CONTROL TECHNOLOGY DEVELOPMENT FOR PRODUCTS/ BY-PRODUCTS OF COAL CONVERSION SYSTEMS

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Abstract

The objective of developing control technologies for the products and by-products of coal conversion systems is to permit the fullest utilization of these materials while controlling environmental pollution within acceptable levels. Products are defined as the primary marketable materials such as low, medium and high Btu gas; liquefied and solvent refined coal. By-products are all other potentially usable components of coal conversion systems.

Coal gasification and liquefaction processes were studied to establish the expected slate of products and by-products. Most processes produce recoverable quantities of sulfur, ammonia, phenol, naphtha, tars, tar oils, and char by-products. Lower temperature gasification processes produce a wide range of by-products; whereas higher temperature processes produce fewer by-products. The operating pressure of the gasifiers is a secondary variable. Almost all coal liquefaction processes yield a full slate of by-products.

Potential pollutants from products/by-products and their control needs are presented. A number of existing and developing technologies for upgrading by-products and for control of effluents are reviewed. On-going work on environmental data acquisition and control technology assessment are discussed.

INTRODUCTION

The economics and environmental impact of coal liquefaction and gasification systems in the U.S.A. will depend to a large extent on effective recovery and use of by-products. Such coal conversion by-products generally include phenol, tar, ammonia, char, ash, and sulfur.

The U.S. Environmental Protection Agency awarded a three-year contract to Catalytic, Inc. in September, 1976 to conduct a program aimed at development of control technology for the products and by-products of fuel conversion and utilization systems based on coal. This paper outlines the project scope, analyzes fuel conversion products and by-products and their pollution control needs, and reviews pertinent recovery and pollution control technologies.

For the purpose of this project, the following definitions apply: coal conversion systems are coal gasification and liquefaction processes. Products are the primary marketable fuel and feedstock materials such as low, medium, and high Btu gas; and solid and liquid hydrocarbons derived from coals. By-products are all other potentially usable components of coal conversion system yields.

PRODUCTS AND BY-PRODUCTS OF FUEL SYSTEMS

Figure 1 for coal gasification and Figure 2 for coal liquefaction define the major boundaries of products and by-products for these coal conversion systems. As indicated, basic process modules such as methanation, compression and dehydration, sulfur recovery, fractionation and hydrotreatment fall within the products and by-products area. Any other process and control techniques that might be applied for the recovery and upgrading of any product or by-product from such coal conversion systems would also be within the project's scope.

Coal Gasification

Table 1 shows coal gasification processes of current and potential interest along with their expected products and by-products. Principal subdivisions of coal gasification processes are in the low, intermediate, and high temperature operations. These may be further subdivided by operating pressure. Table 2 illustrates the quantities of products and by-products generated by a few selected processes.

A definite pattern emerges from examination of Table 1. The low temperature gasification processes tend to show a complete product and by-product slate, extending from fuel gas to ash or slag. As the temperature of gasification increases, recoverable quantities of

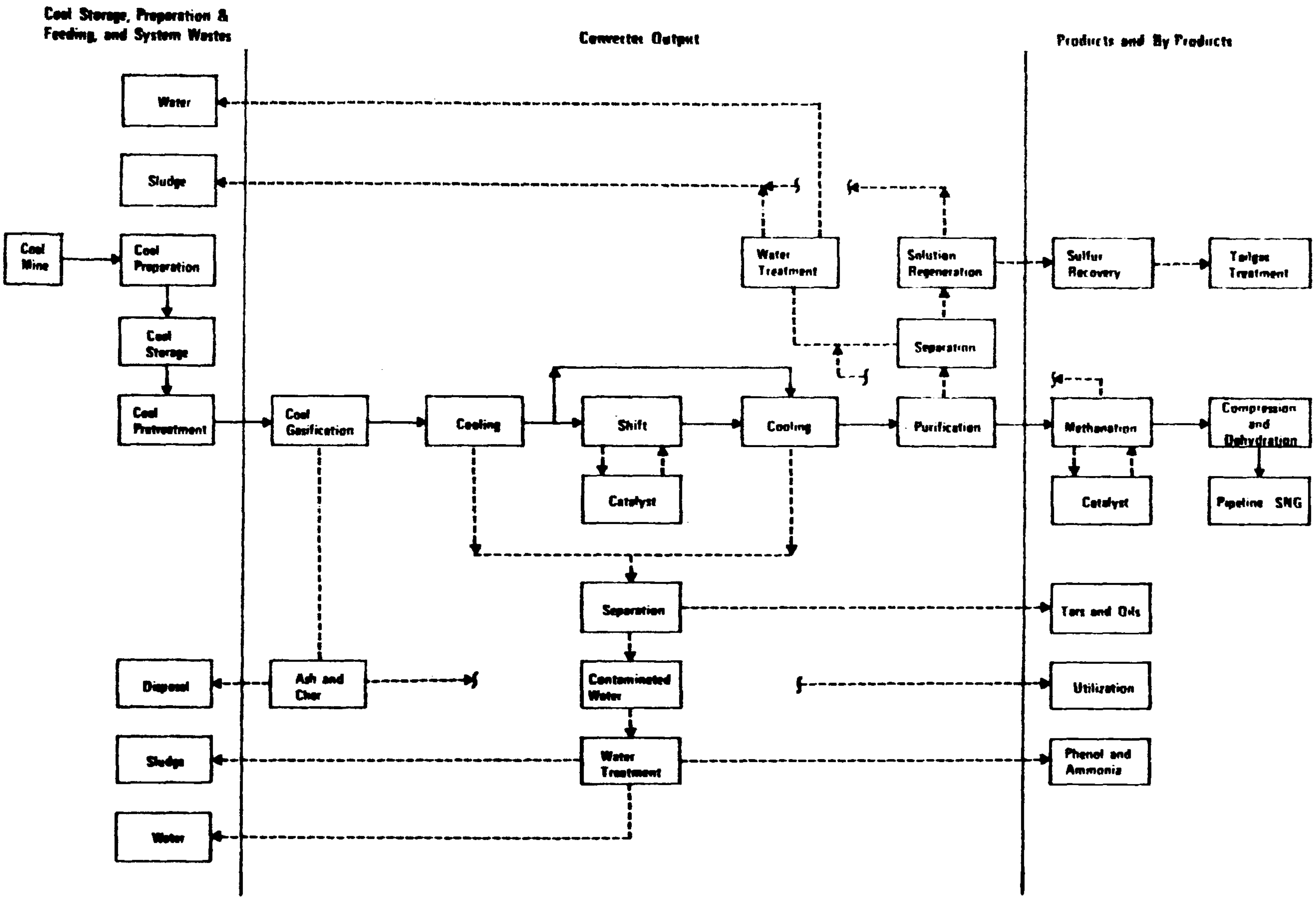

Figure 1. Hypothetical gasification flow diagram.

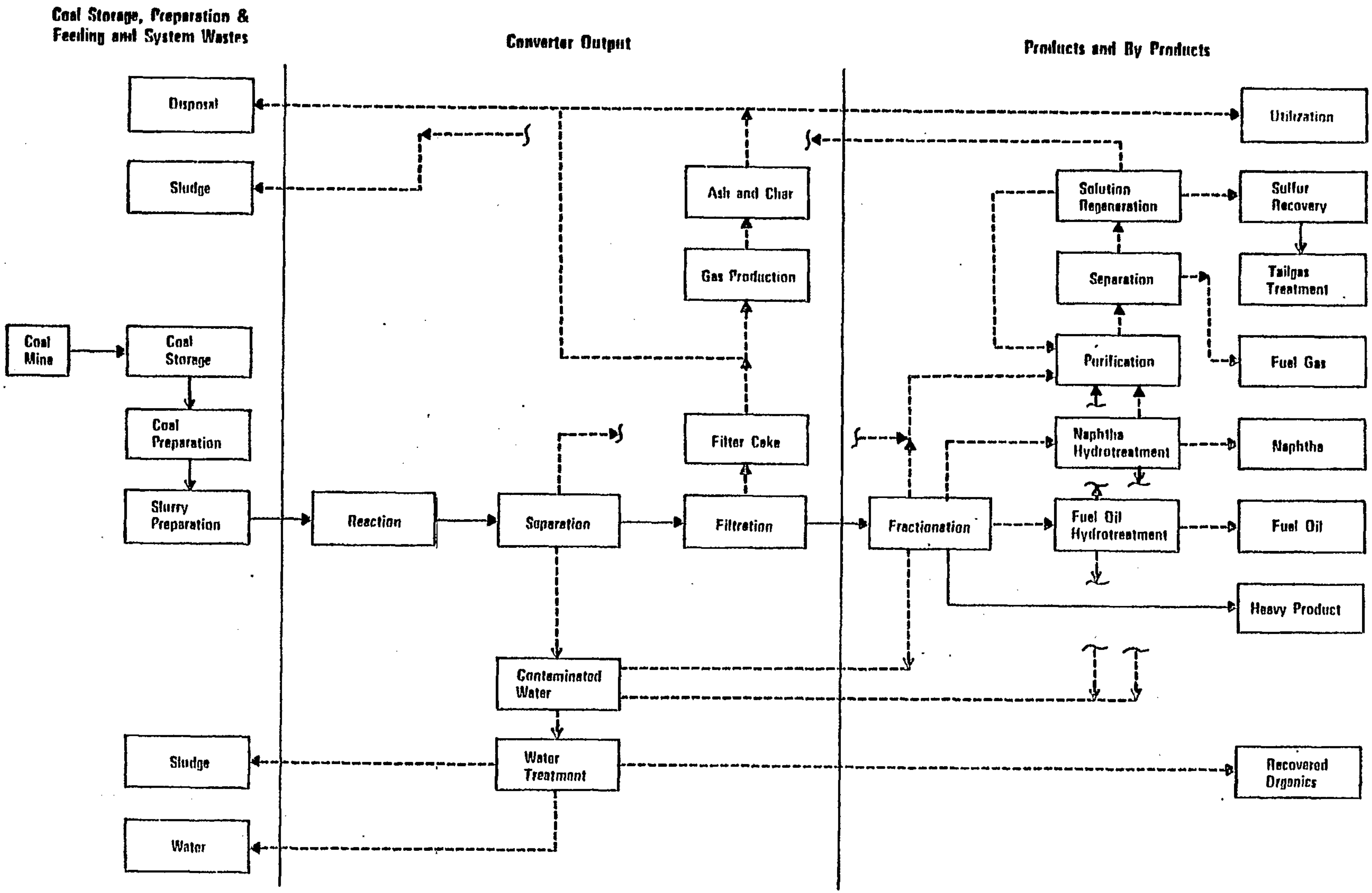

Figure 2. Hypothetical liquefaction flow diagram.

TABLE 1

COAL GASIFICATION PROCESSES PRODUCT/BYPRODUCT AND FUEL SYSTEM SIMILARITIES

LEGEND:

P – Product/By-Product present in recoverable quantities.

Neg. – Negligible or small amounts present.

– Stream present in traces.

N.A. – Information not available, not complete, or not reported at this time.

	CLASSIFICATION OF FUEL SYSTEMS													
	Low Temperature Fixed Bed				Intermediate Temperature Fluidized Bed				High Temperature Entrained Bed		Dolomite Acceptor		Coal Pyrolysis	
	Low Pressure	Intermediate Pressure			Low Pressure	Inter-mediate Pressure	High Pressure		Low Pressure	High Pressure	Intermediate Temperature Intermediate Pressure		Entrained Inter. Temp. Low Pressure	Fluid Bed Inter. Temp. Inter. Pressure
Products/By–Products	Wellman – Galusha	Lurgi	BGC/Lurgi Slagging Gasifier	Pressurized Stirred Fixed Bed – Morgantown	Winkler	U – Gas	Synthane	Hygas	Koppers–Totzek	Bi–Gas	CO_2 Acceptor	Westinghouse–Advanced Gasifier	Battelle – Ash Agglomerating	Garretts Coal Gasification
High BTU Gas – SNG	P	P	P	–	P	–	P	P	P	P	P	–	P	P
Low (Intermediate) BTU Gas	P	P	P	P	P	P	–	–	P	–	–	P	P	P
H_2S – Acid Gas/Sulfur	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Ammonia	P	P	P	P	N A	P	P	P	Neg.	P	P	N.A.	P	N.A.
Phenols	P	P	P	P	Neg.	Neg.	P	P	–	–	N.A.	–	–	–
Naphthas/Benzenes	N.A.	P	P	–	–	N.A.	P	P	–	–	N.A.	–	–	–
Tar Oils/Light Oils	P	P	P	P	–	Neg.	P	P	–	–	N.A.	–	–	–
Tars	–	P	P	P	–	Neg.	P	–	–	–	N.A.	–	–	P
Char/Unreacted Coal	P	–	–	P	P	P	P	P	–	–	P	–	–	P
Ash/Slag	–	P	P	P	–	–	–	–	P	P	–	P	P	–

TABLE 2

PRODUCTS/BYPRODUCTS OF DIFFERENT COAL GASIFICATION PROCESSES

Products/By-Products	Wellman-Gallusha	Lurgi	K-T	Bumines Stirred Bed	Winkler	Synthane	Hygas
Product Gas, SCFD	28.4MM (170 BTU/SCF)	288 MM (SNG)	524 MM (290 BTU/SCF)	995 MM (160 BTU/SCF)	912 MM (280 BTU/SCF)	250 MM (SNG)	260 MM (SNG)
Sulfur, lb/hr	777	15,600	23,600	24,200	50,400	11,400	55,500
Tars, lb/hr	1,153	88,800	neg.	75,600		43,200	
Tar Oil, lb/hr		48,600	neg.				
Phenol, lb/hr	120	11,300	neg.		neg.	4,000	1,300
Ammonia, lb/hr (anhydrous)	219	21,400	neg.	11,100	to claus	13,200	11,300
Hydrocarbon, lb/hr		20,000 (naphtha)				7,400 (BTX, naphta)	39,800
Char/Ash, lb/hr (Slag)	1,768 (ash)	476,000 (ash)	24,400 (ash, slag)	114,100 (ash)	372,500 (char)	362,000 (char)	139,000 (char)
Coal, lb/hr Feed	21,000 Bitum. 3.9% S	1.94 MM 1.07% S	0.7MM 3.8% S	0.7MM W. Ky.#9 3.9% S	1.68 MM Lignite 3.3% S	1.18 MM Pitts.Seam 1.6% S	1.06 MM Ill.#6 4.75% S

heavier tars begin to disappear in favor of lighter products. For the high temperature gasification processes, essentially the only product is fuel gas or products for synthesis; other by-product quantities are too low for recovery to be economic.

Operating pressure also changes yields, as shown in Table 1. As the pressure increases, the product slate becomes heavier. For example, in intermediate temperature processes, products such as naphthas, tar oils, and tars proceed from zero or negligible quantities to significant quantities as operating pressure increases.

For some reason naphtha doesn't appear in the reported products from the Stirred Fixed Bed Process and the Wellman-Galusha process[1,2,3,4,7,8]. From analogy with the other low temperature and intermediate temperature processes, a naphtha cut would be anticipated from both these systems. It is surmised that either the data available are incomplete, or perhaps the yields as reported include the naptha fraction as part of the tar oil stream. The pattern shown in this table indicates that the product slate for other coal gasification processes could be predicted by comparing the gasifier operating conditions with those listed.

Coal Liquefaction

Table 3 shows the relationship between various coal liquefaction processes and the product slates from these processes. In this table distinct patterns of product slates do not readily emerge as in the coal gasification processes. However, the following observations can be made.

- All the liquefaction processes produce an acid gas stream which will contain sulfur and other contaminants. In this regard, they are similar to coal gasification processes, which also produce an acid gas stream. Consequently, H_2S removal and sulfur recovery will be required for all coal processing plants.
- The liquid product distribution shows a range from syncrudes to naphtha and gas oils. However, all will contain varying amounts of sulfur, nitrogen, and metal contaminants which will have to be removed by subsequent upgrading treatments.
- Only the solvent refined coal (SRC) process yields a solid fuel. In all other processes, additional hydrogenation results in the formation of liquid products.
- Almost all the processes produce a char (coke and unreacted coal combined with ash) by-product with some fuel value. These by-products will require additional processing (e.g., specifically-designed combustion units) to utilize the carbon value and, thereby, increase the energy efficiency of the conversion process.
- Phenols and/or ammonia will be present in the aqueous waste streams in most cases and could be recovered as by-products.

Of all the liquefaction processes, solvent refined coal is the most developed. Two SRC pilot systems, 6 and 50 tons/day, are currently operating with various coals. Based on these results, salable product and by-product distribution for a nominal 20,000 ton/day plant using a Kentucky coal, containing 3.45 percent sulfur and 10.4 percent ash on dry basis, was calculated as follows:

Product	Quantity, Ton/day (*)
SRC	9,950
Light Oils (IBP-350° F)	750
Medium Oils (350-450° F)	2,210
Heavy Oils (450-780° F)	166
Fuel Gas	361
Sulfur	450
Ammonia (25%)	37
Phenolics	28

(*) Based on input coal (2% moisture) of 21,011 ton/day.

Effect of Coal Type

While the type of coal charged will not significantly affect the kinds of products and by-products generated by conversion, it will significantly affect how their quantities are distributed. For a particular process, coals with higher sulfur and nitrogen concentrations would obviously give higher proportions of S and NH_3 by-products. More information and testing with different coals will be necessary to establish the effects of coal type on the

TABLE 3

COAL LIQUEFACTION PROCESSES—PRODUCT/BYPRODUCT AND FUEL SYSTEM SIMILARITIES

LEGEND:

P — Product/By-Product present in recoverable quantities.

Neg.— Negligible or small amounts present.

— Stream present in traces.

N.A. — Information not available, not complete, or not reported at this time.

	CLASSIFICATION OF FUEL SYSTEMS								
	Catalytic Hydrogenation			Solvent Extraction		Hydrocarbonization		Pyrolysis	
				Non-Catalytic Solvent Hydrogenation	Catalytic Solvent Hydrogenation	Intermediate Temperature	High Temperature	Low Temperature Fluid Bed	Intermediate Temperature Entrained Bed
Products/By-Products	H–Coal	Synthoil	Gulf Catalytic Coal Liquefaction	Solvent Refined Coal (SRC)	EXXON Donor Solvent Process	Coalcon Hydrocarbonization	Clean Coke Multi-Product Process	Char, Oil Energy Development (COED)	Garrett Process
High B.T.U. Gas — SNG, LPG, ethylene, hydrocarbon, product gas.	P	P	N.A.	P	P	P	P	—	P
Low (Intermediate) BTU Gas — Fuel Gas, Synthesis Gas	—	—	N.A.	—	—	—	—	P	P
H_2S Acid Gas/Sulfur	P	P	P	P	P	P	P	P	P
Ammonia	P	P	P	P	N.A.	P	P	N.A.	N.A.
Phenols	Neg.	N.A.	P	P	N.A.	P	P	P	—
Benzenes	N.A.	N.A.	P	—	N.A.	P	P	P	—
Naphtha, Gasoline	P	—	P	P	P	P	P	—	—
Syncrudes	P	P	P	—	—	—	—	P	P
Middle Distillates, Fuel Oil	P	—	P	P	P	P	—	—	P
Gas Oils, Neutral Oils, Chemical Oils	P	—	P	—	P	P	P	—	—
Residual Fuel Oils	P	P	P	P	—	—	—	—	—
Tars (Tar Acids and Tar Bases)	—	—	—	—	—	P	P	—	P
Solvent Refined Coal	—	—	—	P	—	—	—	—	—
Char/Coke/Unreacted Coal	P	P	N.A.	P	—	P	P	P	P
Ash/Slag	P	—	N.A.	P	P	—	P	—	—

distribution of products and by-products for each coal conversion process.

POLLUTION CONTROL NEEDS

A variety of chemical compounds are generated in the form of products, by-products,and wastes during coal gasification andliquefaction processing. Many are toxic pollutants. For example,

- Sulfur compounds such as H_2S, SO_2, mercaptans, COS
- Nitrogen compounds such as NH_3, HCN, NO_x
- Hydrocarbons, polynuclear aromatics, heterocyclic compounds.

The objective of control technology development is to permit the fullest utilization of the different products and by-products while controlling environmental pollution within acceptable levels.

Products and By-products

As Fuel. The purpose of coal conversion systems is to produce fuels and chemical feedstocks. Combustion gases from the fuel products should preferably be capable of direct discharge to the atmosphere with no further treatment. This will generally require prior removal of sulfur compounds and particulates in the coal conversion process. In addition, nitrogen compounds will also have to be removed tobring NO_x emissions after combustion within acceptable limits.

For example, high temperature H_2S cleanup processes for the purification of low and medium Btu gas will increase the overall energy efficiency of the coal conversion process, but will create NO_x emission problems. The nitrogen compounds (e.g. ammonia) in the raw gas are not removed by these cleanup processes, so if the "purified" fuel gas is charged directly to a furnace, the nitrogen compounds will be converted to NO_x and exit in the flue gas. This calls for development of control technology that can be used in conjunction with high temperature gas purification processes for removing the nitrogen compounds prior to combustion.

A number of by-product streams may also serve as fuel. These include tail gas streams, tarry and oily liquids and chars. Control techniques will be required for sulfur, particulates, and NO_x emissions in these cases also.

As Chemical Feedstocks. Almost all products and by-products from coal conversion units may be used as chemical or petrochemical plant feedstocks. For example, low and medium Btu gas from coal gasification may be used as the starting material for production of hydrogen, ammonia, methanol, or Fischer-Tropsch liquids. For all these processes, pretreatment of the feed to remove the sulfur contaminant is necessary.

The liquids from coal conversion plants can serve as feedstocks for production of benzene, toluene, and xylene as well as for higher aromatics such as naphthalene. In addition, specialty solvents with high aromatic content may be produced. The coal-derived liquids used for aromatic production may be charged either to catalytic reforming units or dealkylation units. Before catalytic reforming, the liquid must be pretreated to remove sulfur and nitrogen impurities. Dealkylation takes place simultaneously with gasification of contaminants. The gaseous contaminants must be removed by control techniques such as scrubbing.

Gaseous Wastes

Generally, gaseous emissions from coal conversion plants originate from the following sources: raw material handling and pretreatment; vent gases from startup, shutdown and lock hopper operations; by-product recovery, storage and upgrading; waste treatment; acid gas removal and sulfur recovery; catalyst regeneration; and power generation. Various sulfur, nitrogen, hydrocarbon compounds, and particulates are present in air emissions.

Air emissions are controlled by the following four basic control modules:

- Sulfur control
- Particulate control
- Hydrocarbon control
- Nitrogen oxide control

At present, sulfur is the only by-product recovered from gaseous emissions to any large extent.

Liquid Wastes

The liquid waste (gas liquor) contains tars, tar oils, phenols, and ammonia as well as virtually every contaminant found in the fuel conversion systems. Large amounts of particulates, CO_2, H_2S, chloride and sulfate are present. Cyanide and ferrocyanide occur in the aqueous layer. Reported trace elements include antimony, arsenic, boron, bromine, cadmium, fluorine, lead, mercury, and nickel.

Little information exists as to how these contaminants will be distributed throughout the recovered by-products. Many contaminants will probably appear in the crude by-products. These pollutants would have to be removed for environmental protection.

At least five different by-product streams are produced from typical Lurgi plant liquid wastes: tar, tar oil, crude phenol, ammonia, and sulfur. The foregoing by-products are recovered from a gas liquor with the following typical composition:

Component	Approximate Composition, ppm
Phenols	3,000-4,000
Ammonia (free)	500-750
Ammonia (fixed)	100-200
Sulfides (total)	200-250
Suspended tar, oil	5,000
Cyanides	50
CO_2	10,000
Fatty acids	500

The proposed El Paso Burnham complex Lurgi plant will produce 288 million SCFD synthetic pipeline quality gas, gasifying 1.07% sulfur coal at the rate of 1.944 million lb/hr. Figure 3 shows the distribution of the various by-products from this plant. A sizable portion of the by-products are absorbed in, or condense out with, the organic and aqueous condensates as the gases are first quenched with water and then cooled. The heavier tars separate out first in the gasifier waste heat boiler and are called "tarry gas liquor." Further downstream, in the gas cooling section, the tar oils with the remaining tars condense out forming the "oily gas liquor." In the acid gas removal step, H_2S and naptha separate out. Naphtha goes directly to a storage tank. H_2S-containing acid gases are processed further to recover the sulfur. Table 4 gives the material balance for the gas liquor treatment[5].

Ammonia and sulfur will be recovered as commercial-grade materials, but further upgrading will be required to meet demands for explosives and fertilizers. Other by-products will also require upgrading[6].

Solid Wastes

Solid wastes are composed of the ash residue plus the accompanying unrecovered carbon or hydrocarbons from the coal charge. If filtration is used in the liquefaction process for ash separation, filter precoat will also be present.

To make coal processing economic, the carbon values from char should be recovered. Two recovery possibilities are on-site combustion of char for steam generation or for hydrogen manufacture. When used in this manner, removal of particulates and sulfur will be required to clean up the stack gases before discharging to atmosphere.

Solid residues such as ash and filtercake will contain trace metals from coal. Recovery of some of these minerals may be possible in the future. If not, then the solid wastes must be disposed of in ways that protect the environment.

In considering pollution control needs, it is necessary to stay cognizant of the interrelationships existing among liquid, gaseous and solid wastes. For example, spent catalysts can present a solids disposal problem if not reused, or cause an air pollution problem when regenerated. The contaminants that normally deactivate catalysts are sulfur compounds, nitrogen compounds, and heavy metals. Catalyst activity can be maintained or lengthened by burning these contaminants off the catalysts. The off gases from catalyt regeneration will contain sulfur, nitrogen, and hydrocarbon compounds and will also require controls to meet air pollution emission requirements.

CONTROL TECHNOLOGY

This section reviews some of the important existing control technologies or classes of technologies.

Earlier discussion established that a full slate of products, extending from fuel gas to ash,

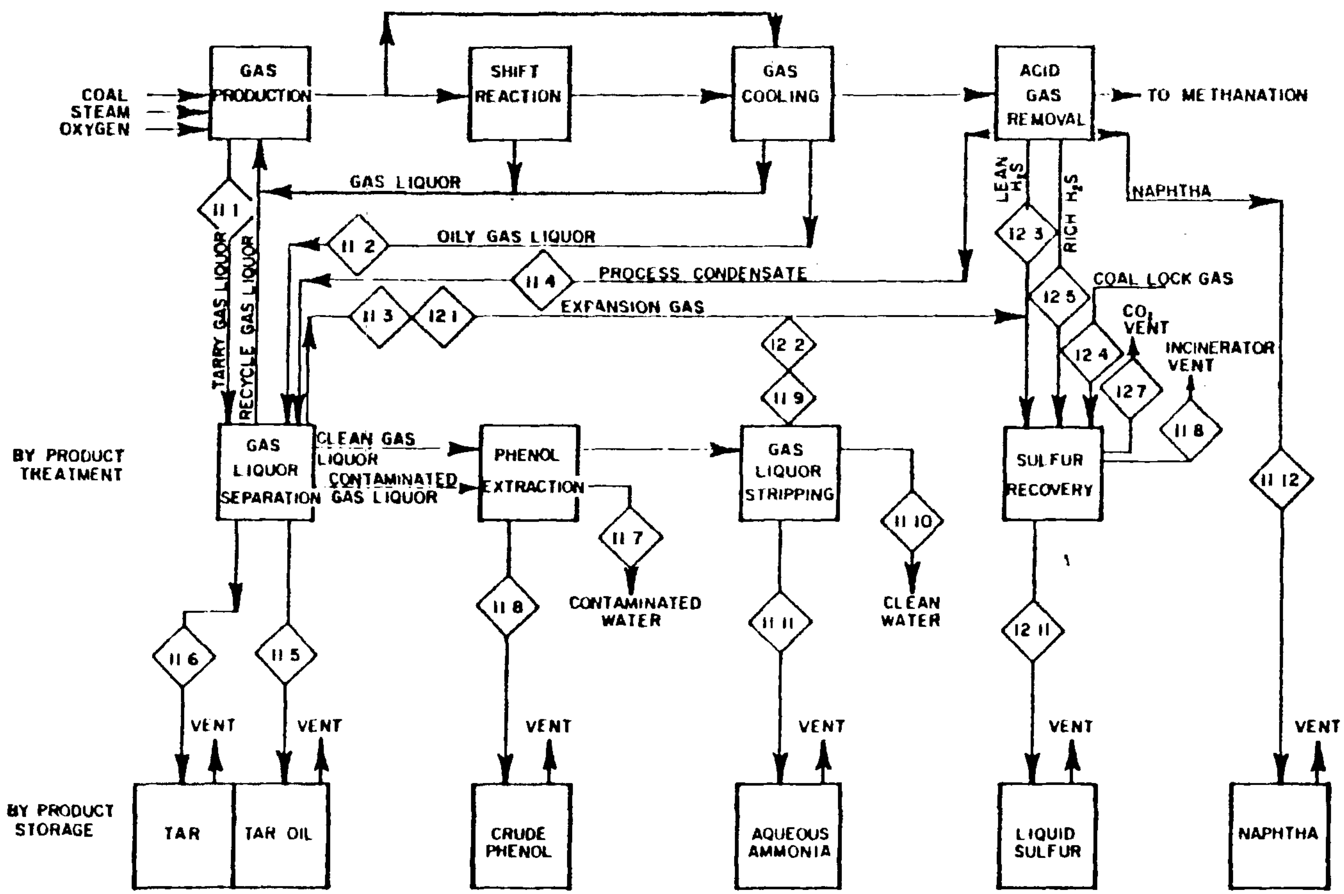

Figure 3. By-product from Lurgi plant.

TABLE 4

MATERIAL BALANCE FOR GAS LIQUOR TREATMENT

Stream Number	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	11.10	11.11	11.12
Stream Description	Tarry Gas Liquor	Oily Gas Liquor	Expansion Gas	Process Condensate	Tar Oil	Tar	Contaminated Gas Liquor	Crude Phenol	Acid Gas	Clean Water	Aqueous Ammonia	Naphtha
Gas Phase, lb/hr												
Component												
Water	--	--	2,030	--	--	--	--	--	8,870	--	--	--
Tar	--	--	--	--	--	--	--	--	--	--	--	--
Tar Oil	--	--	--	--	--	--	--	--	--	--	--	--
Recoverable Crude Phenol	--	--	--	--	--	--	--	--	--	--	--	--
Unrecoverable Phenol & Organic	--	--	--	--	--	--	--	--	--	--	--	--
Ammonia	--	--	--	--	--	--	--	--	--	--	--	--
H_2S	--	--	315	--	--	--	--	--	280	--	--	--
CO_2	--	--	59,700	--	--	--	--	--	8,570	--	--	--
CO	--	--	70	--	--	--	--	--	--	--	--	--
CH_4	--	--	50	--	--	--	--	--	--	--	--	--
Monohydric Phenols	--	--	--	--	--	--	--	--	--	--	--	--
Polyhydric Phenols	--	--	--	--	--	--	--	--	--	--	--	--
Other Organics	--	--	--	--	--	--	--	--	--	--	--	--
Contained Sulfur	--	--	--	--	--	--	--	--	--	--	--	--
Naphtha	--	--	--	--	--	--	--	--	--	--	--	--
Total Dry Gas, lb/hr	--	--	62,165	--	--	--	--	--	17,720	--	--	--
Liquid Phase, lb/hr												
Component												
Water	165,000	1,180,000	--	103,000	--	--	164,000	--	--	1,190,000	82,000	--
Tar	79,900	8,900	--	--	--	88,000	--	--	--	--	--	--
Tar Oil	14,600	34,000	--	--	48,600	--	--	--	--	--	--	--
Recoverable Crude Phenol	210	11,100	--	--	--	--	--	--	--	--	--	--
Unrecoverable Phenol & Organic	130	4,100	--	--	--	--	--	--	--	--	--	--
Ammonia	--	21,600	--	--	--	--	--	--	--	240	21,400	--
H_2S	300	300	--	--	--	--	--	--	--	--	10	--
CO_2	17,200	54,000	--	--	--	--	--	--	--	--	3,660	--
CO	70	--	--	--	--	--	--	--	--	--	--	--
CH_4	40	--	--	--	--	--	--	--	--	--	--	--
Monohydric Phenols	--	--	--	--	--	--	3	9,100	--	24	--	--
Polyhydric Phenols	--	--	--	--	--	--	70	1,600	--	900	--	--
Other Organics	--	--	--	--	--	--	60	560	--	3,200	--	--
Contained Sulfur	--	--	--	--	(73)	(240)	--	--	--	--	--	--
Naphtha	--	--	--	--	--	--	--	--	--	--	--	20,000
Total Liquid, lb/hr	277,450	1,314,000	--	103,000	48,600	88,000	164,133	11,260	--	1,194,364	107,070	20,000

NOTE: Crude estimate based on following assumptions:

1. Monohydric phenols* reduced to 20 PPM per Lurgi
2. 60% of polyhydric phenols recovered
3. 15% of other organics recovered
4. Crude phenol stream contains 5% other organics
5. Phenols recovered are 50% monohydric and 50% polyhydric

* Assumptions 2-4 were presented by Beychok in reference (1) for a *crude* determination of gasification effluent composition.

can be obtained from either the gasification or liquefaction process. Furthermore, the impurities in these streams are generally similar, including sulfur and nitrogen compounds, heavy metals, and particulates.

Identical products from coal gasification and coal liquefaction processes will contain the same contaminants and therefore, may be processed in similar type pollution control systems. For example, sulfur contamination of fuel gas or phenol contamination of aqueous wastewater, whether from coal gasification or coal liquefaction, could have similar treatment and recovery units.

It makes sense then to discuss control technologies primarily in terms of the class of contaminants. Product/by-product identification can serve as a secondary variable while coal gasification or liquefaction is of incidental importance. Control technologies discussed here will be limited to the following classes of contaminants:

- Sulfur and nitrogen compounds
- Particulates
- Heavy metals/trace contaminants

Other pertinent control technologies are touched on briefly, but many such as for hydrocarbon, phenol removal, and wastewater treatment, cannot be covered in depth at this time.

Sulfur and Nitrogen Compounds

Combined sulfur and nitrogen in the products and by-products from coal conversion plants can be converted to H_2S and NH_3 by hydrogenation, or to SO_2 and NO_x by oxidation.

H_2S can be scrubbed from the gaseous products and converted to elemental sulfur. Similarly, SO_2 can be removed from the gases, either by dry or wet scrubbing. The scrubbed SO_2 may then be converted to a variety of different forms, such as elemental sulfur, sulfates, or bisulfites, for disposal or utilization. Control of NO_x compounds by similar scrubbing processes are in the state of development. Currently, various combustion modifications are the best means to control NO_x.

Hydrogenation. In the presence of hydrogen, hydrogenation of the sulfur and nitrogen can occur either thermally (as in coal gasification plants) or catalytically (as in catalytic coal liquefaction plants). For example, the gasification of residue and chars to produce hydrogen results in the formation of H_2S and NH_3.

Catalytic hydrotreating is a well established process in the petroleum industry for the removal of sulfur and nitrogen contaminants. It has been found in the petroleum industry that the operating conditions required for denitrification are much more severe than those required for desulfurization, especially if organic nitrogen is present in thermally cracked stocks. Also, special design care is required for treating some light distillates (as from ethylene plants) because of the gum-forming tendencies of these stocks.

Distillates derived from ethylene plants appear to be the most analogous to those from coal for catalytic hydrogenation treatments. The process flow module should be similar, with hydrotreating followed by fractionation or stripping to remove the H_2S, NH_3, and H_2O formed in the reactors. Prevention of equipment plugging from gum formation is an important design consideration in both cases.

When heavey distillates are hydrotreated in fixed bed reactors, the process module is similar to that for catalytic treating of light distillates--hydrotreating followed by fractionation or stripping. However, the hydrotreating conditions of temperature, total pressure, hydrogen partial pressure, and space rate are more severe than those used for light distillates. At these more severe conditions, and with higher concentrations of sulfur and hydrogen in the process streams, high alloy materials of construction are required. Desulfurization achieved in these units is in the range of 75 to 90%.

The problem with the use of fixed beds for hydrotreating heavy distillates is rapid deactivation of the catalyst caused by heavy metals build-up. Thus, some means of maintaining the catalyst activity by total or partial replacement of the catalyst is necessary. Other reactor designs, such as fluidized or ebullating beds, may circumvent this difficulty. With these designs spent catalyst can be continuously removed from the reactor and replaced by fresh catalyst. Regardless of reactor design, the general overall processing module of hydrotreating followed by stripping would be the same.

Hydrotreating of coal-derived heavy distillates would be expected to follow the same process modules as for petroleum-derived heavy distillates. The concentration of heavy metals in the distillate cut would dictate the type of reactor design necessary. Heavy distillate from both coal gasification and coal liquefaction plants would require hydrotreating units having similar modules.

The catalysts used for hydrotreating are of the cobalt-molybdenum type which resist catalyst poisoning. Catalyst deactivation results from buildup of carbonaceous deposits or heavy metals. Carbonaceous matter can be readily removed from the catalyst in-situ, by steam-air oxidation. Heavy metals cannot be removed. But in the case of light distillates, they are not present in significant concentrations, and should not present a contamination problem. Additionally, catalyst will become deactivated over a long period by loss of active surface area due to time-temperature effects.

H_2S Removal and Sulfur Recovery. A number of commercial processes are available for removing sulfur from fuel gas, as shown in Table 5. These operate at low temperature, so if the scrubbing unit is followed by methanation, the scrubbed gas must be reheated.

To avoid reheating, and thereby increase the energy efficiency of the process, new high temperature H_2S cleanup units are under development (Table 6). One disadvantage of high-temperature cleanup schemes is omission of the initial quench step, which removes NH_3 and particulates from the raw gas. So, removal of the ammonia from fuel gas at high temperature requires further development. High temperature removal of the particulates may be affected by one of the processes shown in Table 7.

Numerous sulfur recovery processes of the direct conversion type exist. These can be classified as either dry oxidation or liquid phase oxidation. The principle of operation involves the oxidation of sulfur compounds to elemental sulfur. The two most widely used direct conversion processes are the Claus (dry oxidation) and the Stretford (liquid phase oxidation) processes.

The commercial Stretford process recovers inorganic sulfur from acid gases containing less than 15% H_2S. A packed absorber removes H_2S from acid gases, using Stretford solution absorbent, which is mainly sodium metavanadate, sodium anthraquinone disulfonate (ADA), sodium carbonate, and bicarbonate in water. Sulfur recovery between 98%-99% is possible. This process is insensitive to H_2S/CO_2 ratio, and operates over wide pressure ranges. Temperature limitations are between ambient to 120° F.

The process does not remove organic sulfur, and it requires pretreatment removal of large quantities of SO_2, HCN or heavy hydrocarbons. It produces a purge wastewater stream containing spent Stretford solution, which will require treatment[9].

The Claus process effectively controls sulfur emissions and recovers elemental sulfur from gas streams containing high concentrations of H_2S (at least 10-15%). In most cases, tail gas treatment is also necessary.

Tail Gas Treatment. Tail gas cleanup processes, when combined with a Claus unit, can provide an overall sulfur removal efficiency of up to 99.9%. Commercially available tail gas cleanup processes include:

Process Name	Type
SCOT Beavon Cleanair Cataban Trencor-M	Catalytic hydrogenation of sulfur compounds to H_2S and then removal by absorption processes or recycle to a Claus unit.
Sulfreen CBA	Continuation of Claus reaction at low temperatures (245-270° F)

An alternative to tail gas treatment is to incinerate the gases and then scrub the resulting SO_2. This set of processes was developed to handle tail gases from furnaces, smelters, and pulp mills, where SO_2 is the main pollutant rather than H_2S.

SO_2 scrubbing systems have several advantages over the H_2S processes. The scrubbers are less affected by process upsets, are not susceptable to catalyst poisons, and can scrub SO_2 from very dilute mixtures. But scrubbing

TABLE 5

LOW TEMPERATURE H_2S CLEANUP PROCESSES

PROCESSES	ABSORBENT	STATUS
Chemical Solvent Type		
MEA	Monoethanolamine	Commercial
DEA	Diethanolamine	Commercial
TEA	Triethanolamine	Commercial
Alkazid	Potassium dimethyl amino acetate	Commercial
Benfield	Activated potassium carbonate solution	Commercial
Catacarb	Activated potassium carbonate solution	Commercial
Physical Solvent Type		
Sulfinol	Sulfolane + di-isopropanolamine	Commercial
Selexol	Polyethylene glycol ether	Commercial
Rectisol	Methanol	Commercial
Direct Conversion		
Stretford	Na_2CO_3 + anthraquinone sulfonic acid	Commercial
Townsend	Triethylene glycol	Commercial
Drybed Type		
Iron Sponge	Hydrated Fe_2O_3	Commercial

TABLE 6

HIGH TEMPERATURE H_2S CLEANUP PROCESSES

PROCESS	ABSORBENT	STATUS
Bureau of Mines	Sintered pellets of Fe_2O_3 (25%) and fly ash	Pilot
Babcock and Wilcox	Fe_2O_3	Experimental
CONOCO	Half calcined dolomite	Pilot
Air Products	Calcined dolomite	Abandoned
Battelle Northwest	Molten carbonates (15% $CaCO_3$)	Pilot
IGT-Meissner	Molten metal (proprietary)	Conceptual
Air Products	Fe_2O_3	Experimental

TABLE 7

HIGH TEMPERATURE PARTICULATE REMOVAL SYSTEMS

TYPE OF REMOVAL SYSTEM	MANUFACTURER	STATUS
Mechanical Collectors		
Cyclones	Buell, Ducon & Others	Commercial
Tornado	Aerodyne	Commercial
Bed Filters		
Granular	Combustion Power Co.	Under Development
	Ducon	Under Development
Panel	C.U.N.Y.	Under Development
Rex	Rexnord	Commercial
Sonic Agglomeration Collection Systems		
Alternating Velocity Precipitator	Braxton	Under Development
Scrubbers		
Fused salts	Battelle	Under Development
Filters		
Metal and Ceramic	Selas and Others	Commercial
Electrostatic Precipitators	Research-Cottrell and others	Commercial

processes are more expensive than other tail gas treatment methods.

Ammonia Recovery. NH_3 formed by the hydrogenation reactions can be scrubbed from the reaction gases by water and subsequently recovered by steam stripping. Several processes are available, for example--Chevron,Phosam-W, and others based on lime treatment to free fixed ammonia for later steam stripping.

Phosam-W, a U.S. Steel Corp. developed process, uses aqueous acid ammonium phosphate solution to scrub ammonia from gases. The scrubbed sour water is then stripped of ammonia with steam and the acid ammonium phosphate solution is recycled.

The Chevron process separates ammonia, carbon dioxide, and hydrogen sulfide from liquid waste streams. Another system, consisting of a pairing of Phosam-W and Firma Carl Still, recovers hydrogen sulfide (for sulfuric acid manufacture) and ammonia from sour water[10].

Particulates

Equipment for controlling particulates in gas streams includes cyclones, bag filters, electrostatic precipitators, and wet scrubbers. Particle size distribution is one of the important parameters necessary to predict the separation efficiency of these devices. High temperature removal of particulates may be effected by one of the processes shown in Table 7.

Heavy Metals/
Trace Contaminants

Heavy metals and trace contaminants are so numerous, and cover such a wide field of physical and chemical properties, that any discussion of control methods should be on an individual basis. Therefore, this paper offers only a few generalized remarks on this class of contaminants.

Determination of the concentration and distribution of heavy metals in the coal feed and in the effluents and product streams of the coal conversion plant is of prime importance. Some preliminary estimate of these values can be attempted by consideration of the physical and chemical characteristics of these elements, and of the compounds they may form in the system. However, ultimate testing and analysis in plant studies will be necessary to establish these distributions. These may then be compared to the allowable safe concentration limits, as set by EPA.

Another concern with regard to heavy metals is their effect on catalyst activity. Heavy metals contained in the feed to catalytic units often will be adsorbed on the surface of the catalyst, causing its deactivation. If, in a particular situation, this occurs at a very slow rate, the catalyst is merely discarded when its activity has fallen to an uneconomic level. In other cases, the catalyst may be protected by placing guard cases ahead of it, or by periodically or continuously drawing off some spent catalyst and replacing it with fresh catalyst. It should be noted here that spent catalyst may have high concentrations of heavy metals or other contaminants, and if regeneration is attempted, these contaminants could be released in a short period of time at high concentrations, causing a health problem.

Additional Control
Technologies

A large number of other control technology techniques not covered here are applicable in upgrading operations of products and by-products. Examples include methanation, catalytic synthesis, catalytic cracking, hydrocracking, catalytic reforming, and fractionation. The other broad control areas are the gas, liquid, and solid waste treatment techniques. These and other control approaches are shown in Table 8[11].

CONTROL TECHNOLOGY ASSESSMENT AND DATA ACQUISITION

Little operating data on control technology for either pilot or commercial scale coal conversion systems exist in the literature. Data acquisition by actual field testing, therefore, should be given top priority for control technology.

In this regard, EPA has initiated projects to (1) design laboratory units needed to evaluate feasible controls for coal conversion products and by-products streams, and (2) develop laboratory treatability screening procedures to

TABLE 8

CONTROL APPROACHES

o Gas Treatment

- Mechanical Collection
- Electrostatic Precipitators
- Filters (fabric, granular, etc.)
- Liquid Scrubbers/Contactors (aqueous, inorganic, organic)
- Condensers
- Solid Sorbents (mol sieves, activated carbon)
- Incineration (direct and catalytic)

o Liquids Treatment

- Settling, Sedimentation
- Precipitation, Flocculation, Sedimentation
- Evaporation and Concentration
- Distillation, Flashing
- Liquid-Liquid Extraction
- Gas-Liquid Stripping
- Neutralization
- Biological Oxidation
- Wet Thermal Oxidation
- Activated Carbon Adsorption
- Ion Exchange System
- Cooling Tower (wet & dry)
- Chemical Reaction and Separation
- Centrifugation and Filtration

o Solids Treatment

- Fixation
- Recovery/Utilization
- Processing/Combustion
- Chemical Reaction and Separation
- Oxidation/Digestion
- Physical Separation (specific gravity, magnetic, etc.)

o Final Disposal

- Pond Lining
- Deep Well Reinjection
- Burial and Landfill
- Sealed-Contained Storage
- Dilution
- Dispersion

o Process Modification

- Feedstock Change
- Stream Recycle

o Combustion Modification

- Flue Gas Recycle
- Water Injection
- Staged Combustion
- Low Excess Air Firing
- Optimum Burner/Furnace Design
- Alternate Fuels/Processes

o Fuel Cleaning

- Physical Separation (specific gravity, surface properties, magnetic)
- Chemical Refining
- Carbonization/Pyrolysis
- Liquefaction/Hydrotreating (HDS, HDN, Demetallization)
- Gasification/Separation

o Fugitive Emissions Control

- Surface Coatings/Covers
- Vegetation
- Leak Prevention

o Accidental Release Technology

- Containment Storage
- Flares
- Spill Cleanup Techniques

TABLE 9

R & D ACTIVITIES TO UPGRADE COAL CONVERSION PRODUCTS/BYPRODUCTS

Investigator	Project Title	Funding
Arco Chemical Co.	Catalytic Hydrotreating of Coal-Derived Liquids	ERDA (Project Completed)
Bartlesvile Energy Research Center	Refining Process Technology	ERDA
The Dow Chemical Co. and Pittsburgh Energy Research Center	Chemicals from Coal Liquids	ERDA
Exxon Research and Engineering Co.	Chemical Properties of Synthoil Products and Feed	ERDA Exxon
Hydrocarbon Research, Inc.	Demetallization of Heavy Residual Fuel Oils	EPA
M.I.T.	Catalytic Desulfurization and Denitrification	EPA
Pittsburgh Energy Research Center	Petrochemicals from Synthesis Gas	ERDA
Sandia Labs	Mechanisms of Deactivation and Reactivation of Catalysts	ERDA
Universal Oil Products, Inc.	Characteristics of Coal-Derived Liquids	ERDA
Air Products	Characteristics of SRC Liquids	ERDA

TABLE 10

LIST OF PRODUCTS/BYPRODUCTS AND SOME OF THEIR FINAL PRODUCT POSSIBILITIES

Products/By-Products	Examples of Final Product Possibilities
1. Aqueous wastewater containing ammonia, phenol and tar, etc.	Ammonia, crude phenol and tar
2. Crude phenol	Natural phenol, refined cresylics, phenolic pitch
3. Tar and tar oil	Benzene, toluene and xylene (BTX)
4. Naphthas	Ethylene
5. H_2S Acid Gas/Sulfur	Sulfur/Sulfuric Acid
6. Spent Catalyst	Regenerated catalyst
7. Char	Hydrogen, or fuel gas
8. Ash	Recovered heavy metals
9. Low BTU gas, medium BTU gas	SNG, fuel, feedstocks for chemicals such as NH_3 and CH_3OH
10. High BTU gas	SNG, chemical feedstock
11. Syncrudes	Refinery products such as gasoline and fuel oil
12. Middle distillate oil	Fuel oil
13. Gas oils	Lubricants, cat-cracker feedstock
14. Residual fuel oils	Coke, fuel oil
15. SRC	Coal fuel, high purity coke

determine how an environmentally harmful stream can be made less harmful through application of appropriate control techniques.

Most of the control technologies discussed earlier are being used in the petroleum, petrochemical, and coke oven by-products industries. It is of utmost interest to know how these technologies are working, and whether their performance characteristics can be duplicated in the synthetic fuels industry.

For this reason, EPA is currently sponsoring a study of the coke oven by-products industry control techniques to determine which are applicable to the coal conversion industry. This work was begun recently and will be reported later. A companion study is being conducted to determine which of the control techniques from the petroleum industry are applicable to coal conversion systems.

A number of research and development activities are being funded by EPA and ERDA to upgrade coal conversion products and by-products. Some of these are shown in Table 9. The impetus for engaging in these activities is illustrated in Table 10 which presents examples of the many marketable chemicals potentially recoverable from the upgrading of coal conversion products and by-products.

CONCLUSIONS

The economic justification of coal conversion systems depends to a large extent on being able to develop technology (1) that will permit upgrading products and by-products into additional marketable chemicals and (2) that will accomplish this goal without substantive adverse impact on the environment.

Generally, product and by-product utilization will require removal of sulfur and nitrogen contaminants before their use as fuel or chemical feedstocks. Some of the more important control needs include H_2S, SO_2, NO_x, hydrocarbon and particulate removal from gaseous effluents; removal of phenol, ammonia, sulfide, dissolved organics, heavy metals, and cyanides from aqueous waste streams; and prevention of solid waste leachate problems. When such pollutants are removed from waste streams and converted to usable products, downstream waste treatment problems and environmental impacts are automatically improved. By-product recovery and upgrading control technologies are, therefore, an important part of the overall environmental management program.

Little operating data on control technology for either pilot or commercial scale coal conversion systems exist in the literature. At the present, most of the control technologies that are applicable for the products and by-products of coal conversion systems are being used in the petroleum, hydrocarbon, and coke oven industries. However, their applicability and limitations have yet to be determined by actual use and field testing with different coal conversion systems.

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