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Fuel Contaminants: Volume 3. Control of Coal-related Pollutants

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Fuel Contaminants: Volume 3. Control of Coal-related Pollutants

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ABSTRACT

Volume III of the series of reports on fuel contaminants is a continuation of the removal technology evaluation studies reported in Volume II. Specifically the objective of the study was to identify possible future control strategies for removal of pollutants in coal and coal-derived liquids based on the findings from reviews on contaminant chemistry (Volume I) and the evaluation of removal technology used for various solid and liquid fuels. Alternative approaches to isolating or removing contaminants were also identified as were new approaches with potential for contaminant removal. Rationale used to select and tentatively rank the various approaches are described. Of the approaches considered, six were selected for preliminary assessment by experimentation. These are:

- Biological action on coal-derived liquids--Although bacteria can tolerate low levels of aromatic hydrocarbons, the addition of aromatic sulfur compounds increases the toxicity of these solvents to bacteria. Hence the prospects of using non-mutated bacteria for sulfur and/or nitrogen removal from coal liquids appears small.
- Enhancement of pyrite removal during immiscible fluid agglomeration--Pyrite removal equivalent to that obtained for float-sink analysis was obtained by pretreatment and oil agglomeration. The same technique was found effective for the recovery of over 90 percent of coal from coal cleaning plant fines.
- Extraction of clean fuels from coal liquids--Light hydrocarbons can be used to extract 83 percent of coal liquid

at super critical conditions to yield a low sulfur and nitrogen fuel.

- Concentration of organic sulfur and nitrogen and ash from coal liquids--Up to 76 percent of the sulfur and about 10 percent of the nitrogen can be removed by passing coal liquids over various special porous media.
- Conversion of coal liquefaction residues to environmentally acceptable fuels--Treatment of coal liquefaction residue with hydrogen-carbon monoxide mixtures reduced nitrogen content by as much as 14 percent.
- Improvements in pyrite liberation from coal--This part of the study was not undertaken because of significant advances by others

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SECTION 1

INTRODUCTION

Major air pollutants have made their presence felt for many years and were the obvious first targets when the Air Quality Act of 1970 was enacted. Thus, a concerted effort is under way with Federal government support to develop practical and effective methods for their control -- especially the elimination of sulfur emissions from the combustion of fuels. Analogous major efforts are also under way on other visible or readily identifiable pollutants such as particulates, oxides of nitrogen, etc. The impact of control of air pollutants on the pollution of water and land became of equal concern and subsequent targets for control.

In accordance with the responsibilities mandated by the Congress, the Environmental Protection Agency is developing information on the control of pollutants emitted to the air, water and land from stationary sources. This includes not only the major pollutants mentioned above, but also other pollutants such as trace metals which, although emitted only a very low concentrations, also pose serious problems because of their toxicity.

Treating fuel to remove contaminants prior to combustion is an attractive technique because of the possibility of removing several contaminants in one processing step. The combustion of a clean fuel would obviate the need for stack-gas treatment methods. It now appears that certain pollutants, especially SO_2 and particulates, can be removed by an integrated stack-gas treatment process, but the removal of other pollutants such as NO_x and volatile trace metals would probably be difficult to integrate into a stack-gas treatment process. While some NO_x is formed from the nitrogen in the combustion air, a considerable portion is also formed from fuel nitrogen. Accordingly, the primary objective of the current research program is to identify and examine the feasibility of fuel contaminant removal prior to combustion, with emphasis on sulfur and nitrogen. However consideration was

given to trace metals, halides, phosphorus, and other potential air pollutants.

The program has provided a survey of the literature on the characteristics of the sulfur, nitrogen, and trace element contaminants in coal, petroleum, shale oil, and tar sand oil, and has classified and analyzed methods employed to remove the contaminants from these fuel types.[1,2] During this study, removal methods were identified that had not been used for various reasons but that may be used today. In addition, alternative approaches for isolating or removing contaminants were also identified, as were new approaches with potential for contaminant removal. As part of the study, it was desirable to verify existing data or obtain new data to support the basis for possibly new and novel removal techniques of the more promising approaches for contaminant removal. This report describes the rationale involved in selecting such approaches based on the review findings. Results of some preliminary assessments of the techniques selected for study in the laboratory conclude the first and second phase effort on the Fuel Contaminant study.

TECHNICAL OBJECTIVES

The objectives of this study, which is a continuation of the removal technology evaluation studies[1,2] are twofold: (1) to identify possible future environmental control techniques for potential pollutants in coal and coal liquids and (2) to make preliminary evaluation of some selected contaminant removal techniques. This study was done to determine the feasibility of using these techniques to produce a fuel low in environmental pollutants prior to combustion of the coal or coal-derived liquids.

SECTION 2

CONCLUSIONS

Some of the contaminant removal methods identified during the review of the chemistry and removal technology of fuel contaminants are not in use today for various reasons but may be used in the future. Alternative approaches to contaminant removal were identified as were new approaches with a potential for contaminant removal. Of the various approaches, ranked according to rationale developed in the study, six were selected for preliminary assessment by experimentation. The conclusions from each of the areas studied and reported in the following sections are summarized below.

- Biological action on coal-derived liquid.
  Both aerobic and anaerobic bacteria can tolerate low levels (0.5 percent or less) of aromatic hydrocarbons but higher levels completely inhibit their growth. The addition of aromatic sulfur compounds to the aromatic hydrocarbons increases their toxicity to the bacteria. The prospects of using non-mutated bacteria to remove organic sulfur and nitrogen compounds from coal derived liquids appears small.

- Enhancement of pyrite removal during immiscible fluid agglomeration.
  Pyrite removal equivalent to that obtained by float-sink analysis (42 percent removal) was obtained by chemical pretreatment of fine coal before oil agglomeration. The oil agglomeration technique was also found to be effective for the removal of 90 percent or more of the coal value in sediments from slurry ponds and black water.
  The process has potential for the control or treatment of effluents from coal cleaning plants and the removal of hazards associated with slurry ponds.

- Extraction of clean fuels from coal liquids.
  Light hydrocarbons (C_2 to C_4) can extract up to 83 percent of coal liquid

at super critical conditions for these hydrocarbons. The extract isolated is very low in sulfur and nitrogen and there is good indication of the concentration of the sulfur and the nitrogen in the residue fraction along with the ash. This was accomplished without any evidence for thermal degradation of the feed material.

- Concentration of organic sulfur and nitrogen and ash forming minerals from coal liquids.
  Porous materials with low surface area but large pore volume have been able to remove up to 76 percent of the sulfur (ash free) from coal liquids when passed through a fixed bed of the material. A 10 percent removal of nitrogen was also obtained. Both nitrogen and sulfur removals appear to occur by separate mechanisms and both seem to be independent of ash removal.

- Conversion of coal liquefaction residues to environmentally acceptable fuels.
  Treatment of coal liquefaction residues or still bottoms with H_2-CO mixture removed as much as 14 percent of the nitrogen originally present. Sulfur removal with hydrogen and ammonia was only minor. More severe conditions than those used in this screening study should increase sulfur removal with ammonia and increase the reactivity of the H_2-CO mixture.

- Improvement in pyrite liberature from coal.
  This part of the study was not undertaken because of significant advances made by others.

SECTION 3

RECOMMENDATIONS

Based on results of this study, it is recommended that the oil agglomeration technique be further developed as a method to control effluents from coal cleaning plants in order to reduce the hazards and environmental impact of increased quantities of wastes that would result as the Nation shifts its energy dependence to coal and strives for the production of clean fuels in an environmentally sound manner. Further work is needed to demonstrate the applicability of the process to various origins of coal wastes and the effluents from coal cleaning plants with varying degrees of complexity. The technique should also be extended to the reduction of mineral matter being fed to coal liquefaction plants by pretreating the coal feed. The development of a bench scale process suitable for the treatment of both sediments and black water effluent should also be undertaken.

Also recommended is further study into the use of light hydrocarbons as solvents for the extraction of clean fuels from coal liquids of various origins, i.e., catalytic and noncatalytic processes without the need for filtration of distillation.

Finally it is recommended that the concept of the use of porous media for the physical removal of low levels of sulfur and nitrogen be expanded to greater range of materials and for the treatment of coal liquids of different origin.

SECTION 4

BACKGROUND

To date the study has reviewed the information on the methods employed to remove the types of contaminants identified from solid and liquid fuels. It has categorized and analyzed these methods. Also, known but unusual contaminant removal methods were identified for possible use in today's world. In addition, new approaches to the liberation, isolation, or removal of contaminants were identified. Criteria had to be developed to aid in selecting approaches or techniques suitable for further study and techniques for immediate evaluation as part of this task. Once techniques were selected, laboratory support studies were needed to verify existing data or obtain new data to support the basis for the potential removal techniques.

To add continuity to the reports, the background information presented here summarizes the findings from literature reviews on contaminant characterization and contaminant removal techniques. This background information was used to develop the selection criteria for possible novel approaches to contaminant removal. Although petroleum, shale oils, and tar sand oils were included in the first part of the study, this work emphasizes the contaminants in coal and coal-derived liquids.

CHARACTERISTICS OF FUEL CONTAMINANTS

Understanding the characteristics and differences of coal, coal liquids, petroleum, shale oil and tar sand oil, aid in characterization of the sources of sulfur, nitrogen, and trace element contaminants in these fuels. As given in Table 1, fuel types typical of those considered in this review exhibit marked differences in the amount of ash-forming matter they contain and in the elemental composition of their combustible part. Coals have a much higher ash content than do petroleum crudes. Coals also have the lowest value for the H/C ratio and are considered in a state of unsaturation with respect to hydrogen. For coal to approach petroleum crude

TABLE 1. ELEMENTAL ANALYSIS OF TYPICAL FUELS

	Weight Percent						H/C
	C	H	O	N	S	Ash	(Atomic)
Coal (moisture-free)							
Subbituminous (Big Horn)	69.2	4.7	17.8	1.2	0.7	6.5	0.81
Bituminous (Pittsburgh)	78.7	5.0	6.3	1.6	1.7	6.9	0.76
Coal Liquids (Big Horn)	89.2	8.9	1.03	0.4	0.04	>1	1.20
(Pittsburgh)	89.1	8.2	1.5	0.8	0.2	>1	1.10
Shale Oil	80.3	10.4	5.9	2.3	1.1	∿1	1.55
Utah Asphalt	82	11	3	2	2	<1	1.61
Petroleum Crude (Pennsylvania)	85	14	1	1	1	<1	1.98

in character, hydrogen must be added to coals or coal liquids. The H/C ratios of shale oil and tar sand oil fall between those for coal and petroleum. Formation of coal liquids by hydrogenation of coal increases the H/C ratio. Such processes also significantly reduce the amount of sulfur and nitrogen remaining in the fuel.

The review of the characteristics of the sources of sulfur, nitrogen, and trace element pollutants in coal, petroleum, tar sand oil, and shale oil suggests that at least part of the sulfur and most of the nitrogen originate from compounds common to all of these fuels.[1] These compounds are primarily organic sulfur and nitrogen compounds. The principal difference between the characteristics of the solid and liquid fuels is the way in which these compounds are combined in the fuel. The noncombustible matter associated with coal distinguishes it from the liquid fuels and

is the source of inorganic sulfur and most of the trace elements. In liquid fuels, the trace elements are present primarily as oil soluble compounds or associated with the colloidal suspensions commonly present in them.

Contaminants in Solid Fuels

In coal, the nitrogen contaminants are present primarily as organic compounds which are part of the three-dimensional carbon skeletal structure that makes up the organic matter of coal. Indirect evidence suggests that the nitrogen compounds exist as both alkyl and aryl derivatives of amines, quinolines, and carbazoles. The sulfur in coal is present both as organic and inorganic compounds. The organic sulfur compounds, also part of the carbon skeleton of coal, consist of both alkyl and aryl derivatives of thiols, thioether, disulfides, and thiophene. The major sources of inorganic sulfur in coal are the pyrites and the sulfate salts. Pyrites and other mineral matter exist in raw coal as discrete phases ranging in size from gross inclusions in the coal seam to micron-size particles disseminated throughout the organic matter of coal. Trace elements that exist in raw coal can be categorized as those found principally with the organic matter of coal and those present principally in the mineral matter associated with coal. However, some trace elements exhibit a dual role and are found in both components. Trace metals and metalloids exist as complexes of the organic oxygen, nitrogen, and sulfur compounds or as crystal-lattice impurities in the mineral matter associated with coal seams. Nonmetallic trace elements are found primarily as part of the inorganic mineral impurities. Some, such as phosphorus, are found also in the organic part of coal.

It can be concluded that nonuniform distribution of impurities exists not only from one coal seam to another but also within the coal seam. Despite this limitation, intrinsic centers of sulfur and nitrogen contamination have been identified. The organic sulfur and nitrogen compounds are uniformly distributed in the organic part of the coal, as are the trace elements associated with it. Inorganic sulfur and the trace elements associated with the mineral matter in the coal vary with the source of coal.

However, with the use of modern mining and coal-preparation techniques, a more uniform product is available for use.

Contaminants in Liquid Fuels

In petroleum and tar sand oil, and to some extent in shale oil, most organic sulfur and nitrogen compounds found in the asphaltene and resin fractions are similar to those found in coal. In petroleum nearly 50 percent of these fractions consist of molecules in the 4,000 to 8,000 molecular-weight range. Between 10 and 50 percent of the nitrogen and 3 and 35 percent of the sulfur in petroleum are found in these fractions. Although coal liquids are known to contain resin and asphaltene fractions, the liquefaction process by the addition of hydrogen to coal also reduces the sulfur content (and at times the nitrogen content) to levels near 1 percent. The contaminants in coal liquids remaining after removal of the solids are present as organic sulfur and nitrogen compounds that are difficult to remove and are usually found in the higher molecular-weight asphaltene and resin fractions of coal liquids.

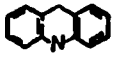
It can be concluded that in the liquid fuels, the intrinsic centers of sulfur and nitrogen contamination are found in the colloidal suspensions (otherwise known as asphaltenes) and in the more soluble resins, both of which make up anywhere from 1 to 43 percent (but more commonly less than 6 percent) of the petroleum, about 37 percent of tar sand oils that have been characterized, 13 to 71 percent of the shale oil, and 10 to 30 percent of the coal liquids. However, the molecular weights of the asphaltenes and resins in petroleum crudes are greater than those in synthetic crudes.

DISTRIBUTION OF CONTAMINANTS IN FUELS

Sulfur and Nitrogen Contaminants

The distribution of sulfur and nitrogen contaminants in the fuel types is shown in Table 2. Large variations in the total sulfur and nitrogen content exist between the fuels and within a fuel type. Coal is unique with respect to the other fuels in that sulfur is also present in the form of pyrites. The organic sources of sulfur in coal have been determined indirectly primarily from studies on depolymerized coal. The exact nature of organic sulfur in solid coal can only be surmised from

TABLE 2. DISTRIBUTION OF S AND N CONTAMINANTS IN FUELS

Contaminants		Fuel				
Type and Source	Parent Structure	Coal	Coal Liquids Primary	Shale Oil[a]	Tar Sand Oil[b]	Petroleum Crude
Sulfur, Total		0.4-13%	<1%	1.1%	0.2-6.3%	0.1-5%
Inorganic						
Pyrites	FeS_2	X[c,d]				
Organic						
Mercaptans	R-SH[e]	X[f]			X	X
Sulfides	R-S-R[e]	X[g]			X	X
Thiophenes		X[f]	X	X	X	X
Benzothiophenes			X	X	X	X
Nitrogen, Total		1-2.1%	>1%	2.3%	<1%	<<1%
Basic						
Pyridines		X[f]				
Quinolines		X[f]	X	X	X	X
Acridines		X[f]				X
Nonbasic						
Pyrroles			X	X	X	X
Indoles		X[f]	X	X	X	X
Carbazoles		X[f]	X	X	X	X
Benzamides				X		

(a) Colorado shale oil.
(b) Tar sands including Utah tar sands.
(c) 48 percent of total sulfur, a mean value for U.S. coals.
(d) X represents the presence of the contaminant in the fuels.
(e) R is an alkyl or aryl group.
(f) As measured in coal tar, depolymerized coal and other indirect methods.
(g) Synthoil product.

these studies. There is strong evidence that mercaptans, sulfides, and disulfides are present in the coal structure. The same type of compounds are usually present in tar sand oils and petroleum but not in coal liquids and shale oils. Thiophenes and benzothiophenes are known to be present in coal liquids and shale oil as well as in tar sand oil and petroleum.

Total fuel nitrogen content is highest in coal and shale oil. Little is known for certain about the types of nitrogen compounds contained in coal since their characterization was determined from studies on coal tars or depolymerized coal. There is good evidence that pyridine, quinoline, acridine, indole, carbazole, and porphyrins or their derivatives account for the nitrogen in solid coal. Thus, it may be concluded that the nitrogen in coal is present as aromatic compounds. Quinolines, pyrroles, indoles, carbazoles, acridines, and porphyrins are present in coal liquids, shale oil, tar sand oil, and petroleum. Benzamides have been found in shale oil and petroleum. The porphyrin compounds may contain trace metals as coordination compounds.

Values for the amount of each type of organic sulfur and nitrogen compound are available for only a limited number of fuels and then for only a few sources of the fuel type (e.g., petroleum). Others have not yet been characterized or are being characterized (e.g., coal liquids, shale oils, and tar sand oils). Until additional data are available, a quantitative comparison would be difficult. But it has been determined that the total nitrogen content of U.S. coals (moisture- and ash-free (maf)) varies in the range of 1 to 1.9 weight percent for lignite and high volatile bituminous coal, respectively. This amount of nitrogen is present as an integral part of the chemical structure of coal.

Trace Elements

The trace elements in the fuels covered in this review can be categorized as either being in fuel's organic matter or the mineral matter. As shown in Table 3, coal has most of the trace elements closely associated with these minerals. Petroleum and tar sand oils by comparison contain much less mineral matter and hence less trace elements are associated with them (e.g., those elements commonly associated

TABLE 3. TRACE ELEMENTS ASSOCIATED WITH MINERAL MATTER IN SOLID AND LIQUID FUELS

Mineral (percent of total)	Trace Elements
Coal	
Shales, kaolins (52)	Si, Al, Ti, K (B, Cu, F, Hg, Sn, V)[a]
Sulfides, pyrites (25)	Fe, Zn, Cd, Pb, Ni, Cu (Hg, B, As, Be, Sb, Ge)[a]
Carbonates (9)	Ca, Mg, Mn (B, Cd, Mo, Se, V)[a]
Chlorides (0.1)	Na, K, Cl (Br, I, Mg, Ca)[a]
Quartz (1-20)	Si (B, Cr, Mn, Cd, Mo, Ge, Se, V, Zn)[a]
Apatite	Ca, P, F (As, V, Cl, Mn, Ce)[a]
Sulfates	Fe, Ca (Mn)[a]
Petroleum (tar sand oils)	
Chloride (trace)	Na, K, Mg, Ca, Cl, Br, I (Mn)[a]
Quartz (trace)	Si
Shales, kaolins (trace)	Si, Al, K
Shale Oils	
Shale minerals	As, Ba, B, Cu, Cr, Pb, Li, Mo, Mn, P, Se, Sr, Tl, Ti, V, Zn, Ag, Au
Coal Liquids (speculation)	
Removed with mineral matter	Hg, Zn, Zr, Cd, As, Pb, Mo, Mn (Co, Ni, Cr, Se, Cu, Sb, V, Ti, Ga, P)[b]

(a) Elements in parentheses are known to have high correlation with minerals but not necessarily detected with minerals.

(b) The elements in parentheses are more commonly found with mineral matter but are also found in organic portion of coal.

with brines and suspended sands and clays). Shale oils contain finely divided shale minerals carried over during retorting and contain trace elements found in the shale minerals. Upon coal liquefaction, the trace elements associated with the mineral matter in coal remain insoluble and are removed along with the mineral matter.

The trace elements more closely associated with the organic matter in coal are shown in Table 4. These trace elements in coal are held in the organic matrix as complexes of organic compounds (containing oxygen, sulfur, or nitrogen), porphyrins or amino acids, or as alkyl or aryl derivatives. Most of the trace metals found in petroleum and tar sand oils are found in the organic phase as oil soluble compounds. They exist primarily as complexes, organic acid salts, and alkyl and aryl derivatives. Shale oil also contains a large number of oil-soluble trace elements which may have formed during retorting. Coal liquids would be expected to contain in solution those elements most closely associated with the organic part of coal or those that enter into solution during the liquefaction process.

SUMMARY OF TECHNIQUES USED FOR REMOVAL OF CONTAMINANTS FROM COAL

Raw coal, which contains large amounts of undesirable mineral matter, undergoes considerable upgrading in modern coal-preparation operations.[2] Significant amounts of sulfur present as gross pyrite inclusion and other ash mineral bodies present in the mined coal are readily removed during coal-washing operations. When such processes are used, 15 to 30 percent of the pyritic sulfur in the run-of-the-mine coal is removed from coal crushed to a top size of 1/4 inch (6 mm). Part of the finely disseminated pyrite can be removed by physical means only if the size of the coal is further reduced. In separations using the dense media cyclone, a bottom size of 32 mesh (0.5 mm) can be treated to remove up to 30 percent of the pyrite. In froth flotation, pyrite removal can reach about 50 percent when the coal is crushed to minus 28 mesh (0.6 mm). Staged froth flotation employing pyrite depressants in the second stage reduces the pyritic sulfur content of coals from 50 to 80 percent. Specialized methods for pyrite

TABLE 4. TRACE ELEMENTS ASSOCIATED WITH ORGANIC MATTER OF SOLID AND LIQUID FUELS

Derivative	Trace Elements
Coal	
Complexes of O, N, S ligands and organic acid salts	Ge, Be, B, Ti, U (Ga, Y, La, Ni, Co, Zn, V, Ca, Al, Si, P)[a]
Porphyrin, amino acids	V, Ni, Cu, Fe
Alkyl or aryl	Ge (P, Se)[a]
Petroleum (tar sand oils)	
Porphyrin	Ni, V
Nonporphyrin	Ni, V, Fe, Co, Zn, Hg, Cr, Cu
Tetradentate complexes (S, N, O)	V, Ni, Fe, Cu, Co, Cr (Cl)[b]
Alkyl or aryl	Hg, Sb, As
Organic acid salts	Na, As, Hg, Fe, Sb (Mo)[a]
Unknown	Se, I
Shale Oils	
Oil soluble	As, Sb, Be, B, Cd, Ca, Cr, Co, Cu, F, Ge, Pb, Mg, Mn, Hg, Mn, Mo, K, Se, Na, Sr, Te, Ti, V, Y, Zn
Coal Liquids (speculation)	
Liquid soluble (?) >50 percent organic affinity	Ge, Ba, Ga, B, Ti (P, U, V, Sb, Co, Ni, Cr, Se, Cu)[c]

(a) Elements forming compounds to a lesser extent are in parentheses.

(b) Cl^- suggested as counter ion.

(c) Elements in parentheses are more closely associated with organic part of coal but are also present in mineral matter.

removal from coal that has been reduced in size to minus 200 mesh (0.074 mm) and even minus 325 mesh (0.044 mm) have met varying success. Typically, 40 to 50 percent of the pyritic sulfur can be removed. In one case in which an oil agglomeration technique was used, the amount of pyrite removal reached 90 percent. However, the minus 325 mesh (0.044 mm) coal was specially preconditioned.

In chemical refining, essentially all of the pyritic sulfur in coal is reported to be removed by treatment with aqueous solutions of sodium hydroxide or ferric sulfate. Both processes require elevated temperature. With sodium hydroxide, partial removal of organic sulfur occurs for selected coals, while ferric sulfate treatment does not attack it. In both these processes pyrite is more efficiently removed when finer sized coal is treated.

Liquefaction or depolymerization of coal to produce a cleaner solid fuel, as in the case of solvent-refined coal (SRC), is an alternative to the extensive size reduction of coal needed to gain access to the finely disseminated pyrite and mineral matter. During such a liquefaction, noncatalytic hydrogenation of coal occurs mostly from the hydrogen-donor type solvent that is mixed with the coal. After the liquefaction, the mineral matter and the finely disseminated pyrite (now reduced to pyrrhotite or ferrous sulfide) originally in coal are released. They and the unreacted coal are removed prior to utilization. Typically, when all of the ash minerals are removed, the sulfur is lowered to values equal to or less than that attributable to organic sulfur in coal. Nitrogen values are usually not lowered in such a process. Most of the cyclic and heterocyclic organic sulfur and organic nitrogen originally present in the coal remain as such in the liquefaction product (SRC). Further removal of this sulfur and nitrogen must be by catalytic hydrotreatment of the SRC to release most of the sulfur as H_2S and part of the nitrogen as NH_3.

Desulfurization and denitrification of coal by carbonization or pyrolysis are only partially effective since, during the processing, the sulfur and nitrogen not removed overhead remain in the coke or char in a form that is bound deeply in graphitic-type structures. Processes employing reactive gases, alkalies, salts, and acids during carbonization or pyrolysis are capable of increasing the amount of sulfur and nitrogen

removed, but complete removal has not been attained. Unless the coal used in these processes is low in ash and pyrite by virtue of their origin or preparation, most of these components will remain in the coke or char.

The gasification of the carbon value in coal releases the sulfur and nitrogen contaminants bound in the coal structure as well as those contaminants present as discrete phases. However, before the low-Btu gas can be utilized, these released gaseous contaminants and the particulates must be removed downstream from the gasifier. Although such an approach would appear to be an effective way to remove the contaminants from coal, the solid fuel is usually converted in the process to a low-grade gaseous fuel.

It may be concluded from these facts on the removal of contaminants from coal that:

- Release from coal of the finely disseminated pyrite requires extensive size reduction of the coal to enable even partial removal of the pyritic sulfur. This is true whether the pyrite-removal method is based on chemical refining or on differences in specific gravity, surfacial behavior, or magnetic properties.
- Only about one-half of the sulfur originally present in coal as pyrite is removed during liquefaction or depolymerization of coal by noncatalytic hydrogenation. The pyrrhotite or FeS must be removed before the product can be utilized as a low-sulfur fuel.
- The sulfur and nitrogen present as cyclic and heterocyclic organic sulfur and organic nitrogen are relatively unaltered by either the physical methods or chemical refining and only a small amount of the organic sulfur is released during the noncatalytic liquefaction process.
- Carbonization of coal is only partially effective for the removal of the sulfur and nitrogen contaminants. Those that remain in the product are tied up in the char structure.
- Gasification of coal releases all of the contaminants contained in coal, but extensive posttreatment of the

gasified coal to remove gaseous and particulate pollutants is required before the gas can be utilized.

SUMMARY OF TECHNIQUES USED FOR REMOVAL OF CONTAMINANTS FROM COAL-DERIVED LIQUIDS

Coal liquids formed during the initial stages of the hydrogenation of coal contain the noncombustible portion and unreacted coal as slurry materials; and they also contain most of the contaminants originally present in the coal.[2] At this point in processing, several alternative approaches for the removal of contaminants become available. As one alternative, the removal of the mineral matter, unreacted coal, and iron sulfide as in the solvent-refined coal (SRC), will provide a product fuel which is reduced in ash and total sulfur and is a solid at ambient temperatures. This same product can be used as a feedstock for a catalytic hydrotreatment process. Another alternative is to catalytically hydrogenate a coal-oil slurry to produce a liquid fuel (liquid at ambient temperatures) and then remove the suspended solids. During the catalytic hydrogenation, much of the organic sulfur and part of the organic nitrogen is removed. Still another alternative is to leave the solids in the liquid after hydrotreatment, then distill the product fuel and leave the insoluble material in the residue (as well as some of the sulfur and nitrogen that is more difficult to remove). Other variations of the process exist, but these alternatives appear to be most common.

Near complete removal of the organic sources of sulfur and nitrogen requires exhaustive hydrogenation using amounts of hydrogen well in excess of the stoichiometric equivalent of the contaminants being removed. The overall hydrogen utilization is poor because the contaminant-removal reaction occurs concurrent with hydrogenation of the coal, and produces less desirable hydrocarbons and light fractions mixed with H_2S and NH_3.

Even though frequently used, the concentrations of sulfur, nitrogen, and trace elements in the coal liquid products probably should not be used as the only measure of the effectiveness of the overall contaminant-removal method, since the final liquid products have different processing histories. The fraction of the coal recovered as an environmentally acceptable fuel should also be considered in the comparisons.

From this summary on contaminant-removal from coal-derived liquids, it may be concluded that:

- Simple organic sulfur contaminants can be removed by chemical (hydrogen) treatment.
- More complex organic sulfur and organic nitrogen molecules existing in coal derived liquids can be removed by catalytic hydrotreatment to form H_2S and NH_3.
- Many of the metals in liquid fuels interfere with catalytic hydrotreatment and must be absent or in very low concentration before such treatment is undertaken.
- Conversion processes in which lighter liquids are recovered from heavy liquid fuels by thermal cracking are relatively ineffective for contaminant removal.
- Hydrotreatment reactions change many of the properties of the fuel as well as remove sulfur as H_2S and nitrogen as NH_3.

INTERRELATIONAL ASPECTS OF CONTAMINANT REMOVAL

An obvious interrelationship exists between the commercial coal-preparation processes used to remove contaminants from run-of-the-mine coal and the need for quality coal feedstock used in other types of contaminant-removal processes. The processes based on liquefaction, chemical refining, pyrolysis, gasification, and some types of physical methods attempt to remove contaminants that usually can be removed only partially or are impossible to remove by the combined commercial preparation processes (i.e., grinding, washing, dense-media separation, and froth flotation). The limit to which the size of the coal can be ground to optimize processing cost and minimize fuel losses during the coal preparation also influences the extent of contaminant removal. However, when feed coal is to be prepared in such a facility for utilization in, for example, chemical refining, trade-offs would have to be made between coal losses and maximum removal of reagent-consuming contaminants prior to chemical processing.

In any study on the contaminant removal from solid and liquid fuels, it is necessary to consider how the removal of one class or type of contaminant affects concurrent or subsequent removal of another contaminant.

For example, liquefaction by catalytic hydrogenation removes the organic sulfur, some organic nitrogen, and half the pyritic sulfur (FeS_2 is converted to FeS) as H_2S. However, removing ash minerals from liquid fuels is a costly and difficult step. If the coal were cleaned to remove pyrite (physical separation or chemical refining) prior to catalytic hydrogenation, it might not be necessary to separate the ash from the liquid fuel after catalytic hydrogenation. Typical combined processes include:

- Pyrite removal by chemical refining followed by coal liquefaction by hydrogenation.
- Iron sulfide removal by magnetic means after coal liquefaction.
- Mineral and pyrite removal by magnetic means before hydrogen treatment.
- Demetallization of coal liquid before catalytic hydrotreatment for sulfur and nitrogen removal.

SECTION 5

SELECTION OF REMOVAL TECHNOLOGIES TO BE CONSIDERED FOR FUTURE STUDY

As part of the objective of the Phase I program, methods for contaminant removal were reviewed and analyzed with regard to their potential for further study. Potentially new and novel techniques based on the chemistry of the fuel contaminants and potential removal mechanisms were considered. A systematic categorization of the methods of contaminant removal according to the contaminants and the type of removal was included in the Task 1 reports.[1,2]

The selection of specific contaminant removal techniques was based on various criteria discussed below. These same criteria were used to finalize and rank a list of techniques suggested for further study.

SELECTION CRITERIA DEVELOPMENT

In choosing the specific areas for study in the initial screening of fuel contaminant removal techniques, several criteria were used. The criteria were developed from the Task 1 review of the information on the chemical and physical characteristics of the contaminants in fuels[1] and the techniques employed to remove them from the fuels.[2] The following criteria, used most frequently to develop a list of techniques for contaminant removal, are related primarily to coal and coal-derived liquids.

- Criteria based on chemical and physical characteristics of the contaminants.
    - Pyritic Sulfur - About 40 to 60 percent of the pyrite present in run-of-the-mine coal can be liberated and removed easily from coal. The remaining pyrite is micron-size particles distributed uniformly in the organic matter. Therefore, release of this pyrite will depend on the extent of size reduction or depolymerization the coal undergoes to expose the fine

particles. The released pyrite might be separated or removed by physical or selective chemical means.

- Organic Sulfur - In order to remove the organic sulfur from the coal structure, either the molecule(s) must be released from the coal polymer and then selectively removed or the molecule must be disrupted to release the sulfur atom. Selective removal would result in substantial loss in fuel value. Disruption of the molecules requires conditions of varying severity depending on the stability of the molecule.
- Nitrogen - To remove the nitrogen present as organic molecules locked into the coal structure, the molecules must be released from the coal polymer. The molecules can then be selectively removed or disrupted to release the nitrogen atom. Removal will result in substantial loss in fuel value. Disruption requires conditions more severe than those for the organic sulfur molecules.
- Trace Elements - Separating the mineral matter distributed in coal will do much to remove trace elements. The problem lies in the extent of release possible at a practical limit of coal size reduction. Removal of trace elements associated with the organic matter requires disruption of coal structure.

- Criteria based on techniques used to remove fuel contaminants.
  - Fuel Value Recovery - Do the techniques used to remove contaminants from fuels produce the maximum possible amount of the desired environmentally acceptable fuel? Is the transfer of fuel contaminants to a residual fuel to provide clean fuel avoided or minimized? Is the energy required in maximizing fuel recovery kept as low as possible?
  - Utilization of Interrelational Aspects - Can two or more contaminant-removal techniques when combined produce a clean fuel with the minimum fuel losses?

For example, can extensive removal of mineral matter and pyrites provide a quality feedstock for use in organic sulfur and nitrogen contaminant removal processes?

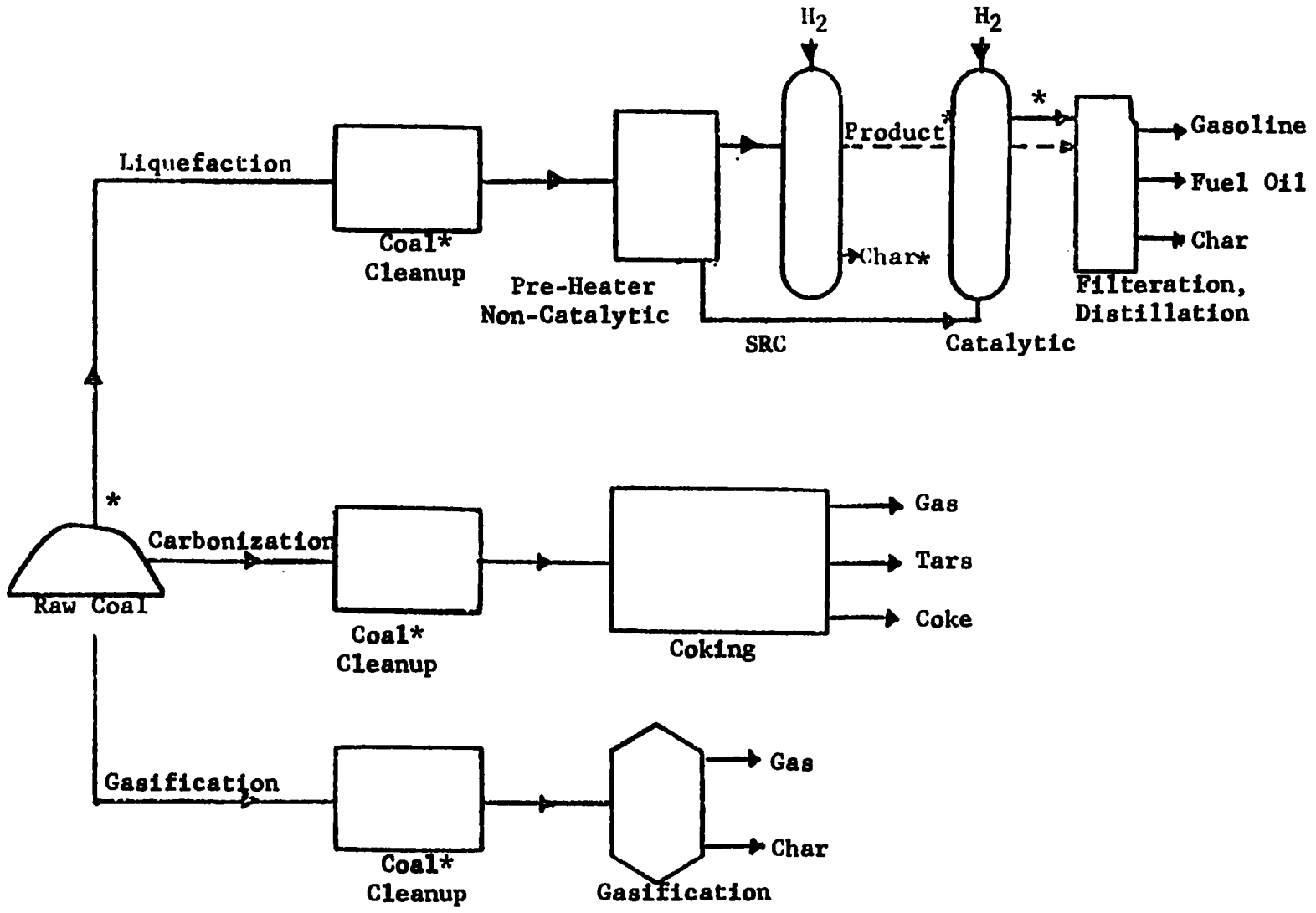
- Optimize Hydrogen Utilization - Can the efficiency with which hydrogen is used in removing organic sulfur and nitrogen from a fuel be improved by treating fractions isolated from coal-derived liquids enriched in these contaminants?
- Transferable Technology - Can a technique of contaminant removal used for petroleum be utilized for coal-derived liquids?
- Contaminant Disposal - Does the process minimize the environmental threat posed by the disposal of the removed contaminants allowing for their chemical nature and form?

Consideration of these criteria provided the basis for ranking several contaminant removal concepts. The ranking was done so that, in any experimental evaluation program, higher ranked concepts that show no immediate success can be replaced by one of intermediate or low rank. Successful approaches would be set aside for larger programs. Thus, as many of the listed areas as possible might be evaluated in a limited time.

Each of the approaches considered could produce an environmentally acceptable fuel. The points in the process where these might operate on a coal-based complex is shown in Figure 1. As an example "Immiscible Fluid Agglomeration of Coal" operates at the coal-cleaning facility, and "Physical Adsorption for Contaminant Removal from Coal Liquids" operates in lieu of filtration of coal-derived liquids.

RESULTS OF SCREENING

After preliminary assessment of the approaches, they were critically reviewed during discussions with other EPA contractors active in coal and coal liquid contaminant removal programs and the EPA Project Officers. Their comments were weighed in the final rationalization which reduced their number to fourteen (14) listed in Table 5. (The order of the



* Potential points in process for contaminant removal method.

FIGURE 1. RELATIONSHIP OF SUGGESTED CONTAMINANT REMOVAL METHODS WITHIN A COAL-BASED COMPLEX

TABLE 5. AREAS SELECTED FOR FURTHER STUDY

No.	Contaminant Removal Study	Description	Comments
1	Determine influence of minerals, trace elements, and metal complexes on hydrotreating	To better understand the role and fate of ash minerals and trace elements during coal liquefaction and subsequent hydrotreating the following areas should be considered for further study. The behavior of model sulfur and/or nitrogen compounds during hydrotreating in the presence of unaltered coal minerals and trace elements with and without the presence of liquids analogous to coal liquids should be investigated. Such minerals would be recovered in an unaltered or only slightly altered state by low-temperature ashing from a coal known to contain most of the trace elements. Variations in selected ratios of the trace elements in coals would be incorporated into the study in order to ascertain correlation of hydrotreating activity, i.e., sulfur and nitrogen removal. Trace metals might be supplied as coordination complexes formed from nitrogen and sulfur containing ligands and/or porphyrin derivatives known to be present in coals.	Pro (1) Would provide fundamental data on mineral activity on hydrodesulfurization and hydronitrogenation and suggest new approaches to hydrotreating catalysts. Con (1) Study would be limited to a study of model sulfur and nitrogen compounds. (2) Results obtained from model compounds may not be directly applicable to hydrotreatment.
2	Effect of reactions of NH_3 or H_2O with organic sulfur compounds	An area which has received little attention is the effect of the products from hydrotreatment of coal upon sulfided catalysts encountered during hydrotreating. The products receiving some attention are NH_3 and H_2S. However, considerable water is also formed especially from lower rank coals and should be added to the list. The back reaction of these products with coal should also be of concern. The potential for the reaction of NH_3 with various organic sulfur compounds to produce the more stable organic nitrogen compounds should be investigated. The study would determine if nitrogen readily removed from more basic amines during catalytic hydrodenitrogenation (HDN) as ammonia is capable of forming organic nitrogen compound from organic sulfur compounds or if the ammonia decomposes and "active" hydrogen is formed to alter the hydrodesulfurization (HDS) rate.	Pro (1) Would provide fundamental data related to the mechanism of HDS and HDN and possible competing reactions. (2) Would determine if overlapping rates exist for the hydrodesulfurization of the more stable sulfur compounds and the less stable nitrogen compounds. Con (1) Study would be done only on model compounds using well known catalysts.
3	Selective insolubilization of coal liquid fractions	Deasphalting of petroleum with low-molecular weight solvents such as propane has been used commercially and is reasonably effective in rejecting metals and sulfur. The commercial use has been limited, particularly in recent years, by the problem of disposing of the rejected asphaltene fraction. The process has not been tested on coal liquids, and the disposal of the reject fraction may not be as much of a problem at a coal liquefaction facility as at a petroleum refinery. For example, recycle of this material to the liquefaction reactors may be feasible.	Pro (1) The hydrotreatment of the isolated fractions would be expected to be more specific for sulfur and/or nitrogen removal since less hydrocarbon would be present to consume hydrogen through saturation of the highly aromatic coal liquid before HDS and HDN would take place (i.e., better hydrogen utilization for HDN and HDS). (2) Ascertain the utility and effectiveness of concentrating organic sulfur and nitrogen by solvent precipitation as compared to distillation of coal liquids [i.e., minimize residue formation (polymerization) and unwanted gaseous hydrocarbon formation due to excessive exposure to high temperatures during distillation].

TABLE 5. (Continued)

No.	Contaminant Removal Study	Description	Comments
			Con (1) Would require selection of solvent system to yield maximum rejection of sulfur and nitrogen compounds and still provide economic advantages for its use over total hydrotreatment of the coal liquid or separation by distillation. (2) Solvent recovery and maintaining pure solvent character may be a problem.
4	Use of pyrite depressants in conjunction with immiscible fluid agglomeration of coal	Immiscible fluids such as kerosene and fuel oil are capable of separating the ash minerals from finely ground coal suspended in aqueous slurry through a process of selective agglomeration. This approach is attractive because the coal does not have to be dried after mining, wet size-reduction and coal-washing operations. However, pyrite removal is poor due to the similarity of its surfacial properties to those of coal. The use of reagents known to alter the surface properties of pyrite or the use of coal wastes known to contain Ferrobacillus Ferrooxidans should be investigated as a means of improving the pyrite removal performance of the agglomeration process. As part of the suggested study, substitution of coal liquids for kerosene or fuel oil should be investigated for those operations preparing coal for liquefaction processes. The process has the added advantage of allowing the isolated coal fraction to be dewatered readily. For this reason, its applicability to brown coals should be investigated.	Pro (1) Can provide a low ash, low pyrite fuel directly or a feed for a coal conversion plant. (2) Oil agglomeration provides a means of producing low moisture feed for conversion processes with minimum thermal drying. (3) Agglomerating oil may be derived from coal liquids. Con (1) Requires size reduction to liberate pyrite and ash minerals. (2) Does not reduce organic sulfur or nitrogen content of coal.
5	Correlation of the mechanism of chemical comminution of coal to the mechanism related to coal dissolution/depolymerization	Both ammonia and methanol are known for their ability to penetrate coal through naturally occurring faults. These chemicals disrupt the bonding forces across the phase boundaries between coal and the impurities it contains, which results in forceless breakage of the coal body. The mechanism causing the disruption is not well understood. A similar action is suggested when coal is dissolved/depolymerized by certain solvents such as pyridine, phenols, aromatic hydrocarbons, etc., to yield a coal liquid. A study should be undertaken to gain a better understanding of the comminution and dissolution/depolymerization mechanisms. This would provide fundamental data useful in selecting improved solvent systems for the liquefaction of coal.	Pro (1) Study would provide fundamental data on the mechanisms of comminution, dissolution, and depolymerization of coal. (2) A model solvent system for enhanced coal penetration may be developed. (3) With a depolymerization process, an alternative to liquefaction by hydrogen treatment at high temperatures might be developed. Con (1) A review of reported rates of coal solubilization would have to precede any laboratory work. (2) Study would have to be limited to known reactive coals. (3) Solvent recovery and stability are critical to success of process.

TABLE 5. (Continued)

No.	Contaminant Removal Study	Description	Comments
6	Physical adsorption for contaminant removal from coal liquids	The high boiling fraction of coal liquids contains trace elements and sulfur and nitrogen contaminants. These fractions would be treated in a fluidized or moving bed of alumina (or similar material) particles that have low surface areas (<100 m^2 g) but large pore size dimensions (>200 Å). Such a material may promote rapid diffusion into the pores and enhance the removal of the contaminants by filtration. Since the adsorption material has a low surface area, it would be strong enough physically to undergo repeated regeneration cycles.	Pro (1) Would provide a means of improving filterability of coal liquids to remove ash minerals as well as a means of concentrating sulfur and nitrogen impurities in residue. Con (1) Yield losses of liquid might be greater than present methods.
7	Treatment of coal with CO or CO-H_2 mixtures to form liquids	As an alternative to hydrotreating, the concept of removing sulfur with CO or H_2-CO mixtures should be considered.	Pro (1) Process would reduce hydrogen requirements for liquefaction. Con (1) If COS formation is substantial, disposal may be difficult.
8	Cleanup of coal liquefaction residues	Coal liquefaction residues would contain, besides the contaminants, some catalyst particles. During coal carbonization it has been found that when the process is carried out in the presence of certain gases (e.g., H_2, NH_3) sulfur and nitrogen contaminants are removed. Then coal liquefaction residues are gasified, the effect of the above gases on sulfur and nitrogen removal may be enhanced because of the presence of the catalyst particles.	Pro (1) Would provide a means of greater hydrocarbon recovery and gas streams richer in H_2S and NH_3 for more efficient removal. (2) Would reduce amount of carbon in the char formed in total liquefaction process. Con (1) Performance of new concept (energy and product quality) would have to exceed performance of existing process of residue pyrolysis/gasification.
9	Acid treatment for coal liquefaction "residue" cleanup	The residue obtained from coal liquefaction is rich in coal ash and trace elements. This residue may be cleaned up by acid washing (e.g., HCl, HF) prior to gasification. The trace elements would be more amenable to acid leaching from the coal liquefaction residue than from the gasification char.	Pro (1) Dissolution of ash minerals in residue would liberate oil and unreacted carbon to improve oil recovery. (2) Provide a means of trace element recovery from liquefaction residues. (3) Produces a reduced ash feed for gasification. Con (1) Disposal of spent acids and unwanted salts presents a potential problem.
10	Hydrothermal action to process oil shale	The concept of short-range solubilization and reprecipitation of the mineral matter in oil shale inherent in a hydrothermal process should be investigated. This would be done to reduce the effect of trace element contamination of shale oil formed during oil shale retorting. It is anticipated that the release of kerogen and other organic constituents of oil shale may occur during the solubilization-reprecipitation sequence.	Pro (1) Provides alternatives to retorting at high temperatures. (2) Reduces contamination of shale oil by trace elements. (3) Reduces losses of hydrocarbon values as char. (4) Provides a means of recovery of alkali value from oil shale. Con (1) Water cleanup required before reuse or disposal. (2) Water losses may be critical.

TABLE 5. (Continued)

No.	Contaminant Removal Study	Description	Comments
11	Use of solid "getters" in hydrotreating	The motivation in this area is the exploratory study on the thermal hydrotreating of tar sand oil in the presence of pulverized coal, which acts as a "getter" for metals in the oil and for coke formed in the process. This study used Canadian tar sand oil and Canadian coal. The properties (primarily porosity) of U.S. western coal indicate that it should work well as a "getter", and this fits well with our western reserves of shale oil and tar sand oil. Other possible "getters" include coke or asphalt from any source and chars produced in coal gasification of liquefaction processes.	Pro (1) Utilizes coal char from liquefaction process to adsorb trace element contaminants from coal liquids. Con (1) Concept would have to show advantage over existing filtration techniques for removal of ash minerals.
12	Oxidative denitrogenation of coal liquids	This represents an extension of the studies on petroleum of selective oxidation with nitrogen oxides followed by extraction of the oxidized species with methanol. Removal of both sulfur and nitrogen were demonstrated, although the nitrogen data were more limited. The potential for nitrogen removal warrants further study, particularly because of the possibility that at least part of the NO_x required for the oxidation might be obtained from the nitrogen removed from the fuel.	Pro (1) Would utilize nitrogen removed from coal. Con (1) Reaction is not selective and coal quality is degraded.
13	Acid/base treatment of coal liquids	The primary motivation in this area is the limited data indicating very good denitrogenation of a shale-oil fraction by a specific combination of acid and base treatments. Also, a base treatment was reported as removing at least one metal (arsenic) from shale oil. No data are available on such treatments of coal liquids. The objective would be the removal of nitrogen or metals, and not sulfur.	Pro (1) Would provide a nonhydrogenation method for the removal of the very stable organic nitrogen compounds in coal liquids. (2) Trace element removal would be possible. Con (1) Acid treatment would produce unwanted sludge that would be difficult to dispose of. (2) Carbon value would be lost with nitrogen compounds.
14	Biological action on coal liquids to remove sulfur and nitrogen contaminants	The studies on the biological action on amino acids and fatty acids show that hydrogenation by anaerobic organisms possessing hydrogenase enzyme systems is possible at room temperature and low pressures of hydrogen. Such action may be transferable to coal liquids for the removal of organic nitrogen and sulfur contaminants by hydrogenation or by other biological action that breaks the carbon-sulfur or carbon-nitrogen bonds.	Pro (1) Bacterial action would provide selective removal of sulfur and nitrogen contaminants. Con (1) Bacterial action inherently slow. However, if the enzyme system responsible for the action could be isolated and concentrated, a viable, low pressure/low temperature process might be devised.

listing does not necessarily reflect the view of the EPA to the importance of the proposed study areas, but it does reflect one of early prioritizations set by Battelle Columbus Laboratories.) In Table 5 the contaminant removal methods or concepts selected for further study are described along with comments about the approach. The descriptions and comments critically discuss the salient features of the study areas which in some cases were selected to answer fundamental questions on the chemical mechanisms and limitations of a process.

SELECTION OF REMOVAL TECHNOLOGIES FOR PRELIMINARY ASSESSMENT

Another of the objectives of this study is to assess rapidly, through either a literature search and preliminary experiments, a selected number of removal technologies. The following six areas were selected for preliminary screening evaluations:

- The biological action on coal-derived liquids.
- Enhancement of pyrite removal during immiscible fluid agglomeration.
- The extraction of clean fuel from coal liquids.
- Concentration of organic sulfur and nitrogen and ash from coal liquids.
- Conversion of coal liquefaction residues to environmentally acceptable fuels.
- Improvements in pyrite liberation from coal.

These six areas at the time of selection were given a higher priority than others being considered. The intent of this prioritization was done so as to permit replacement of the higher priority approaches that show no immediate success with one of the remaining 8 cited in Table 5. Also those approaches that are successful would be set aside for larger programs. In this manner an evaluation of as many of the areas as possible could be made. This approach was not initiated and only the results of the studies cited above comprise the next six sections of the report.

SECTION 6

BIOLOGICAL ACTION ON COAL-DERIVED LIQUIDS

LITERATURE SURVEY

The objective of the literature survey was to develop concepts on the biological approach to removing sulfur and nitrogen from coal and coal-derived liquids on the basis of information in the literature.

The role of microorganisms in forming and degrading petroleum and coal has been the basis for various fundamental studies.[3,4] Another study has shown that asphalt, a by-product of the petroleum industry, can be degraded by certain sulfate-reducing microorganisms.[5-7] Thus, selective degradation of sulfur and nitrogen compounds in coal and coal liquids may be possible by using such microorganisms.

These microorganisms include bacteria, yeasts, and molds. Since most microorganisms are active at or near ambient conditions, sulfur and nitrogen contaminants might be removed from coal and coal liquids under conditions much milder than the high temperatures and pressures required in the conventional hydrodesulfurization and hydrodenitrification processes.

In this survey, wherever possible, the ability of microorganisms to selectively degrade hydrocarbons containing sulfur and nitrogen is compared with the kind of sulfur and nitrogen compounds present in coal.

Sulfur and Nitrogen Contaminants in Coal and Coal Liquids

The report on the characterization of the sulfur and nitrogen contaminants in coal and coal liquids discussed earlier showed that, except for pyrites, the contaminants are primarily organic and consist of aromatic and heterocyclic compounds.[1] The H/C ratio and the total sulfur and nitrogen content for coals, liquids derived from these coals, and liquids derived from a typical petroleum crude were compared in Table 1. Coals as compared to coal liquids and petroleum crude have the lowest H/C

ratio and are considered in a state of unsaturation with respect to hydrogen. The postulated structure of coal "molecule" given in Figure 2 shows the organic sulfur and nitrogen contaminants.

In coal liquids, free of solids, the cyclic and heterocyclic sulfur and nitrogen compounds are found primarily in the high-molecular-weight asphaltenes (benzene soluble and heptane insoluble) and resin (methanol soluble) fractions of coal liquids. Some nitrogen in the coal liquids is present in porphyrin-type structures.[1]

The cyclic and heterocyclic compounds containing sulfur and nitrogen are very stable. When conjugation of a sulfur atom occurs in a ring system, its stability appears to be greater than that in straight-chain compounds. The sulfur atoms display not only electron-releasing but also electron-accepting conjugative effects. Nitrogen, which has five valence electrons, also forms very stable heterocyclic compounds. Two valence electrons are involved in the formation of covalent bonds to the adjacent carbon atoms in the ring; one valence electron is involved in either the bond to a hydrogen atom, an alkyl group, or conjugation in the ring. The two remaining electrons (the "lone pair") are usually not involved in bond formation but account for the basic properties of some amines. These inherent behaviors of electrons of sulfur and nitrogen compounds may be important when considering interaction between these compounds and microorganisms.

Patents on Petroleum Desulfurization Processes Using Microorganisms

The desulfurization of petroleum by using microorganisms is described in many patents.[8-12] The microorganisms used in these patents include aerobic, anaerobic, or a combination of the two. The microorganisms are found in nature, but one patent[12] uses a combination of naturally occurring microorganisms with prepared mutants. In any case the microorganisms are grown under controlled conditions of temperature, pH, and in the presence of specific nutrients.

A brief discussion on the claims of these patents follows.

Strawinskii[8] claimed that crude oils and like substances are desulfurized by bringing them into contact with mineral salt nutrient medium in the proportion of approximately 5 percent oil to 95 percent

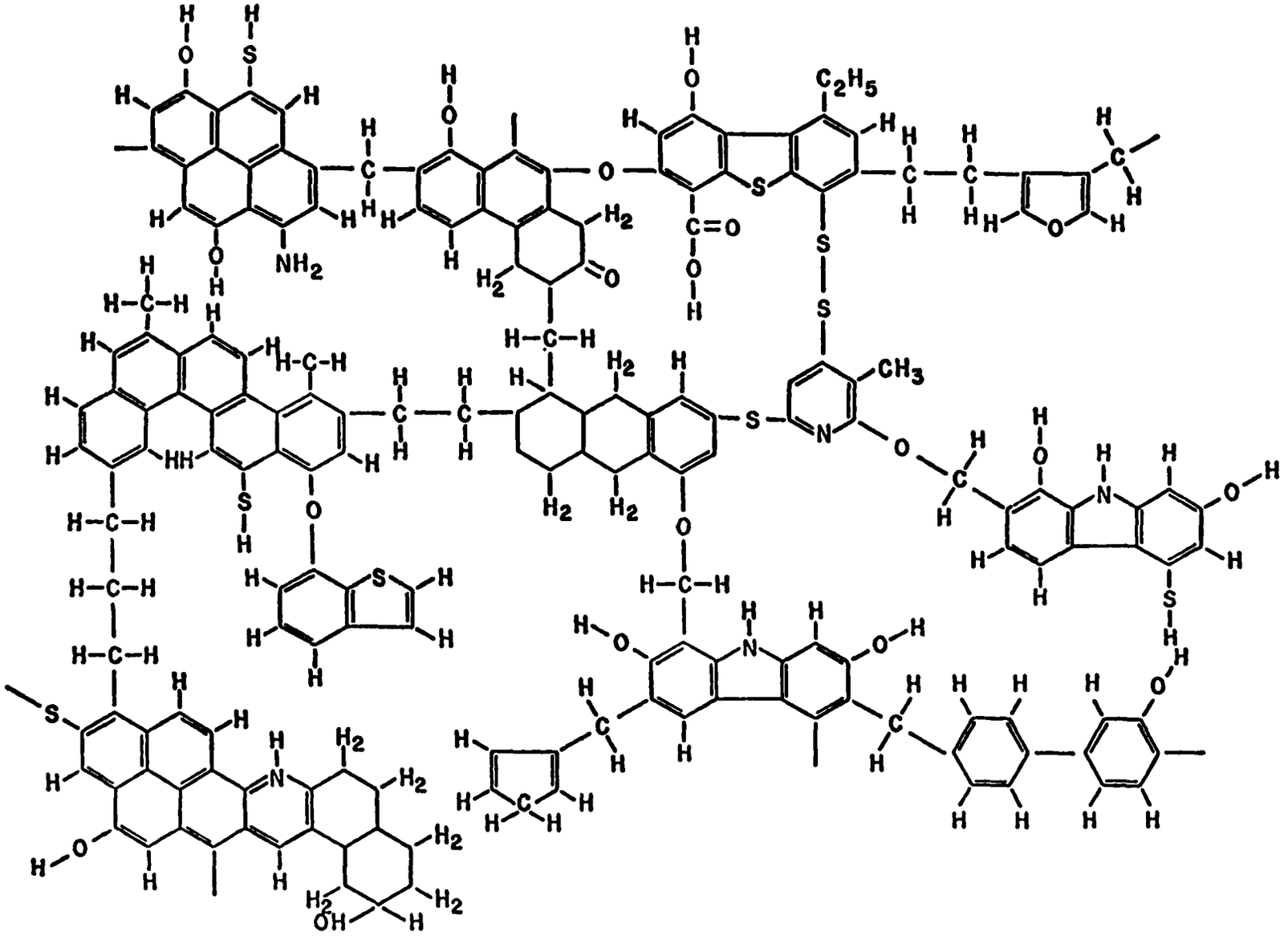


FIGURE 2. STRUCTURE OF BITUMINOUS COAL POSTULATING SULFUR AND NITROGEN OCCURRENCE IN COAL (from Wiser, W. H., EPRI Conference on Coal Catalysis, Sept. 24-25, 1973)

nutrient medium. The nutrient medium contains a diverter, usually a carbohydrate or protein, which the microorganism will consume in preference to the petroleum hydrocarbons. A reduction of sulfur content of 12.5 percent was noted when a crude was treated over a period of 4 days.

Also, Strawinskii[9] proposed the use of aerobic bacteria to convert organic sulfur to sulfate and then anaerobic bacteria to reduce the sulfate to hydrogen sulfide. Aerobic bacteria such as certain species of Pseudomonas, Alcaligenes, Bacillus or any microorganism which is capable of converting the sulfur-bearing complexes in a petroleum hydrocarbon to sulfates are grown in a mineral-salt nutrient. Small increments of the petroleum crude were added to the nutrient. There was no inorganic sulfur in the nutrient-petroleum mixture. The anaerobic bacteria consist of Vibrio desulfuricans, Vibrio estuardi, Vibrio thermodesulfuricans or Desulfovibrio.

The nutrients for aerobic and anaerobic bacteria are shown in Table 6. The medium may be further altered by the addition of pure accessory growth substances, like vitamins and/or amino acids. The pH is adjusted to 7. The addition of certain ions of copper, mercury, zinc bismuth, and iodine to the medium may stimulate the activity of the microorganism only when present in trace concentrations. The patents do not give any sulfur removal data. Most organisms were grown within a temperature range of 24 to 30 C and with the pH in the range of 6.5 to 7.5.

ZoBell,[10] in his patent claimed that sulfur is removed from petroleum hydrocarbons containing relatively complex sulfur compounds by bringing the hydrocarbons into contact with a substantial amount of hydrogen in the presence of hydrogenase producing microorganisms selected from group consisting of Desulfovebrio desulfuricans and Sporovibria and a nutrient medium. In this way sulfur is split off in the form of gaseous products which are removed. The hydrogen can be produced in situ by reaction of Clostridium microorganisms on carbohydrates. The process can be carried out either in batches or continuously and can be controlled by varying the partial pressure of hydrogen, the temperature, pH, etc. The partial pressure of hydrogen is maintained within 25-100 percent of total pressure which is kept below 10 atm. The temperature is maintained between 25 and 75 C and the pH between 6.5 and 7.5. Generally the reaction is exothermic; hence, cooling may

TABLE 6. NUTRIENTS FOR AEROBIC AND ANAEROBIC BACTERIA[9]

For Aerobic Bacteria	Grams
$Na_2S_2O_3 \cdot 5H_2O$	10
$NaH_2PO_4H_2O$	1
K_2HPO_4	2
NH_4NO_3	2
$MgCl_26H_2O$	0.25
$MnCl_24H_2O$	0.01
$CaCO_3$	0.01
$FeCl_2$	0.01
Water	1000 ml
For Anaerobic Bacteria	
K_2HPO_4	0.5
NH_4Cl	1.0
$MgSO_4 \cdot 7H_2O$	2.0
$CaSO_4 \cdot 2H_2O$	1.0
or	
Na_2SO_4	1.0
$CaCl_2 \cdot 2H_2O$	0.1
Mohr's Salt (ferrous ammonium sulfate)	Trace
Water	1000 ml

be required. When hydrogenase is used alone in the absence of other enzymes or catalysts, a mineral salt solution buffer having a pH of 6-8 is used. Catalyst for reducing sulfur-containing compounds can be isolated from marine sediments, the cultures apparently grow best in an aqueous medium of the composition of seawater, enriched by calcium lactate 0.02, ascorbic acid 0.02, ferrous ammonium phosphate 0.02, sodium bicarbonate 0.05, and potassium sulfate 0.5 weight percent.

A patent by Kirshenbaum[11] claimed to desulfurize petroleum crude by using aerobic bacteria. The bacteria convert organic sulfur compounds to inorganic sulfur compounds and these are removed by chemicals, e.g., lime treatment. The microorganisms, Thiophyso-volutans, Thiobacillus thiooxidans and Thiobacillus thioparus, used in this patent are found in nature at places of crude storage and spills. The conditions for desulfurization are similar to those in previous patents. However, certain surface active agents are recommended for increasing the contact between the oil and water layer.

In another patent[12] hydrocarbons are oxidized by using natural and mutant microorganisms. Some of the microorganisms considered in this patent are in Table 7. Adding a mutant to Desulfovibrio aesturii at 38 C resulted in a large increase in the oxygen intake by the microorganism.

The evidence presented in these patents shows that biological desulfurization of petroleum crudes is possible. What is required are controlled process conditions and nutrients. Bacteria from the group, Desulfovibrio, are particularly important. This bacteria dehydrogenates the oil but stops short of complete oxidation. This may be due to hydrogen sulfide buildup which poisons the oxidizing system of Desulfobrio bacteria.[12]

Reaction by Aerobic and Anaerobic Microorganisms--

Some important chemical reactions brought about by microorganisms are as follows.

- Oxidation of sulfur

$$2S + 2H_2O + 3O_2 \longrightarrow 2H_2SO_4 + \text{Energy}$$

TABLE 7. SOME NATURAL BACTERIA USEFUL TO FORM MUTANTS (Reference 12)

Achromobacter aerophilum	*Corynebacterium pseudodiphtheriticum*
Achromobacter citrophilum	*Corynebacterium simplex*
Achromobacter pastinator	*Desulfovibrio desulfuricans*
Achromobacter sulfureum	*Desulfovibrio aestuarii*
Achromobacter thalassius	*Desulfovibrio rubentschikii*
Achromobacter iophagus	*Desulfovibrio halohydrocarbonoclasticus*
Achromobacter delicatulus	*Flavobacterium okeanokoites*
Achromobacter aquamarinus	*Flavobacterium marinotypicum*
Achromobacter cyclocastes	*Flavobacterium marinovirosum*
Achromobacter stationis	*Flavobacterium suaveolens*
Achromobacter delmarvae	*Flavobacterium estcroaromaticum*
Achromobacter agile	*Flavobacterium fuscum*
Achromobacter centropunctatum	*Flavobacterium maris*
Agarbacterium bufo	*Flavobacterium diffusum*
Agarbacterium reducans	*Flavobacterium rigense*
Agarbacterium viscosum	*Flavobacterium rhenanus*
Alcaligenes metalcaligenes	*Flavobacterium lutescens*
Alcaligenes recti	*Flavobacterium proteus*
Bacillus thermoamylolyticus	*Leuconostoc citrovorum*
Bacillus laterosporus	*Methanobacterium soehngenii*
Bacillus brevis	*Methanobacterium omelianskii*
Bacillus thermoliquefaciens	*Methanomonas methanica*
Bacillus tostus	*Methanomonas carbonatophila*
Bacillus hexacarbovorum	*Micrococcus paraffinae*
Bacillus lactorubefaciens	*Micrococcus denitrificans*
Bacillus mycoides corallinus	*Mycobacterium album*
Bacillus druntzii	*Mycobacterium rubrum*
Bacillus toluolicum	*Mycobacterium lacticola*
Bacillus naphthalinicus	*Propionibacterium freudenreichii*
Bacillus phenanthrenicus	*Propionibacterium shermanii*
Bacillus subtilis	*Propionibacterium rubrum*
Bacillus firmus	*Propionibacterium thoenii*
Bacillus polymyxa	*Proteus vulgaris*
Bacillus macerans	*Pseudomonas fluorescens*
Bacillus circulans	*Pseudomonas putida*
Bacillus ethanicus	*Pseudomonas putrefaciens*
Bacillus kaustophilus	*Pseudomonas punctata*
Bacillus thermodiastaticus	*Pseudomonas minuscula*
Bacillus calidolactis	*Pseudomonas mira*
Bacillus michaelisii	*Pseudomonas marinoglutinosa*
Bacillus thermocellulolyticus	*Pseudomonas calcis*
Bacillus thermoalimentophilus	*Pseudomonas claciprecipitans*
Bacillus viridulus	*Pseudomonas fermentans*
Bacillus mesentericus	*Pseudomonas trifolii*
Bacterium naphthalinicus	*Pseudomonas caudata*
Bacterium phenanthrenicus	*Pseudomonas perlurida*
Bacterium stutzeri	*Pseudomonas ochracea*
Bacterium fluorescens liquefaciens	*Pseudomonas arvilla*
Bacterium nidum	*Pseudomonas tralucida*
Bacterium globiforme	*Pseudomonas gelatica*
Bacterium rubefaciens	*Pseudomonas segnis*
Bacterium latericeum	
Bacterium parvulum	
Bacterium idaneum	
Bacterium benzoli	
Bacterium didium	
Bacterium aliphaticum liquefaciens	

- Oxidation-reduction (glucose, potassium nitrate)

$$\underset{\text{(Oxidizable)}}{C_6H_{12}O_6} + \underset{\text{(Reducible)}}{12KNO_3} \longrightarrow \underset{\text{(Reduced)}}{12KNO_2} + \underset{\text{(Oxidized)}}{6H_2O} + \underset{\text{(Oxidized)}}{6CO_2} + \text{Energy}$$

- Oxidation of phenanthrene

$$\underset{\text{(Phenanthrene)}}{C_{14}H_{10}} \longrightarrow \underset{\text{(1-hydroxy-2-naphthoic acid)}}{C_{11}H_8O_2} + CO_2 + \text{Energy}$$

- Reduction of carbon dioxide

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O + \text{Energy}$$

- Reduction of sulfates

$$3CaSO_4 + \underset{\text{(sodium lactate)}}{2(C_3H_5O_3)Na} \longrightarrow 3CaCO_3 + Na_2CO_3 + 2H_2O + 2CO_2 + 3H_2S + \text{Energy}$$

Some reactions mentioned above are included in the earth's carbon cycle shown in Figure 3. The carbon cycle is maintained by the combined activity of plants, animals, and microorganisms. Microorganisms active in the presence and absence of oxygen play an important role in this growth and decay cycle. The normal decay of organic matter and its conversion into carbon dioxide is an aerobic process. The aerobic process uses free oxygen whereas the anaerobic process takes place in the absence of oxygen. In the aerobic process hydrogen is transferred to oxygen to form water while in the anaerobic processes hydrogen may either be transferred to organic molecules or ions like nitrates or sulfates.

Along with the various aerobic and anaerobic degradations of organic compounds, degradation of sulfur and nitrogen compounds also occurs. Aerobic bacteria of the genus Thiobacillus oxidize elemental sulfur to sulfuric acid, which reacts with a base to form sulfates. Thiobacillus and other species also oxidize hydrogen sulfide and sulfides. In such reactions, the intermediate and final products are elemental sulfur and sulfuric acid,

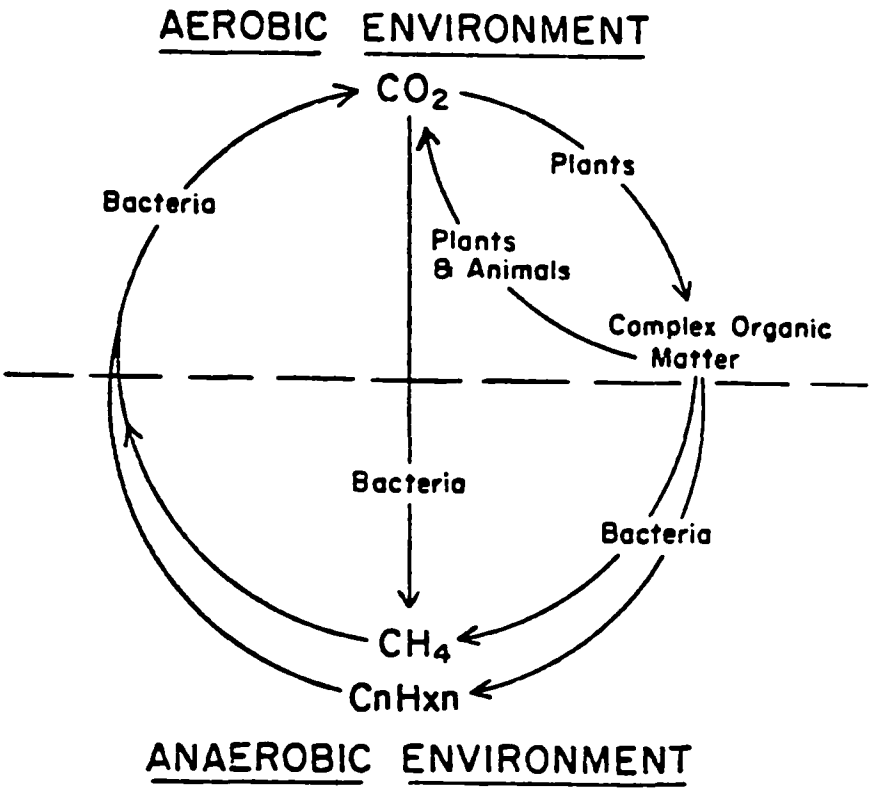


FIGURE 3. THE AEROBIC AND ANAEROBIC ENVIRONMENT IN THE EARTH'S CARBON CYCLE (Reference 3)

respectively. Sulfuric acid is also produced by an anaerobic species of Thiobacillus.[13] This anaerobic species oxidizes sulfur to sulfuric acid and the oxygen for this process is obtained from other salts like nitrates. An anaerobic specie, Desulfovibrio desulfurican, is able to reduce elemental sulfur and sulfates to hydrogen sulfide.

Aerobic and anaerobic microorganisms are also active in the degradation of complex organic nitrogen compounds like proteins and amino acids. The final products of aerobic degradation are ammonia, carbon dioxide, sulfates, and water. The aerobic bacteria can further degrade many of the products formed during an anaerobic degradation.

Several of the patents[8-10] on desulfurization of petroleum by aerobic microorganisms suggest that the desulfurization is achieved in the presence of an enzyme, e.g., hydrogenase, produced by the microorganism and hydrogen gas. The reaction scheme may be represented by

$$\text{Organic-Sulfur Compound} + H_2 \xrightarrow[\text{Enzyme}]{\text{Bacteria}} \text{Altered Organic Compound} + H_2S \quad .$$

The enzyme "activates" the molecular hydrogen which then desulfurizes the petroleum.[8-10]

Thermodynamic Feasibility--

A reaction aided by aerobic or anaerobic microorganisms can be analyzed like a conventional chemical reaction. Thus the more negative the change in Gibbs free energy (ΔG) for a reaction the more thermodynamically favored is the reaction as written. For certain reactions microorganisms seem to act as a catalyst. Like in catalytic reactions, the presence of the microorganisms may be neglected when calculating ΔG, as the concentration of the microorganisms is low with respect to the reactants. In the reactions discussed below, the magnitude of negative ΔG for an oxidation and an oxidation-reduction reaction was calculated. The ΔG values show that the aerobic reaction is thermodynamically more favored than the oxidation-reduction reaction. However, the Gibbs free energy values give no indication of the reaction rates.

In the reactions discussed below, the magnitude of the ΔG for an oxidation and an oxidation-reduction reaction is compared to illustrate the greater potential for aerobic reactions to proceed. The reactions of xylene are considered instead of the classical glucose system, commonly discussed in microbiological degradation, because xylene-type hydrocarbons dominate coal and coal liquids. The xylene-type hydrocarbons include cyclic sulfur and nitrogen compounds found in coal and coal liquids.

- Aromatic (xylene) oxidation by aerobic systems

$$\underset{\text{(Oxidized)}}{C_8H_{10}} + \frac{21}{2}\,O_2 \longrightarrow 8CO_2 + 5H_2O \qquad \Delta G = -999.\text{kcal}$$

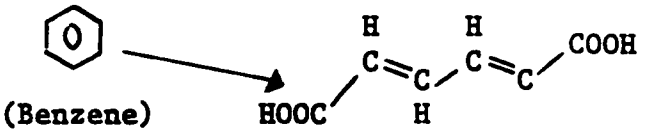
- Aromatic (xylene) oxidation-reduction by anaerobic systems

$$\underset{\text{(Reduced)}}{\frac{21}{2}\,KNO_3} \longrightarrow \frac{21}{2}\,KNO_2 + \frac{21}{2}\,O_2$$

$$\underset{\text{(Oxidized)}}{C_8H_{10}} + \frac{21}{2}\,O_2 \longrightarrow 8CO_2 + 5H_2O$$

$$C_8H_{10} + \frac{21}{2}\,KNO_3 \longrightarrow \frac{21}{2}\,KNO_2 + 8CO_2 + 5H_2O \qquad \Delta G = -723 \text{ kcal}$$

In anaerobic reactions, no free oxygen is available to add directly to the xylene or to act as hydrogen acceptor. With the help of enzymes, the anaerobic bacteria reduce the nitrate and oxidize the xylene. The free energy change is -723 kcal. This value is less than that for the oxidation reaction, which indicates that, although this reaction is favored, it is not as favored as the direct oxidation reaction of the aerobic system. Beerstecher[3] has given examples where microorganisms are able to convert xylene-type hydrocarbons to other products. One such example for benzene is shown below:



This degradation of benzene suggests direct rupture of the ring. Based on such microbial degradation reactions, it can be postulated that organisms may be found that can selectively degrade cyclic sulfur and nitrogen compounds. Thus, when such selective degradation occurs in a coal or coal liquid only the sulfur and nitrogen compounds would be altered by the microorganism.

Factors Influencing the Growth of Microorganisms --

Microorganisms are cultured in various mixtures of mineral salts (phosphates, nitrates, sulfates, chlorides) in water. An adequate source of phosphate is necessary to obtain optimal levels of growth. Some microorganisms can use all types of sources of nitrogen; others require specific

nitrogen compounds. Some hydrocarbon-utilizing microorganisms are known to grow in extreme environments, for example, 25 percent salt solutions.[3]

Other factors, like the pH, temperature, and dispersal of the hydrocarbon in the media, influence growth of the bacteria and the subsequent activity of the enzymes. The dispersal of the hydrocarbon in the liquid media greatly enhances the activity of bacteria as in Figure 4. Various techniques are used to subdivide the hydrocarbons; all involve either the formation of emulsions or adsorption upon suitable materials. As coal derived liquids have the inherent property of forming emulsions in water, they may provide suitable environment for microorganism growth.

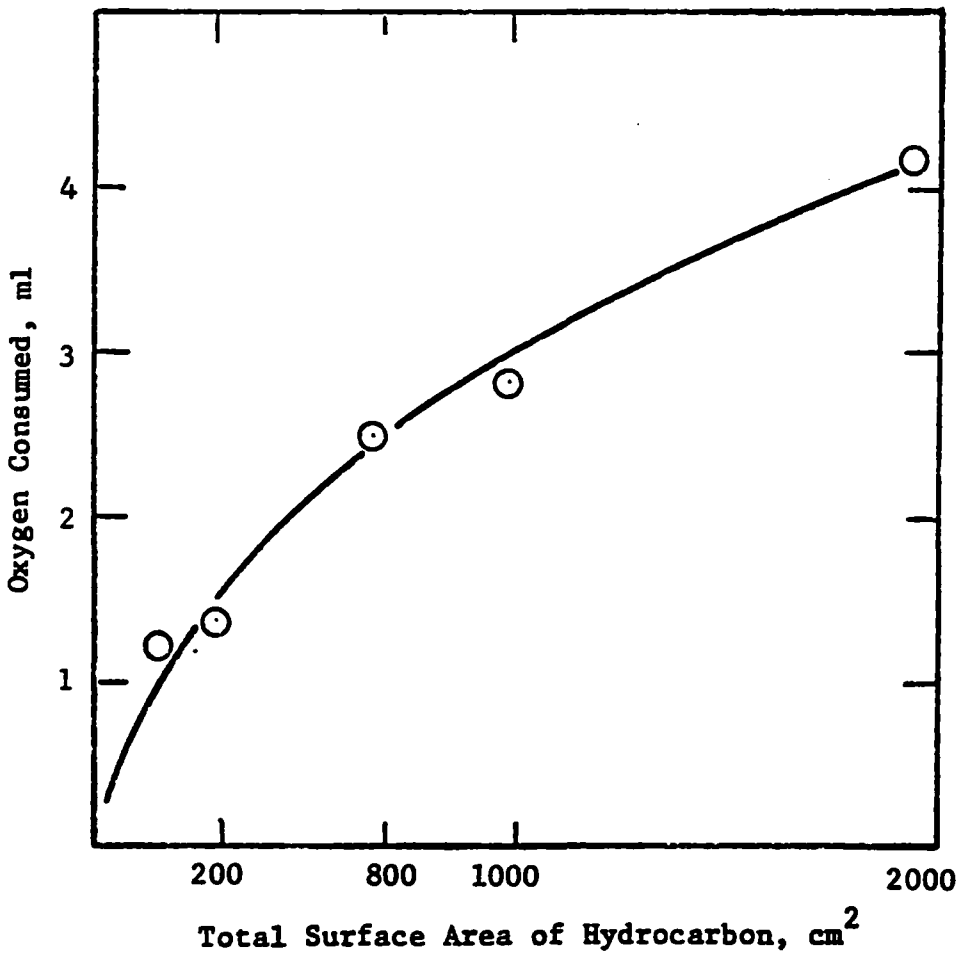


FIGURE 4. THE EFFECT OF SURFACE AREA ON BACTERIAL OXIDATION (Ref. 3)

Biological Action in Coal Derived Liquids

Microbiological degradation of hydrocarbon types found in coal and coal derived liquids by oxidation reactions is well documented.[3,4,14-16] Several patents discussed earlier claim that microorganisms will remove sulfur compounds from petroleum[8-10] and recently it was proposed that microorganisms be used to clean up certain oil spills.[17] In this clean up of oil spills, it was not determined whether the degradation was selective towards certain compounds found in an oil spill.

A majority of the microbial species that are known to consume coal/coal liquid-type hydrocarbons are listed in Table 8. This table illustrates certain characteristics of the more important species and includes fungi, a nonchlorophyll-containing plants. A large number of molds also utilize hydrocarbons.[3]

Oxidation of Hydrocarbons--

There are certain generalizations regarding the oxidizing ability of various microorganisms. Anaerobic sulfate reducers do not oxidize hydrocarbons smaller than decane.[14] This is particularly interesting as the type and size of hydrocarbons found in coal and coal liquids are comparable in size to decane. Organisms such as Mycobacteria are generally restricted in their growth to the hydrocarbon-water interface whereas Pseudomonas grow in a dispersed fashion throughout the medium, Table 8.[3]

The oxidation reactions of various straight-chain (paraffin) hydrocarbons in the presence of aerobic bacteria are of limited importance in this study since coal and coal liquids contain small amounts of paraffinic hydrocarbons.[1] The oxidation reactions of benzene and its derivatives produce various acids prior to the cleavage of the benzene ring as in Figure 5. Certain bacteria oxidize benzene at room temperature, and the product is catechol. However, in the absence of bacteria, benzene is oxidized with air at 600 C, and the product is again catechol.

When a polycyclic aromatic is attacked, a stepwise oxidation involving cleavage of an end ring occurs in a manner analogous to cleavage of the benzene ring. Oxidation of each ring proceeds in turn until the

TABLE 8. MICROBIAL SPECIES AND BIODEGRADATION OF HYDROCARBONS FOUND IN COAL/COAL LIQUIDS[a]

Family	Genus	Hydrocarbon Biodegraded[b]	Remarks
		Fungi	
Nitrobacteriaceae	Thiobacillus T. denitrificans	Crude asphalt	--
Pseudomonadaceae	Pseudomonas Ps. aeruginosa	Kerosene Petroleum Naphthalene	Numerous species
	Ps. boreopolis	Naphthalene	Isolated from soil
	Ps. oleovorans	Petroleum	Isolated from cutting oils
	Desulfovibrio D. desulfuricans	Hydrocarbons Phenanthrene	Obligate anaerobe isolated from oil field waters
Micrococcaceae	Sarcina S. species	Petroleum	--
Achromobacteriaceae	Achromobacter A. centropunctatum	Kerosene Petroleum	--
Bacteriaceae	Bacterium B. phenanthrenius	Phenanthrene	Isolated from oil-soaked soil
Mycobacteriaceae (Actinomycetales) filamentous bacteria	Mycobacterium	Most hydrocarbons	Numerous species Isolated from soil
Streptomycetaceae	Micromonospora	Most hydrocarbons	Isolated from Wisconsin lake bottoms
		Yeast and Molds	
Endomyces		Petroleum	Isolated from soil
Hansenia		Petroleum	Isolated from soil

(a) From Tables 19 and 21 of Reference 3 and Table 7 of Reference 4.

(b) Biodegradation may not be complete in some cases.

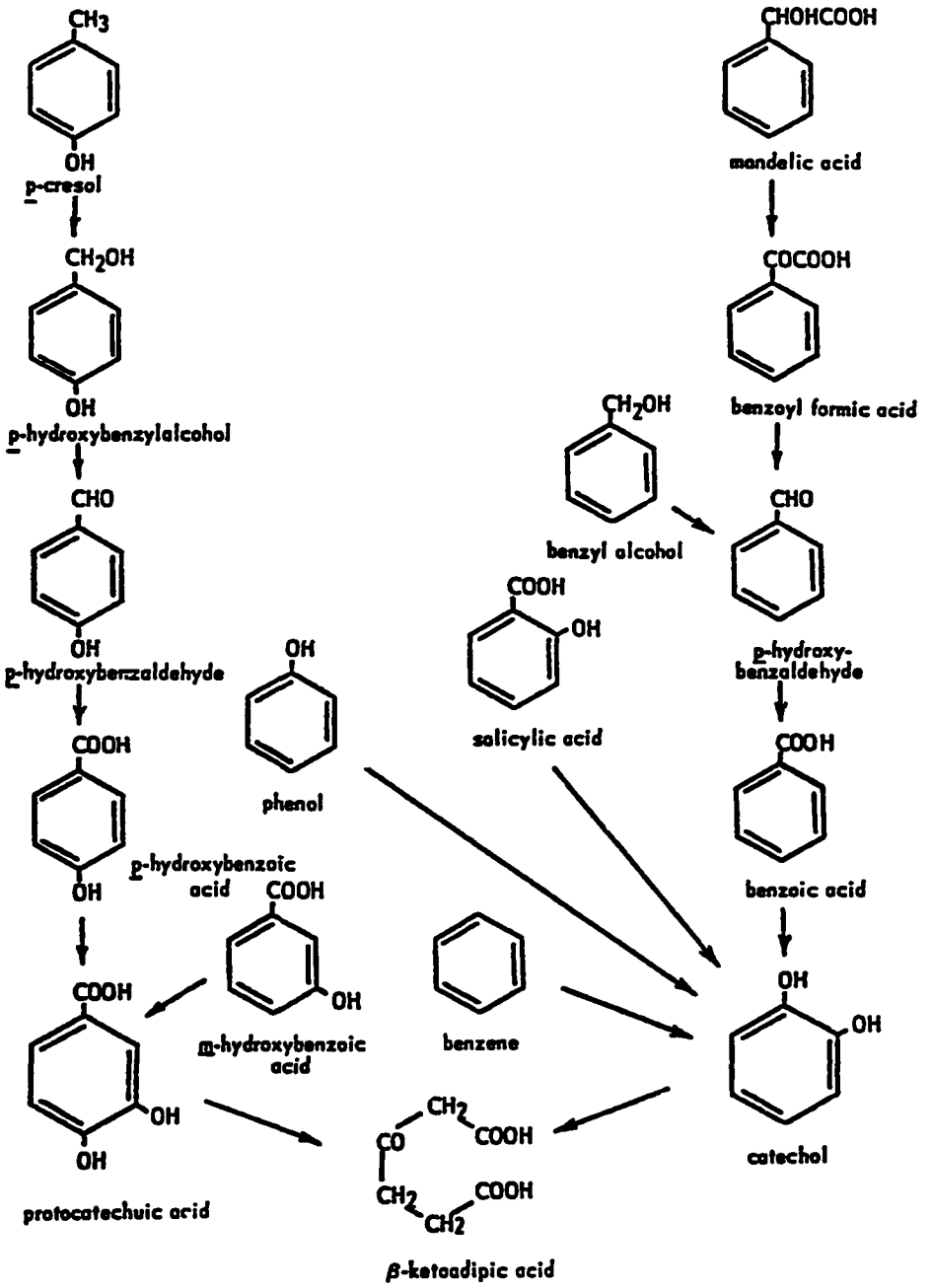


FIGURE 5. CATECHOL AND PROTOCATECHUIC ACID AS KEY INTERMEDIATES IN THE OXIDATION OF BENZENE DERIVATIVES (Reference 4)

rings are broken.[4,16] Thus, in the oxidative degradation of the polycyclic aromatics, they will pass through the salicyclic acid and catechol derivatives of benzene as shown in Figure 5.

Enzyme Activity--

The activity of the microorganisms in using hydrocarbons depends on the enzymes the organisms produce. The ability of an enzyme to catalyze a certain reaction and activity is determined by several factors:[3,13]

- Enzymes are specific and will catalyze only certain kinds of reactions; in addition, they act on but one kind of substance. For example, enzyme deaminases reacts with amino acids to produce ammonia and acids.
- The activity of an enzyme is directly related to the operating temperature. Enzymes have an optimum operating temperature which is usually below 60 C. At higher temperatures, most enzymes are rapidly deactivated.
- Enzyme activity is sensitive to the pH of the solution although specific enzymes are active in acid, alkaline, or neutral solutions.
- Certain neutral salts like NaCl and KNO_3 enhance the activity of some enzymes, but salts of heavy metals, such as $HgCl_2$ and $CuSO_4$, will, in time, inactivate most enzymes.[3,8] However, small amounts of heavy metal salts were considered necessary nutrients in the patents discussed earlier.

Microbiological Activity in Coal and Petroleum Deposits

Microbiological activity probably played a significant part in the formation and accumulation of coal and petroleum.[3,4] In the carbon cycle discussed earlier, the available carbon is constantly recycled, providing energy and building material for life. This cycle allows little carbon to be accumulated. However, the various rates of microbiological activity and unfavorable conditions of pH, oxygen, and nitrogen have probably

led to the accumulation of carbon as coal and petroleum. For coal, the first stage of this accumulation is peat formation.[3,4]

Microbial Activity in
Conversion of Peat to Coal--

Most microbial species found in peat are similar to the species identified in the biodegradation of hydrocarbons, Table 8. The species belongs to the family of Mycobacteria and Streptomycetes. The peat deposits support two forms of microorganisms: aerobic microorganisms found near the surface and anaerobic microorganisms found near the bottom of the peat deposit as in Table 9. In this table, the sphagnum peat is acidic compared to woody peat and thus supports different types of microorganisms. The anaerobic microorganisms count in acidic peat is higher than that for woody peat. The cellulose-decomposing and -nitrifying bacteria present in woody peat are absent from the acidic peat. Fungi in both peats are active at the surface of the deposit. This table also shows that the total number of organisms increases with depth and suggests that the containers used in any possible microbial treatment of coal to remove sulfur and nitrogen should not be shallow.

One theory of coal formation postulates that the difference in activity of aerobic and anaerobic microorganisms could influence the nitrogen content of coals.[18] According to this theory the anaerobic conditions promote the decomposition of the nitrogenous complexes in the peat. If this is so, then some anaerobic microorganisms present in peat may be used to decompose selectively organic nitrogen compounds in coal and coal derived liquids.

The activity of microorganisms that leads to variations in products in peat and coal deposits is an important finding for this study. Such an activity suggests that microorganisms may be found that may selectively attack certain types of sulfur and nitrogen compounds in coal or coal liquids. Rogoff[4] has summarized the microbial activity in peat deposits as follows:

- Differential decomposition occurs as a result of inherent resistance of the original plant matter to decay. The waxy and resinous materials in coal contain substances which inhibit the growth of microorganisms (biocides).

TABLE 9. TYPES OF MICROORGANISMS FOUND IN PEAT AS DETERMINED BY DIFFERENTIAL MEDIA COUNTS (Reference 4)

Depth (cm.)	pH	Microorganisms per g moist peat				
		Bacteria				
		Capable of developing in air	Anaerobic[a]	Cellulose decomposing[a]	Nitrifying[a]	Fungi
			Woody Peat			
0	6.2	[b]6,200,000	6,000	12,000	18,000	26,000
26-40	6.4	25,600,000	12,000	12,000	12,000	2,000
50-62	6.5	2,300,000	12,000	12,000	12,000	0
110-120	6.3	1,600,000	18,000	6,000	6,000	0
			Sphagnum Peat			
2.5-10	4.4	[c]100,000	200,000	-	-	-
22.5-30	4.0	260,000	100,000	-	-	-
90-120	4.1	650,000	200,000	-	-	-
150-180	4.2	750,000	300,000	-	-	-
240-220	5.7	1,250,000	200,000	-	-	-
270-330	6.0	2,000,000	300,000	-	-	-

[a]Approximate.
[b]Includes facultative aerobes.
[c]Includes facultative anaerobes.

- Different products are produced from the same plant matter under different environmental conditions. This may be demonstrated by the attack of microorganisms on lignin under aerobic conditions giving carbon dioxide and water as products as opposed to anaerobic attack in which the lignin structure is merely altered.

Microbial Activity in Petroleum Reservoirs--

Living microorganisms have been isolated from oil field waters originating several thousand meters below the earth's surface. At least 50 species of such microorganisms are known. These microorganisms can grow under diverse conditions: (1) within a temperature range of 0 to 85 C, (2) under hydrostatic pressures of up to 150,000 psi, and (3) in various saline solutions.[3] The interest in the various microorganisms found in

petroleum crudes is prompted by efforts to determine the origin of the crudes. However, certain microorganisms, like the sulfate reducing bacteria, play various roles in a petroleum reservoir: (1) they dissolve carbonates from the rock thus releasing the oil, (2) they produce certain detergent-type chemicals that help release oil from the rock, (3) they attach themselves to the rock and prevent the movement of oil, and (4) they attack long-chain paraffin compounds converting them to smaller chains.[3,19]

Conclusions on Biological Actions on Coal-Derived Liquids Based on Literature Survey

The literature reviewed for this study suggests that microorganisms may be found that are effective in desulfurizing coal and coal derived liquids. This desulfurizing activity of microorganisms is based on information found in; (1) studies on the metabolic activity of certain aerobic and anaerobic microorganisms and (2) data from the various patents on desulfurization of petroleum.

The aerobic microorganisms that are active in desulfurizing hydrocarbons function by converting the organic sulfur to a sulfate (SO_4^{--}) ion. This sulfate ion is then removed from the solution. The desulfurization reactions of anaerobic microorganisms may be catalyzed by enzymes. These enzymes convert molecular hydrogen to an 'active' hydrogen that reacts with sulfur compounds to form hydrogen sulfide. The microorganisms need nutrients and controlled conditions for growth. The nutrients include inorganic salts particularly phosphates. The conditions necessary for the growth of these microorganisms are that (1) the temperature be in the range of 0 to 85 C and (2) the pH be maintained in the range of 6.5 to 7.5; however, many microorganisms will grow at other pH values. Besides the nutrients, temperature, and pH of the solution, growth of the microorganisms is influenced by certain organic compounds in the coal and coal liquids which are preferred over the others by these microorganisms.

Besides the desulfurization of coal and coal derived liquids, denitrification by microorganisms may also be possible as is observed during the formation of coal.

EXPERIMENTAL STUDIES

Outline of Experimental Program

Based upon the information obtained in the literature search, a five-step experimental program was initiated with the intention of demonstrating biological removal of organic sulfur and nitrogen-containing compounds from coal-derived liquids.

The experimental program is outlined below:

Step 1. Grow microorganisms on defined media (salts media containing inorganic sulfur salts) to determine the growth rates of the organisms

Step 2. Add approximately 1 percent hydrocarbon characteristic of coal-derived liquids (benzene or toluene) to the salts media and determine the growth rates on the modified media

Step 3. Add approximately 1 percent model sulfur compounds (thiophene, thianaphthene, methylthiophene) to the hydrocarbon(s) used in Step 2 and determine growth rates in the presence of the organic sulfur compounds

Step 4. Repeat Step 3 but remove all inorganic sulfur salts from the media

Step 5. Grow microorganisms on actual coal-derived liquids.

Steps 2 and 3 of the experimental program were needed to demonstrate that aromatic hydrocarbons and organic sulfur compounds typical of those found in coal-derived liquids were not toxic to the microorganisms. No attempt was to be made in Step 3 to demonstrate sulfur removal -- only that the sulfur compounds were not toxic at concentrations typical of those found in coal-derived liquids. If no growth could be achieved in

Step 3 with 1 percent model compounds in the hydrocarbon phase, the concentration of the model compounds would be reduced to determine their toxic level. Assuming Steps 1-3 were successful, analytical verification of organic sulfur removal would be made in Steps 4 and 5. The same experimental program could then be repeated with model nitrogen compounds to determine if microorganisms could be used to remove nitrogen-containing compounds in coal-derived liquids.

Bacteria Cultures

Both aerobic and anaerobic sulfur-utilizing bacteria were selected for the laboratory study based upon the frequency of their referral in the literature and patent claims. The microorganisms and their sources and cultivation media are given in Tables 10, 11, and 12. The pure cultures, which were obtained from the American Type Culture Collection (ATCC) and from Dr. Patrick J. Dugan (Ohio State University), were maintained on the growth media recommended by ATCC and Dr. Dugan. Stock cultures were maintained in 10 ml of their respective medium and transferred to fresh medium on a biweekly schedule. The anaerobic bacteria were maintained in a Gas Pac 100 anaerobic jar, backflushed with a hydrogen-carbon dioxide gas mixture

The mixed culture, which was obtained from a settling pond at a coal cleaning plant in Ohio, was maintained on ATCC medium No. 450 (under aerobic conditions) and on commercially prepared, sulfate API broth (under anaerobic conditions) which was obtained in sterile, 10 ml serus vials.

The *Thiobacillus* are characterized as being: gram-negative, strict aerobes, short rods with a single polar flagella, and occurring singularly or in pairs. They obtain their energy by oxidizing reduced sulfur compounds to sulfuric acid. Their optimum temperature for growth ranges between 28 to 30 C and their optimum pH range is between 2 and 3.5.

Desulforibrio desulfuricans is characterized as a strict anaerobe, and derives its energy for metabolic activity by chemical reduction of sulfate to hydrogen sulfide. Its optimum temperature for growth is 25 to 30 C and its optimum pH range is 6 to 7.5. *D. desulfuricans* is a gram-negative, mobile, short curved rod, occurring either singly or in short chains.

TABLE 10. AEROBIC SULFUR-UTILIZING BACTERIA

Organism	Source	Growth Media[a]
Thiobacillus thiooxidans	ATCC No. 19377	ATCC No. 238
Thiobacillus thiooxidans	J. Dugan, Ohio State University	ATCC No. 450
Thiobacillus intermedius	ATCC No. 15466	ATCC No. 152
Unidentified Mixed Culture	Coal Cleaning Plant Settling Pond	ATCC No. 450

(a) ATCC -- American Type Culture Collection, 12th Edition, 1976.

TABLE 11. ANAEROBIC SULFUR-UTLIZING BACTERIA

Organism	Source	Growth Media
Desulfovibrio desulfuricans	ATC No. 13541	ATCC Medium No. 42 Sulfate API[a] broth
Unidentified Mixed Culture	Coal Cleaning Plant Settling Pond	Sulfate API broth

(a) API - American Petroleum Institute recommended practice 38, 3rd Edition, 1975, prepared by Difco Laboratories, Cat. No. 0500-86.

TABLE 12. CULTURE MEDIA

ATCC 238

Thiobaccilus Medium B

NH_4Cl	0.1	g
KH_2PO_4	3.0	g
$MgCl_2$	0.1	g
$Na_2S_2O_3.5H_2O$	5.0	g
Distilled water	1.0	L

Adjust pH to 4.2 Sterilize by steaming for 30 minutes on three successive days.

ATCC 450

T2 Medium for Thiobacillus

Solution A:

$Na_2S_2O_3.5H_2O$	5.0	g
NH_4Cl	1.0	g
KNO_3	2.0	g
Distilled water	250.0	ml

Solution B:

KH_2PO_4	2.0	g
Distilled water	250.0	ml

Solution D:

$MgSO_4.7H_2O$	0.8	g
$FeSO_4.7H_2O$ (2%, w/v, in N HCl)	1.0	ml
Trace Metals (see Med. 426)	1.0	ml
Distilled water	250.0	ml

The four solutions are sterilized separately and combined aseptically for the completed medium. The pH of the final medium is 7.0.

ATCC 125

Thiobacillus Medium

$(NH_4)_2SO_4$	0.2	g
$MgSO_4.7H_2O$	0.5	g
$CaCl_2$	0.25	g
KH_2PO_4	3.0	g
FeSO	0.005	g
Tap Water	1.0	L

1.0 g sulfur (precipitated) is placed in each dry flask. The salt solution is prepared, and 100 ml amounts are carefully poured down the side of the flask without wetting the sulfur. Flasks are then sterilized in flowing steam on three consecutive days, 1/2 hour per day. Care must be taken to ensure that the sulfur remains on the surface throughout sterilization.

ATCC 426

Thiobaccillus Medium

Trace Metal Solution

EDTA	50.0	g
$ZnSO_4$	22.0	g
$CaCl_2$	5.54	g
$MnCl_2$	5.00	g
$FeSO_4$	4.99	g
Ammonium molybdate	1.10	g
$CuSO_4$	1.57	g
$CoCl_2$	1.61	g
Distilled water	1.0	L

Adjust pH to 6.0 with KOH

TABLE 12. (Continued)

ATCC 152

Thiobacciullus Medium

Chlorophenol Red	0.08	g
$Na_2S_2O_3 \cdot 5H_2O$	10.0	g
NH_4Cl	1.0	g
$MgCl_2$	0.5	g
K_2HPO_4	0.6	g
KH_2PO_4	0.4	g
$FeCl_3$	0.02	g
Yeast extract	1.0	g
Distilled water	1.0	L

API SULFATE BROTH*

Sulfate-Reducing Medium

Sodium lacate, USP, millimeters	4.0
Yeast extract, grams	1.0
Ascorbic acid, grams	0.1
$MgSO_4 \cdot 7H_2O$, grams	0.2
K_2HPO_4 (anhydrous), grams	0.01
$Fe(SO_4)_2(NH_4)_2 \cdot 6H_4O$, grams	0.2
NaCl, grams	10.0
Distilled water, milliters	1,000.0

*Ten ml volumes are packaged in sterile serum vials by Difco Laboratories

ATCC 42

Desulfovibrio Medium

Peptone	5.0	g
Beef extract	3.0	g
Yeast extract	0.2	g
$MgSO_4$	1.5	g
Na_2SO_4	1.5	g
$Fe(NH_4)_2(SO_4)_3$	0.1	g
Glucose	5.0	g
Tap water	1.0	L

Adjust pH to 7.0.

The mixed culture used in this study was not characterized except that cell growth was obtained using the API broth and ATCC medium No. 450.

Model Organic Sulfur Compounds

Two representative organic sulfur-containing compounds were selected for the laboratory tests: thiophene and 2-methyl thiophene. For biological evaluation, these compounds were dissolved in reagent-grade toluene and benzene appropriate to the test design. The thiophene and the 2-methyl thiophene are analytical-grade reagents from Aldrich Chemical Company.

Experimental Technique

Standard microbiological equipment and technique were used throughout the experimental work. In the experiments involving the *Thiobacillus*, 100 ml of the appropriate media were aseptically dispensed to sterile 500 ml flasks fitted with a gas sparging tube. These flasks, after inoculation and addition of the test reagent, were placed in a New Brunswick Gyrotory incubator-shaker and continuously sparged with water-saturated compressed air. Temperature was set at 30 C and oscillations at 80 rpms. With the aerobic mixed culture, glass-stoppered flasks were selected so that the volatile organic sulfur compounds would be retained in the medium and would not evaporate during the test period. Oxygen was supplied to the actively growing cultures by opening the flasks to the atmosphere for short periods of time (10 minutes/day) during the experiment.

In the experiments involving the anaerobic-mixed culture, anaerobic conditions were maintained by performing all experiments in the Difco-API-sulfate-broth vials. Inoculations and additions of the organic sulfur compounds were made with syringe injections. Caution was exercised to exclude the introduction of air bubbles into the vials.

Detection and Estimation of Growth

Bacterial growth in the test media was determined by: (1) observing the increase in turbidity, (2) measuring the change in pH, (3) microscopic examination, and (4) observing the color change of pH indicators.

Characteristically, the sulfur utilizing bacteria are relatively slow-growers -- their doubling times are usually measured in days. Thus, to positively establish that growth has occurred, a combination of the four criteria mentioned above were used. Observing the increase in turbidity alone is not a positive indicator since sulfur salts can either precipitate or form colloids which can be misinterpreted as microbial growth. Therefore, growth was confirmed by both measuring the medium's pH change and by phase microscope examination. Several of the ATCC mediums for aerobic bacteria include a pH indicator, chlorophenol red. This indicator responds to the presence of sulfuric acid production and effects a color change within the medium. The API sulfate broth includes a ferrous ion which precipitates as black iron sulfide. The sulfide is produced when the bacteria reduce sulfate; thus, the formation of the black precipitate indicates bacterial growth within the medium.

EXPERIMENTAL RESULTS

The results from four shake-flask experiments performed with pure cultures of Thiobacillus are summarized in Table 13. In Experiment 1, a series of 10 flasks each containing 100 ml of ATCC Medium No. 238 was inoculated with Thiobacculus thioxidans. After inoculation, toluene and benzene (at 0.25 and 0.50 percent) were added to duplicate flasks which were aerated and shaken at 30 C for ten days. No growth was observed throughout the test period in any of the flasks, including the inoculated controls which did not contain any test solvents.

In Experiment 2, 100 ml of ATCC Medium No. 152 were inoculated with approximately 1 ml of Thiobacculus intermedus stock culture. The objective of this experiment was to measure the growth rate for this organisms. Within 24 hours of incubation, growth was observed as indicated by the decrease in the pH of the medium. Sulfuric acid is a metabolic by-product and its presence was observed by the color change of the pH indicator, chlorophenol red.

In Experiment 3, a series of 10 flasks each containing 100 ml of ATCC Medium No. 152 was inoculated with Thiobaccilus intermedius at the 1 percent level. Toluene and benzene (0.25 and 0.50 percent) were added to the

TABLE 13. SUMMARY OF SULFUR-UTILIZATING THIOBACCILUS GROWTH EXPERIMENTS, WITH AERATION AND SHAKING

Experiment No.	Organism	ATCC Media No.	Inoculum, %	Experimental Variables	Remarks and Results
1	T. thiooxidians	238	1	Toluene, 0.25 v/o " 0.50 v/o Benzene, 0.25 v/o " 0.50 v/o Controls (no solvent)	No growth was observed in either experimental or control flasks--no change in pH or in optical density after 10 days
2	T. intermedius	152	1	Controls (no solvent)	Growth occurred within one day after inoculation as indicated by color change of chlorophenol red
3	T. intermedius	152	1	Toluene, 0.25 v/o " 0.50 v/0 Benzene, 0.25 v/o " 0.50 v/o Controls (no solvent	No growth occurred in any of the flasks within 13 days
4	T. thiooxidians	238	4	Controls (no solvent)	A series of 10 replicate flasks were set up. The objective was to establish growth, then challenge the active growing cultures with toluene and benzene. No growth occurred in any of the flasks after 40 days as measured by pH change

test flasks and incubation at 30 C, with shaking, continued for 13 days. No growth occurred in any of the flasks, including the controls.

In Experiment 4, a series of 10 flasks containing 100 ml of ATCC Medium No. 238 was inoculated with Thiobaccilus thioxidans at the 4 percent level. It was planned to obtain an active growing culture, then challenge the test flasks with toluene and benzene. However, no growth occurred in any of the flasks during the 40-day incubation period.

No experiments were conducted with the Desulforibrio desulfuricons pure culture because a viable stock culture of the organism could not be established.

Various attempts were made to stimulate the growth of the Thiobaccillus stock cultures. Most were concerned with medium variations such as: (1) substitute tap water for the double distilled water, (2) adjust the pH to 3 with sulfuric acid rather than 4.2, as in ATCC medium No. 238, (3) substitute cotton plugs for the urethane foams, (4) add sterile glucose to the medium so that a supply of organic carbon is available, (5) oxygenate and carbonate the mediums with oxygen and carbon dioxide, (6) filter sterilize, rather than steam sterilize, and (7) increase the volume of inoculation to the fresh mediums. None of the variations tested improved the viability of the stock cultures.

Since the stock cultures did not propagate reliably, the unidentified mixed culture, isolated from a coal cleaning plant lagoon, was used in all subsequent experiments.

The results of experiments in which the unidentified mixed culture was challenged with benzene or toluene and these same solvents containing thiophene or 2-methyl thiophene are summarized in Tables 14 and 15. The anaerobic bacteria in the culture tolerated a higher level of toluene than benzene (Table 14), whereas the aerobic bacteria were more tolerant of benzene. In no case was growth observed in cultures containing more than 0.5 percent solvent.

Addition of the model sulfur compounds to toluene and benzene increased the toxic effect of the solvents (Table 15). Toluene containing as little as 5 percent thiophene completely inhibited growth of the bacteria. 2-methyl thiophene was slightly less toxic to the anaerobic bacteria.

TABLE 14. RESULTS WITH UNIDENTIFIED MIXED CULTURE-EXPERIMENTS IN DEFINED MINERAL MEDIA PLUS SOLVENT ONLY (7 Days)

Solvent Concentration (v/o)	Toluene				Benzene				Medium
	0.1	0.5	1.0	5.0	0.1	0.5	1.0	5.0	
Anaerobic	+++	++	-	-	+++	-	N.D.	N.D.	API Sulfate broth
Aerobic	-	-	N.D.	N.D.	++	-	N.D.	N.D.	ATCC No. 450

+++, ++, + indicates degree of growth (observed visually)

-, indicates no growth.

N.D. - Not determined.

TABLE 15. RESULTS WITH UNIDENTIFIED MIXED CULTURE-GROWTH EXPERIMENT IN DEFINED MINERAL MEDIA CONTAINING SOLVENT AND EITHER THIOPHENE OR 2-METHYL THIOPHENE (7 Day)

System[a]	Toluene (0.5 v/o)			
	Thiophene	2-Methyl Thiophene		
	5 v/o	5 v/o	10 v/o	20 v/o
Anaerobic	-	++	-	-
Aerobic	-	-	N.D.	N.D.

System	Benzene							
	(0.1 v/0)					(0.5 v/o)		
	Thiophene			2-Methyl Thiophene		Thiophene		2-Methyl Thiophene
	5 v/o	10 v/o	20 v/o	5 v/o	10 v/o	5 v/o	10 v/o	10 v/o
Anaerobic	-	N.D.	N.D.	+	-	-	-	-
Aerobic	+	-	-	+	N.D.	-	-	-

(a) Aqueous media given in Table 12.

+++, ++, + indicates degree of growth.

-, indicates no growth.

ND - not determined.

Solutions with two levels of benzene (0.1 and 0.5 percent) in which bacterial growth occurred were tested. At the 0.1 percent level, addition of 1 percent 2-methyl thiophene to benzene inhibited growth of the bacteria. Thiophene was less toxic to aerobic than the anaerobic bacteria, but growth of bacteria cultures was inhibited by 10 percent thiophene present in benzene. No growth was observed, at the concentrations of model sulfur compounds tested, when the benzene level was increased to 0.5 percent.

The results of experiments in which the aerobic mixed culture was challenged with benzene or toluene and these same solvents containing thiophene but with no other source of sulfur are summarized in Table 16. The aerobic organisms did not appear to grow in the medium that contained no sodium thiosulfate despite the fact the sulfur was available in the form of thiophene.

CONCLUSIONS

The following conclusions are based on the laboratory experiments with naturally-occurring sulfur-utilizing bacteria:

(1) Both aerobic and anaerobic bacteria can tolerate low levels (0.5 percent or less) of aromatic hydrocarbons (toluene and benzene) but higher levels completely inhibit growth of the bacteria.

(2) The addition of aromatic sulfur compounds (thiophene and 2-methyl thiophene) to toluene and benzene at levels typical of those that might be found in coal-derived liquids increases the toxicity of these solvents.

(3) The naturally-occurring, aerobic bacteria used in the experimental program could not utilize thiophene as their sole source of sulfur.

(4) The prospects for using non-mutated bacteria to remove organic-sulfur- and nitrogen-containing compounds from coal-derived liquids appear to be small because of the toxic nature of the aromatic constituents of these liquids.

TABLE 16. RESULTS WITH AEROBIC MIXED CULTURE-GROWTH EXPERIMENTS IN DEFINED MINERAL MEDIA, WITH THIOPHENE IN TOLUENE OR BENZENE AS SOLE SULFUR SOURCE (9DAY)

	Controls[a]		Experimental[b]	
	Complete Medium with Thiosulfate	Incomplete Medium, no Thiosulfate	Toluene 0.1 v/o 1 v/o Thiophene	Benzene 0.1 v/o 5 v/o Thiophene
Growth	++	-	-	-
pH (7 days)	5.7	7.5	7.9	7.9

(a) No solvents or organic model sulfur compounds added to salts medium (ATCC No. 450).

(b) ATCC Medium No. 450 containing solvents and model sulfur compounds but no thiosulfate.

(c) Initial pH 7.0.

+++, ++, - indicates degree of growth.

-, indicates no growth.

SECTION 7

USE OF AGGLOMERATION TO RECOVER CLEAN COAL VALUES FROM PREPARATION PLANT WASTES AND THE ENHANCEMENT OF PYRITE REMOVAL

INTRODUCTION

In the first phase of the program on fuel contaminants a review was made of the utility and limitations of several technologies reported in the literature for the removal, before combustion, of contaminants in coal that produce pollutants when coal is utilized as a fuel.[1] The oil agglomeration technique was one of those that appeared to have the potential for the removal of trace elements and under special conditions the physical removal of pyritic sulfur liberated from coal during grinding. The results of the review also suggested that the technique might be used to clean up coal slurry pond sediments accumulated during coal cleaning plant operations by removing the coal values they contain. The two areas are related in that pyrite removal from old coal slurry pond sediments is enhanced by the autotrophic bacterial actions on the surface of pyrite that are supported in these sediments.[1] Understanding the cause of these effects could be useful for developing a technique for removing pyrites from freshly ground fine coal slurries by oil agglomeration. Conversely, any technique developed to enhance pyrite removal from fresh coal could in effect be used to speed up natures process and the recovery of low pyrite coal from coal waste streams, both fresh and aged.

This part of the report summarizes the experimental results which extend the state of the art of oil agglomeration to the recovery of coal from coal cleaning plant wastes and the removal of pyrite from freshly ground coal to the extent that they can be removed during float-sink analysis.* In this

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* Detailed description of the experimental program are the subject of Volume 4 of the series on Fuel Contaminants. Only a summary of the findings are presented here.

program, both an Illinois No. 6 coal and an Ohio Pittsburgh Seam Number 8 coal were investigated.

Objective

The objectives of this study were to determine the feasibility of coal recovery from coal cleaning plant wastes by immiscible fluid agglomeration technique and to evaluate the effects of physical and chemical treatments on enhancement of pyrite removal during agglomeration of these wastes.

Background

Water immiscible liquids, usually hydrocarbons, have been used to separate coal from its impurities.[1] In principle it is an extension of principles of froth flotation where the hydrocarbons wet the hydrophobic surface of coal and the mineral impurities which are mostly hydrophilic remain in aqueous suspension. Separation of the two phases takes place after agglomeration or coalescence occurs and produces agglomerates of clean coal containing the oil and an aqueous suspension of the mineral matter nearly free of combustible material. Effective separation can be made with coal with a size of minus 28 mesh (0.149 mm) and often with sizes too small for any other recovery scheme. Hydrocarbon fluids such as kerosenes and fuel oils have been found very effective for enhancing the separation of the mineral matter from finely divided coal suspended in an aqueous slurry (i.e., reduce ash). The selective agglomeration process is attractive because the coal does not have to be dried after wet face mining, wet size reduction and conventional coal preparation operations. In addition the agglomerated coal can be readily dewatered by mechanical action providing energy tradeoffs between oil use and drying.

CONCLUSIONS

This study has demonstrated that coal recoveries of 90 percent or greater are attainable from fine coal slurry wastes using the oil agglomeration technique. These high levels of recovery are attainable from fresh black water sediments generated during coal cleaning, aged sediments

accumulated in slurry ponds and excavated, weathered, and partially dried slurry pond sediments. The quality of the coal was good and had lower ash and sulfur content than the coal shipped from the mine.

The residue from the agglomeration process contained between 2 to 5 percent of the oil used in agglomeration and very little coal, i.e., 90 percent ash or greater. The residue suspension obtained after agglomeration settled more rapidly than the original slurry. The residue material appears to be well suited for land disposal.

The experimental results suggest the following environmental and conservation advantages of the agglomeration process based on these current results and on understanding of the relationships between various contaminants, mineral matter and organic matter.

- Recovered coal contains lower ash and reduced sulfur (and trace heavy metals) than the parent coal.
- Recovered coal is easily dewatered and the product remains dust free.
- Volumes of waste from coal cleaning facilities can be significantly reduced resulting in less impoundment and thus less land utilization.
- Waste management characteristics are improved since residues are faster settling, more compatible with soil since they are not altered, and less prone to support bacterial activity that cause acid drainage.
- Rather than disposal of the concentrated mineral matter it may be amenable as a raw material for ceramics, cement and other construction purposes or for the recovery of useful mineral values such as alumina.

Coal derived liquids such as the distillate recovered from SRC dissolver product is able to yield 90 percent or greater coal recoveries. Its behavior is not any different than that of the petroleum derived liquids such as No. 2 fuel oil, No. 6 fuel oil-kerosene mixture and kerosene alone.

With regard to the enhancement of pyrite removal during agglomeration, use of sodium metaphosphate will remove 42 percent of the pyritic

sulfur from freshly ground minus 48 mesh coal. This is the same as that obtained by float-sink analysis suggesting removal of all the liberated pyrite in the ground coal. Equally good results were obtained when a coal slurry was treated with oxygen in the presence of sodium carbonate at 25 C. These same treatments could be applied to black water and slurry pond sediments to enhance pyrite removal during coal recovery.

An estimation of the product cost recovered from agglomeration step as an add-on to an existing coal cleaning plant or as a portable facility is about $14/ton.

Benefits that might be realized by the adaptation of the oil agglomeration technique by the coal industry include the following:

- Reduces the hazards and environmental impact of existing coal slurry ponds.
- Recovers valuable resources from wastes.
- Allows environmental control of effluents from coal preparation plants faced with increased throughput to meet energy needs and environmental constraints.
- Applicable to coal preparation plants used to prepare feed for coal conversion plants.
- Dewaters wet coal fines.
- Permits direct application of technology developed for clay stabilization to residues.
- In principle, may reduce risks of catastrophic dam failure when used as a replacement for raw wastes.

SECTION 8

EXTRACTION OF CLEAN FUELS FROM COAL-DERIVED LIQUIDS

The objective of this study is to develop a solvent extraction process for treating coal-derived liquids to produce a fuel that is low in contaminants (ash, sulfur, and nitrogen).

INTRODUCTION

Coal-derived liquids, such as those produced by the Solvent Refined Coal (SRC), H-Coal, and Synthoil processes, are highly aromatic. Their average molecular weight depends on the coal liquefaction process. A primary coal liquid prepared in any of these processes consists mostly of two- and three-ring aromatics and heterocyclic compounds. Only 60 percent of one type of SRC can be vacuum distilled in the range of 90-300 C as shown in Table 17. This limited recovery during distillation of coal liquids is probably due to thermal degradation of the coal liquid, the by-products being gases (e.g., methane and ethane) and a residue which is highly graphitic in nature and which holds the sulfur and nitrogen deep in its structure. This residue is not suitable for further liquefaction, recycle, or hydrotreatment for sulfur and nitrogen removal. Furthermore, separation by distillation alone depends solely upon the vapor pressure of the constituents overhead. While distillation is well suited for petroleum upgrading, its use for upgrading coal-derived liquids is considered marginal. This is especially true when one considers the separation of non-coal solids, attrited catalysts, and unreacted coal from the liquefied coal. The distillation temperatures are high enough to promote hydrocracking of the high boiling hydroaromatics and tend to promote reactions leading to by-product hydrocarbon gas, char formation, and hydrogen loss.

Use of selective extractions with solvents conducted at relatively low temperatures where degradation is minimized should permit

TABLE 17. CONSTITUENTS OF SOLVENT REFINED COAL[20]

Feed

Colonial Mine, Hopin County, Kentucky
Sulfur 3.33 percent, dry basis
Nitrogen 1.62 percent, dry basis

Product	Percent	
	Feed	Raw Coal
Gas	5.29	14.58
Water	2.29	6.31
Volatiles	0.19	0.52
Cold trap oil	1.00	2.76
Cut I oil (distilling to 90 C, 3 mmHg)	6.44	6.34
Cut II oil (distilling 90 C to 300 C, 3 mmHg)	59.58	--
Heavy residue	0.23	0.63
Vacuum bottom	18.33	50.52
Dry minerals	7.42	20.45
	100.77[a]	102.11[a]

[a]Greater than 100 percent because of hydrogen addition.

isolation of a hydrogenated, contaminat-free fraction (a clean fuel). Such fractionation would enhance any subsequent upgrading by allowing the use of hydrotreatment methods which take into consideration the chemical makeup of the various fractions.

Ideally, extraction should lead to portioning the primary coal liquid into streams containing:

1. Aliphatics, naphthenes, and light aromatics
2. Aromatics, including polynuclear compounds
3. Asphaltenes, preasphaltenes, and ash components.

To minimize hydrogen consumption and the production of gas and char, the first group should not be subjected to the hydrogenation/hydrocracking necessary to produce smaller molecules from condensed ring systems. Nor should the third group be treated for heteroatom (S and N) removal by hydrotreatment in the presence of the first two, since this would be costly in hydrogen consumption due to hydrogenation of the nonheterocyclic compounds.

This study reviews the extraction of coal-derived liquids with such solvents as benzene, tetralin, toluene, and acetone and summarizes the background information leading up to the experiments that suggested extraction with light hydrocarbon solvents near or above their critical pressure and can be used to isolate the fuel contaminants from clean fuel.

The development of some theoretical basis for the super critical extraction technique is given in the Appendix.

BACKGROUND

Solvents

Various solvents have been used to extract components of coal and coal liquids[2]. The solvents can extract oils (Heptane soluble material), resins (methanol soluble), and asphaltenes (benzene soluble) from coal liquids.

Solvents are of various types, e.g., aliphatic, aromatic, hydroaromatic, as shown in Table 18. The aliphatic solvents are considered poor solvents for coal liquids primarily because the coal and coal liquids contain only small amounts of oils soluble in aliphatic solvents. But the aromatic solvents (e.g., benzene) dissolve large fractions (60-70 percent) of coal liquids. The other classes of solvents, the hydroaromatic (e.g.,

TABLE 18. SOLVENT TYPES FOR SELECTIVE SOLUBILIZATION OF COAL

Solvent Type	Function
Aliphatic	Extract oil[a]
Heptane	
Hexane	
Pentane	
Propane	
Ethane/Ethylene	
Aromatics	Extract asphaltenes
Benzene	
Toluene	
Xylene	
Cresol, Phenols	
Aromatics, Active O, N, H Group	Extract asphaltenes, solublize more coal
Pyridine	
Tetrahydrofuran (THF)	
Tetralin, Anthracene Oil	
Other Solvents	Extract asphaltenes/paraffins
Acetone	
Trichloroethylene	

[a]Extracts oil under conventional solvent extraction conditions.

anthracene oil, tetralin), aromatic bases (e.g., pyridine), and aromatic acids (e.g., phenols), can solubilize undissolved coal present in the coal liquid. The hydroaromatic "hydrogen donor" solvents improve the quality of the coal liquid by increasing the H/C (atomic) ratio of the coal liquid. During such an improvement in the H/C ratio, the coal liquid is partially desulfurized.

Aliphatic solvents appear to be solvents in the true sense for coal and coal liquids, that is, they are chemically inert towards both the extract and the residue (unreacted coal). The extract and residue obtained by the action of aromatic solvents are more susceptible to oxidation than the original feed. This indicates that aromatic solvents probably extract coal and coal liquids by chemical action.

Rodgers[21] evaluated various types of solvents for extracting feeds of SRC and COED (Char Oil Energy Development) products for periods of 10-20 minutes at room temperature and found that aromatics containing a nitrogen atom in the ring structure (pyridine, quinoline) and polar molecules containing oxygen (acetone, tetrahydrofuran) were excellent solvents. Solvents like cresol, pyridine, and quinoline extracted large amounts of COED and SRC products. The solid residue, after the extraction, had an ash content of 21 percent and 50 percent, respectively, as in Table 19. The sulfur in the solid residue varied from 2.3 to 7.4 (weight percent) and the ratio of sulfur in solids to sulfur in feed was in the range of 0.28 to 0.57. Some solvents, e.g., cresol and pyridine, that produce 4 to 9 weight percent solids compared to the 22 weight percent solids with acetone and toluene did not selectively concentrate the sulfur in the soluble or insoluble fraction of the feed. The iron content of the dry solids, as in Table 18, is too low to account for sulfur as FeS or FeS_2. This indicates that sulfur in solid residue is organic in nature.

Solvent Deasphalting

Solvent deasphalting of petroleum fractions has been used extensively in petroleum refining. In such a process, petroleum residuum is contacted with a light hydrocarbon (the solvent), such as propane, normally

TABLE 19. FILTRATION SOLIDS FROM SOLVENT FRACTIONATED COAL LIQUIDS[21]

Solvent	Dry Solids Collected, wt percent Feed	Ratio,[a] $\left[\frac{A}{B}\right]$	Analysis of Dry Solids, wt percent		
			Ash	Sulfur	Iron
	SRC (Solvent Refined Coal)				
Toluene	22.1	0.55[b]	14.1	2.3	3.1
Acetone	20.0	0.67	12.8	2.6	6.9
Cresol	4.0	0.25	50.1	5.7	9.0
Pyridine	4.6	0.26	55.0	5.3	6.9
Tetrahydrofuran	8.6	0.38	33.4	4.2	3.9
Quinoline	4.5	0.28	57.7	5.8	8.3
SRC (Feed)		1.0	3.2	0.9	0.5
	COED (Char Oil Energy Development)				
Toluene	13.6	0.39	13.6	4.4	2.8
Acetone	9.0	0.28	20.4	4.6	13.7
Cresol	7.7	0.38	21.8	7.4	5.0
Pyridine	9.0	0.28	21.0	4.6	15.3
Tetrahydrofuran	9.1	0.28	21.1	4.6	14.5
Quinoline	9.1	0.28	21.5	4.6	14.6
COED (Feed)		1.0	2.1	1.5	

(a) A is the sulfur in solid product, B is sulfur in feed

(b) Example: Calculation of A/B ratio. Feed, SRC, 100 g; Solvent, Toluene. Then A = (22.1 x 0.023) and B = 0.9 and the ratio A/B = 0.55.

in a temperature range of 65-120 C and at pressures of up to 600 psi. Deasphalting is a liquid-phase extraction process. The phases are separated and the extract is flashed to recover the solvent, which is then recompressed and recycled.

The amount of asphalt free oil produced during propane deasphalting of petroleum residuum depends on the operating temperature. For a residuum there is a temperature that will produce almost a deasphalted residuum. Some typical data on solvent deasphalting are shown in Table 20. The primary objective of deasphalting the residuum is to remove metals, and it is found that sulfur and nitrogen compounds are also removed.

Solvent Extraction Above Critical Temperature

One novel method that may produce a contaminant free product from a coal liquid, e.g., SRC, extracts at temperatures above the critical temperature of the solvent. The extraction thus occurs when the solvent is in the gas phase.

This mode of solvent extraction is being used by the National Coal Board, U.K., to study the structure of coal. In one of their recent studies, up to 17 percent of a low rank coal was extracted at 350 C. The extract consisted of aromatic hydrocarbons and the yield of gas was very small. This indicated that during such an extraction the degradation of coal to gas was small.[22,22a]

In related study on the extraction of two- and three-ring aromatic hydrocarbons that are present in coal liquids, it was found that ethylene was a good solvent for removing these hydrocarbons from mixtures[23]. The degree of extraction was a function of temperature and pressure. In one pressure range investigated, higher pressures increased the solubility of the hydrocarbon to a value which was greater than the concentration at the normal vapor pressure.

Diepen and Scheffer[23] investigated the extraction of naphthalene (2 ring aromatic) by ethylene (solvent). At extraction conditions of 12 C and 100 atm, the naphthalene extracted was 25,600 times that obtained during conventional extraction at 12 C and 1 atm pressure. Higher pressures increased

TABLE 20. TYPICAL DATA ON SOLVENT DEASPHALTING OF RESIDUUM[20]

Crude Oil Type	Gach Saran	Gach Saran	West Texas	California
Residuum feedstock				
Specific gravity at 16 C (60 F)	1.030	1.030	0.986	1.027
Sulfur (weight percent)	2.66	2.66		
V (ppm)	372	372	27.6	136
Ni (ppm)	120	120	16.0	139
Cu + Fe (ppm)			14.8	94
Heptane insolubles (weight percent)	10	10		
Deasphalted oil product				
Yield (volume percent of feed)	51.5[a]	75[b]	66.0	52.8
Sulfur (weight percent)	1.89	2.25		
V (ppm)	8.0	89	1.3	2.3
Ni (ppm)	7.6	40	1.0	8.1
Cu + Fe (ppm)			0.8	3.5
Heptane insolubles (weight percent)	< 0.006	< 0.006		
Asphaltene fraction				
Sulfur (weight percent)	3.25	3.8		
Heptane insolubles (weight percent)	20	48		
Metals rejection to asphaltene fraction (percent)	98.5	81.0	96.6	98.2
Sulfur rejection to asphaltene fraction (percent)	66	41		

(a) This yield value is low in V and Ni.
(b) This yield value is high in V and Ni.

The solubility and a pressure versus composition plot for the ethylene-naphthalene system, Figure 6, shows that at 35 C and 1660 psig, 6.1 weight percent of naphthalene is solubilized in ethylene compared to about 2 weight percent at 1500 psig.

Ellis[24] extracted a mixture of hydrocarbons, dodecane and naphthalene by ethylene. In this extraction, at 75 C and 2100 psig, the vapor contained 34 weight percent of the dodecane/naphthalene mixture, as is shown in Figure 6. Also in this study, the concentration of the mixture in the vapor was found to be a function of pressure. The hydrocarbons extracted increased from 1.6 weight percent at 1175 psig to 34 weight percent at 2100 psig.

Zhuze[25] used a propane-propylene mixture for deasphalting petroleum. At extraction conditions of 100 C and 1500-1600 psig the yield of deasphalted petroleum from petroleum asphalt and cracked residue was 30 and 50 weight percent, respectively. Also it was shown that diverse products of petroleum refining, from residues to lighter fraction, could be deasphalted with compressed gases.[25]

The above-mentioned solvent extraction studies utilized ethylene and propane-propylene as the solvent. In similar extractions other gases (e.g., methane, carbon dioxide, ethane, carbon tetrafluoride) were successfully used.

The extractions of 2 to 3 ring aromatics by various gases show that the critical temperature of the gas may be an important criterion in determining the degree of extraction by the gas. When phenanthrene (M.W. 178) was extracted at 40 C (313 K) and 40 atm by certain gases, e.g., nitrogen, methane, carbon tetrafluoride, ethylene, carbon dioxide and ethane, it was observed that the extract (phenanthrene) increased markedly with increasing critical temperature of the gases as shown in Figure 7. However, the extraction with ethylene was greater compared to that by carbon dioxide even though ethylene and carbon dioxide have similar critical temperatures. This suggests that the physical and chemical nature of the gas (solvent) molecule should be considered when selecting an effective solvent system[26,27].

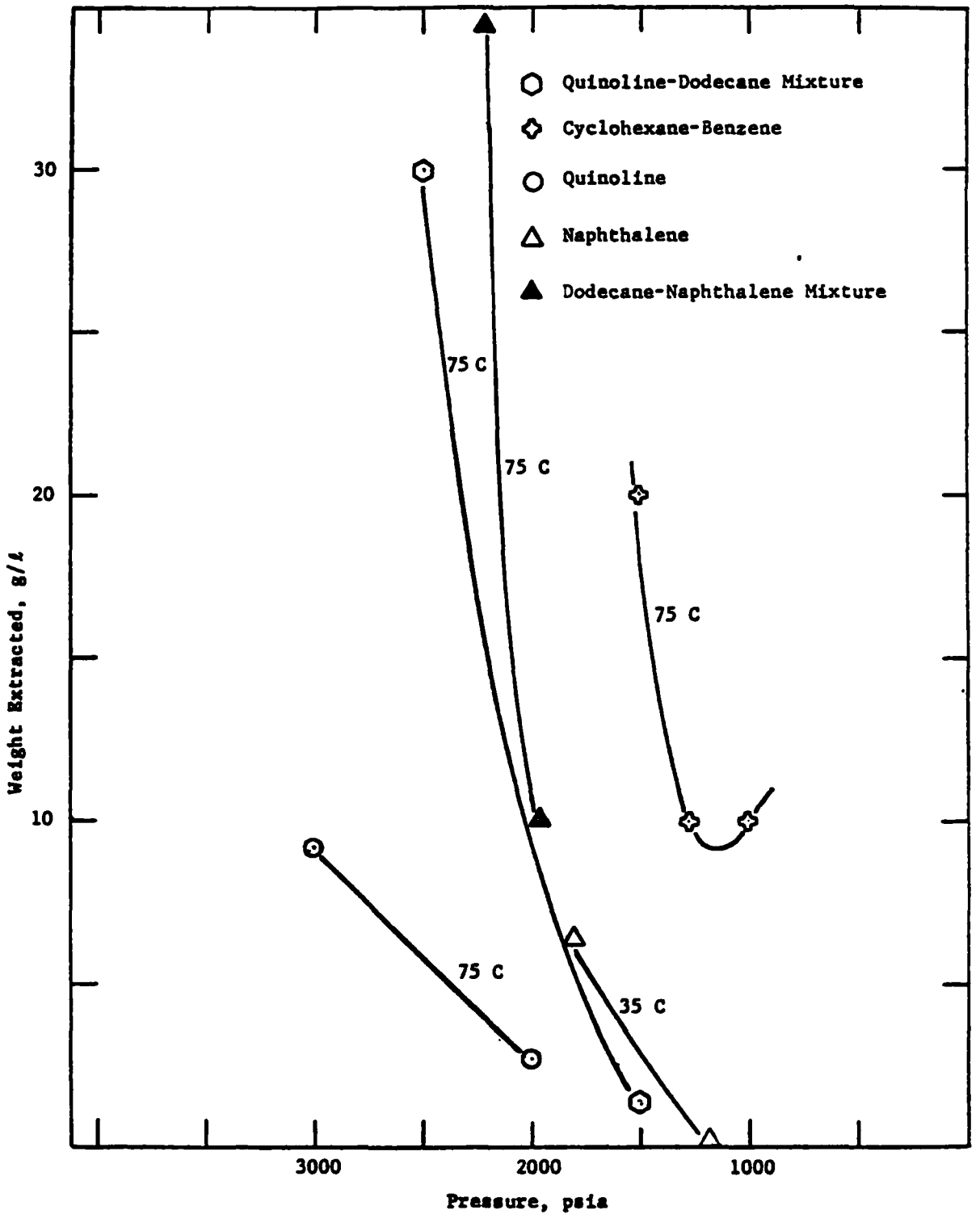

FIGURE 6. SOLUBILITY OF HIGH MOLECULAR WEIGHT HYDROCARBONS IN ETHYLENE GAS AS A FUNCTION OF TEMPERATURE AND PRESSURE[23,24]

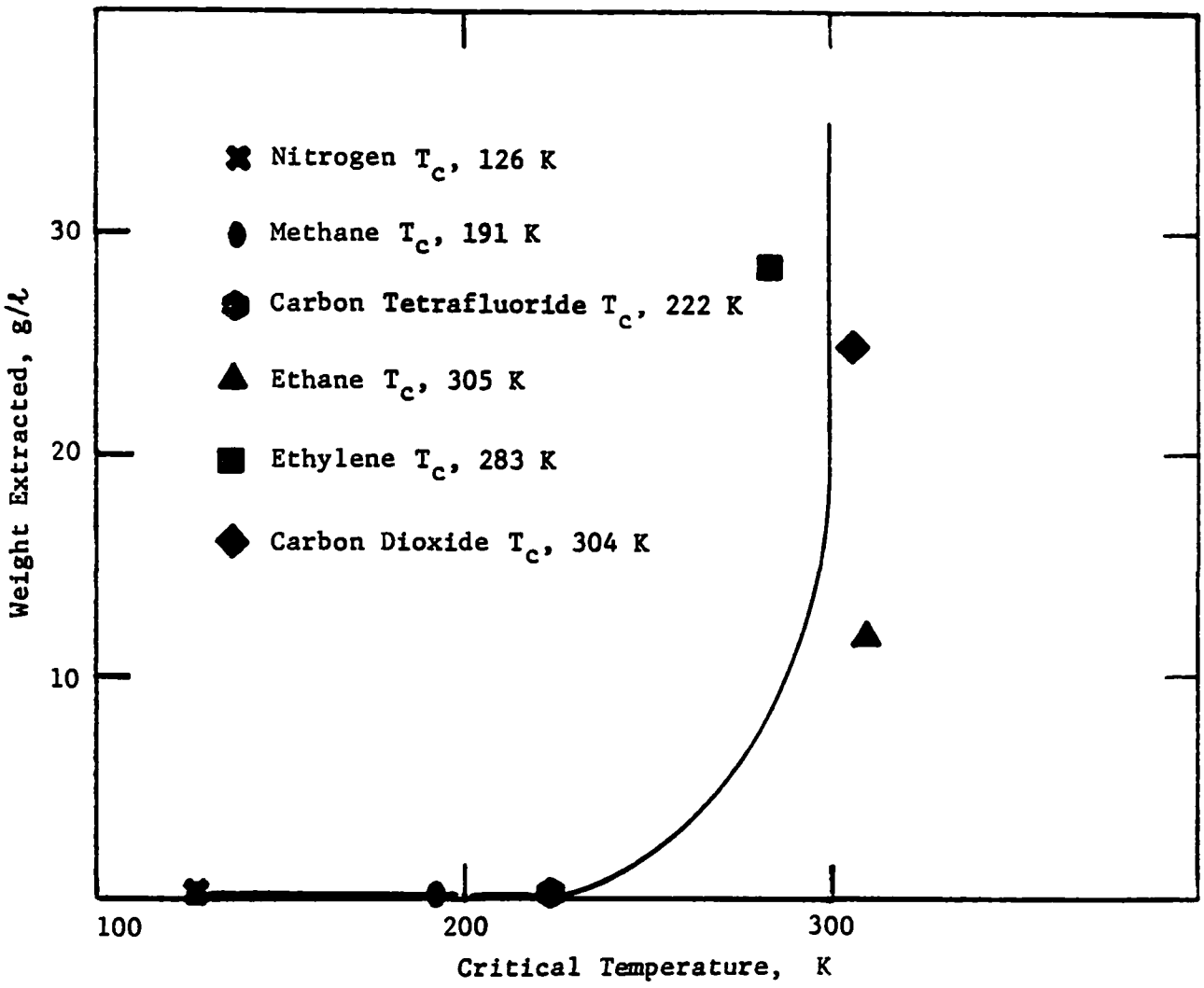

FIGURE 7. EFFECT OF CRITICAL TEMPERATURE OF GASES ON EXTRACTION OF A COAL TAR COMPONENT (PHENANTHRENE) AT 40 ATM AND 40 C (313 K)[27]

The Effect of Pressure on Solubility--

In various binary and ternary systems, it is observed that the solubility of high-molecular-weight components in the solvent, at temperatures above the critical temperature of the solvent, increases rapidly with pressure (Figure 6). It is observed that the increase in solubility is greater for nonpolar components[24].

The Effect of Temperature on Solubility--

The effect of temperature, as compared to pressure, on the solubility of high-molecular-weight components is not well documented. Diepen and Scheffer[23] show that in the pressure range of 60-80 atm the solubility was increased as temperature was raised from 12 to 35 C. Todd and Elgin[28] observed similar results.

Thus, it appears that at relatively low pressures, increasing temperature slightly above the critical temperature (of the solvent) decreases the solubility, but at higher pressures, increasing the temperature will increase the solubility of the hydrocarbon in the solvent (gas).

EXPERIMENTAL PROGRAM

The coal liquid selected for this study was obtained from the Wilsonville, Alabama, SRC plant. The sulfur, nitrogen, and ash concentrations in the feed coal are given in Table 21. This coal liquid, as it leaves the dissolver at the SRC plant, is usually flashed to remove most of the solvent. The solvent is then recycled in the process. The residue obtained after the initial flashing operation is filtered at elevated temperatures and pressures to remove the ash and the product is SRC (solvent refined coal).

The experimental program included preliminary investigations to determine the feasibility of producing a clean fuel (low in ash, sulfur, and nitrogen) from a coal-derived liquid. The clean fuel was extracted from the coal liquid by using the following hydrocarbon gases: methane, ethane, ethylene, propane, propylene, and butane. The selection of the above gases for the program was based on the following criteria:

TABLE 21. FEED MATERIAL FOR EXTRACTION OF COAL LIQUIDS

Source: Southern Services, SRC Technical Report 6, Wilsonville, Alabama SRC Pilot Plant

Feed Coal - W. Kentucky #14

Ash	8.93%
Sulfur (pyrite)	1.12%
Sulfur (sulfate)	0.10%
Sulfur (organic)	1.85%
Nitrogen	1.14%

Dissolver Product[a]

Ash	S	N	Remarks
0.22	0.23	0.74	Used on Runs 1-17
1.48	0.35	0.76	Used on Runs 18-35
2.58	0.49	0.76	Used for Distillation

(a) Values for smaller samples taken from main sample storage as percent.

- These gases are readily available, e.g., a product of coal liquefaction
- These gases are readily recoverable from the heavier product
- This gas-liquid extraction will require conventional extraction conditions, e.g., temperatures and pressures similar to those being used in present refinery extraction operations like propane deasphalting.

Nitrogen gas was used only for comparison purposes.

Extraction of Unfiltered Coal Liquid

The experimental arrangement for the extractions is shown in Figure 8. The high pressure source was a small (20-25 scfm) compressed air-operated high pressure pump.

A typical experiment consisted of charging the reactor with 50 g of the coal liquid and then introducing the gas, e.g., ethane, into the reactor. The reactor was then heated to the reaction temperature and maintained at that temperature for 10 minutes (reaction time). At the end of the reaction time a valve was opened and the gas and dissolved coal liquid flashed into ice-cooled condensers. The clean fuel was then recovered from the condensers.

The weight of the gas introduced into the reactor was calculated from the following equation:

$$pv = ZnRT,$$

where

p = pressure, atm	T = temperature, K
v = volume, l	R = gas constant, 0.082
Z = compressibility factor.	

The volume of gas in the reactor, in some cases, was verified by slowly venting the contents of the reactor through a wet test meter.

The gas to feed (coal liquid) ratio was in the range of 0.8 to 8. The extraction experiments and reaction conditions are summarized in Table 22. In this table, the column titled "percent extracted" gives the quantity of clean fuel extracted form the coal liquid based on its weight loss. The

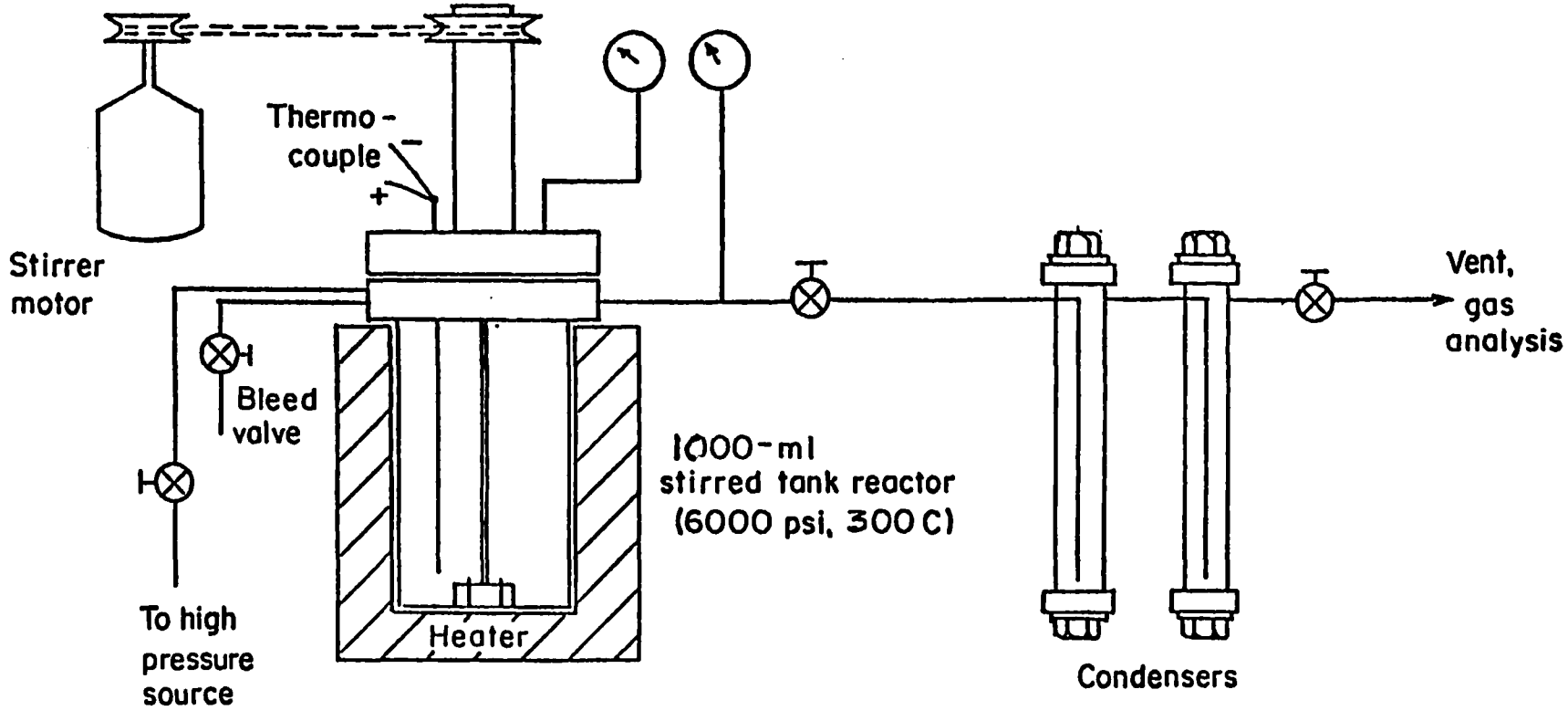

FIGURE 8. EXPERIMENTAL ARRANGEMENT FOR SOLVENT EXTRACTION AT ELEVATED TEMPERATURES AND PRESSURES

quantities extracted when the gas was methane, nitrogen, ethane, or ethylene, at pressures of 3400 psig, are shown in Figure 9. It is seen that ethaane and ethylene were equally effective in extracting a clean fuel comprising as much as 76 percent of the feed at 300 C. The yield of clean fuel is a function of temperature. The extraction capacity of ethane/ethylene increased from 12 percent at 100 C to 76 percent at 300 C. Nitrogen and methane showed poor extraction results with only 12 percent and 32 percent clean fuel extracted respectively at 300 C.

The results of extraction of clean fuel from the coal liquid with such as propane, propylene, and butane are compared with the results for ethane and ethylene in Figure 10. Butane was effective in extracting 83 percent of the feed at a temperature of 300 C. The effect of pressure on the degree of extraction for butane and ethylene is compared in Figure 11. This comparison shows that at a pressure of 3400 psig ethylene extracted 76 percent of the feed, and butane gave similar results but at a pressure of 1500 psig.

Atmospheric pressure distillation experiments with 120 to 160 g of feed (sp. g. 1.075) at a maximum pot temperature of 315 C, yielded about 50 g of light liquids. This yield is only about half that obtained by extraction with gases. Hydrogen, methane, and ethane were detected in measurable amounts in the overhead vapors, thus indicating some degradation during the recovery.

Quality of Liquid Product (Clean Fuel) and Residue

Samples of the condensed liquid product and residue (material remaining in the reactor) selected from experiments with the highest extraction yields were analyzed to determine their quality. The analyses of the products and residue after extraction of the coal liquid with ethane and ethylene are given in Table 22. The sulfur in the product is 20 percent of that in feed, the nitrogen varies between 40 to 80 percent of that in the feed, and the product is essentially ash free. The residue had 5 to 20 times as much ash as feed material. The analyses of products and residue after extraction of feed with butane are also given in Table 22. The ash content of the liquid product is essentially zero whereas the residue now

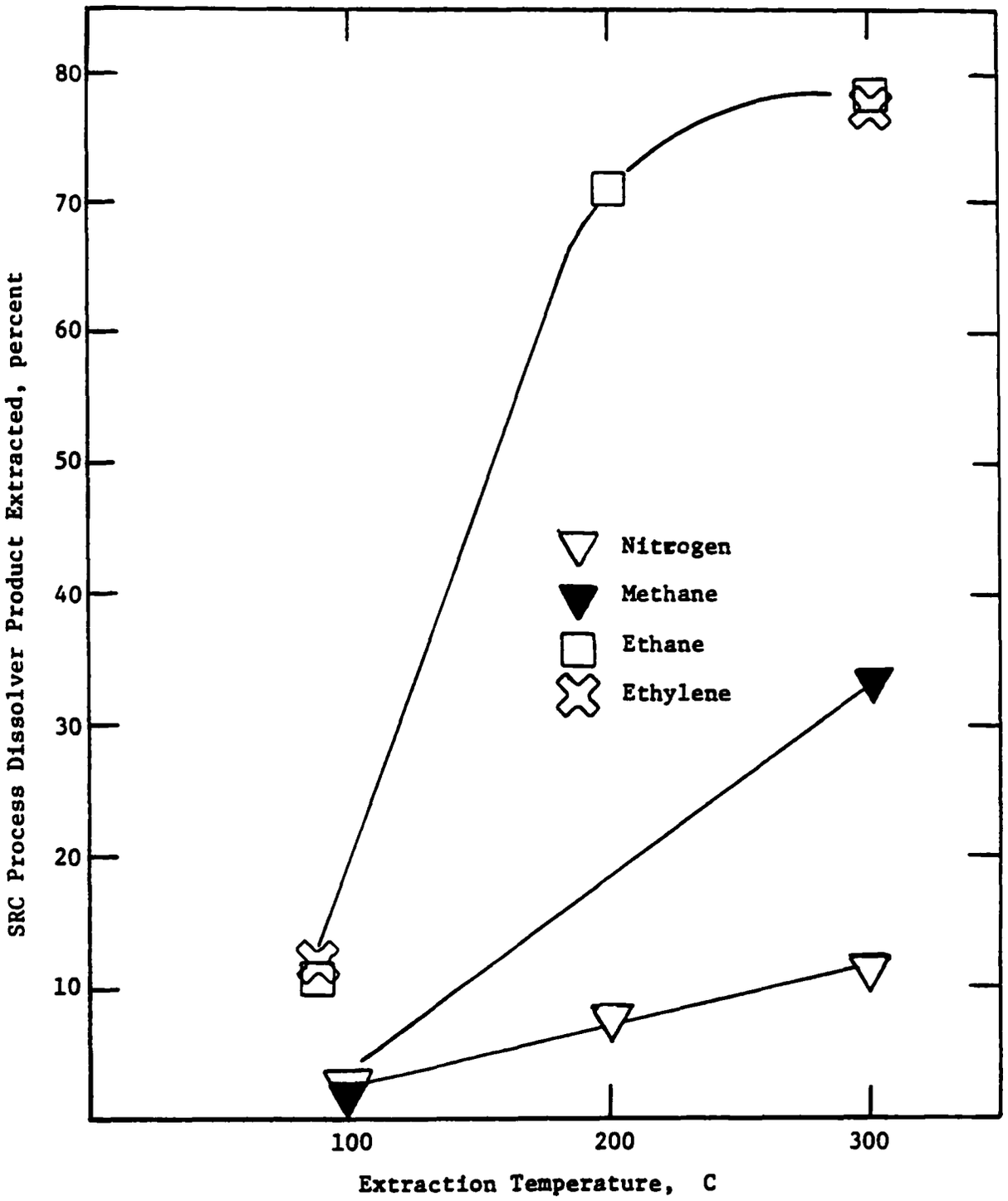

FIGURE 9. EXTRACTION OF SRC PROCESS DISSOLVER PRODUCT BY GASES AS A FUNCTION OF TEMPERATURE (3400 psig)

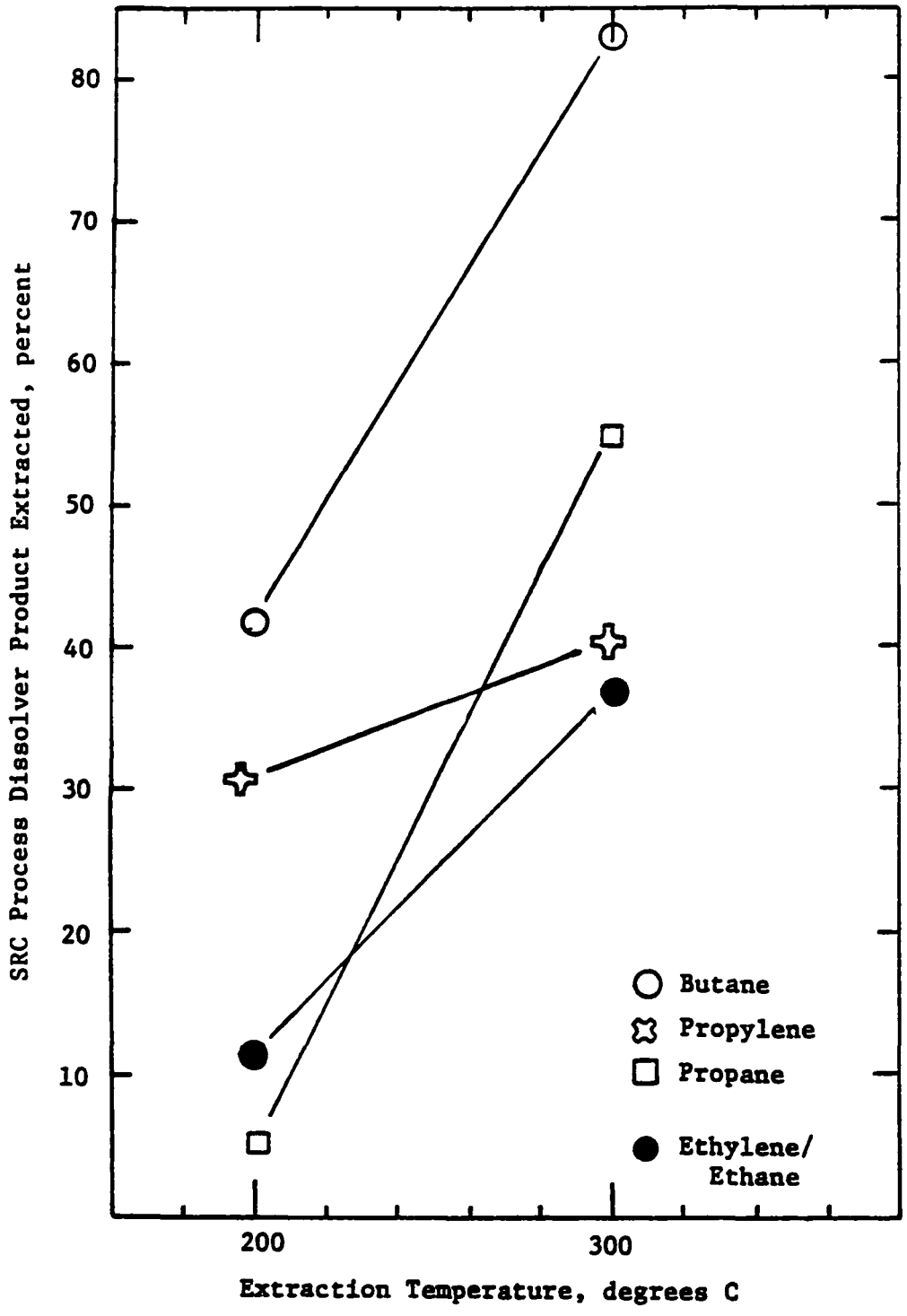

FIGURE 10. EXTRACTION OF SRC PROCESS DISSOLVER PRODUCT BY GASES AS A FUNCTION OF TEMPERATURE (PRESSURE ≈ 1500 psig)

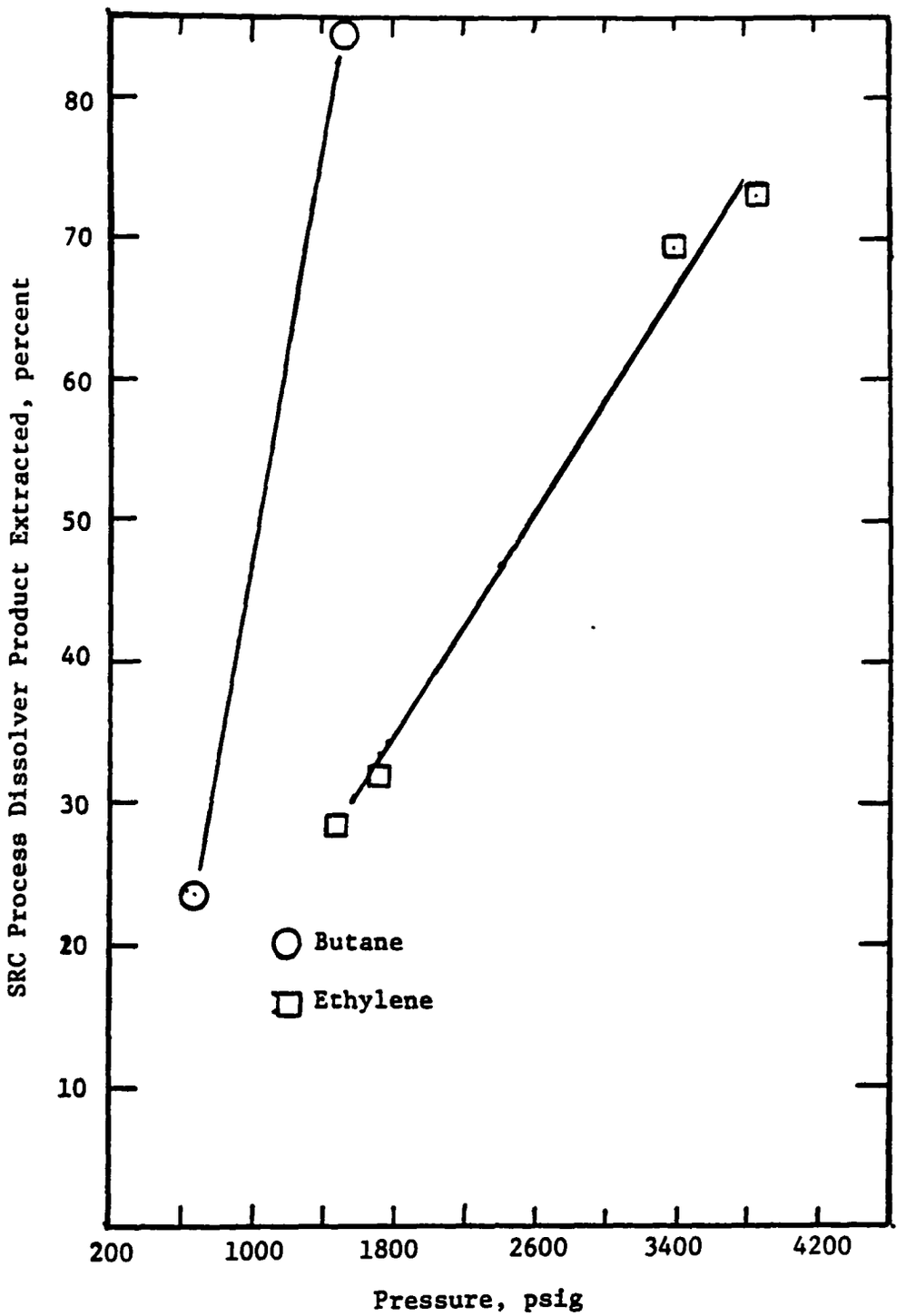

FIGURE 11. EXTRACTION OF SRC PROCESS DISSOLVER PRODUCT BY BUTANE AND ETHYLENE, AT 300 C, AS A FUNCTION OF PRESSURE

TABLE 22. SUMMARY OF REACTION CONDITIONS, PERCENT EXTRACTED, AND PRODUCT RECOVERY FOR GAS EXTRACTIONS

Sample No.	Run No.	Weight Loss	Percent Extracted	Wt of Gas / Wt of SRC	Temp, C	Pressure, psig Initial	Pressure, psig Final	Gas	Product Recovery: Final Weight, g	Product Recovery: Initial Weight, g	Product Recovery: Prod, g	Product Recovery: Autoclave Wash, g	Product Recovery: Total Recovery, g
32727-15	1	0	0	3	193	2000	3000	N_2	ND	ND	ND	ND	--
32727-16	2	3	6	4.6	114	3000	4100	N_2	ND	ND	ND	ND	--
32727-17	3	1.1	2.2	3	18	2000	2000	N_2	ND	ND	ND	ND	--
32727-18	4	0.9	2.0	4.6	18	3000	3000	N_2	ND	ND	ND	2.35	--
32727-19	5	0.6	1.2	3.0	100	2000	2700	N_2	ND	ND	ND	ND	--
32727-23	6	5.6	11.2	7.8	69	1500	3850	C_2H_6	222.6	221.5	1.1	ND	1.1
32727-24	7	36.1	72.2	4.5	184	700	3800	C_2H_6	229.2	225.1	4.1	ND	4.1
32727-25	8	38.3	76.6	4.5	280	700	4300	C_2H_6	235.5	225.5	10.0	ND	10.0
32727-27	9	4.4	8.8	2.14[a]	177	700	1700	C_2H_4	223.6	227.5	ND	--	--
32727-28	10	6.2	12.4	7.8	100	1500	2300	C_2H_4	229.1	225.1	4.0	3.1	7.1
32727-29	11	21.0	42.0	1.2[b]	300	700	1500	C_2H_4	232.9	222	10.9	5.9	16.8
32727-31	13	0	0	0.98	100	1500	1800	CH_4	157.5	157.0	0.5	2.5	3.0
32727-32	14	11.1	22.2	1.6	300	1000	2000	CH_4	164.5	157.1	7.4	2.5	9.9
32727-33	15	38	76	4.5	300	700	3400	C_2H_4	171.6	157.9	13.7	4.3	18.0
32727-34	16	5.6	11.2	1.6	300	1000	1950	N_2	162.8	157.9	4.9	4.6	9.5
32727-35	17	7.5	15	0.77	200	500	1500	N_2	158.9	158.0	0.9	4.4	5.8
32727-36	18	22.1	44.2	4.5	300	700	1500	C_2H_4	167.5	158.3	9.2	8.5	17.7
32727-37	19	11.0	22.0	4.5	200	700	1600	C_2H_4	160.6	157.8	2.8	9.8	12.6
32727-38	20	19.9	39.8	4.5	300	700	1750	C_2H_4	168.2	158.8	9.4	7.5	16.9
32727-39	21	36.6	73.2	4.5	300	700	3900	C_2H_4	171.9	157.8	14.1	0.9	15.0
32727-40	22	39.7	79.4	4.5	300	700	4600	C_2H_6	162.1	150.2	11.9	0.9	12.8
32727-42	23	42.0	84.0	5.53	300	4[c]	1500	C_4H_{10}	157.7	151.0	6.7	1.2	7.9
32727-43	24	28.7	57.4	5.53	200	4[c]	800	C_4H_{10}	162.1	150.2	11.9	5.8	17.7
32727-45	25	19.2	38.4	4.00	200	4[c]	1300	C_3H_6	154.8	150.9	3.9	9.8	13.7
32727-46	26	24.4	48.8	4.00	300	4[c]	1300	C_3H_6	156.8	148.6	8.2	7.8	16.0
32727-46	27	5.4	10.8	4.19	200	4[c]	1300	C_3H_8	152.5	150.7	1.8	5.8	7.6
32727-49	28	32.5	65.0	4.19	300	4[c]	1500	C_3H_8	169.4	150.8	18.6	7.8	26.4
32727-50	29	19.3	38.6	2.1	300	2000	3700	CH_4	163.6	150.6	13.0	6.1	19.1
32727-51	30	3.0	6.0	5.3	200	900	1500	C_2H_4	--	--	--	--	--
32727-52	31	26.8	53.6	5.3	200	900	3400	C_2H_4	161.3	151.0	10.3	5.3	15.6
32727-53	32	26.7	53.4	5.3	200	900	5000	C_2H_6	158.5	149.0	9.5	4.5	14.0
32727-54	33	18.2	36.4	7.3	200	5[c]	4900	C_4H_{10}	153.2	150.1	3.1	4.6	7.7
32727-56	34	16.4	32.8	2.8	300	2[c]	600	C_4H_{10}	152.5	148.4	5.1	6.4	11.5
32727-57	35	27.3	54.6	4.5	200	700	3600	C_2H_6	158.5	148.0	10.5	5.8	16.3

(a) Calculated from 1700 psi pressure, 177 C.

(b) Calculated from 1500 psi pressure, 300 C.

(c) Cu ft.

has 7.7 weight percent ash compared to 1.5 weight percent ash in the feed. The sulfur and nitrogen concentrations in the residue are 15 and 4 times, respectively, those in the product. Thus, by using butane extraction yields as high as 84 percent of the feed are feasible and the product is low in ash, sulfur, and nitrogen.

The results in Table 23 may only be representative of the minimum quality of products obtained because the amounts of product recovered in Experiments 32727-25 and -42 represent only about 20 percent of the material extracted, i.e., the heavy oils. The remaining part of the extract (i.e., light oils) were not captured under the experimental conditions employed. Despite this experimental limitation, an estimate of the sulfur and nitrogen contaminants the light oils contained was made by performing a sulfur and nitrogen balance. Since the quantities of feed material, residue from extraction the product captured in the traps were measured for Experiments 32727-25, -29, and -42 and they had been analyzed for sulfur and nitrogen, it was a simple matter to estimate the quantity of sulfur and nitrogen they contained and their percentage. The results of these calculations are given in Table 24. The sulfur was estimated to be 0.14 percent in the volatilized material and 0.23 percent in the feed (see Table 21), while the nitrogen decreased to 0.65 percent from 0.74 percent. In Experiment -42, the sulfur was estimated to be 0.28 percent, while the nitrogen was about 0.71 percent (compared to 0.35 percent and 0.76 percent in the feed). If these estimates are valid, then sulfur values appear to remain with the residue while the concentration of nitrogen is only slightly less than it was in the feed material. Further characterization of these fractions is needed before this can be shown conclusively. Furthermore, the conditions during extraction may not have been optimum for maximum rejection of sulfur and nitrogen compounds.

Cracking of Light Oils

Gas samples, taken after the pressure was released, were analyzed by gas chromatography. The analysis showed that no apparent chemical degradation occurred as measured by the presence of light gases, e.g., hydrogen, methane, and ethane. This is in contrast to the gas analysis of the products during atmospheric pressure distillation of the coal liquid at 300 C, when

TABLE 23. ANALYSIS OF LIQUID PRODUCT AND RESIDUE AFTER EXTRACTION OF COAL LIQUID

Experiment No./Gas	Percent of Coal Liquid Extracted	Analysis, Product, weight percent					Analysis, Residue, weight percent				
		Ash	C	H	N	S	Ash	C	H	N	S
32727-25/ Ethane	76	0	85.7	7.4	0.3	0.07	6.9	87.6	6.1	1.3	0.58
32727-29/ Ethylene	36	0	89.0	7.7	0.6	0.04	0.1	89.4	6.7	0.8	0.24
32727-42/ Butane	83	0	88.7	7.3	0.3	0.11	7.7	75.7	4.9	1.3	1.64

TABLE 24. SULFUR AND NITROGEN BALANCE FOR SELECTED EXTRACTION EXPERIMENTS

Experiment No. (Run)	Feed[a], g		Residue, g		Product Caught, g		Total Volatilized Products[b]			
							Sulfur		Nitrogen	
	Sulfur	Nitrogen	Sulfur	Nitrogen	Sulfur	Nitrogen	g	%	g	%
32727-25(8)	0.121	0.388	0.073	0.163	0.007	0.030	0.041	0.14	0.195	0.65
(Percent of Feed)			(60)	(42)	6	8	(34)		(50)	
32727-29(11)	0.125	0.403	0.084	0.279	0.004	0.065	0.037	0.43	0.059	0.68
(Percent of Feed)			(67)	(69)	(3)	(16)	(30)		(15)	
32727-42(23)	0.269	0.416	0.153	0.121	0.007	0.020	0.109	0.28	0.275	0.71
(Percent of Feed)			(57)	(29)	(3)	(5)	(40		(66)	

(a) Estimated from analysis of single sample.

(b) Estimated based on sulfur and nitrogen differences and weight of material not captured.

hydrogen, methane, and ethane were detected in measurable amounts. The presence of such gaseous products suggests that distillation at 300 C will produce gases by cracking light hydrocarbons in the feed, thereby reducing the yield of total liquids. This does not appear to be the case when gaseous extraction of coal-derived liquids is used.

OPTIMUM EXTRACTIONS OF CLEAN FUEL FROM A COAL LIQUID

Compared to a liquid fuel, the feed coal is deficient in hydrogen. A typical high-volatile bituminous coal has a hydrogen to carbon (H/C) atom ratio of 0.8, whereas a liquid fuel, e.g., fuel oil No. 1, has a hydrogen to carbon (H/C) ratio of 1.88. This indicates that hydrogen must be added to coal to produce liquid products. For a self-contained process, this hydrogen must be produced from the coal; this is possible by reacting coal with steam as:

$$C + H_2O \rightarrow CO + H_2.$$

Although this reaction is endothermic and thus requires an external source of energy, the stoichiometry of this reaction still may be used to estimate the amount of carbon in coal that is needed for hydrogen production. The percent of carbon in coal required for hydrogen production when 40, 50, and 60 percent of the coal is converted to a fuel oil with various H/C ratios can be determined from Figure 12. When 40 percent of a high volatile bituminous coal (H/C = 0.797) is converted to a liquid fuel (H/C = 1.6), the rest is a residue with a H/C = 0.8, then 14 percent of the carbon in the coal must be converted to hydrogen. Similarly when 60 percent of the coal is converted to a liquid (H/C = 1.9) then 33 percent of the coal must be converted to hydrogen to supply the extra hydrogen required by the fuel oil. These quantities of coal required for hydrogen production will be higher when due consideration is given to the heat requirements of the carbon (coal) - steam reaction.

With consideration given to these classical requirements for a self-contained process which is in hydrogen balance overall, it is generally agreed that a coal liquefaction/liquid recovery step that converts greater than 50 percent of the feed coal to the fuel oil type liquids is not practical.

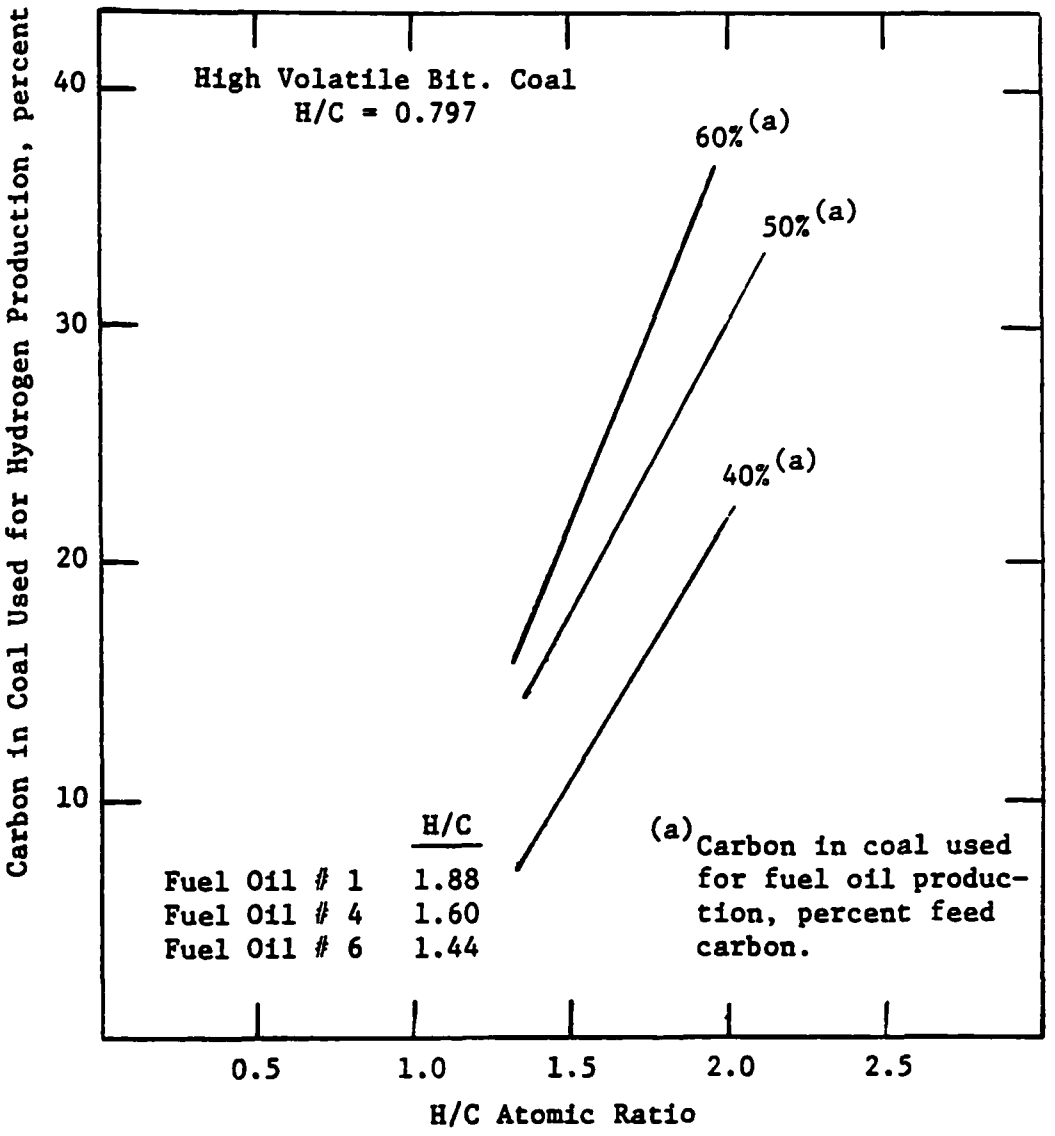

FIGURE 12. CARBON IN COAL USED FOR FUEL OIL PRODUCTION (BY HYDROGENATION) AND THE REQUIREMENT FOR CARBON IN SAME COAL FOR HYDROGEN PRODUCTION

However, given the opportunity to recover over 80 percent of the converted feed as a clean fuel as is the case in the liquefaction/extraction process reported here, shortages in the coal-hydrogen balance might be made up by adding coal to the residue gasifier. This is especially true when the liquefied coal is recovered with minimal thermal decomposition and most of the hydrogen in the converted coal is retained as the clean heavy fuel formed in the process. Recycle oil requirements of a liquefaction process could be met by the recovered extract.

PROCESS AND ECONOMIC CONSIDERATIONS

The experimental data have shown that a clean fuel can be extracted from a coal liquid. In this evaluation, design data for a clean fuel demonstration plant[29] were taken and a comparison is made between a conventional process that uses filtration and distillation and a new process that uses extraction by gases as means for separating a clean fuel from the bulk feed. The essential components of a conventional plant flow sheet, with feed and product quantities, are shown in Figure 13. The coal to recycle oil ratio is 0.5 and the coal dissolution occurs at 850 F (490 C) and 1000 psig (68 atm).

A hypothetical flow sheet for the new plant that would use extraction by gases is shown in Figure 14. A gasifier is common to both processes since part of the coal liquid residue from the extraction must be gasified to produce hydrogen. The liquefaction vessel remains unchanged, but two options are considered as alternates to filtration and distillation: (1) extraction with a light gas, e.g., ethane or ethylene, and (2) extraction with a heavier gas, e.g., butane. The major cost savings for this type of plant results from the elimination of filtration and distillation.

The extraction with light gases has shown that at temperatures of 300 C and pressures of 3500 psig (238 atm) the weight ratio of the gas to coal liquid feed should be high, e.g., 5, and for a plant with 10,000 t/d coal feed[29] the corresponding quantity of gas to be handled would require too many compressors. (The required output of the compressor was estimated to be 1×10^6 cu ft/min or more of ethane/ethylene.)

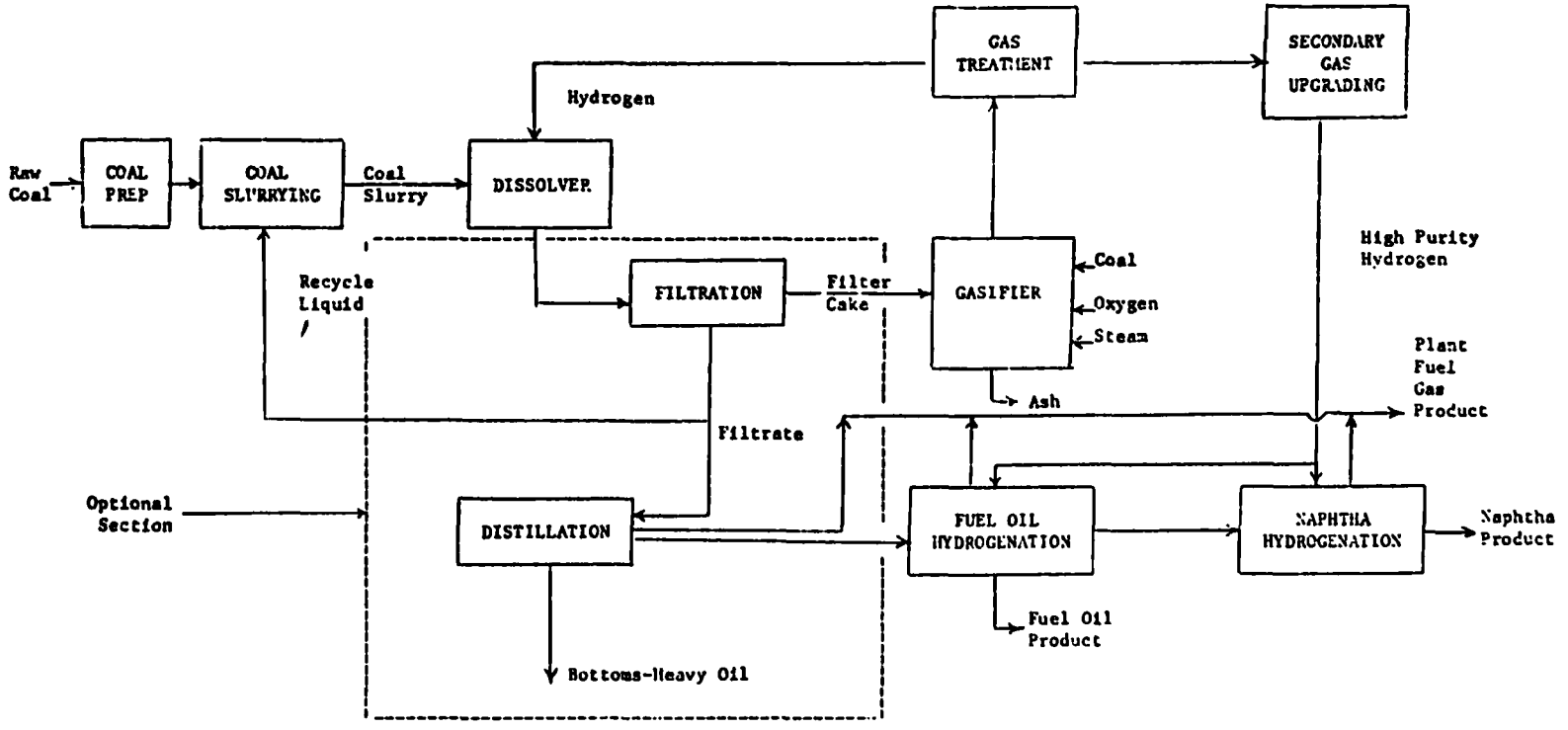

FIGURE 13. "CONVENTIONAL" SOLVENT REFINED COAL LIQUEFACTION PROCESS FOR BOILER FUEL PRODUCTION[29]

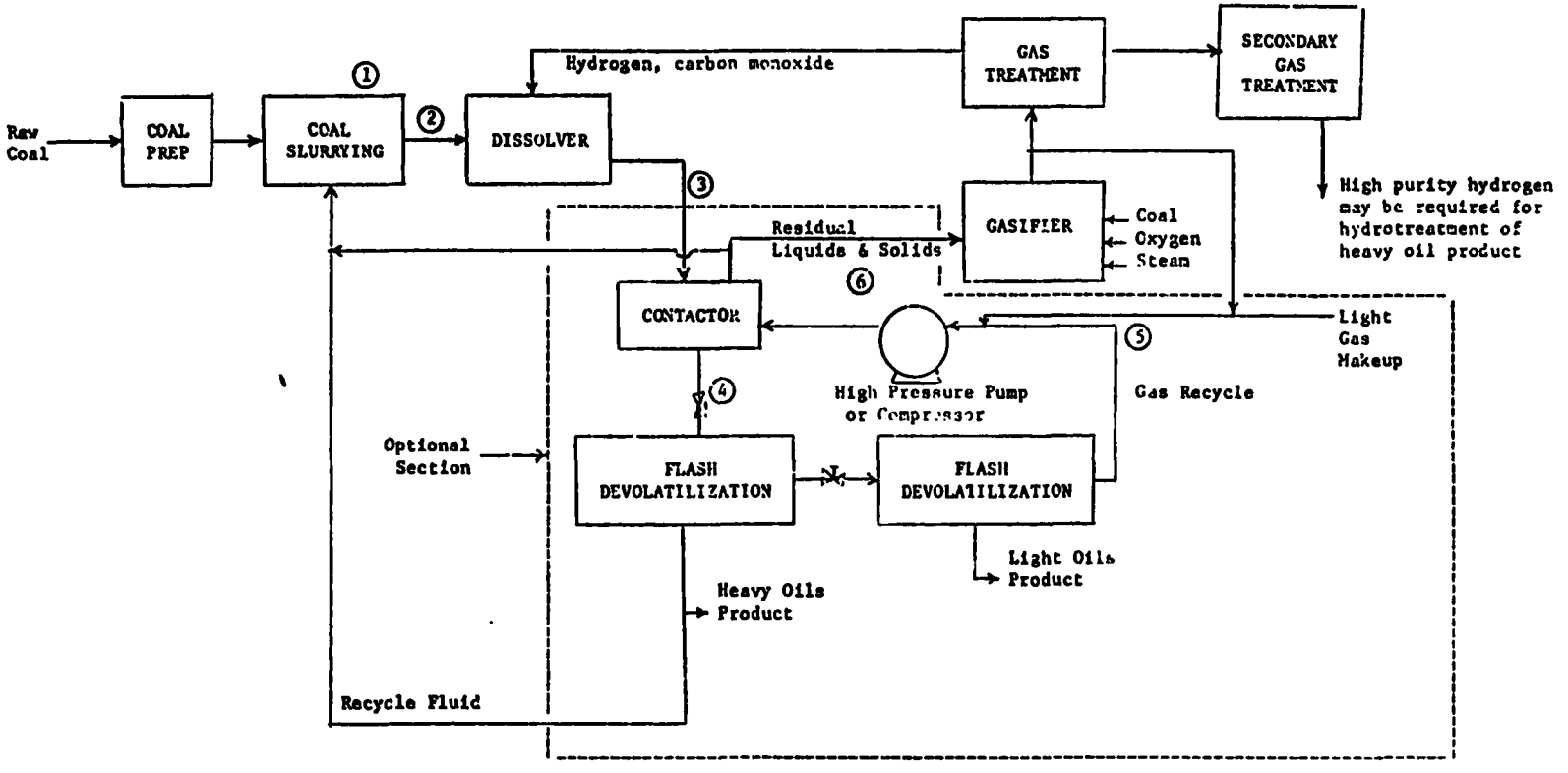

FIGURE 14. PROPOSED BATTELLE EXTRACTION PROCESS

When a heavy gas, e.g., butane, is used for extraction instead of a light gas, this material actually exists at standard conditions as a liquid, so that a conventional pump may be used instead of a compressor. The pumps are inherently lower cost units than are compressors and considerable savings could be realized if extractions were done using readily liquefiable hydrocarbons. The capacity of the pumps will be dictated by the extent of extraction desired in the process, i.e., from 50 to ~100 percent of the feed coal liquid. Arguments relating to the magnitude of the extraction relative to an overall coal to hydrogen balance were discussed earlier. The issue was purposely left unresolved because the extraction of coal liquid with gases may be more efficient and faster than conventional filtration and distillation for the separation of ash from the coal liquid and the separation of light and heavy fuel fractions from the residue. The overall impact of such a process change on clean fuel recovery and the energy efficiency of the total process would have to be assessed.

DESCRIPTION OF BATTELLE EXTRACTION PROCESS (see Figure 14)

1) Raw coal is slurried with residual liquids and solids from the contactor and heavy oil product.

2) Slurry is pumped to the dissolver which is under hydrogen pressure. Operating conditions normally used in the SRC process, i.e., 1000 psig, 490 C (850 F).

3) Materials exit the dissolver and are sent to the contactor where hydrocarbon gases (butane, ethylene or C_3-C_4 mixtures) are used to extract the clean fuels from the coal liquids.

4) The liquids from the contactor are pumped to devolatilizers (flash tanks) where the pressure is rapidly reduced in a 2-stage system. Heavy oils are collected from the first stage, part of which is recycled as solvent to the coal slurrying tank. The remaining heavy oil product may require hydrotreatment for additional sulfur and nitrogen removal. Light oils are recovered in the second stage and may not require further treatment. (As yet the quality of the light fuel fractions, i.e., %S, %N, MWt, etc., are

not known). The heavy fuel is typical of the values forund in Table 23, i.e., $\leq$0.1 percent S and 0.3 percent N.*

5) Gas which is released during the devolatilization process is compressed to the operating pressure and returned to the contactor. The C_2 to C_4 hydrocarbon gases produced in the gasifier are also used. Additional light gas may have to be added to the system. If butane or C_3-C_4 mixtures are used as the extraction medium, a pump could be used instead of compressors.

6) Part of the residual fluids from the contactor are gasified to produce hydrogen for the dissolver. Some gas treatment is required to purge H_2S from the system. If high purity hydrogen is required for hydrotreatment of the heavy oils, shift conversion, and CO_2 removal will be required as secondary gas treatment. Such a system is common to both processes.

COMPARISON OF BATTELLE EXTRACTION PROCESS TO "CONVENTIONAL" SOLVENT REFINED COAL/ LIQUEFACTION PROCESS

The front end of the Battelle process is similar to a conventional system (see Figure 14) in that coal is slurried with a recycled liquid and sent to a dissolver. However, material leaving the dissolver in a conventional system is filtered. The filtration step is very time-consuming as well as labor intensive. The ash load to the gasifier is also reduced by the elimination of the diatomaceous earth in the filter cake. In the conventional process, part of the filtrate is recycled with the raw coal in the coal slurrying tank. Filtering the stream which is recycled puts an added burden on the filters (i.e., the product and recycle must be filtered). This is eliminated by the use of the extraction process. Following filtration in the "conventional" process, part of the filtrate is distilled to produce fuel gas, fuel oils, and naphtha. The distillation is known to degrade the light and medium liquids to hydrogen, fuel gases, and heavy liquid fuels.

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*Such values of S and N are typical of the Wilsonville SRC recycle solvent.

The extraction process eliminates the distillation and related thermal degradation. The Battelle process appears to produce better grades of fuels with good recovery of desirable products.

The Battelle extraction process suggests the following benefits:

- Cleaner fuel with greater recovery
- Simpler process
- Eliminates filtration and distillation steps
- Better efficiency may be realized. (Heat and material balances are needed to help decide.)
- Possibly eliminates need for hydrotreatment of the oils to produce environmentally acceptable fuel
- Part of residue after extraction is recyclable to coal dissolver or can be feed for further hydrotreatment. It is enriched in sulfur and nitrogen contaminants and amenable to more severe hydrotreatment for their removal.

CONCLUSIONS

It has been shown that light hydrocarbon gases such as ethane, ethylene, propane, propylene, and butane may be used to extract a clean fuel from a coal liquid. The clean fuel product has the following characteristics:

- Ash content is low (almost zero)
- Sulfur content is 10-14 percent of total sulfur in feed
- Nitrogen content is 19-50 percent of total nitrogen in feed.

When a heavy gas, e.g., butane, is used up to 83 percent of the feed is extracted at pressures of 1500 psig (102 atm) and at a temperature of 300 C.

Lighter gases, e.g., ethane and ethylene, require pressures of 3500 psig (238 atm) to achieve 76 percent extraction at a temperature of 300 C.

There does not appear to be any thermal degradation of the coal liquid to hydrogen and light hydrocarbons during extraction of the clean fuel as is the case with distillation.

A process that uses butane instead of ethane/ethylene for the production of clean fuel may be more economical with respect to both capital and operating costs.

SECTION 9

USE OF POROUS MEDIA TO CONCENTRATE ORGANIC SULFUR, NITROGEN AND MINERAL MATTER CONTAMINANTS IN COAL DERIVED LIQUIDS

The objective of this part of the program was to determine if a major fraction of sulfur, nitrogen and mineral components of a coal-derived liquid stream can be adsorbed and retained on a porous material.

INTRODUCTION

The role of catalysts in the mechanism of hydrodesulfurization (HDS) and hydrodenitrification (HDN) of both petroleum and nonpetroleum feedstocks have been comprehensively reviewed in the literature as reported earlier in this study.[2] The mechanistic and kinetic models developed for petroleum HDS have been postulated for the HDS reaction occurring during coal hydrogenation and liquefaction. However since both HDS and HDS reactions are interdependent, especially on sulfided metal catalysts, both processes must be included in the model. These dual-function catalysts contain both metallic and acidic sites at which special interactions occur to promote HDS and HDN reactions. For sulfur and nitrogen contaminant removal, a critical step in the reaction is the adsorption of sulfur or nitrogen compounds on the active catalyst sites (usually acidic).

The support for many catalyst systems used in HDS and HDN treatment are alumina, Fuller's earth, iron oxide and similar materials which possess in their own right high surface areas and significant pore volume. By exposing coal liquids to porous materials with low surface areas (< 100 m^2/gm) but large pore dimensions (> 200 Å) such as alumina particles with various calcining histories, the ash minerals and sulfur and nitrogen contaminants might be removed. Such a material may promote rapid diffusion into the pores and enhance removal of these contaminants by preferentially adsorbing sulfur and nitrogen compounds much as they are in the initial stages of catalyzed HDS and HDN reactions. The mineral matter would be occluded by the bed of particles

of adsorbent and retained. If these processes occur, then the spent substrate would be expected to contain a high concentration of sulfur and nitrogen contaminants suitable for further processing under conditions more amenable to conversion to clean fuels by hydrotreatment. Since the porous adsorption material was selected for its low surface area, the spent adsorbent would be expected to be strong enough physically to undergo repeated gasification regeneration cycles in a fluidized or moving bed.

Such a separation could provide a clean liquid from high boiling fractions of coal-derived liquids and serve as a means of concentrating organic sulfur and nitrogen contaminants into a fraction for more severe HDS and HDN treatment (i.e., higher temperature and pressure reaction conditions). However, losses of liquids would have to be held to levels below that now being lost in filtration and/or distillation of coal liquids.

EXPERIMENTAL PROGRAM

The coal liquid selected for this study was obtained from the Wilsonville, Alabama, SRC Plant and is the same material used in the extraction experiments described in Section 8, i.e., it is the SRC dissolver product containing solvent.

The equipment used in the study is shown schematically in Figure 15. The pump was operated at a flow rate of 10 ml/min. The SRC liquid flowed up through the reactor containing the fixed bed or porous material. The porous material could be maintained in the temperature range of 25 to 200 C.

The materials selected for this study are listed in Table 25. The choice of the materials was based on the activity of the alumina, the silica-alumina content, porosity and availability. Material of a minus 6 plus 10 U.S. Standard Sieve size was used in all experiments. Some of the materials had to be crushed to obtain this size range. Volumes of 22 and 10 ml were used to charge the reactor. When a volume of 10 ml was used, the remaining reactor volume was filled with nonreactive ceramic fish spines.

Procedure

A typical run consisted of packing the reactor with a known volume of the porous material. Then the reactor was heated to the predetermined temperature. When this temperature was reached the SRC-liquid was pumped

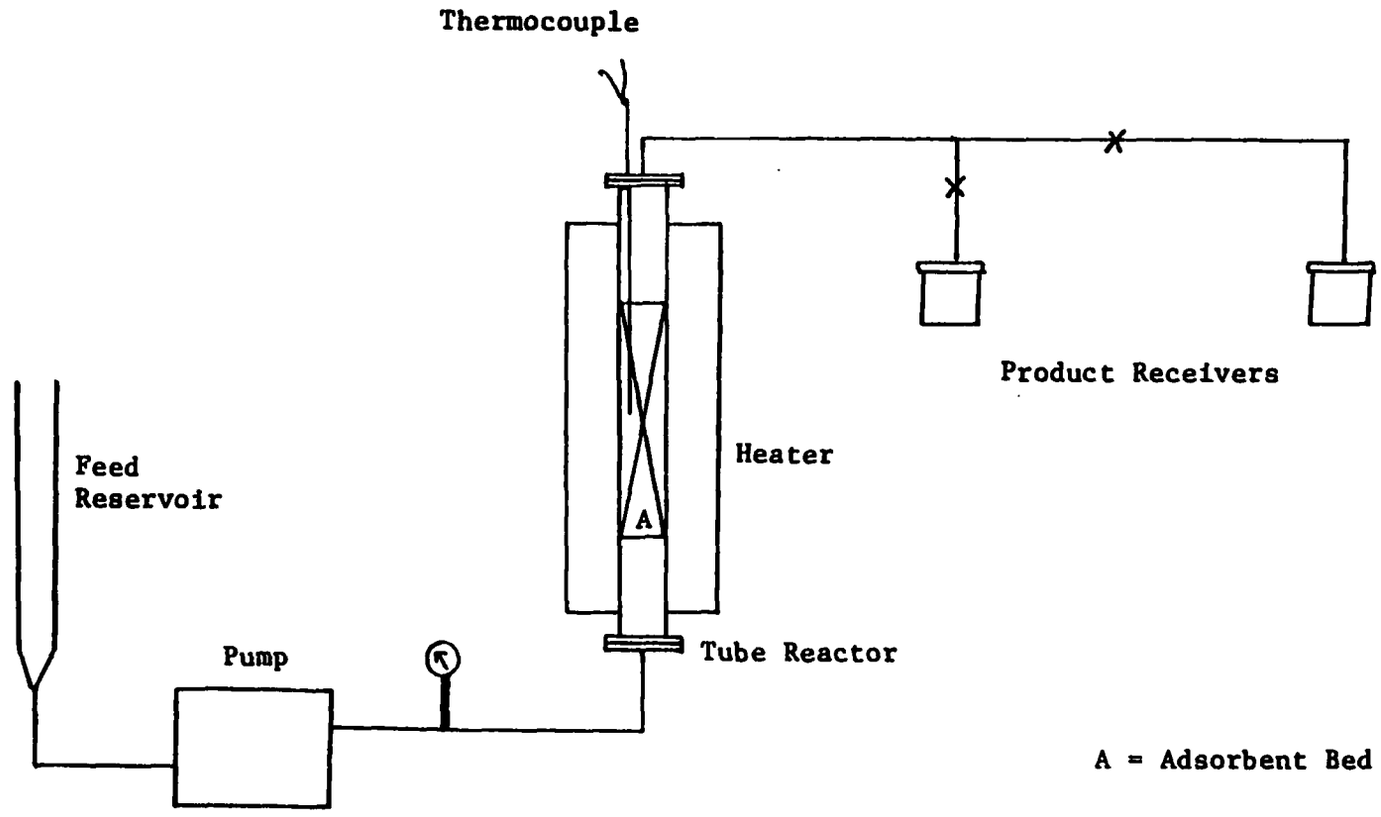


FIGURE 15. EQUIPMENT ARRANGEMENT USED FOR POROUS MATERIAL ADSORPTION STUDIES

TABLE 25. MATERIALS USED AS POROUS MEDIA

Manufacturer	Number	Chemical Analysis, % Al_2O_3	Chemical Analysis, % SiO_2	Porosity %	Bulk Density g/cc	Surface Area m^2/g	Chemical Nature
Norton	SH-5102	99.6	< .05	50-56	1.7-2	0.7-1.3	Inactive
	SH-5123	87.2	11.1	40	2.2-2.4	0.02	Inactive
	H-Zeolon	$SiO_2/Al_2O_3 = 10$		N.A.[a]	0.6	450	Active
Harshaw	Al-X-649 -65-5-S	≈ 99	N.A.	N.A.	1.5	1.0	Inactive
Alcoa	F-1	≈ 95	N.A.	N.A.	1.5	5	Active
BCL	A-4[b]	75	(Fe_2O_3 25)	N.A.	0.61	1.69	Inactive
W.R. Grace	Expanded Perlite	∿15	∿70	(c)	0.2	(c)	Inactive

(a) N.A. = not available

(b) 25 percent Fe_2O_3 - Bauxite Mixture Sintered

(c) 80-90 percent void space

through the bed at a predetermined rate. A total of 120 ml of the SRC liquid was treated in each experiment. Three liquid samples were collected and analyzed for sulfur, nitrogen and ash. The first liquid sample (Cut 1) was the first 10 ml of liquid which passed through the bed, the second liquid sample (Cut 2) was the 100 ml of liquid following and the third liquid sample (Cut 3) is the last 10 ml of liquid that passed through the bed. The porous material is recovered from the reactor and stored. The spent bed was regenerated by heating to 400-450 C in a controlled stream of air. The performance of the regenerated materials were evaluated under similar conditions to that used for fresh material.

The first and third cuts were all analyzed for their ash content first. From these values the amount of ash removal was calculated. Initially only those samples which had a 50 percent reduction in ash content were to be analyzed for sulfur and nitrogen. This criteria was later modified in order to determine if sulfur and/or nitrogen removal was independent of ash removal.

Results

A total of 33 experiments were completed at 25, 100, and 200 C using fresh and regenerated adsorbents with the objective of reducing the ash content by at least 50 percent. The results of the ash determinations for selected samples of the first and third 10 ml cut of the 120 mls passed through the adsorbent bed are compared to ash values for the feed materials in Table 17. Also included in the table are the ash-free sulfur and nitrogen values determined for samples selected for analysis and the feed materials. Feed materials with the ash content of 2.58 and 3.25 percent had higher sulfur content (0.50 and 0.44 percent S, respectively) than the feed material with an ash content of 0.360 percent (0.23 percent S). This suggests that the sulfur content is attributable to both organic and inorganic forms.

It should be noted that increases in ash content were observed when adsorbents SA-5102, F-1, inactive Al_2O_3 and bauxite were used. This was assumed to be due to the presence of fines formed during crushing, screening and/or loading of these materials. After regeneration of the absorbent, the tendency to increase the ash content was not as severe or absent (see SA-5102). However, beds of regenerated bauxite, F-1, and H-Zeolon become plugged when used again for treatment.

DISCUSSION

Ash Removal

A comparison of the ash removals indicates that a reduction of about 50 percent of the ash content occurs only when the ash content of the feed material is low, in this case 0.360 percent. This occurs for a known chemically active adsorbent (H-Zeolon) and for an inactive form (SH-5123). It also occurs at 25 C and 100 C.

In the case of SH-5123 the smaller bed of 10 ml seemed to be the best giving a 55.5 percent removal for the first 10 ml and even a greater removal by the end of the run of 61.9 percent.

For the filled reactor (22 ml of adsorbent) the removal remained the same while for H-Zeolon it decreased. The reason for these variations is not clear. One may speculate that the voids between adsorbent particles are filled by the end of the run and the filtration is more effective. This would happen more quickly in the smaller bed treating equal volumes. (Ceramic fish spines alone were found to be ineffective for ash-forming mineral removal.) The ash removal for the other materials studied, even those contributing to the ash in the first cut, was improved by the end of the run in 9 of the 13 experiments reported in Table 26. Of the four that showed an increase in the ash removal two were for regenerated adsorbents.

When coal liquids with ash contents of 2.58 and 3.25 percent were fed through the adsorbents, removal never approached 50 percent. For H-Zeolon removal reached 14.2 percent, while SH-5123 reached 22.2 percent. These results suggest that the fresh porous materials are not as effective on coal liquids with higher ash content. The removal did improve slightly at the end of the run in most experiments using fresh porous material. Regenerated materials were not as effective at the end of the run as at the beginning or became plugged. With the material SH-5102, no significant difference was observed while operating at 25 C rather than 100 C. With SH-5123, however, the ash removal of 42 percent at 25 C fell to 2.1 percent at 100 C and 2.6 percent at 200 C. The material F-1 was found to be more effective for ash removal at 100 C than at 200 C. (No experiments were done at 25 C with F-1.)

TABLE 26. RESULTS OF EXPERIMENTS ON THE USE OF POROUS MEDIA TO REMOVE CONTAMINANTS FROM COAL LIQUIDS (Feed Rate 10 ml/min)

Material	Active Bed		Ash Values, Percent			Ash Reduction (Increase), percent		Sulfur/Nitrogen, percent, Ash Free		
	Volume, ml	Temp., C	Feed	Product Cut 1	Product Cut 3	Cut 1	Cut 3	Feed	Product Cut 1	Product Cut 3
H-Zeolon[a]	22	100	0.360	0.178	0.262	50.5	27.2	0.23/0.74	0.13/0.74	0.13/0.73
H-Zeolon	22	100	3.25	3.05	2.79	6.2	14.2	0.44/0.75	0.48/0.78	0.39/0.72
H-Zeolon (Regen)[b]	22	100	3.25	2.41	--[c]	25.8	--	0.44/0.75	0.52/0.75	(0.47/0.74)[e]
SH-5123[a]	22	25	0.360	0.210	0.210	41.6	41.7	0.23/0.74	0.20/0.75	0.20/0.74
SH-5123	10	25	0.360	0.16	0.137	55.5	61.9	0.23/0.74	0.20/0.75	0.20/0.74
SH-5123	22	100	2.58	2.56	2.52	0.8	2.1	0.50/0.78	0.46/0.88	0.45/0.79
SH-5123	22	200	2.58	3.08	2.51	(1.9)	2.6	0.50/0.78	0.43/0.76	0.34/0.74
SH-5123	22	100	3.25	2.53	2.95	22.2	9.2	---	---	---
SA-5102[a]	22	100	2.58	2.71	2.74	(5.2)	(6.4)	0.50/0.78	0.14/0.79	0.12/0.83
SA-5102	22	25	2.58	2.94	2.69	(14.1)	(4.5)	---	---	---
SA-5102 (Regen)[b]	22	100	3.25	2.80	2.95	13.2	9.2	---	---	---
F-1[d]	22	100	3.25	3.26	2.80	(0.3)	14.0	0.44/0.75	0.52/0.75	0.45/0.72
F-1	22	200	2.58	2.73	2.64	(6.1)	(2.8)	0.50/0.78	0.13/0.80	0.12/0.80
Inactive Al_2O_3[d]	22	100	2.58	2.69	2.51	(4.5)	2.5	0.50/0.78	0.47/0.79	0.47/0.71
Bauxite	22	100	3.25	3.31	2.58	(1.7)	20.6	0.44/0.75	0.49/0.78	0.47/0.79
Bauxite (Regen)[b]	22	100	3.25	Plugged				---	---	---
Perlite	22	100	3.25	2.90	2.83	10.8	12.9	0.44/0.75	0.49/0.73	0.46/0.68
Perlite (Regen)[b]	22	100	3.25	2.75	3.07	15.4	5.5	---	---	---

(a) Supplied by Norton
(b) Regenerated at 400 C with flow of excess air
(c) Sample lost
(d) Supplied by Alcoa
(e) With ash

Sulfur and Nitrogen Removal

Sulfur in the coal liquid was reduced to the 0.12 to 0.14 percent level (ash free) with the use of H-Zeolon, SA-5102 and F-1 but the treatment conditions and relationship to ash content differ for each material. This was the lowest level attained in these experiments. Nitrogen removal was essentially zero except that in the third cuts using inactive Al_2O_3 or perlite about a 10 percent reduction was measured.

H-Zeolon reduced the ash-free sulfur of 0.23 percent to 0.13 percent for the feed with 0.36 percent ash but did not prove too effective for the feed with 3.25 percent ash where the values appeared essentially the same (feed = 0.44 percent; Cut 1 = 0.48 percent; Cut 3 = 0.39 percent). After regeneration the H-Zeolon appeared to contribute sulfur to the coal liquid. By contrast the material SA-5102 (which is not very effective in removing ash forming minerals) was able to reduce the sulfur to 0.12 to 0.14 percent from a feed with 0.50 percent sulfur (2.58 percent ash) at 100 C. However porous material, F-1, could reduce the sulfur to 0.12 to 0.13 percent from a feed with 50 percent sulfur only at 200 C. At 100 C, using a feed with 0.44 percent sulfur (3.25 percent ash), no removal was measured. Bauxite and perlite were found ineffective with the other porous media studied exhibiting only a small tendency to remove sulfur.

The ability of inactive Al_2O_3 and expanded perlite to reduce nitrogen from two high-ash-containing coal liquids by 10 percent is significant since they did not affect the sulfur content. This suggests that the removal mechanism for organic nitrogen may be different than for some of the sulfur (organic or inorganic) and is not directly related to ash removal.

It should be noted that in those cases where high ash coal liquids were fed and ash removals of 14 to 20 percent were obtained, sulfur reduction did not occur. Even in the case of SH-5123 where a low-ash feed was used and a large percentage of ash was removed, the sulfur only decreased from 0.23 to 0.20 percent. Therefore one could speculate that sulfur removal does not necessarily follow effective ash removal if pyrrohtite were the source of sulfur. In fact, the opposite seems to be true (see SA-5102 and F-1 results).

CONCLUSIONS

Some porous materials with low surface areas but large pore dimensions have been found to remove up to 76 percent of the sulfur (ash free) from coal liquids passed through them in a fixed bed. These same materials can also remove about 20 percent of the ash-forming minerals from feeds containing about 3 percent. From feeds containing about 0.4 percent ash, 50 percent or better can be removed. A 10 percent removal of nitrogen can be accomplished using expanded perlite. Both nitrogen and sulfur removals appear to occur by separate mechanisms and both seem to be independent of ash removal.

SECTION 10

CONVERSION OF COAL LIQUEFACTION RESIDUE TO ENVIRONMENTALLY ACCEPTABLE FUEL

The objective of this study was to ascertain whether techniques used by the coal carbonization industry to produce clean coke can be used for the cleanup of coal liquefaction residues.

INTRODUCTION

As reported earlier in this study, the thermal decomposition reactions of coal during carbonization for coke formation are favorable to the enrichment of most contaminants in the solids.[2] Up to 65 percent of the sulfur and 60 percent of the nitrogen originally present in the coal end up in the coke. This fraction was reduced by special treatment with gases during carbonization. Removal of 80 percent of the sulfur was realized by exposure of the coal during carbonization at 800 to 1000 C with either ammonia, hydrogen, water gas or steam. Changes in nitrogen content were not reported. The same principals are believed to be applicable for the removal of sulfur and nitrogen from coal liquefaction residues which are usually enriched in sulfur and nitrogen and trace elements originally in the feed coal. The sulfur and nitrogen are considered to be refractory or too difficult to remove at reasonable HDS and HDN treatment conditions but still not fixed in the carbon matrix as in coke.

Coal liquefaction residues are defined as the materials obtained after removal of liquids during solids separation and the heavy oils left after distilling off light cuts (i.e., bottoms). Characteristics of contaminants usually present in residues are as follows:

- Sulfur - present as FeS and as organic sulfur compounds (2-4 member aromatic rings); usually difficult to convert by hydrogenation.

- Nitrogen - present as organic nitrogen compounds; usually difficult to remove by hydrogenation; enriched in residues, especially bottoms.
- Trace elements - normally those present are those contained in mineral matter of raw coal.
- Catalyst - eroded or attrited catalyst if used in the process.

Prevalent methods proposed or anticipated for utilization of these residues are as follows:

- Typically insoluble solids would be retorted to obtain added liquids and char. The char would be used for fuel or reacted with water to form hydrogen. Such solids typically contain 5 to 30 percent fixed carbon.
- Still-bottoms would be coked to provide additional recoverable liquids and solid coke for fuel and/or hydrogen production (would be enriched in sulfur and nitrogen and undesirable as a fuel).

If the coal liquefaction residue can be converted into liquid hydrocarbons (rather than gas) and a char which is made low in sulfur and nitrogen by treating the residues with active gases, greater recovery of clean fuel value would be possible Removal of the sulfur and nitrogen during the conversion of residues or still bottoms to char will reduce the amount of sulfur and nitrogen eventually fixed into the coke-like matrix during carbonization (coking). The cleaner char would be used to produce hydrogen stream requiring less cleanup down stream. In addition, such an approach could provide for greater yield of carbon as hydrocarbons and could provide gas streams richer in H_2S and NH_3 for more efficient cleanup during the treatment. No energy penalty for cooling the gas stream would have to be considered. However, such a process would have to exceed the performance of existing processes using pyrolysis and gasification with respect to overall environmental impact, energy requirement, and the quality of the fuel products.

EXPERIMENTAL PROGRAM

Residues of coal liquids used in this study were from two sources. One was prepared from SRC dissolver product described in Section 8 by topping

the liquid at a 400 C bottom temperature. (One batch, prepared under vacuum, gave a residue which was 18.4 percent of the original weight charged; the other batch was prepared at atmospheric pressure and was 21 percent of the original weight charged. Both batches were crushed and blended thoroughly before analysis and use.)

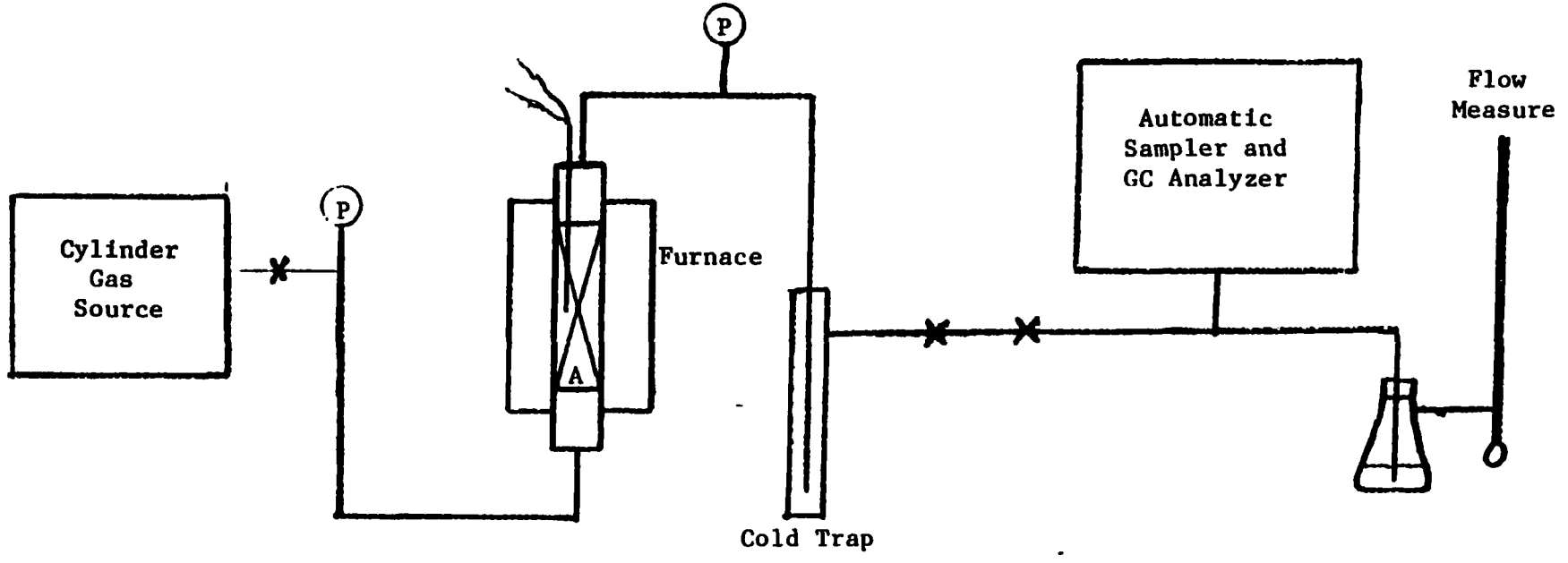
The other residue was supplied by Hydrocarbon Research, Inc. (HRI) at Lawrenceville, New Jersey (Sample No. LO-1052 from their syncrude run 130-79-168 which processed Illinois No. 6 coal). The HRI residue is from the vacuum bottoms. The analysis of both materials is shown in Table 27.

The equipment used in the study is shown in Figure 16. The system could be pressurized to 80 to 100 psi from the cylinder of gas being used for the treatment.

Flow of the gases at pressure were controlled by double-valving and the flow rates of 10 and 100 ml/minute were measured at the vent of the reactor train by measuring the rate of rise of coap bubbles in a burette at atmospheric pressure. The cold trap was cooled to -78.5 C with a solid carbon dioxide-acetone slurry to trap condensable material released during the run. An automatic sampling gas chromotograph was used to detect the release of noncondensable (at -78.5 C) products formed during the reaction. The temperature in the reactor was controlled at either 400 or 500 C in a resistance heated furnace.

TABLE 27. ANALYSES OF COAL LIQUEFACTION RESIDUES, PERCENT

Material	Moisture	Ash	Total S	Nitrogen
SRC Residue	0.20	19.5	2.29	1.76
HRI LO-1052	0.08	25.8	2.41	1.28



A = Residue packed column

FIGURE 16. ARRANGEMENT OF EQUIPMENT USED IN COAL LIQUEFACTION RESIDUE TREATMENT WITH GASES

Procedure

In a typical run, about 22 ml of crushed residue was weighed and packed into the reactor. Then the reactor was fastened into place and checked for leaks at the operating pressure. The furnace and cold traps were put into place and the flow of gas adjusted to the desired rate. As the reactor was heated to operating temperature, and as the cold trap was warmed to room temperature at the end of the run, samples were taken automatically for gas chromotographic analysis every 6 minutes. While at temperature, two or three samples were taken every 6 minutes at intervals of 30 to 90 minutes during the 3 hours the reactor was at temperature. At the end of the run, the reactor was cooled quickly and the treated residue removed from the reactor for analysis. The odor of the liquids caught in the cold trap was noted and the volume estimated.

In those runs using NH_3 where decomposition of the NH_3 was desired, about 2 percent of the charge weight consisted of activated alumina (Alcoa, F-1) mixed thoroughly with the residue.

Results

A summary of the analytical results for the product from each experiment is given in Table 28. The values for sulfur and nitrogen are presented on a moisture and ash free basis (MAF). The results from the gas chromatographic analysis were not definitive except that they demonstrated the temperature at which the hydrocarbons began to be released by the residues during exposure to the treatment gases. Release of methane and ethylene began at about 400 C in all cases. Detection of H_2S and/or NH_3 when H_2 and a H_2-CO mixture was used was at best sporadic and could not be correlated to changes in the sulfur and nitrogen values in the residue.

When the percentage of nitrogen and sulfur found in the treated residue increased from that originally present in the feed and N/S weight ratio remained essentially the same (0.768 versus 0.884), it was assumed that the increase was due to the loss of volatile hydrocarbons from the residue. This behavior was found especially characteristic for hydrogen. When a mixture of hydrogen and carbon monoxide was used (H_2 to CO volume ratio = 1), a measurable reduction in the amount of nitrogen in the residue was observed despite an apparent increase in the percentage of sulfur present due to

TABLE 28. EFFECT OF TREATMENT OF COAL LIQUEFACTION RESIDUES WITH VARIOUS GASES ON THEIR SULFUR AND NITROGEN CONTENT

Treatment	Percent, Moisture and Ash Free N	S	Weight Ratio N/S
Original Char (SRC Residue)	2.19	2.85	0.768
H_2 at 400 C, high flow[a]	2.19	2.83	0.774
H_2 at 500 C, low flow[a]	2.30	2.98	0.772
H_2 at 400 C, low flow	2.29	2.96	0.774
H_2 at 500 C, high flow	2.44	3.18	0.767
NH_3 at 500 C, high flow	3.49	2.72	1.283
low flow	2.62	3.04	0.862
H_2-CO[b] at 500 C, low flow	1.89	3.04	0.622
high flow	2.17	3.03	0.716
low flow	1.89	3.01	0.628
NH_3 at 500 C with active alumina			
low flow	3.19	3.01	1.060
high flow	2.85	2.95	0.966
Original Still Bottoms[c]	1.73	3.25	0.532
H_2-CO[b] at 500 C, low flow	1.61	3.18	0.506
H_2-CO at 400 C, high flow	1.58	3.30	0.479
NH_3 at 400 C, low flow	2.00	3.32	0.602
NH_3 at 500 C with active alumina			
high flow	2.24	3.44	0.651
H_2 at 500 C, low flow	1.75	3.09	0.566
H_2 at 400 C, high flow	1.71	3.22	0.531

(a) High flow = 100 ml/min; low flow = 10 ml/min.

(b) H_2 to CO volume ratio = 1.

(c) Hydrocarbon Research Sample No. LD-1052.

hydrocarbon loss. The lower N/S weight ratio was obtained for both coal liquefaction residues treated with the H_2-CO mixture. Treatment with ammonia gave a slight reduction of sulfur, but since the treated residue was cooled in ammonia, there was an increase in the nitrogen present in both residues. The presence of active alumina appeared to enhance the loss of hydrocarbons since the sulfur values increased significantly. However, nitrogen was retained by the residue in these experiments also.

DISCUSSION

The experimental results suggest that when ammonia is passed through the SRC residue at 100 psi and 500 C, small reductions in sulfur occur. At 400 C no sulfur removal was obtained. Hydrogen and a mixture of hydrogen and carbon monoxide were not effective for the removal of sulfur.

Treatment with the mixture of hydrogen-carbon monoxide at 400 and 500 C was found to remove nitrogen from both the SRC and the HRI residues (it was not possible to determine the effect of carbon monoxide alone). The 10 ml/min flow rate gave better removal. Reasonable agreement between duplicate runs were obtained for the SRC residue at 500 C. The longer residence time appeared to favor the denitrification reaction and produced a 4 percent reduction. In the case of the HRI residue, treatment at the high flow rate but at 400 C provided the greater nitrogen reduction--about 9 percent. Both higher temperatures and pressures may enhance nitrogen removal.

Treatment with ammonia gas in the presence of an activated alumina which is known to promote the decomposition of NH_3 at 500 C was more effective for removing hydrocarbons than just ammonia alone, but it did not show the activity reported in the literature during coal carbonization. Higher temperatures might have helped.

CONCLUSIONS

Nitrogen in coal liquefaction residues can be reduced by treatment with a mixture of hydrogen and carbon monoxide at 100 psi and at 400 C. Treatment of residues with ammonia at even 500 C did not remove sulfur to the extent that the literature reports suggest during the carbonization of coal at 1000 C.

Higher temperatures and pressures may help both sulfur and nitrogen removal and promote the conversion of a greater faction of the carbon value to hydrocarbons. Further work in this area would be desirable.

SECTION 11

IMPROVEMENTS IN PYRITE LIBERATION FROM COAL

The objective of this study was to enhance pyrite liberation by chemical comminution compared to mechanical grinding.

DISCUSSION

Quite early in the program, it became apparent that work in this area should not be initiated because the progress made in chemical comminution by others would only be duplicated by the planned effort. Although there was no activity in the area, it seemed appropriate to summarize the finding that prompted our action.

Bench-scale studies with ammonia-treated coals at Syracuse Research Corporation indicate that chemical comminution is capable of liberating more pyrite and a comparable amount of ash-forming minerals than conventional mechanical crushing to the same size consistency.[30,31]

The chemical comminution process is basically an improved method for pyrite liberation. Although the mechanism is not well defined, it seems that chemical comminution involves rapid migration of the molecules of the comminuting agent throughout the naturally occurring system of faults in coal. This weakens and disrupts the interlayer forces. The net result is fracture of the coal, the breakage being induced selectively along the bedding planes and mineral boundaries. The fragmented coal and mineral matter can then be separated by some conventional cleaning processes.

The chemical comminution of coal with ammonia has been studied by the Syracuse Research Corporation since 1971. Comparative washability data for an Upper Freeport coal showed that 96.6 percent of the pyrite was removed at 1.3 specific gravity from the chemically comminuted coal, while 90 percent of the pyrite was removed from the mechanically crushed coal (-14 mesh) at the same specific gravity. It was also shown that the chemically comminuted

sample contained only 5.5 percent fines (-100 mesh) compared to 21 percent fines (-100 mesh) for the mechanically crushed sample.

The researchers estimated the process requirements for a chemical comminution plant producing 1000 tons per hour as:

Ammonia (1 percent of recirculated NH_3)--0.5 ton/hr

Electricity--7830 kW

Steam--70 ton/hr

Manpower--3 men/shift.

The estimated capital cost for a plant capacity of 1000 ton/hr was $12,500,000. The operational cost was $1.06 per ton of cleaned coal. This covered only the chemical comminution units added to an existing coal cleaning plant.

Syracuse Research Corporation reported that the nitrogen content of coal increased by 5 to 7 percent after the chemical comminution, depending upon the type and extent of ammonia recovery treatment. However, it is not known whether the nitrogen is in a form that would result in NO_x emissions during combustion.

SECTION 12

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APPENDIX

APPENDIX

THEORY OF EXTRACTION WITH COMPRESSED GASES

THERMODYNAMICS

It would be useful to know of the extraction capacity for a compressed gas. But compressed hydrocarbon gases, when used for extraction, form non-ideal vapor phase mixtures. Prausnitz[1] discusses the implications of non-ideality of the vapor. The fugacity, f, is not generally equal to the partial pressure, but rather it is necessary to apply corrections for the non-ideality of mixing as well as for the non-ideality of the pure vapor. The fugacity coefficient, Θ, is used to correct for the non-ideality of the system.

Various methods[1,2] for predicting the properties of gaseous mixtures have been proposed, but for the most part these have been strictly empirical. It will be shown later that the solubility of a hydrocarbon (MW 128) in a hydrocarbon gas (MW 30) can be calculated by various methods, e.g., Lewis fugacities, Redlich and Kwong equation and virial equation of state. Only the solubility values calculated by the virial equation agree with the experimental values. The virial equation of state is a series in the reciprocal volume

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \; . \; . \; . \; . \; . \qquad (1)$$

where Z is the compressibility factor.

When Equation (1) is applied to a mixture, the virial coefficients are functions of composition as well as temperature. The composition dependence of the virial coefficient is given by

$$B_m = \sum_{ij} y_i y_j B_{ij} \qquad (2)$$

$$C_m = \sum_{ijk} y_i y_j y_k C_{ijk} \tag{3}$$

In the case of a simple binary mixture, Equations (2) and (3) become

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad . \tag{4}$$

$$C_m = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_2^2 y_1 C_{122} + y_2^3 C_{222} \qquad \text{etc.} \tag{5}$$

where coefficients, B_{11}, C_{111}, B_{22}, C_{222}, depend on the forces acting between like molecules. The remaining coefficients, called cross-coefficients, depend on the forces acting between unlike molecules.

It has been shown that when there is ideal mixing of the gases, the cross-coefficients are zero. Such a simplification implies that the compressibility factor of a mixture at constant temperature and pressure is a straight line function of the composition. But even for a simple mixture of methane and ethane at 50 C and 60 atm, the plot (compressibility factor versus mole fraction) is not a straight line but a parabola. Thus, even this system does not involve ideal mixing.

A method has been developed by Prausnitz[3] for calculating the virial coefficients. To calculate the cross-coefficient, for a binary mixture, the virial coefficient is represented by the following equation:

$$\frac{B_{ij}}{V_{cij}} = \Theta \left(\frac{T}{T_{cij}}, W_{ij}\right) \tag{6}$$

where

V_{cij}, characteristic initial volume, $= 1/2(V_{ci} + V_{cj})$.

Θ, a generalized function, computed values available as in Table A-1.

T_{cij}, characteristic critical temperature, $= k_{ij}(T_{ci}T_{cj})^{1/2}$. k_{ij} values are calculated from Statistical Mechanics. T is temperature.

W_{ij}, accentric factor, $= 1/2(W_i + W_j)$, values tabulated in Reference (4).

By using the critical values of temperature, volume, and accentric factor, the terms T/T_{cij}, V_{cij}, and W_{ij} are calculated, and then from Table A-1 it is possible to determine the value of Θ. Thus, from Equation (6) the cross-coefficient is calculated.

The third virial coefficient (e.g., C_{122}) may be neglected when the density of the vapor is similar to that of the compressed pure gas.[3]

There is good agreement, as shown in Figure A-1, between calculated and experimental solubility values of ethylene and naphthalene mixtures. It needs to be determined whether the virial equation of state can be used to predict extraction of coal liquids by compressed gases.

TABLE A-1. COMPUTED VALUES OF $-\Theta$

Partially Reproduced from Reference (3)

Reduced Temp, T/Tc	Accentric Factor, W					
	0.0	0.1	0.2	0.3	0.4	0.5
0.5	4.008	5.412	6.896	8.473	10.144	11.923
1.0	1.155	1.213	1.274	1.339	1.408	1.481
1.5	0.483	0.451	0.418	0.382	0.345	0.304

Solubility Isotherms (Empirical)

Studies in the deasphalting of petroleum crude by a compressed gas shows that a typical solubility isotherm of the petroleum crude in a gas is qualitatively described by the equation:[4]

$$\left(\frac{d\ln\eta}{dp}\right)_{T} = \frac{V^{o} - V}{RT} \qquad (7)$$

$$\eta \rightarrow 0$$

where

η = mole fraction.

p = saturation vapor pressure.

V^{o} = molar volume of hydrocarbon in condensed phase, the greater V^{o} the lower the pressure corresponding to minimum solubility.

V = partial molar volume of hydrocarbon in gaseous phase.

R = gas constant and

T = temperature.

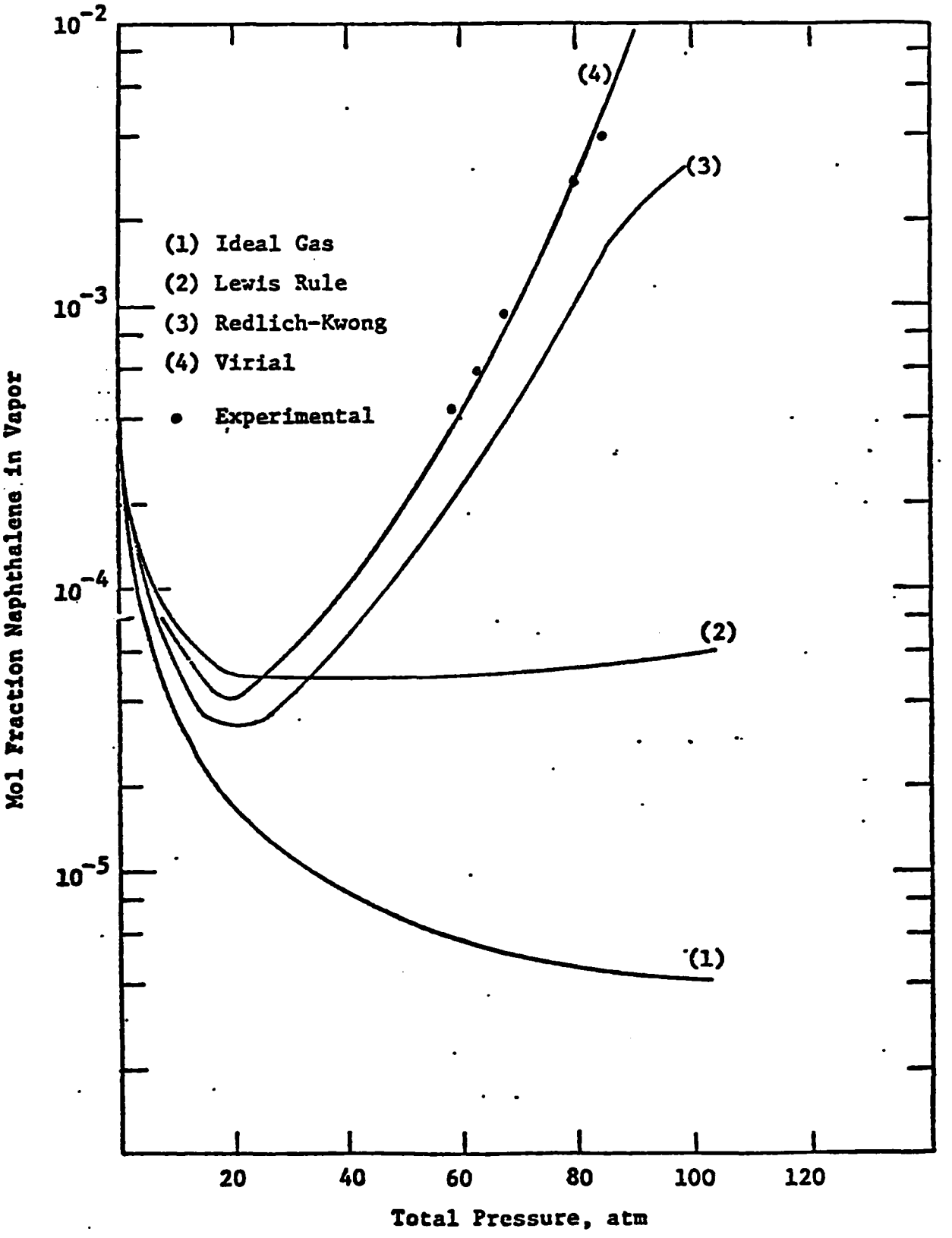

FIGURE A-1. VAPOR-PHASE SOLUBILITY OF NAPHTHALENE IN ETHYLENE, CALCULATED AND EXPERIMENTAL VALUES AT 35 C (Ref. 5)

The isotherm for the solubility can be described by the observations that when p is equal to the saturated vapor pressure of the substance at the given temperature then the mole fraction of the hydrocarbon is unity. As pressure is increased, the solubility curve shows a downward trend until a minimum value in η is reached. Further increase in pressure leads to an increase in mole fraction of the hydrocarbon in the vapor.

The Effect of Pressure on Solubility

The limited data on binary and ternary systems shows that solubility of high-molecular weight components in the solvent, at temperatures above the critical temperature of the solvent, increases rapidly with pressure.[5]

The Effect of Temperature on Solubility

It appears that at relatively low pressures, increasing temperature slightly above the critical temperature (of the solvent) decreases the solubility, but at higher pressures, increasing the temperature will increase the solubility of the hydrocarbon in the solvent (gas).[5]

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16. ABSTRACT The report gives results of a study to identify strategies for removing pollutants from coal and coal-derived liquids. Of the approaches considered, five were selected for preliminary assessment by experimentation (a sixth, improvements in pyrite liberation from coal, was not studied because of significant advances by others). Study findings include: (1) biological action on coal-derived liquids--prospects of using nonmutated bacteria for sulfur and/or nitrogen removal from coal liquids appear small; (2) enhancement of pyrite removal during immiscible fluid agglomeration--removal equivalent to that obtained for float-sink analysis was obtained by pretreatment and oil agglomeration, the same technique found to be effective for recovering $\geq 90\%$ of coal from coal cleaning plant fines; (3) extraction of clean fuels from coal liquids--light hydrocarbons can be used to extract 83% of coal liquid at supercritical conditions to yield a low sulfur and nitrogen fuel; (4) concentration of organic sulfur and nitrogen and ash from coal liquids--up to 76% of the sulfur and about 10% of the nitrogen can be removed by passing coal liquids over various special porous media; and (5) conversion of coal liquefaction residues to environmentally acceptable fuels--treatment of coal liquefaction residue with H_2/CO mixtures reduces nitrogen content by as much as 14%.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Bacteria	Pollution Control	13B	06M
Coal	Pyrite	Stationary Sources	21D, 08G	
Coal Preparation	Agglomeration	Denitrogenation	08I	
Liquefaction	Hydrocarbons	Bacterial Action	07D	07C
Desulfurization	Hydrogen	Coal Cleaning	07A	
Nitrogen	Carbon Monoxide		07B	
Biodeterioration			06A	

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