●	X	X	X	●
A. Preheating	o	o	o	+	o	+	+	o	o	o	+	o	o	o	+	o	o	o	+
B. Catalytic Reaction	o	o	o	+	o	+	+	o	o	o	+	o	o	o	+	o	o	o	+
C. Cooling	o	o	o	+	o	+	+	o	o	o	+	o	o	o	+	o	o	o	+
8. FRACTIONATION	●	●	X	●	X	●	●	X	●	●	X	●	●	X	●	●	●	X	●
A. Product Separation	+	+	o	+	o	+	+	o	+	+	o	+	+	o	+	+	+	o	+
B. Condensation	+	+	o	+	o	+	+	o	+	+	o	+	+	o	+	+	+	o	+
9. ACID GAS REMOVAL	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
A. Absorption	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
B. Regeneration	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
10. SUPERCRITICAL GAS EXTRACTION	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	●	X	X	X
A. Extraction	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	+	o	o	o
B. Quenching	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	+	o	o	o

KEY:

● - Modules Required; X - Modules Not Required; + - Module Components Required; o - Module Components Not Required
Y - Optional Module Components

TABLE 1 (Continued)

LIQUEFACTION PROCESS

MODULE/ MODULE COMPONENT \ LIQUEFACTION PROCESS	SRC I	SRC II	H-COAL	EXXON	SYNTHOIL	COED	CSF	COSTEAM	CLEAN COKE	FISCHER-TROPSCH	GARRETT	COALCON	METHANOL	TOSCOAL	ADL	GAS EXTRACTION	BERGIUS	SOLID PHASE HYDROGENATION	LIQUI-COAL
11. AUXILIARY SYSTEMS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
A. Oxygen Generation	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	+	+
B. Makeup & Cooling Water Treatment	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
C. Steam & Power Generation	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
D. Product & Byproduct Storage	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

TABLE 2

SOURCES AND CHARACTERISTICS OF AIR EMISSION

Module	Source	Emission Characteristic
Coal Preparation	Grinding, Pulverizing, and Drying	Particulate, Hydrocarbon vapors
Hydrogenation	Preheater Flue Gas	CO, NO_x, H_2S, NH_3, hydrocarbons
Pyrolysis and Hydrocarbonization	Preheater Flue Gas	CO, NO_x, H_2S, NH_3, hydrocarbons
Hydrotreating	Preheater Flue Gas Catalyst Removal and Replacement	CO, NO_x, H_2S, NH_3, hydrocarbons particulates, NH_3, H_2S
Catalytic Synthesis	Heater Flue Gas	CO, NO_x, N_2S, NH_3, hydrocarbons
Extraction	None	None
Phase Separation	Flash Drum Vapors	Hydrocarbons, sulfides, Sulfur dioxide, Ammonia, particulate
Fractionation	Uncondensed Gases From Condenser	H_2S, CO_2
Gas Cleaning Module	CO_2 Gas Stream	CO_2, H_2S, CO, Hydrocarbons, Sulfides
Synthesis Gas/Hydrogen Generation	Acid Gas CO_2 Stream Driers Flue Gas	CO_2, CO, Hydrocarbons, Sulfides, CO, NO_x, H_2S, NH_3, hydrocarbons
Auxiliary Systems and Utilities	Cooling Tower Drift Boiler Combustion Gases	Biocides, Anticorrosive, Agents, Solids, NO_x, SO_x, Hydrocarbons, Fly ash

TABLE 3

COMMON CONTROL TECHNOLOGIES

Particulate Controls	SO_2 Controls
Dry inertial separators	Wet Limestone Scrubbing
cyclones	Limestone Injection
multiclones	
baffle chambers	
settling chambers	
impingement separators	
gravity settling chambers	**Sulfur Recovery**
Electrostatic precipitators	Claus Plants
Bag (Fabric Filters) Houses	Stretford Plants
Wet Scrubbers	
NO_x Control	**Gaseous Pollutant Control**
Reduction in excess air and temperature	Flares Absorbtion
Evaporation Controls (Mainly Hydrocarbons)	
Storage tank modifications	
Inspections and maintenance	
Vapor collection and recovery equipment	

and wastewater may be treated and reused. In such cases, less of the water utilized will leave the plant as effluent. The type of control and/or treatment required depends on the physical, chemical, and biological properties of the waste stream. All waste streams do not have the same characteristics thus the control technology applicable to waste streams from certain modules will be more extensive than from others. Wastewater streams from some modules may be combined prior to treatment or pretreated separately and then combined for further treatment and discharge.

The sources and characteristics of wastewater streams are shown in Table 4. Coal storage piles have large surface areas and problems may arise as a result of stormwater runoff. Water may react with coal and minerals to form acids or to extract organics, sulfur, and soluble inorganics. Suspended matter are commonly carried by runoff water.

In the pyrolysis and hydrocarbonization module, a significant amount of foul water is generated by the quench operation. Such water contains phenols, tar, light oil, ammonia, sulfides, chlorides, phenolics, and any other products of coal pyrolysis. Vapors separated from pressure let down systems are condensed and such condensates form waste streams also containing phenols, ammonia, light hydrocarbons, and dissolved salts, however the concentration of dissolved salts is lower than that of quench water. Water from the overhead condenser of the hydrotreater has ammonia and sulfides as the primary contaminants but phenols also may be present. Condensate water from fractionation contains sulfides, ammonia, oil, phenols, and dissolved solids. Cooling tower and boiler blowdown may contain high levels of dissolved solids.

Trace elements may appear in both the product and waste streams. Most of the heavy metals will remain in the ash but some of the trace elements will volatilize and may build up in the quench water. Others may be further carried over with acid gases and then appear with purge streams from the acid gas removal module. Of particular interest is the possibility of mercury, selenium, arsenic, molybdenum, lead, cadmium, beryllium, and fluorine in wastewater streams.

The complexity of the wastewater streams from coal liquefaction indicates a need for the utilization of a broad control technology which includes the various treatment processes shown in Table 5. The best practical control technology currently available (BPCTCA) will be a combination of some of these processes. Again, some waste streams will be treated through only part of the whole treatment system depending on the origin of the stream and its characteristics.

Wastewater from the coal preparation module is sent to a separate retention pond to permit the settling of suspended solids. Coagulants may be added for better removal efficiency. Acidity can be controlled by adding limestone. A low biological activity in the retention pond will control any organics that may be present. Higher concentrations of pollutants can be avoided by good housekeeping and by use of silos for storage of small quantities of coal on a day-to-day basis and by covering the coal storage piles with a coating of polymer or asphalt.

TABLE 4

SOURCES AND CHARACTERISTICS OF WASTEWATER STREAMS

Module	Source Description	Wastewater Stream	Constituents
Coal Preparation	Coal storage piles, crushing and grinding operations	Storm water runoff	Suspended particles, dissolved solids
Hydrogenation	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Pyrolysis and Hydrocarbonization	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Hydrotreating	Condensing overhead vapors	Condensate	Phenols, ammonia, sulfides
Synthesis Gas Generation	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
	Shifting Operation	Condensed unreacted water	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Catalytic Synthesis	Condensing overhead vapors	Condensate	Phenols, ammonia, sulfides
Phase Separation	Two or three stage pressure reduction	Condensate from overhead condensor	Oils, light hydrocarbons, phenols, ammonia, dissolved sulfides
Fractionation	Cooling overhead vapors.	Condensate	Light hydrocarbons, dissolved salts
Gas Cleaning	Absorption and regeneration operations	Purge Flows	Dissolved sulfides in gas removal solvent
Hydrogen Generation	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides, and chlorides
	Shifting Operation	Condensed unreacted water	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Supercritical Gas Extraction	Char quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Auxiliary Systems and Utilities	Cooling towers and boiler	Blowdown	Dissolved solids
	Plant yard area	Storm water runoff	Suspended particles, dissolved solids, traces of phenols, oils and tars

TABLE 5

WASTEWATER TREATMENT PROCESSES

Physical	Chemical	Biological
Sedimentation	Neutralization	Activated Sludge
Flotation	pH Adjustment	Trickling Filter
Oil Separation	Coagulation	Aerated Lagoons
Stripping	Precipitation	Waste Stabilization Ponds
Solvent Extraction	Oxidation	
Adsorption	Ion Exchange	
Combustion		
Filtration		

For oily waste streams containing high amounts of phenols and ammonia, recovery is generally desired. Ammonia is recovered by stripping. After the oil is separated, phenols are recovered by solvent extraction. A probable sequence of processing steps and control process(es) to clean up sour water is as follows:

Removal of H_2S, NH_3, CO_2, light gases
- Stripper

Initial oil and solids removal
- API separators
- Baffle plate separators

Further oil and solids removal
- Clarifiers
- Dissolved air flotation
- Filters

Organic waste removal
- Activated sludge
- Aerated lagoons
- Oxidation ponds
- Trickling filters
- Activated carbon
- Combination

Solid Wastes

Of the many waste streams rejected from various coal liquefaction modules, five basic types of solids waste can be identified. These are particulate coal, ash and slag residues, char, spent catalyst and spent absorbents. Treatment sludges are considered as solid waste generated by control technologies and are discussed below. Particulate coal is generated in the coal preparation module of each liquefaction process. Unreacted coal particles are present in the existing waste streams of other modules as well. Ash consists primarily of metallic oxides, compounds of silicon, aluminum, calcium, iron, magnesium, titanium, sodium, potasium and nickel being the major constituents. In addition, a variety of trace elements are present. Char, although utilized as fuel and to synthesize other process reactants, exits certain modules as waste in minute quantities. Spent catalyst is periodically discharged from modules utilizing them, as is spent absorbent from modules which use absorbents to protect catalysts from acid gases. The solid wastes exiting each module are summarized in Table 6.

Several modules have similar solid waste streams exiting. Spent catalyst and/or spent absorbent are the only solids exiting the hydrogenation, hydrotreating, catalytic synthesis, and gas cleaning modules. Both of these wastes are discharged intermittently. Some catalysts will need changing only every two to three years. The synthesis gas generation, phase separation, fractionation, and hydrogen generation modules will continuously reject ash residue with small amounts of coal and char particles. These streams are the major source of solid waste generated during coal liquefaction process.

In addition, control technologies will generate solid waste streams, including limestone sludges from sulfur dioxide removal systems and water treatment sludges. Calcium sulfite and calcium sulfate are the primary components of limestone sludges. The wastewater sludges will consist primarily of coal tars, sand, coal fines, and water treatment byproducts.

Coal dust particles are generated in the coal processing module. Bag house filters are generally considered the best method of controlling particulate emissions during processing operatons such as grinding and crushing. However, for transferring coal within the preparation module, other vacuum cleaning systems may be preferred. All remaining solid waste streams may be collected without specialized equipment.

Landfilling is the primary technique utilized in solid waste disposal. Ideally, landfill sites will

TABLE 6

MODULAR SOLID WASTE DISCHARGES

Module	Solid Waste: Particulate coal	Spent catalyst	Ash/slag (Mineral Matter	Char	Spent (sulfur guard) Absorbent (Zinc sulfide)	Remarks
Coal Preparation	+	0	0	0	0	
Hydrogenation	0	+	0	0	0	Spent catalyst not continuously generated
Pyrolysis/Hydrocarbonization	+	0	+	+	0	
Hydrotreating	0	+	0	0	0	Spent catalyst particles in gas or liquid stream
Synthesis Gas Generation	+	+	+	+	0	Spent catalyst not continuously generated
Catalytic Synthesis	0	+	0	0	+	
Extraction (Supercritical Gas Extraction)	0	0	+	0	0	
Phase Separations	+	0	+	+	0	Small amounts of unreacted char/oil may be present
Fractionation	+	0	+	+	0	Solids from donor solvent processes only
Gas Cleaning (Acid gas removal)	0	0	0	0	+	Some systems use sulfur guard absorbents
Hydrogen Generation	+	+	+	+	0	
Auxiliary Systems Utilities	+	0	+	+	0	Particulate product losses during handling, ash and particulates from coal/char burning boilers

+ denotes waste stream is generated in module
0 denotes waste stream is not generated in module

naturally prevent horizontal or vertical migration of solid waste constituent materials to ground or surface waters. Impervious liners may be necessary to assure this. Periodic sampling and analysis of potential leachates is an additional preventive measure.

Utilization of solid wastes to produce useful byproducts is also being considered, with primary emphasis on utilizing ash as a constituent of construction materials, such as asphalt and concrete blocks. Ash has also been used successfully, in the revegetation of mined-out areas. Scrubber sludges, elemental sulfur, phenols, naphtha, and ammonia are other byproducts which could be used beneficially.

Transient Pollutants

Waste streams produced during normal process operation are expected and provisions are made for their disposition on a continuous basis. Consideration must also be given to waste streams generated as a result of intermittent occurrences. These releases may be unplanned or accidental, caused by leaks, spills, upsets, startups, shutdowns, power failure, process equipment failures, slugging, surging, and overloading. They may also be caused by or occur during maintenance operations. Such releases have been termed transient pollutants. Because of their nature they are difficult to sample, analyze, and classify. However, if some thought has been given to these events, it is more likely that the impact of fugitive emissions can be minimized when they do occur. In many cases the best disposition of the waste stream is to return it to the process.

Spills and leaks will occur and provisions for cleanup and containment should be made. Pumps and valves are known sources of leaks. Solids handling equipment can cause problems. Belt conveyors or bucket elevators can break or jam causing spills or fires. In such cases, it may be necessary to dump materials in order to make repairs for resumption of normal operations. Vacuum cleanup trucks could be used to reclaim the spilled solids for reuse. Water flushing can be provided to wash residual solids and to flush oil spills to an "oily water" sewer system for recovery.

During startup, shutdown, or a plant upset, off specification products may be made. Rather than dispose of these materials through the waste treatment facilities, it will probably be much more desirable to store them and rework them into the proper specifications. This procedure, however, will require adequate storage. Enclosed storage will be needed for many of the liquids removed at shutdown. Vapors and particularly odors may be released. Water layers from separations will contain various sulfur, nitrogen, and oxygen compounds that should not be allowed to escape to the atmosphere. These liquids can be stored until a subsequent startup and used for recharge or they can be worked off through the wastewater treating systems.

Before maintenance is performed, the equipment or system will have to be purged to remove toxic and combustible gases. Purge gases should be sent to an incinerator or furnace. This will also be true for shutdowns. Certain catalysts or carbonaceous materials may be pyrophoric at high temperatures. Inert gas purge and cooling will be required to prevent fire.

In the case of plugging, it may be necessary to flush the system with a light oil or with water. Provision must be made to collect and store the cleaning stream until it can be either recycled or treated for disposal. Slugs of liquids may be sent to the flare because of upsets or surges. Serious fires or explosions could be caused if separators are not sized to prevent entrainment.

In general, inspection, monitoring, and maintenance programs are an essential part of controlling transient pollutants.

SUMMARY

A generally applicable modular approach to dividing coal liquefaction processes into groupings of unit operations based on function is proposed. The approach promises to be an effective way of comparatively assessing the waste streams from the wide variety of liquefaction processes. The advantages over alternative, in-

dividual process approaches are the ability to comparatively evaluate waste streams from dissimilar unit operations on the basis of module function and to allow for process designs changes as they evolve from conceptual pilot scale to full commercial size.

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