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FINDING SOLUTIONS TO POTENTIAL HEALTH AND ENVIRONMENTAL PROBLEMS ASSOCIATED WITH COAL LIQUEFACTION MATERIALS

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ABSTRACT

Chemically complex materials produced by different coal liquefaction processes and under various stages of process design and operating conditions have been screened for potential health and environmental effects. Biologically active components of these materials have been identified, and the environmental fate of problematic agents is currently being determined.

Coal-derived liquids are generally more active than shale oil and petroleum crudes in biological test systems. Biologically active agents include primary aromatic amines, polynuclear aromatic hydrocarbons, phenols and others. However, both synergistic and antagonistic interactions occur among constituents of chemically complex mixtures. Hydrotreating, a refining or upgrading process, selective distillation, other process conditions and environmental factors also influence chemical characteristics and biological activity of coal-derived materials. Eliminating toxic input of coal liquids to ecological test systems results in partial system recovery.

The growing health and environmental data-base has provided input for assessment, and has been used by developers to design occupational health and industrial hygiene programs and to select process modifications and product slates that minimize risk to man and the environment. The data may also aid selection of control technologies, mitigative strategies, special handling and accident prevention procedures or spill-cleanup options to enhance the environmental acceptability of a coal liquefaction industry.

1. INTRODUCTION

Increasing energy demands, rising prices, and an unstable world oil market have stimulated international interest in developing alternative sources of fuel. Hydrogenation of coal under high temperature and pressure produces gaseous, liquid and solid products that may serve as substitutes for coal or oil. Four major direct coal liquefaction processes have been under development in the United States [1] and may be available for large-scale use in the future. These include two solvent refined coal (SRC-I and -II) processes, EDS and H-coal. Although all produce liquid fuel products, the SRC-I process also produces a low-sulfur, low-ash, solid fuel.

Both SRC process options were evaluated at a 30- to 50-ton/day pilot plant at Ft. Lewis, Washington. The SRC-I process and its Two-Stage Liquefaction (TSL) variation have been evaluated at a 6-ton/day pilot plant at Wilsonville, Alabama. An Integrated TSL (ITSL) option is also being studied at a smaller-scale process development unit (PDU) in New Brunswick, New Jersey. The H-coal process was evaluated at a 200- to 600-ton/day facility at Catlettsburg, Kentucky, while the EDS process was studied at a 250-ton/day pilot plant at Baytown, Texas. Other coal liquefaction options (Fig. 1) are being developed and evaluated in England, West Germany, Japan and South Africa, where a commercial indirect liquefaction facility is now operable.

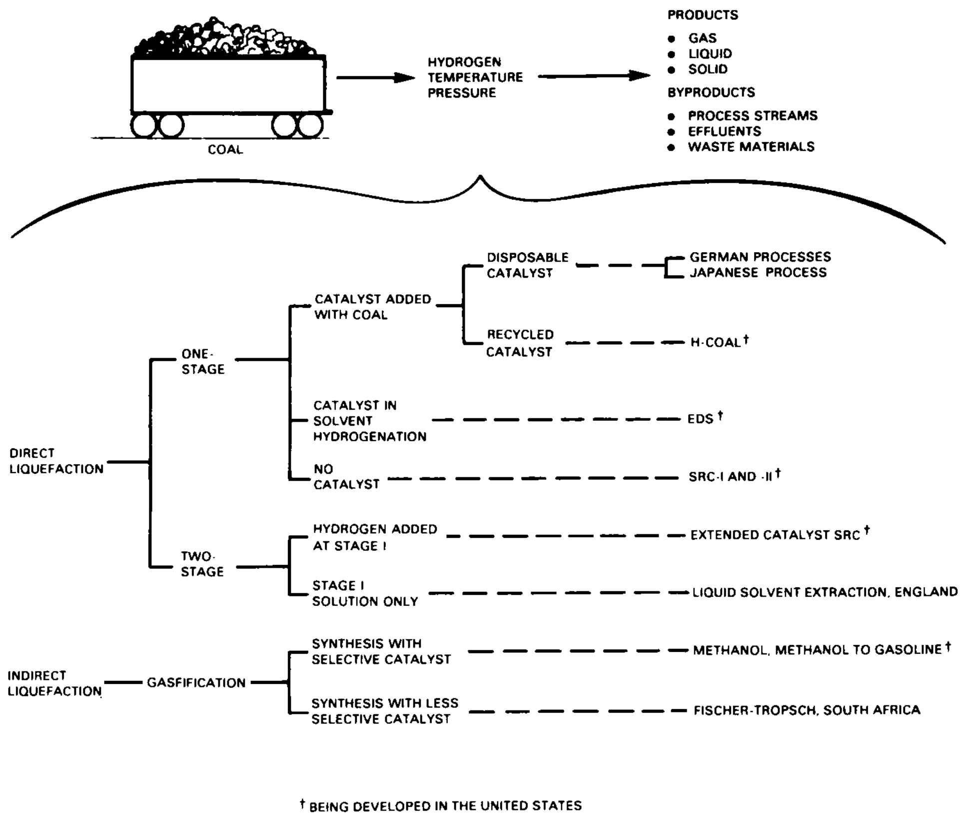

Fig. 1. Coal liquefaction and classification of major process options under development [2], derived from [3].

Along with engineering design and development, the U.S. Department of Energy (DOE) established a program to evaluate the environmental acceptability of coal liquefaction processes being developed in the United States [4,5]. Epidemiological studies and toxicological research on coal liquefaction, gasification and coking process materials had indicated that constituents of coal tars and heavy coal liquids were carcinogenic [6-9]. Studies on direct coal liquefaction processes supported this conclusion [4,5]. Additionally, the high phenol content and complex nature of coal liquids implied greater acute and chronic toxicity if these materials were released to the environment than that observed for crude petroleums [10].

DOE selected several organizations to study the health, environmental and safety aspects of direct coal liquefaction processes. Battelle's Pacific Northwest Laboratories were assigned responsibility for evaluating SRC materials and initiated comprehensive health and environmental effects research programs [11,12]. Similar programs were initiated by the Oak Ridge National Laboratory for the H-coal process [13] and by Exxon Research and Engineering

Co. for the EDS process [14]. Battelle subsequently established working relationships with several process developers and obtained materials representing all major U.S. and two foreign coal liquefaction process options.

2. PROGRAM OBJECTIVES

Objectives of the DOE programs were to: 1) identify and evaluate long-term health and environmental issues associated with direct coal liquefaction; 2) evaluate options to permit environmentally acceptable design; and 3) assess risk to man and the environment from deployment of a large-scale industry.

3. RESEARCH STRATEGY

Although DOE's objectives focused on assessing potential health and environmental effects of a coal liquefaction industry, there have never been

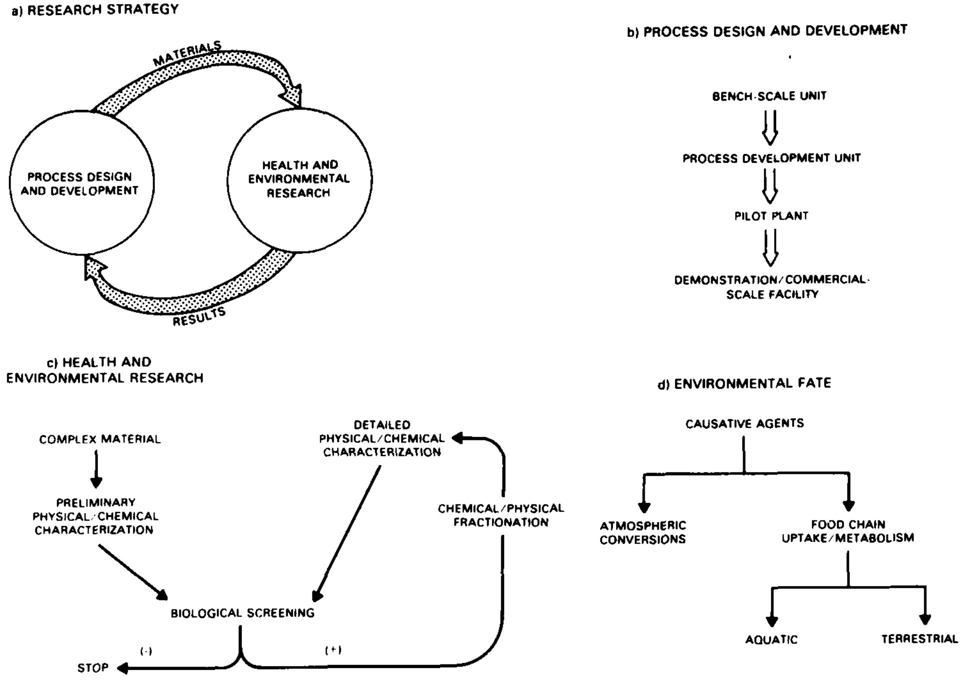

Fig. 2. Linking health and environmental research with technology development [15]. (a) Health and environmental studies are integrated with early process design and development. (b) Complex organic materials produced under various stages of process design and scale are (c) screened with various chemical, health and environmental assays. Materials showing potential biological activity undergo more detailed analysis to identify causative agents. (d) Environmental fate and potential food chain transfer of agents responsible for biological activity are evaluated.

any operating large-scale (i.e., demonstration- or commercial-scale) coal liquefaction facilities in the United States. Therefore, research and assessment have utilized materials produced at small-scale facilities (bench, PDU, pilot plants), that were considered generically representative of large-scale operations. Health and environmental research has accompanied engineering development (Fig. 2) so that results may influence final process designs. For comparative purposes, other fossil-derived materials and selected chemicals have also been evaluated. These reference materials which include shale oil, crude and refined petroleums, and pure forms of known mutagens and carcinogens, help to place in clearer perspective results obtained with coal liquefaction materials.

At Battelle, research on coal-derived materials has been performed in chronologically overlapping phases [11,12,16].

3.1 Phase I

Initially, materials from existing coal liquefaction facilities were screened using a battery of short-term health and environmental assays (Table 1). Chemical fractionation and detailed chemical analyses were performed on those materials showing biological activity, to identify components responsible for effect. Results of the short-term screening assays indicated the environmental properties and potential effects of coal liquefaction materials, identified materials that may require special handling or additional processing to minimize environmental risk before they are widely distributed, and aided in the design of longer-term, more expensive studies.

Table 1. Short-term Health and Environmental Screening Studies

Assay	Test Organism(s)	Detects
Health		
In Vitro	Bacteria (various species and strains)	Mutation, chromosome damage, chromosome recombination, toxicity
	Cultured mammalian Cells	Cell transformation, mutation, chromosome damage, toxicity
In Vivo	Rodents	Acute oral and dermal toxicity, teratogenicity, carcinogenicity
Environmental		
Aquatic	Algae, invertebrates, fish	Acute and chronic toxicity, behavior
Terrestrial	Plants	Acute and chronic toxicity

3.2 Phase II

Longer-term research has emphasized materials considered most representative of a potential large-scale industry. These materials have been studied in whole-animals to evaluate their potential carcinogenicity and teratogenicity, and in more complex ecological systems to evaluate toxic effects and environmental fate (Table 2). Again, chemical fractionation and detailed chemical analyses have been used to identify components of greatest concern. Results of longer-term experiments are being correlated with those of shorter-term studies and will provide a firmer basis for assessing health and environmental risks.

Table 2. Long-term Health and Environmental Studies

Health Studies (Whole Animal)	Environmental Studies
Skin carcinogenicity	Model ecosystems
Inhalation toxicology	Biological fate (bioconcentration, biomagnification, biodegradation)
Reproductive effects	Chemical Fate (mobility, persistence/degradation, environmental concentration)
Teratology and developmental toxicology	Food Chain Transfer
Neurobehavioral toxicology	Environmental Pathways Modeling

3.3 Phase III

A third phase of research is evaluating the influence of process or operational conditions (i.e., temperature, catalyst condition, recycle configuration, etc.), and control technology options on potential health and environmental effects of coal liquefaction materials. Short-term health and environmental assays used in Phase I that correlate with longer-term assays used in Phase II are being used in Phase III. As in Phases I and II, integrated chemical fractionation and detailed analytical methods are being used to determine which components affect biological activity. Results of these studies have provided a basis for determining the efficacy of process or operational modifications and control technology options to minimize potential health and environmental effects.

3.4 Phase IV

Finally, data from Phases I, II and III may be used to select methods with which to monitor the workplace and local environment at a large-scale coal liquefaction facility. This effort is needed to validate predictions of environmental risk based on laboratory data, and to assure a safe environment for the work force and general populace.

4. FINDINGS

DOE-sponsored efforts to evaluate potential health, and environmental fate and effects of coal liquefaction materials have recently been reviewed [4,5]. Selected data are summarized below to demonstrate the approach used to study complex mixtures, and how the data may aid the design of an environmentally acceptable technology.

4.1 Health Effects and Causative Agents

Coal-derived materials are chemically complex and, compared to crude petroleums, are enriched in polynuclear aromatic hydrocarbon (PAH), basic, acidic and insoluble constituents. Higher-boiling-range materials are enriched in both basic nitrogen-containing and highly polar materials believed to be responsible for biological activity.

Higher-boiling-range coal liquids such as SRC-I process solvent (PS), SRC-II heavy distillate (HD), and PDU-derived H-coal distillates are mutagenic in microbial test systems; lower-boiling-range coal liquids such as SRC-I light oil (LO) and wash solvent (WS), SRC-II light (LD) and middle distillates (MD), and PDU-derived H-coal materials are not. Studies with distillation cuts show that the mutagenically active constituents of coal liquids (e.g., SRC-II HD) occur in those materials boiling above 371°C (700°F). The latter make up about 20% of the full-boiling-range material. Chemical fractionation and analysis, coupled with microbial assays in which polycyclic, primary aromatic amines (PAAs), as pure compounds and in complex coal liquids, were selectively activated (using mixed function amine oxidase) and deactivated (using nitrous acid), and where biological activity was correlated with PAA concentration, suggested that the highest specific mutagenic activity was associated with the PAAs. However, genetically active fractions are also enriched in azaarenes and polar-substituted aromatics that may affect genetic activity. Other studies indicate that materials showing mutagenic activity in microbial assays also cause transformation (biochemical and morphological changes) in cultured mammalian cells.

When applied to the shaved backs of mice, higher-boiling-range coal-derived materials (SRC-II HD, SRC-I PS, H-coal distillates, EDS liquids and others) and shale oil and benzo[a]pyrene (BaP), a known carcinogen, produced high incidences of skin tumors. Lower-boiling-range coal liquids do not appear to possess this tumorigenic activity.

Studies to evaluate potential teratogenicity, where pregnant rats were exposed to coal liquids (SRC-II LD, MD and HD, SRC-I LO, WS and PS) either orally or through aerosols, showed that fetal growth and survival were decreased. Administration of SRC-I PS and SRC-II HD also increased the incidence of fetal malformations, primarily cleft palate, hypoplastic (immature) lungs and herniated diaphragms. Coal-derived materials were also teratogenic in amphibian and insect test systems [4].

4.2 Ecological Effects and Environmental Fate

Toxicity studies [4,5,17] with aquatic test species (phytoplankton, invertebrates, fish) show that various coal liquids (SRC-I, SRC-II, ITSL, EDS) may be several hundred times more toxic than comparable petroleum products (i.e. No. 6 or No. 2 fuel oil or Prudhoe Bay crude). Acute toxicity (lethality) of the water-soluble-fraction (WSF) of coal liquids reflects high concentrations of low-molecular-weight, easily degradable phenolic compounds. Chronic toxicity (effects on growth, reproduction, etc.) appears due to higher-molecular- weight and more persistent compounds which may also include phenols. Although some fish species avoided acutely lethal concentrations of an SRC-II WSF, they did not detect or avoid concentrations causing chronic effects.

When coal liquids were released into experimental ponds or streams, extensive changes occurred in the structure and function of the biological community. Many zooplankton species were eliminated, and diatoms were replaced by blue-green algae. Patterns of ecosystem metabolism were also affected (i.e. a food web based on plant production was replaced by one based on detritus). However, termination of toxic input resulted in partial recovery of the ecological system. In simpler test systems where algae were exposed to concentrations of coal liquid causing chronic effects, the population also recovered once the toxicant was removed.

Studies in which barley was exposed to an SRC-II liquid in soil indicated potential for significant toxicity in a terrestrial habitat. However, toxic effects were reduced following overwintering. Similar studies with the SRC-I solid product showed it was nontoxic, although layering this material under a soil overburden retarded root growth.

4.3 Effects of Chemical Matrix on Biological Response

Recent findings suggest that biological responses to a particular chemical agent vary, depending on whether that material is presented to the organism or environment as a pure compound or in a complex mixture. Selected data comparing biological responses (mutagenicity, carcinogenicity, biouptake, acute toxicity, fish avoidance) to coal-liquid constituents tested as pure compounds and in complex mixtures are shown in Fig. 3. The developing data- base suggests that both synergistic and antagonistic interactions occur among constituents of chemically complex organic materials. Thus, results of studies with pure compounds alone cannot be used with confidence to predict effects of complex materials. Current research efforts are addressing this problem.

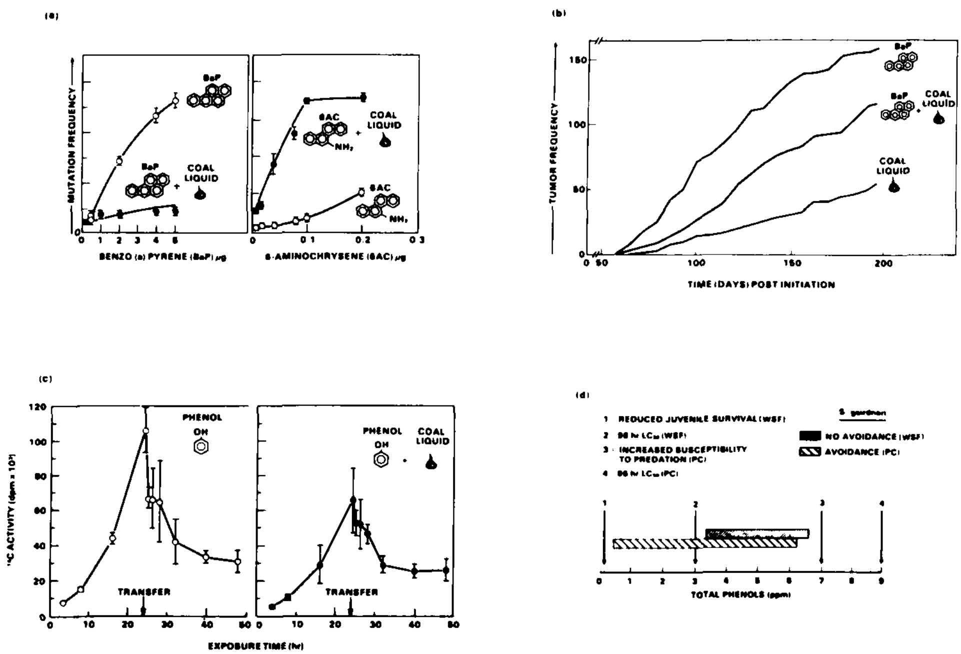

Fig. 3. Effects of chemical matrix in coal liquids on biological activity of selected compounds [18]. (a) Mutagenicity of benzo(a)pyrene (BaP) and 6-aminochrysene (6-AC), derived from [19]. (b) Carcinogenicity of BaP, derived from [19]. (c) Biouptake of phenol, derived from [20]. (d) Behavioral response of fish and acute toxicity to phenol as a pure compound (PC) and in a coal-liquid water-soluble fraction (WSF), from [21].

5. TECHNOLOGICAL IMPLICATIONS

Results of these studies have significant implications for coal-liquefaction process designers and developers who are concerned with minimizing risks to the work force, general populace and the environment. Full-boiling-range coal-derived materials are generally more biologically active than shale oil and petroleum. High-boiling-range coal-derived materials are mutagenic, teratogenic and carcinogenic in laboratory test systems. Coal liquids also cause acute and chronic effects in organisms representing various ecological trophic (feeding) levels. Chemical constituents of coal liquids, responsible for biological effects include PAAs, PAHs, phenols and others. Knowledge of these potentially detrimental health and environmental effects, and their causative agents, can be used to design environmentally acceptable coal conversion processes.

For example, hydrotreating (a process which catalytically stabilizes liquid hydrocarbon products and/or removes objectionable elements by reacting them with hydrogen) is one potential method of refining or upgrading raw coal liquids prior to marketing. Hydrotreating also reduces the mutagenicity, and carcinogenicity of coal liquids. Hydrotreating reduced the mutagenicity of an SRC-II distillate blend by more than 100-fold. Hydrotreating also reduced the concentrations of two genetically active chemical classes, the PAAs and PAHs. The PAAs detected in the distillate blend, were below the limits of detection in hydrotreated materials. Concentrations of BaP, a known mutagen/carcinogen, were reduced at least 75% by hydrotreatment. Hydrotreating also reduced the concentration of phenols responsible for toxicity to aquatic organisms. Finally, removal of nitrogen compounds by hydrotreating may reduce teratogenic activity.

Hydrotreating is an expensive operation and processing a full-boiling-range coal liquid is currently not economically feasible. However, because mutagenic activity of coal-derived materials is due primarily to PAAs that are found only in materials boiling above 371°C (700°F), distillation cuts might be adjusted so that the commercial coal liquid product contains little mutagenic potential. Alternatively, distillation cuts could be selected to concentrate mutagenically active compounds in a high-boiling relatively small process stream, that might then be hydrotreated economically, recycled to extinction inplant, or gasified.

Studies with PDU-derived materials representing a TSL option suggest that process variables (residence time in the liquefaction reactor, reaction temperature, catalyst condition, etc.) contributing to extraction severity, influence chemical characteristics and biological activity [22]. Thus, it may also be possible to modify process variables to minimize biological activity of coal-derived products.

Although engineering and economic factors must also be considered, the growing health and environmental data base can now be incorporated into the decision-making process. It is noteworthy that, except for acute toxicity, coal liquids currently projected for commercial use are not expected to have higher biological activity than shale oil or petroleum. If process modifications, adjusting distillation cuts, and/or hydrotreating, are not technically or economically feasible, process designers can begin, now, to develop special handling and accident prevention procedures to minimize health and environmental risks.

Accidental spills of coal liquids and other coal-derived materials during transport are a potential threat to the environment. Aquatic organisms exposed to coal liquid components for long periods of time will experience a constantly changing spectrum of organic compounds, and different species will experience different toxic effects. Coal liquids are also toxic to terrestrial plants. Some constituents of coal-derived materials will be taken up and translocated through food chains leading to man. Low-molecular-weight compounds, such as phenols, which are responsible for acute effects, degrade rapidly. Higher-molecular-weight compounds are more persistent and bind to soils and sediments, causing long-term effects at low concentrations. Although some species of fish, avoided acutely toxic concentrations of SRC liquids, they did not avoid concentrations causing chronic effects. Thus, assuming that accidental spills of coal liquids will occur, cleanup procedures need to be developed to minimize potential chronic effects in aquatic and/or terrestrial systems. Some aquatic populations (e.g., algae) can recover following exposure to toxic concentrations of coal liquids in water after the material is removed.

6. SUMMARY

Potential health and environmental risks associated with deployment of a large-scale coal liquefaction industry are being assessed during the early design stages of technology development. Chemists, biologists, ecologists and engineers have been involved in a cooperative interdisciplinary effort to solve environmental problems before process designs are finalized and facility construction begins, rather than waiting until regulatory agencies require studies or until after construction when costs are higher. These efforts have provided guidance for identifying marketable products (materials that boil below 700°F), and for selecting process modifications (e.g. recycle configurations), control technology options, mitigative strategies, accident prevention, spill cleanup and solid-waste disposal procedures to minimize adverse human health and environmental risks. Although the example given is related to developing a coal conversion industry, the research strategy or approach is equally applicable to development of other energy-related processes that produce organically complex materials (petroleum, shale oil, fuels from biomass etc.). In fact, the concepts described can be applied to the development of any technology or the environmentally safe exploitation of any resource.

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