RTGI-008

OCCUPATIONAL HEALTH ASSESSMENT
STATUS AND REQUIREMENTS FOR
DIRECT AND INDIRECT COAL LIQUEFACTION

Purchase Order
Report

FINAL REPORT

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1.0 SUMMARY

Coal liquefaction has been a sporadically commercial technology since the World War I era, targeted primarily to feedstock production for the chemical industry. Because of this market orientation, coal liquefaction for a synthetic fuels industry will require far greater production capacity and larger plants than traditional technologies. Current DOE programs are designed to resolve hardware and process problems anticipated in the scale-up procedure to demonstrate (beginning around 1984) the technologies as commercially feasible.

Two generic coal liquefaction technologies offer paralell paths for synthetic liquid fuels -- direct (coal hydrogenation) and indirect (gasification/"Fischer-Tropsch" reaction). Important process stream constituents which are common to both types of coal liquefaction technology include:

- Tar fractions, including polynuclear aromatic hydrocarbons (PAH) Most of the PAH is composed of 2-ring and 3-ring non-mutagenic aromatics.
- Tar acids, primarily simple phenols.
- Tar bases, primarily aromatic amines and heterocyclics.
- Ammonia (NH_3).
- Hydrogen sulfide (H_2S).

Direct liquefaction processes frequently contain these agents in their products, as well as intermediate steps. Certain components of the plant may also generate carbon monoxide (CO). Indirect liquefaction processes produce more CO and less tar, but as a result of the downstream conversion reactions also generate:

- Methanol (CH_3OH)
- Formaldehyde (HCHO)
- Metal carbonyls, particularly iron carbonyl, $Fe(CO)_5$.

In general, areas of greatest occupational exposure risk involve:

1) Feedstock entry into pressurized sections of the plant;
2) Waste product/by-product pressure letdown;
3) Process sampling ports under pressure;
4) Reactor interiors during shutdown/maintenance.

For direct liquefaction plants, these maximum hazard sites (from industrial hygeine surveys) correspond to the solids separation/recovery units, solvent recovery units, coal/solvent preparation units.

Industrial hygeine studies to date have identified carcinogenic tar fractions as The major occupational health hazard, the highest-molecular weight fractions being the most carcinogenic. To date, however, no PAH constituent accuragely reflects this potential hazard.

Best estimates for a susceptible worker population for a 1.2 Mbbl/day synthetic fuels industry range from 20,000-400,000 on-site personnel, depending on plant size. Cancer cases have been reported for workers in at least one liquefaction plant, but cancer mortality statistics generally do not show convincingly any occupational trend.

Most health effects research related to occupational criteria for coal liquefaction technology has focused on surrogate materials which are found in the process stream constituents. A majority of these represent rapid bioassay screening tests for mutagenicity, carcinogenicity and the like.

Bioassay tests are valuable for determining whether a material is toxic in some way, but are not intended to serve as a basis for exposure dose-response hazard evaluations in support of occupational criteria. Additional research (generic to all forms of coal conversion) to quantify exposure dose-responses characteristics can provide the proper foundation for worker risk assessments.

The principal research needs with respect to major criteria constituents (CO, H_2S, NH_3, phenol and cresol) revolve around the establishment of an appropriate fugitive emission marker substance or hazard indicator. For tar fractions, generally, the tradeoff dilemma between analytical sophistication/information content, and sampling errors due to incomplete extractions, must be satisfactorily resolved.

Integration of the requisite occupational health-related research and monitoring/characterization activities into the technology developments schedule offers the best prospect for building worker protection into the coal liquefaction-synthetic fuels industry. A plan for implementing these activities in coordination with the technology development schedules is recommended.

> *The synthetic fuels development schedule offers NIOSH an opportunity to factor occupational health safeguards into the emerging technology from the outset.*

2.0 INTRODUCTION

Over the next ten years, it is planned that coal liquefaction will reappear as a viable commercial technology in the United States. Although liquefaction technology has existed since World War I, its application in industry has been dormant in the U.S. since the early 1960's. However, the long-standing national need for liquid fuels has spurred the development of new generation direct and indirect liquefaction technologies as an alternative to petroleum imports.

This new phase of technology development offers NIOSH a unique opportunity to build solutions and safegaurds to adverse occupational health consequences into the emerging technologies as a front end activity.

NIOSH has actively pursued industrial hygeine and medical surveillance criteria for defining worker safeguards as the liquefaction technologies mature. To date, five documents have emerged from this NIOSH involvement (Refs. 1-5). These reports draw heavily upon industry data and literature for facilities no longer in operation; also information obtained first-hand during a walk-through study at a current Department of Energy (DOE) pilot plant facility. There are, in addition to the facilities described above (Refs. 1-5), several relatively small commercial liquefaction plants in Europe and the SASOL plants located in South Africa.

In this report, we complement the earlier NIOSH efforts by providing the following new emphases:

- *A generic overview of present and emergine coal liquefaction technology -- for both direct and indirect liquefaction.*
- *A programmatic focus on relating future NIOSH activity to the Department of Energy (DOE) timetables for liquefaction development.*
- *An orderly basis for incorporating industrial hygeine requirements into the technology developments, with emphasis on expected R & D needs.*
- *A prediction of susceptible worker populations based on previous experience with the technology.*

3.0 TECHNOLOGY STATUS

Coal liquefaction has been a sporadic commercial technology since the World War I era. Direct liquefaction, in which coal is dissolved and hydrogenated under high pressures and temperatures, was first described by Bergius (Ref. 6) in 1915. Indirect liquefaction, in which coal is gasified and subsequently converted to methanol (CH_3OH) or other liquid products, dates back to the BASF process (Ref. 7). These two technologies sustained the German economy during the latter phases of World War II (Ref. 6); they have also been prominent in the production of chemical feedstocks, both in the U.S. and abroad, since the 1930's (Ref. 8).

Except during the World War II period in Germany, with its economic disruptions, coal liquefaction output has generally been targeted to the synthetic chemicals industry (Refs. 6-8). For these purposes, very large facilities were not usually necessary. However, the current emphasis on coal liquefaction for fuels production represents a major departure from the traditional technology deployment strategy.

3.1 Generic Characteristics of Liquefaction Technology

Figure 1 shows a typical process flowsheet for a direct coal liquefaction facility (Ref. 9). Coal is mixed with a carrier oil, heated under pressure with hydrogen (H_2), and the resulting products are cleaned and separated. Product distributions depend on the end use for which the plant is designed Table 1 summarizes these for three such direct coal liquefaction plants.

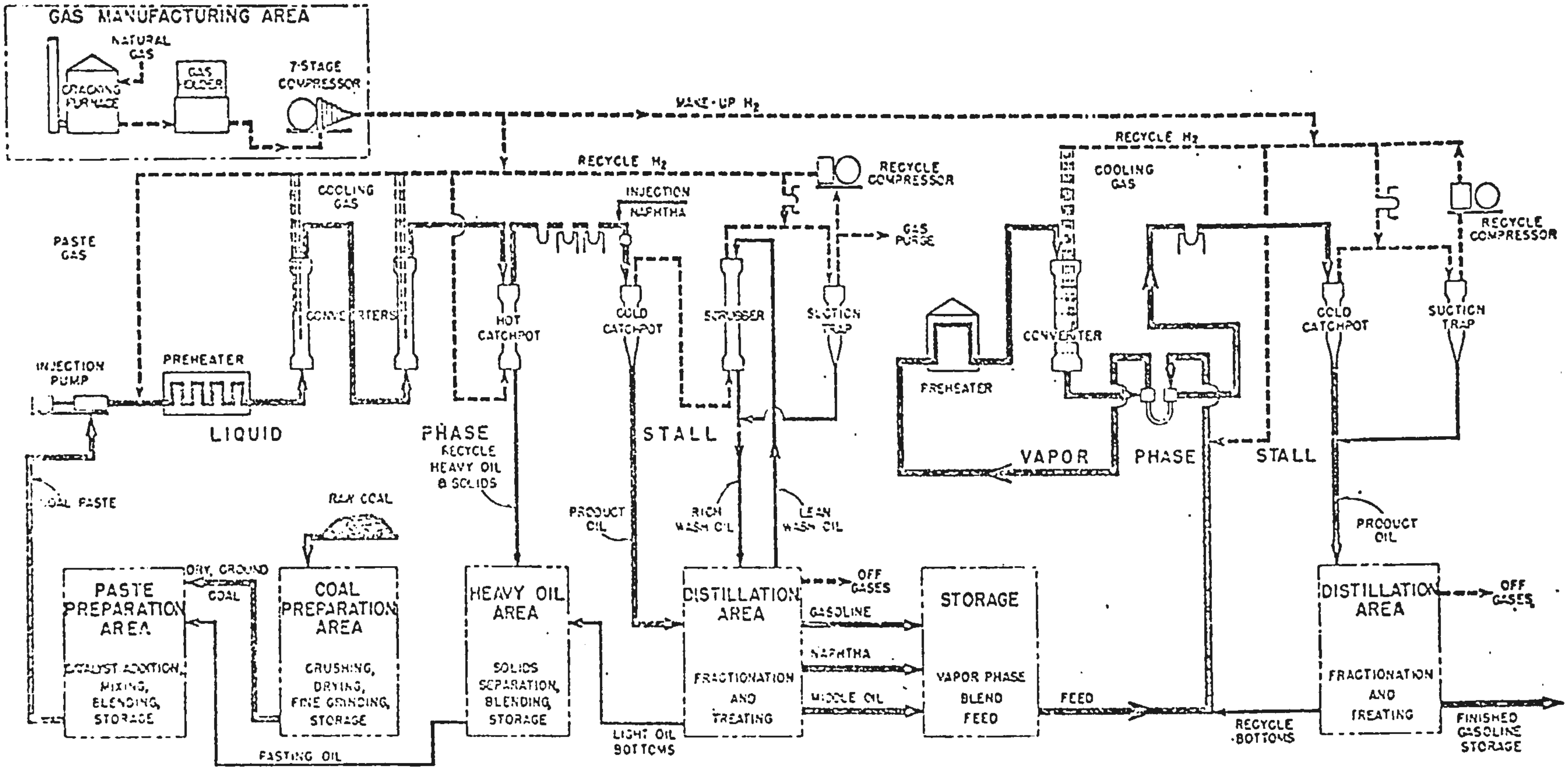


Figure 1. Process Flowsheet for a Direct Coal Liquefaction Facility.

Bureau of Mines - Louisiana, Missouri coal hydrogenation plant, which was constructed as a replica of the World War II German Bergius (Ref. 6) plants.

TABLE 1

Commercial Products of Direct Coal Liquefaction (Ref. 11)

UNION CARBIDE (Ref. 10), Institute, W.V.	BUREAU OF MINES (Ref. 9) Louisiana, MO	GULF OIL CO., SRC II (Ref. 11) Morgantown, W.V.*
LIGHT OILS: Benzene, C_5 - C_7 hydrocarbons, phenols, arylamines, napthalenes, C_7-C_{13} hydrocarbons, vapors. *Separated later.* *MIDDLE OILS:* Napthalenes, biphenyls, fluorenes, acenapthalenes. *Separated later.* *HEAVY OILS:* Anthracenes, PAH compounds. *Separated later.* *PITCH.* *COKE.*	*VAPORS:* C_1-C_4 hydrocarbons, Recycled, Cracked *In Refinery on-site.* *GASOLINE:* C_{5+} hydrocarbaons, aromatics. *Refined on-site.* *NAPHTHA:* C_{5+} hydrocarbons, aromatics. *Refined on-site.* *LIGHT OILS:* Benzene, napthalenes, phenols, arylamines, anthracenes. *HEAVY OILS:* PAH compounds, etc. *ASPHALT.*	*VAPORS:* Methane, C_2-C_4 hydrocarbons. *Separated on-site.* *NAPHTHA:* C_{5+} hydrocarbons, aromatics. *Separated later.* *LIGHT OILS:* Benzene, napththalenes, phenols, C_7-C_{13} hydrocarbons, Grade #14.4°API. *HEAVY OILS:* Anthracenes, PAH, C_{13+} hydrocarbons, Grade #7.2°API *CHAR.*
Coal throughput=300 T/d 300 T/d	Coal throughput=60 T/d Gasoline Output=11000 gal/d	Coal throughput=6000 T/d **Proposed*

NOTE THAT AMONG THE THREE COAL LIQUEFACTION SYSTEMS COMPARED ABOVE, ONLY ONE -- THE BUREAU OF MINES PROGRAM OF THE EARLY 1950's -- WAS EVER DESIGNED TO PRODUCE AND ACTUALLY DID PRODUCE MOTOR FUELS.

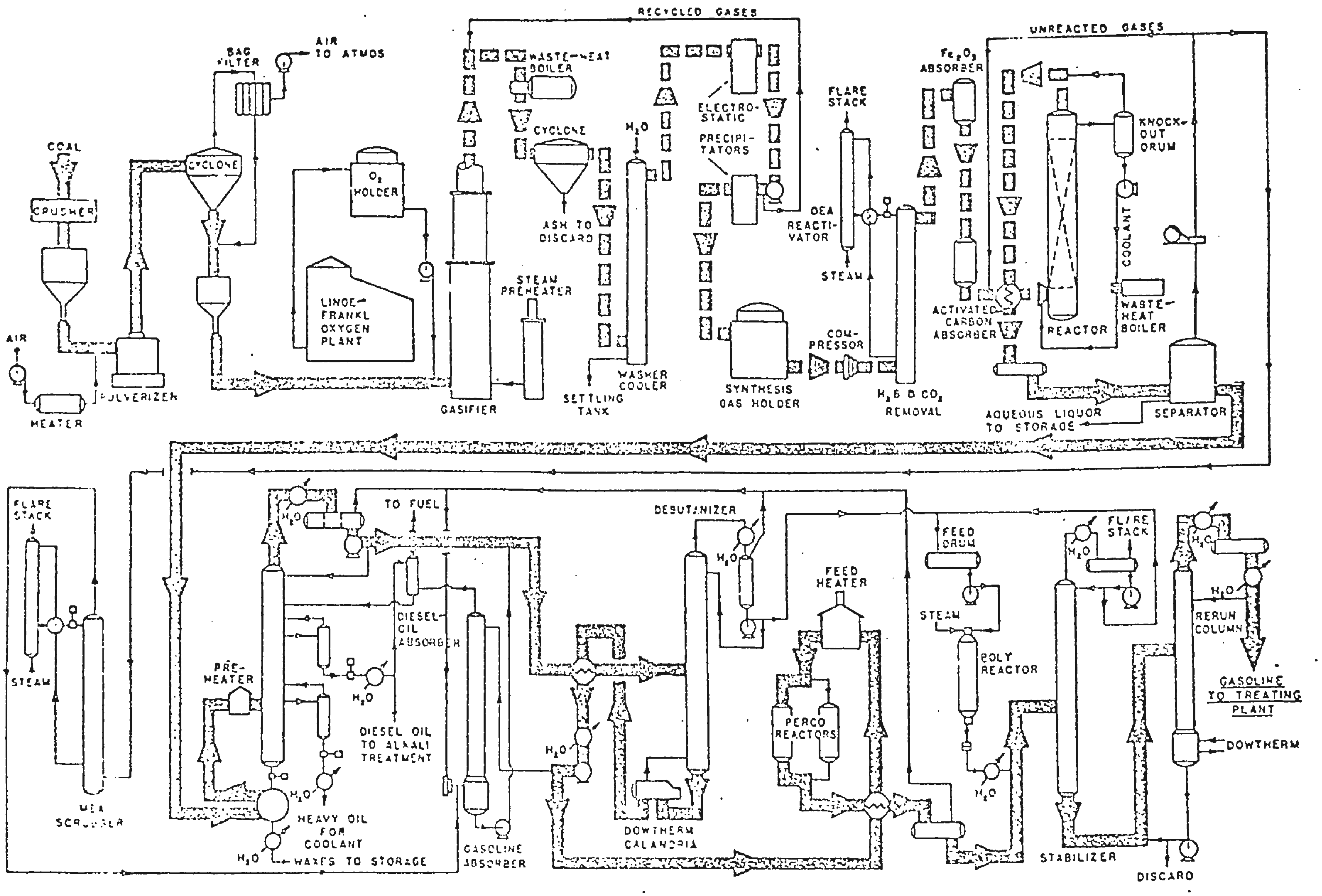


FIGURE 2. Process Flowsheet for an Indirect Coal Liquefaction Facility. Bureau of Mines - Louisiana, Missouri gas generation/ammonia plant (Ref. 7). Design conforms to World War II German Fischer-Tropsch plants for liquid fuels and methanol feedstock production.

Indirect liquefaction facilities, likewise, have been designed for a multiplicity of end use options. Figure 2 shows a typical process flowsheet for an indirect coal liquefaction plant (Ref. 9). Coal or coke is gasified under oxygen (O_2) to produce carbon monoxide (CO) and hydrogen (H_2), which are converted under pressure in a Fischer-Tropsch type reactor to any particular combination of end products, depending on the type of catalyst used. Table 2 exemplifies this variety (Ref. 8).

TABLE 2

Product Distributions for Indirect Coal Liquefaction

"FISCHER"TROPSCH" Catalyst	MAJOR PRODUCTS	MINOR PRODUCTS
zinc chromite	Methanol (CH_3OH)	None
Ni or Ru	Methane (CH_4)	None
Zn/Mn/Cr Alkali	Methanol (CH_3OH)	Higher alcohols
Iron oxide (True F-T)	C_5-C_{12} Alkanes	C_1-C_4 Alkanes, Alcohols, Waxes.
Ruthenium	Alkane polymers	Waxes
Rhodium Carbonyl/Pyridine	Ethylene glycol	Poly-glycols
Copper	Formaldehyde (HCHO)	?

3.3 *Commercial Applications*

In the U.S., coal liquefaction has historically supported the chemical synthesis industry. The Union Carbide (direct liquefaction) plant in Institute, W.V. (Ref. 10), and the DuPont (Indirect Liquefaction) facility in Belle, W.V. (Ref. 8), represent two particularly important cases in point. Both plants were captive suppliers to nearby chemical plants. With the exception of SASOL in South Africa and plants in World War II Germany, the chemical industry market orientation has epitomized coal liquefaction worldwide over the last fifty years. In this light, the present-day push toward coal liquefaction for substitute fuels represents a major industry departure, for which the German and South African experiences are the precedent.

Future trends in coal liquefaction technology development will depend on the nature of market demand for the products. For fuels production, considerable product refining and reprocessing will be required after the primary products have left the liquefaction plant. The need to upgrade these products will require a secondary industry (Ref. 12):

- *For direct liquefaction plant products, special refineries to handle and separate naphthas.*
- *For indirect liquefaction plants, methanol-to-gasoline conversion plants (such as "Mobil-M) or chemical refinery techniques for separating Fischer-Tropsch products.*
- *In either case, removal of undersirable (sulfurous and amine) contaminants will have to be carried out.*

In many instances, coal liquefaction plants were used primarily for the production of ammonia (NH_3) -- the organic by-products being of secondary importance (Ref. 13). Prior to the advent of cheap oil and natural gas in the 1940's, in fact, coal liquefaction -- and particularly indirect liquefaction -- accounted for virtually all of the world's nitrogen fertilizer production (Refs. 8, 13). Today, indirect liquefaction plants are still noted for their copious ammonia output (Ref. 8).

Not until the World War II German plants, replicated by the Bureau of Mines Louisiana, Missouri demonstration (Refs. 6, 9), was gasoline considered a prime product of liquefaction. It is reported (Refs. 9, 14) that the Bureau of Mines plant, during one continuous 3-month run, produced 1 million gallons of gasoline. Today, the largest existing coal liquefaction facility in the world, SASOL-2 in South Africa, is undergoing shakedown (Refs. 15, 16). The plant is designed to produce, by indirect liquefaction, 1.5 million tons/year of gasoline, plus 0.6 million tons/year of other commercially important chemicals. Interestingly, NH_3 is expected to account for about 5 percent of the total plant output (Ref. 15).

> *In spite of the commercial maturity of coal liquefaction technologies, numerous operational problems remain unsolved.*

Table 3 summarizes the important operational problems involved with direct or indirect coal liquefaction (Refs. 8, 11, 15). Note that materials listed as process stream constituents are not necessarily released to the environment. However, the potential for some particular, hazardous fugitive emissions may exist if these processes are not properly controlled and contained.

Table 3

FEATURE	DIRECT LIQUEFACTION	INDIRECT LIQUEFACTION
Major Components (Refs. 11, 15)	Preheaters Gasifier Hydrogenation Reactor Vapor-Liquid Separator Liquid-Solid Separator Sulfur Cleanup Tar Knockdown	Preheaters Gasifier Fischer-Tropsch Reactor Vapor-Liquid Separator Products Separator Sulfur Cleanup Tar Knockdown
Process Streams (Refs. 11, 15)	Gas from Gasifier Coal liquids slurries Wastewater Ash/char/spent catalysts	Gas from Gasifier Alcohols/Hydrocarbons Wastewater Ash/char/spent catalysts
Gremlins (Refs. 12, 18)	Particles = Plugging Erosion Repolymerization	CH_4 + loss from system Carbonyl Corrosion Carbon Black Deposition Catalyst Poisoning by Tars, S.
Products and By-Products (Refs. 8, 11, 15).	Naphthas Heavy Oil Hydrocarbon Fuel Gases Light Fuel Oil Sulfur Ammonia and Amines Phenols	Methanol Alcohols/Ethers Waxes Aldehydes Sulfur Ammonia Organic Amines

Most of the operational difficulties encountered in direct liquefaction are traceable either to process line plugging due to viscosity changes (i.e., viscosity increases with time and temperature in the process), or to erosion by the suspended solids (Refs. 9, 18 - 22). The service life of plant components sensitive to plugging or erosion therefore usually defines the intervals between plant shutdowns for maintenance and repairs. For the Bureau of Mines Louisiana, MO demonstration plant (Refs. 9, 14) this interval was approximately 3 months. For modern direct liquefaction (DOE-supported) pilot programs (Refs. 20 - 21), this interval is presently 3 days. If a new Gulf Oil Co valve design (Ref. 21), which is to be incorporated into future test operations, can successfully withstand the wear and tear of liquefaction process streams, the maintenance interval can be extended to about 3 months (Ref. 21).

Worker exposure hazards are greatly magnified during these maintenance shutdowns, because fugitive safeguards are breached whenever components are dismantled for repair, cleaning, or replacement.

Reliability limitations in indirect coal liquefaction facilities ensue from totally different circumstances, which are virtually unknown in any other industry. Present day unresolved problems (Ref. 8) include:

- *Carbon deposition on catalyst:* This factor typically limits (Fischer-Tropsch) catalyst service life to one year or less.

- *Carbonyl corrosion:* The high pressures and relatively low process stream temperatures dirve the reaction between CO and process vessel walls. No predictable maintenance interval has yet been defined.

- *Metal carbonyl fugitives:* According to Stiles (Ref. 6) "Other problems were for the most part solved, but the iron carbonyl problem remains and seems to defy an economic solution". Had stainless steel been used in these plants instead, the principal hazard would have been emissions of nickel carbonyl. These may accompany methanol fugitives.

- *Tar fogs, scrubber mists, entrained ash particles severely impair downstream performance.* Process stream cleanup options can therefore be restricted.

Any innovation in indirect liquefaction technology development which solves any of the first three of the above problems will most likely solve all three.

3.3 Government Sponsored Programs and Technology

Federal government-sponsored R & D activity in coal liquefaction stems from the Bureau of Mines investigations at Louisiana, MO (Ref. 9), and a number of subsequent development programs have evolved since the 1950's. In general, these programs were directed toward the production of fuels instead of chemical feedstocks. Recent perturbations in the U.S. energy economy have resulted in the proliferation of Federal Government-sponsored R & D programs in direct coal liquefaction (see Figure 3). Today, however, these have been narrowed to four pilot plant and demonstration projects: SRC-I, SRC-II, the Exxon Donor Solvent (EDS) Process, and the H-Coal process.

Figure 3 shows projected milestone schedules for the DOE coal liquefaction program (Refs. 20, 23).

While direct coal liquefaction processes sponsored by DOE have much in common with systems which have operated commercially in the past (compare flowsheets in Figure 1 with Refs. 10-11, for example), several features of the DOE-supported technology for direct liquefaction stand out as important new developments and scenarios:

- Size. *The proposed SRC-II Demonstration plant (Ref. 11) will be far larger than any coal liquefaction facility built to date (Refs. 6, 11). In many cases, units which form the components of the plant (pressure vessels, oxygen plant, gasifier, water treatment, etc.), will be the largest in existence.*

- Novel Components or Different Feedstocks. Many of the hardware components have never been tested with coal-derived liquids, but were developed and/or modified from other industrial purposes (Ref. 24).

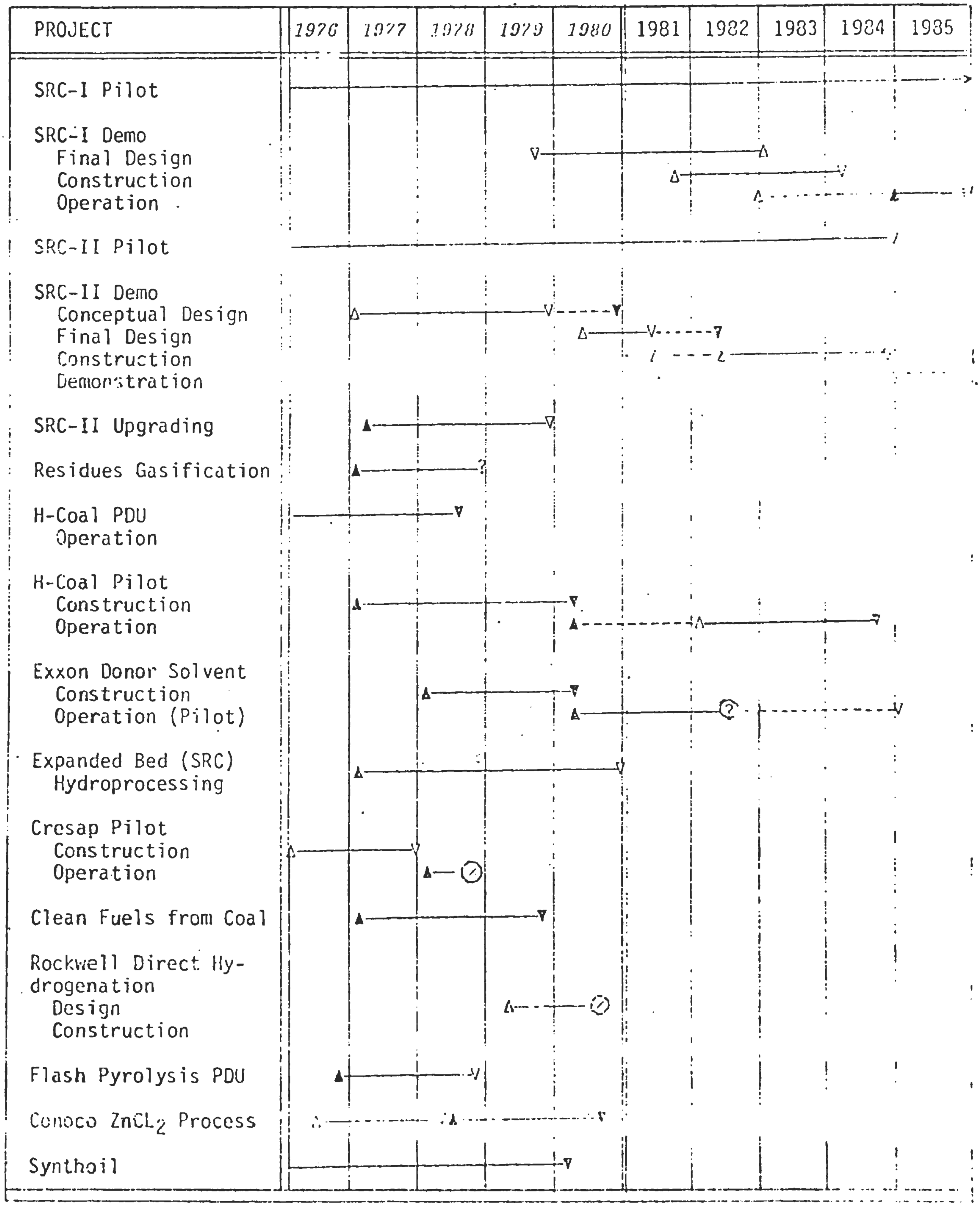
- Environmental and Industrial Hygiene Concerns. Until recently, protective measures were not routinely considered in the design, operation, and economics of coal liquefaction plants (Refs. 6, 10, 25-28). The Union Carbide example (Refs. 10, 25-28) was exceptional. These will have to be factored into the DOE-supported technology, however (Ref. 11).

- Hardware Failures. Certain components of current direct coal liquefaction pilot plants have typically exhibited short service lives, and have been sources of leaks and fugitive emissions. Specific examples (Refs. 28, 29) include:

    - erosion in slurry pumps;
    - corrosion of heat exchangers;
    - erosion and corrosion, freezing and repacking of valves;
    - viscosity-dependent plugging of process lines.

FIGURE 3

Development Schedule for Direct Liquefaction as of June 1980.
(Refs. 20, 23, 29)



At the present time, valves represent the weakest link in direct liquefaction hardware technology (Refs. 4, 21, 24). *Routine maintenance procedures necessitated by hardware failures represent sources of occupational and environmental exposure hazards.*

The DOE pilot plant and demonstration programs in direct coal liquefaction are intended to remedy the weaknesses presently encountered in the hardware components (Ref. 20), and to provide a successfully proven alternative to crude petroleum as the source of residual and distillate fuel oils.

Federal Government-sponsored R & D activity in indirect liquefaction, unlike the more mature direct liquefaction program, is currently in a formative stage. One demonstration facility, to be built in North Dakota and to operate (beginning in FY1984) on western coals, will be supported by DOE (Ref. 30). However, the present DOE opinion that water and reclamation will limit the growth of an indirect liquefaction industry in the West (Ref. 30) remains to be tested. A number of small laboratory and bench-scale studies to develop improved Fischer-Tropsch catalysts are also proceeding under DOE support (Ref. 31). Indirect liquefaction catalyst development studies are also being vigorously and independently pursued (Ref. 20) by Imperial Chemical Industries, Ltd. (ICI), Badische-Anilin and Soda-Fabrik GmbH (BASF), Exxon, and a consortium of New Zealand firms. A DOE-supported pilot plant for the Mobil-M and Union Carbide processes is in preliminary design to develop key downstream products conversion steps (Ref. 31B).

4.0 CHARACTERIZATION OF POTENTIALLY HAZARDOUS CONSTITUENTS

Direct or indirect liquefaction of coal can generate variable amounts of hydrogen sulfide (H_2S), cyanides, ammonia (NH_3), mutagenic/carcinogenic tars and phenolics, toxic trace elements, and in some cases, toxic vapors of alcohols, aldehydes, and metal carbonyls (Refs. 8, 11, 15, 32). Furthermore, the bioavailability and toxicity of particle-bound trace elements may differ among processes even when the bulk compositions are similar. *To date, no quantitative data is available relating bioavailability and toxicity to actual liquefaction materials, although work does exist on exposures of animals to extracts prepared from these materials (Ref. 33).*

Table 4 summarizes the production of environmentally important substances in coal liquefaction. Careful measurements of the process stream constituents of direct coal liquefaction have been reported for the Ft. Lewis pilot plant (Ref. 34), and show at least qualitatively the same materials as in laboratory coal pyrolysis experiments (Refs. 35-39). Organic N is an

TABLE 4

Typical Contaminant Profiles in Coal Liquefaction

PARAMETER (wt/coal)	SRC-II (Ref. 11)	USBM Louisiana, MO (Ref. 9)	SASOL (Ref. 15)
Sulfur (kg/T)	225.	0.8	1.0
Ammonia (kg/T)	5.0	4.8	1.1
Phenols/Tar Acids(kg/T)	1.1	46.	+
Tars/PAH (kg/T)	≐ 50	48-66	2.2
Organic N (kg/T)	Probable	∿ 20	+
Metal Carbonyls	—	—	+

important liquefaction by-product, but most S evolves as H_2S (Ref. 12). Table 5 shows the kinetics expressions for gas and tar formation predicted for coal liquefaction (Refs. 35 - 39).

TABLE 5

Kinetics and Yield Predictions for Coal Liquefaction

FUNCTIONAL GROUPS IN COAL	PYROLYSIS PRODUCT	RATE CONSTANT, $k(sec^{-1})$ ARRHENIUS FORM (T in K)
R-OH	H_2O	$(45)\ \exp(-4950/T)$
Aliphatics	$R-C\equiv CH$	$(1.9\times10^{10})\ \exp(-35000/T)$
Aliphatics	Olefins	$(2.0\times10^{7})\ \exp(-20000/T)$
Aliphatics	Paraffins	$(750)\ \exp(-8000/T)$
Aliphatics	CH_4	$(9.5\times10^{10})\ \exp(-35000/T)$
Coal	Soot	$(2300)\ \exp(-9700/T)$
R-COOH	CO_2	$(6)\ \exp(-4000/T)$
Ethers, Ketones	CO	$(7000)\ \exp(-10300/T)$
Ethers, Ketones	CO	$(890)\ \exp(-12000/T)$
Aromatics	Tar	$(750)\ \exp(-8000/T)$
Ar-H	H_2	$(36000)\ \exp(-12700/T)$
"Loose" - N	NH_3	$(200)\ \exp(-7699/T)$
"Tight" - N	HCN	$(290)\ \exp(-12700/T)$
All - N	N_2	$(0.13)\ \exp(-4220/T)$

According to Solomon (Ref. 39), the composition of liquefaction tar products conserves the aromatic subunit structure of the feed coal; however, the production of tar strictly depends on the availability of aliphatic hydrogen. This explains why anthracite coals form very little tar when utilized, in spite of their very high coal rank and aromatic content. *Thus, the (qualitative) similarities between direct coal liquefaction products and coke oven volatiles (Ref. 40) can be attributed to a common basis* *in the physical-chemical fundamentals (Refs. 35-39).* Coke oven tars contain many of the same PAH compounds, phenols, and carcinogenic fractions. Figure 4 shows some typical tar/aromatics characteristics of coal liquefaction materials. If one merely considers the distribution of benzene-soluble organics (Ref. 42), the data create the impression that most of the aromatics produced in coal conversion are small and simple. However, this is merely an artifact of the solubilization procedure. Careful examination of the organic products of coal liquefaction (Ref. 41) shows the average molecular weight distribution to be much heavier than would otherwise be expected on the basis of solvent extraction studies.

> Figure 4 indicates that the true median molecular weight M is close to 400, as opposed to about 150 for the solvent extracts. *This distinction is extremely important in light of other studies which implicate the high-molecular weight fractions as the most carcinogenic (Ref. 34).*

Figure 4 also indicates that approximately half of the carbonaceous matter in coal is "coked" during the liquefaction step (Ref. 41). This fact has been designed into the SRC-II Demonstration Plant (Refs. 11, 43).

To date, NIOSH has conducted on-site industrial hygeine characterizations at the SRC-I Pilot Plant at Wilsonville (Ref. 3A), the now-defunct Cresap Test Facility, Cresap, WV (Ref.3B), and at the SRC-II Pilot Plant at Ft. Lewis (Ref. 4). In addition, NIOSH efforts to provide an industrial hygeine assessment at the SASOL-I plant have been documented (Ref. 44) but have yet to provide a comprehensive survey.

In general, results of these studies (Refs. 3-5) have shown measured levels for single-ring, or fused-ring aromatic compounds to be in the parts-per-billion (micrograms-per-cubic-meter) range. At these levels, the major hazard is expected to be due to polynuclear aromatic hydrocarbons (PAH) or their derivatives (Ref. 4). Other more conventional criteria pollutants were present at levels generally below detection limits (Ref. 4). Eight compounds, mostly 2-ring and 3-ring non-mutagenic aromatics, make up 75% of the total PAH found (Ref. 4).

A central part of an exposure sampling strategy is to determine the exposure level of the employee found to be at maximum risk within a given area (Ref. 45). For liquefaction plants, the positions of high risk will involve among other places (Ref. 14):

- Areas of feedstock entry to pressurized sections of the plant;
- Regions of waste product and by-product pressure letdown;
- Process sampling ports which are at high temperature and pressure;
- Reactor interiors during shutdown.

DOE has an ongoing effort (Ref. 21) to evaluate the performance and longevity of selected components in gasification units such as valves, directed toward the improvement of component reliability from a process viewpoint. These results, however, are also important from an industrial hygeine standpoint. Additional work is also required on the safety aspects of high-temperature/high-pressure sampler design and on worker protection measures for those using those systems.

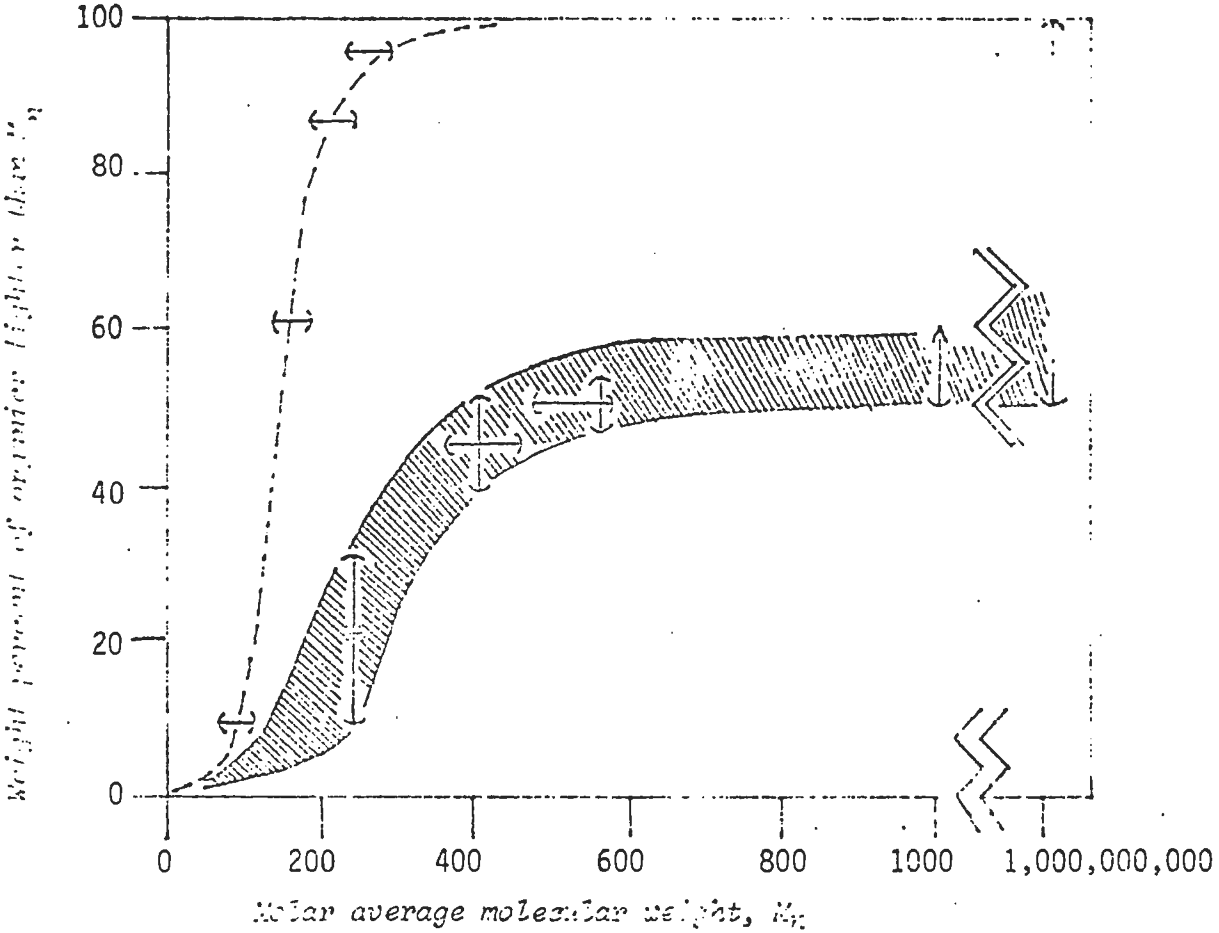


FIGURE 4. Size Distribution Curves for Coal Conversion Organics. (▨), Data [illegible] by Skowronski et al (Ref. 41) for coal liquefaction materials: light oils, asphaltenes, benzene/methanol solubles, and char fractions, in ascending order of M_n. (– – –), Data of Forney et al (Refs. 32, 42) for benzene extracts of Synthane tars. Data (←→) refer to 1-ring, 2-ring, 3-ring, and 4-ring aromatics, repectively with increasing M_n.

5.0 OCCUPATIONAL HEALTH-RELATED STUDIES

Occupational health and safety criteria for direct and indirect coal liquefaction plants will be predicated, in large measure, on laboratory studies of surrogate materials, plus experience obtained in other (related) industries such as:

- Coal gasification plants (Ref. 32, 46).
- Coke ovens (Ref. 40)
- Methanol synthesis plants (Ref. 47)
- Coal tar products (Ref. 48).

Thus, results of investigations conducted for coal liquefaction facilities specifically (Refs. 1 - 5, 10, 25 - 28) need not be considered in isolation.

5.1 Technology-Specific Investigations

Because of the considerable attention shown for coal liquefaction as a synthetic fuels alternative, numerous studies supported by EPA, DOE, NIOSH, and other agencies (Refs. 49 - 50) have been undertaken to assess the occupational and environmental health consequences of the industry. One can generalize these studies in three groupings:

- Occupational epidemiology,
- Industrial hygeine characterizations,
- Basic toxicology.

5.1.1 Epidemiology

The most notable occupational epidemiology study of coal liquefaction workers was reported for the Union Carbide plant at Institute, WV (Refs. 10, 25-

28). Of the 350 persons employed in this facility over the period 1952-1960, some 50 cancer morbidity cases were reported. However, a recent NIOSH-supported followup study (Ref. 2) of these workers failed to detect any latent systemic cancer cases or excess mortality 17 years after closing of the plant.

Recent epidemiological investigations at the SUC-II Fort Lewis Pilot Plant (Refs. 34, 43), on the other hand, have shown a significant incidence of folliculitis on the forethighs and shoulders or workers, but no confirmed occupational cancer cases among the 500 person study population since startup of the plant in 1974. This apparent contrast with the Union Carbide study (Refs. 10, 25-28) must be viewed in terms of latency and exposure characteristics. Numerous epidemiological investigations have also been reported for other coal conversion industries (Ref. 32, 40, 51-58, among others), a sample of which is described in Table 6. Excess mortality rates were reported in most of these studies. Worker populations at gas works and coke ovens were followed in these studies for periods of up to 25 years to evaluate the impacts of work-related factors on cancer mortality rates.

While most of the occupational epidemiology literature concludes an excess cancer mortality risk for workers in coal conversion facilities, close examination of the primary data shows considerable noise in the statistics. One must therefore question whether cancer mortality data adequately reflects the actual occupational health risks for those worker populations. In view of the demonstrated incidence of (relatively non-lethal) skin cancer morbidity for coal liquefaction facilities, conclusions based on mortality statistics may underestimate the real cancer hazards.

TABLE 6. OCCUPATIONAL EPIDEMIOLOGY STUDIES FOR COAL CONVERSION FACILITIES

Facility Type	Investigators	Contemporary/ Prospective	Retrospective	Results	Comments
Coal Liquefaction	Sexton (Ref.10,27)	(1960) Morbidity	———	Elevated skin cancer morbidity, no mortality.	Statistical significance high for morbidity, low for mortality.
	Palmer (Ref. 2)	———	(1979) Mortality	No latent trends among the 50 skin cancer victims.	
Producer Gas Works (Gasification)	Kuroda *et al* (Ref. 51)	(1936) Mortality	———	Excess mortality, lung cancer	Statistical significance of data questioned (Ref. 57)
	Kawai *et al* (Ref. 52)	———	(1967) Mortality	Latent lung cancer mortality	
Gas Works	Doll (Ref. 53)	(1952) Mortality	———	Excess mortality, lung cancer	Statistical significance of data questioned (Ref. 57)
	Doll *et al* (Ref. 54)	———	(1965) Mortality	Possible latent cases of lung cancer	
Gas Works	Kennaway & Kennaway (Ref.55)	(1936) Mortality	———	Excess mortality, cancer of lung and larynx	Statistical significance of data questioned (Ref. 57)
	Kennaway & Kennaway (Ref.56)	———	(1948) Mortality	Latent lung cancer mortality, but at lower rate	Statistical significance of data questioned (Ref. 57)
Coke Ovens	Reid & Buck (Ref. 57)	(1956) Mortality	———	Excess mortality due to cancer of lung possible but not proven	Confirmed by Redmond et. al. (Ref. 58)
Coke Ovens	Redmond *et al* (Ref. 58)	(1969-75) Mortality	———	Excess cancer mortality for non-white workers, but not for white coke oven workers	Reference population bases were: (1) U.S. total; and (2) Allegheny Co. steelworker

A major drawback of many epidemiological investigations is the absence of an established exposure dose-response relationship (Ref. 59). Indeed, the differences between the Ft. Lewis observations (Refs. 4, 34) and the Institute, WV Studies (Refs. 10, 25-28) may be traceable to this fact. Two additional lines of evidence must be present in order to permit a cause-effect assessment of the occupational and environmental health consequences of coal liquefaction:

- *Assay of the exposure history of the subject population*
- *Pathways and adverse health effects of identified toxic constituents.*

5.1.2 Industrial Hygeine Characterizations

Industrial hygeine characterizations have been reported for Union Carbide, Institute, WV (Refs. 10,25-27); SRC-I Pilot Plant, Wilsonville, AL (Ref. 3A); Consol, Cresap, WV (Ref.3B); and SRC-II, Fort Lewis, WA (Ref. 4) -- in order to identify sources and quantify hazards to workers in these facilities. Table 7 compares the potential hazard sites in each of these three plants. Areas of maximum exposure risk common to all three facilities include:

- Solids separation and recovery.
- Solvent recovery.
- Coal/solvent preparation.

TABLE 7

OCCUPATIONAL HAZARD POTENTIAL IN DIRECT LIQUEFACTION PLANTS

High-Risk Areas for Pollutants	Union Carbide, Institute, WV (Ref.26)	Consol, Cresap, WV (Ref.2)	Gulf SRC-II, Ft. Lewis, WA (Ref.4)
Polycyclic Aromatic Hydrocarbons (PAH) BaP does not correlate with PAH (Ref. 4).	Pitch Treatment (2-6$\mu g/m^3$ as BaP); Paste Pumps (.1 $\mu g/m^3$ as BaP); Solids Removal (12-19$\mu g/m^3$ as BaP)	Solvent extraction area; Solids separation solvent recovery; Tank farin; Sulfur removal	Coal Preparation: (41$\mu g/m^3$); Preheater, Dissolver (19$\mu g/m^3$); Mineral separation (224$\mu g/m^3$); Solvent Recovery (93$\mu g/m^3$); Product Storage (6$\mu g/m^3$)
Phenolics/Tar Acids		Solvent extraction area; Solvent recovery; Catwalk above tanks;	B.D.L.
Trace Elements			B.D.L.
Aromatic Amines		Solvent extraction area; Residue separation catwalk above tanks;	B.D.L.
Benzene/Toluene/Xylenes		Extraction area; Residue separation unit; Pressure letdown valves; Coal-slurry feed; Solvent recovery; Carbonization Section	Coal Preparation (.08 ppm); Mineral Separation (0.19ppm); Solvent Recovery (0.2 ppm)
Criteria Gases (CO, NH_3, H_2S, SO_2)		B.D.L.	H_2S up to 93,000 ppm at Naphtha Loading Port. Others B.D.L.
TSP Respirable Dust			Coal Prep. (1mg/m^3) Coal Prep. (.06mg/m^3)

B.D.L. = Below Detection Limit. All data from area monitoring.

Other direct liquefaction facilities might present a comparable potential occupational exposure hazard to those reported in Table 7 and Refs.(3A,3B,4,26) For indirect liquefaction plants, industrial hygeine surveys of a scope comparable to that for direct liquefaction facilities have not been reported to date. Preliminary attempts at the SASOL-1 plant (Ref. 44) have provided insufficient information for realistic evaluation of worker exposure hazards.

For a mature coal liquefaction industry for synthetic fuels production, the population of workers susceptible to known/suspected occupational hazards is estimated from existing technology. Table 8 shows a compilation of existing data on facilities staffing for several direct and indirect liquefaction plants. If one correlates on-site worker population (P) with plant size (x), the data points fit the function $P=20 \cdot 10^{0.4x}$ (Fig.5) with $r^2=0.91$. The fact that the Exxon data points for the EDS process over the scale-up from PDU to commercial design all fall on the line appears to justify this function as a predictive tool. Furthermore, the worker population estimates are the same for either liquefaction technology.

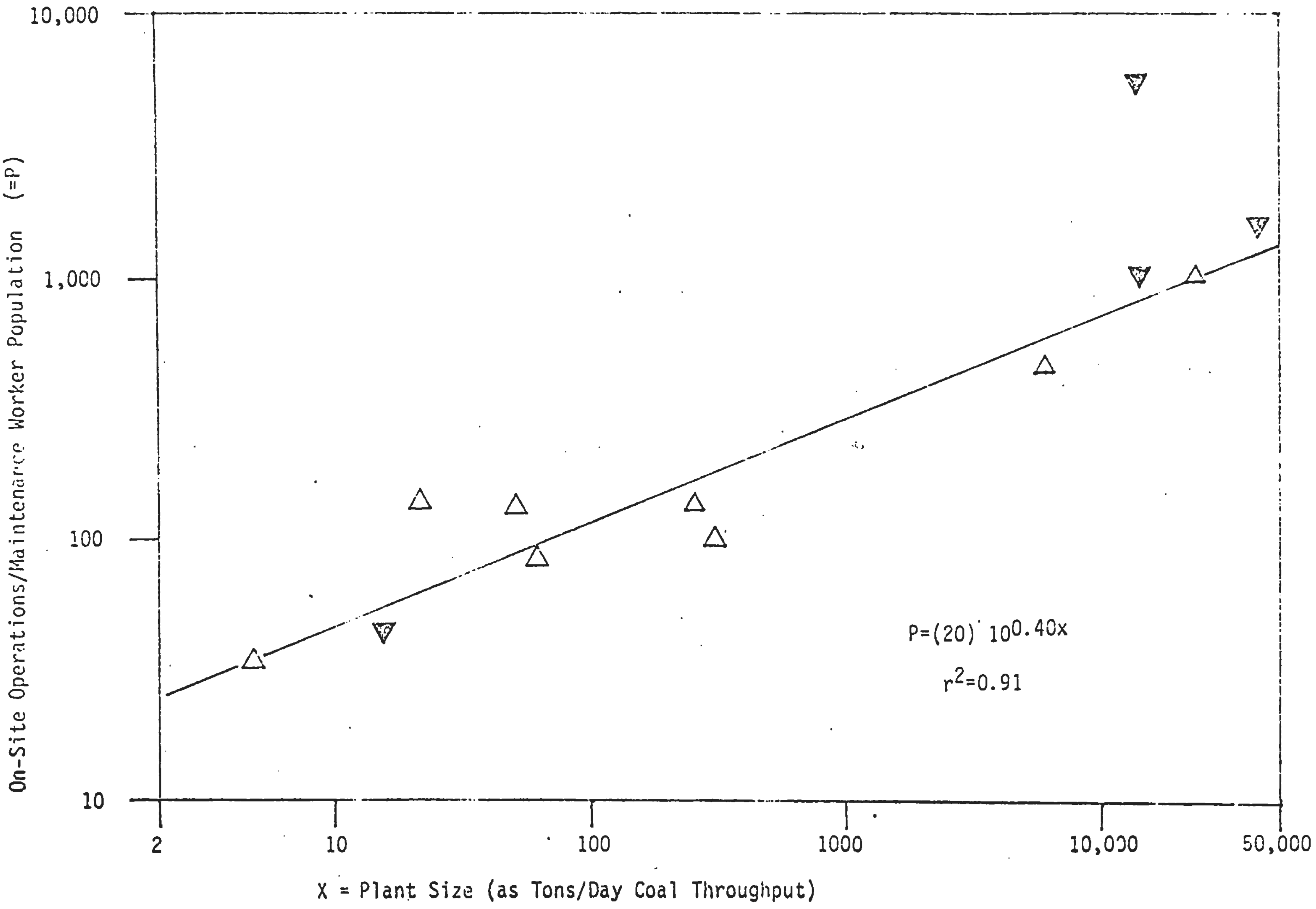
If one now attempts to predict the susceptible worker population in a liquefaction industry, the number depends heavily on the sizes of the synthetic fuels plants. For a market penetration of 1.2 million bbl/day by synfuels, the required on-site worker population would be: 20,000 workers in 20 plants as large as SASOL 1 or SASOL 2 (Refs. 5, 15); or 400,000 workers in 4000 plants of the size of the German or USBM

TABLE 8

Liquefaction Facitility	Direct/ Indirect (D/I)	Cumulative Worker Population	On-Site Work Force	Plant Size (Tons/day Coal throughput)	Operational Status	Information Source
Union Carbide	D	359	173	300 T/d	C→1962	Sexton (Ref. 27)
USBM Louisiana MO	D	?	100-120	60 T/d	D→1953	USBM (Ref. 9)
SRC-II Pilot	D	500	133	50 T/d	1974→P	Refs. (4,34,43)
SRC-II Demo	D	?	550	6000 T/d	Proposed	DOE (Ref. 11)
Consol, Cresap	D	≳180	140	20 T/d	P→1978	NIOSH (Ref. 2)
H-Coal	D	?	?	540 T/d	1980→P	DOE (Ref. 60)
Exxon EDS - PDU	D	?	35	4½ T/d	1972→P	Exxon (Ref. 61)
Exxon EDS - Pilot	D	125	125	240 T/d	1980→P	DOE (Ref. 60)
Exxon EDS - Comm.	D	?	1000	24000 T/d	Conceptual	DOE (Ref. 62)
USBM Louisiana MO	I	?	40-80	15 T/d	P→1953	McGee (Ref. 14)
SASOL-1	I	?	5600	14000 T/d	1955→C	Refs. (5,15)
SASOL-2	I	2000	2000	40000 T/d	1980→C	Refs. (15,16)
Fluor-U.S.	I	?	1000	14000 T/d	Conceptual	DOE (Ref. 62)

Designations under "Operational Status" are defined as follows: B=bench scale or PDU: P=pilot plant; D=demonstration plant; C=commercial facility. For letter preceding a year, date indicates termination of plant operation. For letter following a year, date indicates startup of operation for plant currently still in operation.

Cumulative worker populations will be higher than numbers shown in Figure. Both scales are logarithmic.



liquefaction plants (Ref. 9). The smaller sized plants have been demonstrated and will operate under U.S. conditions (Refs. 9, 14). The larger plants are operable only in South Africa.

A further consideration in an assessment of the occupational health characteristics of coal liquefaction plants is the rate of personnel turnover. As Table 8 shows, the Union Carbide, Institute, WV plant employed a total of 359 workers over its ten-year life span; but only 173 of these were currently on-site at a given time (Ref. 27). This corresponds to an average turnover rate of about 7.5 per cent per year. In contrast, the average annual personnel turnover rate at the SRC-II Fort Lewis pilot plant (Refs. 4, 34, 43), was at least 20.5 per cent. While precise numbers for SASOL 1 are not presently available, the turnover rate is reportedly very high -- especially among the highest-risk groups (Ref. 44).

Personnel turnover complicates the assessment of occupational health risks by expanding the worker population base which must be followed in a medical surveillance program. Heavy turnover can also artificialy obscure plant hazards because fewer workers are subjected to prolonged or repeated exposures to fugitives. This may partially account for the discrepancy between the Union Carbide (Ref. 27) and SRC-II (Refs. 4, 34, 43) epidemiologic observations.

5.1.3 Toxicology

The primary emphasis to date for toxicity assessment of coal liquefaction materials has been rapid bioassay screening of the various product fractions. Most of this work has been ongoing at a number of National Laboratories, most notably BPNL (Ref. 34) and ORNL (Refs. 63-65). Table 9 gives the details of the bioassay tests performed to date on coal liquefaction materials. These tests conform, in general, to the EPA "tier system" (Ref. 66) for bioassay screening.

Bioassay screening is primarily useful for determining which substances are toxic in one way or another. Their principal advantage, and the primary reason for their use, is the ability to ascertain within days or weeks -- as opposed to the latency periods of 3-40 years experienced in epidemiological investigations (Refs. 2,27,51-58) -- whether a serious occupational health risk might be encountered with a test material. As Table 9 indicates, rapid screening bioassays are not limited to mutagenicity or carcinogenicity tests, although these happen to be the simplest and most direct. Consequently, most of the health effects efforts directly relatable to coal liquefaction technology occupational criteria have focused on potential mutagenic and carcinogenic organic constituents, or on trace elements contaminants (Ref. 70). However, recent industrial hygeine surveys of direct liquefaction facilities (Ref. 3-5) have pointed out possible worker hazards from the criteria pollutants H_2S and CO in addition to the suspected aromatic carcinogens. Problems encountered in indirect liquefaction facilities also center around criteria pollutants like iron carbonyl (Ref. 8), which coincides with formation of carbon black and methanol/formaldehyde leaks. Table 10 summarizes the criteria pollutants which could comprise fugitive emissions in future synfuels plants.

Table 9

Bioassay Tests Performed on Coal Liquefaction Products

Tests	Test Method	Process Examined	Evaluation Source	Results/ Comments
Carcinogenicity	Mouse Skin Painting	Synthoil SRC-II	ORNL BPNL	++++ Heavy Mainly, +
Mutagenicity	Ames Ames Styles Zimmerman	SRC-II Synthoil Synthoil Synthoil	BPNL ORNL ORNL ORNL	Heavy Only, + ++++
Teratogenicity				
Acute Toxicity	Oral Feed	SRC-II	BPNL	
Subacute Tox.	Oral Feed	SRC-II	BPNL	
Chronic Tox.	Oral Feed	SRC-II	BPNL	
Bioaccumulation			ITRI‡	
Synergistic Properties			ORNL‡	
Clinical Effects	Periodic Exam	SRC-II	BPNL	Folliculitis
Epidemiological Effects	Occupational Occupational Occupational Occupational	SRC-II SRC-II Union Carbide Union Carbide	BPNL NIOSH Union Carbide SRI	— —, Uncharacter.‡ 50 cases, current 17-yr retrosp, —
Ecological effects	Area Sampling	SRC-II	BPNL	Terpenes from pine trees interfere.
Transformability* (Normal cells → Tumor)	Monkey Kidney Hamster Embryo	SRC-II SRC-II	BPNL BPNL	All + Heavy Mainly, +

*Not specifically listed originally as TSCA candidate.

†Tests performed on surrogate materials.

‡Observed exposure criteria uncharacteristic of a commercial scale facility.

Table 10

Criteria Documents for Contaminants in Liquefaction

CONTAMINANT	LIQUEFACTION PROCESS		EXISTING CRITERIA DOCUMENTS
	Direct	Indirect	Occupational
CO*	✓	✓	NIOSH 73-11000
H_2S*	✓	✓	NIOSH 77-158
HCN*		✓	NIOSH 78-213
NH_3*	✓	✓	NIOSH 74-136
Thiols*	✓	✓	NIOSH 78-213
Phenol*	✓	✓	NIOSH 76-196
Cresol*	✓	✓	NIOSH 78-133
CS_2*	?	✓	NIOSH 77-156
Nickel Carbonyl*	?	✓	NIOSH (Ref. 74)
Iron Carbonyl*	?	✓	NIOSH (Ref. 73)
Coal Tar Products	✓	✓	NIOSH 78-107
Coke Oven Emissions	✓	✓	NIOSH 73-11016
Coal Gasification	✓	✓	NIOSH 78-191
Methanol*		✓	NIOSH 76-148
Formaldehyde*		✓	NIOSH 77-126
Hydrocarbons	?	✓	NIOSH 78-204
Combustible Liquids	✓	✓	NIOSH 78-206

*Toxic Thresholds and modes of action understood and defined.

✓Indicates a probable contituent of any fugitive emissions. Circle indicates a confirmed hazard.

An accurate assessment of the environmental health and safety consequences of coal liquefaction technology will require substantial cross-fertilization of epidemiological studies, bio-chemical toxicology investigations, rapid bioassay screening results, and process and environmental monitoring of emissions. Combination of these levels of investigation into a unified exposure dose-response assessment has not been a common occurrence in this context (Ref. 59).

5.2 Studies on Constituents and Surrogate Materials

Most toxicological investigations relevant to liquefaction have been controlled laboratory experiments outside the context of definable occupational health criteria. Their results can be considered equally applicable to other coal conversion technologies such as gasification, coke-making, and even direct or advanced combustion. Consequently, what is concluded from these studies affects all coal use. However, experimental conditions have frequently fallen outside the range of realistic or even catastrophic occupational exposure conditions. It remains an open question, for example, how one relates available toxicity or carcinogenicity information to the exposure-dose conditions and routes of administration likely to occur in an occupational setting.

Nevertheless, the results of existing studies designed to establish the toxicity, mutagenicity and carcinogenicity of liquefaction product constituents qualitatively define those substances whose interactions need to be addressed more clearly. Three principal classes of toxic agents known to exist in variable concentrations in products and process fugitive emissions are described below for indirect and direct liquefaction.

Hazardous gases such as CO, H_2S, CS_2, NH_3, HCN, thiols, nickel carbonyl, phenol and cresol, for which well defined and documented occupational criteria and standards already exist (Table 10). Toxic thresholds and modes of action for these compounds are reasonably understood for acute exposures.

Organic compounds with suspected carcinogenic activity, such as polycyclic aromatic hydrocarbons (PAH), N-heterocyclic aromatics, and their derivatives (Refs. 1,32,68,70).

Trace elements bound to or condensed on fly ash, such as Cd, Ni, Hg, Pb, and others (Refs. 70,75,76). Occupational exposure criteria and standards for individual elements have been defined and documented for essentially every trace element shown to have a toxic threshold (Refs. 77-83). In general, liquefaction process stream trace element concentrations (Ref. 1, 3-5, 32, 70) fall orders of magnitude below the toxic thresholds defined in the NIOSH criteria documents (Refs. 77-83). On a bulk concentration basis, therefore, adverse health effects due to trace elements are not expected in a worker population. The absence of detectable trace element levels in area monitoring studies (Ref. 4) confirm this conclusion.

Most of the health effects effort directly or indirectly relatable to gasification technology occupational criteria have focused on potential mutagenic and carcinogenic organic constituents in the fuel gas, or on trace elements contaminants.

Past and present efforts to assess the hazards of organic constituents/tars have concentrated on the establishment of rapid mutagenicity screening, direct carcinogenesis testing, metabolism/fate and distribution pathways. Tar fractions from coal conversion have been known to cause skin cancer in mice since 1921 (Ref. 67). Since that time, hundreds of constituent organic compounds tested for carcinogenicity have been documented (Ref. 68). Disproportionately higher mutagenic activity appears in the high-molecular.weight tar factions, and in the basic extracts (Refs. 63,64,69,70), similar to observations previously reported for organics from coal liquefaction. Ongoing carcinogenisis studies (Ref. 64) appear to confirm the earlier work (See Refs. 68,70, 71 for review). Rapid mutagenicity screening procedures for tar fractions and polycyclic aromatics using bacterial testor strains were introduced in the early 1960's (Ref. 84) and the methods developed in sophistication by Ames and coworkers (Refs. 85,86). *Efforts to correlate mutagenicity with carcinogenicity have been partly successful (Refs. 87,88) for substances requiring metabolic activation with microsomal mixed-function oxidases. It is generally agreed that this test provides qualitatively accurate identifications of carcinogens as mutagens in those instances. Substitutions of bacterial testor strains or microsome source (lung for liver, for example) or differences in microsome induction procedures, however, have been reported to substantially alter the results of these bioassay tests (Ref. 69).*

A number of additional rapid bioassay screening procedures for suspected carcinogens are currently under development or in use which complement the bacterial mutagenicity tests. Mutagenesis tests using yeast strains

(Ref. 89), mammalian cells in tissue culture (Refs. 90,91), in vivo chromosomal aberrations (Ref. 92), hamster and human cell transformation assays (Ref. 93), among others have been developed and correlated with carcinogenicity. Thus far, none has provided more reliable or quantitative measure of mutagenicity/carcinogenic hazard potential than the Ames bacterial mutagenesis tests (Refs. 35-86). At the present time, a massive effort involving scores of research groups (Refs. 49-50) supported by EPA, DOE, NIOSH, NIEHS, and the National Cancer Institute is underway to develop and validate some or all of these rapid bioassay screening procedures, to expand their use in the public and private sector activities, and to develop regulatory policies based on their results.

Remember that PAH markers such as benzo(a)pyrene do not correlate with the carcinogenicity of liquefaction tar (Ref. 1).

In order to provide a reliable cancer hazard evaluation of the tar constituents from direct or indirect liquefaction, however, it is important to understand the actual uptake, distribution, metabolism and fates of these compounds in the body. Chang in 1943 (Ref. 94) demonstrated that the uptake of PAH compounds depends heavily on the vehicle. Water, for example, is a poor transport medium, while oils and detergents greatly facilitate the uptake of PAH. PAH derivatives apparently accumulate in the gastrointestinal tract and are excreted in the feces, regardless of their route of administration -- be it skin exposure (Ref. 95), inhalation (Refs. 95,96), or ingestion (Refs. 94,95). Recent work at the Lovelace Inhalation Toxicology Research Institute (ITRI) suggests that PAH materials are cleared from lung tissues (Refs. 69,95) long before microsomal aryl hydrocabon hydroxylase (AHH) induction can begin after a single pulse dose. Parallel mutagenicity screening tests using lung microsomes (Ref. 69) show that induction is necessary (PAH mutagenicity tests give negative results unless prolonged or repeated exposures of animal lungs to PAH occur prior to isolation of the microsomes.).

An occupational health implication of these results is that liquefaction workers exposed to a single catastrophic exposure to PAH may be subject to little or no additional cancer risk unless they smoke or otherwise have pre-induced AHH activity. Long-term low-level exposures to PAH, on the other hand, might provide the necessary AHH pre-induction. Unfortunately, current basic/bioassay data cannot define a significant harm theshold for PAH exposures.

The toxic effects of trace elements have been reviewed extensively (Refs. 1,32,59,70), and the reader is referred to these publications. However, because bulk toxic trace element production rates in coal conversion systems (See Refs. 1,4,32,75 for example) are insufficient to produce a significant acute exposure hazard potential, [illegible] *element effects should cause less concern than effects due to other contaminants such as CO or PAH derivatives. In this regard, existing NIOSH studies for coal liquefaction and gasification plants (Refs. 1,3,4, 32) do not mention toxic trace metals in their industrial hygeine protocols.*

Hazardous gases produced in gasification plants for indirect liquefaction can include CO, H_2S, HCN, phenol, cresol, CS_2, and thiols in decending order of importance. Downstream, process gas constituents may include iron carbonyl, nickel carbonyl, methanol, formaldehyde, and a variety of hydrocarbons, in addition. Because the occupational health criteria for these substances have already been documented by NIOSH (Table 10), relatively little effort is currently being devoted to toxicological or health effects research. Studies relating to occupational health criteria for these gases in coal conversion plants have concentrated on CO because of its concentration dominance as a major product. Recent investigations in this area include a DOE-supported blood CO evaluation in workers (Ref. 49) and an interlaboratory comparison of blood CO analysis methods, under EPA support (Ref. 97). Blood CO measurements represent a body-burden analysis technique for actual worker exposures to CO, which are sufficiently accurate and reliable at the level corresponding to existing occupational health standards (Table 10, also Ref. 97) to establish a CO hazard index for workers in indirect liquefaction plants.

Whether the CO hazard index can accurately reflect the occupational health risks associated with other toxic contaminants remains to be established. The absorption and equilibrium kinetics for CO might differ from those for other, accompanying toxic constituents. Establishment of the proper correlating factors between CO exposure indices and those for other species such as PAH would simplify the monitoring and interpretation of occupational exposures.

For direct liquefaction plants, H_2S (and to a lesser extent CO) are demonstrated (Ref. 4) as actual exposure hazards due to criteria gases (Table 10). Phenol and cresol, among other substances, probably also merit some concern along with PAH compounds. For direct liquefaction plants, CO probably will not suffice as an occupational hazard indicator, unless the gasifier used as H_2 and heat source is so large (see Refs. 11,43, 98) as to dominate the facility.

6.0 OCCUPATIONAL HEALTH ASSESSMENT REQUIREMENTS

A great deal still needs to be learned before one can quantitatively connect the composition of coal conversion streams with occupational health criteria. Existing data are not yet adequate to establish, for example:

- Whether present or planned monitoring protocols are adequate.

- What, if any, significant threshold level values should exist for suspected carcinogens.
- Whether present or planned medical surveillance and industrial hygiene procedures are adequate.

6.1 Characterization needs

In general, analytical data for liquefaction product compositions are inadequate. One is faced with a tradeoff between sampling artifact and analytical sophistication (See Figure 4). Moreover, the reliability of some analytical measurements is compromised when routine calibration steps are ignored. Overall, documentable quality assurance practices are sparse.

Process stream characterization efforts to date have been supported primarily by DOE. Most of that support has gone to instrumentation development projects (Ref. 49). DOE is presently planning an interlaboratory sampling and analytical program on coal liquefaction materials to be carried out through the Pittsburgh Energy Technology Center in collaboration with several private industry laboratories. Results of this work are intended to clarify which process stream procedures will assure the most reliable output for direct liquefaction facilities, but also should provide useful source characterization data. Implementation of liquefaction/pyrolysis kinetics models developed under DOE support should facilitate the extension of process stream characterization among all of the liquefaction systems being supported to commercialization. Coupling this source composition data with emission failure mode and rate data, such as that under development by the DOE-Morgantown Energy Technology Center Component Test Program, should offer some level of emission modeling capability.

6.2 Area, Personal, and Body Burden Characterization

Area sampling and personal dosimetry have already been used in industrial hygeine characterizations of some direct coal liquefaction facilities (Refs. 3,4,26). However, it remains necessary to link these observations to process stream compositions in order to determine the origins of exposure hazards on a commercial plant. For indirect liquefaction plants, monitoring needs will be very similar to those for coal gasification facilities (Ref. 46) Most of the DOE work is being conducted at the Oak Ridge National Laboratory (ORNL) and is focused on the development of personal dosimeters and the automation of area monitors (Ref. 49). For validating personal and area monitoring strategies, it may be sufficient to draw upon the large body of existing NIOSH experience through modifying the sampling and monitoring protocols developed for other industries. Body burden analysis procedures will be needed to calibrate personal monitoring data, and these dosimetry results will in turn direct the siting and calibration of area monitors. Useful output from these activities will be needed within two years. Identification of a single reliable marker substance will accelerate this effort. However, as has already been shown, benzo(a)pyrene will not suffice as a PAH or tar/carcinogen marker (Ref. 4), and CO will probably not suffice as a marker for direct liquefaction facilities (Refs. 4,11).

6.3 Research Needs in Occupational Health Effects

Traditional problems in occupational health studies have included (See Chapter 5 of Ref. 59 for details):

- Confounding variables in epidemiological studies.
- Inadequate monitoring strategies.
- Lack of resolution among the bad actors.
- Hit-or-miss characteristics of bioassays.
- Absence of metabolism/detoxification data.

As a result, cause-effect relationships have generally been very difficult to establish. These difficulties are common to all coal conversion technologies, as are the remedial solutions.

> *The present state of bioassay and toxicology information on coal conversion process stream constituents indicates qualitatively the need for stringent industrial hygiene measures, but (except for CO and other criteria gases) fails to offer any quantitative dose-response indicators. With the possible exception of three very small NIEHS projects, studies which effectively address this problem are only now beginning. In spite of the sophistication of carcinogen/mutagen screening procedures and the breadth of their application, we have little better understanding of the carcinogenic hazards of coal liquefaction constituents today than we had twenty years ago. (Compare Refs. 1,28,64,66, 70 with earlier work cited in Refs. 67;68,71,72,100-103.)*

Additional multidisciplinary research will be needed to quantitatively link the occupational health effects identified in epidemiological investigations (Table 6) with the causal factors established in bioassay screening tests (Table 9). Generic activities which address this need can be categorized as:

- Research on exposure dose-response relationships.
- Resolution of health effects of pollutants in combination, and of confounding variables for occupational epidemiology.
- Risk assessment -- determination of worker exposure hazards.

The ultimate output of these activities is a medical surveillance program for coal liquefaction facilities which maximizes the opportunity to prevent occupational hazards from appearing as occupational illness or poisoning. An additional benefit from these activities is design criteria for worker protection in commercial liquefaction plants.

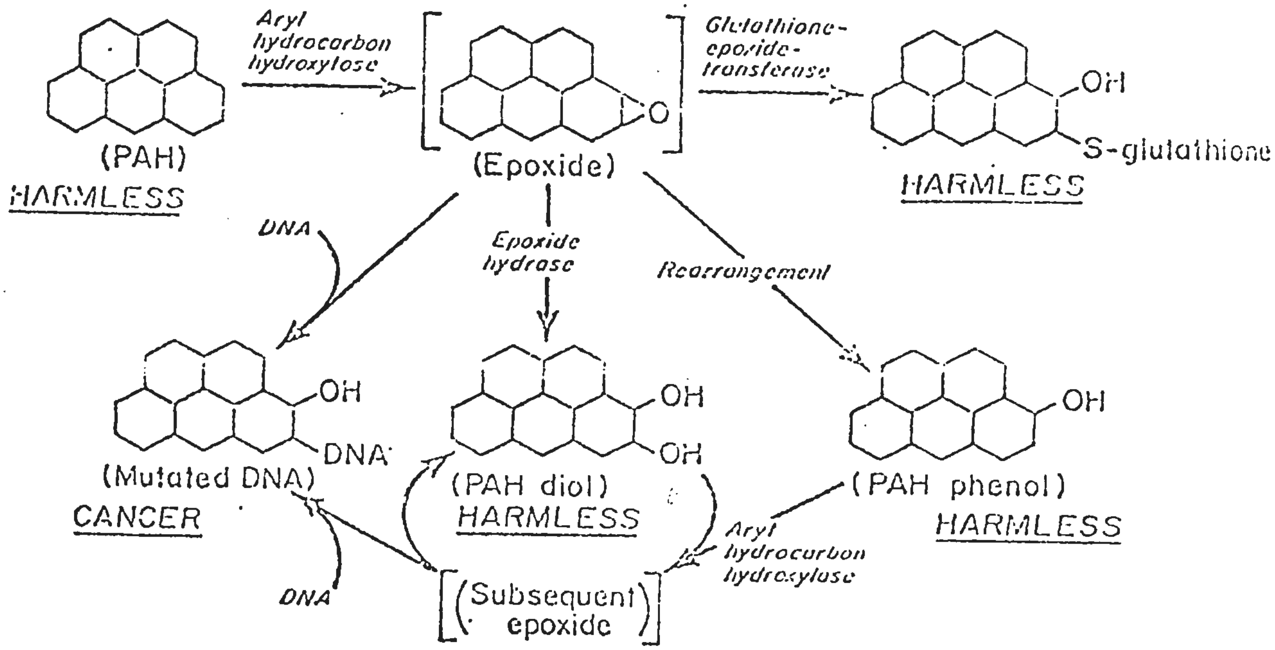
Research on exposure dose-response relationships is intended to supplement the results of present-generation bioassay screening test programs, so that quantitative assessment of the consequences of short-term and long-term occupational exposures can be carried out. Most of the studies supported under this category are expected to involve surrogate materials, and should therefore apply to all coal conversion technologies. Research tasks which will be particularly important in the development of quantitative exposure dose-response relationships include, among other things:

- *Transport, fate, and excretion of hazardous substances in process products and by-products.* Such information is routinely generated in pharmacology research (Ref. 105), especially for FDA testing of new drugs. Similar kinds of information will be required for surrogate compounds relating to coal conversion constituents, such as PAH derivatives. Several groups (Refs. 94-96) have tagged the movement of pyrene and benzo(a)pyrene, for example, in animals. They found that ultimate accumulations occur in the gastro-intestinal tract, regardless of the route of administration. However, this route of transport needs to be verified for a wider spectrum of surrogate PAH compounds before one can generalize this conclusion to coal conversion aromatics.

- *Metabolism and detoxification of pollutants.* Metabolic conversions of pollutants can dramatically alter their potential toxicity or mutagenic/carcinogenic characteristics. Oxidation of PAH compounds, for example (Refs. 59,65,107), represents both a route to mutagenesis and a pathway for detoxification. Figure 6 depicts these competing fates for PAH, based on the epoxide mechanism of Ames *et al* (Ref. 104). Relative activities of aryl hydrocarbon hydroxylase (AHH) and epoxide hydrase can vary from organ to organ, as can their induction properties (Refs. 107,108,109). *Consequently, one cannot a priori associate accumulation sites for PAH derivatives as target organs for occupational cancer.* Detoxification mechanisms for other coal conversion pollutants such as H_2S (Ref. 4) have been identified (Ref. 110), and therapeutic applications reported (Ref. 111).

FIGURE 6

Metabolic (Oxidation) Pathways for Polycyclic Aromatic Hydrocarbons (Ref. 59)



- *Co-contaminant interactions.* Other coal conversion process constituents can affect the uptake and metabolism of particular toxic or mutagenic substances. These companion materials may act as:
  - Vehicles -- substances which accelerate uptake and transport.
  - Promoters -- substances which accelerate metabolic processes.
  - Inducers -- stimulants for the synthesis of metabolic machinery.
  - Inhibitors -- subtances which poison the metabolic machinery.

  Key examples of these kinds of interactions among surrogate compounds known to occur in coal conversion processes have already been documented out of context. *Phenols* are excellent vehicles for PAH compounds, and therefore may accentuate the mutagenic and carcinogenic potential of PAH derivatives (Ref. 106). *Carbon monoxide* (Ref. 112) and certain toxic *trace elements* (Ref. 113) have been shown, on the other hand, to inhibit microsomal mixed-function oxidase activity. Alternatively, vitamin A may retard carcinogenesis (Ref. 114) without specifically affecting other metabolic routes for aromatics. Additional research is needed to determine the relative importance of these potential pollutant-pollutant interactions in the occupational health effects assessment for coal conversion systems.

Results of these efforts will support all of the other occupational health effects activities by providing a data base to:

- *Systematically interpret the effects of coal conversion constituents in combination -- "synergisms", "antagonisms", "co-carcinogenesis", and so on.*
- *Estimate health consequences and worker risks to particular exposure hazards in coal conversion systems.*
- *Select particular targets for medical surveillance.*

Research activities to resolve the health effects of pollutant combinations are intended to incorporate exposure dose-response data into a causal relationship framework for interpreting occupational epidemiology results and for implementing the medical surveillance program for coal liquefaction. Particular tasks toward this end may include:

- *Modeling of exposure dose-response information.*
- *Laboratory verification.* Low-level exposure experiments using coal liquefaction (surrogate) mixtures, to determine which exposure dose-response factors are important for occupational conditions.
- *Occupational epidemiology comparison.* Establish degree of consistency between predicted and reported occupational health effects for workers in coal liquefaction facilities.

Risk assessment activities to determine occupational exposure hazards to coal liquefaction plant workers require input from monitoring activities as well as quantitative occupational health effects data. The results of this work will identify areas of high risk which can be remedied by plant redesign and modification, and will target particularly susceptible job categories for medical surveillance.

6.4 Medical Surveillance Program

Development of a medical surveillance program for demonstration phase and commercial coal liquefaction technology will be aided greatly by input on occupational health effects which links the toxicology data base to the medical manifestations of occupational exposures. The systematic identification of target organs and adverse health effects from these inputs may improve the sensitivity and reliability of morbidity determinations in the medical surveillance and epidemiological studies of coal liquefaction workers.

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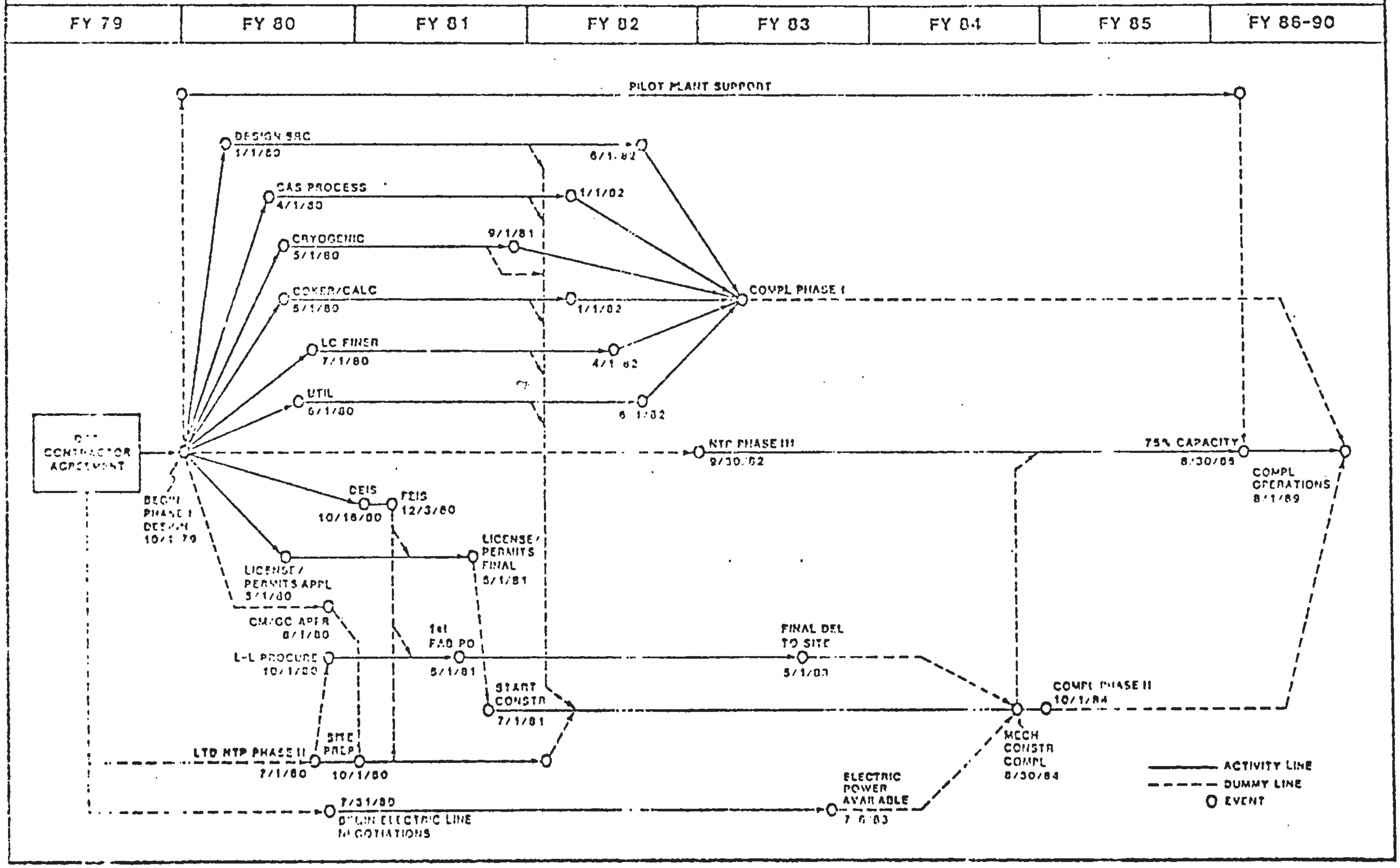
9.0 APPENDIX: U.S. DEPARTMENT OF ENERGY DIRECT LIQUEFACTION SCHEDULES

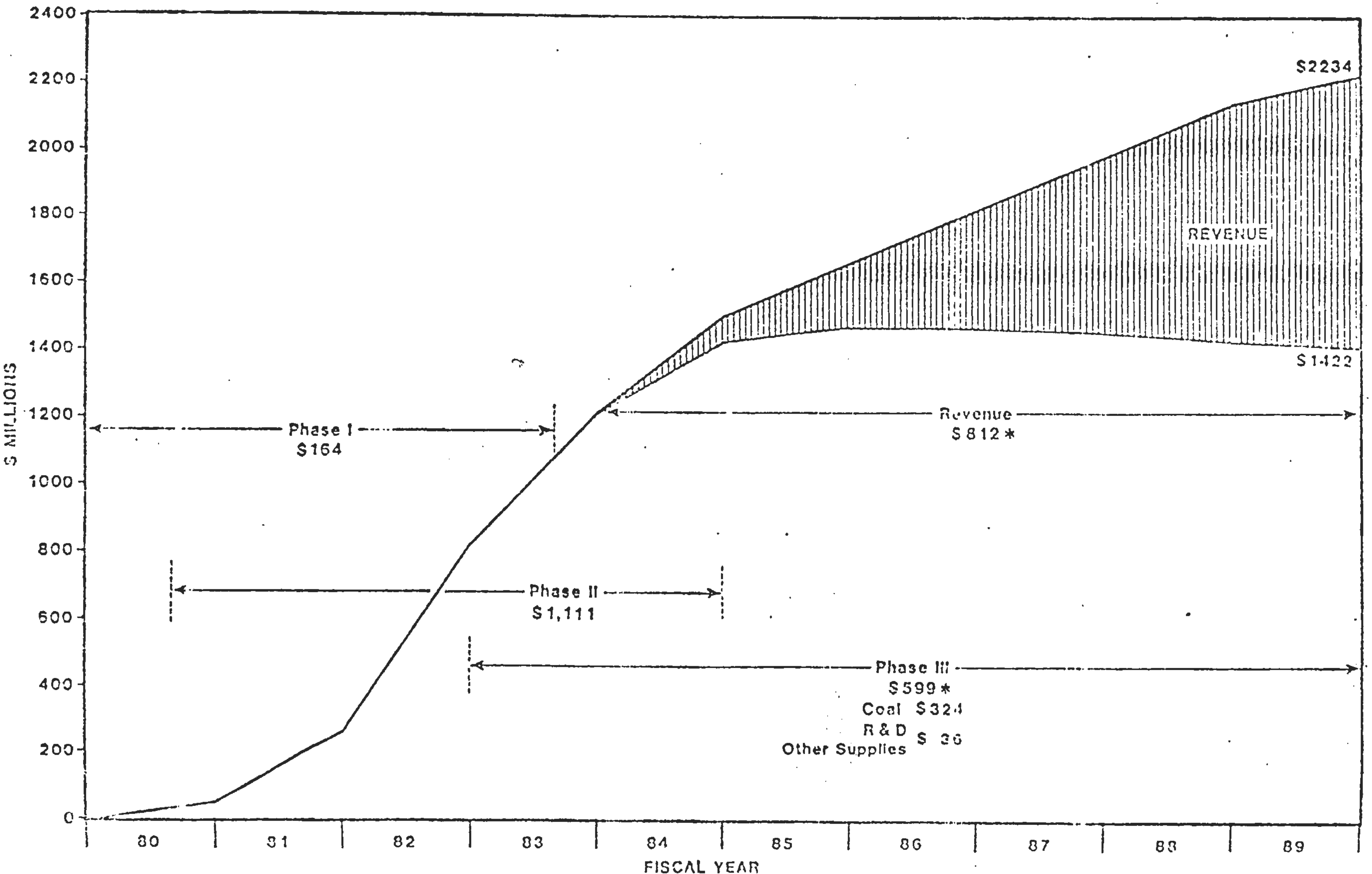
(From Ref. 238)

SRC I EXECUTIVE SUMMARY NETWORK



SRC I
COST ESTIMATE

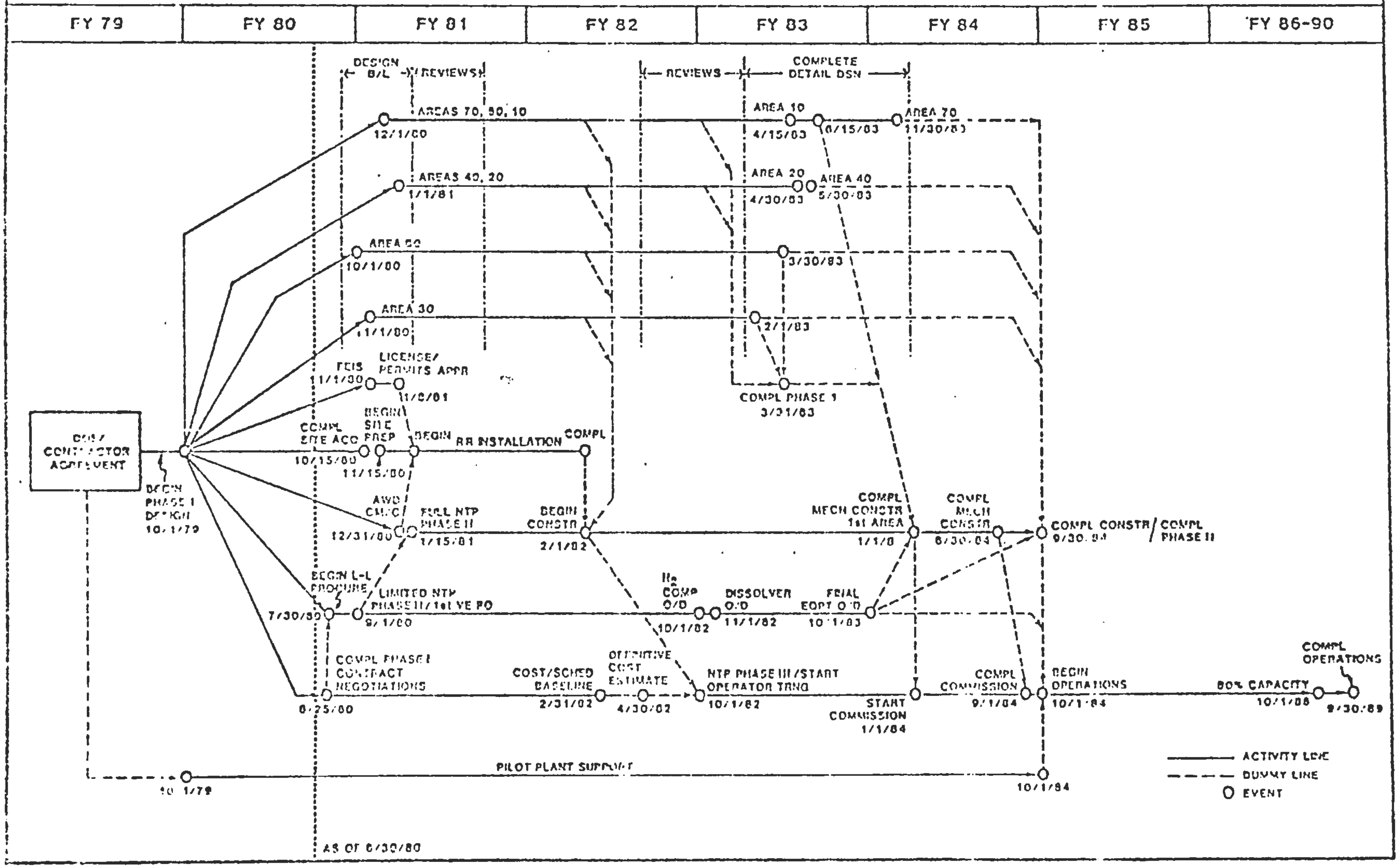
PHASES I, II, III



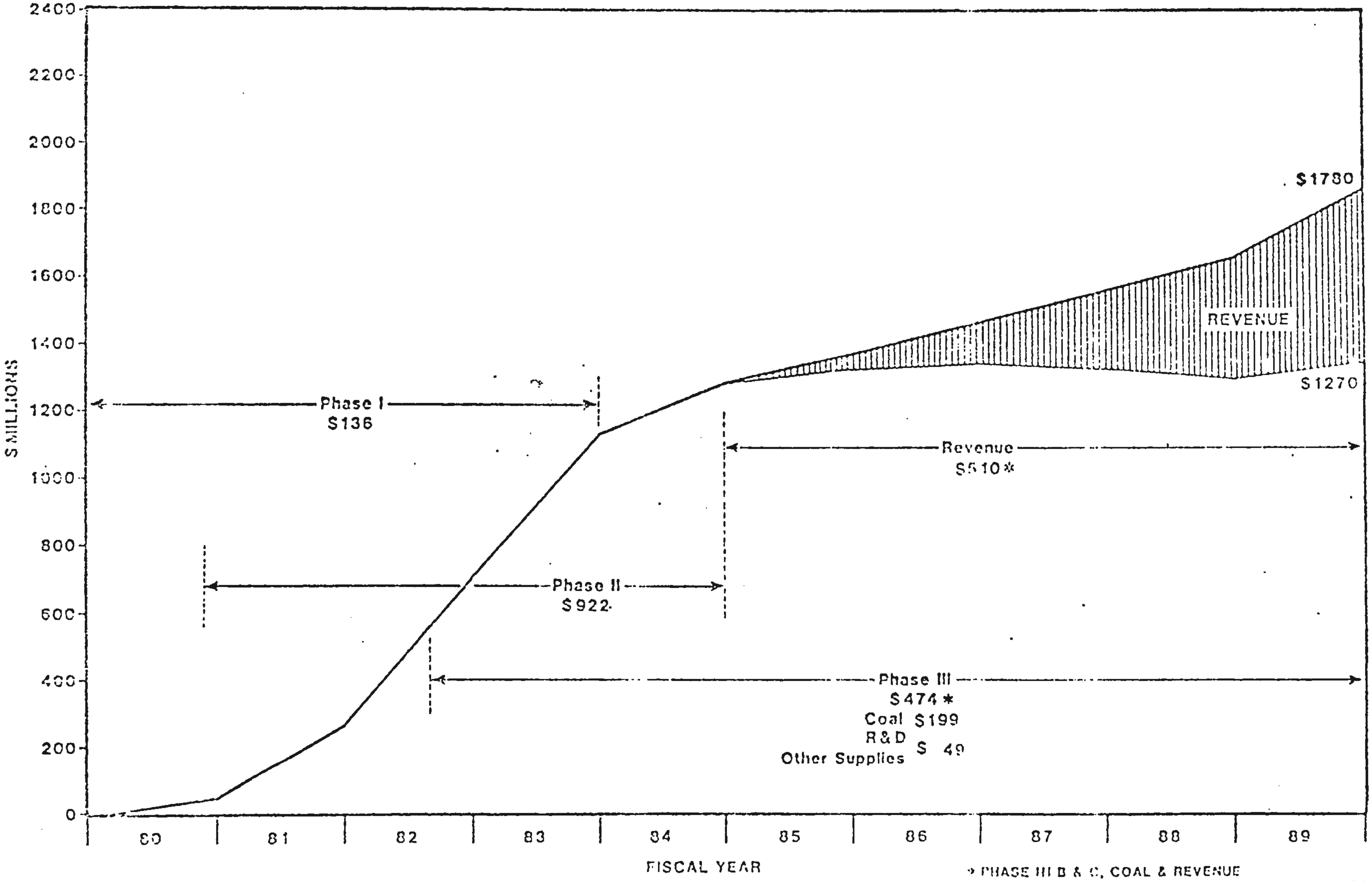
*PHASE III D & C, COAL & REVENUE
ARE NOT ESCALATED

7-13-80

SRC II EXECUTIVE SUMMARY NETWORK



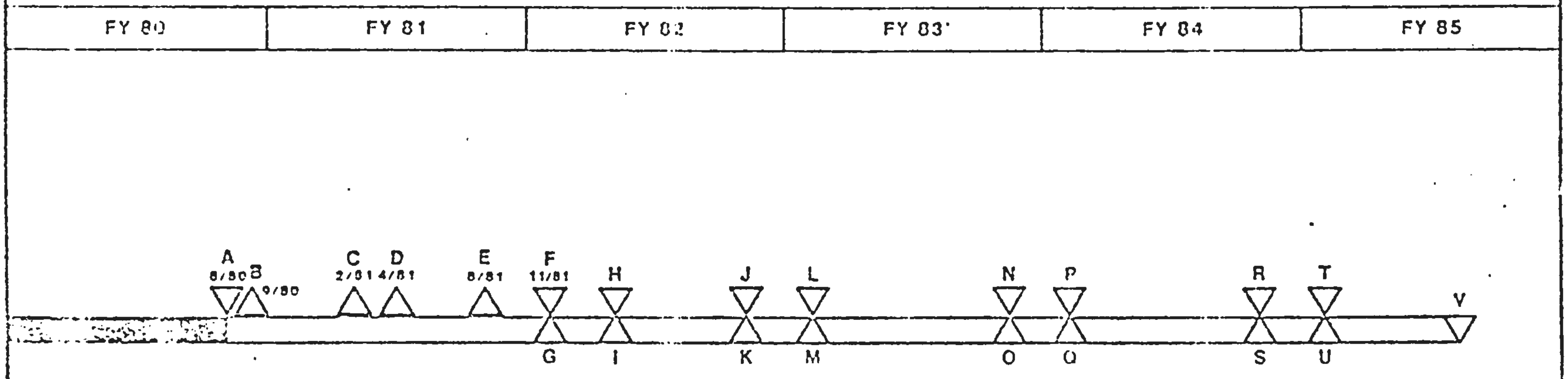
SRC II
COST ESTIMATE
PHASE I, II, III



* PHASE III B & C, COAL & REVENUE ARE NOT ESCALATED

10-1-79

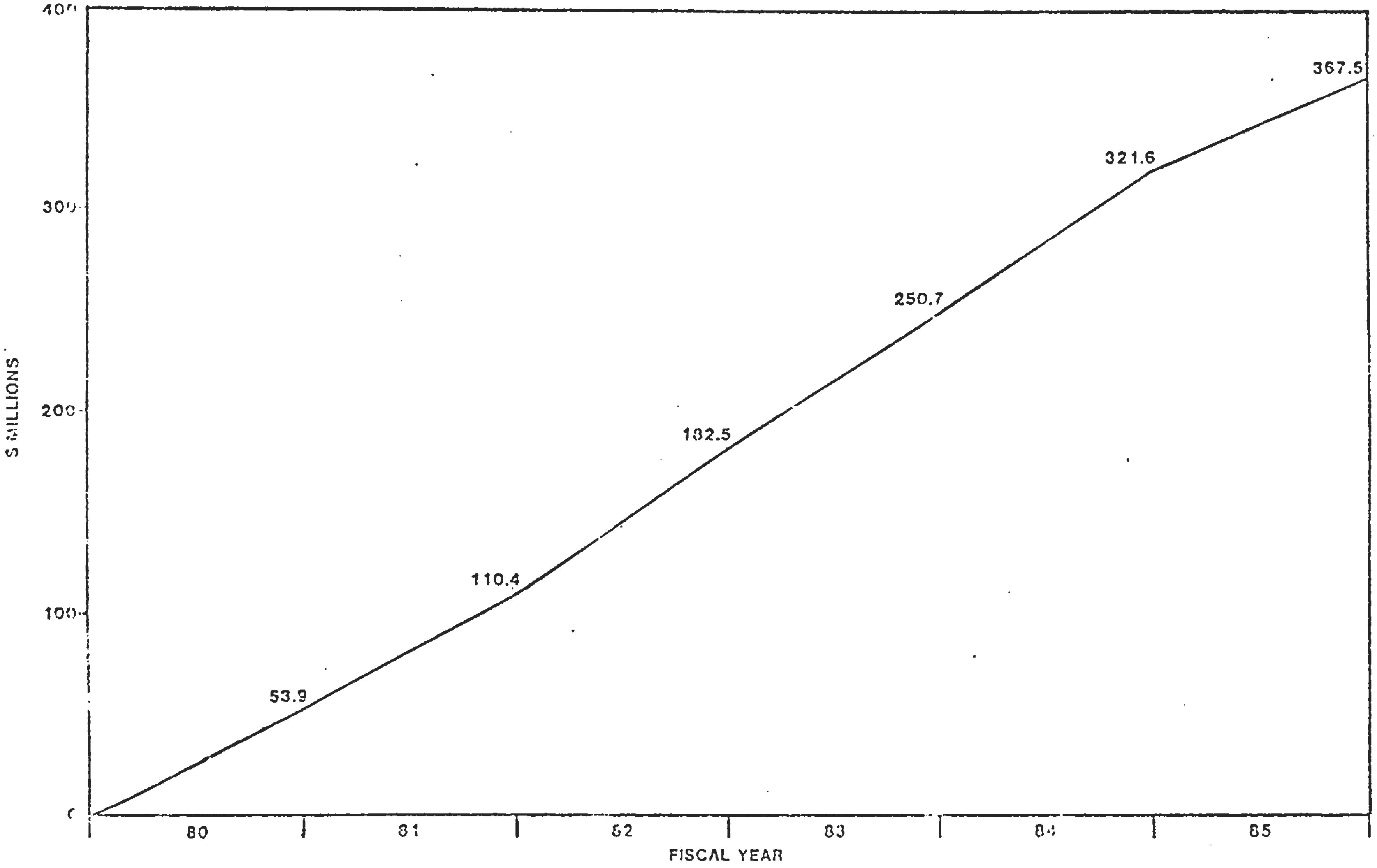
H-COAL EXECUTIVE SUMMARY SCHEDULE



A. COMPLETE BREAKIN - KY COAL
B. BEGIN SYNCRUDE RUN - IL #6 COAL
C. BEGIN FUEL OIL RUN - KY COAL
D. BEGIN FUEL OIL RUN - IL #6 COAL
E. BEGIN SYNCRUDE RUN - WYODAK COAL
F. END SYNCRUDE RUN - WYODAK COAL

FY 82 - 3 MONTHS SHUTDOWN (G-H)
6 MONTHS OPERATION (I-J)
FY 83 - 3 MONTHS SHUTDOWN (K-L)
9 MONTHS OPERATION (M-N)
FY 84 - 3 MONTHS SHUTDOWN (O-P)
9 MONTHS OPERATION (Q-R)
FY 85 - 3 MONTHS OPERATION (S-T)
6 MONTHS FOR MOTHBALLING (U-V)

H-COAL
COST ESTIMATE
PHASE IV



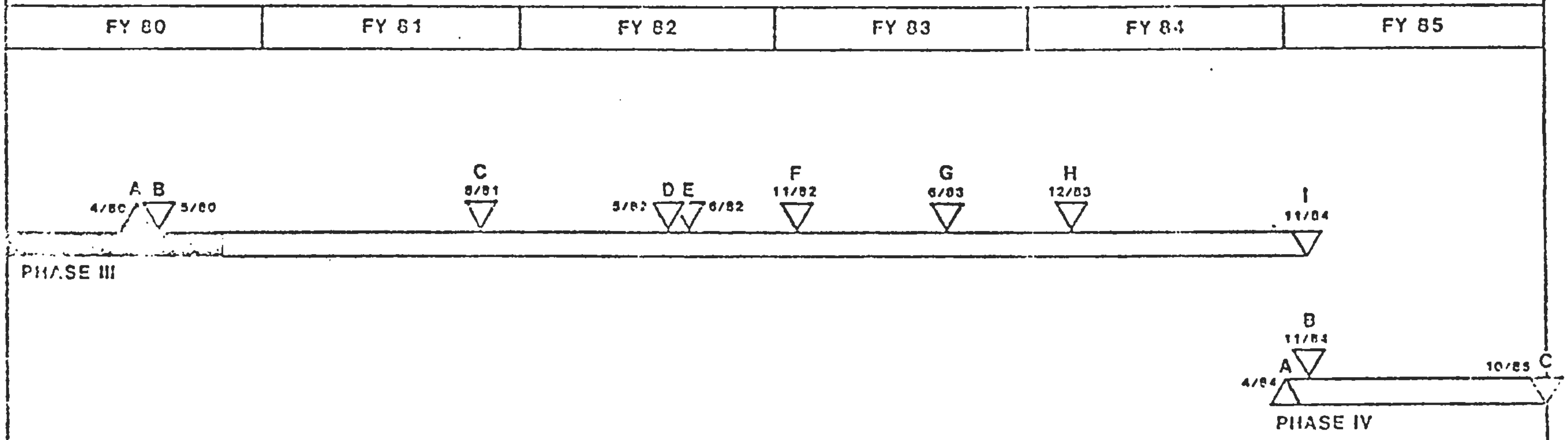
H-COAL PROJECT COST ESTIMATE

(MILLION $)

PHASE IV

	FY 80	FY 81	FY 82	FY 83	FY 84	FY 85	TOTAL
PHASE IV (OPERATION)	53.9	56.5	71.1	69.2	70.9	45.9	367.5

EDS EXECUTIVE SUMMARY SCHEDULE



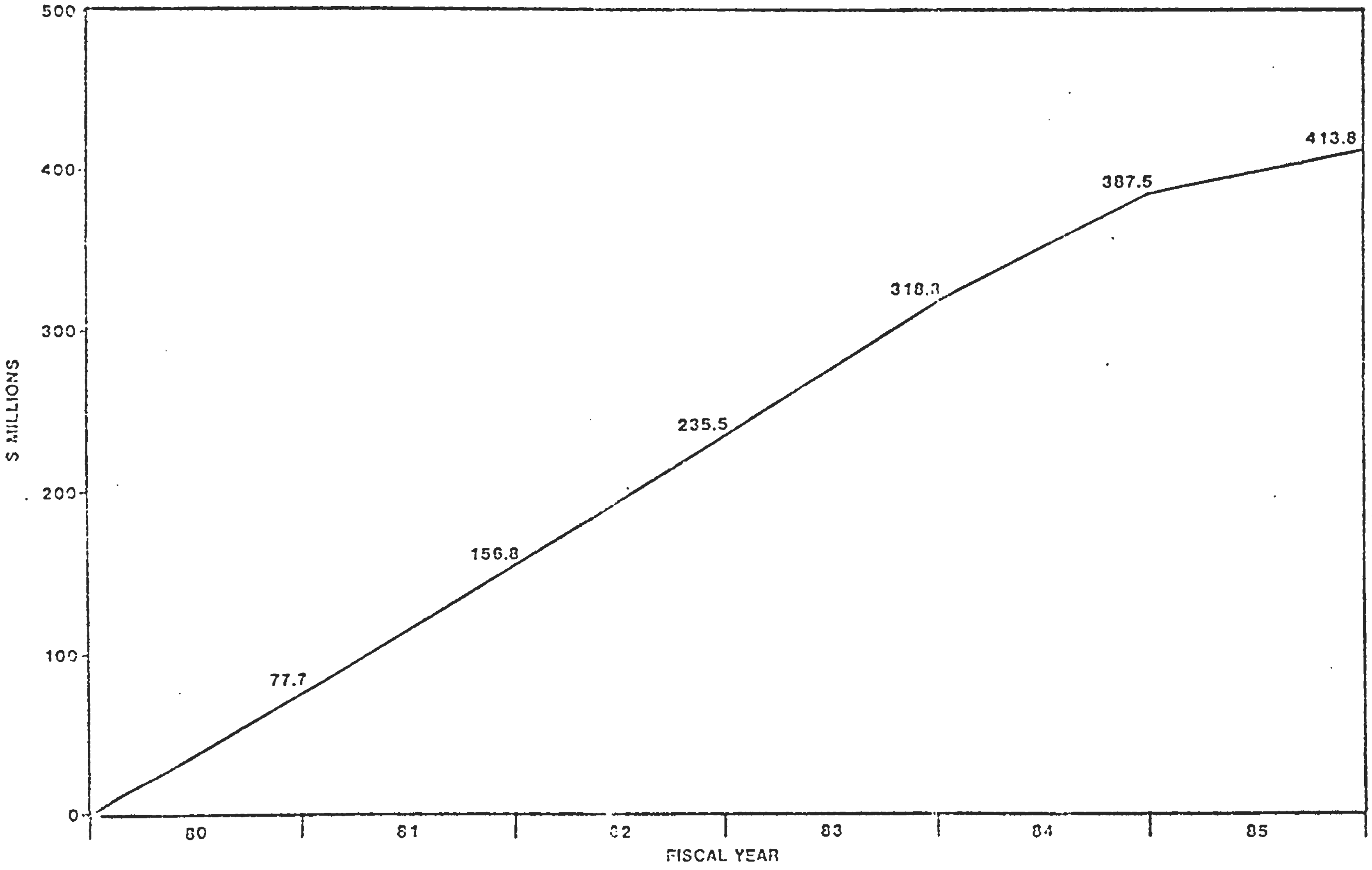
PHASE III

A. START OPERATIONS
B. TWO YEAR ADDITIONAL OPERATIONS APPROVED
C. COMPLETE OPERATIONS BITUMINOUS COAL/START SUBBITUMINOUS COAL OPERATIONS
D. APPROVAL OF ADDITIONAL OPERATIONS
E. START FLEXICOKING OPERATIONS
F. COMPLETE ELCP OPERATION ON THIRD COAL/START ADDITIONAL OPERATION
G. COMPLETE OPERATIONS FIRST ELCP BOTTOMS
H. COMPLETE OPERATIONS SECOND ELCP BOTTOMS
I. COMPLETE OPERATIONS

PHASE IV

A. DECISION ON DISPOSITION
B. START DISPOSITION
C. COMPLETE DISPOSITION

EDS
COST ESTIMATE
PHASE IV



EDS PROJECT COST ESTIMATE

(MILLION $)

PHASE I, II, III & IV

	FY 80	FY 81	FY 82	FY 83	FY 84	FY 85	TOTAL
PHASE 0							
PHASE I FINAL DESIGN	13.0						13.0
PHASE I CONSTRUCTION	32.7	27.3	23.4	28.0			111.4
PHASE III OPERATIONS	32.0	51.8	55.3	53.2	69.2	26.3	287.8
PHASE IV SHUTDOWN				1.6			1.6
TOTAL	77.7	79.1	78.7	82.8	69.2	26.3	413.8

EXPENDITURES PRIOR FY's - $139.3 MILLION