Western Low-Rank Coal Development Analysis

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Introduction

An analysis of the technical, environmental, and economic constraints to expanded development of the U.S. low-rank coal resource is in progress. The primary objective of the study is to propose a comprehensive national R&D program focusing on technology development for enhanced utilization of lignite and subbituminous coal. Utilization of these fuels has expanded rapidly in recent years and will continue to expand in line with national energy priorities. This will require technological improvements and developments to solve unique problems associated with the physical and chemical properties of low-rank coals. These properties include high moisture content, dispersed alkaline mineral matter content, high reactivity, and low sulfur content. The majority of coal R&D programs in this country are oriented towards bituminous coal, which exhibits significantly different behavior in most extraction, combustion, and conversion processes.

The study is being directed by the Grand Forks Energy Technology Center (GFETC), which has the lead mission within the Department of Energy for technology "applications for low-rank coals." To fulfill this assignment, GFETC must:

1. Identify the properties of low-rank coals that affect the applicability and economics of technologies;

2. Identify R&D needs unique to low-rank coals, and establish priorities based on potential impact on expanded development; and

3. Ensure that DOE's coal R&D programs address those needs.

Historically, GFETC has focused on lignite R&D, primarily on Northern Great Plains lignite. This has included programs in coal combustion, preparation, liquefaction, gasification, and environmental control technologies. The Center has also sponsored a biennial lignite Symposium, designed to encourage the transfer of low-rank coal technology data between government, industry, and academia (1,2). The present study was initiated as a means to identify other needed R&D areas associated with the whole spectrum of U.S. low-rank coals.

As a result, the scope of the study is broad, encompassing all of the major lignite and subbituminous coal deposits in this country, and including

some attention to peat as well. The technical analysis includes assessment of resources; technologies, from extraction through final utilization (including environmental control); and regulatory, environmental impact, and market factors. The R&D requirements definition will be based on these assessments plus a review of current R&D programs, costs, and impacts.

Study Approach

The study approach is summarized in Table 1, which shows the eight major tasks or areas of investigation. As a rough indicator of the relative emphasis being placed on these various tasks, the percentage of the total contract funding allocated to each task is indicated on the table.

The initial task, labelled "Development Scenarios," includes a literature review, definition of key issues and analytical methodologies, and establishment of the study's data base. In Task 2, the U.S. low-rank coal resources are being defined in terms of their occurence, quantity, quality, characteristics, and physical/chemical properties. An effort is being made to classify the resources according to their behavior in various utilization processes, which influences their development potential. This effort is closely tied to Task 3, the technology evaluation. A comprehensive list of technologies applicable to low-rank coals is being evaluated to ensure that the resulting preliminary R&D "wish list" is as exhaustive as possible.

Table 1
Major Tasks in the Low-Rank Coal Study

1. Low-Rank Coal Development Scenarios (6%)
   - 1.1 Literature Review
   - 1.2 Technology Definitions
   - 1.3 Regulatory/Environmental/Market Definitions
   - 1.4 Low-Rank Coal Data Base
2. Resource Characterization (8%)
   - 2.1 Occurrence
   - 2.2 Properties/Characteristics
   - 2.3 Classification
3. Technology Evaluation (42%)
   - 3.1 Extraction
   - 3.2 Transportation Systems
   - 3.3 Preparation and Storage
   - 3.4 Processing and Utilization
   - 3.5 Environmental Control Technology
4. Regulatory Requirements/Constraints (4%)
   - 4.1 Definition
   - 4.2 Roadmap
   - 4.3 Effects on Development
5. Environmental Impact Analysis (3%)
   - 5.1 Land Use/Reclamation
   - 5.2 Air Quality
   - 5.3 Water Quality
   - 5.4 Ecological Effects
   - 5.5 Socio-Economic Effects
6. Market Analysis (6%)
   - 6.1 Existing Markets and Penetration
   - 6.2 Potential Markets
7. RD&D Program Evaluation (11%)
   - 7.1 Definition and Priorities
   - 7.2 Review of Current RD&D Programs
   - 7.3 Cost and Impact Analysis
8. Task Force Utilization (20%)
   - 8.1 Development Scenarios Evaluation
   - 8.2 Technical Analysis Evaluation
   - 8.3 RD&D Program Definition
   - 8.4 RD&D Program Impacts and Recommendations

In addition to these purely technical considerations, there are various social, economic, and environmental factors in the regions containing low-rank coals that will affect the development of these resources. These factors are the subject of Tasks 4, 5, and 6. Each of these analyses is being conducted on a regional basis, with detailed calculations being made for a few carefully selected examples, in contrast to the more comprehensive approach being utilized in Tasks 2 and 3.

In Task 7, we will define and establish priorities for the R&D activities necessary to stimulate the effective development and utilization of low-rank coals in this country. This will be done in light of the present related governmental and industrial research and development efforts, and will include a preliminary analysis of costs and impacts of the proposed program. The practical difficulties of evaluating and ranking R&D projects, even when the most rigorous decision/analytical techniques are used, are great but do not diminish the need for this type of exercise.

Because of the scope and difficulty of the effort, we have enlisted a task force of recognized experts on the technical and regional issues germane to the study to meet with the study team at four critical points. At the periodic formal review meetings, interim results are discussed and decisions are made regarding emphasis, priorities, and methodologies for the analysis. In particular, the task force will participate actively in the development of R&D recommendations. This task force utilization effort is listed on Table 1 as Task 8.

The schedule for the study is June 1979 through June 1980, and is such that preliminary R&D recommendations will be in the formulation stage at the time of the American Chemical Society meeting in late March. The authors expect to summarize some of the key conclusions and recommendations of the study at that time. It is not possible to do so in this preprint because the work is in progress. Therefore, the remainder of this paper provides some preliminary findings and background information on some of the study areas.

Occurrence and Properties of Low-Rank Coals

The locations of the major lignite and subbituminous coal deposits in the U.S. are shown in Figure 1, and the magnitude of the resources contained in the largest low-rank coal-bearing regions is indicated in Table 2. The two major lignite-bearing areas are the Fort Union Region and the Gulf Coast Lignite Region, with the predominant surface-minable reserves being in the states of North Dakota, Montana, and Texas. The largest subbituminous coal deposits are in the Powder River Region of Montana and Wyoming, the San Juan Basin of New Mexico, and in Northern Alaska. Whether one considers the total identified resources (over one trillion tons) or just the strippable reserve base (over 100 billion tons), the potential supply of energy from low-rank coals is enormous.

Figure 1
United States Low-Rank Coal Resources

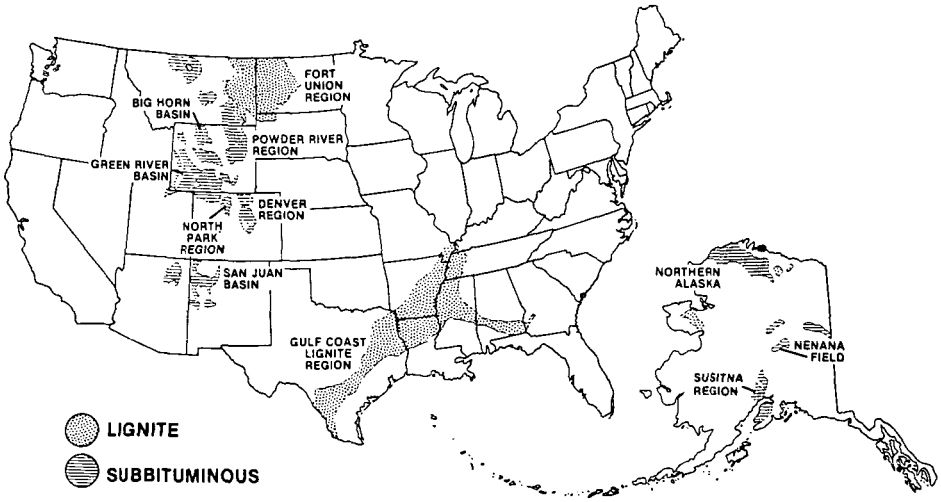

Figure 2
New Source Performance Standards for SO_2 Emissions from Electric Utility Steam Generators

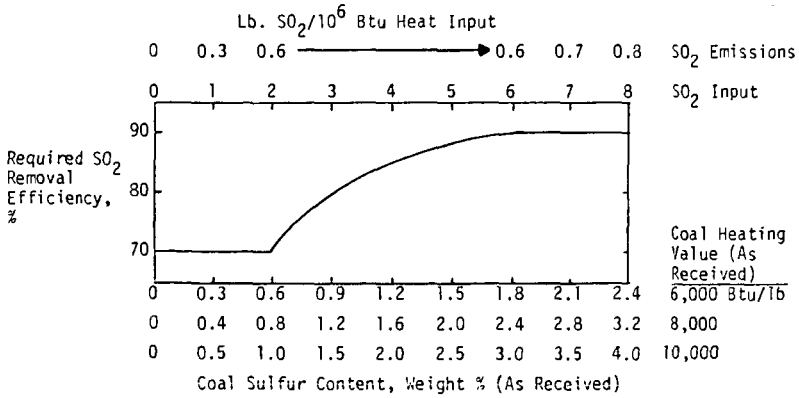

Table 2
Major United States Low-Rank Coal Regions

Region	Predominant Coal Rank	Identified Resources, Billion Short Tons	Strippable Reserve Base, Billion Short Tons
Fort Union Region	Lignite	465.3	31.9
Powder River Region	Subbituminous	238.1	57.5
San Juan Basin	Subbituminous	50.6	1.8
Northern Alaska	Subbituminous	100.9	5.0
Gulf Coast Lignite	Lignite	68.3	11.6
Others (see Fig. 1)	Subbituminous, some Lignite	165.2	0.9
		1,088.4	108.7

Sources: References 3-9

The distinguishing properties of low-rank coals are derived from their fundamental composition. Coals are complex aggregations of physically distinctive and chemically different organic materials (macerals) and inorganic materials (minerals). Strictly speaking, the rank of coal expresses only the degree to which geologic alteration processes (metamorphism) have affected the properties of the organic substances. In this sense, rank classification is independent of inorganic content; nevertheless, U.S. low-rank coals do exhibit characteristic differences from high-rank coals in their mineral matter content and therefore in their ash properties. This is apparently a coincidental or indirect relationship caused by the respective geologic ages and geographic locations of the U.S. low-rank coals and high-rank coals (10,11).

Some important properties of the organic and inorganic fractions of U.S. coals are summarized in Table 3. The data on organic content are based on samples of essentially pure vitrinite, which is the predominant maceral in U.S. coals (10). All of the properties listed have an impact on the coal's behavior in extraction, utilization, or conversion processes; the most noticeable properties are the high inherent moisture and oxygen contents of low-rank coal macerals, and their corresponding low heating values.

The data on mineral matter content are reported as ash, which is the residue left after complete incineration of the combustible constituents. The ash compounds are reported as oxides; however, they may actually occur as a mixture of silicates, oxides, and sulfates (11). Due to the wide variations in coal ash composition, the data are presented as ranges. A notable trend is the higher proportion of the alkali components CaO, MgO, and Na_2O in low-rank coals. The acidic components SiO_2 and Al_2O_3 are more prominent in the higher rank coals. The generally higher proportions of SO_3 in low-rank coal ash reflect the high retention of coal sulfur by the alkaline ash, which averages 78% for lignites, 26% for subbituminous coal, and 10% for the generally higher sulfur bituminous coals (11).

Table 3
Selected Analyses of U.S. Coals of Different Ranks

Organic Content (Vitrinite Samples)	Lignite	Subbituminous	Bituminous	Anthracite
Moisture Capacity, Wt.%	40	25	10	< 5
Carbon, Wt.% DMMF*	69	74.6	83	94
Hydrogen, Wt.% DMMF	5.0	5.1	5.5	3.0
Oxygen, Wt.% DMMF	24	18.5	10	2.5
Vol. Mat., Wt.% DMMF	53	48	38	6
Aromatic C/Total C	0.7	0.78	0.84	1.0
Density (He, g/cc)	1.43	1.39	1.30	1.5
Grindability (Hardgrove)	48	51	61	40
Btu/lb, DMMF	11,600	12,700	14,700	15,200
Inorganic Content (Weight % of Total ASTM Ash)				
Acidic Components: SiO_2	6-40	17-58	7-68	48-68
Acidic Components: Al_2O_3	4-26	4-35	4-39	25-44
Acidic Components: Fe_2O_3	1-34	3-19	2-44	2-10
Acidic Components: TiO_2	.0-.8	.6-2	.5-4	1-2
Acidic Components: P_2O_5	.0-1	.0-3	.0-3	.1-4
Alkali Components: CaO	12.4-52	2.2-52	.7-36	.2-4
Alkali Components: MgO	2.8-14	.5-8	.1-4	.2-1
Alkali Components: Na_2O	.2-28	-	.2-3	-
Alkali Components: K_2O	.1-1.3	-	.2-4	-
SO_3	8.3-32	3.0-16	.1-32	0.1-1

*Dry, mineral-matter-free basis.

Sources: References 10 and 11

These mineral matter properties of U.S. low-rank coals have wide-ranging effects, such as: 1) high fouling rates on boiler tubes, primarily linked to high sodium content; 2) high fly ash resistivity, thus relatively poor ESP performance; 3) unique opportunities for sulfur removal, such as ash-alkali wet scrubbing, dry scrubbing, and ash recirculation in fluid bed combustors; and 4) catalytic effects on certain reactions such as coal hydrogenation (liquefaction).

One additional characteristic of U.S. low-rank coal is its typically low sulfur content, as shown in Table 4. When these percentages are converted from a dry to an as-mined basis, about 90 percent of the reserve base of U.S. low-rank coal is shown to have less than one percent sulfur (13).

Table 4
Distribution of U.S. Low-Rank Coal Reserve Base by Sulfur Content

Sulfur Content, % (Dry Basis)	1.0 or Less	1.1-1.8	1.8-3.0	Over 3.0	Total
Subbituminous	89.5	8.1	2.0	0.4	100.0
Lignite	40.7	33.4	23.4	2.5	100.0

Source: Reference 12

Utilization and Processes

Present use of low-rank coal is concentrated in electric utility steam generating units fed by surface-mined coal. This conventional application of the resource is experiencing rapid change. As the data in Table 5 indicate, existing small stoker and cyclone-fired units have given way to very large pulverized-coal-fired, dry bottom furnaces. All of the new plants will incorporate SO_2 removal systems as mandated by the recently issued New Source Performance Standards (see Figure 2). The same regulation also requires highly effective particulate removal systems, and combustion system modifications to meet NOx emission limits, in all new or modified electric utility steam generating units larger than about 25 MWe (250 million Btu/hr. input).

The dominating near-term R&D issues for low-rank coals revolve around the environmental control technologies that are being developed to meet these requirements. In the area of SO_2 control, the variable percentage removal requirement shown in Figure 2 (which translates to a 70% removal requirement for the majority of low-rank coals) was instituted for the express purpose of encouraging the further development of dry scrubbing techniques for low- and medium-sulfur coals (14). The combined stack gas cleaning strategy of dry SO_2 scrubbing plus the use of baghouses for particulate removal has a number of apparent advantages over today's wet scrubber/ESP systems, and appears to be strongly encouraged by the NSPS. However, the lack of operational experience with such systems provides ample opportunity for well-directed R&D. Wet scrubbers (particularly ash-alkali systems for low-rank coals) and electrostatic precipitators (combined with novel conditioning or removal devices) will both continue to have applications for specific coals; however, many problems relating to enhanced removal efficiencies, sludge disposal, sulfate and sulfuric acid mist carryover, and trace element emissions, remain to be solved. Potential operating problems associated with combustion modifications for NOx control also need R&D. Finally, the task of integrating the study of these interrelated problems and opportunities through a systems engineering approach is just beginning, for example in the EPRI Arapahoe program (15).

Ash fouling of boiler tubes continues to be a major problem encountered in burning lignites and subbituminous coals. Sodium content has been identified as the most important of a number of factors that contribute to the fouling problem. The possible control methods to decrease chances of fouling include: 1) boiler designs involving low volume heat release and low furnace exit temperature; 2) restrictions on the sodium level in the coal by selective mining, blending and upgrading, 3) the use of additives; and 4) possibly the use of overfire air with fuel-rich burners (16).

Table 5
U.S. Low-Rank Coal-Fired Electric Power Plants

Fuel Location Plants, Capacity	Lignite				Subbituminous Coal			
	Fort Union Reg.		Texas		West		Midwest	
	No.	MWe	No.	MWe	No.	MWe	No.	MWe
Operating Plants (1979)	19	3,357	11	5,660	20	7,389	79	10,627
Furnace: PC	8	1,614	11	5,660	20	7,389	58	6,705
Stoker	7	205	-	- -	-	- -	9	97
Cyclone	4	1,538	-	- -	-	- -	7	1,265
Unknown	-	- -	-	- -	-	- -	5	2,560
Wet Scrubber:								
Limestone	5	1,720	5	3,575	12	3,783	10	3,477
Ash-Alkali	2	670	-	- -	-	- -	4	2,116
Spray Dryer	2	716	-	- -	-	- -	-	- -
Particulate Removal:								
ESP	16	3,329	11	5,660	17	7,192	48	7,131
Baghouse	-	- -	2	1,150	-	- -	8	1,788
Mechanical	5	210	-	- -	2	230	21	518
Unknown	7	72	-	- -	-	- -	5	1,929
Plants Under Construction and Announced	6	1,947	18	10,390	5	1,349	34	15,372
Furnace: PC	6	1,997	9	5,175	4	1,249	2	1,100
Stoker	-	- -	-	- -	-	- -	6	107
Cyclone	-	- -	-	- -	1	100	1	200
Unknown	2	1,050	9	5,215	-	- -	25	13,004
Wet Scrubber:								
Limestone	-	- -	8	4,600	-	- -	1	800
Ash-Alkali	-	1,100	-	- -	-	- -	5	3,100
Spray Dryer	2	880	-	- -	1	330	-	- -
Particulate Removal:								
ESP	-	- -	9	5,175	2	450	-	- -
Baghouse	-	- -	-	- -	1	350	-	- -
Mechanical	-	- -	-	- -	-	- -	3	18
Unknown, ECT	1	410	14	8,675	2	589	31	15,934

Numerous advanced technologies are being pursued in a wide range of government and industry R&D programs. Many of these technologies will contribute to enhanced utilization of low-rank coals in the future. Extraction of the abundant thick, deep coal seams in the western U.S. will eventually be pursued. A variety of techniques, including advanced longwall and in situ conversion systems (such as underground coal gasification), are currently being researched.

Coal cleaning and preparation techniques have historically not been applied to U.S. low-rank coals because of cost considerations and the relatively low ash content of the coals. The fact that most of the mineral matter in low-rank coals tends to be highly dispersed and/or organically bound means that typically only 15-30% of the mineral matter is separable in a carbon tetrachloride float-sink separation (17). Lignite is characterized by high moisture content which is also bound in the coal structure. Upon drying, the

structure of low-rank coal tends to change and to produce smaller, friable particles which may be either highly oxidized (when air-dried) or highly reactive (when inert-dried) (18). Nevertheless, wider geographic marketability and improved over-all process economics could potentially be achieved if energy-efficient techniques for selective removal of moisture or mineral matter were developed.

Fluidized-bed combustion (FBC) systems are receiving major emphasis as the potential next generation of industry, and possibly utility, boilers. Almost all major projects are utilizing bituminous coal. The technology has a good apparent fit with low-rank coals because of their inherent sulfur absorption capability. A particularly promising market appears to be developing in Texas, which has a high concentration of industry fuel users juxtaposed with large lignite deposits. Some of the FBC research needs specific to low-rank coals include selection of bed materials, use of ash recycle, control of ash agglomeration, and possible corrosion/erosion problems.

In the highly visible synfuels area, none of the major developing U.S. processes for liquefaction or gasification appears to be optimized or tailored to the unique properties of low-rank coals, with the possible exception of the CO_2 Acceptor gasification process. Low-rank coals are well suited for fixed-bed gasification because they do not agglomerate or cake when heated. The high inherent moisture content of low-rank coal has a variety of effects on gasification processes. Plant water requirements may be lower if coal moisture is recovered. High moisture, however, can cause heat balance problems and pre-drying of the coal can produce an excessive amount of fines which cannot be included in feed for fixed-bed reactors. Large volumes of gas liquor may be produced, affecting waste water treatment requirements. These factors, plus the reactive nature of low-rank coals and the presence of catalytically active mineral matter, justify the need for development of low-rank coal specific processes (19).

Coal liquefaction processes also need to be adapted to special problems posed by low-rank coals. The high content of functional groups (particularly oxygen) affects liquefaction chemistry. Low-rank coals react very rapidly with carbon monoxide providing the basis for development of processes using synthesis gas instead of more expensive hydrogen. High moisture content adds to reactor pressure. Drying can deactivate the coal because of surface oxidation and collapse of the pore structure (20). The special forms of low-rank coal mineral matter may catalyze liquefaction reactions; they can also lead to formation of calcium carbonate deposits in the reactors. Viscosity of the distillation bottoms is higher for low-rank coals, which affects process design and operability (21). All of these factors affect the optimization of recycle solvent composition and product separation techniques, which are important research areas for liquefaction processes in general.

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CURRENT RESEARCH ON THE INORGANIC CONSTITUENTS IN NORTH DAKOTA LIGNITES AND SOME EFFECTS ON UTILIZATION

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Introduction

Although coal is often considered to be simply an organic rock, most coals contain appreciable quantities of inorganic materials. With the resurgence of interest in coal utilization and conversion processes in recent years has come an increased appreciation for the need to understand both the mineralogical characteristics and the chemical behavior of the inorganic constituents of coal. The recent coal literature contains numerous discussions of the importance of knowing the character, distribution, and behavior of the inorganic species; these discussions span the whole spectrum of coal technology-- preparation and storage, combustion, liquefaction, gasification, and environmental studies.

This paper discusses results of laboratory studies on the characterization of inorganic constituents in low-rank coals and on elucidation of the role of these constituents in combustion and conversion processes. The laboratory studies were undertaken in support of pilot plant activities at the Grand Forks Energy Technology Center (GFETC) of the U.S. Department of Energy. Engineering and process-related details of the various projects have appeared in previous publications, which are noted in the reference section.

Inorganic Constituents in Lignite

Samples from two major lignite mines in western North Dakota were obtained (4) and studied by polarized light microscopy, x-ray diffraction, scanning electron microscopy, and electron microprobe analysis. The initial results of the laboratory studies of these two samples show that the inorganic constituents occur as minerals or combined with organic substances; are closely related in origin to the overburden and underclay; and illustrate part of a complex series of events in the geochemical evolution of the lignites. While the systematic variations that are presented are believed to be significant, they are not claimed to be necessarily representative at this point in the study.

The abundant lignite in North Dakota is contained in the upper part of the Fort Union group within the Bullion Creek formation and the overlying Sentinel Butte formation. Recent summaries of the general geology of the lignite-bearing rocks in western North Dakota are available (1-3).

Lignite, lignite overburden, and underclay were collected from measured, vertical sections on the highwalls at the South Beulah mine, Beulah, and the Baukol-Noonan mine, Center (4). Both mines produce lignites from the Sentinel Butte Formation with major production from the 3.8 m Beulah-Zap bed at South Beulah and the 3.5 m Hagel bed at Baukol-Noonan. Inorganic constituents in the two lignites are similar and contain detrital and authigenic minerals, listed in Table 1 and illustrated in Figure 1, as well as organically bound materials. The bulk chemistry of overburden, lignite, and underclay has been obtained by a rapid microprobe method.

At the South Beulah mine, four samples of overburden above the Beulah-Zap bed consist largely of clayey silt grading downward to organic-rich clay. Illite, quartz, and montmorillonite are the major minerals and kaolinite, chlorite, plagioclase, and mica are present in lesser amounts. Calcite is present in the uppermost sample while dolomite occurs in the other three samples; both decrease in abundance downwards. The Beulah underclay contains major illite, kaolinite, and quartz and lesser montmorillonite and calcite.

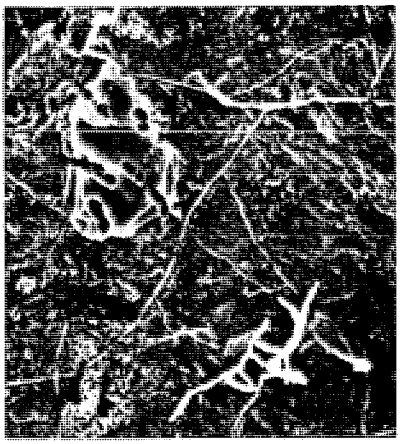
TABLE 1. - Minerals Identified in Two North Dakota Lignites

Common (in approximate order of abundance)	Rare or uncertain
Kaolinite	Montmorillonite?
Quartz	Dolomite?
Pyrite	Barite
Gypsum	Enstatite
Calcite	Corundum
Hematite	Ca, Mg Aluminosilicate?
Na Plagioclase	Ca, Na Aluminosilicate?
Alkali Feldspar?	
Chlorite?	
Hornblende	
Augite?	
Illite?	
Biotite?	

The twelve samples of overburden and the sample of underclay from the Baukol-Noonan mine are mineralogically similar to the Beulah samples. The lower part of the overburden is silty sand and the upper part, clays and silty clays. Overall montmorillonite is somewhat less abundant than at Beulah but is highly variable.

The mineralogical and chemical studies combined with the observation that lignites are aquifers suggest that hydrogeochemical processes have strongly affected the sodium and calcium distribution by removal of calcium by dissolution of carbonate minerals in the lower part of the overburden, concentration of sodium and calcium in the central parts of the lignite seams, and increase in the CaO/Na_2O ratio in the upper parts of the lignite seams (5). Groundwater processes also appear to be a major factor in oxidation and reduction reactions as suggested by sulfide and sulfate distribution in fracture zones at the Baukol-Noonan mine (6). Pyrite development in fractures followed by growth of small gypsum crystals on the pyrite (Figure 1) indicates that groundwater carried and deposited iron and sulfur under reducing conditions, and carried and deposited calcium at a later stage under oxidizing conditions.

The original detrital minerals and organically bound inorganic constituents in lignite have been strongly affected by hydrogeochemical processes in the depositional and post-depositional history of lignite and the associated sediments. Current laboratory studies emphasize cataloging and characterization of inorganic constituents in lignite; establishment of mineralogical and chemical distribution patterns in overburden, lignite, and underclay; and evaluation of the geochemical history of the lignite-bearing sediments.



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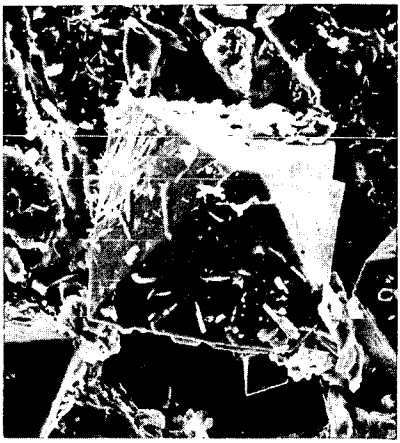

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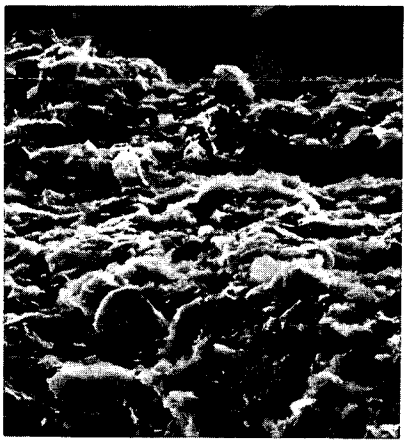

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Figure 1. Scanning electron microscope photographs of inorganic constituents in lignite-bearing strata. Sentinel Butte Formation, North Dakota.
A. Detrital quartz (?) in ion-etched Beulah lignite. 1540X.
B. Secondary pyrite with gypsum crystals on surface from fracture zone in Baukol-Noonan lignite. 770X.
C. Secondary barite in fracture zone in Baukol-Noonan lignite. 270X.
D. Montmorillonite in overburden at Beulah mine. 1400X.

Gasification

The inorganic constituents of lignite can have several effects in gasification processes. Numerous articles have appeared in the recent literature describing the catalysis of gasification reactions by various inorganic species. Studies at GFETC have focused on the development of an understanding of the relationship between coal ash slag composition and viscosity. These studies have been done in support of the slagging fixed-bed gasification pilot plant at GFETC. Details of the pilot plant project have been given in a series of publications, most recently by Ellman and co-workers (7). Maintaining slag viscosity low enough to allow continuous discharge from the gasifier is crucial to successful operation.

Direct measurement of slag viscosity is a demanding operation, and few laboratories are equipped with suitable high-temperature viscometers. Therefore the development of predictive or correlative techniques for relating viscosity to composition is an important component of gasification research. A previous publication (8) has demonstrated that it is possible to develop empirical equations which give a good fit of experimental viscosity data provided that the equations are developed for, and their use restricted to, slags of a given petrographic classification.

The petrographic normative calculation (9) is a formation used to calculate a set of standard, or normative, mineral species, which then establishes the types of silicate structures to be expected in the slag. The degree of polymerization of silicate species has an important role in determining viscosity behavior (10).

The transformations involved in the formation of slag from the inorganic species in the coal have been partially elucidated in laboratory studies of char and slag samples obtained from the gasifier hearth after a test had been ended and the bed contents quenched. The data presented here were obtained from samples collected from a 1.4 MPa test with Indian Head lignite. Process data from this test, number RA-12, have been published (11).

Discreet slag particles were found in samples collected 0.9 m above the bottom of the bed. The composition at this point was 22% Na_2O, 24% Al_2O_3, and 53% SiO_2. This composition lies in the nepheline region of the Na_2O-Al_2O_3-SiO_2 ternary (12) and has a melting point of approximately 1200°C. This is consistent with typical temperatures of about 1260°C observed 1.2 m above the hearth bottom. Samples collected at 0.3 and 0.6 m were complex mixtures of silicates and sulfates. Total melting occurred in the bottom-most 0.3 m of the bed, where temperatures exceeding 1700°C have been observed. Some slag components are volatilized in this region, particularly sulfur (approximately 80% is lost), sodium and potassium (30-35%), and phosphorus (25%). Smaller amounts of magnesium, calcium, and silicon are also volatilized.

At 0.1 to 0.3 m above the hearth bottom some reduction of iron compounds to metallic iron occurs. Normally the iron metal drains with the slag and does not appear to interfere with slag flow. However, formation of iron metal removes a potential source of FeO, which is considered to be an excellent slag flux.

The viscosity behavior of the slag with temperature will be determined by its composition; specifically, by the relative amounts of polymer-forming constituents such as SiO_2 and Al_2O_3 and of polymer-breaking species such as Na_2O or CaO. The slag composition is in turn determined by two factors. The composition and nature of the inorganic constituents in the lignite feed broadly determines the relationships between polymer formers and polymer breakers. The thermal and chemical environment established by the gasification and combustion reactions in the gasifier hearth then "fine tune" the slag composition through such processes as volatilization of SO_3 and Na_2O and reduction of Fe_2O_3 to FeO or metal.

Liquefaction

The product distribution from coal liquefaction will vary between a heavy distillate, a light oil, and a gas depending on the extent and method of treatment of the intermediate products. The catalytic effect of naturally occurring inorganic species and minerals on the conversion and product yield is being investigated extensively with Eastern coals and also with low-rank Western subbituminous and lignitic coals. In general certain inorganic constituents of Eastern coals have shown a self-catalyzing effect on the liquefaction yield. High yields have been achieved by adding pyrite, magnetite plus pyrite, sulfur plus magnetite, and coal ash plus sulfur to coals which initially gave a low yield.

The lignites in the Northern Great Plains are distinguished from the higher rank coals by having high moisture, lower sulfur, and high inherent ash content. Most of the alkali and alkaline earth cations exist as humic acid or phenolic salts. These cations are ion exchangable and are uniformly distributed throughout a coal particle. The majority of the extraneous ash exists as small particles of quartz, pyrite, hematite, and clay. In addition lignites have a large amount of oxygen-containing functional groups. These properties affect the liquefaction behavior of lignite in terms of reactivity, product quality, product yield, catalyst life, and solid residue.

The role of these unique properties of lignite in liquefaction is being investigated in a program at GFETC which seeks to develop a chemical and engineering data base for liquefaction of lignites and subbituminous coals. The programmatic background and process engineering results have been presented in a recent paper by Willson and co-workers (13).

Some of the parameters being studied with the batch autoclave and continuous process unit at GFETC are temperature, pressure, residence time, slurry coal concentrate recycle, solvents, and mineral effects. Extensive research on the effects of individual minerals on the product yield has not been performed thus far. However, a significant increase in the overall product yield was observed when the reaction solids were recycled in the continuous unit. In a recent run using a lignite from the Beulah mine in Mercer County, ND, a deposit formed in the feed slurry and was analyzed for possible minerals and inorganics using a polarizing light microscope and a scanning electron microscope (SEM). Calcium carbonate was initially suspected as a main ingredient in the deposit. However, quartz was the only mineral identified in the product. An elemental analysis of the bulk product using the SEM resulted in a composition not unlike that of the ash in the original coal. Analysis for calcium by atomic absorption also showed no preferential buildup of calcium. Thermogravimetric analysis indicated the presence of some carbonates but no particular cation could be associated with the carbonate. Other workers in liquefaction have reported calcium carbonate deposits when using lignites but thus far no major accumulations have been observed at GFETC. The implications of a low-level carbonate buildup using lignites should be fewer shut downs caused by carbonate plugging.

Combustion

Ash fouling-- the buildup of ash deposits on walls and heat exchange surfaces of boilers-- is a major problem associated with the use of lignite. The causative effects of sodium content in the fouling behavior of low-rank coals has been discussed in previous publications (14-15). Some of the current laboratory research at GFETC relating to ash fouling involves the chemical and physical characterization of ash deposits to develop a better understanding of the mechanisms involved in deposit formation and to predict fuel additives to control fouling.

A typical profile of an ash deposit formed in the 34 kg/hr, PC-fired pilot plant combustor at GFETC is shown in Figure 2 (16). The deposit was collected on an

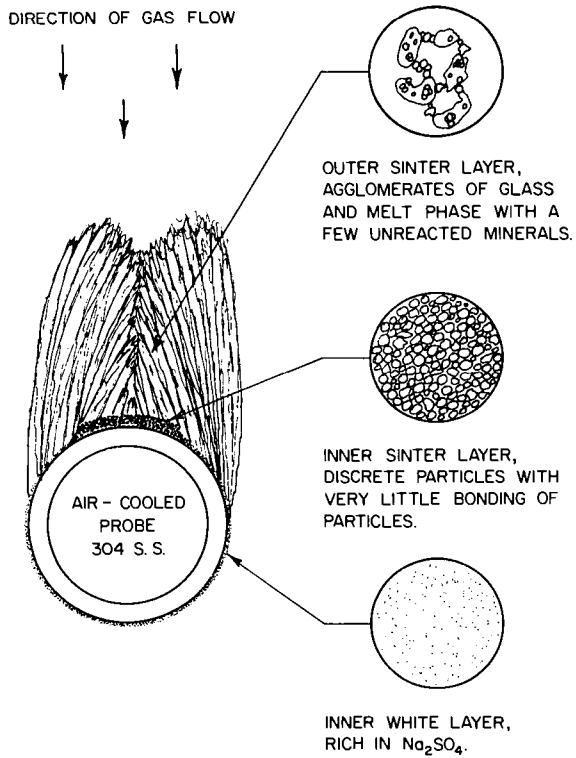

FIGURE 2. - Physical structure of a typical ash deposit formed in the GFETC combustor.

FIGURE 3. - SEM photomicrograph (3000X) showing particles in the initial stages of attachment.

air-cooled probe maintained at 540°C. X-ray diffraction studies have shown that sulfates, mainly Na_2SO_4 and $CaSO_4$, predominate near the probe and in the inner sinter layer. The sulfates are present on the surfaces of the ash particles and in the inner white layer immediately surrounding the probe. The melt and reaction of these surface sulfates to form an intermediate $Na_2Ca(SO_4)_2$ eutectic has been proposed (18,19). Figure 3 illustrates the particle-to-particle bonding which occurs upon the melt and reaction of the various sulfates (16).

A second mechanism involving sodium has been observed: the fluxing action of sodium with aluminosilicate (presumably kaolinitic clay) mineral assemblages. Volatilized sodium is believed to react with kaolin particles in the combustion zone to form low-melting (900-1100°C) sodium aluminum silicate compounds. These species react with the molten sulfates in the deposit to form complex melilites $(Na,Ca,K)_2$ $[(Mg,Fe^{+2},Fe^{+3},Al,Si)_3$ $O_7]$. X-ray diffraction studies of deposits from the GFETC combustor have shown that melilite formation increases as the distance from the probe increases (16).

The physical strength of the deposits has been observed to increase as a result of continued exposure to SO_2 and SO_3 at high temperatures. This phenomenon is referred to as the sulfating process. X-ray diffraction analysis of deposits obtained from the Hoot Lake Power Company, Fergus Falls, Minnesota, has shown that more anhydrite was present than melilites.

Fouling problems in fluidized bed combustors are not expected to be as severe due to the lower combustion temperatures in FBC's (700-950°C) compared with PC-fired or cyclone combustors (1650°C). Scanning electron microscope studies have been made of bed agglomerates from the GFETC pilot plant FBC from a test burning Beulah lignite with Al_2O_3 bed material, and from the pilot scale FBC of Fluidyne Engineering Corporation of Minneapolis, burning Indian Head lignite with an SiO_2 bed. The agglomerations from the GFETC FBC showed thin films of Na_2SO_4, $CaSO_4$, and $Na_2Ca(SO_4)_2$ surrounding a layer of complex silicates (a typical composition is 11% Na_2O, 9% MgO, 21% Al_2O_3, 11% CaO, 45% SiO_2) with a core which is predominantly Al_2O_3. No sulfates were observed in the agglomerations from the Fluidyne combustor (17). A calcium-rich coating surrounded a sodium-rich layer which in turn contained core material that was predominantly SiO_2 and Al_2O_3.

This preliminary evidence suggests that agglomerates form around particles of bed material via reactions with the inorganic materials in the coal or ash, and may react further with SO_2 or SO_3. Laboratory investigations of the mechanism of agglomerate formation are expected to provide continuing support to FBC research.

Summary

The results presented here exemplify the types of broad-ranging studies, which, it is hoped, will eventually provide an extensive data base on the origin, distribution, characteristics, and process behavior of the major inorganic species in lignites. For example, the hydrogeochemical history of a lignite deposit and the mineralogy of the overburden and underclay play an important role in determining the amount and distribution of sodium in the lignite. That sodium may then have a detrimental effect on the utilization of the lignite-- by contributing to ash fouling - or it may have a beneficial effect-- by reducing slag viscosity in a slagging gasifier. Continued research will allow coal scientists to follow the fate of the inorganic species from the Paleocene epoch to tomorrow's synfuels technology.

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ANALYSIS OF THE INORGANIC CONSTITUENTS IN AMERICAN LIGNITES

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INTRODUCTION

The relatively untapped reserves of lignite coals in the western United States have generated a large amount of interest in the past few years. In general, lignites exist in relatively thick seams which are close to the surface. Thus they are amenable to extraction at a low cost. These coals tend to react quite differently in coal conversion processes than coals of higher rank. All of the reasons for this behavior are not well understood. One of the characteristics peculiar to low rank coals is the amount of ion-exchangeable inorganics. These inorganics are usually taken to be cations in association with carboxyl groups. These cations are believed to be responsible for catalysis of gasification, formation of calcite during liquefaction, and the behavior of lignite ash during combustion. However, characterization of this organic-inorganic system has not been satisfactorily accomplished for American lignites.

The research described here was concerned with the characterization of the ion-exchangeable cations and the carboxyl groups with which they are associated for three important deposits of American lignites. This has been accomplished by ion-exchange techniques, utilizing ammonium acetate and barium acetate, respectively. The cations analyzed for were Na, K, Mg, Ca, Sr, and Ba. Also the amounts of the major discrete mineral phases present in the lignites have been determined. This was accomplished by the use of semi-quantitative x-ray diffraction and infrared spectroscopy techniques.

EXPERIMENTAL

The carboxyl group analysis was modeled after that of Schaefer (1,2). Briefly, demineralized coal (3) which has been ground in N_2 to pass 200 mesh is mixed with 1N barium acetate solution at a pH equaling 8.25 to 8.30. The slurry is refluxed in a flask through which purified N_2 is passed to prevent oxidation of the coal and subsequent formation of barium carbonate. After 4 hr, the solution is cooled, the pH recorded, and enough 0.05 N barium hydroxide is added to restore the original pH of the solution. After three 4 hr periods, the slurry is filtered under N_2 and washed with 1N sodium acetate at a pH equaling 8.25 to 8.30. The hydrogen ions released from the exchange are quantified by the total amount of barium hydroxide added to the solution. The exchanged barium is then removed by boiling the coal in 0.2 N perchloric acid for 20 min. The barium released is quantified by emission spectrometry.

The cations were analyzed by extraction of the coal with 1N ammonium acetate as suggested by Miller (4). Using this procedure, the coal is stirred at room temperature in the ammonium acetate solution (pH equals 7.0 to 7.2) for 3 hr. The slurry is then filtered and the coal transferred back to the beaker with fresh ammonium acetate for another 3 hr extraction. This is followed by three more 3 hr extractions, followed by extraction overnight and a final 3 hr period in the morning. Each of the extracts is then analyzed for Na, K, Mg, Ca, Sr, and Ba by emission spectrometry. The use of fresh ammonium acetate is essential to achieve complete exchange since the existence of any cations in the slurry will result in an equilibrium value on the coal.

Characterization of discrete mineral phases present in the low temperature ash (LTA) of the lignites was accomplished by x-ray diffraction and infrared spectroscopy. The procedure for LTA follows that described by Miller (4). Calcite, quartz, and pyrite are analyzed by x-ray diffraction, while kaolinite and anhydrite are analyzed by infrared spectroscopy. Techniques for these analyses are described by Jenkins and Walker (5). It has been shown (4,5) that mineral phases can form in the LTA process when lignites are ashed. That is, cations present fix sulfur, carbon, and oxygen to form carbonates and sulfates. In order to study this phenomenon, mineralogical analyses of both the raw lignites and the ammonium acetate treated lignites were performed.

RESULTS AND DISCUSSION

Table 1 shows the results of the carboxyl group analysis. Each value, calculated from the titration results, represents the average of six to eight runs, with the value of one standard deviation also shown. In order to investigate the accessibility of the carboxyl groups to the reagent, both minus 80 and minus 200 mesh fractions of PSOC 623 were investigated. There was no effect of particle size on the results. Table 1 also shows carboxyl group values calculated using the barium release method for selected runs. Carboxyl group contents are calculated assuming that two carboxyl groups are exchanged with one barium ion. Close agreement of these results supports this assumption and confirms the accuracy of the technique. The choice of three 4 hr refluxes was based on the finding that, in all cases, less than 5% of the carboxyl groups were exchanged in the final 4 hr period. The oxygen contained in the carboxyl groups of these coals accounts for 46% (North Dakota), 37% (Texas), and 42% (Montana) of the oxygen by difference value calculated in the ultimate analysis.

TABLE 1. CARBOXYL CONTENTS OF LIGNITES

PSOC Coal	State	Seam	Carboxyl Content, Mequiv/g DMMF Titration	Ba Released
246	N. Dakota	Hagel	3.13 ± 0.05	3.24
623	Texas	Darco	2.11 ± 0.08	2.22
833	Montana	Fort Union	3.00 ± 0.07	3.07

Table 2 lists concentrations of cations associated with carboxyl groups found on the lignites. The values shown represent the average of four runs and have a precision of ± 3% or better. Calcium and Mg are the predominant cations. However, there are significant variations in concentration of the cations among the coals studied. For these coals, it was estimated that 43% (North Dakota), 44% (Texas), and 60% (Montana) of the total carboxyl groups are associated with the cations listed in Table 2. The basis for the selection of a 27 hr total exchange time is displayed in Figure 1, where the cumulative percentage of the total exchange versus time is plotted for Mg and Ba. Magnesium is essentially totally exchanged in 12-15 hr, while Ba exchange proceeds more slowly to completion. These results confirm the evidence of other investigators (4,6) who show that Ba should be more strongly held than Mg. Among the divalent cations, the ions with smaller hydrated ion radii have been found to be held most strongly.

Since the cations are thought to be active catalytically in gasification and liquefaction processes, it is of interest to estimate the fraction of total surface area covered by the total cations present. Table 3 shows the CO_2 (total) surface

areas calculated from adsorption at 25°C, the surface areas occupied by the carboxyl groups calculated by assuming 7.7 A^2 per site or carboxyl group, and the perecentages of the CO_2 surface area occupied by the total carboxyl groups and cations associated with carboxyl groups. A significant portion of the CO_2 surface area is covered by the carboxyl groups and by those associated with cations.

TABLE 2. CATION CONTENTS OF LIGNITES ASSOCIATED WITH CARBOXYL GROUPS

PSOC Coal	Cation Concentrations, 10^{-4} g/g DMMF						
	Mg	Ca	Na	K	Ba	Sr	Total
246	34.4	171	27.8	1.89	6.51	3.30	244.9
623	22.6	129	8.69	3.42	3.36	2.38	169.5
833	59.8	212	10.0	5.30	10.9	3.34	301.3

TABLE 3. SURFACE AREAS OF AND GROUP COVERAGES ON LIGNITES

PSOC Coal	Surface Areas, m^2/g DMMF		Coverage of CO_2 Surface Area, %	
	CO_2	Carboxyl	Carboxyl	By Cations
246	200	130	65	28
623	180	78	43	19
833	210	128	61	37

Results of the mineral matter analysis are summarized in Table 4. Each value corresponds to triplicate determinations. In general, a reproducibility of ± 2-4% (absolute) is found. Infrared spectroscopy showed a greater degree of precision than x-ray diffraction, and the larger values are more relatively precise than the smaller ones. The effect of the presence of cations in the raw lignites on the mineral matter analysis is seen. The amount of LTA decreased by up to 50%, when the cations were removed from the lignites prior to ashing. The disappearance of calcite and anhydrite can also be seen. These results show clearly that the yield of LTA produced from raw lignites is enhanced by the formation of sulfates and carbonates. One would predict the existence of other carbonates and sulfates, but their concentrations would be too low to observe by the techniques used.

CONCLUSIONS

1) The ion exchange techniques described in this paper to define the carboxyl groups and exchanged cations are relatively precise, simple, and suitable for characterization of American lignites.

2) Calcium and Mg are the major cations in the coals studied, but considerable variations in absolute and relative concentrations exist among the cations analyzed.

3) The cations and carboxyl groups cover a significant fraction of the CO_2 surface areas of the lignites.

4) Up to 50% of the LTA of the raw lignites studied is an artifact of the ashing procedure, which is mainly due to cation fixation of CO_2 and SO_2 to form carbonates

and sulfates.

5) The real significance of this work lies in the ability to correctly characterize the inorganics in lignites. With the information gained by such analyses, effects of inorganics on coal conversion processes and combustion can be more fully understood.

TABLE 4. MINERAL MATTER IN LTA RESIDUES OF LIGNITES

	LTA, wt %/g Coal Dry	wt %/g LTA					
		Kaolinite	Quartz	Pyrite	Calcite	Anhydrite	Others
			PSOC 246				
Raw	11.5	5	9	nil*	11	21	54
NH_4Ac	5.9	8	15	nil	nil	1	76
			PSOC 623				
Raw	20.5	41	12	nil	2	14	21
NH_4Ac	16.9	41	12	nil	nil	1	46
			PSOC 833				
Raw	17.4	20	19	nil	16	10	35
NH_4Ac	8.7	41	26	nil	nil	4	29

*minerals detected but in quantities too small to quantify.

ACKNOWLEDGEMENTS

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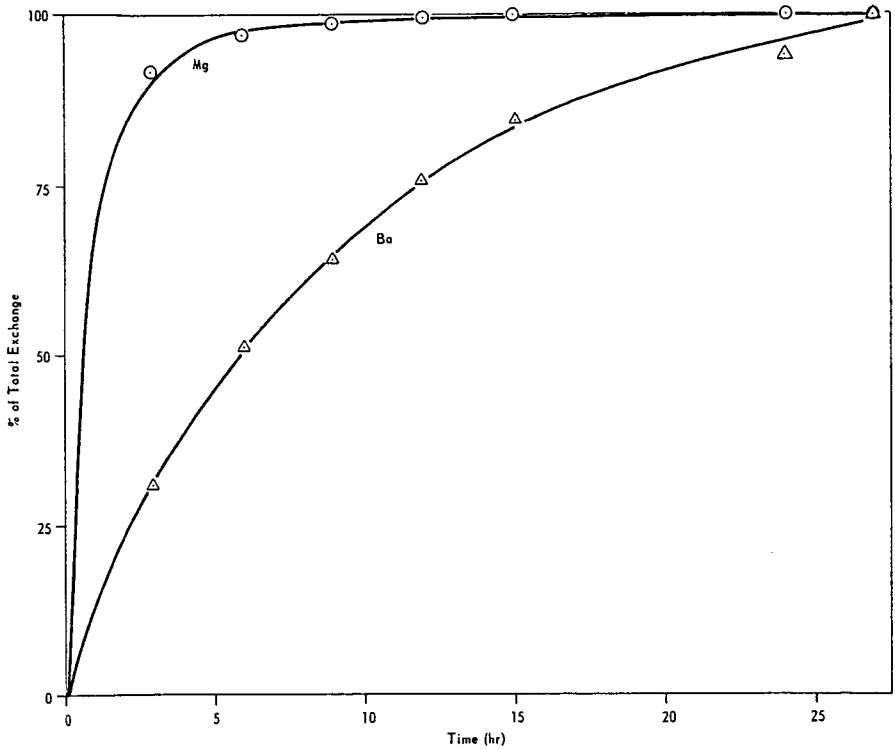

Figure 1. REMOVAL OF CATIONS FROM CARBOXYL GROUPS ON LIGNITE PSOC–246 IN AMMONIUM ACETATE SOLUTION

REMOVAL OF SODIUM FROM LIGNITE BY ION EXCHANGING WITH CALCIUM CHLORIDE SOLUTIONS

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Lignite resources in North Dakota are estimated at 350 billion tons, comprising 20 percent of the nation's total coal resources on a tonnage basis. Using present technology, 16 billion tons of this lignite is mineable (1). Analyses of over 400 samples of coal taken throughout the region show that the average sodium oxide content is 5.5 percent of the ash (2).

The major use of lignite is as fuel for electric power generation. These large power plants (up to 450 MW) cannot operate efficiently burning high sodium lignite because of fouling of heat transfer surfaces. Field tests and boiler experience have shown that when sodium oxide content in the ash becomes greater than 5 percent, excessive boiler fouling can be expected (3).

Sodium does not occur as in the discrete mineral particles in lignite but is evenly dispersed throughout the coal matrix (4,5). Sodium, along with calcium, magnesium, iron and aluminum cation, is attached to exchange sites on the lignite structure and can be replaced by ion exchange with other elements (6). Combustion tests using lignite in which sodium has been replaced by calcium in ion exchange have shown less fouling than untreated lignite.

This paper presents selected results based on laboratory batch tests in which calcium from calcium chloride solution is used to replace sodium in a high sodium lignite. Test parameters include coal moisture content, particle size, solution concentration, temperature, solid-to-liquid ratio and contact time.

EXPERIMENTAL PROCEDURE

Lignite selected for the tests was from the Beulah mine (North Dakota) and contained 8.7 percent sodium oxide in the ash. Ash analysis, as determined by x-ray fluorescence, is shown in Table 1. Ash content of the coal was 10.8 percent on a dry basis.

Table 1. - Ash Analysis of Test Coal by X-ray Fluorescents: (Beulah mine, North Dakota)

Element	Percent
SiO	19.7
Al_2O_3	12.0
Fe_2O_3	7.6
TiO_2	0.5
P_2O_5	0.3

CaO	19.3
MgO	5.2
Na_2O	8.7
K_2O	0.7
SO_3	25.0
TOTAL	99.0

The test coal was crushed to desired size and stored in double plastic bags to minimize moisture loss. The test procedure consisted of combining the desired weight ratio of lignite with calcium chloride solution in a 400 ml beaker and stirring with a propeller-type mixer for the specified length of time. The lignite was separated from solution by filtering with a Buchner funnel using Whatman No. 41 filter paper. The filtrate was analyzed for pH and specific gravity, and the dissolved elements were measured by an inductively coupled argon plasma spectrometer (ICAP). The lignite was rinsed with 200 ml deionized water and filtered. This filtrate was also analyzed. The coal sample was dried and ashed, and the ash analyzed by x-ray fluorescence spectrometry.

RESULTS AND DISCUSSION

Each of the test parameters is discussed individually.

Coal Moisture

The relationship between the extent of sodium removal by ion exchange and lignite moisture content is shown in Figure 1. Moisture reduction was accomplished by air drying the lignite at 25°C. In this set of tests, coal sized to 80 x 0 mesh was contacted with .05 molar calcium chloride solution for 5 minutes. The coal-to-liquid weight ratio was 1 to 4. The moisture content of the coal varied from 34 to 15 percent. Results indicate that reducing the coal moisture to 28 percent had little effect on the rate of exchange. Below 28 percent moisture, the rate of exchange was reduced considerably.

Lignite has a porous structure and the inherent water is believed to be trapped in capillaries (7). Organically bound ions such as sodium may adhere to the surface of the capillaries. In the ion exchange process, calcium diffuses from the solution into the water-filled passages and replaces sodium. Reducing the lignite's moisture content collapses and seals off a portion of the capillary thus reducing ion exchange potential.

Particle Size

The effect of particle size on the rate of ion exchange is shown in Figure 2. In this set of tests, various sized coal was treated with .05 molar $CaCl_2$ for 5 minutes at solid to liquid weight ratio of 1 to 4. Coal moisture content was 34 percent.

Results show that treating 40 x 0 mesh lignite reduced the sodium content in the lignite by 80 percent, while treating 8 x 0 mesh, at the same test conditions, reduced the sodium by 63 percent. Treating ¼ x 0 inch sized lignite removed only 15 percent of the sodium originally in the coal. The lignite's particle size determines the distance that the exchanging ion must travel through the capillary network and, for that reason, effects the rate and extent of exchange.

Solution Concentration

The sodium content of the treated lignite (dry basis) as a function of starting calcium concentration in solution is shown in Figure 3. The calcium content of lignite resulting from the treatment is also shown. In this series of tests, calcium chloride solution in molar concentration varying from 0 to .2 molarity was mixed with 80 x 0 mesh lignite for 3 minutes. The solid-to-liquid weight ratio was 1 to 5.

Results indicate a direct relationship between solution concentration and sodium removal. The calcium content of the lignite increases proportionally to the decrease in sodium content.

Temperature

The relationship between the temperature of the calcium solution and sodium removal is shown in Figure 4. In this test series, 8 x 0 mesh lignite was treated with .05 molar $CaCl_2$ solution for 5 minutes. The solid-to-liquid ratio was 1 to 4. The solution temperature was varied from 70 to 145 degrees F. Results indicate that 63 percent of the sodium was removed from the lignite at 70 degrees F., while 72 percent was removed at 120 degrees F. Temperatures higher than 120 degrees F. did not increase the removal efficiency.

Figure 5 shows the moles of sodium removed from the lignite per mole of calcium added as a function of temperature. Under these test conditions, one mole of calcium will replace 1.15 to 1.25 moles of sodium. Under ideal conditions, this ratio should be two sodiums removed for every calcium added. In the present case, other metals in the lignite, such as magnesium or iron, which are also ion exchangeable, may have been replaced, thus reducing the molar ratio of calcium replacing sodium.

Solid-Liquid Weight Ratio

The solid-to-liquid ratio effects sodium removal efficiency as is shown in Figure 6. In this series of tests, lignite sized 8 x 0 mesh was contacted with .05 molar calcium chloride for 5 minutes. The solid-to-liquid weight ratios were 1 to 2, 3 to 8, and 1 to 4.

Results in Figure 6 show that increasing the quantity of liquid (thus increasing the quantity of calcium present) in proportion to solids will increase the sodium removed. The reason is that with higher ratios more calcium is in contact with the coal. Figure 7 shows the ratio of moles of sodium removed to moles of calcium added to the lignite for this set of tests. As shown, the molar quantity of sodium removed to calcium added to the coal varied from 1.25 to 1.35 and compared favorably to that previously shown in Figure 5.

Contact Time

The effect of solid-liquid contact time on sodium removal efficiency is shown in Figure 8. In this series of tests, .05 molar $CaCl_2$ solution was mixed with 8 x 0 mesh lignite in a weighed solid-to-liquid ratio of 1 to 4. Contact time was 5, 30 and 120 minutes.

Results show that the quantity of sodium removed for this size coal increased with contact time up to 30 minutes. After 30 minutes, there was no significant increase. This indicates that equilibrium under these test conditions with this size limit has been achieved in less than 30 minutes.

SUMMARY

The quantity of sodium removed from lignite by ion exchange with calcium is a function of the coal's moisture content, particle size, quantity of calcium present in solution, solution temperature and contact time. The greatest exchange occured with lignite containing more than 28 percent moisture and smallest particle size (80 mesh x 0). The rate of exchange increases slightly with temperature to 120°F. The sodium removal is a direct function of solution calcium concentration. Solution concentration and solid-liquid ratio are interdependent variables which determine total quantity of calcium which contacts a unit quantity of lignite.

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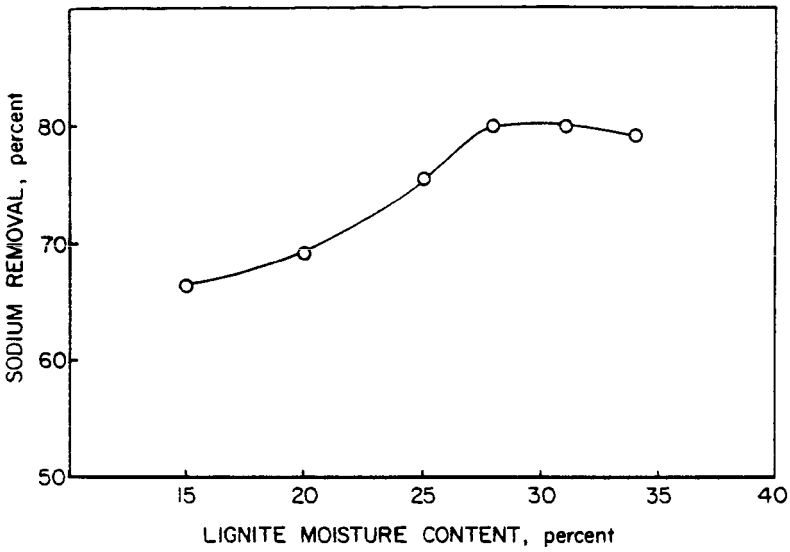

FIGURE 1. - Sodium removal as a function of lignite moisture content.

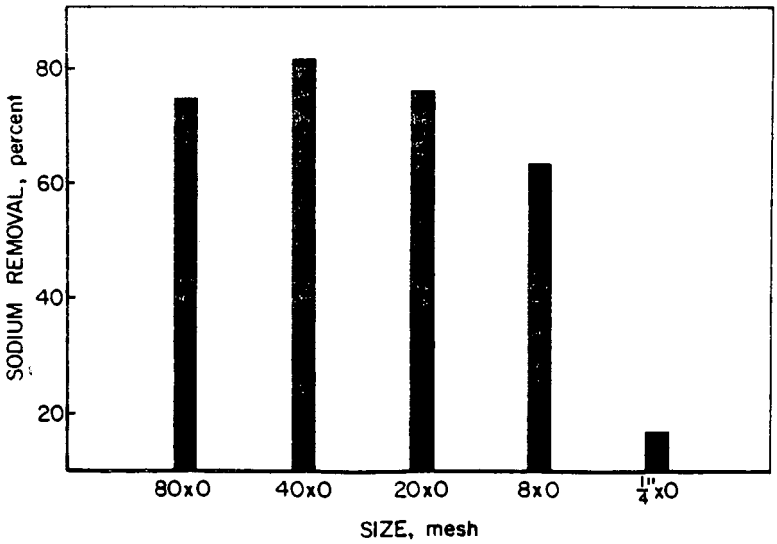

FIGURE 2. - Sodium removal as a function of lignite particle size.

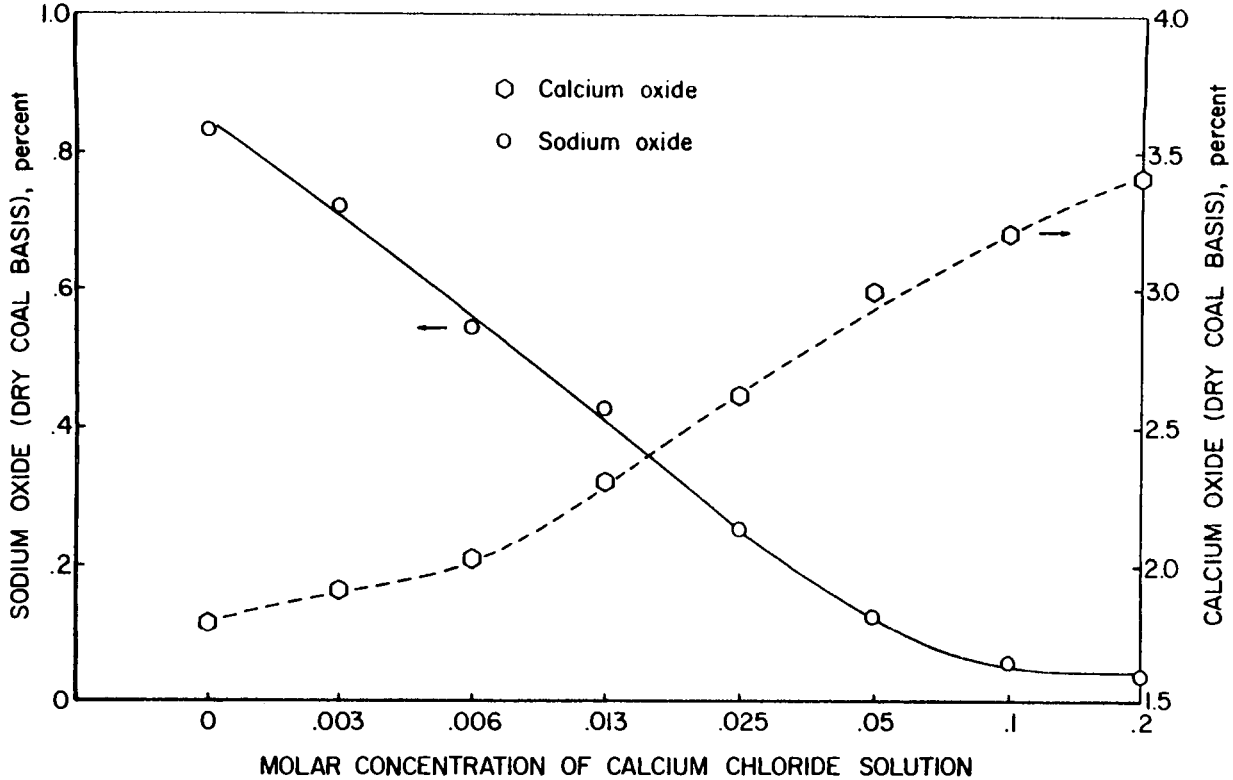

FIGURE 3. - Sodium removal and calcium addition to lignite as a function of calcium chloride solution concentration.

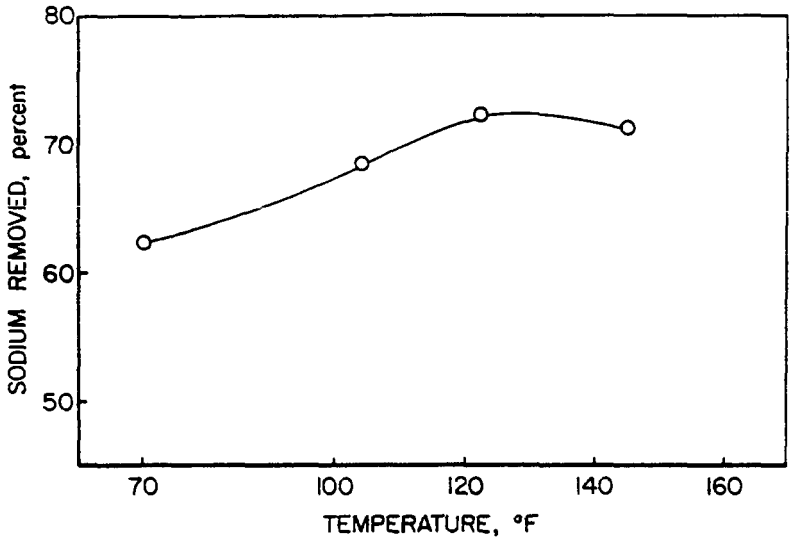

FIGURE 4. - Sodium removal from lignite as a function of temperature of treating solution.

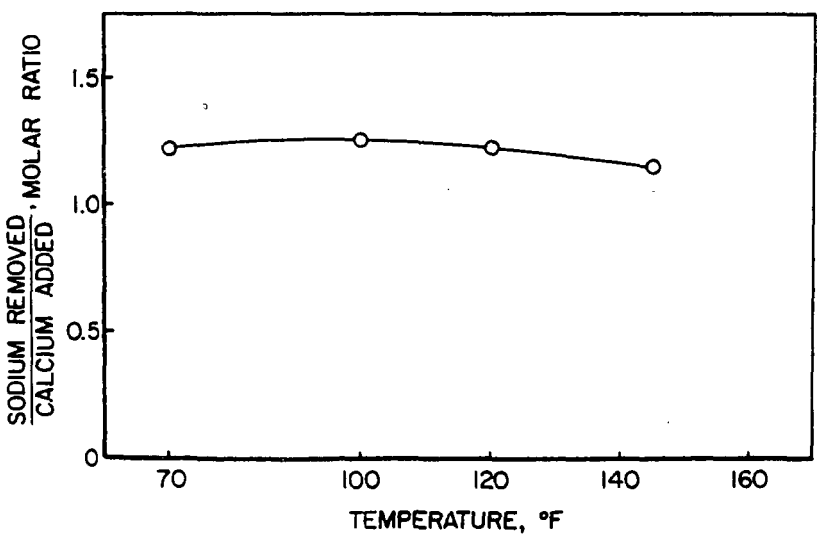

FIGURE 5. - Ratio of sodium removal from lignite to calcium added as a function of solution temperature.

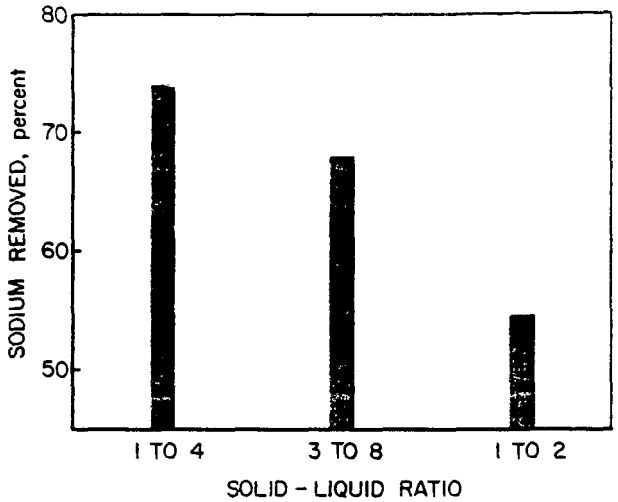

FIGURE 6. - Sodium removal from lignite as a function of solid to liquid ratio.

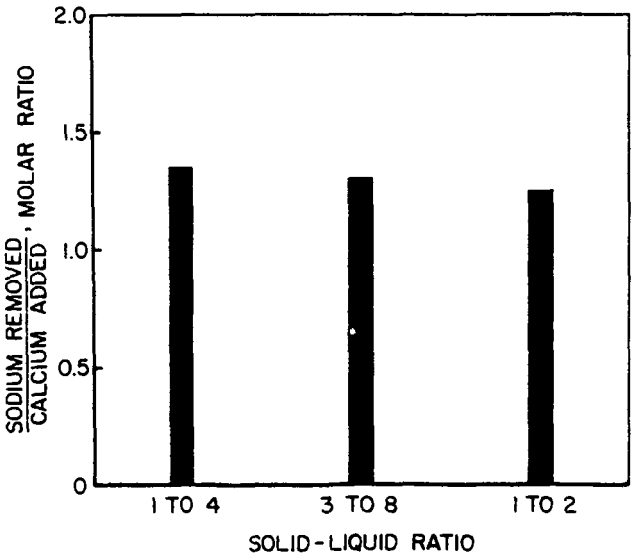

FIGURE 7. - Ratio of sodium removal from the lignite to calcium added as a function of solid to liquid ratio.

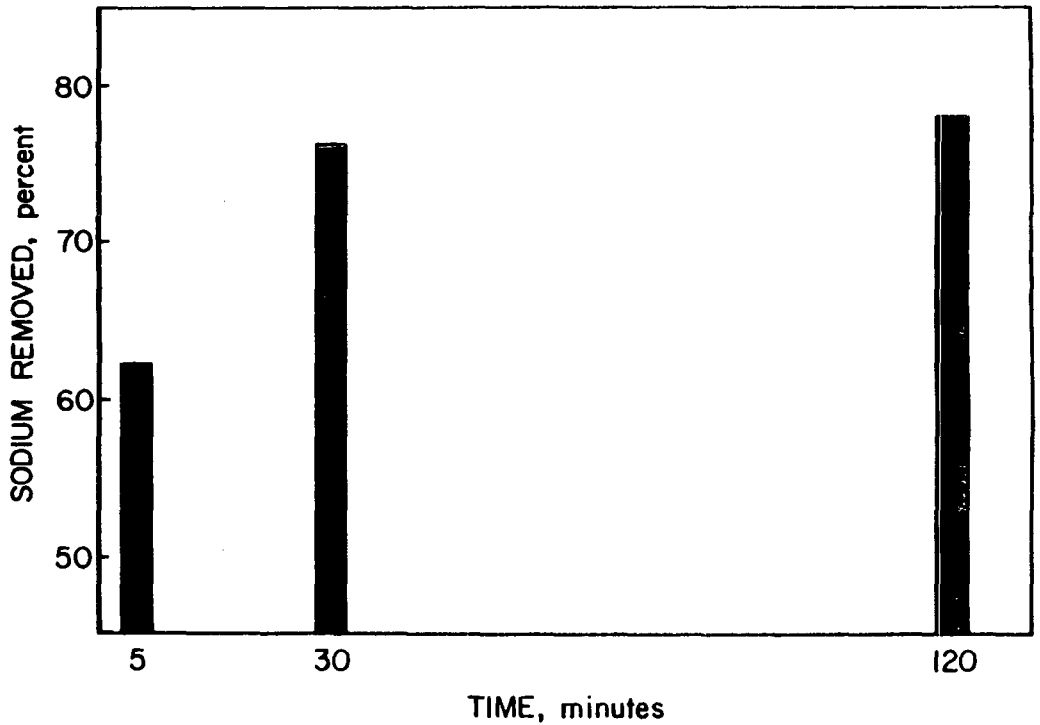

FIGURE 8. - Sodium removal from lignite as a function of solid-liquid contact time.

Laboratory Batch Liquefaction of Low Rank Coals

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INTRODUCTION

Laboratory autoclave studies of low rank coals, particularly lignitic coals, have been conducted in the Department of Chemical Engineering at the University of North Dakota over a period of nearly 15 years. Recent research work is focused on providing process support data for the "surviving" liquefaction technologies with particular emphasis on western low rank coals. Early work in the current program was directed to screening several liquefaction solvents. Two solvents were selected for subsequent work; one was a distilled anthracene oil (AOD1 and AOD2) and the second was hydrogenated distilled anthracene oil.

One of the objectives of the research program is to study the effect on liquefaction yields of the identity and quantity of mineral constituents of the coal.

Five North Dakota lignites (Beulah, Gascoyne, Zap, Larson, and Velva), three Montana or Wyoming subbituminous coals (Absaloka, Wyodak, and Decker), and a single Alaska subbituminous coal (Usibelli) were investigated. Analyses of the coals and of the coal ashes are given in Tables 1 and 2, respectively. The elements often considered to be important in liquefaction are iron, calcium, magnesium, sodium, potassium, and sulfur. There is a considerable body of opinion that the various forms of iron sulfides are the primary catalysts in liquefaction. Tables 1 and 2 show that the high ash lignite (BEU 3) and subbituminous (ABS 1) are also high in both iron and sulfur, while the calcium and magnesium contents are in the range of the other coals. The sodium level is relatively high for the Beulah (BEU 3) and Zap lignites, and for the Absaloka coal when it is compared with the other subbituminous coals.

PRODUCT AND SLURRY ANALYSES

Analyses of liquefaction solvent and of reaction products are largely physical in nature. Solvent and slurry are characterized by vacuum distillation (ASTMD-1160) and by dissolution of the undistillable portion in tetrahydrofuran (THF). Slurry material not soluble in THF was considered to be unconverted lignite or ash, and the ash was determined independently.

Three distillate fractions were determined in the vacuum (5 torr) distillation. These were the initial boiling point (IBP) to 120°C - light oil; 120°C to 260° C - middle oil; and the fraction distilled above 260°C - heavy oil. The THF soluble, but nondistillable, portion of the product slurry was called soluble residuum. Condensable vapors that were discharged with the reactor gases were collected in cold traps and are also considered to be light oils. It will be noted that the solvents consist primarily of material in the middle oil range. For purposes of data reduction it was assumed the ash was unchanged during the reaction.

EXPERIMENTAL RESULTS

Cold Charge Autoclave

In cold charge autoclave experiments, solvent, lignite, and gas (nominally

an equimolar mixture of CO and H_2) were charged to the autoclave. The autoclave was heated to the desired reaction temperature at the rate of approximately 3°C/minute. When the maximum temperature was reached the power was immediately shut off. Reactor gases were discharged through cold traps when the reactor temperature dropped to 400°F.

Figures 1 and 2 show the effects of maximum reactor temperature on the product distribution when using Velva lignite in the cold charge autoclave. Distilled anthracene oil (AOD 1) was used as the solvent for the runs presented in Figure 1, while hydrogenated anthracene oil (HAD 29) was the solvent for the data shown in Figure 2. As the temperature exceeds 420°C, the yields of gas and light oil increase, while the heavier distillate yields decrease dramatically and the overall conversion is unchanged or slightly diminished. This indicates that heavier products (soluble residuum and heavier distillates) are converted to lighter products, but some of the solvent or products are polymerized, coked, or charred and thus rendered insoluble in THF. Figures 3 and 4 show the results obtained when using Absaloka subbituminous coal at the same temperatures and with the same solvents. The same general observations can be made although there are some differences apparent between the lignite and the subbituminous coal. The results for the various products of the two types of coal are shown in Figure 5 through Figure 10.

Figure 5 shows that the yield of soluble residuum is high at the lower temperatures, but decreases with increasing temperature for the Absaloka coal, while the soluble residuum yield reaches a maximum at about 420° for Velva lignite. Additionally, the overall conversion of Absaloka coal is largely unaffected by reaction temperature, but the conversion increases from 69 percent to 89 percent when reaction temperature is raised from 380°C to 420°C for the lignite. Differences in the yields of THF soluable product and of distillate show a greater effect of reaction temperature for the lignite than for the subbituminous coal (Figure 6). The yields of the components of the distillate products follow similar trends although the yield of the middle and heavy oil fraction shows greater variation with temperature changes for the lignite coal (Figure 7).

Figures 8, 9, and 10 show the same general trends when hydrogenated anthracene oil (HAD 29) was the solvent and the same two coals were used.

The highest distillate yield obtained was with Zap lignite using the distilled anthracene oil solvent (AOD 1), while the Larson and Beulah lignites showed the lowest distillate yields. The overall conversion was also highest for Zap lignite. Changing to the hydrogenated solvent (HAD 29) caused a decrease in distillate yield for Beulah lignite, while the yield of gas increased. Overall conversion increased slightly, and the yield of soluble residuum was nearly constant. It appears that distillate (including solvent) was converted to lighter products while other products were unaffected. For the Larson and Velva lignites, the distillate and gas yields and the overall conversion increased, and the yield of soluble residuum decreased.

Comparing the conversion and product yields when using the anthracene oil solvent (AOD 1) for North Dakota lignites and for the subbituminous coals show that the conversion of lignite is generally higher. Correspondingly, the distillate yields are higher for lignite. Changing to the hydrogenated solvent (HAD 29) caused the conversion for the subbituminous coals to increase noticeably; the conversion of lignite increased, but to a lesser extent. Thus, it appears that the presence of a solvent containing greater amounts of hydrogen has a greater effect on the higher rank (subbituminous) coal.

Although the coal screening work has not been completed, results obtained so far do not seem to indicate a positive relation between ash content of the feed coal and overall conversion or production of distillate product. More work will be done

in looking at the effects of the various ash constituents on conversion and yields.

Hot Charge Autoclave

Gas (equimolar CO/H_2 mixture) and the solvent/coal slurry were charged to the hot one-gallon autoclave, and periodic samples of both reactor gas and slurry were taken during a run. The same lignites and subbituminous coals and the same solvents were studied. Nominal temperatures were 420°C and 460°C.

Recovery of products on the hot charge system ranged from 88.0 to 96.5 percent, with closure generally in the 92 to 95 percent range. Failures in the runs were generally caused by plugging in the slurry sampling system. In some of the runs, the time samples exhausted the product slurry, so that no end-of-run results were obtained. In other runs, the sampling system plugged so that all of the time samples were not obtained, but end-of-run results could be determined. It is interesting to note that with Decker subbituminous coal and hydrogenated solvent the sampling system plugged each time a run was attempted. However, some end-of-run results were obtained.

The end-of-run data for Beulah, Velva, Larson, and Gascoyne lignites and for Wyodak and Absaloka subbituminous coals are shown in Figures 11 and 12, where yields of distillable oil, soluble residuum, and unconverted coal are plotted against temperature over the range 420° to 460°C. The most obvious difference is the much higher conversion (lower yield of unconverted coal) and much higher yields of distillable oil realized with the hydrogenated solvent HAD 20 as compared with the unhydrogenated anthracene oil, AOD 1 or 2. When comparing results with the different coals, first with the hydrogenated and then with the unhydrogenated solvents, there appears to be little significant difference between any of them. However, the data from the slurry time samples show some differences between lignites and between the two subbituminous coals.

The results of the slurry time sample data were calculated on an MAF coal basis on the assumption that the ash content of the slurry sample is the same as the total ash in the coal charged (this is the so-called "ash-conversion"). This is not strictly accurate, but information on trends was obtained by cross-averaging the data for the three lignites and for the two subbituminous coals for each solvent at each of the two temperatures.

The averaged data are plotted in Figure 13 for the lignites and in Figure 14 for the subbituminous coals. At the lower temperature of 420°C with both solvents and both coals, total conversion (THF solubles and lighter) increases with time, whereas the conversion to distillates and lighter decreases slightly with time. There appears to be no significant difference, considering the scatter of the data, between the lignites and the subbituminous coals. At the higher temperature of 460°C, with the unhydrogenated solvent, total conversion is initially high with the lignites and then decreases, whereas with the subbituminous coals it increases to a maximum and then decreases with time. With the hydrogenated solvent, conversion of the lignites increases with time, whereas conversion of the subbituminous coals is initially high and remains high. The apparent decreasing conversion is the result of repolymerization or condensation reactions to produce THF insolubles occurring to a greater extent than the solubilization reactions.

Here again, future work will be concerned with the effects of the mineral matter constituents on conversion and yield distribution.

TABLE 1

ANALYSES OF COALS

Mine	S. Beulah	S. Beulah	Peerless	Noonan	Velva	Indianhead	Wyodak	Absaloka	Decker No.1	Usibelli
Town	Beulah	Beulah	Gascoyne	Larson	Velva	Zap	Gillette	Sarpy Creek	Decker	Usibelli
County	Mercer	Mercer	Bowman	Burke	Ward	Mercer	Campbell	Big Horn	Big Horn	(Nenana Dist.)
State	N. Dak.	N. Dak.	N. Dak.	N. Dak.	N. Dak.	N. Dak.	Wyoming	Montana	Montana	Alaska
Abbreviation I.D.	Beu 2	Beu 3	Gas 1	Lar 1	Vel 1	Zap 1	Wyo 1	Abs 1	Dec 1	Usi 1
Grand Forks No.	77-0712	78-4556	78-4555	78-4867	78-4866	78-4868	78-4467	78-4557	78-4558	
Sample Date	2/77	10/78	10/78	11/78	11/78	11/78	7/78	10/78	10/78	10/78
Bin No.	Drum	3518	3528	3499	3514	3519	3500	3527	3530	Drum
Proximate Analysis										
As Received										
Ash, Wt %	7.05	13.02	7.90	6.71	5.69	8.10	5.82	16.01	4.41	8.03
Moisture, Wt %	25.59	28.46	27.81	29.68	32.30	27.19	25.91	19.70	21.05	23.66
Volatile Matter, Wt %	39.47		32.96	31.37	32.94	37.75	38.63	28.94	34.45	
Fixed Carbon, Wt %	27.89		31.33	32.24	29.07	26.96	29.64	35.35	40.09	
Heating Value, Btu/lb	7515	7311	7859	7833	7415	8154	8743	8314	9772	8006
MF Basis										
Ash, Wt %	9.47	18.20	10.94	9.54	8.40	11.12	7.86	19.94	5.59	10.52
Heating Value, Btu/lb	10100	10219	10886	11139	10953	11199	11800	10354	12378	10492
Ultimate Analysis										
MAF Basis										
Carbon, Wt %	72.24		65.44	60.81	72.27	68.12		73.84		
Hydrogen, Wt %	5.78		5.14	5.65	4.55	4.29		4.45		
Nitrogen, Wt %	0.66		0.76	0.93	1.08	1.14		0.98		
Sulfur, Wt %	1.05		1.74	0.38	0.63	1.13		0.93		
Oxygen, Wt % (by difference)	20.27		26.92	32.23	21.47	25.32		19.80		
Heating Value, Btu/lb	11157	12493	12223	12314	11957	12600	12807	12933	13111	11726
H/C Ratio	0.96		0.94	1.11	0.76	0.76		0.72		

TABLE 2

ANALYSES OF COAL ASHES

Mine	S. Beulah	S. Beulah	Peerless	Noonan	Velva	Indianhead	Wyodak	Absaloka	Decker No.1	Usibelli
Town	Beulah	Beulah	Gascoyne	Larson	Velva	Zap	Gillette	Sarpy Creek	Decker	Usibelli
County	Mercer	Mercer	Bowman	Burke	Ward	Mercer	Campbell	Big Horn	Big Horn	(Nenana Dist.)
State	N. Dak.	N. Dak.	N. Dak.	N. Dak.	N. Dak.	N. Dak.	Wyoming	Montana	Montana	Alaska
Abbreviation I.D.	Beu 2	Beu 3	Gas 1	Lar 1	Vel 1	Zap 1	Wyo 1	Abs 1	Dec 1	Usi 1
Grand Forks No.	77-0712	78-4556	78-4555	78-4867	78-4866	78-4868	78-4467	78-4557	78-4558	
Sample Date	2/77	10/78	10/78	11/78	11/78	11/78	7/78	10/78	10/78	10/78
Bin No.	Drum	3518	3528	3499	3514	3519	3500	3527	3530	Drum
Ash Content, Wt %										
As Received	7.18	13.44	7.49	6.60	5.15	8.56	5.76	15.51	4.32	6.15
Dry Basis	10.02	19.95	13.09	9.76	8.25	13.41	8.23	19.72	5.55	27.80
Ash Composition										
Oxides as Wt % of Ash										
SiO_2	6.7	27.6	29.8	31.8	19.6	26.2	33.8	45.9	24.9	31.9
Al_2O_3	40.9	14.0	19.4	18.5	12.7	10.7	16.7	21.9	19.5	17.5
Fe_2O_3	18.4	14.2	2.0	5.0	5.8	14.0	5.1	11.3	11.9	7.7
TiO_2	0.2	0.6	0.9	0.9	0.4	0.5	1.0	0.8	1.2	0.8
P_2O_5	0.2	0.2	0.2	0.4	0.6	0.4	1.4	0.1	1.7	1.4
CaO	12.1	14.5	22.9	23.2	36.0	16.0	22.5	7.5	15.1	28.3
MgO	3.3	3.9	6.9	6.3	10.2	4.9	6.5	1.7	2.9	4.8
Na_2O	2.8	5.5	3.3	3.5	2.1	8.0	1.8	2.9	6.5	0
K_2O	0.1	0.4	0.2	0.4	0.3	0.9	0.3	0.9	0.4	1.0
SO_3	15.3	19.1	14.4	10.0	12.3	18.4	10.9	7.0	15.9	6.6
Metals as Wt % of MF Coal										
Si	0.31	2.57	1.82	1.45	0.76	1.64	1.30	4.22	0.65	1.27
Al	2.17	1.47	1.34	0.96	0.55	0.76	0.73	2.29	0.57	0.79
Fe	1.29	1.98	0.18	0.34	0.33	1.32	0.29	1.56	0.46	0.46
Ti	0.01	0.07	0.07	0.05	0.02	0.04	0.05	0.09	0.04	0.04
P	0.01	0.02	0.01	0.02	0.02	0.02	0.05	0.01	0.04	0.05
Ca	0.86	2.06	2.14	1.62	2.12	1.53	1.32	1.06	0.60	1.72
Mg	0.20	0.47	0.54	0.37	0.50	0.39	0.32	0.20	0.10	0.25
Na	0.21	0.82	0.32	0.25	0.13	0.79	0.11	0.43	0.27	0
K	0.01	0.02	0.02	0.03	0.02	0.09	0.02	0.14	0.02	0.07
S	0.61	1.52	0.75	0.39	0.41	0.99	0.36	0.55	0.35	0.22

Figure 1

Liquefaction of Velva Lignite with Distilled Crowley Chilled Anthracene Oil (AOD 1) 50/50 H_2/CO 3200 - 4000 psig

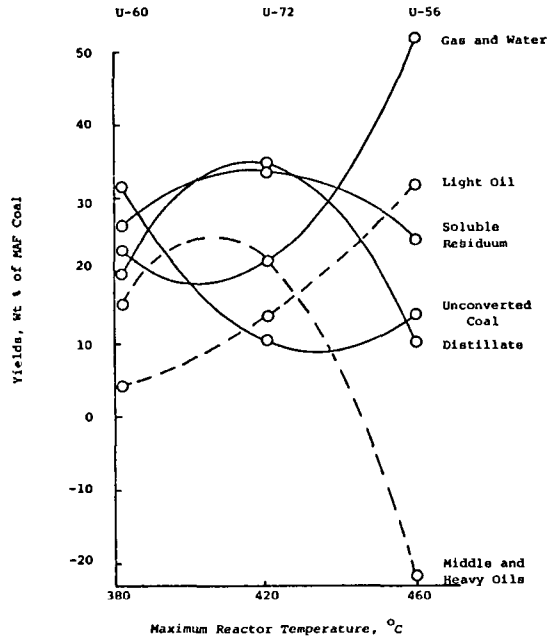


Figure 2

Liquefaction of Velva Lignite with Hydrogenated Distilled Crowley Chilled Anthracene Oil (HAD 29) 50/50 H_2/CO 4000 - 4200 psig

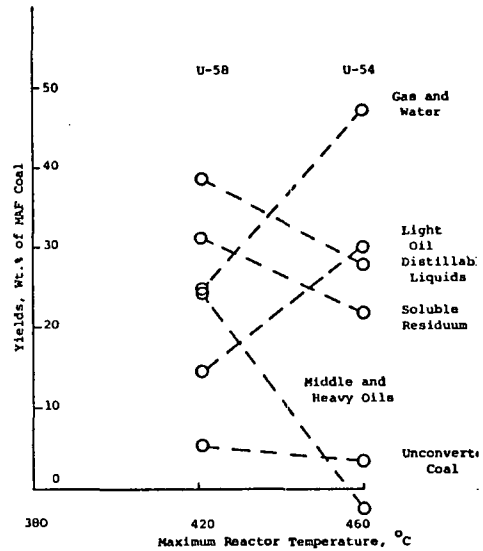


Figure 3

Liquefaction of Absaloka Subbituminous Coal
with Distilled Crowley Chilled Anthracene Oil
(AOD 1) 50/50 H_2/CO 3150 - 3350 psig

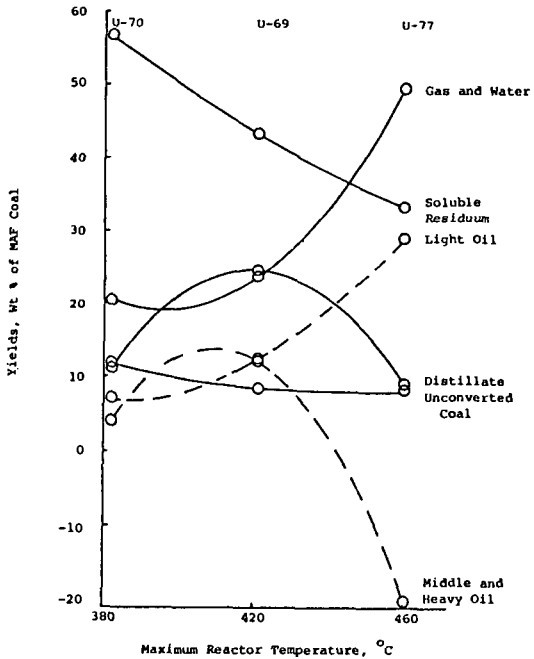


Figure 4

Liquefaction of Absaloka Subbituminous Coal with
Hydrogenated Crowley Chilled Anthracene Oil (HAD 29)
50/50 H_2/CO 3500 - 3600 psig

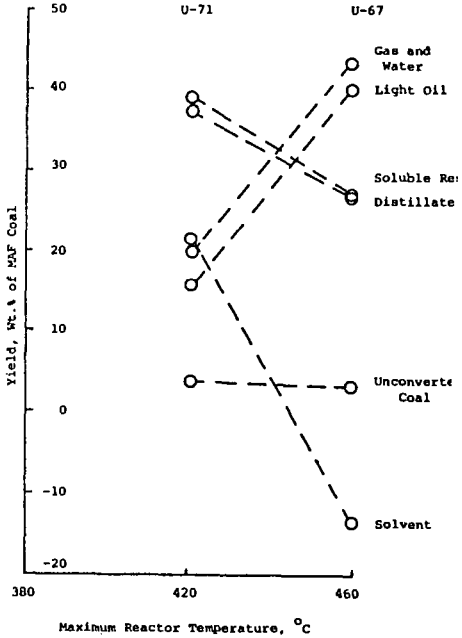


Figure 5

Liquefaction of Velva Lignite and Absaloka Subbituminous Coal with Anthracene Oil (AOD 1) 50/50 H_2/CO 3200 - 4000 psig

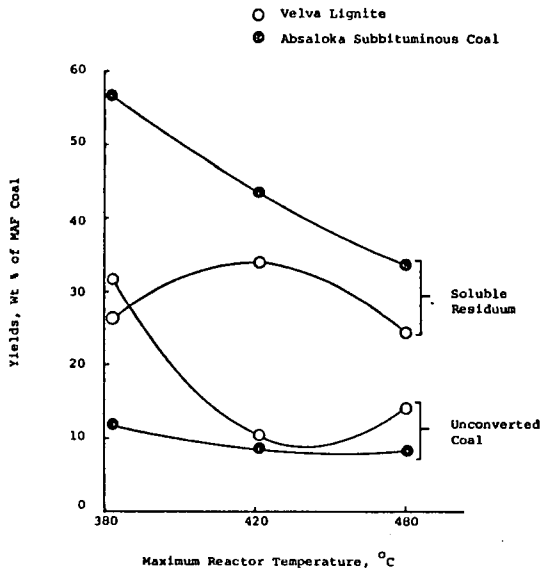


Figure 6

Liquefaction of Velva Lignite and Absaloka Subbituminous Coal with Anthracene Oil (AOD 1) 50/50 H_2/CO 3200 - 4000 psig

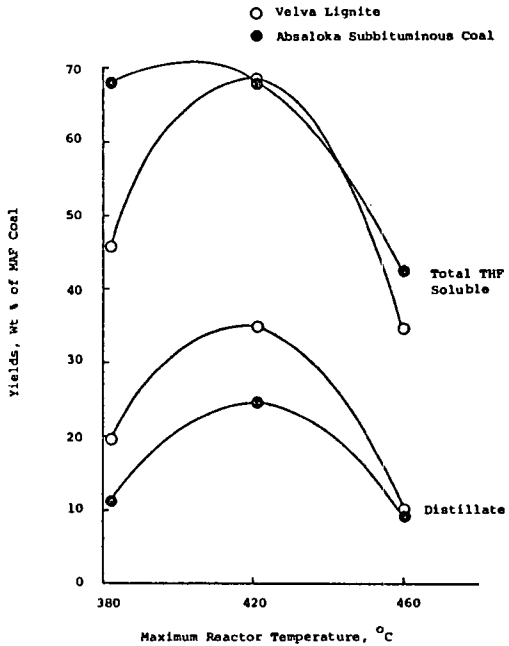


Figure 7

Liquefaction of Velva Lignite and Absaloka Subbituminous Coal with Anthracene Oil (AOD 1)
50/50 H_2/CO 3200 - 4000 psig

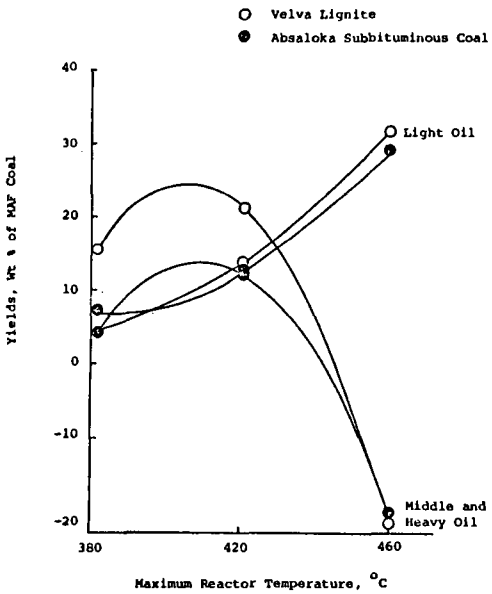


Figure 8

Liquefaction of Velva Lignite and Absaloka Subbituminous Coal with Hydrogenated Anthracene Oil (HAD 29)
50/50 H_2/CO 3500 - 4200 psig

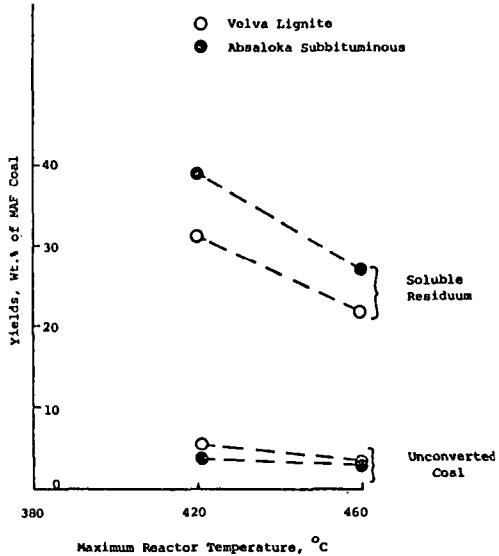


Figure 9

Liquefaction of Velva Lignite and Absaloka
Subbituminous Coal with Hydrogenated Anthracene Oil (HAD 29)
50/50 H_2/CO 3500 - 4200 psig

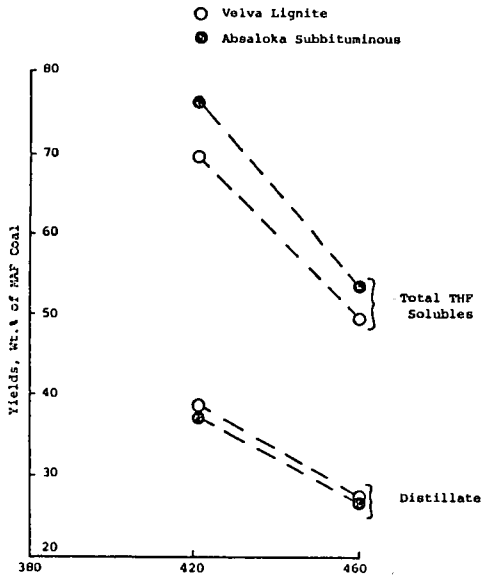


Figure 10

Liquefaction of Velva Lignite and Absaloka
Subbituminous Coal with Hydrogenated Anthracene Oil (HAD 29)
50/50 H_2/CO 3500 - 4200 psig

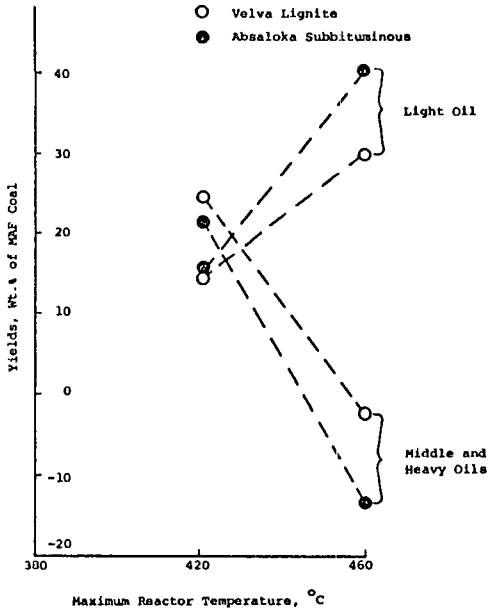


Figure 11

Liquefaction of Beulah, Velva, and Gascoyne Lignites in the
Hot Charge Autoclave
End of Run Results

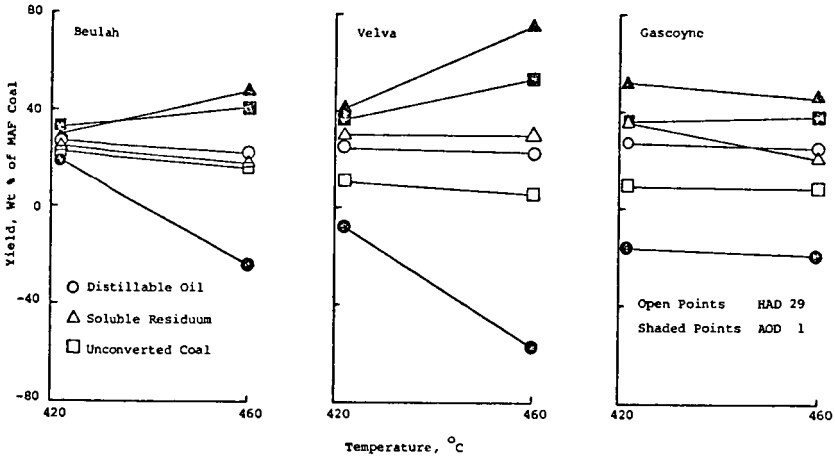


Figure 12

Liquefaction of Larson Lignite and Wyodak and Absaloka Subbituminous
Coals in the Hot Charge Autoclave

End-of-Run Results

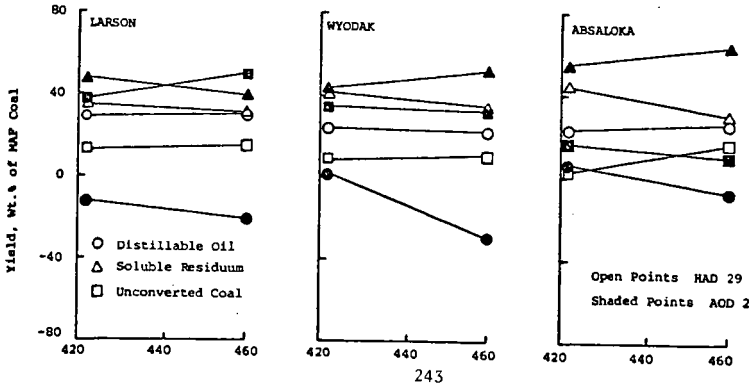


Figure 13

Hot Charge Autoclave Studies with Beulah, Gascoyne, and Velva Lignites, using AOD1 and HAD 29 Solvents at 420 and 460°C.
Yields for all coals averaged with each solvent at each temperature.

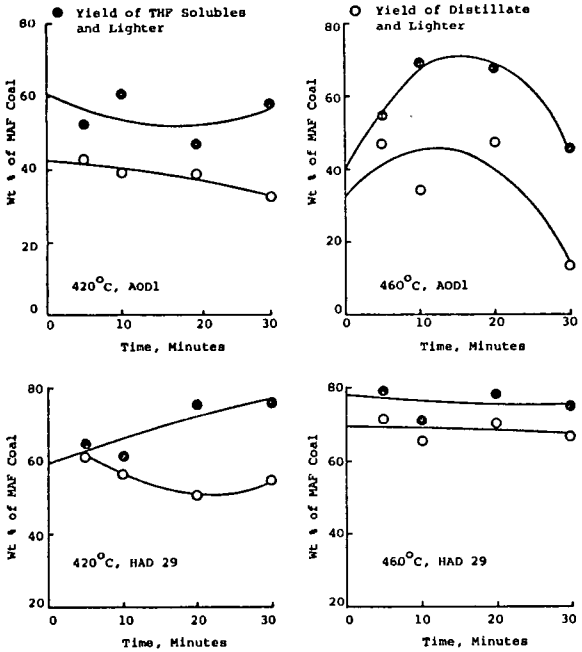
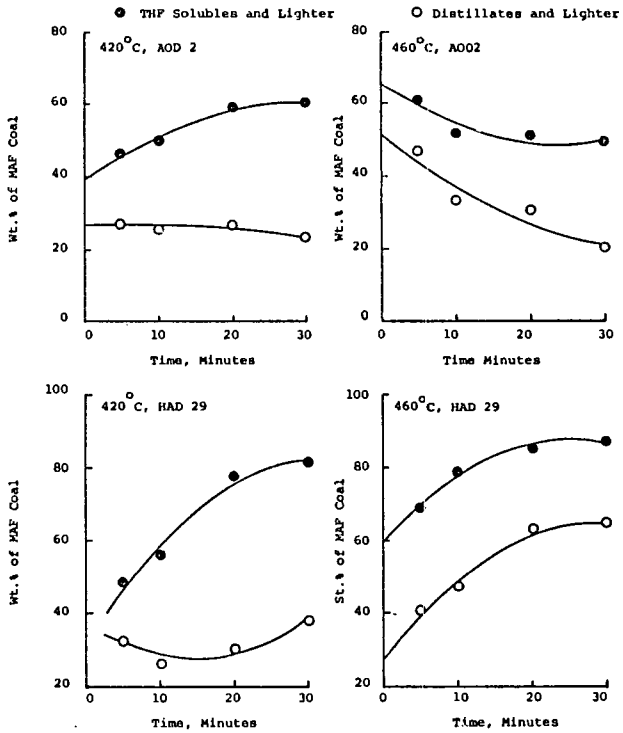


Figure 14

Hot Charge Autoclave Studies with Absaloka and Wyodak Subbituminous Coals Using AOD 1 and HAD 29 Solvents at 420 and 460°C
Yields for Both Coals Averaged with Each Solvent at Each Temperature



CHARACTERIZATION OF LIGHT OILS FROM LIQUEFACTION OF LIGNITE

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Introduction

Liquefaction of North Dakota Beulah seam lignite (Table 1) was carried out in a 2.3 kg coal/hr continuous processing unit at the Grand Forks Energy Technology Center. The design and engineering details of this unit have been described previously (1). Light oil (BP<300°C @ 27.5 MPa) which accounted for about 19% of the yield calculated on a MAF coal basis was withdrawn at the end of each pass and not added back to the recycle solvent. Slurry was prepared for each recycle pass by adding 30% by weight, pulverized (100% minus 60 mesh) as received (~30% moisture) lignite to the heavy product (BP>300°C @ 27.5 MPa) containing unreacted lignite and ash as well. Slurry feed rate to a 4.55 liter autoclave acting as a continuous stirred tank rank reactor (CSTR) at 2.3 kg/hr gave a nominal residence time of one hour. CO and H_2 gas (1:1) were added at 14.2 l/min. The pasting solvent for the first pass was redistilled anthracene oil (IBP 296°C @ 1.3 Pa). The light oil sample studied was collected on the 24th recycle pass, and represents an essentially lined-out steady state product. A description of the detailed reactor conditions and of the composition of the other products was given by Farnum, Knudson and Koch (2).

Experimental

Separations

The light oil was condensed from the gases after depressurization via two let-down valves into a water cooled product receiver, separate from the heavy product let-down. The water vapor that condensed with the oil was separated in a separatory funnel.

The oil was further fractionated by extraction using the scheme suggested by Fruchter et al. (3) modified by the use of n-pentane rather than iso-octane. A flowsheet of the method with the percent recovery of each fraction is given in Figure 1. The number of components determined by capillary GC using a 50-meter OV-101 glass column (Table 2) indicates that the total detectable number of components is less than 277 since there is some overlap between fractions. There are less than 85 components above 1% in this lignite conversion product.

Separations of the four fractions using reverse phase HPLC with a MeOH-H_2O gradient (Altex Model 420) produced major component separations. The light oil was fractionated using the scheme of Dooley et al. (4), yielding fractions including weak acids, phenolics, basics, hydrocarbons and heteroaromatics. Gradient HPLC separation of the weak acids gave approximately 40 peaks; the phenolics, 45 peaks; and the basics, 36 peaks. The hydrocarbon fraction was resolved into 30 compounds. This separation was developed for use as an analytical scale separation technique with automatic fraction collection.

Analyses

Elemental and water analyses of the oil and the four fractions were carried out by combustion (C,H,N,S), Karl Fischer titration (H_2O), and neutron activation and

coulometry (O) (Table 3). The fractions were dried over anhydrous magnesium sulfate before analysis.

Spectroscopy

IR spectroscopic analyses were carried out on thin films of the oils between NaCl disks using a Perkin-Elmer 283* IR spectrometer.

UV studies were conducted using appropriate dilutions of the light oil and its fractions in CH_2Cl_2. The Perkin-Elmer Hitachi model 340 with Data Handler was used either in the absorbance mode or programmed for the fourth derivative mode.

^1H NMR spectra were taken at 200 MHz with a Varian XL-200. The solutions were diluted 1:8 with $CDCl_3$ containing 1% of TMS. They were pulsed 25 times at flip angles of 45° or 90°. The integrated areas are shown in Table 4.

^{13}C NMR spectra were also acquired with the Varian XL-200, operating at 50 MHz using the broad band probe. The solutions were 30% oil in $CDCl_3$ with 1% TMS and 5×10^{-3} M $Cr(AcAc)_3$. The pulse angle was 60° with 5000 to 15,000 pulses accumulated before integration. The results are presented in Table 5.

Trifluoroacetic Acid - Hydrogen Peroxide Oxidations

A trifluoroacetic acid - hydrogen peroxide oxidation (5) of the light oil was carried out. The resulting acids were derivatized to the p-bromophenacyl esters (6) to provide UV absorbance. They were then separated by solvent gradient ($MeOH-H_2O$) reverse phase HPLC and identified by comparison with the same sequence carried out with standards.

Results and Discussion

Basic Fraction

The basic fraction, 5% of the total, is dark in color, with heterocyclic character. The ^1H NMR has several resonance lines between 8.2 and 8.6 ppm as well as a large area between 6.5 and 7.8 ppm indicating pyridines. Some prominent lines between 2 and 3 ppm suggest methyl substituents. The IR contains all of the pyridine - quinoline stretching frequencies and also indicates ring substitution. As was expected, a very broad band appears in the NH, N^+-H stretching region. The richly populated ^{13}C NMR spectrum of this fraction, however, shows a complex mixture of carbon types from 115 ppm to 160 ppm. Pyrolles, if present, are probably substituted since no ^{13}C peak is seen at 106-108 ppm. Indoles are possible.

Phenolic Fraction

The phenolic fraction, 25%, appears to be mainly phenols with cresols and other substituted phenols present in wide variety. Naphthols, if present, are a minor component.

The IR of this fraction, in addition to a broad OH stretching vibration, has a prominent C-H stretching vibration. The other characteristic bands of phenol are all present.

The UV (Figure 2) shows a maximum near 275 nm that is the absorption due to phenols. The fourth derivative UV (Figure 3) is well defined giving a characteristic pattern with a peak corresponding to the absorbance at 275 nm after wavelength correction.

Heteroaromatic Fraction

The ^{1}H NMR of the heteroaromatic fraction, 22%, (Figure 4b) is dominated by symmetrical multiplets at 7.8 and 7.5 ppm which are characteristic of naphthalene. The ^{13}C NMR (Figure 6a) shows two peaks of similar area at 127.8 and 125.7 ppm with a peak at 133.4, agreeing well with the assumption that unsubstituted naphthalene is present. The IR supports this assumption also in that the spectrum closely resembles that of naphthalene and the methylnaphthalenes with all of the frequencies represented. The weak N-H frequency in the IR along with the nitrogen present in the elemental analyses indicates that carbazoles may be present in this fraction. The ^{1}H and ^{13}C NMR, UV (Figures 2,3) and IR also suggest the presence of phenanthrenes.

All of the sulfur-containing compounds are present in this fraction (Table 3). Aromatic ethers are also indicated; however, no evidence of aliphatic ethers is seen.

Hydrocarbon Fractions

The hydrocarbon fraction is almost one-half of the light oil by weight. It is apparently a mixture of aliphatic molecules with some aromatic character, probably benzenoid substitution. The material is light in color, does not have an unpleasant odor, and is low boiling. The IR of the hydrocarbon fraction is very simple, dominated by the C-H aliphatic stretching frequencies and the CH_3 and CH_2 bending vibrations at 1465-1450 cm^{-1} and 1380 cm^{-1}. The major CH_2 rocking vibration appears at 745 cm^{-1}, $(CH_2)_2$. The aromatic C-C stretching is weakly represented at 1495 cm^{-1}.

The ^{1}H and ^{13}C NMR (Figure 6b) spectra are the simplest spectra seen for any of the four fractions. The aromatic protons are 15% of the total number of protons with the measured C_{ar}/C_{total} = 0.33 (Tables 4 and 5).

Unseparated Light Oil 28-14

The fourth derivative UV was used to compare the oil with its separated fractions. The two main UV-absorbing fractions, the phenolic and heteroaromatic fractions (Figure 2), show characteristic fourth derivative fingerprints (Figure 3). This characteristic fine structure of the fourth derivative UV is easily seen in the pattern for the complete light oil LO 28-14. The absorption near 275 nm is the main phenolic band which increases in concert with the increase in phenolic content as line-out is approached. Since the fourth derivative follows Beer's Law, the changes seen as the process proceeds may be quantitatively measured.

IR studies of the CH stretching region in the oil itself along with ^{1}H NMR are also very useful for monitoring the approach to line-out. The asymptotic approach of the IR ratio to a constant value as a function of recycle passes indicates that a lined-out product was obtained (2).

Trifluoracetic acid - hydrogen peroxide oxidation of the light oil was carried out. Reverse phase solvent gradient HPLC was used to qualitatively separate the p-bromophenacyl esters of the acids formed during the oxidation. The following diacids were inferred from comparison with standards: 2C, 3C, 4C, 5C and 10C. Also seen were acetic, butanoic, pentanoic, cyclohexenecarboxylic and cyclohexylacetic acids.

Summary

The light oil 28-14 was separated into four fractions. The basic fraction was heterocyclic in nature containing most of the nitrogen compounds from the oil. The phenolic fraction was shown to be mostly phenols with naphthols only a minor consti-

tuent. The phenolic fraction is about 25% of the total weight of oil. The hetero-aromatic fraction, 22%, contains few components with more than three rings. It is largely composed of naphthalene and naphthalene derivatives, probably some aromatic ethers, neutral or slightly acidic nitrogen compounds and all of the sulfur compounds. The hydrocarbon fraction is the major fraction, 48%. It has no functionality as the elementary analysis shows no O, N or S. This fraction is aliphatic in nature with some benzenoid substituents.

In addition to the observed yield distribution approaching a constant value, which is one indication of line-out, by monitoring the aromatic to aliphatic proton ratio as a function of recycle pass number with IR or NMR spectrometry, the approach to constant composition can be determined.

Acknowledgement

We would like to express our appreciation to Dr. Warren Reynolds for the capillary GC separations.

* Reference to specific brand names and models is done to facilitate understanding and neither constitutes nor implies endorsement by the Department of Energy.

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4. Dooley, J. E., C. J. Thompson, and S. E. Scheppele. "Characterizing Syncrudes From Coal" in Analytical Methods for Coal and Coal Products, C. Karr, Jr. Editor, Academic Press, N.Y., 1978.

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6. Umeh, E. O.. J. Chromatography, 56, 29, 1971.

TABLE 1. - Analyses of Coal for Beulah 3, North Dakota, Lignite

Basis of reported analysis:	Coal Analysis (GF-79-2147)		
	As-received	Moisture-free	Moisture- and ash-free
Proximate analysis, pct.:			
Moisture	29.48	--	--
Volatile matter	30.21	42.84	50.53
Fixed carbon	29.58	41.94	49.47
Ash	10.73	15.22	--
TOTAL	100.00	100.00	100.00
Ultimate analysis, pct.:			
Hydrogen	6.20	4.15	4.89
Carbon	42.87	60.79	71.71
Nitrogen	0.48	0.68	0.80
Oxygen	37.91	16.59	19.57
Sulfur	1.81	2.57	3.03
Ash	10.73	15.22	--
TOTAL	100.00	100.00	100.00

* An "atypical" Beulah Lignite chosen specifically for its high ash content.

TABLE 2. - Capillary G.C. analysis of LO 28-14 fractions

Fraction	# Components			
	>1%	0.5-1.0%	0.25-0.5%	Total
Basic	12	7	21	48
Phenolic	26	23	10	84
Heteroaromatic	21	18	19	124
Hydrocarbon	26	14	20	121

TABLE 3. - Elemental analysis of light oil 28-14 and its fractions based on LO as 100%

	% C	% H	% O	% N	% S	% H_2O
28-LO-14	84.34	10.69	0.37	3.70	0.22	0.23
Basic	19.94	2.64	0.09	3.35	0.01	--
Phenolic	19.77	2.49	0.25	0.03	0.01	--
Heteroaromatic	22.38	2.21	0.035	0.32	0.20	--
Hydrocarbon	22.26	3.35	0.001	0.00	0.01	--

TABLE 4. - ^1H NMR areas for 28-LO-14 and fractions, $CDCl_3$, TMS

Fraction	% Har (8.8-5.7 ppm)	% Hα (4-1.9 ppm)	% Ho (1.9-0.3 ppm)	% Hphe (varies)
28-LO-14	23.1	23.0	53.3	--
Basic fraction	34.1	34.1	31.8	(part of Har)
Phenolic fraction	31.3	32.3	25.9	10.5
Heteroaromic fraction	48.1	29.0	22.5	--
Hydrocarbon fraction	15.3	19.0	65.7	--

TABLE 5. - Integrated ^{13}C areas for LO 28-14 and fractions

Fraction	Car/Ctotal	Car/Caliph
LO 28-14	0.45	0.83
Basic fraction	0.56	1.30
Phenolic fraction	0.66	1.93
Heteroaromatic fraction	0.81	4.24
Hydrocarbon	0.33	0.49

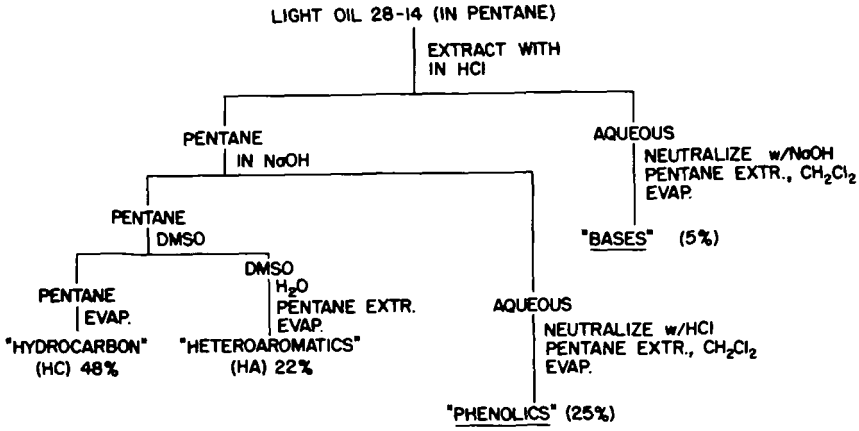


FIGURE 1. - Separation and recovery of the light oil fraction by extraction

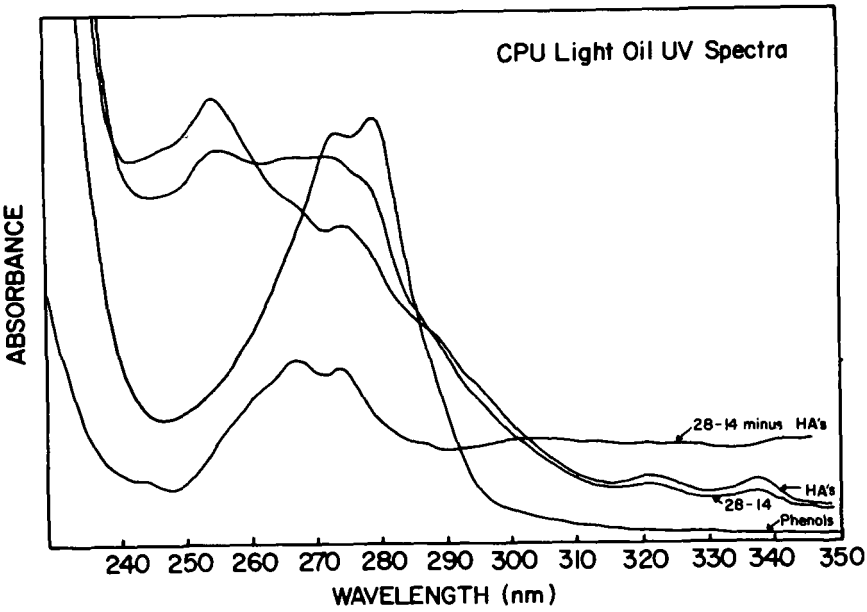


FIGURE 2. - UV spectra of LO 28-14 and fractions

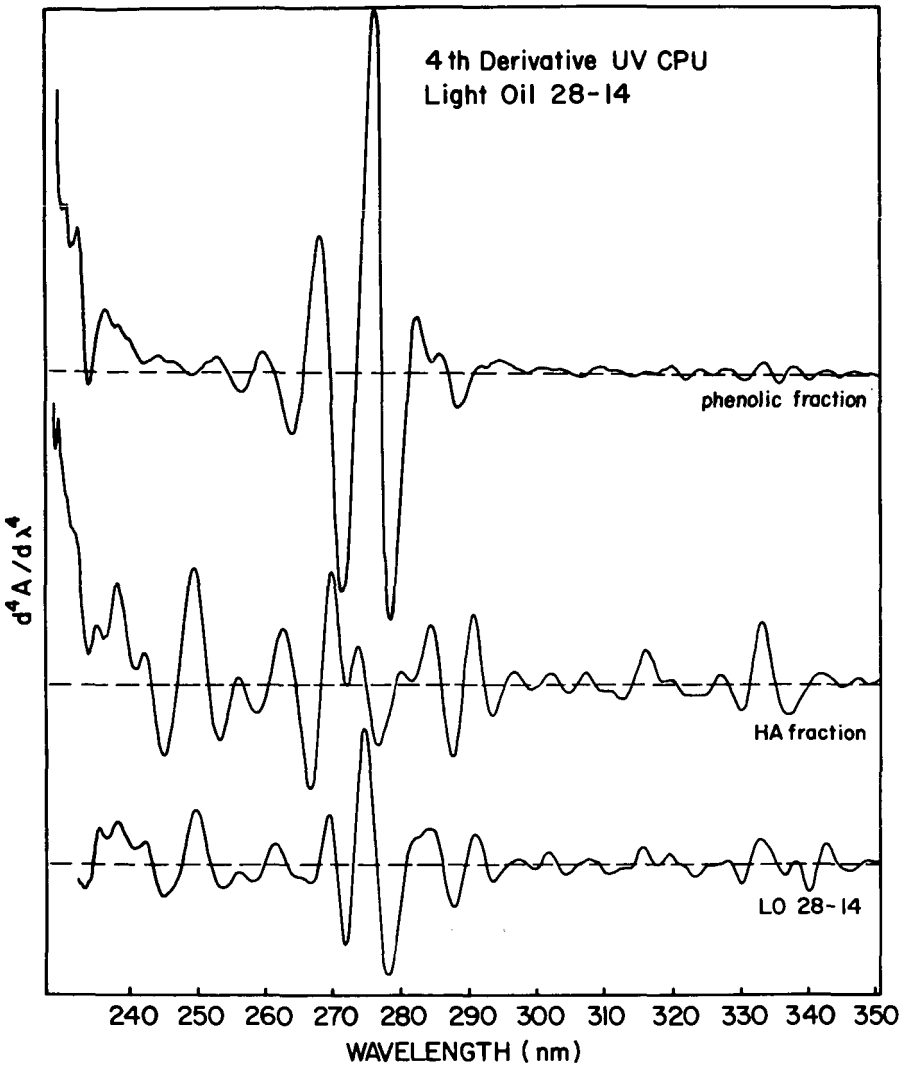
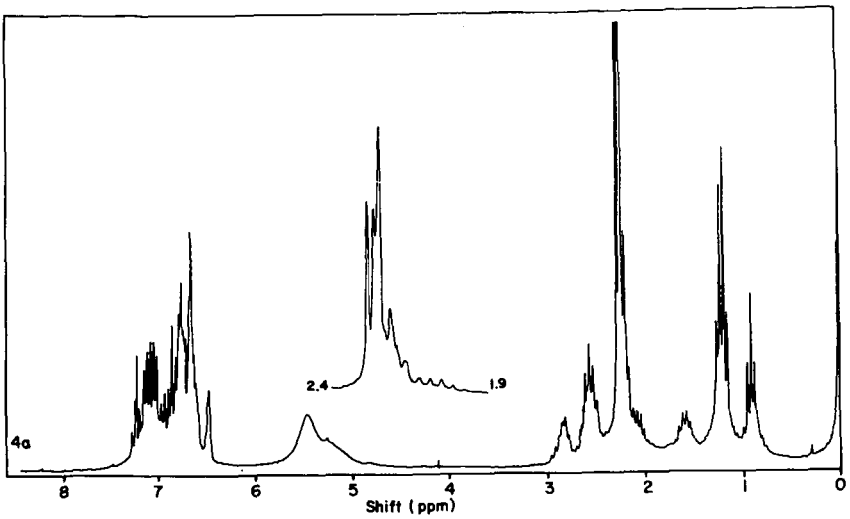


FIGURE 3. - Fourth derivative UV of light oil 28-14 and fractions



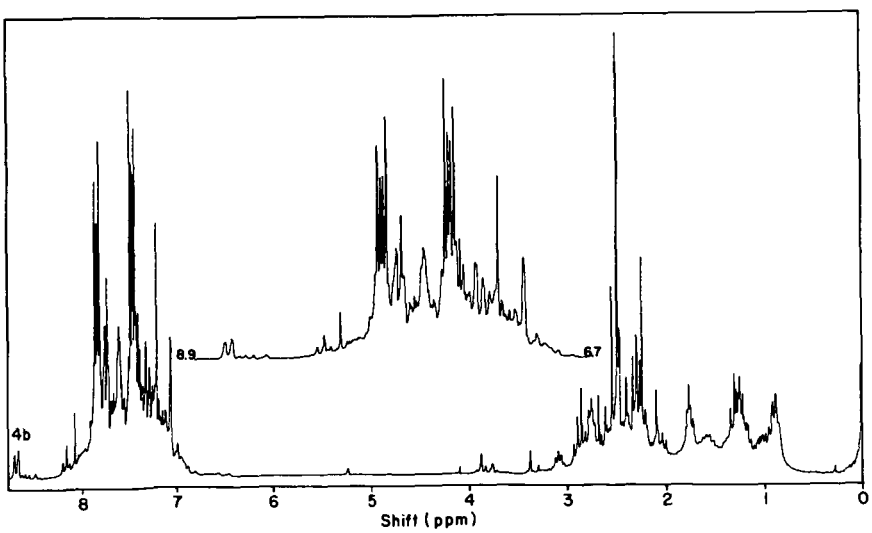
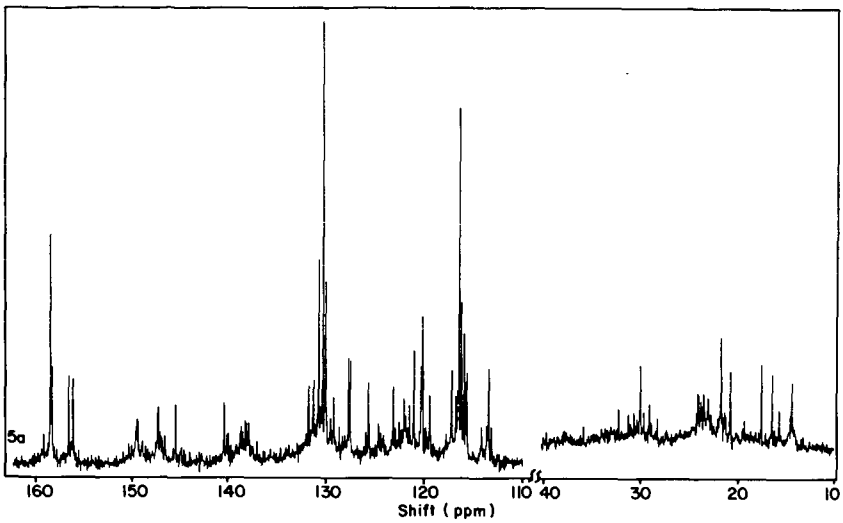


FIGURE 4. - 200 MHz ^{1}H NMR of light oil 28-14, a) phenolic fraction, b) heteroaromatic fraction



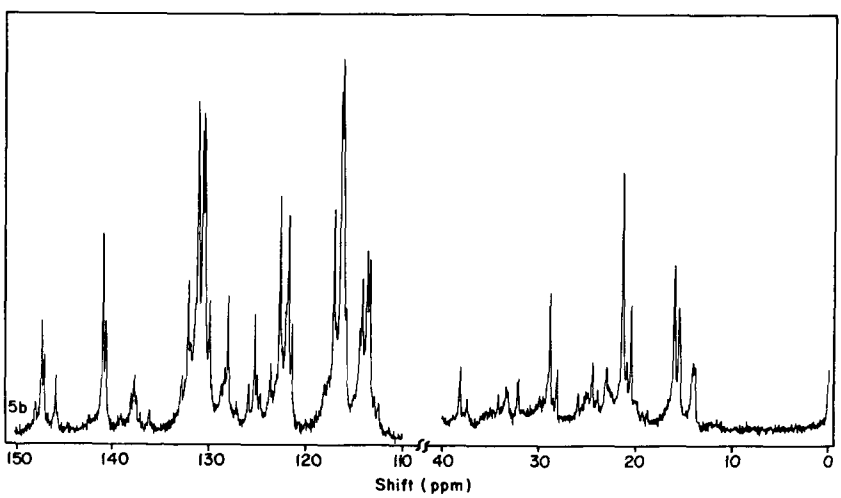
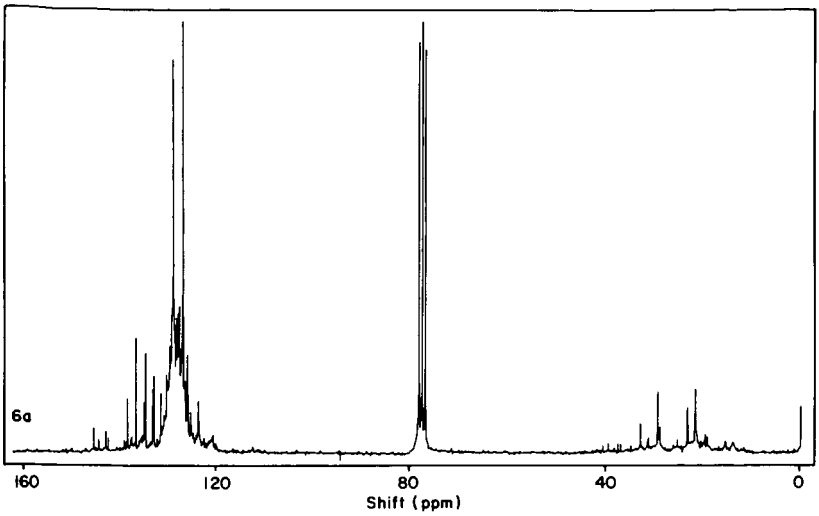


FIGURE 5. - 50 MHz ^{13}C NMR of the aliphatic and aromatic regions of light oil 28-14 (without NOE, $Cr(AcAc)_3$, $CDCl_3$), a) basic fraction, b) phenolic fraction



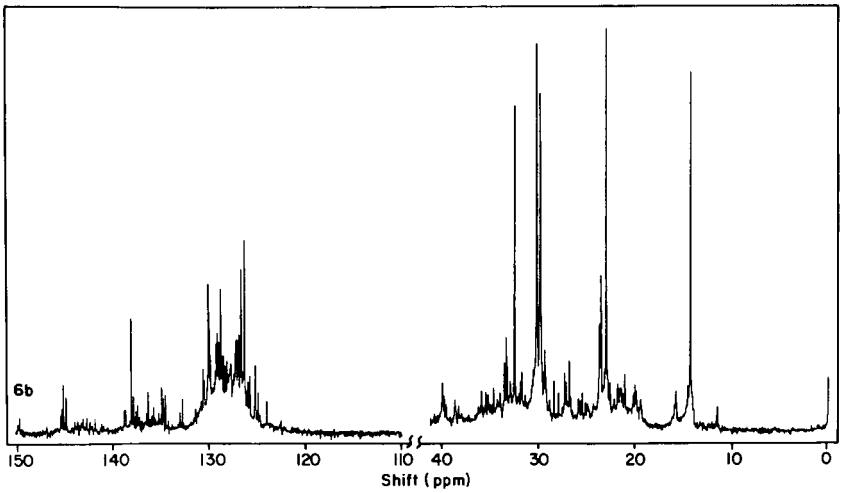


FIGURE 6. - 50 Mz ^{13}C NMR, a) of the heteroaromatic fraction, completely proton decoupled in $CDCl_3$, b) aliphatic and aromatic regions of the hydrocarbon fraction (without NOE, $Cr(AcAc)_3$, $CDCl_3$), of light oil 28-14

ORGANIC STRUCTURAL STUDIES OF LIGNITE COAL TARS

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INTRODUCTION

The Grand Forks Energy Technology Center is operating a 900 kg/hr slagging fixed-bed gasification pilot plant. The pilot plant was installed in 1958 and was first operated until 1965 (1). The renewed interest in producing synthetic natural gas and the environmental concerns associated with commercial-scale gasification facilities led to resumption of operations of the Grand Forks gasification pilot plant in 1976. A major objective of the renewed gasification program was to utilize the gasifier to acquire environmental assessment data for a variety of low-rank coals (2). Of particular interest was the identification and characterization of effluents. It has been shown that tar composition can be correlated with the chemical properties of the lignite gasified (3). A detailed understanding of the chemical composition and structure of effluents, such as coal tar, is of two-fold importance. First, such understanding, when coupled with information about reaction conditions such as temperature and partial pressure of hydrogen, provides clues for deducing structural relationships in the lignites. Second, knowledge of the tar composition also provides guidance for designing down-stream effluent treatment or by-product recovery unit operations.

A previous publication (4) presents data on the low-voltage mass spectrometric analysis of nine tar samples, obtained from the gasification of four low-rank coals at a variety of gasification conditions. Extensive statistical analysis of the data, similar to that presented here, showed that the major factors affecting on tar composition are the partial pressure of hydrogen and the residence time of the coal in the gasifier. These results agree with conclusions developed in other laboratories (5). The success obtained in deriving these relationships from the mass spectrometric analyses and the agreement with known behavior of other systems led to the present study in which attention was focused on two tar samples obtained from the gasification of similar lignites under identical conditions. The results reported here are compared with data from other laboratories to suggest relationships between tar composition and possible structural features in the parent lignites.

EXPERIMENTAL

Sample Preparation

Samples of as-received gasifier tar were distilled at reduced pressure to remove water and volatile light oils. Saturate determinations were performed by column chromatographic elution with hexane from neutral alumina. Fractions for high resolution mass spectroscopic analysis were prepared by a method previously described (6).

Mass Spectrometry (HRMS and LVMS)

The instrument used was an AEI MS-30* single-beam high-resolution mass spectrometer interfaced with a DS-50 data system. Approximately 1 mg of gross sample or of column chromatography fractions was introduced into the mass spectrometer using an all-glass heated inlet system operating at 300°C. Source temperature was 300°C, the ion source pressure was $2.0\text{-}2.7\times10^{-4}$ Pa and the ionizing

voltage was 70 eV. A medium resolution spectrum (8000-9000 resolving power) was obtained for each fraction and for the gross sample for molecular formula assignment.

Quantitative data was obtained by lowering the ionization potential to 10 eV (7) and decreasing the resolution to 1500. A minimum of six scans are averaged and calibration with known hydrocarbons, oxygen compounds and nitrogen compounds was used to calculate concentrations from the low-voltage intensity data.

Gas Chromatography - Mass Spectrometry (GC-MS)

Materials were analyzed by GC-MS using a Varian 2740 gas chromatograph coupled with a DuPont 21-491B mass spectrometer. A 1.2 m x 2 mm i.d. glass column packed with 3% OV-17 on 80/100 Supelcoport was used for compound separation. The helium carrier gas flow rate was 30 ml/min and the column temperature was programmed from 70-300°C at 6°C/min. GC peak areas were determined using a Spectra Physics System I computing integrator and response factors were measured with appropriate pure standards. The ion source was at 250°C and ionizing voltage was 70 eV.

* Reference to specific brand names or models is done to facilitate understanding and neither constitutes nor implies endorsement by the Department of Energy.

RESULTS AND CONCLUSIONS

The mass spectrometric analysis of tars from the gasification of two North Dakota lignites, Indian Head (IH) and Baukol-Noonan (BN), provide the basis for this study. The as-received proximate analyses of these coals are nearly identical as shown in Table 1. The ultimate analyses, also shown in Table 1, indicate that Indian Head lignite has a much lower carbon/hydrogen atomic ratio than does Baukol-Noonan lignite, 1.2 and 2.3 respectively. However, the maf oxygen and nitrogen content of these coals are nearly identical. The operating conditions for gasification of the two lignites were nearly identical: 2.1 MPa operating pressure, 170 m^3/hr oxygen feed rate, 1.0 oxygen/steam molar ratio, and 41 minutes average coal residence time. The two tests from which these samples were obtained are RA-52 (IH) and RA-66 (BN) in the current gasification program. Details of these tests have been published elsewhere (8).

Table 2 gives the low-voltage mass spectrometric carbon number data for the aromatic portion of Indian Head (35%) and Baukol-Noonan (37%) tars. Comparison of the tar analyses indicate several trends. Baukol-Noonan

TABLE 1. - Analyses of coals gasified

	Indian Head lignite Mercer Co Central, ND	Baukol-Noonan lignite Burke Co Northwest, ND
Proximate analyses, % as rec'd		
Moisture[1/]	29.1	32.6
Volatile matter	28.0	26.5
Fixed carbon	34.7	34.6
Ash	8.2	6.3

Ultimate analyses, % maf		
H	4.8	2.7
C	70.8	73.7
N	0.9	0.9
S	1.8	0.7
O (by difference)	21.7	22.1

1/ These values do not represent as-mined moisture because of partial drying during storage and handling.

tar contains generally larger amounts of compounds with no substitution and larger amounts of two-, three-, and four-ring compounds. Indian Head tar generally tends to have more one-ring compounds. Table 3 shows some of the comparisons.

Indian Head and Baukol-Noonan tar analyses were compared with data obtained by Hayatsu and co-workers (9). They reported the results of gas chromatographic analysis of the hydrocarbon-rich fraction of 3:1 benzene/methanol extraction of Decker lignite. Their chromatograms identified approximately 25 compounds isolated from the lignite extract. The mass spectrometric analysis of the gasifier tar contains 17 of the same compound types, based on Z number and molecular weight matches. The major difference between the lignite extract and the gasifier tar is that the latter lacks the highly substituted compounds, such as C_{10} benzenes or C_5 tetralins. This difference is expected when conditions under which the samples were produced are taken into account since it is generally considered that aliphatic side chains are vulnerable to thermal cleavage during coal tar formation (10).

Ranking compounds in gasifier tar by quantity found provides a correlation with published data for the thermal stability of various polynuclear aromatic hydrocarbons. Sharkey and co-workers (11) determined the thermal stability of 20 compounds from the product ratio of the liquid-phase pyrolysis of polynuclear aromatic hydrocarbons. Table 4 shows the comparison between the published thermal stability ranking and quantities observed in Indian Head gasifier tar.

In general, only those compound types that could be identified unambiguously are included in the table. For example, compounds with a Z number of -16 may be fluorenes or acenaphthalenes; and therefore are not included in the table. An exception is 2,6-dimethylnaphthalene (Z= -12, MW=156); although an unambiguous assignment was not made, the 2,6-isomer is reported to be more stable than some other dimethylnaphthalenes (12) and is one of only two isomers reported in low temperature carbonization tar in an extensive compilation (13). The similarity of tar from the GFETC gasifier to that of other low-temperature carbonization processes has been shown previously (14).

Since unequivocal identifications were not made as a part of the study reported here, no attempt was made to correlate these compounds with other data. The Spearman rank correlation (15) found for this ranking was 0.725; a value of this magnitude could occur by chance with less than 0.01 probability.

The tar samples used in this study were chosen from tests at identical gasification conditions to eliminate the effects of operating conditions on tar composition which have been reported previously (16). The major difference between the two lignites, carbon/hydrogen ratio, indicates that Baukol-Noonan has a more aromatic nature than does Indian Head lignite. Thermal cracking of these coals during gasification results in distinctly different tars. Baukol-Noonan lignite produces a more aromatic tar, presumably as a result of the initial loss of smaller aliphatic units during carbonization. An indication of this reaction may be the greater amounts of methane produced during the gasification of Baukol-Noonan lignite as compared to Indian Head lignite (Table 5). It has been shown previously

TABLE 2. - Low Voltage Mass Spectrometric Analysis of the Aromatic Portion of Indian Head and Baukol-Noonan Tars

Probable Structural Type	Z#	Carbon Number 6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	Total
Benzenes	-6	0.04	0.17	0.22	0.40	0.00												0.83
		0.02	*0.16*	*0.18*	*0.33*	*0.00*												*0.69*
Indanes/Tetralins	-8				0.07	0.71	1.27	1.05	0.69	0.40								4.19
					0.14	*0.65*	*0.94*	*1.00*	*0.78*	*0.48*								*3.99*
Indenes	-10				0.00	0.32	0.00											0.32
					0.05	*0.24*	*0.00*											*0.29*
Naphthalenes	-12					3.00	2.16	1.34	0.98	0.87	0.66	0.46	0.31	0.24				10.03
						0.58	*1.23*	*1.18*	*1.10*	*1.17*	*0.98*	*0.65*	*0.45*	*0.31*				*7.65*
Acenaphthene/Biphenyl	-14					0.83	0.62	0.48	0.37	0.24	0.16	0.11						2.81
						0.92	*0.74*	*0.61*	*0.49*	*0.32*	*0.23*	*0.15*						*3.46*
Fluorene/Acenaphthalenes	-16							2.01	2.86	0.69	0.43	0.39	0.25	0.21	0.18			7.02
								1.76	*3.03*	*0.92*	*0.61*	*0.51*	*0.36*	*0.26*	*0.22*			*7.67*
Phenanthrene/Anthracenes	-18									2.28	0.91	0.61	0.33	0.31	0.21	0.13		4.78
										3.23	*1.24*	*0.89*	*0.60*	*0.55*	*0.30*	*0.16*		*6.97*
Pyrenes/Fluoranthenes	-22											1.81	0.58	0.25	0.16	0.08		2.88
												2.45	*0.83*	*0.36*	*0.19*	*0.12*		*3.95*
Chrysenes	-24													0.59	0.23	0.14		0.96
														0.76	*0.29*	*0.16*		*1.21*
Benzopyrenes	-28															0.93	0.26	1.19
																0.94	*0.25*	*1.19*

Indian Head
Baukol-Noonan

TABLE 3. - Comparison of Indian Head and Baukol-Noonan tars

	Z#	Mass	IH (%)	BN (%)
1 Ring				
	-6	92	0.2	0.2
		106	0.2	0.2
		120	0.4	0.3
	-8	132	0.7	0.6
		146	1.3	0.9
		160	1.1	1.0
	-10	130	0.3	0.2
2 Ring				
	-12	128	3.0	0.6
		142	2.2	1.2
		156	1.3	1.2
	-14	154	0.8	0.9
		168	0.6	0.7
		182	0.5	0.6
	-16	152	2.0	1.7
		166	2.8	3.0
		180	0.7	0.9
3 Ring				
	-18	178	2.3	3.2
		192	0.9	1.2
		206	0.6	0.9
4 Ring				
	-22	202	1.8	2.4
		216	0.6	0.8
	-24	228	0.6	0.7
		242	0.2	0.3

TABLE 4. - Comparison of thermal stability with observed quantity in Indian Head tar

Thermal stability ranking		Quantity observed in Indian Head tar	
Compound	Rank	Quantity	Rank
Naphthalene	1	3.00	1
Pyrene	2	1.81	3
Chrysene	3	0.59	8
2 - Methylphenanthrene	4	0.91	5
Acenaphthene	5	0.83	6
1 - Phenylnaphthalene	6	0.47	10
2,6 - Dimethylnaphthalene	7	1.34	4
α - Methylnaphthalene	8	2.16	2
1,2 - Diphenylethane	9	0.48	9
Dihydroanthracene	10	0.69	7
1 - (o-tolyl) - Naphthalene	11	0.31	11
Indene	12	0.00	13
Indane	13	0.07	12

TABLE 5. - Analyses of hydrocarbons in product gas

Component (%)	IH	BN
CH_4	5.1	6.0
C_2H_4	0.2	0.2
C_2H_6	0.3	0.3
C_3H_6	0.1	0.1
C_3H_8	0.0	0.0
C_4H_{10}	0.0	0.0
Total HC's	5.7	6.6

(17) by two-sided comparison of the means that the difference is statistically significant at the 95% confidence level. Conversely, Indian Head lignite, a more aliphatic coal, produces a tar consisting of primarily small and highly substituted aromatic compounds. This is possibly due to cleavage of hydro aromatic units in the coal at methylene bridges and reactions with available hydrogen.

The good correlation between the quantities of compounds in Indian Head tar and the thermal stabilities of those compounds indicates that the organic units found in the tar are the survivors of thermal degradation processes in the gasifier. At the same time, however, the relationships between the compound types in the tar and those obtained from mild solvent extraction conditions suggest that the molecular structures in the tar are determined not only by thermal processes but also by structural relationships in the parent lignite.

Since tar structures very likely reflect coal structures, differences in the tar analyses can be related to structural differences in the coals. The development of an understanding of the effect of the molecular frameworks in coal and the likely mechanisms of tar formation will assist in assessing and predicting the chemical nature of such effluents.

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THE DISSOLUTION OF LIGNITE IN ANHYDROUS LIQUID AMMONIA

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INTRODUCTION

The rapid depletion of gaseous and liquid fossil fuels has focused attention on the problems associated with using the existent vast quantities of coal-substances for equivalent purposes, e.g. the production of energy and as a source of useful carbon compounds. Although our primary interest here is in the latter area, the ideas presented may have useful implications in certain aspects of the former.

The general strategy involves using the unusual solvent properties of liquid ammonia as a means to solubilize relatively large fractions of coal-substances at low temperatures and thereby providing (1) a method of obtaining potentially useful carbon-containing compounds directly and (2) information on the chemical nature of the original coal-substance.

The Chemical Nature of Coal-Substances

It is generally conceded that coal-substances originated primarily from plants through a series of evolutionary changes. The plant matter is transformed sequentially into humic acid, peat, lignite, subbituminous coal, bituminous coal, and anthracite. During this series of transformations, the carbon content increases while the oxygen content decreases. The precise chemical composition of coal-substances is unknown (indeed it may be unknowable in the chemical sense) because it may be derived from a variety of sources by numerous combinations of physical and/or chemical processes which lead to a nearly continuous variation of mixtures of carbon-containing (1) compounds. Nonetheless, a combination of techniques has led to the identification of broad classes of compounds present in coal-substances; viz., waxes, resins, terpenes, cellulose, protein, flavonoids, tannins, lignins, alkaloids and sterols as deduced from solvent extraction studies, (2) precursors of the heterocycle nitrogen bases, obtained by vacuum distillation of coal tar, (3) and humic acids (4). A large portion of carbon present in coal occurs in the form of saturated 6-membered condensed ring systems (napthenes) linked together by oxygen bridges (4). Chemical analysis involving a variety of standard methods (5) has shown that coal-substances contain -OH groups (predominantly as phenolic units), carboxylic (as metal salts), ether, and carbonyl groups in varying proportions depending upon the rank of the sample; nitrogen (6) is believed to exist almost completely in cyclic structures whereas sulfur (6d, 7) appears as thioethers (-S-) or bis thioethers (-S-S-) groups. A model structure (8) for the coal-substance which summarizes the relationship among the known functional groups, consists of 6-7 aromatic ring clusters held together by saturated carbon chains (1-4 atoms long), ethers, sulfides, disulfides and bipheyl groups; the model suggests a predominantly 2-dimensional structure in the vicinity of the 6-7 aromatic rings, but the individual aromatic sections are not necessarily co-planar.

The Solvent Properties of Liquid Ammonia

Solubility in a two-component system involves a consideration of the attractive forces which exist between solute and solvent, solvent and solvent, and solute and solute; the attractive forces in the first instance favor the solubility of one substance in another, whereas the last two types of interactions oppose solubility. Because of its moderate dielectric constant, high dipole movement, ability to hydrogen bond, and relatively high basicity, liquid ammonia is a remarkably versatile solvent (9). The potential of ammonia to react with certain functional groups to produce soluble products also provides an additional advantage in the solubilization processes.

A consideration (9) of the polarity of the ammonia molecule as well as the dispersion forces generated by it suggest that ammonia should be a good solvent for covalently bound polar groups. In addition, arguments (9) based on internal pressure considerations (10) indicate that aromatic hydrocarbons and molecules containing polarizable atoms should exhibit a reasonable degree of solubility in liquid ammonia. Molecules which contain highly polar functional groups such as the carbonyl moiety (aldehydes, ketones, acid amides, and esters) that can interact strongly with the solvent dipole might be expected to interact strongly with ammonia. In addition, an enhancement of solubility would be expected in the presence of groups which can form hydrogen bonds to ammonia ($X\text{-}H \cdot \cdot NH_3$, e.g. alcohols, primary, and secondary amines) or be hydrogen-bonded by ammonia ($X \cdot \cdot \cdot HNH_2$, e.g., ethers, tertiary amines, oxygen functions, and nitrogen heterocycles). Lastly, molecules possessing acidic hydrogen atoms such as carboxylic acids or phenolic groups react with liquid ammonia to form ammonium salts which should be soluble in liquid ammonia.

The solubility principles developed here are illustrated by the data summarized in Table 1; these data are selected examples of a more extensive series available (9).

It is from this point of view that we decided to investigate the possibility of dissolving substantial fractions of coal substances in liquid ammonia under mild conditions using Rockdale (Texas) lignite for our preliminary experiments.

EXPERIMENTAL

The apparatus used for extraction of Rockdale (Texas) lignite with pure liquid ammonia is shown in Figure 1. The lignite ground to 100 mesh is placed in a Whatman extraction thimble which is then sealed by a staple. Sealing the extraction thimble prevents accidental mixing of the solid, unextracted lignite with ammonia. The thimble is placed in a conventional Soxhlet extractor; a condensing Dewar placed on top of the Soxhlet extractor and an empty flask placed below. The entire apparatus is purged with anhydrous gaseous ammonia; then a dry ice slush is added to the Dewar condenser on top, allowing the ammonia to condense and drip from the Dewar condenser onto the sample in the thimble. As extraction continues, an insulating layer of ice condenses on the outside of the apparatus. After six to ten hours the extraction is complete (25% by weight) for ca. 100 mesh samples. Extraction was conducted on samples weighing up to 50 grams.

After extraction of the lignite was complete, the precipitated tar from the ammonia solution, and the brown-black ammonia solution were let stand in air until only solid residue remained. The lignite remaining in the extraction thimble (75%) we term "treated lignite", whereas that which dissolved in the ammonia we term the ammonia extract.

Proton magnetic resonance spectra on d_6-DMSO solutions of the ammonia extract were obtained using an NT200 spectrometer.

Infrared spectra of the samples prepared as KBr pellets were obtained with both Beckman IR5A and Beckman IR9 spectrometers.

Elemental analysis was conducted at Schwarzkopf Microanalytical Laboratory, Inc.

OBSERVATION AND RESULTS

The addition of ammonia gas to the system described in Figure 1 led to warming of the lignite sample. Later, when the first drops of liquid ammonia fell on the lignite, the outside of the Soxhlet extractor became quite hot. It was at this time that spattering of the lignite sample took place in open extraction thimbles which led us to the current method of sealing the thimbles. After about 10-20 minutes, the Soxhlet extractor was cooled by the liquid ammonia to below room temperature.

An extraction was attempted at room temperature using a pressure bomb. After several days, the mixture was filtered at room temperature, yielding 26% extract and 74% solid residue (treated lignite). Whereas the solid extract obtained from extraction at -33°C was a brown powder; the solid obtained at room temperature was black and lustrous. However, when the -33°C ammonia extract was dissolved in DMSO, which was then allowed to slowly evaporate, the appearance of the resulting product was identical to the room temperature reaction.

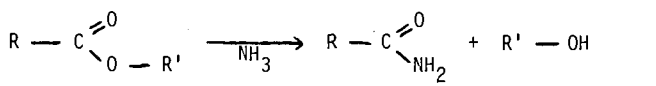
Preliminary GC-mass spectroscopic data indicated that the DMSO soluble extract contains well over 100 compounds, none of which could be resolved sufficiently for identification. Proton magnetic resonance spectroscopy revealed absorptions at 7.5, 1.2 and 0.9 τ (downfield from TMS). The ratio of the area of the 7.5 τ absorbance to the sum of the areas of the 1.2 τ and 0.9 τ absorbances, which is usually assigned as the ratio of aliphatic to aromatic protons, was ~1.3 for the ammonia-soluble fraction.

Elemental analysis (Table 2) suggests that at least some components in the lignite react with liquid ammonia, since both the extract and the treated lignite exhibit increased nitrogen content as well as increased atomic H/C ratios. The increased content of sulphur in the extract suggests preferential extraction of those portions of the lignite with a high hetero-atom content.

The solubility behavior of the treated lignite and the ammonia extract shows gross differences from the solubility behavior of the untreated lignite. The untreated lignite and treated lignite are not totally soluble in any solvent attempted, but they are both partly soluble in pyridine. The treated lignite has enhanced solubility in DMSO and dimethylformamide, which are considered good solvents for high molecular weight substances. The ammonia extract is at least partly soluble at room temperature in all solvents tested except water.

DISCUSSION

As mentioned in the introduction, one important consideration in these experiments is the solubility characteristics of functional groups in ammonia. We might expect that the lower rank coal-substances like lignite, which have a higher oxygen content, presumably in the form of functional groups that enhance solubility, would have a moderate solubility in ammonia. Another consideration is the ability of ammonia to react with certain functional groups, breaking a large unit into two smaller moieties. For example, ammonia reacts with esters (12) to create alcohols and amides (scheme 1) both of which should exhibit high ammonia solubility. If esters, or



1)

similar compounds, are constituents of coal, ammonia will react, breaking the coal into smaller fragments. A recent study (11) on Texas lignite showed that hydrogenation of this coal-substance provides phenols, thus supporting the possibility that some of the linking groups in Rockdale (Texas) lignite are esters or ethers. Further support can be inferred from the observation that a saturated DMSO solution of the ammonia extract is more highly colored than a saturated solution of untreated lignite in DMSO. This observation implies that upon extracting with ammonia reactions took place, changing the nature of the remaining lignite as well as the ammonia extract, and creating more soluble moieties.

Yasukatsu Tamai and co-workers (12,14) treated bituminous coal with liquid ammonia; no more than 4% of the coal was actually extracted into the ammonia at 100-120°C. It is interesting to note that the coals they used had atomic hydrogen to carbon ratios of from 0.55 to 0.98. The ammonia extract always had a significantly higher atomic H/C ratio, whereas the treated coal maintained approximately the same

H/C ratio as the untreated coal. The same general trends are found for our lignite experiments (Table 3), although lignite has a much higher H/C ratio, thus perhaps explaining the greater amount extracted by ammonia. It should be noted that our method provided continuous extraction of 100 mesh particles whereas Matida, et.al. (13) extracted larger particles by 5 successive contacts of pure ammonia for one hour each. A priori, our method would be expected to extract more than this even at the lower temperature involved, but not as great a deviation as is observed. The difference must be accounted for in the chemical difference between lignite and bituminous coal.

There are similarities to our lignite-ammonia extract and the coal-ammonia extracts of Tamai and co-workers; infra-red bands at 3300, 1720 and 1660 cm^{-1} are characteristic of the ammonia extract obtained from coal. In our experiment the methanol soluble portion of the extract has broad bands at 1640 cm^{-1} with a shoulder at 1700 cm^{-1}, and 3400 cm^{-1} with a shoulder at 3200 cm^{-1}; the C-H streaches are all below 3000 cm^{-1}. The ammonia extract itself had a strong band at 1380 cm^{-1}, a small broad band at 1460 cm^{-1}, large broad bands at 1620 cm^{-1} and 1700 cm^{-1}, large bands at 2950-2980 cm^{-1} and a large broad band at 3400 cm^{-1}.

The primary difference in the infrared spectra of the untreated lignite and of the ammonia extract was the growth of the band at 1380 cm^{-1} and a decrease in the ratio of heights of the bands at 3400 cm^{-1} to those at 2950 cm^{-1}, indicating an increase of alkyl group hydrogens to hetero-atom hydrogens in the ammonia soluble portion compared to the treated lignite portion. Of course, the treated lignite portion showed an increase in height of the band at 3400 cm^{-1} relative to the bands at 2950 cm^{-1}.

Even though the infrared results seem to indicate an increase in the aliphatic content of the ammonia extract relative to the OH and NH content, the NMR results indicate more aromatic protons than aliphatic.

CONCLUSION

It is clear that the original lignite structure can be modified and lignite separated into its component moieties by treatment with liquid ammonia. The usefulness of liquid ammonia to better identify lignite components has been demonstrated. The solubility of different coals should be further tested; the identity of the species dissolved in the ammonia should be more explicitly identified. We are currently engaged in both types of experiments.

ACKNOWLEGDEMENTS

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Table 1

Solubilities of Selected
Compounds in Liquid Ammonia

Substance	Solubility	Reference	Atomic H/C
C_6H_6	Moderately Soluble	a	1.00
$C_6H_5CH_3$	Slightly Soluble	a	1.14
$C_6H_5CH{=}CH_2$	Soluble	a	1.00
$C_6H_5CONH_2$	Soluble, 35%	b	1.00
$C_6H_5CH_2CO_2CH_3$	Miscible	b	1.11
$C_6H_5OCH_3$	Miscible	a	1.14
$(C_2H_5)_2O$	Miscible	a,c	2.50
$(C_4H_9)_2O$	Soluble	d	2.25
$C_6H_5NH_2$	Miscible	a	1.17
C_6H_5OH	Very soluble	a	1.00

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Table 2

Solubilities of Lignite[1]

Solvent	Untreated Lignite	Treated Lignite	Ammonia Extract
methyl sulphoxide	I[2]	P	S
pyridine	P	P	S
acetone	I	I	P
methanol	I	I	P
water	I	I	I
chloroform	I	I	P
propylene carbonate	I	I	P
dioxane	I	I	P
acetonitrile	I	I	P
ethylenediamine	P[3]	I	S
nitrobenzene	I	P	P
dimethylformamide	I	P	S

[1]All solubilities except where noted at room temperature. S = totally soluble, ca. 1 mg. in ca. 1 ml; P = solvent becomes colored, but not all of the lignite dissolves; I = no discoloring of the solvent is observed.

[2]If the lignite is maintained in contact with DMSO at 100°C., the DMSO becomes colored. Concentrated solutions of the soluble lignite in DMSO are much less colored than concentrated solutions of the ammonia extract in DMSO.

[3]Lignite appears to react with ethylenediamine.

Table 3

Elemental Analysis

Samples	C	H	N	S	Ash	Atomic H/C
Rockdale lignite[1]						
Untreated lignite[2]	51.70	4.85	1.03	1.27	12.0	1.12
Treated Lignite[2]	53.37	5.18	2.71	1.72	11.8	1.16
Ammonia Extract[2]	46.46	5.36	4.45	2.74	9.0	1.37
Mazachi coal[3]						
Untreated coal	83.9	6.9	1.5	-	-	0.98
Treated coal[4]	83.0	6.0	1.9	-	-	0.86
Ammonia Extract[5]	87.2	10.1	1.4	-	-	1.38

[1]Rockdale (Texas) lignite has been reported to contain up to 30% oxygen.

[2]Analysis by Schwarzkopf Microanalytical Laboratory.

[3]M. Matida, Y. Nishiyama and Y. Tamai, Fuel 1977, 56, 177.

[4]One hour in liquid ammonia at 120° C.

[5]One hour contact with untreated coal.

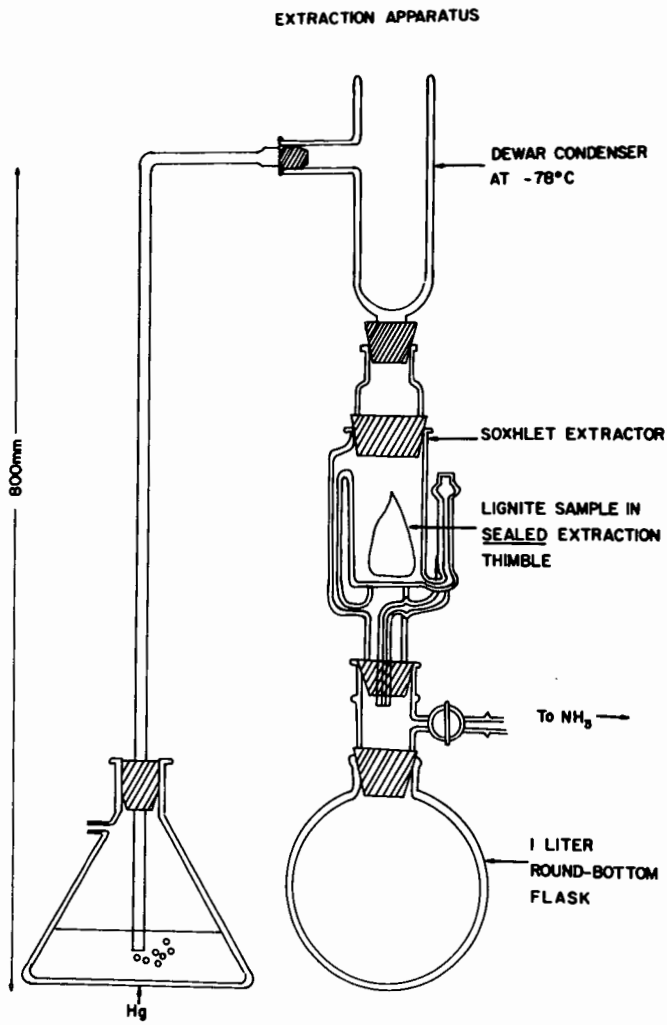

FIGURE 1. The apparatus used for extraction of Rockdale (Texas) lignite.

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PEAT BENEFICIATION AND ITS EFFECTS ON DEWATERING AND GASIFICATION CHARACTERISTICS.

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In its natural state peat contains up to 90 weight percent water. Traditional methods of dewatering such as filtration and drying are unacceptable for large-scale peat utilization on an economic and technical basis. Wet-carbonization, a chemical pretreatment method using peat-water slurry, facilitates dewatering of peat in the effluent slurry by conventional pressure filtration. Decarboxylation and dehydralization reactions during wet-carbonization yield a beneficiated product which has higher energy value than the raw peat.

A wet-carbonization study, being performed at the Institute of Gas Technology with financial support from the Minnesota Gas Company and the U.S. Department of Energy, will determine the effects of wet-carbonization parameters (temperature, pressure, and reaction time) on the dewatering and gasification properties of the beneficiated peat. Peat from Minnesota, Maine, and North Carolina will be tested. The study will investigate the effects of reaction conditions upon the 1) energy value, 2) gasification characteristics, and 3) mechanical dewatering characteristics of wet-carbonized peat. One of the goals of the study is to identify wet-carbonization reaction conditions which permit mechanical weight. More severe conditions further enhance the energy value and dewatering characteristics of beneficiated peat, but would adversely affect the thermal efficiency of integrated peat gasification, liquefaction, and direct combustion facilities.

KINETICS AND CORRELATIONS FOR PEAT HYDROPYROLYSIS. S.A. Weil, D.V. Punwani: Inst. of Gas Technology, Chicago 60616; M.J. Kopstein: U.S. Dept. of Energy, Washington, D.C. 20545; and A.M. Rader: Minnesota Gas Company, Minneapolis 55426.

The kinetics and correlations for rate and extent of conversion of peat to carbon oxides and light hydrocarbons during hydropyrolysis have been extended to cover North Carolina and Maine peats. The primary variations due to feedstock characteristics can be accounted for in terms of the ultimate yield of each product species. These limiting values can be approximately estimated from the ultimate and proximate analyses of the feedstocks.

The liquid products of hydropyrolysis of Minnesota peat have been analyzed. They are essentially aromatic. Higher temperatures and hydrogen pressures favor the formation of the lighter fractions (i.e., BTX) both relatively and absolutely. The heavier compounds as well as phenols and pyridines are reduced with the greater severity.

EXPERIMENTAL INVESTIGATION OF PEAT HYDROGASIFICATION. W.S. Hines, L.P. Combs, and F.D. Raniere. Rockwell International, 8900 DeSoto Avenue, Canoga Park, California 91304.

This paper describes a series of experiments sponsored by the Department of Energy in which dried, pulverized Minnesota peat was hydrogasified in an engineering-scale (3/4 TPH) hydrogasifier system designed for pulverized coal feed. Pulverized carbonaceous solids are fed in dense phase (i.e., minimum transport gas) to the Rockwell 3/4 TPH entrained-flow hydrogasifier where they are very rapidly and thoroughly mixed with a high temperature hydrogen stream. The hot hydrogen heats and pyrolyzes the individual solid particles. Reactor operating pressure and temperature, together with reactant feed rates and residence time, are varied to achieve a desired performance, viz., overall carbon conversion and relative distribution of converted carbon among gaseous and liquid products.

Very interesting and promising hydrogasifier performance has been experienced with peat. Overall carbon conversion levels, substantially higher than previously observed with coals under comparable conditions, ranging to as high as 84.2%, were previously reported. This paper is an update of the continuing peat hydrogasification test program being conducted by Rockwell International. Overall conversion is measured with respect to reactor temperature, residence time, and pressure. Reactor conditions will be optimized to permit the most economical conversion of peat to substitute natural gas.

Detailed results of the peat hydrogasification experiments are presented and discussed. Included are comparisons with other investigators' findings.

DEVELOPMENTS IN PEAT BIOGASIFICATION. M.G. Buivid, D.L. Wise, Dynatech R/D Co., Cambridge, MA 02139, A.M. Rader, Minnesota Gas Co., Mineapolis, MN 55426, M.J. Kopstein, U.S. Dept. of Energy, Washington, DC 20545.

A four-phase development program is underway to confirm that biogasification is a technical and economical process for the conversion of peat into pipeline quality methane (SNG). The biogasification of peat is based on a two-stage process. In the first processing stage (assumed to follow hydro-mining) an oxidative pretreatment of peat breaks down the lignocellulosic structure to soluble, low molecular weight acids, wood sugars, and other soluble organic fragments. Unreacted peat solids are separated while the recovered liquid, containing the soluble organic material is converted to methane and carbon dioxide by conventional anaerobic fermentation in the second stage of the process. Phase I was a preliminary experimental investigation which indicated that a substantial percentage of the energy value in the solubilized peat from the first stage was fermented to methane in the second stage. Phase II was a preliminary process design and economic analysis that showed a 75 billion BTU/day peat biogasification plant to be cost competitive with other sources of natural gas. Presented are the details of the 8-month Phase I and II study. Phase III, which started October 1979, co-funded by Minnesota Gas and the U.S. Dept. of Energy, will optimize a continuous multistage bench scale biogasification process (18-month program). The objective is to provide scale-up data necessary for a process development unit (PDU) of approximately 1 ton/day (Phase IV). A significant advantage of the biogasification process appears to be that technical difficulties of dewatering necessary for peat utilization in conventional gasification or direct combustion, are eliminated.

ENHANCED REACTIVITY OF METAL-IMPREGNATED PEAT CHAR AND SEMICOKE DURING GAS PHASE HYDROGENOLYSIS

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INTRODUCTION

Chars and semicokes of different origins show a definite although moderate reactivity in hydrogenolysis and hydrogenation reactions. Early studies have substantiated this fact (1 - 3). This situation is in contrast with the low of reactivity of ordered structures (graphite) as it has been documented by Walker et al. (4). Our attention has focused on the reactivity of peat char and semicoke and more precisely we have tried to improve the hydrogenolysis and hydrogenation of these materials by addition of metals in rather massive amounts (about 15% by weight using the ion exchange properties of humic materials). This follows our previous work on the preparation of finely dispersed metals on peat char and semicoke (5). It was felt that by a proper combination of metal characteristics, dispersion and operating conditions increased amounts of methane could be produced from our preparations even at pressures near atmospheric.

Former work on metal catalyzed hydrogen-char reactions has shown the importance of pretreatment conditions (6). Accordingly our study starts with some considerations on the peat char pretreatment followed by a study on the hydrogen-char reaction with and without addition of metals. Iron, nickel and cobalt have been considered as would-be catalysts for this reaction. The overall reactivity study was carried out using thermogravimetric methods.

EXPERIMENTAL

The impregnation and the carbonization conditions used were developed in our former study (5). By ammoniation of the peat prior to impregnation the amount of metal which can be incorporated in the peat structure is quite significant. In the present work preparations having 16.1% Ni, 14.9% Co and 17.9% Fe (weight percentage of anhydrous peat) have been achieved. After carbonization of the peat-metal preparations at 540°C specific surface areas of 365, 224 and 364 m^2/g have respectively resulted. The surface area of the carbonized peat (without any metal added) is only 69 m^2/g. Yields upon carbonization are of about 40%. The non-impregnated peat char contains 0.02% Fe either as pyrite or oxide.

The devolatilization and H_2 reactivity studies have been carried out in a Mettler thermobalance. 200 to 300 mg of sample were used for each run. Temperature programming was conducted between 2°C/min and 10°C/min with most runs at 4°C/min. H_2 and He flow rates were of 60 mℓ/min. Both gases were purified by passage through a molecular sieve and a Deoxo unit prior to introduction in the thermogravimetric cell. Atmospheric pressure was used in all the hydrogenolysis experiments. On-stream chromatography allowed intermittent sampling of the gases entering or produced during the reactions.

A typical run consisted of:

a) Introduction of the sample in the thermobalance cell. Heating at 105°C under vacuum and in the presence of helium to eliminate all traces of moisture.

b) Heating under helium up to the desired devolatilization temperature.

c) Return to 20°C under helium, introduction of H_2 and programmed heating up to the desired temperature.

Our criteria for a valid experiment required less than 10% error in the overall material balances.

RESULTS

1. Heating rate effects

Weight losses during hydrogenolysis are strongly influenced by the heating rate. Thus on non-impregnated chars weight losses of 33%, 31.5%, 30.5% and 25.5% accompany heating rates of 2, 4, 6 and 15°C/min respectively for identical devolatilization conditions. On a Ni-doped char the weight losses are of 48% and 33% for 4 and 10°C/min respectively. Two levels of influence seem clear at this point: moderately low heating rates do result in higher overall reacted material as shown in Figure 1 and the presence of the metal enhances considerably the reactivity of the char.

2. Devolatilization studies prior to hydrogenolysis

Pretreatment (devolatilization) of the metal-char preparations has an important influence on further hydrogenolysis: when devolatilization under He is conducted at 750°C, 500°C, 250°C and 150°C, weight losses on further hydrogenolysis with programmed temperature up to 1200°C are 8%, 24.5%, 33.5% and 35% respectively.

During devolatilization under He of the peat chars initially prepared at 540°C only CO_2 and CO appear to be produced. Similar observations had previously been made on graphite where CO requires temperatures of 300°C to be produced (7, 8). With peat chars at temperatures as low as 105°C the presence of CO is easily detected, suggesting weak chemisorption of oxygen and low stability of surface oxides. The higher the temperature of devolatilization, the higher the amount of CO given off and thus the lower the concentration of oxygenated species on the surface. This seems to have a crucial effect on the rate of CH_4 formation upon subsequent hydrogenolysis. Figure 2 illustrates this point. Devolatilization at the lowest temperatures results in higher CH_4 hields. Moreover, the temperature of maximum CH_4 formation is also function of the devolatilization temperature which could be explained by a higher concentration of oxygenated surface species on the samples devolatilized at the lower temperatures.

3. Hydrogen reactivity of non-impregnated peat chars

Even on the samples devolatilized at high temperatures (500°C and 700°C) three major species are detected upon subsequent hydrogen-char reactions. CO_2 appears initially at temperatures around 185°C; it reaches a maximum rate of formation at about 390°C and slowly vanishes at about 500°C. Between 400°C and 500°C, CH_4 and CO begin to appear in such a way that the rise in the rate of formation of CH_4 also corresponds to a rise in the rate of formation of CO. Both species follow similar trends although quantitatively CH_4 is present in larger amounts (a factor of 3 to 4 times larger). This trend suggests that the formation of CH_4 from the reaction between peat char and hydrogen (with no O species externally added as O_2 or H_2O) proceeds via the methanation reaction between CO and H_2 using the O species still present at the surface rather than by direct reaction between the carbon atoms and hydrogen.

4. Hydrogen reactivity of peat chars impregnated with Fe, Ni and Co

The catalytic influence of transition metals has been studied following devolatilization at 150°C. Weight losses upon subsequent hydrogenolysis of the samples by temperature programming (4°C/min) up to 1200°C are as follows: uncatalyzed peat

char, 34%; Fe-peat char, 42%; Ni-peat char, 46.5%; Co-peat char, 84%. The case of cobalt is remarkable since it can be concluded that the hydrogenolysis of the organic matter in the char is nearly complete when taking into account the initial ash content of the char (8.5%).

Figure 3 shows the profiles of CH_4 formation during the hydrogenolysis. The reactivity is defined as $R_s = mg_{CH_4}$ formed x g_{char}^{-1} x min^{-1} in which the g_{char} is taken at any time t during the experiment (and not at initial t = 0). For each of the three chars studied, the CH_4 profile shows two maxima: a low temperature peak (625°C for Co and 650°C for Ni and Fe) and a high temperature peak (1010°C for Co, 1020°C for Ni and 1050°C for Fe). In all three cases there is a marked decrease in the temperature of maximum CH_4 formation relative to the non impregnated char (750°C in this case). Furthermore the second peak is absent in the latter samples.

It is important to notice that both maxima are higher for cobalt impregnated chars than for iron or nickel preparations. Also, the effect of iron is more marked at the higher temperatures. Comparatively to observed literature results the impregnated peat chars do present some unique features as shown in Table 1.

Table 1: Temperatures of maximum rate of methane formation

Metal	Low Temperature Peak (°C)	High Temperature Peak (°C)	Ref.
None	700*		
Fe	650*	1050*, 1020	(9)
Co	625*, 693	1010*, 950	(6), (9)
Ni	650*, 550, 535, 540, 685	1070*, 950, 683	(7), (9) (10), (11)

* - this work

It is interesting to note that the raw peat char and the Fe preparation show a low temperature peak which has not been previously observed on graphite (9). Also the low temperature peak occurs at lower temperatures on the Co than on the Ni chars, contrary to previous observations on graphite. Metal dispersions might be responsible for this behaviour.

To emphasize the distinct behaviour of peat chars, Table 2 shows the percentage of reacted char (% conversion) as a function of selected temperatures. Appropriate literature references have also been included (9, 11).

Table 2: Percentage of reacted peat chars during hydrogenolysis at a programmed temperature of $4^{o}C$/min and 1 atm.

Metal	650°C		750°C		950°C		1050°C	
	(11)	this work	(9)	this work	(11)	this work	(9)	this work
None	0	21	0	26	2	29	8	31
Fe	0	22	0	27	3	33	9	37
CO	0	68	0.1	74	5	76	25	79
Ni	2	20	36	29	7	37	62	41

Differences between literature values used for comparison reflect distinct carbon structures (9, 11). It is important to realize that in all cases, except for Ni, peat chars, impregnated or not, show higher conversion figures at a given temperature. Although differences between the heating schedules might be partly responsible for the observed results, we favor nevertheless an explanation based on the concentration of oxygenated species in the chars. Thus, peat chars contain >10% oxygen. Whereas the carbons used as comparison range from 6.2% (9) to 1.4% (11). Moreover, a unique metal effect is observed in the sense that CO catalyzes the hydrogenolysis reaction in a very efficient way. Such catalytic action could be explained by the state of the metal on the carbon support. In fact X ray studies on the sample have shown that CO is present as a highly dispersed metal not having achieved a definite crystal structure. Ni is present as a crystalline metal wheras Fe is present both as a metal and as a mixture of oxides. Thus it is quite probable that the highly dispersed "amorphous" cobalt acts as a nucleus both for H_2 chemisorption and its subsequent dissociation and also its reaction with surface carbonyls or formed CO to produce methane.

Since the maximum rate of CH_4 formation takes place in between 625°C and 700°C a series of runs was carried out by programming the temperature ($4^{o}C$/min) up to 700°C and letting the chars react at this temperature until no methane was evolved. Maximum reactivity values were very similar to those shown in Figure 3. Total conversions were: 77.5%, 31.0%, 25.0% and 24.5% for CO, Ni, Fe and raw char respectively. The significance of CO in hydrogenolysis of peat chars is thus again emphasized.

Modelling of the conversion vs time profile was attempted using the generalized model put forward by Chornet et al. (12). The parameter $\tau = t/t_{0.5}$ as defined by Mahajan et al. (13) could only be applied to the CO-char preparation since it was the only sample which resulted in f>0.5. The generalized kinetic expression is: $df/dt = kf^{a}(1-f)^{b}$, where f is the conversion; t, the hydrogenolysis reaction time and k, a and b are constant characteristics of a particular reaction. For the CO-peat char sample and using the experimental run in which the temperature is held constant at 700°C a computer simulation yields the following values: $k = 1.65\ min^{-1}$, a = 0.5 and b = 0.4, with a correlation coefficient of 0.95 between the experimental values and those derived from the model. Evidence of the excellent fit for CO is presented in Figure 4. Similar profiles were also obtained for the other samples. No attempt has been done so far to interpret these profiles which

suggest some sort of autocatalytic reaction sequences.

DISCUSSION

Proposed mechanisms of direct CH_4 formation from carbon and hydrogen are numerous (1, 14, 16). The existence of two distinct reaction paths as evidenced from the two peaks observed in the present work on peat chars has also been documented on other carbon supports (1, 8, 9, 17). Its explanation is still a challenging problem. Several authors have suggested that the heterogeneity of the carbon surfaces way be responsible for the presence of two or several peaks during the hydrogenolysis: first the reaction focusses on the amorphous fractions, later on the crystalline sections (7, 9, 17, 8, 18, 11). Dissociation of hydrogen on the surface and further reaction with surface carbon atoms has been mainly proposed as the dominant mechanism (9, 19, 20). Direct reaction between weakened surface carbon atoms and gaseous hydrogen has also been considered (21).

In this study the role of oxygenated species present in the char is of paramount importance. The indications derived from our experiments can be summarized as follows: a) influence of the heating rate on CH_4 formation: a higher rate of CH_4 formation at the low heating rates is a consequence on increased surface reaction times which result in more CO reacted; b) the negative role of higher devolatilization temperatures on the rate of CH_4 formation is a result of a lower concentration of oxygenated surface species; c) the decrease in the formation of CO_2 is accompanied by an increase in CO; and d) the simultaneous presence of CH_4 and CO in the first reaction stage, tends to indicate that CH_4 formation is closely linked to the presence of CO.

A tentative reaction sequence consistent with the observed results can then be suggested as follows:

1- Decomposition of basic surface oxides (carbonyl or ether types) with formation of CO_2 starting at about 150°C, as suggested by Boehm and co-workers (22, 23).

2- Reaction between the CO_2 formed and the char to yield CO as proposed by Shaw (24). Some CO is probably also present as surface carbonyl.

3- Reaction between the surface CO and hydrogen as a true methanation step (25, 26). The in-situ production of steam during this reaction will allow regeneration of the oxygenated surface species via its subsequent interaction with the surface carbon atoms and eventually produce either CO_2 (27) or CO (24, 28). It is during this step that the impregnated metal plays a major role since Fe, Ni and Co are excellent catalysts for the methanation reaction when present in a peat-derived carbon matrix (28).

4- At high temperatures (>>700°C) direct reaction between hydrogen and the char takes place, the metal probably facilitating the dissociation of the incoming hydrogen and its migration toward adjacent carbon atoms for further methane formation.

CONCLUSIONS

In the present study, the gas phase hydrogenolysis of peat chars prepared at about 540°C and previously impregnated with Fe, Ni and Co has been investigated. The following points summarize the main findings of this work:

devolatilization of the char is an important factor for its subsequent reactivity toward hydrogen. The lower the devolatization temperature prior to hydrogenolysis, the higher the rate of methane formation during hydrogenolysis.

- the catalytic effect of the metals is important at two levels: higher conversions to methane and lower temperatures of maximum rate of methane formation.

- the conversion versus time profiles can be very well fitted by the following expression $df/dt = k\ f^a\ (1-f)^b$ suggesting a kinetic sequence closely related to autocatalytic steps.

- the oxygenated surface species play a major role in the methane formation, which probably takes place at the lower temperatures (625-700°C) via reaction between surface CO and chemisorbed hydrogen catalyzed by the metals. Co is the very most active of the metals at this level. At higher temperatures (>>700°C), direct reaction of hydrogen with the surface carbon atoms also seems to occur.

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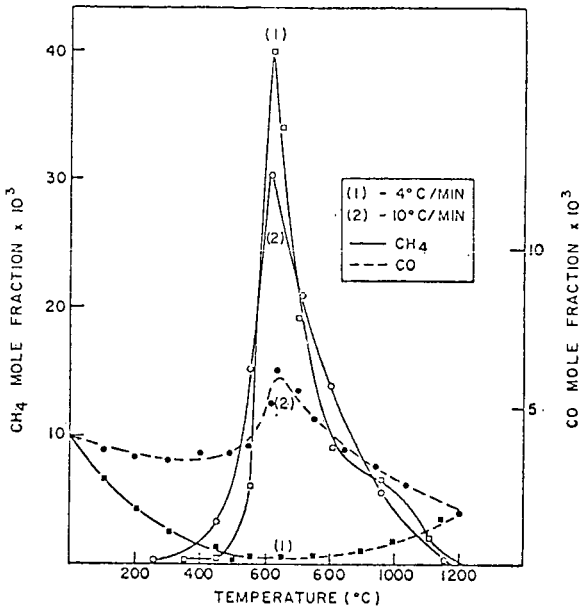

Figure 1 Heating rate effects on Ni-peat char hydrogenolysis as measured by the CH_4 mole fraction in exit gas

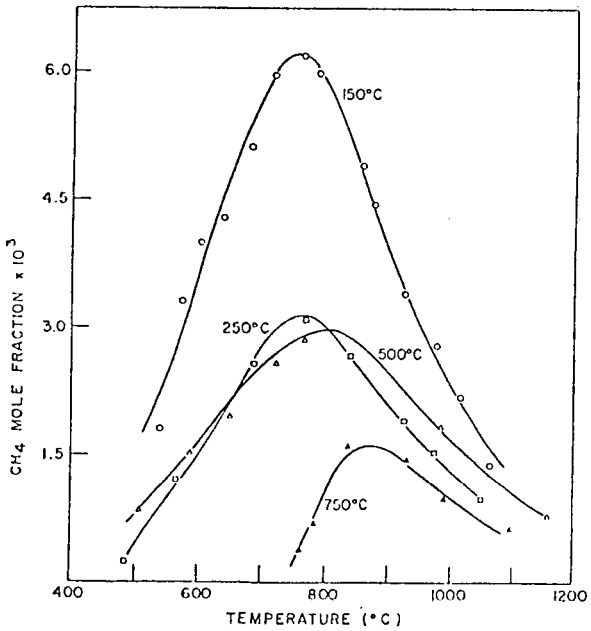

Figure 2 Methane formation during hydrogenolysis of peat char as a function of devolatilization temperature

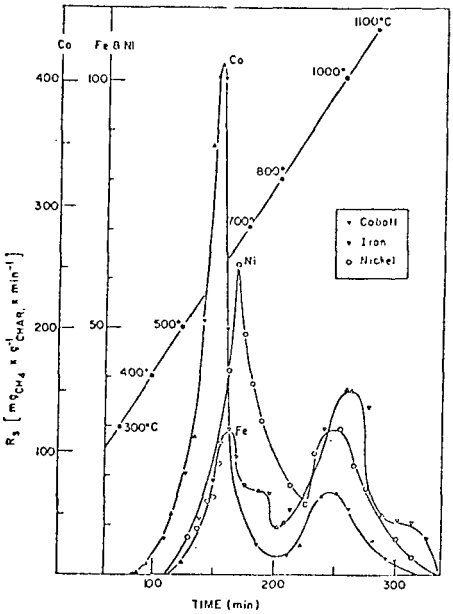

Figure 3 Hydrogen reactivity of metal impregnated peat chars as measured by CH_4 formation

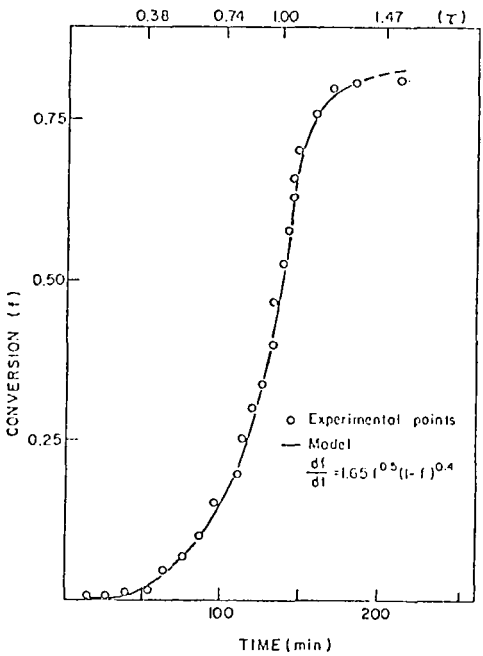

Figure 4 Conversion, f, as a function of time, t, and standardized time $\tau = t/t_{0.5}$ for the hydrogenolysis of Co-impregnated peat chars