

## LOW COST FUEL FROM DEGASIFICATION OF COALBEDS

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### INTRODUCTION

Coalbed degasification can provide significant quantities of low cost fuel with none of the difficult problems associated with other processes for unusual fuel production. The most compelling reasons for coalbed degasification focus on conservation, compatibility, and predictability, but other positive factors such as the use of existing technology, low cost of production, proximity to markets, favorable environmental circumstances, immediate availability, and a resultant enhancement in the ease and safety of producing coal are no less important.

The scientific and technical basis for coalbed degasification as a source of pipeline quality gas has already been established. All that now remains is the refinement of the techniques of gas production from coalbeds and further evaluation of the gas content of the lower rank deep subbituminous coalbeds of the Western States and of the anthracite of eastern Pennsylvania. The current work on coalbed degasification is a natural consequence of a methane control research program initiated by the U.S. Bureau of Mines in 1964 to develop methods of making coal mines safe from explosions of methane-air mixtures.

### GAS CONTENT OF COALBEDS

The gas content of coalbeds, mostly methane, can be directly determined by measurement of samples of freshly collected coal cores ( ). It is becoming clear now that the amount of methane in coal is roughly proportional to the rank of the coal and the depth of the coal. Although most of the studies to date have been conducted in bituminous coals, there is no reason to expect that much of what Mott postulated ( ) about the methane produced during coalification will not be supported by further investigation. Certainly the deeper Pittsburgh, Pocahontas, Beckley, Mary Lee, and Hartshorne coalbeds all contain enough gas to warrant serious consideration.

The composition of coalbed gas is compatible with pipeline quality gas. Kim's report ( ) gives analyses of 13 coalbed gases, only one of which had a heat of combustion less than 900 Btu/ft<sup>3</sup>.

The absence of H<sub>2</sub>S and SO<sub>2</sub> in coalbed gas makes it especially desirable because no special gas scrubbing is required before mixing with other pipeline gas.

### CONSERVATION

The gas in coalbeds, especially in minable coalbeds, will be lost ultimately, unless degasification is practiced. More than 200 million cubic feet a day of methane is lost in the exhaust from bituminous coal mines. Almost all of this gas could be collected for use.

A ton of bituminous coal will yield about 25 million Btu upon combustion. If the average content of 250 ft<sup>3</sup> of gas per ton of bituminous coal were to be recovered, this would amount to a 1 pct increase in our fuel resources for such coals; but since only a fraction of coal in any coalbed is extracted and nearly all the gas can be recovered, the increase in usable resources attributable to the contained gas is more like 3 pct of the produced coal. In an age of declining productivity, a 3 pct increase is indeed significant.

## PREDICTIBILITY

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Coalbeds can be located readily. The major bituminous coalbeds are well delineated and the deeper coalbeds are only now being exploited in this country. The gas content of an entire coalbed can be estimated and the resource base evaluated with only a modest investment as compared with that required for conventional gasfield exploration.

The Bureau of Mines has developed methods for routinely determining the gas content of coalbeds and as our techniques become more refined and a larger data base is established, even less effort will be required to estimate accurately the gas that can be recovered from bituminous coalbeds in the United States.

### USE OF EXISTING TECHNOLOGY

The technology developed by the oil and gas industry can be applied now to produce gas from permeable coalbeds such as the Pittsburgh coalbed in western Pennsylvania and West Virginia, the Mary Lee coalbed in Alabama, and the Beckley coalbed in West Virginia. Gas wells have been producing gas from the Pittsburgh coalbed for many years ( ) on structural highs, much as from favorable gas sands. We know now that such geologic structures are not essential. The gas wells drilled into coalbeds are not very productive initially but with hydraulic stimulation, a well established oilfield technique, productivity can be increased from 5- to 20-fold ( ).

Early experimental work has already shown that it will be possible to produce from more than one coalbed from a single borehole. It is not uncommon for several coalbeds to be found within a few hundred feet of vertical stratigraphic section. Almost all coal-bearing strata contain multiple beds and although multiple seam mining is not common in the United States as it is Europe, it is now being practiced with more frequency in the states of Kentucky, central Pennsylvania, Ohio, and West Virginia.

Even old ideas for producing oil from strata by horizontal drilling is being successfully applied to producing gas from coalbeds. Two notable examples are experiments conducted in the Pittsburgh coalbed by the Bureau of Mines where two sets of horizontal holes drilled radially into the coalbed from shaft bottoms have already produced more than 1 billion cubic feet of pipeline quality gas ( ).

Another technique, widely used by the petroleum industry, for producing oil from offshore oilfields by drilling angle holes from sites on the mainland, has been successfully applied to extracting gas from coalbeds.

The recitation of these successful efforts does not mean that further development work is unnecessary. It means only that refinements in these methods must be sought and that such refinements require no massive investment in research and development.

## THE UNDERGROUND GASIFICATION OF A SUBBITUMINOUS COAL

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## INTRODUCTION

The recently recognized energy shortage has generated an upsurge in government research devoted to both improving current technology to better utilize known energy reserves and providing new technology which will allow the country to convert energy resources to reserves. Underground coal gasification (UCG) technology may play an important role in both of the above categories.

Sufficient technology is at hand to successfully produce a low-Btu gas from relatively shallow (<1000 ft.) deposits of bituminous, subbituminous and lignitic coal (1, 2, 3). Most recently the Bureau of Mines' Laramie Energy Research Center has conducted an underground gasification experiment at Hanna, Wyoming, in a 30 ft. thick seam of subbituminous coal at a depth of 400 ft. The results from Hanna have been more favorable than previous results in the U. S. and other countries (4) in two important categories: a gas of higher Btu content (125 Btu/scf) has been produced and during a 6½-month period of optimum operation there was little or no gas leakage from the underground system (3). However, applicability to deeper deposits (>1000 ft.) is not yet proven.

In order to evaluate UCG's feasibility, methods of measuring the physical and chemical occurrences in an inaccessible reaction zone must be developed. While experiments are underway to implant sophisticated instrumentation in the gasification pathway in the second UCG experiment at Hanna, such instrumentation would probably not be economically feasible in a commercial process. Consequently, it is of paramount importance to develop both inexpensive remote sensing and material and energy balance techniques to continuously evaluate the in situ process in order to maximize gasification efficiency and resource utilization. A material balance method derived by Elder et. al. (1) has been applied to data obtained from the first UCG experiment at Hanna. Results of these material balance calculations are presented as well as the problems involved in measuring factors necessary for performing a material balance.

## GEOLOGICAL CONDITIONS

In attempting to build an underground reactor in a coal seam, important factors to be considered are the rate and pressure of water influx and the directional permeability of the coal. In addition, strata above and below the coal seam must have significantly lower permeabilities than the coal in order to prevent leakage from the reaction zone. The rate of water influx is related to both the permeability of the seam and to the hydrostatic pressure. In the experiment at Hanna, the seam of choice, the Hanna #1, is 180 to 200 feet below the water table. A 80-90 psig hydrostatic pressure is thereby imposed upon the reaction zone. Another important factor in the movement of water and gases within the seam is the directional nature and extent (both vertical and horizontal) of the natural

fractures within the coal seam (5, 6). A thorough understanding of these natural fractures should aid in development of true in situ process control.

The Hanna #1 seam used during this experiment is a 30-foot thick subbituminous coal seam lying at a depth of 350 to 400 feet. It dips to the northeast at 6 to 9°, is isolated by outcrop on three sides, and displaced by faulting on the fourth (2). Strata above and below the coal consist of less permeable shales with 15 feet above and 4 feet below the coal.

#### GASIFICATION TECHNIQUE USED AT HANNA

While many techniques have been used in UCG (7), the chosen method in the Hanna experiment was the percolation or filtration method. Success of this method depends on the development of sufficient permeability between vertical boreholes to maintain a sufficient flow of gasification agent and product gas. The critical step in development of the underground reactor is establishing the initial linkage between vertical boreholes, i.e., increasing air acceptance by some means. Therefore, the water and the natural fracture direction in the coal play obvious roles in affecting the UCG experiment. The initial permeability of the coal seam to injected air is quite low (1-10 millidarcys). However, injection of air at pressures in excess of hydrostatic pressure expels water from the natural fracture system thereby increasing permeability. The degree of permeability increase is not predictable unless the natural fracture directions and the transmissivity of the coal are known. An experiment is planned to evaluate these parameters (8).

The most reliable method of linking boreholes prior to gasification is that of reverse combustion(3). A fire is ignited in the borehole to be vented and air is fed to this combustion zone by injection into an adjacent borehole. Thus the combustion front propagates countercurrent to the gas flow. This is in contrast to forward combustion wherein the combustion front proceeds in the same direction as the gas flow. The practical advantages of a reverse combustion mode over a forward combustion mode are:

1. The possibility of tars, produced from carbonization, plugging the natural fractures in the coal is obviated because the tars are not driven into the coal ahead of the combustion zone.
2. Directional control of combustion front movement is attained because the combustion front will proceed toward the source of air.

During establishment of linkage between wellbores using reverse combustion, two distinct phases have been found by monitoring air injection rate and pressure. Initially air is injected at relatively high pressure (250-300 psig) and low flow rates for a period of several days. During this time a narrow combustion front proceeds toward the source of air. When breakthrough between wellbores occurs, an abrupt drop in pressure occurs after which the flow of gas is relatively unrestricted. The gas produced during the linkage process is usually of high Btu content (approx. 175-200 Btu/scf) with high methane and low carbon monoxide content characteristic of a carbonization gas. However, once breakthrough is achieved allowing high volume-low pressure gas flow, gasification rather than carbonization becomes the predominant mode. Gasification is characterized by high carbon monoxide and low methane content in the product gas.

Thus a gasification scheme using the percolation method consists of two regimes, one of linking at high pressure and the other of gasification at low pressure. The linking process, being of short duration and low gas flow rates,

utilizes only a small fraction of the coal that is eventually affected between a pair of boreholes. Due to the high pressure involved, leakage from the system can be severe (75% gas loss) during the linking phase. Leakage during gasification has not been observed at Hanna. The seam water apparently acts as an effective gas seal during this low pressure operation (3).

#### FACTORS INVOLVED IN A MATERIAL BALANCE

A prerequisite for calculating a material balance on a system is a detailed knowledge of the reactants and products. In the case of UCG, it is impossible to determine the precise stoichiometry of the coal to be gasified. A chemical and mineralogical examination of a core taken from the Hanna #1 coal seam reveals the lack of homogeneity with respect to depth. Table 1 lists the ash content, fixed carbon/volatile matter ratio, and C/H ratio of samples from a 30-foot core.

TABLE 1. - Core Analysis of Hanna #1 Coal Seam as a Function of Depth

Depth	% Ash <sup>1/</sup>	Fixed Carbon/ Volatile Matter	C/H Ratio <sup>2/</sup>
378.7	27.4	1.00	12.5
379.3	21.6	1.05	12.9
381.5	39.4	0.70	11.7
383.0	4.6	1.29	13.8
383.5	8.8	1.04	12.6
384.0	19.2	1.00	12.5
384.5	11.8	1.13	12.9
385.5	19.7	1.04	12.8
386.0	24.5	0.94	12.0
386.5	14.0	1.07	13.2
387.0	9.0	1.06	12.4
387.5	9.4	1.19	13.2
388.0	6.2	1.08	12.9
388.5	9.7	1.04	13.3
389.0	21.7	1.02	12.9
390.0	20.5	1.03	12.1
391.5	36.7	0.21	14.3
392.0	14.5	0.77	13.4
393.0	3.8	1.06	12.8
393.5	9.7	1.00	13.0
394.0	14.4	1.06	12.9
394.5	29.3	0.86	11.9
395.0	24.1	1.03	12.8
396.0	15.1	1.04	12.9
396.5	14.9	1.10	13.1
397.0	15.7	1.09	13.4
399.0	16.8	1.26	13.6
400.0	6.4	1.33	13.8
400.5	7.1	1.19	13.4
401.0	4.3	1.17	13.5
402.0	11.5	1.13	13.1
402.5	23.2	1.06	12.9

<sup>1/</sup> Moisture free basis

<sup>2/</sup> Moisture and ash free basis

## MATERIAL BALANCE CALCULATIONS

Material balance equations may be written as follows:

$$\begin{aligned} \text{Hydrogen Balance (H): } & H \text{ (from char)} + H \text{ (from volatile matter)} + H \text{ (from formation water)} \\ & = H \text{ (total in products)} \end{aligned} \quad 1)$$

$$\text{Carbon Balance (C): } C \text{ (from char)} + C \text{ (from volatile matter)} = C \text{ (total in products)} \quad 2)$$

$$\begin{aligned} \text{Oxygen Balance } (\emptyset): & \emptyset \text{ (from char)} + \emptyset \text{ (from volatile matter)} + \emptyset \text{ (from formation water)} \\ & = \emptyset \text{ (total in products)} - \emptyset \text{ (from air)} \end{aligned} \quad 3)$$

Then let:

- x = pounds of char entering the reaction zone
- y = pounds of volatile matter entering the reaction zone
- z = pounds of water entering the reaction zone

Substituting the data from Table 2 into the material balance equations:

$$H = 0.0083x + 0.116y + 0.111z$$

$$C = 0.970x + 0.498y$$

$$\emptyset' = 0.0003x + 0.347y + 0.889z$$

$$\text{Where } \emptyset' = \emptyset \text{ (total in products)} - \emptyset \text{ (from air)}$$

Solving these equations for x, y and z with quantities expressed in pounds:

$$x = 1.10C + 0.93\emptyset' - 7.45H$$

$$y = -0.12C + -1.82\emptyset' + 14.55H$$

$$z = 0.05C + 1.84\emptyset' - 5.67H$$

From Table 2 the weight ratio of volatile matter to char is 0.92; the weight ratio of moisture and ash free (maf) coal to char is 1.92; and the weight ratio of maf coal to volatile matter is 2.08.

Therefore:

$$1.92x = \text{weight of maf coal completely gasified and}$$

$$2.08(Y - 0.92x) = \text{weight maf coal carbonized only}$$

This material balance has been applied to a 6½-month operational period in five day increments. During this period both nitrogen and argon balances showed that there was little or no leakage from the underground system and thus a leak free system is assumed in the material balance. Additional assumptions are steady state conditions during the period considered, carbonization at 900°C, no condensation of products prior to gas sampling at the surface, no reactions of oxygen with any materials other than coal, and the laboratory carbonization assays indicate the stoichiometry of the char and volatiles under seam reaction conditions. The results of this material balance are listed in Table 3 along with average air injection rates, average gas production rates and average product gas heating values for the periods indicated.

The total amount of coal affected during the period considered was 2986 tons with 1171 tons carbonized only and 1815 tons completely gasified. These results are based on the linkage and gasification of three pathways of 80, 90, and 100 feet, respectively, radiating from the original ignition point to three different wellbores used as air injection points. Assuming that a cylinder of coal 30 ft. in diameter was accessible to gasification for each pathway, approximately 4700 tons of maf coal were available for gasification. Therefore, the coal utilization efficiency was 63%. From Table 3 the average energy recovered from the coal affected was 58%. The product of these two efficiencies yields an overall energy

These data indicate that while the ash content varies widely with respect to depth in the seam of interest, the ratio of fixed carbon to that of volatile matter and the C/H ratio remain relatively constant.

In assessing a material balance for a UCG experiment, several assumptions must obviously be made. It is difficult to measure the total quantities of water which are gained or lost by the system. More importantly it is difficult to directly measure the amount of coal affected and the manner in which it was affected. However, excavation of previous UCG experiments and laboratory simulations have shown that the process occurs in two discrete steps: carbonization only and complete gasification. In UCG a stream of the gasification agent is passed over the surface of the coal with carbonization occurring first followed by complete gasification of the remaining char. Water from the coal itself or natural ground-water influx from the seam is present at or near the region of reaction. For practical purposes air, volatile matter from coal, char from coal, and water are present in the reaction zone where the carbonization-gasification processes occur.

Although it is not difficult to set up a material balance in theory, practical considerations of UCG make it extremely difficult to measure all of the quantities involved. Obtaining a material balance thus involves:

1. Measurement of the gasification agent (air).
2. Assuming that the material to be gasified enters the system in two discrete parts: (a) the products of carbonization of the coal at 900°C, and (b) the char remaining after carbonization.
3. Estimating the quantity of water entering the underground system.
4. Measuring the volume and composition of the products.

The application of Elder's method (1) of material balance to the Hanna #1 coal is based on a precision carbonization assay at 900°C, the results of which are listed in Table 2 along with the ultimate analysis.

TABLE 2. - Elemental distribution in coal, char and volatile matter from 100 pounds of moisture and ash free Hanna #1 Coal

Element	Coal		Char		Volatile Matter	
	wt. %	Pounds	wt. %	Pounds	wt. %	Pounds
H	6.04	6.04	0.83	0.43	11.60	5.61
C	74.33	74.33	97.02	50.34	49.82	23.93
O	16.67	16.67	0.03	0.02	34.65	16.65
N	1.94	1.94	0.93	0.48	3.04	1.46
S	1.02	1.02	1.19	0.63	0.81	0.39
Totals	100.00	100.00	100.00	51.90	99.92	48.04

TABLE 3. - Five Day Averages of Operating Data and Material Balance Results

Starting Date of 5 Day Period	Air Injection Rate (MM scf/day)	Dry Gas Production Rate (MM scf/day)	Heating Value (Btu/scf)	Tons of MAF Coal Carbonized Only (tons/day)	Tons of MAF Coal Completely Gasified (tons/day)	Total MAF Coal Affected (tons/day)	Energy Recovery Efficiency (%)
9/16/73	1.20	1.40	61	16.0	0.9	16.9	20
9/21/73	0.69	0.97	134	13.5	1.6	15.1	33
9/26/73	0.82	1.26	150	15.7	2.9	18.6	39
10/01/73	0.99	1.48	138	2.6	9.3	11.9	67
10/06/73	1.06	1.78	163	8.7	9.9	18.6	61
10/11/73	1.11	1.89	162	13.0	8.9	21.9	54
10/16/73	1.08	1.76	153	11.0	8.4	19.4	54
10/21/73	1.03	1.56	136	9.6	6.9	16.5	50
10/26/73	1.06	1.60	134	7.5	7.9	15.4	54
11/01/73	0.83	1.44	158	9.3	6.7	16.0	55
11/06/73*	0.71	1.04	112	-4.2*	8.1	--*	--*
11/11/73	1.08	1.63	132	4.2	9.3	13.5	61
11/16/73	1.23	1.79	129	6.9	9.4	16.3	55
11/21/73	1.20	1.76	129	5.9	9.5	15.4	56
11/26/73	1.36	1.91	114	4.2	10.5	14.7	57
12/01/73	1.15	1.69	125	8.4	8.4	15.2	53
12/06/73	1.09	1.57	109	3.6	8.1	11.7	56
12/11/73	1.25	1.91	136	-1.6*	13.7	--*	--*
12/16/73	1.22	1.81	126	7.2	9.0	16.2	55
12/21/73	1.29	1.86	110	0.2	11.2	11.4	69
12/26/73	1.22	1.72	103	-4.7*	12.0	--*	--*
1/01/74	0.79	1.01	75	-4.6*	7.3	--*	--*
1/06/74	0.96	1.21	68	-5.9*	8.6	--*	--*
1/11/74	0.96	1.13	52	-5.1*	7.5	--*	--*
1/16/74	0.94	1.14	70	1.4	5.5	6.9	44
1/21/74	0.78	0.77	96	3.3	3.3	6.6	44
1/26/74	0.58	1.13	125	5.7	5.3	11.0	50
2/01/74	1.09	1.84	168	7.7	11.2	18.9	63
2/06/74	1.20	1.98	176	16.9	9.2	26.1	51
2/11/74	1.39	2.14	153	7.0	13.1	20.1	62
2/16/74	1.43	2.35	187	14.4	14.4	28.8	59
2/20/74	0.69	1.66	200	28.7	13.5	42.2	42
2/24/74	2.06	2.85	118	-4.4*	20.4	--*	--*
3/01/74	1.56	2.21	117	-9.8*	18.1	--*	--*
3/06/74	1.89	2.75	128	3.2	17.2	20.4	67
3/11/74	0.66	1.48	182	-8.5*	14.3	--*	--*
3/16/74	1.51	2.25	131	-2.3*	16.0	--*	--*
3/21/74	0.10	0.34	229	-6.9*	5.5	--*	--*
3/26/74	0.00	0.05	275	--*	--*	--*	--*

\* These data are not significant because abrupt variations in flow rates preclude a steady state system.

recovery efficiency of 37% based on results of this material balance calculation.

This material balance is only a chemical interpretation of the process based on many assumptions. The areal and vertical sweep efficiencies are unknown. In addition, this first experiment was designed not to optimize operating parameters but to provide preliminary information for designing other experiments to evaluate UCG feasibility. Even so, the results are encouraging. The overall energy efficiency for the period considered is higher than that achieved in any previous UCG experiment for the length of time considered here. Physical assessment will include coring and downhole measurements to better establish the sweep efficiencies and the geometry of the coal area affected. These data will give a much better idea of the overall resource utilization efficiency than the material balance calculations.

#### FUTURE RESEARCH

A second experiment (8) at Hanna is presently underway utilizing an oxygen blown system, an improved well linkage system, and in situ instrumentation consisting of both active and passive acoustic techniques, surface and subsurface resistivity, and in situ temperature and pressure measurements to better define the combustion zone. A "line drive" system will be initiated. This involves movement of a 60-foot long combustion front at right angles to the major natural permeability direction in the coal providing intimate contact between the gasification agent and the coal. Coal utilization efficiency should be improved over that estimated from the first UCG experiment. A target of 50% overall energy efficiency rather than the 37% estimated here for the first experiment has been set. This second experiment should lead to development of process control and process evaluation techniques as well as significantly improved process interpretation for determining the feasibility of UCG.

#### CONCLUSIONS

A UCG experiment has been successfully conducted in a thick seam of subbituminous western coal with encouraging results. Problems of gas leakage and the ability to link wellbores successfully have not occurred during the Hanna project so long as reverse combustion was used to link adjacent wellbores. Seam water, rather than posing a problem, appeared to be an asset in preventing gas leakage in the underground reaction system. A material balance technique based on the carbonization properties of coal has been used to estimate an energy recovery efficiency of 58% from the coal affected, a coal utilization efficiency of 63%, and an overall energy recovery efficiency of 37%. Many problems remain to be solved in UCG such as a greater degree of process control, but results of the first UCG experiment are especially encouraging even though it was not designed to optimize operating parameters. The second UCG experiment now underway should yield higher coal utilization efficiencies and offer a feasible technique for recovering energy from coal seams unsuited to current coal mining techniques.

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## THE GEZRO PROCESS FOR OPEN-CYCLE HYDROGEN PRODUCTION

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Various scenarios using hydrogen as a general energy medium in the future have been proposed based upon its outstanding environmental compatibility, its ultimate derivation from an inexhaustible feedstock material ( $H_2O$ ) and its high flexibility. At least until the next century, however, the overwhelming uses of hydrogen will be as a chemical feedstock, in chemical and metallurgical processing operations and the production of clean synthetic fuels. In particular, the conversion of coal into synthetic natural gas and liquefied synthetic fuels will require large amounts of hydrogen. Both present and projected demands for hydrogen require that new, higher efficiency and lower cost production methods be developed.

Currently the vast majority of hydrogen produced is made by open-cycle processes that consume natural gas, oil or other petroleum products as the feedstock material. The principal methods include steam reforming and partial oxidation both of which are followed by the shift reaction<sup>(1)</sup>. Thermal efficiencies of such processes in terms of the combustion value of hydrogen produced compared to that of the input fossil fuels typically range from 50-80%. Only a small fraction of the hydrogen consumed presently is produced by water electrolysis in spite of the simplicity of the process, the product purity, and the good efficiency achievable in the electrolysis step itself by advanced methods (up to ~70-90%). This is due largely to the low overall efficiency (i.e., <35%) when electric generation and DC conversion steps from a base load thermal power plant are included. Much attention has recently been given to the closed cycle thermochemical decomposition of water in which heat at moderate temperatures (<1000°C) is used to carry out a series of reactions,<sup>(1)</sup> the net result of which is:  $H_2O + H_2 + 1/2 O_2$ . All other chemical intermediates in the process are recycled, ideally. Detailed analysis indicates that overall thermal efficiencies of 40-60% might be achieved. While numerous closed cycle processes have been theoretically proposed, none have yet been successfully operated in an integrated mode. Serious technical barriers, including corrosion, kinetics, system stability and design, combined with licensing uncertainties, the projected high cost of high temperature nuclear heat and process components shed serious questions on the viability of multi-step closed cycle processes for hydrogen generation, at least in this century. Thus it appears that open-cycle processes to make hydrogen will be very important for the foreseeable future.

The primary objective of this paper is to describe a new open cycle technique which will utilize coal or coal char from gasification to produce electrolytically pure hydrogen. The concept stems from our earlier high temperature fuel cell program, during which an electrolytic water dissociation cell using an oxygen ion conductive membrane was proposed<sup>(2)</sup> and demonstrated<sup>(3)</sup>. By introducing a reducing gas at the cell anode, the voltage required to produce hydrogen from water is lowered. The new method is to use a ceramic membrane that is both an electron conductor as well as oxygen ion conductor. Thus the cell can operate in a "self-driven" mode, i.e., no

electrical driving force or electrodes are needed. Such a cell is shown schematically in Figure 1. Steam is passed over one side of the membrane while carbon monoxide is passed over the opposite side of the membrane. On the "cathode" side, the steam reacts at the surface with two electrons to yield hydrogen gas plus an oxygen ion, which is transported through the electrolyte to combine at the "anode" surface with carbon monoxide to form carbon dioxide plus two electrons. This process, operating without electrical input, has been named GEZRO. It should achieve overall thermal efficiencies, as defined earlier, of at least 60-70%.

The net reaction for the process is the well-known water gas shift reaction:  $H_2O + CO = CO_2 + H_2$ . Because the reactants are separated, the product hydrogen does not have to be purified with respect to CO or  $CO_2$ . This has important implications to ammonia synthesis, for example, where CO impurity in the hydrogen acts as a catalyst poison. Also, the input carbon monoxide need not be pure. For this reason, GEZRO is particularly adaptable for integration into coal liquefaction or gasification technology. Figure 2 shows a possible cycle using gas obtained from coal which has been partially oxidized in air as the feed to GEZRO. Nitrogen from the air and coal contaminants such as sulfur also enter the GEZRO reactor; gas clean-up is accomplished subsequently at lower temperatures. On the steam side, a portion of the steam is reduced to hydrogen and the remainder is recycled. Heat exchangers, not shown in the diagram, would be used so that minimal heat input would be required. Figure 3 shows a cycle in which GEZRO is incorporated into a high BTU coal gasification scheme, such as HYGAS. In this cycle, hydrogen and steam from GEZRO are fed directly into the second stage gasifier (both hydrogen and steam are required to maintain proper heat balance in the gasifier) to react with coal and char and yield methane. The remaining char is partially burned in air to provide the input gas for GEZRO.

The GEZRO reactor can be considered as an electrochemical cell in which the cell voltage is zero (short circuit condition). For this case an effective average thermodynamic cell voltage,  $\bar{v}$ , may be defined by  $\bar{v} = r\bar{j}$ , where  $r$  is the electrolyte specific resistance, and  $\bar{j}$  is the average current density. Thus,  $r$ , which depends on the membrane material, and  $\bar{v}$  which is related to the driving force for the reaction (proportional to temperature and oxygen partial pressure differential) integrated over the reactor length, determine the output of the cell in terms of oxygen ions transported per unit area of membrane. For typical membrane compositions, it can be shown that by operating with countercurrent gas flows, it is theoretically possible at 800°C, to oxidize 80% of the CO to  $CO_2$  while converting half of the input steam to hydrogen when the input steam flow rate is twice the input CO flow rate. In general, the process is expected to operate at between 700°C and 1000°C at any required pressure.

The critical problem in the development of a GEZRO reactor is the selection of a suitable membrane and our experimental program has centered in this area. Materials requirements include the following:

- (1) High oxygen ion conductivity,
- (2) High electronic conductivity,
- (3) Thermal stability,
- (4) Stability toward reactants and products,
- (5) Stability toward contaminants,
- (6) Mechanical stability and strength, and
- (7) Fabrication capability (thin and gas tight).

These properties are similar to those required by high temperature fuel cells, with the important exception that electronic conductivity, instead of being undesirable, is required. Indeed, the optimum condition for GEZRO is that the transport number for electrons ( $t_{e^-}$ ) is equal to that for oxygen ions ( $t_{O^{2-}}$ ), so that  $t_{O^{2-}} = t_{e^-} = 0.5$ . The severe operating environment, which includes corrosive and reactive gases (e.g.,  $H_2S$ ,  $SO_2$ ,  $COS$ ) as well as a wide range of reducing conditions ( $10^{-20}$  atm  $< P_{O_2} < 10^{-7}$  atm) at high temperatures, rules out many possible materials.

Because of its well-established use in experimental fuel cells, zirconia has been chosen as the initial candidate membrane base material. When certain oxide materials containing a cation in the +2 or +3 oxidation state are added to monoclinic  $ZrO_2$ , the  $ZrO_2$  is stabilized in a cubic fluorite crystal structure. The stabilization process leaves several percent oxygen ion vacancies in the structure and leads to significant ionic conduction. The ionic conductivity at a given temperature generally increases with the nature of the additive in the order  $CaO < Y_2O_3 < Sc_2O_3$ . The use of  $Y_2O_3$  as a stabilizer appears attractive as a compromise between cost, long-term stability, reactivity toward sulfides, and reasonable conductivity. A maximum in the conductivity of the  $Y_2O_3$ - $ZrO_2$  system occurs at about 7-8 m/o  $Y_2O_3$ , at which point the purely ionic conductivity is about  $0.1 \Omega^{-1} cm^{-1}$  at  $1000^\circ C$ . The addition of compatible transition metal oxides into the ionically conducting fluorite lattice is expected to introduce electronic conductivity, provided the additive goes into the structure and is not merely segregated along grain boundaries..

A program to synthesize and screen various three and four component ceramic compositions by means of microstructure analysis, electrical conductivity measurements, and transport number measurements is in progress. Table I summarizes some of the compositions which have so far been successfully prepared and which have been sintered into dense, gas-tight shapes. The sintering conditions were found to be critical in achieving good materials properties. In general, sintering was carried out at temperatures between  $1500^\circ C$  and  $1900^\circ C$  in an atmosphere of either air or wet hydrogen; wet hydrogen atmospheres generally approximate the oxygen partial pressures used in the GEZRO process. Oxides of Mn, Zn, Ce, U, and Fe have been successfully added to yttria-stabilized zirconia to form pure single phase materials. Additive contents have ranged from 4.1 m/o to 13.4 m/o in compositions based on 7-8 m/o  $Y_2O_3$ -stabilized zirconia. Other preparations involving 2-20 m/o of additive, and using other transition metals have been attempted or are in progress.

Electrical conductivity measurements have been completed on several of the above compounds using a two-probe AC technique. Platinum paste electrodes (Engelhard #6082) were applied to sintered bar samples which made pressure contact with platinum foil spacers in a sample holder constructed of alumina. Measurements were carried out as a function of temperature in the range between  $500^\circ C$  and  $1000^\circ C$  and as a function AC frequency in the range between 400 Hz and 50 kHz, in either pure nitrogen or carbon monoxide atmospheres. Figure 4 shows the results for selected compositions. In most cases, the plot of the logarithm of conductivity ( $\sigma$ ) vs reciprocal temperature is linear. The most conductive and the lowest activation energy (0.47 ev) material yet measured is the 7 m/o  $Mn_2O_3$  composition. Unfortunately, a severe decrease in the conductivity resulted within 70 minutes after carbon monoxide was introduced at high temperature. Post-run

examination revealed that reduction, probably to poorly conducting  $Mn^{+2}$  oxidation state, had occurred. Both ZnO and  $CeO_2$  additives are more promising. As shown in Figure 4 the composition containing 8.1 m/o ZnO is somewhat more conductive than the 13.4 m/o ZnO material. Measurements for the 13.4 m/o ZnO composition in carbon monoxide revealed no significant deterioration in the conductivity even after several hours exposure. Similar results were obtained in the case of 8.1 m/o  $CeO_2$  where measurements in both CO and  $N_2$  are shown for comparison in Figure 4; in this case, the reducing atmosphere lowered the conductivity somewhat, but there was no change in activation energy. Finally, one four component system, containing 2.8 m/o  $UO_2$  and 7.6 m/o  $Fe_3O_4$ , was measured since earlier work had indicated this material to be a potential mixed conductor. Although this material has been prepared in the form of dense, gas tight discs, such preparations are not always repeatable. In addition, efforts to prepare tubular shapes by means of plasma spray techniques have not led to suitably dense material.

Measurement of transport numbers for oxygen ions and electrons for the above and other potential materials, is also underway. These measurements are being made by the emf-technique in which the voltage generated by differing known oxygen partial pressures on either side of a disc sample is measured and compared with the theoretical voltage obtained for pure oxygen ion conduction.

Table I

<u>Additive*</u>	<u>m/o</u>	<u>Sintering Temperature Time, Atmosphere to Produce Dense Sample</u>
ZnO	8.1	1510°, 5 hr., air
	13.4	1510°, 5 hr., air
	8.1	1700°, 5 hr., wet H <sub>2</sub>
CeO <sub>2</sub>	8.1	1510°, 5 hr., air
	8.1	1500°, 5 hr., wet H <sub>2</sub>
	4.1	1510°, 5 hr., air
Mn <sub>2</sub> O <sub>3</sub>	7.0	1510°, 5 hr., air
UO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub>	2.8/7.6	1900°, 16-1/2 hr., wet H <sub>2</sub>

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\*All compositons based on 7-8 m/o  $Y_2O_3$ -stabilized  $ZrO_2$ .

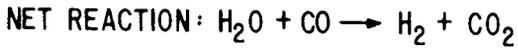
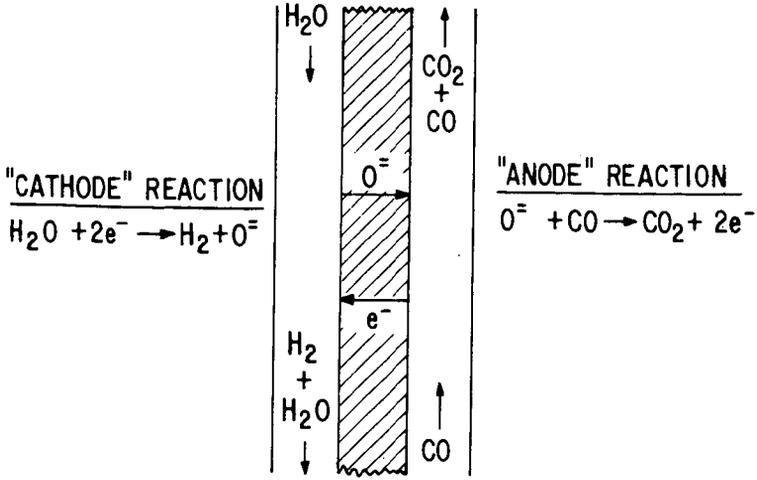


FIG. 1

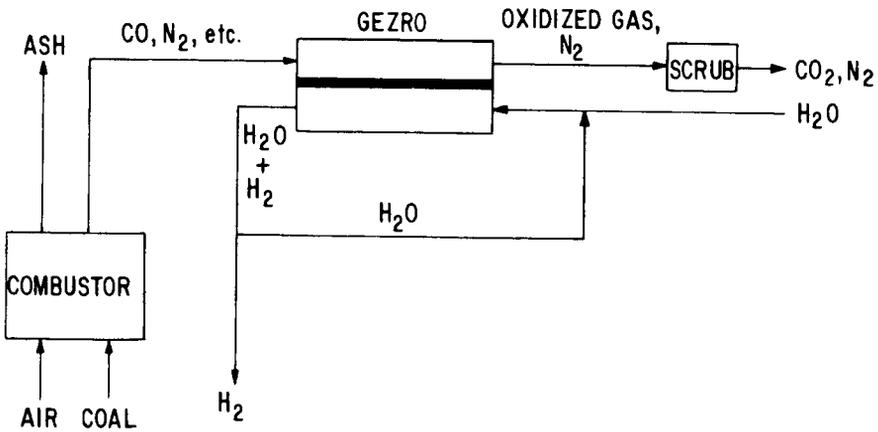


FIG. 2

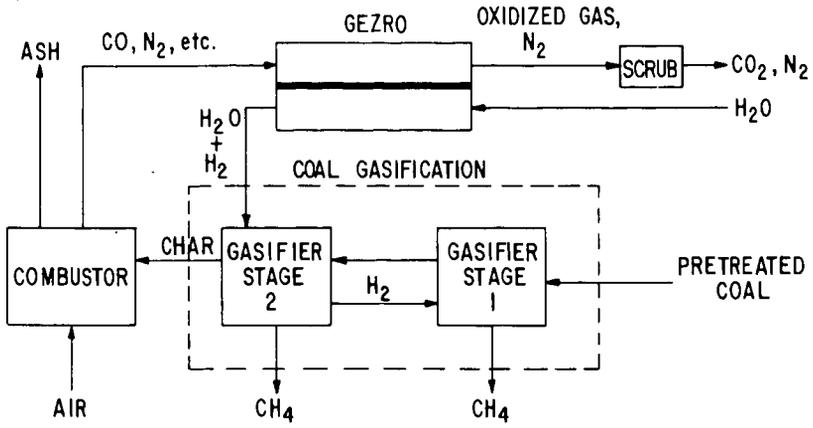


FIG. 3

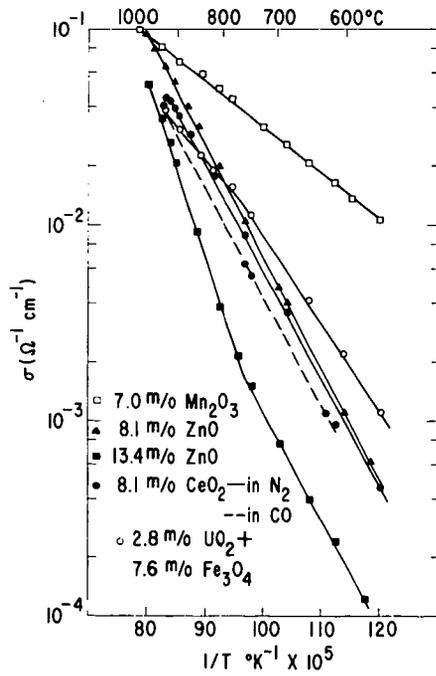


FIG. 4

## DESIGN OF A WOOD WASTE-TO-OIL PILOT PLANT

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The Pittsburgh Energy Research Center of the U.S. Bureau of Mines has, for a number of years, been involved in programs for the conversion of coal to fuel oil. One such process, based on the findings of Fischer & Schrader<sup>1</sup> that low-rank coals could be hydrogenated with carbon monoxide and steam, is currently being developed. An interesting and significant offshoot of this work was the observation that lignin, cellulosic materials, and plastics could be converted to oil by the same chemical processing. Thus, the potential exists for the disposal of vast amounts of environmental pollutants and the creation of a replenishable energy source. Estimates indicate that the equivalent of one billion tons of dry, mineral matter-free organic waste will be generated in the U.S. in 1974. The energy value of this waste is  $12-16 \times 10^{15}$  Btu or approximately 17 pct of the total estimated 1974 energy consumption in the country. Basically the waste-to-oil process involves the reaction of carbon monoxide and steam with organic waste material in the presence of sodium carbonate catalyst at temperatures of 250°-400° C and 2,000-4,000 psig pressure. The technical feasibility of the process was demonstrated in batch autoclave and bench-scale continuous process unit runs<sup>2,3</sup>; the results and observations from this work was the basis for the design of a pilot plant for converting 1-3 tons per day of wood chips to oil. This pilot unit is currently being constructed on the site of the Bureau of Mines Metallurgical Station at Albany, Oregon. An overall process-flow diagram is presented in Figure 1.

#### Wood Chips Drying and Grinding

The wood chips (1/4" x 2" x 2" maximum size) will be withdrawn from the storage bin by the table feeder and fed into a rotary dryer where the moisture content will be reduced from 45 to 4 wt pct. The dry chips will be pulverized to -50 mesh in a hammermill and then conveyed pneumatically in an inert gas stream to the wood flour surge bin.

#### Feed Systems

The area of principal difficulty encountered in the operation of the bench-scale continuous units was the feeding of the wood oil slurry into the reactor. This problem is caused by the fibrous nature of the cellulosic waste material and its low-bulk density. Accordingly, three separate feed systems were designed into the wood-to-oil pilot plant; namely,

1. Wood-oil slurry feed
2. Pretreated wood-oil slurry feed
3. Solids feed

In the wood-oil slurry feed system, the pulverized wood will be continuously mixed with some of the product oil to form a slurry containing 30 wt pct solids. This slurry, which is extremely stiff, will be injected into the reactor feed lines by a high-pressure plunger pump with special check valves to minimize fouling.

The pretreated wood-oil slurry system is very similar to the wood-oil slurry feed technique with the exception that the raw wood chips will first undergo a partial carbonization to increase their bulk density. Hopefully, slurries of greater than 30 wt pct concentration of wood can be prepared through this technique. The pretreatment will involve heating the raw wood chips with some additional water to 500° F in a closed vessel. A pressure of approximately 700 psig will be developed from the steam. After process conditions have been maintained for a fixed time period, the pretreater and its contents will be cooled to 150° F by means of an external pump loop and an air cooled heat exchanger. The pretreated wood will then be separated from the water by vacuum filtration, dried, pulverized to -50 mesh, mixed with recycle oil, and fed to the reactor as described previously.

Direct solids feeding of wood flour will be accomplished by a lock-hopper system. This method of operation permits the greatest throughput per reactor volume but is quite complex and difficult to operate. Basically the feed system consists of two pressure-balanced lock hoppers which will be used alternately. The process gas, carbon monoxide, must be used to pressurize the feed system because of partial pressure considerations; i.e., the partial pressure of the carbon monoxide in the reactor would be reduced considerably if inert gas were used to pressurize the lock hoppers. Metering of the solids will be effected by a rotary feeder installed on the exit side of each lock hopper. During operations, a lock hopper at atmospheric pressure will be filled with -50 mesh wood flour from the storage bin. The unit will then be pressurized to operating pressure and the solids fed to reactor via the rotary feeder. When a lock hopper is empty, the pressure in the vessel is reduced to atmospheric by first venting to a carbon monoxide surge tank and finally to a flare stack. The surge tank, which is not shown in figure 1, is used to capture most of the carbon monoxide from the lock hopper for re-compression and reuse in the next cycle. In this feed system, recycle oil will be pumped separately into the reactor so that the desired ratio of wood-to-oil can be maintained.

#### Catalysts and Process Gas

Sodium carbonate solution will be prepared and pumped continuously into the reactor by means of a high-pressure plunger pump.

Carbon monoxide process gas will be taken from 35,000 scf tube trailers and compressed to operating pressure in a non-lubricated, non-contaminating diaphragm-type compressor. The compressed process gas will be preheated in a gas-gas interchanger and sparged into the reactor. Later, synthesis gases of various H<sub>2</sub>:CO molar ratios will be used as the process gas.

#### Reaction and Subsequent Processing

The reaction will take place continuously at temperatures in the range of 250°-400° C and pressures of 1,500 to 4,000 psig. The liquid flow from the reactor will be cooled to 200° C in an air-cooled bottoms cooler and pressure reduction will be effected by a pressure reducing valve operating on a reactor liquid level controller. As the pressure is reduced, some liquid will flash and the remaining will be collected in a bottoms tank and then pumped to a centrifuge where oil and water are separated. The oil will then be filtered to remove any solids and transferred to a hold tank. Residual gases from the flash tank will

be measured, analyzed continuously for carbon monoxide, carbon dioxide, and hydrogen and flared in the flare stack.

The reactor off-gases will be cooled in a gas-gas interchanger and then undergo a pressure reduction by means of a reducing valve operating on a pressure controller. The gas will then be cooled to 80° C in an off-gas cooler, measured, analyzed continuously for carbon monoxide, carbon dioxide, and hydrogen, and finally flared.

The plant has the capability of producing 3 barrels of oil per day from wood waste. The product oil will be collected in an oil hold tank and then transferred to 55-gallon drums. Routine product oil analysis will include water and solids content, benzene solubles and insolubles, asphaltenes, viscosity, and heating value. Present plans call for the processing of other organic waste products upon completion of the wood-to-oil program.

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## Photosynthesis as a Model for Photochemical Hydrogen Generation

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Introduction

Using solar radiation as an energy source has been considered for years, and a large number of attempts have been made to harness this seemingly "free" and clean energy directly. Most of the successful techniques rely on the heating effect of long wavelengths or on direct photovoltaic production of an electric current. Attempts at conversion of solar radiation to a chemically stored form of energy have been largely unsuccessful for one or a number of the following reasons: 1) the energy of a single photon of most of the light which reaches the earth's surface is insufficient to bring about a reasonably endothermic reaction; 2) the stored reaction products tend to recombine too readily before they should; 3) the reaction products do not combine readily enough at the desired time; 4) the reactants or reaction products are highly corrosive, toxic, expensive or otherwise difficult to work with; 5) since only a weakly endothermic photochemical reaction can be brought about, a large volume of reaction products must be stored for use during dark periods.

We have recently begun a feasibility study on a closed-cycle photochemical process for splitting water into hydrogen and oxygen. The novelty of the proposed method lies in the fact that the energy of two photon captures is added together in the cycle just as plants add photon energies during photosynthesis. In this way, a highly endothermic reaction, such as the photolysis of water, can be brought about by photons of relatively low energy and the five problems just mentioned can be largely eliminated. Hydrogen is an especially interesting reaction product, as many recent articles have pointed out, because it can be burned to produce heat, used in a fuel cell to produce electricity directly, or used as a chemical feedstock for coal liquefaction, etc.

Energetics of Photolysis and the Solar Spectrum

At 25°C, the free energy change for the conversion of liquid water to oxygen and hydrogen is 56.7 kcal/mole (1.23 electron volts). However, from the relationship  $E = hc/\lambda$ , one can calculate that only photons of a wavelength less than about 504 nm will have sufficient energy to do this and only about 15% of the incident solar energy at the earth's surface satisfies this criterion. (See Figure 1). The differential curve, which shows absorption bands for H<sub>2</sub>O, O<sub>2</sub>, etc., is taken from Levine *et al.* (1). An integrated curve also is shown. Even a 100% efficient conversion process would fail to be of much interest. If two equally energetic photons could funnel their energies into one reaction, though, the wavelength limit would be doubled and about 64% of the incident radiation could be utilized. A three-photon process in which the energy requirement is equally divided would result in a wavelength limit of 1512 nm, and about 84% of the incident radiation would be suitable.

The efficiency of such conversion processes as well as the fraction of the spectrum which can be utilized must, of course, also be

considered. To do this we can construct from Figure 1 a second plot (Figure 2) which decomposes the energy flux as a function of wavelength into photon flux vs. wavelength relationships, both differential and integral. We will next assume that the amount of energy which can be captured from any given photon is no more than that of the least energetic photon in whatever photon population we are considering. Such an assumption is quite realistic and parallels what we would expect to obtain in a photochemical excitation process. (The manufacturers of solar cells face a similar dilemma. To capture a larger fraction of the solar spectrum, they must decrease the band gap and thus the output voltage of the cell.) By multiplying the integral photon flux at a given wavelength by this minimum photon energy and comparing with integral energies found from Fig. 1, we can find a conversion efficiency and also an efficiency based on the total solar energy flux. For the single photon process, these efficiencies are 90% of the photons with sufficient energy, but only about 10% relative to the whole spectrum. For a two-photon process the efficiencies are 67% for the population (up to 1008 nm) and 37% for the entire spectrum. For three photons, the population efficiency (for wavelengths to 1512 nm) has dropped to 52% because so little energy is extracted from each photon, that the spectrum efficiency increases only to 38%. As an alternate to drawing each of the two or three photons from the same population, we can divide the total population into two (or more) sub-populations, a short wavelength high energy band and a long wavelength low energy band. Since we have already found that two-photon processes can use a reasonably large fraction of the spectrum, we will henceforth limit ourselves to such schemes. We also will assume that the low wavelength limit is set low enough to capture all of the high energy photons. The efficiency of a two-photon process depends on two factors: the upper wavelength cutoff point for the entire population,  $\lambda_u$ , and the wavelength,  $\lambda_c$ , at which the change from one sub-population to another takes place. The overall efficiency can be limited by too few photons in the high energy band, too few in the low energy band, or insufficient photon energy in the low energy band to make up a total of 56.7 kcal/mole. Using the data in Figures 1 and 2, the influence of  $\lambda_u$  and  $\lambda_c$  on efficiency has been calculated and is shown in Figure 3. Efficiency is a rather strong function of  $\lambda_c$  which determines the number of photons in each band. For wavelengths below 1008 nm, the peak efficiency corresponds exactly to the efficiency obtained by drawing photons from the same population because each photon has at least half of the required energy. However, it is now possible to use photons beyond 1008 nm by dividing the energy unequally. An interesting result which emerges is that a new upper wavelength limit of 1280 nm exists. Beyond this point the photon energies are insufficient even though the total number of photons is increased. At this wavelength and the optimum  $\lambda_c$  of 830 nm the efficiency is 59% of the whole spectrum and 75% of the photon population absorbed, a considerable improvement over the two-photon efficiencies obtained from a single population division. In closing this section we should point out that we have completely neglected fluorescence, competing reactions, etc. which produce non-unitary quantum yields. Actual efficiencies may be considerably lower than those which we have given here.

### The Photosynthetic Cycle

Having decided that a two-photon process can efficiently capture a significant fraction of the solar radiation, particularly if wavelengths up to 1280 nm can be used and different populations are chosen

for each of the two photons, we now consider how to couple their energy. The cycle is very similar to that involved in photosynthesis, so a brief description of nature's scheme as it is presently understood, will be given first (see Figure 4) (2, 3, 4).

Chlorophyll a 670 is a pigment which when photochemically excited forms a strong oxidant (chl a<sup>670</sup>) and a weak reductant (reduced plastoquinone). The strong oxidant regenerates the original chl a 670 by an unknown series of reactions (collectively called the Hill Reaction) which ultimately extract an electron from water in the presence of Mn<sup>++</sup> and Cl<sup>-</sup>, liberating oxygen gas and hydrogen ions. The plastoquinone regenerates itself by contributing its electron to a chain of cytochrome compounds. As the electron falls toward a more oxidized state, part of its energy is trapped by converting ADP (adenosine diphosphate) to ATP (adenosine triphosphate) an energy source molecule used in cellular reactions. The electron eventually winds up in a compound called plastocyanin. This entire scheme of photon trapping and electron transport reactions is referred to a photosystem II.

The second series of reactions is called photosystem I. A pigment P700 is excited by the second photon, contributing its electron to an unknown compound X and thereby creating a very strong reductant. The weak oxidant, P700<sup>+</sup> returns to its original state by extracting the electron from plastocyanin. The compound X contributes its excess electron to a slightly less strong reductant, ferredoxin. The reducing energy of ferredoxin is used to create a second type of energy storage and transport molecule, NADPH, from NADP. This compound then supplies the energy to create carbohydrates from carbon dioxide and carry out other endothermic cellular reactions.

#### The Proposed Photolytic Cycle

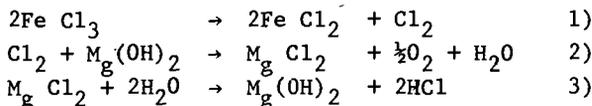
The cycle shown in Figure 5 is quite similar in principle to photosynthesis. Specific dyes are shown, but these are for convenience only and their choice was dictated primarily by what has already been described in the literature. Corresponding to photosystem II is a scheme based on the dye methylene blue. Excited by a photon, it extracts an electron from Fe<sup>++</sup> forming the colorless leucomethylene blue and Fe<sup>+++</sup>. (Actually the reaction occurs in two steps and 2 electrons are transported.) This reaction is well documented in the literature (5). We then postulate that a carrier molecule, such as one or more cytochromes, would extract the electron and carry it to a second system containing a dye such as acridine.

Upon photon excitation, the acridine is converted to an acridan. Unlike the methylene blue system, there is little or no tendency for the reaction to spontaneously reverse itself. Leucomethylene blue plus Fe<sup>+++</sup> tend to react and regenerate the ferrous ion plus original dye. Although to our knowledge cytochromes have not been tried as electron donors for acridine, a wide variety of compounds including allylthiourea, isopropyl alcohol, ethanol, toluene, ethylene diamine tetraacetic acid, and ascorbate are effective (6, 7), so the carrier and donor molecules probably will not be too critical.

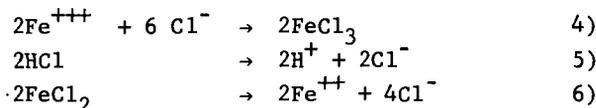
The reduced acridan molecule has a redox potential more negative than that of the hydrogen electrode. It is therefore thermodynamically capable of producing hydrogen gas given a source of protons. We postulate that it will be quite easy to use the energy of the reduced acridan to reduce one of the viologens (methyl viologen,

benzyl viologen, etc.) which is slightly less negative in redox potential than the acridan. It is known that reduced viologen molecules plus protons will regenerate the oxidized viologen, liberating hydrogen gas, in the presence of the enzyme hydrogenase (8).

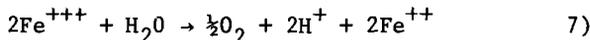
The scheme as shown is incomplete because the electron has been obtained by the conversion of  $\text{Fe}^{++}$  to  $\text{Fe}^{+++}$  and the proton source has not been shown. Obviously the Hill Reaction would be the ideal answer to this problem, but since it is unknown, we will borrow a few reactions from a proposed thermochemical hydrogen cycle to illustrate how the problem could be handled with known reactions (9):



The temperatures at which these reactions proceed are 300°C, 50 to 90°C, and 350°C respectively. Now we add three simple reactions representing crystallization and dissolution of a gas and solid:



The net result of all six reactions is therefore



Our cycle is therefore closed, the ferric ion returned to ferrous ion, oxygen liberated, and the hydrogen ions needed for hydrogen production are supplied. Such an additional set of reactions could be supplied with low grade heat from photons not used in the primary photochemical reactions.

An important consideration in successfully carrying out all of the foregoing reactions is obviously separation of the various steps. Ferric ion, a strong oxidant, certainly would react very vigorously and rapidly with the acridan or viologen, strong reductants. Fortunately, coupling the dyes and even the hydrogenase enzyme to a solid surface presents little difficulty, so the circulation of fluids over beds of solid material can be carried out readily. This is one simple expedient to separate the reactants, but of course there are others too.

In summary, an examination of the mechanisms involved in photosynthesis, of previous work on photosensitive synthetic dyes, and of some pertinent theory suggest that it should be possible to split water into hydrogen and oxygen with moderate efficiency using a significant fraction of the photons in sunlight. Considerable experimental work is needed to verify the possibility of coupling certain steps in the suggested sequence and to determine the ease with which individual reactions could be segregated to prevent undesirable energy "short-circuiting" reactions.

Acknowledgment

We are pleased to acknowledge support of this work by the National Science Foundation (Grant GK43641).

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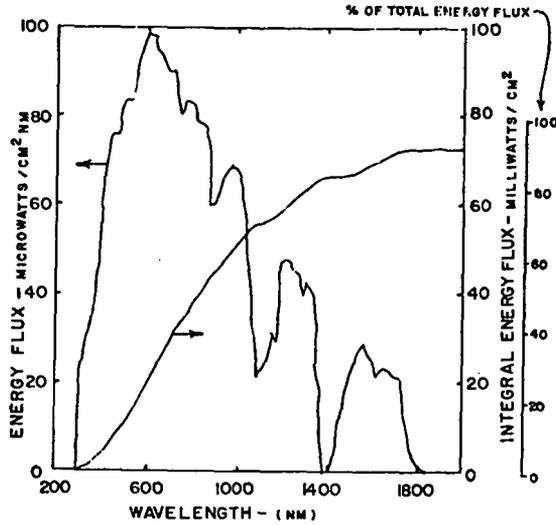


Figure 1. Solar Energy Flux at the Earth's surface (1) between 200 and 2000 nm and the integrated flux curve. About 10 percent of the total radiation has a wavelength greater than 2000 nm and is not shown.

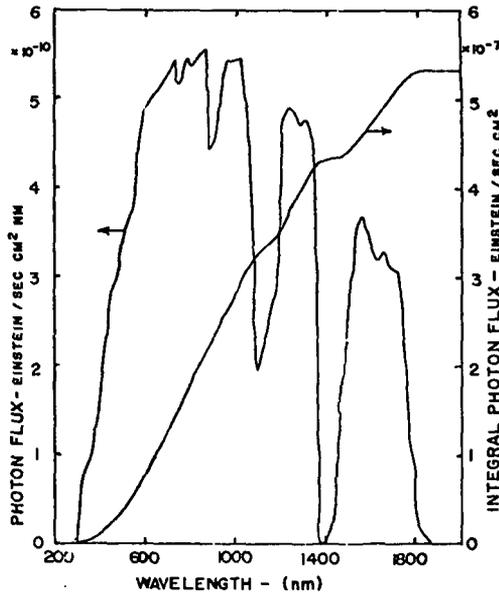


Figure 2. Photon Flux at the Earth's surface, differential and integral. This data was derived from Fig.1 using  $E = h\nu$ .

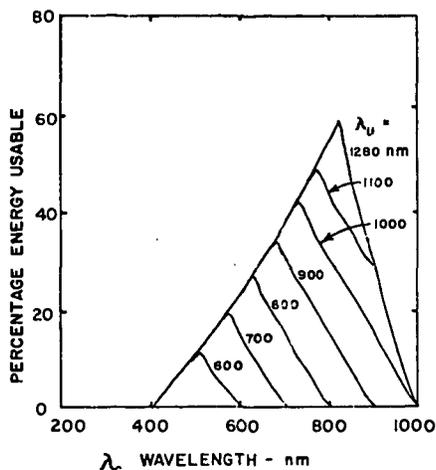


Figure 3. Percentage of the total Solar Flux which can be used in a two-photon process in which each photon is drawn from a different population. The upper cutoff wavelength ( $\lambda_u$ ) is a parameter and the wavelength at which the change ( $\lambda_c$ ) is the independent variable.

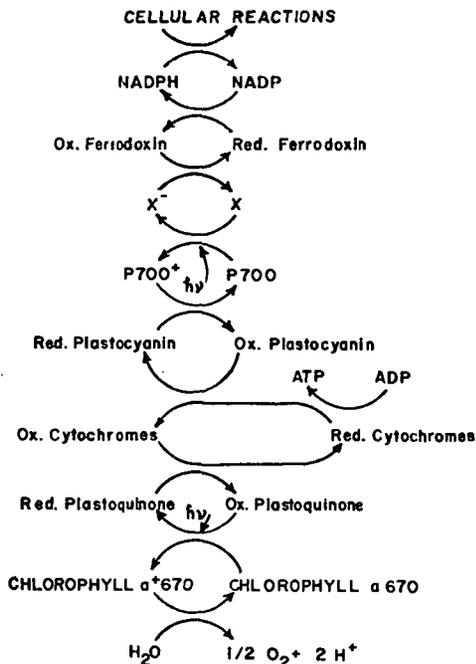


Figure 4. The coupled reactions of photosynthesis as presently understood.

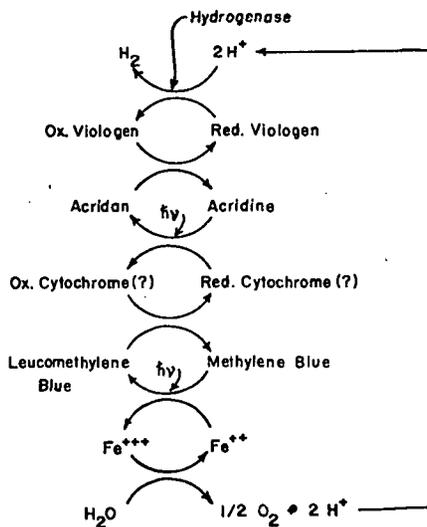


Figure 5.

The proposed photochemical cycle to split water. The ferric to ferrous conversion with attendant release of oxygen is discussed in the text.

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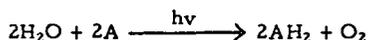
April 6-11, 1975  
 Philadelphia, Pennsylvania

BIOPHOTOLYSIS OF WATER TO HYDROGEN AND OXYGEN

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The concept of the biophotolysis of water with the formation of oxygen and hydrogen is the bringing together of two biological fields of scientific endeavor, each of which has made phenomenal progress during the last decade or two. The two areas of progress referred to are: (1) a greater understanding of the molecular events which occur in photosynthesis, and (2) a greater understanding of molecular events in microbial metabolism. Although thermodynamically feasible, heretofore not much thought has been given to the possibility of biophotolysis.

The photosynthetic apparatus which consists of two photosystems operating in series can, by capturing two quanta of radiant energy, place an electron from the water-oxygen couple (+0.8 volts pH 7.0) to a negative value as much as -0.7 volt which is 0.3 volts more negative than the hydrogen electrode. A minimum of eight quanta of radiant energy are required for the following photosynthetic equation:



where A is an electron acceptor (Hill reagent). A variety of compounds may serve as Hill reagents. For the purpose of employing these photosynthetic electrons for the reduction of protons to hydrogen by the action of a bacterial hydrogenase, the acceptor must have an oxidation-reduction potential near the potential of the hydrogen electrode and in its reduced state serve as a substrate for the hydrogenase. Several anaerobic non-photosynthetic and photosynthetic bacteria form hydrogen during some of their metabolic processes. Usually the immediate precursor of electrons for the reduction of protons as catalyzed by these hydrogenases is reduced ferredoxin, a small molecular weight iron-sulfur protein. A similar species of protein although smaller in molecular weight is in the normal pathway of electron transfer in the photosynthetic apparatus. In this latter case the reduced ferredoxin reduces

triphosphopyridine nucleotide (TPN) which in turn is the source of electrons for the reduction of carbon dioxide to plant materials. With some anaerobic bacteria it has been demonstrated that reduced TPN can reduce ferredoxin with sufficient kinetics in spite of the unfavorable thermodynamic barrier of approximately 0.1 volt. The electrons of reduced ferredoxin are the precursors of hydrogen as catalyzed by the bacterial hydrogenase.

The first experiments which demonstrated the biophotolysis of water to oxygen and hydrogen consisted of a two-stage reaction mixture. The first stage employed the classical method of San Pietro and colleagues who demonstrated that spinach chloroplasts could photosynthetically reduce TPN by the oxidation of water, providing ferredoxin was present. Five  $\mu$ moles of TPNH were prepared and added to the second mixture containing the components listed in Table 1.

Table 1

HYDROGEN FORMATION FROM TPNH  
-- NO GENERATING SYSTEM

	<u>per ml</u>
Tris buffer pH 7.6	100.0 $\mu$ moles
Glutathione (SH)	2.0 $\mu$ moles
TPNH	5.0 $\mu$ moles
Na pyruvate	20.0 $\mu$ moles
DPN	1.0 $\mu$ moles
Lactic dehydrogenase	9 units
<i>C. kluveri</i> hydrogenase	0.4 ml
Ferredoxin	500 $\mu$ g

Total volume 10 ml, argon atmosphere, temp. 35°C

	<u>Hydrogen evolved</u> ( $\mu$ moles)
15 min	3.2
30 min	3.2
45 min	3.2

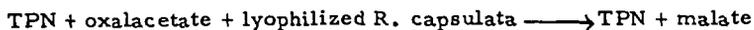
The important components for this discussion are TPNH, the bacterial hydrogenase preparation from *Clostridium kluveri* and buffer. At the bottom of the table is given the quantity of hydrogen evolved from TPNH. Control experiments demonstrated that hydrogen evolution was totally dependent upon the presence of TPNH. The quantity of hydrogen is less

than the TPNH added but it could be shown that the activity of the hydrogenase was lost shortly after the beginning of the experiment. A general characteristic of hydrogenases is that they are labile, particularly to the presence of oxygen. In this case, although the experiment was conducted under an atmosphere of argon, the oxidized TPN formed from the oxidation of TPNH to hydrogen inactivated the enzyme.

In an attempt to overcome the inhibition by TPN of hydrogenase activity and the thermodynamic barrier between TPNH and the hydrogen electrode in these anaerobic bacteria, we investigated the probability of employing photosynthetic bacteria. Photosynthetic bacteria although they cannot use water as an electron source use reduced organic or inorganic substances for photosynthetic electron donors and in many cases can form hydrogen photosynthetically from these substrates. Rhodospseudomonas capsulata, a photosynthetic bacterium, can form copious quantities of hydrogen from malate under anaerobic conditions providing no elemental nitrogen or fixed forms of inorganic nitrogen are present. The photochemical systems present in spinach chloroplasts are also labile, having a short-lived mechanism for forming TPNH. The photosystems present in the blue-green alga, Anacystis nidulans, were therefore employed. Freshly harvested cells of the alga are impermeable to most organic substrates. Lyophilization under appropriate conditions render the cells permeable to several substances including TPN and photosystems I and II remain active and reasonably stable. These cells were employed to prepare reduced TPN (TPNH) photosynthetically, using water as the electron donor. No reduction of TPN occurred in the dark or in the presence of 1,1 dimethyl-3-(3,4 dichlorophenyl) urea (diuron), a specific inhibitor for photosystem II.

Lyophilized cells of R. capsulata are permeable to reduced TPN and contain a very active malate dehydrogenase. These cells by well known biochemical reactions can reduce oxalacetate to malate with the reduced TPN. In contrast to freshly harvested cells the lyophilized cells cannot photosynthetically form hydrogen from malate. With a mixture of freshly harvested cells and the lyophilized cells, small quantities of oxalacetate and substrate amounts of reduced TPN (obtained photosynthetically with the algae) hydrogen was obtained photosynthetically in quantities equivalent to the amount of reduced TPN added. For example, with 10  $\mu$ moles of TPNH, 20 mg (dry weight) freshly harvested R. capsulata, and 5.0 mg lyophilized cells in a total volume of 2 ml under an atmosphere of argon and exposed to 22,000 lux of white light, 10  $\mu$ moles of hydrogen were obtained in 45 minutes.

The events may be summarized as follows:



Omitting the microorganisms and electron carriers, the sum of the equations become:



In a one-stage experiment, by combining the following components: 40.0 mg Anacystis nidulans, 2.5  $\mu$ moles TPN, 50.0 mg (dry weight) freshly harvested R. capsulata, 12.0 mg lyophilized R. capsulata in a total volume of 5 ml under an atmosphere of argon with 175,000 lux of white light, 2  $\mu$ moles of hydrogen were formed in 30 minutes. Apparently the hydrogenase of the photosynthetic bacterium is sufficiently stable to the oxygen liberated by the photosynthetic activity of algae to form hydrogen from the photosynthetically formed TPNH.

The experiments cited here as well as other conclusively show that hydrogen can be formed by the biophotolysis of water.

## A LONG-RANGE APPROACH TO THE NATURAL GAS SHORTAGE UTILIZING NONFOSSIL RENEWABLE CARBON

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### INTRODUCTION

The production of substitute natural gas (SNG) from petroleum liquids, coal, and oil shale to alleviate the natural gas shortage has received considerable developmental effort. Commercial SNG processes based on these fossil feeds will undoubtedly play important roles in the future of the U.S. gas industry and help to maintain it as a methane marketer over the next few decades. But fossil feeds for the production of SNG are still finite natural resources, and ultimately depletion will occur. A very promising long-range practical solution to this problem is to convert a major source of continuously renewable nonfossil carbon to SNG.<sup>1,2</sup>

One source of nonfossil carbon that has been considered is organic wastes.<sup>3</sup> The growing environmental and pollution problems caused by the generation of organic wastes in the United States provides an opportunity to combine improved waste-disposal technology, for recycling valuable waste components into the economy, with energy recovery in the form of SNG. Table 1 summarizes the results of a recent study to survey the various types of organic wastes generated in the United States and the amounts that are collected and available for conversion to synfuels.<sup>4</sup> At SNG yields per ton of dry waste of 10,000 cubic feet, about 8.8 trillion cubic feet of SNG could be produced each year if all of the wastes could be processed. This is obviously not possible; all of the wastes could not be collected for this purpose even if laws were passed requiring total collection and a concerted effort were made to achieve it. However, if total collection did occur, the amount of SNG that could be produced would still fall far short of the U.S. annual demand for natural gas, which is currently about 24 trillion cubic feet. Organic wastes offer a significant source of supplemental synfuels, but are not the total answer to fossil fuel depletion. Another source of nonfossil renewable carbon must be utilized.

The most promising source of this carbon is water- and land-based biomass produced from ambient carbon dioxide and solar energy by photosynthesis.<sup>1,2</sup> Biomass is defined as all growing organic matter, such as plants, trees, grasses, and algae, and, in a real sense, is perpetually renewable. The production of SNG from low-cash-value, high-fuel-value biomass would offer a major, controllable, nonpolluting, storable source of fossil fuel substitutes. It has been estimated that 146 billion tons of biomass, most of which is wild and not controlled by man, is produced on the earth each year,<sup>5</sup> so at the same SNG yield used for organic wastes above, about 1.6% of this amount of biomass would provide enough raw material to meet all of our natural gas demand. With the advanced state of U.S. agricultural practice, it is conceivable that the conversion of solar energy to SNG via biomass could be achieved to establish what might be called "A Perpetual Methane Economy."

The concept of A Perpetual Methane Economy reduces itself to the development of suitable methods for planting, growing, harvesting, transporting, and converting biomass to SNG. The purpose of this paper is to review the important factors related to the development of this concept. Although liquid fuels and syncrudes can also be produced from biomass,<sup>2</sup> they are not included in the review.

Table 1. ESTIMATES OF AVAILABLE ORGANIC WASTES, 1971

Source	Total Organic Wastes Generated	Organic Solids Available
	10 <sup>6</sup> tons/yr	
Manure	200	26.0
Urban Refuse	129	71.0
Logging and Wood Manufacturing Residues	55	5.0
Agriculture Crops and Food Wastes	390	22.6
Industrial Wastes	44	5.2
Municipal Sewage Solids	12	1.5
Miscellaneous Organic Wastes	50	5.0
Total	880	136.3
Net Oil Potential, 10 <sup>6</sup> bbl	1098	170
Net Gas for Fuel Potential, 10 <sup>12</sup> CF	8.8	1.36

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### SYSTEM DESIGN

The overall design of a biomass-to-SNG system depends on several parameters such as the type, size, number, and location of the biomass growth and processing areas. In the ideal case, the SNG production plants would be located in or near the biomass growth areas to minimize the cost of transporting the harvested biomass to the plants, all the nonfuel effluents of which are recycled to the growth areas. If this kind of "synfuel plantation" could be developed, it would be equivalent to an isolated system with inputs of solar radiation, air, carbon dioxide, and minimal water, and one output, SNG. A schematic design of such a system is depicted in Figure 1. The nutrients are kept within the ideal system so that the addition of external fertilizers and other materials is not necessary. Also, the environmental and disposal problems are eliminated.

Onsite production of synfuel from the biomass would be facilitated in land-based synfuel plantations and near water-based growth areas where the natural water currents might function as a transport vehicle for the biomass to move it to the conversion plant sites. The gasification plants would be strategically located onshore with respect to biomass supply, recycling, and SNG transmission or transportation facilities.

The achievement of optimum system designs will be necessary to make the manufacture of SNG from biomass a commercial reality. The scope and size of commercial SNG plantations alone will demand careful planning and total integration of each operation because any errors in design will result in operating difficulties that can seriously affect the continuity of production, efficiencies, and economics.

The risks in such a large venture will have to be minimized by evolutionary development in a logical sequence of steps, such as system synthesis, preliminary analysis, small-scale demonstration, second-stage analysis, moderate- to large-scale demonstration over a prolonged time period, final analysis and system optimization, and full-scale commercialization. The business and political problems associated with each system cannot be overlooked either, because any new industry of

this magnitude will undoubtedly have its quota of skeptics among those who can benefit from the technology. The development program must produce the information needed to prove the viability of the concept beyond any doubt.

## BIOMASS PRODUCTION

In the last few decades, the production of biomass for foodstuffs applications has been significantly improved through the use of modern techniques and equipment. Higher yields and more nutritious strains of crops have been developed as a result of these advanced methods, and much of the information could be applied to the development of low-cash-value, high-fuel-value biomass for SNG production. Also, our basic knowledge of photosynthesis has advanced so that specific biomass crops and growth methods can be optimized together to improve production.

A broad range of biomass production technology is available because the crops can either be land- or water-based. Suitable crops might include certain land-based, high-yield grasses and water-based algae, which can be grown in either fresh water or seawater. The goal of any program undertaken to develop and select the best biomass forms for SNG manufacture is to choose the highest yield, highest fuel-value crops that require minimum labor during planting, growth, and harvesting, and that not only survive but thrive in most climates. Also, it is desirable to use crops that have no large-scale markets as foodstuffs or materials. As expected, no one crop meets all of the desired characteristics, but, fortunately, numerous biomass species meet many of the idealized requirements.

A preliminary assessment of biomass production as it relates to SNG has been performed, and a few in-depth studies are in progress to assist in the selection of optimum biomass forms.<sup>1,6</sup> Some of the important parameters that were studied included biochemical energy transfer classification, solar energy capture efficiency, growth rate and cycles, yields, nutrient needs, water needs, carbon content and fuel value, insolation, temperature, and rainfall. These studies have attempted to quantify the relationship of these parameters and their importance in selecting the proper biomass types and production methods. It is not the purpose of this paper to review this information in detail; instead, the major conclusions will be summarized.

One major conclusion is that it appears sufficient yields of certain plants can be obtained to provide suitable raw material for conversion to large quantities of SNG. Examples of biomass that may prove to be optimum crops include land crops of Sudangrass, napiergrass, sorghum, sugarcane, sunflower, kenaf, and eucalyptus, sycamore, and poplar trees; freshwater crops of water hyacinth and the unicellular algae, Chlorella and Scenedesmus; and seawater crops such as Macrocystis pyrifera (giant kelp). Several of these crops are capable of production at yields of 20 to 30 tons dry organic matter/acre-year, and some have been reported to be produced at yields over 60 tons/acre-year. Also, the fuel values generally range from about 5000 to 8000 Btu/dry lb. These crops are believed suitable for SNG production.

Another important conclusion from these studies is that relatively large areas of land or water are needed to grow enough biomass to supply the U.S. fuel needs. For example, at a yield of 50 tons/acre-year of dry biomass, about 169,000 square miles are required at an overall thermal efficiency of conversion of 35% to SNG to replace all of the U.S. natural gas demand with SNG as indicated in Table 2.<sup>1</sup> This area corresponds to a square 411 miles on each edge and might be considered to be a major roadblock to commercialization of a biomass-to-synfuel industry. But, on further examination, it does not seem to be an insurmountable barrier, especially when considered in light of the problem solved. First, this area is about 5.6% of the Lower-48-State area. Idle farmland and deserts comprise about 6.4% of the Lower 48 States now. When compared with the surface areas of the oceans, a small portion of which might be devoted to biomass production, a

411-mile square seems to be an insignificant part of the whole. Also, it is possible to conceive of combined foodstuffs and biomass-for-fuel production, so some growth areas might serve dual functions. In some cases, symbiotic relationships might lead to further improvement in both biomass forms. Finally, it should be realized that the preliminary studies that have been made are based primarily on existing information. Major improvements in yield, fuel value, and other important properties might emanate from field-test programs.

Table 2. POTENTIAL SNG PRODUCTION FROM BIOMASS\*

PERCENT OF PRESENT DEMAND <sup>†</sup>	AVERAGE AREA REQUIRED, sq miles		
	10 ton/acre-yr	25 ton/acre-yr	50 ton/acre-yr
1.66	12,000	5,000	2,800
10	72,000	30,100	17,000
50	361,500	150,500	84,500
100	723,000	301,000	169,000

\*Based on indicated dry yields at overall thermal efficiency of conversion to SNG of 35% and fuel value of 6500 Btu/dry lb.

<sup>†</sup>Calculations based on annual demand of  $22 \times 10^{12}$  cubic feet.

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No field tests of any significant size are yet in progress to optimize biomass production methods and specific biomass crops for SNG manufacture. However, the U.S. Navy has announced plans to begin such a program with giant kelp off the California coast.<sup>7</sup>

#### BIOMASS CONVERSION TO SNG

Methane can be produced from biomass by digestion, pyrolysis, and hydrogasification as shown in Figure 2. Digestion is a biological process that occurs in the absence of oxygen and in the presence of anaerobic organisms at ambient pressures and at temperatures of 95<sup>o</sup>to150<sup>o</sup>F. The biomass is supplied to the anaerobic digesters as a water slurry and is converted to an intermediate-Btu gas (450 to 800 Btu/cubic foot) that is essentially a two-component gas containing methane and carbon dioxide. This product is easily upgraded to pipeline gas (SNG) by removal of carbon dioxide in conventional amine scrubbers or by other methods. IGT's Biogas<sup>TM</sup> Process (Figure 3) is an example of such processes.<sup>3</sup>

Biomass can also be converted to SNG by pyrolysis. Pyrolysis consists of thermal decomposition of the feed at low pressure in the 900<sup>o</sup> to 1700<sup>o</sup>F range. However, the initial product gas is generally a low-Btu gas (100 to 450 Btu/cubic foot) that contains low concentrations of methane and higher concentrations of carbon monoxide, carbon dioxide, and hydrogen. In addition, by-products of char and oxygenated liquids are formed; these are often used to supply the heat for the pyrolysis units. If SNG is the desired end product, the pyrolysis gas must first be adjusted in composition by "shifting" the molar ratio of hydrogen to carbon monoxide in a shift converter to about 3:1, which corresponds to the stoichiometric ratio needed to convert the carbon monoxide to methane in the methanator. The gas is then scrubbed to remove carbon dioxide, and the resulting gas, which contains methane, carbon monoxide, and hydrogen, is methanated to yield SNG. The process developed by West Virginia University for solid-waste pyrolysis should also be suitable for biomass pyrolysis.<sup>8</sup>

In the hydrogasification process, part of the biomass feed is first converted to hydrogen by partial oxidation or steam-reforming followed by shifting to increase the hydrogen content as high as

possible. The hydrogen-rich gas is then reacted with the remaining biomass at 500<sup>o</sup> to 1500<sup>o</sup>F and 500 to 2500 psi to hydrogenate it and yield a product gas high in methane. The gas is then upgraded to SNG by shifting, scrubbing, and methanating as in the pyrolysis process.

As might be expected, each of these three processes is not energetically suitable for all types of biomass. Some types of biomass, especially those in the water-based category, usually contain large quantities of intracellular water, as high as 90 to 95%. If this type of feed is pyrolyzed or hydrogasified, the water must be removed before thermal treatment, or a large amount of feed energy is consumed in the process simply in driving off the water before gasification.<sup>1</sup> The curves in Figure 4 illustrate the effect of moisture content on the energy available for conversion of heat-dried biomass to SNG. For example, if a biomass containing 70% moisture is heat-dried to a moisture content of 30%, only 62% of the energy content is available for conversion to SNG. Anaerobic digestion is preferred for those feeds high in moisture because the process requires large amounts of water. Air-drying of biomass is the most economical drying method if it is needed.

Table 3 lists representative examples that have been reported of methane-containing products made from various biomass plants. Available information on actual experimental data is limited because the biomass-to-synfuels concept has only recently begun to receive attention. Only a few research groups are developing data at present, but the data base is expected to expand rapidly in the near future.

Table 3. EXAMPLES OF FUEL GAS PRODUCTION FROM BIOMASS

Biomass	Conversion		Fuel Products <sup>a</sup>
	Reaction	Approximate Conditions	
Pine Bark <sup>9</sup>	Pyrolysis	900 <sup>o</sup> C, ambient pressure	Low-Btu gas, char, oil <sup>b</sup>
Rice Straw <sup>9</sup>	Pyrolysis	200 <sup>o</sup> -700 <sup>o</sup> C, ambient pressure	Low-Btu gas, char, oil <sup>b</sup>
Cellulose (Refuse) <sup>10</sup>	Hydrogasification	540 <sup>o</sup> C, 1000 psi	High-Btu gas (after CO <sub>2</sub> ), char
Wood (Excelsior), Paper <sup>11</sup>	Digestion	30 <sup>o</sup> C, 30 days	Intermediate-Btu gas
Grass <sup>12</sup>	Digestion	48 <sup>o</sup> C, 10-28 days	Intermediate-Btu gas
Water Hyacinth <sup>c, 12</sup>	Digestion <sup>d</sup>	48 <sup>o</sup> C, 28 days	Intermediate-Btu gas
Seaweed Algae <sup>e, 12</sup>	Digestion	33 <sup>o</sup> and 48 <sup>o</sup> C, 20-50 days	Intermediate-Btu gas
Unicellular Algae <sup>f, 13</sup>	Digestion	35 <sup>o</sup> and 55 <sup>o</sup> C, 30 days	Intermediate-Btu gas

<sup>a</sup>Low-Btu gas, 100-450 Btu/CF; intermediate-Btu gas, 450-800 Btu/CF; high-Btu gas, >800 Btu/CF.

<sup>b</sup>Minor product.

<sup>c</sup>*Eichhornia crassipes*.

<sup>d</sup>After caustic treatment.

<sup>e</sup>*Macrocystis pyrifera*; commonly called giant kelp; grown in seawater.

<sup>f</sup>Principally *Scenedesmus* spp. and *Chlorella* spp.; grown in fresh water.

## ECONOMICS AND ENERGETICS

The economics of biomass conversion to SNG are in a preliminary stage of development. However, some idea of the cost structure can be obtained from existing information. Table 4 illustrates the energy cost of several selected biomass species. With the exception of the edible portion of corn,

whose energy cost was calculated from current market prices, the price range varies from \$0.42 to \$1.88/million Btu, which places biomass energy in a range competitive with the current costs of fossil fuel energy. Of course, the cost of converting biomass to SNG must be added to the biomass energy costs.

Table 4. SELECTED COST ESTIMATES OF BIOMASS ENERGY

Biomass	Yield, dry tons/acre-yr	Fuel Value, Btu/dry lb	Estimated Cost, \$/10 <sup>6</sup> Btu
Corn	2.27*	6,500*	9.70 <sup>†</sup>
Corn Silage <sup>15</sup>	15.9	6,500	1.31
Corn Silage <sup>15</sup>	6.5	6,500	1.88
Conifer <sup>15</sup>	—	7,000	1.25-1.75
Poplar <sup>15</sup>	10	7,800	0.90-1.00
Sugarcane <sup>6</sup>	25	7,500	0.63
Kenaf <sup>6</sup>	20	7,500	0.61
Kenaf <sup>6</sup>	6	7,500	1.40
Land or Water Based <sup>1</sup>	20	8,000	0.79-1.46 <sup>‡</sup>
Land or Water Based <sup>1</sup>	50	8,000	0.42-0.87 <sup>‡</sup>
Land Based <sup>6</sup>	30	7,500	0.65

\*Assumed values based on current yield and market information.<sup>14</sup>

<sup>†</sup>Calculated from assumed values and market price of \$3.53 per bushel of No. 2 yellow corn (Chicago).<sup>14</sup>

<sup>‡</sup>Calculated from Table 11 in Reference 1.

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A few cost estimates have been reported on the conversion of biomass to SNG as shown in Table 5. There is a wide diversity of plant sizes, conversion efficiencies, and capital requirements in this particular tabulation, but the SNG price ranges from only \$0.73 to \$3.50/million Btu. One of the available SNG-from-coal projections is also included in this table for comparison.

An interesting factor in the production of biomass alluded to in Table 4 concerns the energy budget of the system, i.e., the total energy into the system and the product energy returned. Few studies of this type have been made. One of the in-depth studies computed the energy budget of U.S. corn production and included all of the nonsolar energy inputs into the system such as electric power, equipment fuels, and the energy needed to manufacture ammonia fertilizer which is made primarily from natural-gas-derived synthesis gas.<sup>17</sup> Some of the information developed in this study has been converted to thermal energy production efficiency (energy in/energy out) and nonsolar energy input/lb of corn produced and plotted versus year (Figure 5). Less energy was expended to produce a pound of corn in 1940, which means that the energy input is utilized less efficiently today.

This kind of energy budget treatment is directly related to SNG because one of the important factors that has largely been ignored in the development of new energy supplies concerns the net

Table 5. PRELIMINARY COST ESTIMATES OF BIOMASS-DERIVED SNG

Biomass	Biomass Yield, dry ton/acre-yr	Biomass Fuel Value, Btu/dry lb	Gasification Process	SNG Production, CF/day	Area Required, acre	Eff. % <sup>b</sup>	Capital Requirement, \$	SNG Cost, \$/10 <sup>6</sup> Btu
Land or Water Based <sup>1</sup>	20	8,000	Digestion	$1.0 \times 10^{12}$ <sup>a</sup>	$3.26 \times 10^6$	35	$1.6 \times 10^9$	1.10-1.77
Land or Water Based <sup>1</sup>	50	8,000	Digestion	$1.0 \times 10^{12}$ <sup>a</sup>	$1.30 \times 10^6$	35	$0.98 \times 10^9$	0.73-1.17
Giant Kelp, Floating <sup>1b</sup>	2.8 <sup>b</sup>	5,160 <sup>c</sup>	Digestion	$3.56 \times 10^{12}$ <sup>d</sup>	$64.0 \times 10^6$	70	$5.0 \times 10^9$	2.48
Giant Kelp, Anchored <sup>1c</sup>	49	5,160	Digestion	$19.2 \times 10^{12}$	$22.4 \times 10^6$	62	$105 \times 10^9$	3.50
Land Based <sup>b</sup>	30	7,500	Air Dry, Pyrolysis	$76.0 \times 10^{12}$ <sup>a</sup>	$89.6 \times 10^3$	69	$0.325 \times 10^9$	2.09
Coal <sup>b</sup>	-	-	Hydro- gasification	$250 \times 10^6$	-	-	$0.350 \times 10^9$	1.61

<sup>a</sup>Biomass is assumed to be gasified onsite at growth area, transportation costs of biomass and SNG not included.

<sup>b</sup>Calculated from referenced area of 250 miles x 400 miles in which it was estimated that 80% of kelp is harvested.

<sup>c</sup>Calculated from referenced information which indicates kelp yield of  $1.8 \times 10^8$  dry tons/yr, conversion of 70% of its energy content to SNG, and SNG yield of  $1.3 \times 10^3$  CF/yr.

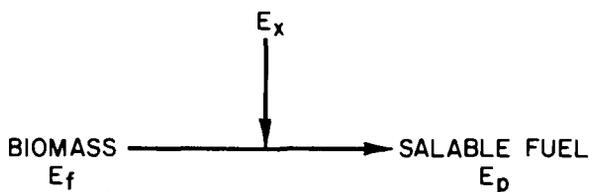
<sup>d</sup>As liquefied SNG.

<sup>e</sup>Calculated from ratio of energy produced as SNG and fuel value of biomass feed:  $100 E_p/E_f$ .

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energetics of the system. \* Valid comparisons of different systems cannot result from only synfuel cost estimates and capital and operating cost projections; these factors do not necessarily correlate with net energy production. Nor can valid comparisons be made simply by calculating the thermal efficiency or the energy in and out of a process. All of the energy inputs involved in planting, harvesting, transportation, fuel production, and recycling of product streams should be considered. It is essential that these factors be lumped together with economics in the fully integrated system. Since the primary objective is to produce new fuel supplies, more fossil fuel substitutes must be produced as salable end products than the fossil fuels consumed in the system. Even then, the selection of the best of several systems is a difficult one to make.

For example, let  $E_f$ ,  $E_x$ , and  $E_p$  represent the energy content of the dry biomass, the sum of the external nonsolar energy inputs into the total system, and the energy content of salable fuels, respectively. Diagrammatically, the system can be represented as follows:



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Then the ratio,  $(E_p - E_x)/E_x$ , which can be termed the Net Energy Production Ratio, indicates how much more (or less) salable fuel energy is produced than that consumed in the integrated system if the external energy consumed is replaced, and it is assumed that the biomass feed energy is zero. This is a reasonable assumption because the energy value of the biomass is derived essentially 100% from solar radiation. Net Energy Production Ratios greater than zero indicate that an amount of energy equivalent to the sum of the external energy inputs and an additional energy increment of salable fuel are produced; the larger the ratio, the larger the increment. The ratio  $100 E_p/E_f$  is the Fuel Yield Efficiency and is a measure of how much biomass energy is diverted to other than salable fuels in the system. The ratio  $100 E_p/(E_f + E_x)$  is the overall Fuel Production Efficiency of the system.

\*The rationale presented here is also applicable to synfuels from fossil feeds.

In Table 6, a comparison of selected end product costs, as either SNG or biomass energy, and the calculated Net Energy Production Ratio for each end product is presented. A correlation exists between these ratios and the biomass energy costs listed, namely, the higher the energy cost, the lower the ratio. However, the corresponding correlation does not apply to the listed SNG cases. The Net Energy Production Ratio is therefore a useful tool when considered together with the energy costs to evaluate synfuel systems and, especially, to bring out the importance of the external energy inputs.

Table 6. COMPARISON OF ESTIMATED END PRODUCT COST AND NET ENERGY PRODUCTION RATIO

Biomass	Conversion Process	Fuel Efficiency Yield, % <sup>a</sup>	End Product	End Product Cost, \$/10 <sup>6</sup> Btu	Net Energy Production Ratio <sup>b</sup>
Rice (U.S.A.) <sup>18, 19</sup>	None	-	Rice	26.70 <sup>c</sup>	0.67 to 0.80 <sup>e</sup>
Corn (U.S.A.) <sup>17</sup>	None	-	Corn	9.70 <sup>d</sup>	1.82 <sup>f</sup>
Giant Kelp, Floating <sup>16</sup>	Digestion	70	LNG	2.48	5.07 <sup>g</sup>
Land Based <sup>6</sup>	None	-	Biomass	0.65	17.40 <sup>h</sup>
Land Based <sup>6</sup>	Air Dry, Pyrolysis	69	SNG	2.09	2.34 <sup>i</sup>
Land or Water Based <sup>20</sup>	Digestion	35	SNG	0.73 to 1.77	3.79 <sup>j</sup>

<sup>a</sup>100 E<sub>p</sub>/E<sub>r</sub>

<sup>b</sup>(E<sub>p</sub> - E<sub>x</sub>)/E<sub>x</sub>

<sup>c</sup>Average price of \$20.00/100 lb and 7500 Btu/dry lb assumed.

<sup>d</sup>From Table 4.

<sup>e</sup>Calculated from References 18 and 19 that state that 1/5 to 1/3 of energy input returned as end product. NEPR = (0.2 - 1.0)/1.0, and (0.33 - 1.0)/1.0.

<sup>f</sup>Calculated from in-depth analysis in Reference 17 for year 1970 that states that 2.82 kcal returned/kcal input; NEPR = (2.82 - 1.0)/1.0.

<sup>g</sup>Calculated from Table 1 in Reference 6 utilizing reported estimate that 16.48% of end product fuel content consumed by system; NEPR = (1.0 - 0.1648)/0.1648.

<sup>h</sup>Calculated from Table 5, p. 51, in Reference 6, using reported estimate that total energy yield for case analyzed was 45 X 10<sup>7</sup> Btu out and 2.45 X 10<sup>7</sup> Btu consumed; NEPR = (45 - 2.45)/2.45.

<sup>i</sup>Calculated from conditions assumed in Reference 6: 5.6% biomass energy content required as energy input in growth phase, 15.0% of biomass energy content required as energy input on gasification, and Fuel Yield Efficiency of 69.0%; NEPR = (0.69 - 0.206)/0.206.

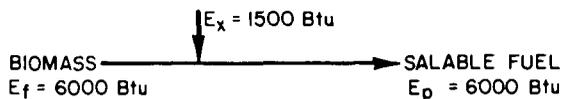
<sup>j</sup>Calculated from conditions assumed in Reference 20 for waste conversion in which 2.7% of feed energy equivalent required as external energy input on gasification, Fuel Yield Efficiency is 35%, and assuming 5.6% of biomass energy content is required as energy input in growth phase as in Reference 6; NEPR = (0.35 - 0.073)/0.073.

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For biomass having an energy content of 6000 Btu/dry lb, a plot of Net Energy Production Ratio versus the total external energy input as a percentage of the feed energy equivalent (100 E<sub>x</sub>/E<sub>r</sub>) provides the two curves shown in Figure 6 for Fuel Yield Efficiencies of 66.6% and 100%. If the following two systems selected from Figure 6 are compared, which is preferred?

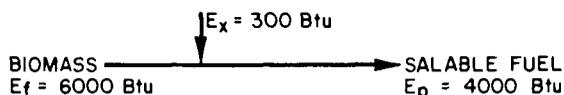
Is the first system preferable because it has a higher Fuel Production Efficiency, or is the second system preferable because it has a higher Net Energy Production Ratio? Consideration of this kind of information in conjunction with economics is necessary to make an intelligent choice. Also, in this simplified treatment, the boundary is not drawn regarding the size of the system. Thus, tractors may be used to plant and harvest biomass. The fuel requirements of the tractors are certainly part of E<sub>x</sub>, but is the energy expended in manufacturing the tractors also part of E<sub>x</sub>? In-depth studies are necessary to decide these questions.

*ENERGETICS OF TWO SELECTED SYSTEMS*



$$(E_p - E_x)/E_x = 3.0$$

$$100 E_p/(E_f + E_x) = 80\%$$



$$(E_p - E_x)/E_x = 12.3$$

$$100 E_p/(E_f + E_x) = 63\%$$

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**SUMMARY**

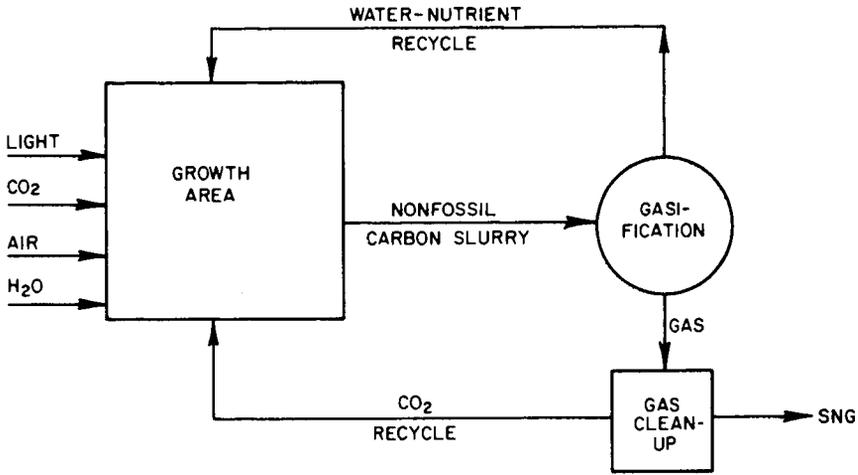
The concept reviewed in this paper to attain A Perpetual Methane Economy by conversion of biomass to SNG is technically feasible. After suitable development, the commercialization of an SNG industry using low-cash-value, high-fuel-value biomass raw materials will probably be economically attractive and permit conservation of our valuable fossil fuel reserves. Since the basic technology is already on hand, large-scale programs to refine the technology and to develop intergrated systems should be started without delay before fossil fuel depletion causes greater energy supply problems.

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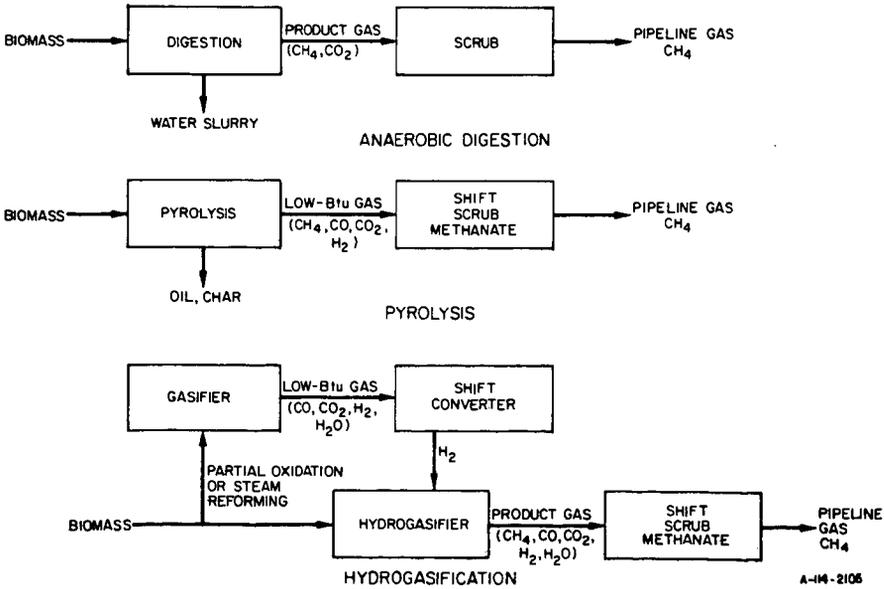
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FIG. 1. SCHEMATIC DIAGRAM OF BIOMASS-TO-SNG SYSTEM



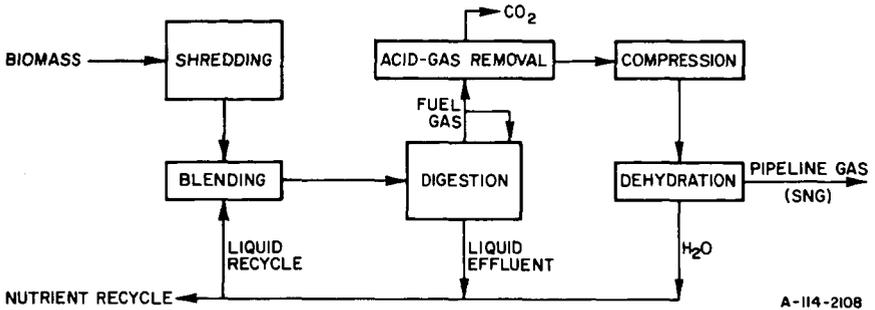
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FIG. 2. SCHEMATIC DIAGRAM OF THE THREE PRINCIPAL METHODS OF METHANE PRODUCTION FROM BIOMASS



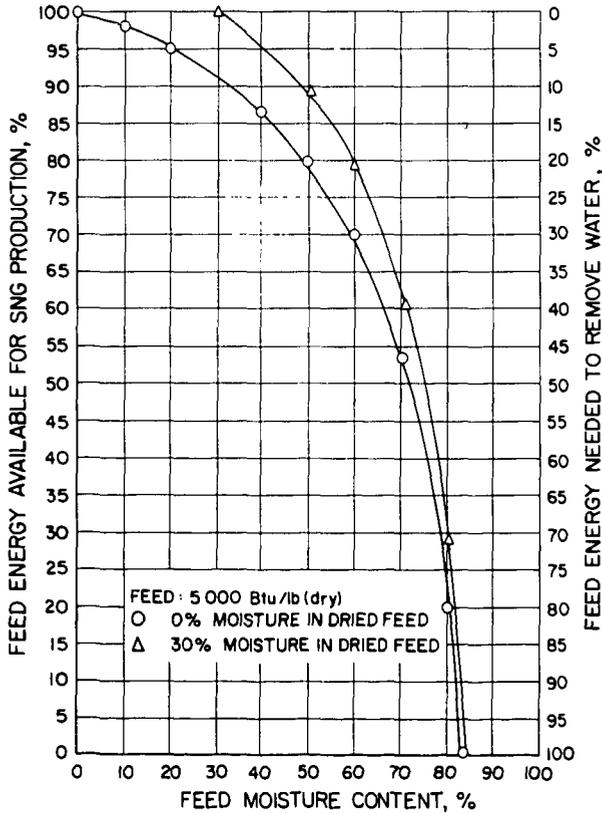
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Fig. 3. EXAMPLE OF BIOGAS™ PROCESS DESIGN USING BIOMASS FEEDS



A-114-2108

Fig. 4. EFFECT OF FEED MOISTURE CONTENT ON ENERGY AVAILABLE FOR SNG PRODUCTION



A-114-2110

Fig. 5. THERMAL ENERGY PRODUCTION EFFICIENCY AND ENERGY INPUT FOR U.S. CORN FROM 1945 TO 1970

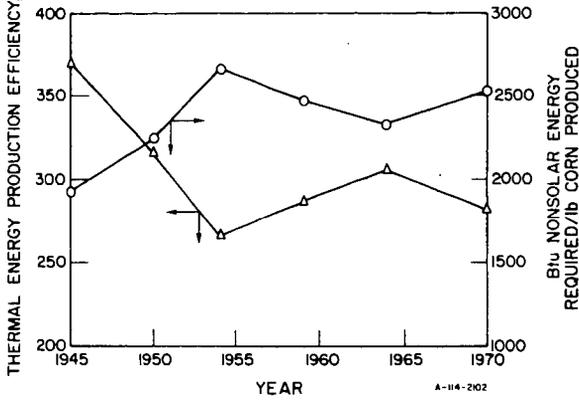
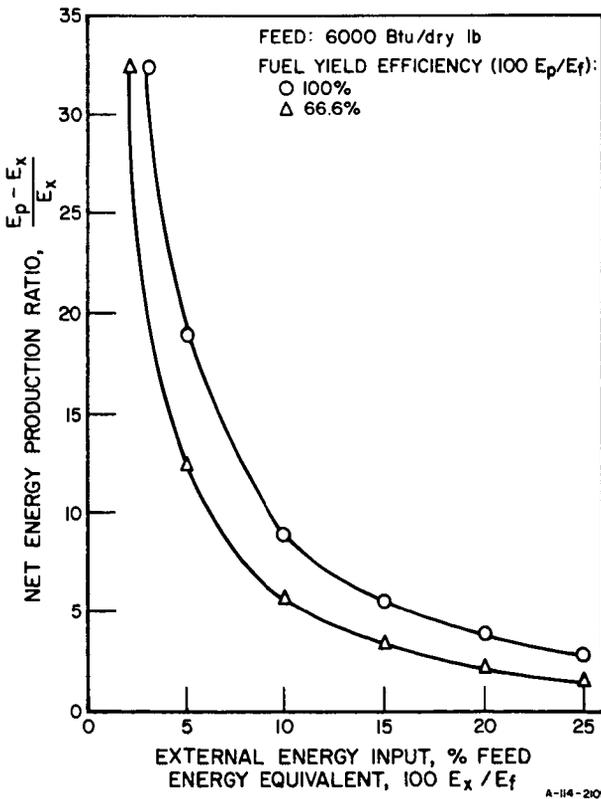


Fig. 6. NET ENERGY PRODUCTION RATIO vs. EXTERNAL ENERGY INPUT



METHANOL OR AMMONIA PRODUCTION FROM SOLID WASTES  
BY THE CITY OF SEATTLE

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## I. INTRODUCTION

Solid waste disposal on an acceptable environmental and cost basis is one of the most nagging, costly, and unpleasant problems facing Seattle and other cities in America. Escalating costs for disposal labor and transportation and the difficulty of finding suitable landfill sites has caused what was simply an unhandy problem a decade ago to become a major problem for the City.

In the 1960's, the federal government and industry began to emphasize development of major new alternatives to the historic methods of solid waste disposal. A number of new handling and disposal methods have reached development maturity and are available for application. The past decade has also seen widespread acceptance of the fact that affluence and waste need no longer be synonymous. Terms like "recycling" and "urban ore" typify a changing attitude toward what was once simply garbage. Public demands for environmental reform, prudent land use, and economy in public services, have all simultaneously crested in a time of fuel cost increases, power shortages, and a recognition that terrestrial resources are finite.

In this context, the Mayor of Seattle and the Chairman of the Utilities Committee of the Seattle City Council, in December of 1973, commissioned the Engineering and Lighting Departments of Seattle to aggressively undertake a program of utilizing the latent material and energy potential of Seattle's municipal solid wastes.

In May of 1974, an interdepartmental report appropriately titled *SEATTLE'S SOLID WASTES...AN UNTAPPED RESOURCE* (1) was presented to the Mayor with the revelation that of numerous solid waste disposal options, the conversion of solid waste to methanol, as suggested by T. Reed (2,3), appeared to be the most environmentally advantageous and economical. Table 1 summarizes the comparative economic findings of the Seattle study.

Briefly stated, all practical disposal alternatives except conversion to methanol or to a bulk confetti-like air-classified fuel, were found to be as costly or more costly for Seattle than continued waste disposal in landfills. It was later found that the bulk fuel alternative is impractical, leaving methanol production as the most promising alternative from an economic standpoint. Conversion of waste into methanol may also be a method for achieving fuel independence for the City's motor fleet and a modest reduction of air pollution from City vehicles. These potential benefits, plus the opportunity for eliminating dependence on landfills, except for inert materials, caused the City to undertake more intensive investigations of the feasibility of solid waste conversion.

In June of 1974, the Seattle firm of Mathematical Sciences Northwest, Inc. (MSNW), was retained to do an intensive study of the technical feasibility, economics, and environmental impact of conversion of Seattle solid waste to methanol, and use of methanol as a vehicle fuel. (4) The MSNW study confirmed that the proposed conversion process was technically feasible; however, neither the quantity of methanol produced nor the system economics were found to be as attractive as

initially believed. Nevertheless, the process still showed promise as being superior to landfill. In addition, the study disclosed an opportunity for using the same basic technologies for the manufacture of ammonia. These findings, plus further verification that methanol is a potentially practical automotive fuel (5,6,7), have caused the City of Seattle to intensify project planning.

## II. PROCESS DESCRIPTION

The process as envisioned for the City consists of grinding the solid waste to make it more convenient to convey and pyrolyze. Following coarse grinding, ferrous materials are removed magnetically, following which the remaining residues--paper, wood, glass, yard wastes, domestic wastes, organics, and plastics--are charged into a pyrolysis system.

There are several pyrolysis systems currently being developed. One system that is in the late stages of large scale and successful demonstration is the Union Carbide Corporation's Purox system (8). In this system, solid waste is charged into the top of a structure similar to a blast furnace. As the solid waste migrates downward, it is heated by rising gases generated from the oxidation of residues at the bottom of the vessel. This hot gas permeates upward through the solid waste, providing the necessary heat for the conversion of the cellulosic materials into additional carbon monoxide plus hydrogen. The gas leaving the top of the reactor, which consists largely of carbon monoxide, hydrogen, and water vapor, is then processed through a closed gas-cleaning system in which water and other impurities are trapped. The product gas leaving the system consists of approximately two-parts carbon monoxide to one-part hydrogen plus impurities.

The first step for subsequent treatment of the gas as currently envisioned is an absorption process to remove sulfur compounds and convert the sulfur to its elemental state. This is to be done for pollution control reasons and to protect the catalysts used in subsequent synthesis operations. The objective of this step should be to achieve a gas concentration of 0.5 ppm or less sulfur. Following this step, a water-gas shift is employed to alter the carbon monoxide-hydrogen ratio. In this traditional process, steam is added to the gas stream in the presence of a catalyst and under appropriate pressure and temperature conditions. The quantity of hydrogen and carbon dioxide in the inlet clean gas is approximately doubled and halved, respectively, so that the shifted gas has a composition of about one-part carbon monoxide to two-parts hydrogen, the stoichiometric ratio required for methanol synthesis. The amount of carbon dioxide produced in the shift reaction is large and must be purged down prior to the synthesis step.

The product synthesis step, while requiring complex equipment, is relatively straightforward. Under conditions of heat and pressure and in the presence of a catalyst, the carbon monoxide and hydrogen are spontaneously combined into methanol. Alternatively, the shift reactor may be designed to more completely shift carbon monoxide in the inlet gas to carbon dioxide and hydrogen. The hydrogen, in combination with nitrogen, may then be reacted by the traditional method, using catalysts, to produce ammonia gas. By-product nitrogen resulting from oxygen production in the head-end pyrolysis step is more than sufficient to meet the requirements of ammonia synthesis in this case.

The product yields computed in this study were 370 pounds of methanol per ton of solid waste, or 445 pounds of ammonia per ton of solid waste. On an annual basis, these amounts represent potential yields of approximately 100,000 tons of methanol per year (31-million gallons per year) or 120,000 tons of ammonia per year, starting from 550,000 tons per year of municipal solid waste. While these amounts of chemical products seem large to city government, they represent only a small percentage of national production for these products. What is of interest, of course, is that they represent potential revenues with which to reduce the future cost of solid waste disposal.

Both the methanol and ammonia processes are established commercial processes. The raw material now used for their manufacture is primarily natural gas. In the context of fuel conservation, then, the production of chemical methanol or ammonia from solid waste represents conservation of natural gas which might otherwise have been used for these products. The Btu content of the products was found to exceed the external energy required by a factor of 2.5 to 3.0, depending on the product. This factor is measured at the plant boundary; the overall energy balance of the process may be positive or negative, depending upon the ultimate product uses and related thermal efficiencies.

### III. PROJECT ECONOMICS

Solid waste disposal - not chemical production - is the project's primary purpose. Therefore, the project financial target to equal or beat is the combined cost of long-haul transport and sanitary landfill operations. In Seattle, this combined cost is currently \$4.90 per ton and projected to increase significantly by 1978. The indifference point for this project is that situation prevailing when the pyrolysis facility and the chemical synthesis plant operate at an annual net cost of \$3.3 million per year (1978). This will be the cost to the City if landfill disposal is continued. From a project accounting standpoint, a revenue credit can be made to the project for disposal service in an amount equal to what conventional disposal would have cost. This credit is expressed in Table 2 as a "disposal gain" of \$3.3 million.

Obviously, the financial feasibility of the project is dependent upon product prices. Based on late 1974 prices (\$0.38/gallon for methanol and \$150/ton for ammonia), one may postulate that with the diminishing supply and rising cost of natural gas (the usual feedstock for such plants), either plant alternative offers the definite possibility of significantly bettering the marginal economics indicated above. For example, a price of \$0.44/gallon for methanol or \$130/ton for ammonia would entirely offset the disposal gain, yielding free solid waste disposal (1978). Even more favorable prices were developed using assumed escalation values over the entire project lifetime. Such expectations are not unrealistic and should leave an attractive profit margin for any industrial participant in the project. The reliability of solid waste supply and the potential advantage of City financing of the project makes it a potentially attractive product source for the private sector. In assessing product risk, one must consider preservation of the cellulose content of solid waste. If that content were to decrease as a result of paper being extracted from the solid waste supply stream, product production would suffer. A decrease in cellulose feed results in more than a proportional loss in the methanol or ammonia production rate.

### IV. CITY BENEFITS AND CONSIDERATIONS

Solid waste disposal cost is a major consideration to any city contemplating a change in its disposal system. Most professionals in solid waste management view any change as inevitably more costly simply because until recent years, that has been the history of the industry.

Recent rapid changes in the economics of energy--the rising cost and scarcity of fuel for long-haul disposal plus the greater opportunities for entering the energy marketplace as an energy producer--have begun to change that traditional view of disposal economics. This is occurring at a time when public attitudes toward landfill disposal are bordering on hostility because of the environmental and land use compromises that characterize such operations.

Another lesson learned by city governments during the 1973/1974 oil shortage is that public services are dependent on automotive fuel. The City of Seattle, for example, found itself with only 60 percent of its usual gasoline for City

fleet use, and in the minds of many City officials, the situation bordered on one of City government being unable to provide adequate public services. With this memory still fresh in mind and with the possibility of future fuel supply interruptions and even higher fuel prices, there is genuine appeal to the concept of City fuel independence by way of fleet conversion to 100 percent methanol made from municipal solid wastes. Studies performed to date indicate technical feasibility and a need for a fleet testing program to define vehicle conversion requirements and to confirm estimated vehicle performance parameters.

A modest reduction in urban air pollution is another benefit that can be realized from the utilization of methanol as an automotive fuel. (5,6) While the improvement may be minor, it is nevertheless a step in the right direction.

Clearly, there are significant incentives and benefits inherent in a solid waste disposal process that yields either methanol or ammonia.

- Cessation or reduction of landfill disposal.
- Potentially attractive economics.
- City fuel independence and reliability of public services.
- Fuel conservation.
- Reduced urban air pollution.

Preliminary studies show that the recovery plant can be sited next to one of the City's large transfer stations. Neutralization of several plant waste liquid streams will be required for discharge into the regional liquid waste system. Current air pollution standards can be met and noise levels are not expected to exceed 65 dBA at the plant boundary, a level of noise within proposed City standards.

#### V. SYSTEM APPLICABILITY ELSEWHERE

The question frequently arises as to possible widespread use of "The Seattle Concept." In an earlier paper (9), one of the authors projected the potential national benefits of converting municipal wastes to methanol in terms of equivalent automotive fuel and imported crude oil. That projection assumed that 70 percent of all municipal solid waste could ultimately find its way into conversion to methanol and, that product yield (if all were used as automotive fuel) could displace 150-million barrels per year of imported crude oil, for a national balance of trade saving in excess of a billion dollars per year. Aside from the fact that calculated product yields were probably too high, there is legitimate reason to question whether such wide use of the process is likely to be undertaken.

The environmental and energy appeal of converting wastes to methanol or ammonia tend to confuse the practical realities of solid waste disposal. The energy profile of every city is different, and conversion of waste to these products is not likely to be the best solution in every case. The use of solid waste for steam and power generation is an established technology, and where pulverized coal is now used in existing urban plants on a year-around basis, it makes economic and environmental sense to follow the lead of the City of St. Louis and the Union Electric Company where pulverized and air-classified solid waste fuel is suspension-fired in base-load electric utility boilers. Similarly, the Baltimore Landguard installation, where steam is generated from a pyrolysis process and displaces steam that would otherwise have been generated by burning oil in an urban power plant, makes both financial and environmental sense. (10) In both of these cities, electric power demands are heavy during the Summer when solid waste generation is greatest. Also, fossil-powered plants are located close to the source of solid waste. In situations such as these, the economics of producing methanol or ammonia may be less attractive than steam or power generation, at least in the

near future. In arid areas where there is ample land for landfill disposal and the hazards of leachate are minimal, relatively little incentive may exist--except the ethical matter of resource conservation--for a city to undertake any energy recovery system, particularly one as unfamiliar to the lay public as conversion to methanol or ammonia. The studies on which this paper are based also considered the possibility of installing facilities to pyrolyze solid waste coupled with sale of the clean gas for direct fuel use, thus avoiding the expense of chemical synthesis plant installation. In this case, markets for the clean gas were not identified. In other locales, where customers for the fuel gas exist close to the pyrolysis plant, this solution may prove optimal. Clearly, every city must determine the best solution in the light of its own particular circumstance.

Seattle is situated in a region that utilizes methanol in its wood products industry and ammonia for agriculture. Electric utility loads are minimum in Summer when solid waste generation is maximum and, in most years, hydropower is more than adequate to satisfy demands for electricity through much of the year. Therefore, a process leading to the generation of electricity does not appear to be competitive at this time. Moreover, large close-in fossil-fuel power plants suitable for solid waste combustion are nonexistent. Another factor that enhances the economics of methanol or ammonia conversion processes in this area is that both products are imported at considerable cost (methanol from the Gulf Coast, ammonia from Alaska). Also, ammonia and related fertilizer products are dependent primarily on natural gas which is experiencing dramatic price increases and declining availability. Simply stated, Seattle's situation appears to be tailor-made for the concept of converting solid waste to either methanol or ammonia.

#### VI. SUMMARY

The utilization of municipal solid waste as feedstock for the manufacture of either methanol or ammonia has been found to be technically feasible for the City of Seattle. Further effort is underway to confirm the initial findings of economic feasibility. Such an installation should reduce future disposal costs while simultaneously providing the City with a source of methanol for City motor fleet use. The use of methanol for vehicle fuel will assure continuity of public services during periods of fuel shortages and aid in reducing urban air pollution. After diverting 6,000,000 gallons per year of methanol for City fleet use, 25,000,000 gallons per year of methanol, or 100,000 tons per year of ammonia can be made available for marketing through existing commercial channels. The suitability of this process for other cities depends upon local energy and product markets which must be carefully analyzed on a case-by-case basis.

The list of those academic and industry people who willingly and generously shared their knowledge and offered encouragement for this project, especially during its embryonic stages, would be too long to include here. This opportunity is taken to extend appreciation to them as a group for their important contributions to the Seattle studies.

TABLE 1  
SUMMARY OF DISPOSAL ALTERNATIVES<sup>1</sup>

SYSTEM ALTERNATIVE (1)	NET OVERALL DISPOSAL COST \$/TON (2)
A. Unprocessed Solid Waste Steam-Electric Plant	-16.10
B. Processed Solid Waste Steam-Electric Plant	-13.77
C. Processed Solid Waste/Pulverized Coal Steam-Electric Plant 60,000 KW	-15.62
D. Processed Solid Waste/Pulverized Coal Steam-Electric Plant 100,000 KW	-18.62
E. Processed Solid Waste/Pulverized Coal Steam-Electric Plant 200,000 KW	-25.97
F. Processed Solid Waste/Existing Coal Fired Steam-Electric Plant (Centralia, Washington)	- 6.30
G. Unprocessed Solid Waste Steam Plant (Steam Only)	- 8.15
H. Processed Solid Waste Steam Plant (Steam Only)	- 7.62
I. Processed Solid Waste Pyrolysis Gas Turbine-Electric Plant	-11.07
J-1. Limited Solid Waste Processing Pyrolysis-Oxidation-Gas Turbine-Electric Plant	-10.92
J-2. Processed Solid Waste Pyrolysis-Oxidation-Gas Turbine-Electric Plant	- 9.97
K-1. Limited Solid Waste Processing Pyrolysis-Oxidation System for Methanol Production	- 0.32
K-2. Processed Solid Waste Pyrolysis-Oxidation System for Methanol Production	+ 0.63
L. Processed Solid Waste as a Marketable Fuel	+ 1.03*
M. Unprocessed Solid Waste Landfill Disposal No Energy Recovery	- 7.90

<sup>1</sup>City of Seattle, "Seattle's Solid Waste...An Untapped Resource," May, 1974.

\*NOTE: Does not include haul cost.

TABLE 2

MARGINAL OR "BREAK-EVEN" ECONOMICS OF SEATTLE SOLID WASTE  
METHANOL OR AMMONIA PROJECT (1978)

(1)	METHANOL PLANT (2)	AMMONIA PLANT (3)
Plant Nominal Product Size	300 T/Day	350 T/Day
Annual Product Yield	100,000 T/Year (31,000,000 Ga1/Yr)	120,000 T/Year
<u>CAPITAL COST</u> <sup>1</sup>	\$ 56,000,000	\$ 65,000,000
Debt Service <sup>2</sup>	6,600,000	7,500,000
Operation and Maintenance	<u>7,100,000</u>	<u>8,100,000</u>
<u>FIRST-YEAR COSTS</u>	\$ 13,700,000	\$ 15,600,000
Product Sales	\$ 10,400,000	\$ 12,300,000
Disposal Gain <sup>3</sup>	<u>3,300,000</u>	<u>3,300,000</u>
	\$ 13,700,000	\$ 15,600,000
Marginal (Break-Even) Product Price, First Year	33.6¢/Ga1	\$103/Ton

<sup>1</sup>Gasifiers, gas cleanup, shift process, synthesis plant, site, tankage, and associated facilities.

<sup>2</sup>15-year life, 8% interest.

<sup>3</sup>Disposal cost for equivalent transport and landfill.

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PRODUCTION OF ETHANOL AND VEGETABLE  
PROTEIN BY GRAIN FERMENTATION

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INTRODUCTION

Since the end of World War II the use of synthetic ethanol for industrial purposes in the United States has grown at a steady pace displacing ethanol produced by the fermentation of grain and molasses. In 1970 less than 5% of the U.S. industrial ethanol was produced by fermentation. Because of FDA regulations that require ethanol for human consumption be produced by the fermentation of grain, fruit or sugar, the synthetic ethanol industry has not penetrated the beverage market. In 1972 approximately 37 million bushels of grain were fermented to produce 94.2 million gallons of ethanol expressed as 200°proof (100%) alcohol. During the same year approximately 241 million gallons of ethanol (as 200°proof) were produced synthetically from ethylene and ethyl sulfate. The bulk of the ethanol consumed by industry outside of the United States is produced by fermentation of fruit, grain, and molasses. In 1972, 800 million gallons of fermentation ethanol (as 200°proof) were consumed by industry outside of the U.S.A.

Synthetic ethanol has had a very stable price history. Between 1959 and 1969 the price was 52¢/gallon for 190°proof alcohol. In 1970 the price increased to 54¢/gallon and remained there into 1973. 200°proof synthetic ethanol typically costs 7¢/gallon more than 190°proof. These prices are quoted without the federal beverage alcohol tax.

The dramatic increase in the price of energy which came about in late 1973 has caused the price of ethylene to increase sharply. This in turn has caused a substantial price increase for synthetic ethyl alcohol. An estimate of the 1974 price for synthetic ethanol is shown in Table I. The increase in fuel prices added 10.3¢/gallon to the alcohol cost and the increase in the price of ethylene has added another 28.7¢/gallon to the cost bringing the 1974 price to \$1/gallon. Actual quotations on tank car prices of synthetic ethanol have been difficult to obtain. Two major producers of synthetic ethanol, Exxon Corporation and Tennessee Eastman, have announced that their synthetic ethanol plants would be shut down at the end of 1974. These plants represent about 22% of the U.S. synthetic ethanol production capacity.

The price of ethanol produced by fermentation in the beverage trade is not generally available. A rough estimate can be made if we consider that a fifth of 80°proof vodka sells for as little as \$2.79 including the federal alcohol tax. If one deducts the taxes and, recognizing that vodka is only a 40% blend of ethanol and water, corrects the price to pure ethanol he obtains about \$10/gallon. Recognizing that bottling, packaging, shipping and distribution expenses are significant, it might be reasonable to assume that the fermentation ethanol as 200°proof alcohol is worth at least \$1/gallon

in the distillery storage tanks. This is comparable to the current price estimated for synthetic ethanol.

Because ethanol produced by both processes is chemically equivalent and now cost the same, fermentation ethanol need no longer be limited to the beverage market. Furthermore, with the potential for recovering a valuable protein concentrate from the by-products of fermentation alcohol manufacture it now appears that fermentation ethanol can actually become cheaper than synthetic ethanol. With increasing fuel prices and increased world demand for protein sources fermentation ethanol may have the potential for being produced at a price based on its fuel properties which will make it attractive as a blending component in automotive fuel.

#### PRODUCTION OF ETHANOL BY GRAIN FERMENTATION

The process for the production of ethanol by the fermentation of grain is well established. Starch containing grains such as wheat; corn, milo, etc. are ground to expose the interior of the kernel and cooked to gelatinize the natural starches. The cooked grain is cooled and an enzyme is added to convert the starch to sugar. The sugars are then fermented to ethanol anaerobically with yeast and the alcohol recovered from the mixture by fractional distillation.

Two by-products result from this fermentation process, carbon dioxide and distillers dried grains with solubles. The distillers dried grains represent the insoluble materials in the original grain such as fiber, ash, and protein. The soluble components such as unconverted starch and soluble proteins are concentrated and dried with the distillers dried grains to yield this by-product. The distillers dried grains plus solubles (DDG&S) are a desirable high protein content (25-30%) cattle feed. In 1972 slightly more than 400 thousand tons of DDG&S were produced and in 1973 their average selling price was \$117/ton. The carbon dioxide produced is of high purity and if a market is available this gas can be sold at \$2/ton or more at atmospheric pressure.

The cost of converting grain into 200°proof ethanol is about 28.6¢/gallon of alcohol. This cost includes utilities, labor, supervision, maintenance, etc. but does not include the cost of the grain nor depreciation. The investment for an alcohol plant to produce 20 million gallons/year of 200°proof ethanol from milo (a feed grain belonging to the corn family) is approximately \$18 million. Milo contains about 70% starch and a typical price that agricultural economists estimate in the next 12 months is \$2.29/bushel at a moisture content of 15.5 weight per cent. The process would also produce 174 tons/day of carbon dioxide and about 218 tons/day of DDG&S at a 14% moisture content.

Table III shows an economic evaluation for the production of 20 million gallons/year of 200°proof ethanol from 21,490 Bu/day of milo. With ethanol valued at \$1/gallon and distillers dried grains at \$120/ton, the total annual income from such a plant is \$29.68 million. The expenses for such a plant include the cost of milo, and the conversion cost. These total \$23.68 million per year. This then gives a profit of \$6 million/year before depreciation and taxes which in turn gives a payout of 3 years for the investment of \$18 million.

## RECOVERY OF PROTEIN FROM DDG&amp;S

As mentioned above, the DDG&S contains between 25% and 30% protein depending on the protein content of the original grain. A portion of this protein may be solubilized by treating the DDG&S with a pH greater than 11.0. If the pH is then lowered to about 4.0 a sizable portion of the protein will precipitate. The process equipment requirements are not complex. The amino acid profile of the protein concentrate depends to a great extent on that of the original grain.

Table III contains an economic evaluation for a process to produce 20 million gallons/year of 200° proof ethanol and to recover 66,200 lb/day of protein concentrate (85% protein) from the distillers dried grains and solubles. In this case the value of the DDG&S is reduced to \$90/ton after the protein has been removed. The protein concentrate has been estimated by an agricultural economist to have a value in the human food market of about 60¢/lb. The incremental investment for the protein plant is \$4 million and the conversion cost for recovery of the protein is \$1.09 million per year. The value placed on ethanol in this case is that which will provide a three year payout on the total investment for the alcohol plant plus the protein plant i.e. a profit of \$7,370,000/year. From the figures shown in Table III it can be seen that the 20 million gallons per year of ethanol must bring an income of \$11,600,000/year or 58¢/gallon.

## ETHANOL IN GASOLINE

As a component in gasoline anhydrous ethanol has a blending octane number of 123. If the differential value between 94 octane regular gasoline and 100 octane supreme gasoline is 2¢/gallon at the wholesale level then ethanol as a blending component in gasoline is worth 9.7¢/gallon more than the price of 94 octane regular. This in turn means that when the wholesale price of regular gasoline excluding state and federal taxes is 48.3¢/gallon ethanol at 58¢ per gallon can be used as an economical blending component based on its fuel properties. Allowing for a 35¢ mark-up to retail price and adding 12.5¢/gallon state and federal taxes we come to a retail price of 77.7¢/gallon of gasoline at the pump as being consistent with an alcohol price of 58¢/gallon at the distillery. Table II is a comparison of price (including taxes) of 94 O.N. regular gasoline at the pump with the alcohol price at the distillery which is necessary for anhydrous ethanol to be an economical gasoline blending component.

## CONCLUSIONS

Based on laboratory studies it has been shown that protein of a quality suitable for human consumption can be extracted from vegetable materials such as distillers dried grains and solubles, the by-product of the production of ethanol by grain fermentation. Economic evaluations of the investment and operating cost requirements for the production of anhydrous ethanol from grain and the recovery of protein concentrate from distillers dried grains and solubles indicates that the protein recovery can reduce the selling price of alcohol without adversely affecting the return on investment. In the case where milo was used as the feed grain to the fermentation process the selling price of anhydrous ethanol could be reduced from \$1/gallon to 58¢/gal. while maintaining a 3 year payout on investment. If ethanol were

available at 58¢/gallon it would be economical to use as a blending component in gasoline if the price of regular gasoline at the pump including state and federal taxes were 77.7¢/gallon. Lower grain prices would permit lower ethanol costs which in turn would make the ethanol attractive at lower gasoline prices. Recovery of the protein concentrate from the distillers dried grains results in an increase of about 46% in the total amount of protein produced over feeding the grain directly to cattle. The energy deficit associated with farming and fermentation ethanol production has been shown elsewhere to be less than that associated with ethanol production from light gases via ethylene.

Table I  
Current Price Estimate  
For Synthetic Ethanol

Base Price in 1972	61.0¢/gal
Increase in Fuel Prices of 90¢/million Btu	10.3
Increase in Ethylene Price from 3¢/lb to 10¢/lb	<u>28.7</u>
1974 Price	<u><u>\$1.00/gal</u></u>

Table II  
Value of Ethanol as  
a Gasoline Component

<u>Gasoline</u> 94 O.N. Reg. (Incl. Tax)	<u>Ethanol Value</u> at the Distillery
52¢/gal	39.0¢/gal
60	44.9
80	59.7
100	74.5

Table III

Economic Evaluation for the Production  
of 20 Million Gallons per year of 200°Proof Ethanol

	<u>Without Protein Recovery</u>	<u>With Protein Recovery</u>
Feed: Milo (Bu/Day)	21,490	21,490
Products: Ethanol (Gal/yr)		20,000,000
Distillers Dried Grains & Solubles (Ton/Day)	218	180
Carbon Dioxide (Ton/Day)	174	174
Protein (Lb/Day)	---	66,200
Income: Ethanol		@ 58¢/gal
DDG&S	\$20,000,000/yr	@ \$90/ton
CO <sub>2</sub>	9,550,000	@ \$2/ton
Protein	130,000	@ 60¢/lb
	---	14,500,000
Total Income	<u>\$29,680,000</u>	<u>\$32,140,000</u>
Expenses: Milo		
Conversion Cost	@ \$2.29/Bu	\$17,960,000/yr
	5,720,000	<u>6,810,000</u>
Total Expenses	<u>\$23,680,000</u>	<u>\$24,770,000</u>
Profit: Before Taxes and Depreciation	\$ 6,000,000/yr	\$ 7,370,000/yr
Capital Investment:	\$18,000,000	\$22,000,000
Payout: Before Taxes and Depreciation	3.0 yrs	3.0 yrs

## THE USE OF METHANOL AS A MOTOR VEHICLE FUEL

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I. Blends of Methanol and Gasoline as Motor Vehicle Fuels

The use of methanol has been suggested as a means of extending the nation's supply of liquid fuels. The transportation sector of the economy is one of the largest users of liquid fuels today, and several investigations have been made of the possibility of blending portions of methanol with gasoline to extend the supply of that fuel. The data reported from several of these investigations together with the particular experiences encountered have been gathered together in a report prepared for the City of Seattle by Mathematical Sciences Northwest, Inc. The sections of this report are summarized here together with pertinent references.

Fuel Consumption (1, 2, 3, 4, 5, 6, 7, 9, 14, 17, 18)

The energy content of methanol is less than that of gasoline (8640 Btu/lb vs 19,080 Btu/lb) so that higher fuel consumption would be theoretically predicted for blends of methanol and gasoline than for straight gasoline. However, these blends will burn more satisfactorily at sub-stoichiometric fuel to air ratios than will gasoline, and this fact together with their better anti-knock qualities and cooler, more efficient engine operation may offset this theoretical prediction. Depending upon the automobile engine tested, fuel economy has been shown to be improved slightly or slightly decreased by the addition of methanol to form blended fuels. Since the blend contains less Btu per gallon, there is a slight but significant increase in efficiency of operation on a mile per Btu basis. This increase is generally reported, and may be of importance economically depending upon the comparative prices of gasoline and methanol on a dollars per million Btu basis.

Power or Acceleration (6,8,9,10,14)

The high latent heat of vaporization of the methanol (474 Btu/lb vs 141 Btu/lb for octane) cools the air charge of an engine and increases its density. This causes an increase in volumetric efficiency and available power from an engine. However, the methanol also lowers the combustion temperature in the cylinder, resulting in lower combustion efficiency. It has been shown that the addition of practical amounts of methanol to gasoline should not appreciably affect the power output of an unmodified automobile engine.

Vapor Pressure (9, 11, 13, 14, 18)

Because of the disruption of hydrogen bonding in methanol when it is mixed with a hydrocarbon, the vapor pressure of a mixture of methanol and gasoline deviates greatly from ideal behavior as predicted by Raoult's Law, exhibiting a much higher vapor pressure than would be expected. This excess vapor pressure can lead to vapor lock problems, difficulties with hot starts, stalling, hesitation, and poor

acceleration. The evaluation of these problems is highly subjective, however. This question will be discussed after three more factors affecting driveability are mentioned.

Solubility (2,6,7,8,9,11,15,17)

Another factor affecting the driveability of an automobile fueled with a methanol-gasoline blend is the degree of solubility of the methanol in the base gasoline. Methanol is least soluble in paraffins and naphthenes, and more soluble in aromatics and unsaturates. Therefore, the amount of aromatics in the base gasoline greatly affects the degree to which the methanol will blend. At lower temperatures the solubility of methanol in gasoline is decreased. Operation in sub-freezing environments will be a problem, and suitable solubilizers such as higher alcohols will have to be added to the fuel.

Separation (1, 3, 4,6,7,9,11,14,15,17,19,20,21,22,23,24)

The presence of very small amounts of water can cause methanol-gasoline mixtures to separate into gasoline and water-alcohol phases. These separate phases are vastly different in their combustion properties. Some of the aromatics from the base gasoline will also separate with the alcohol-water leaving the gasoline phase very low in octane number. The separation becomes more pronounced at low temperatures so that the primary effect will be very difficult, if not impossible, cold starting and stalling in cold weather. As with solubility the properties of the blend are dependent upon the aromatic content of the base gasoline. As the methanol fraction increases in a blend so does the water tolerance. The presence of higher alcohols in the blend increases its water tolerance. The problem of phase separation of methanol-gasoline blends can be a serious one. The solution may lie in the addition of higher alcohols to the blend.

Octane Number (1,3,6,7,8,9,11,14,15,17,18,20,21,28)

Pure methanol has a very high blending octane value (BOV). This number reflects the fact that the blending of methanol with gasoline is a very effective method of increasing the octane number of the fuel. The effect is less pronounced in newer automobiles. The elimination of knocking has been demonstrated as the result of this effect. Higher compression ratios may be utilized and the attendant increases in fuel economy realized. The effective increase in octane number depends upon the octane number of the base gasoline used in the blend. Methanol is more effective in raising the octane number of an originally lower octane number fuel. One of the most interesting effects of this octane number boost is the possibility of replacing tetra-ethyl-lead as an anti-knock compound in gasoline with a low percentage of methanol in a blend, helping to minimize lead pollution. The substitution of methanol for TEL in gasolines as an anti-knock agent will prevent the accidental poisoning of catalytic mufflers by lead.

Subjective Road Tests (1,3,6,7,8,14,15,17,19,20,24,25,29)

The overall effect upon driveability resulting from the properties of methanol gasoline blends that were discussed in the preceding

sections can only be assessed through subjective fleet tests in which some qualitative judgments of overall driveability are given by drivers of automobiles in actual field tests. These qualitative judgments can only be subjective, and as such are open to the effects of bias; however, care is taken (blinds) to minimize these effects.

One specific area that has been investigated is the effect upon cold starting. Difficult cold starting has been predicted. Cold start problems are decreased by the addition of higher alcohols to the fuel. Subjective judgments of the effects of methanol blends used as fuels on driveability seem as mixed as the driver's assessments of automobiles themselves. Perhaps it can be safely stated that the substitution of a 7 percent blend of methanol would exhibit enough beneficial effects to overshadow most detrimental effects. However, this number depends strongly upon the specific automobile considered and the severity of the cold weather to be encountered in service.

#### Corrosion and Compatibility (1,2,6,7,9,11,13,14,15,17,24,26,27,29)

The automotive fuel system has been developed for the use of petroleum distillates and the substitution of blends of methanol for fuels opens the possibility of corrosion of fuel system parts. The gasket materials and elastomer seals used in the automotive fuel system must also be examined for compatibility with methanol fuel blends. Several test programs have been carried out in this area, and also observations have been made of the effects of corrosion during most of the fleet tests that have been performed.

Methanol and methanol blends have been seen to attack the terne plating on automobile fuel tanks. Deterioration of copper, aluminum and magnesium has also been reported.

There appear to be serious corrosion and compatibility problems associated with the use of methanol blends in some automobile fuel systems. There are similar problems when pure methanol is used as a fuel; however, the greater problem is experienced with blends primarily because of the water separation problem. The corrosion and compatibility problems listed above are not universally observed, however. It appears as if the severity of the corrosion and compatibility problem depends strongly upon the particular vehicle and fuel system being considered. Certain specific problems such as those with methacrylate fuel filters and Viton float valve seats can be identified; however, it is very difficult to generalize further.

#### Modifications and Reliability (1,3,6,8,11,14,15,21,24)

One of the beneficial aspects of the use of methanol as a blend with gasoline should be the fact that engine modifications are not necessary. The degree of adherence to this dictum depends upon the percentage of methanol considered, the age of the automobile, and the tolerance of the driver. Problems of driveability that point to the necessity of equipment modifications increase with methanol concentration. Older, richer cars are more tolerant of the leaning effect of methanol blends. Equipment reliability has not been sufficiently examined in the time scale of the experiments that have been carried out, except for the corrosion problems mentioned in the previous section. Further testing needs to be done before sufficient data are

available to make valid conclusions concerning equipment reliability.

### Emissions

One of the most beneficial effects of the use of methanol blends as automotive fuels is the reduction in the emission of air pollutants afforded. This reduction, together with the octane number boost, has been the motivating factor in most of the investigations of the use of methanol blends as automotive fuels.

#### Carbon Monoxide Emissions (2,3,5,6,8,14,21,23,24,25,30)

The emission of carbon monoxide (CO) from an automotive engine is decreased when methanol blends are substituted for straight gasoline as a fuel without vehicle modifications because of the leaning effect of the blend and the more complete burning of the fuel that is afforded. The blending of methanol with gasoline has been shown to decrease the emissions of carbon monoxide in the vehicle exhaust if the vehicle is unmodified and allowed to take advantage of the leaner operation possible with methanol blends. Indeed, the fact that the engine need not be modified for the use of methanol blends is one of the motivating factors for the use of such blends and should be considered a ground-rule for vehicle testing in which the use of blends is investigated. Comparison of the data with the Federal Standards points out the fact that the use of methanol blends will not obviate the incorporation of catalytic converters in order to meet the 1977 standard for CO emissions.

#### Hydrocarbon Emissions (2,5,6,9,14,21,24,30,31)

The effect of the use of methanol blends as fuels upon the emissions of hydrocarbons is not as easily discerned as the effect upon carbon monoxide emissions. Part of the reason can be found in the fact that the constituents of "unburned fuel" in the case of methanol are different than those for gasoline. Considerable care must be taken in the hydrocarbon emission measurement procedure to account for all of these constituents that may be present.

When methanol blends are used as fuels, the possibility of increased emissions of formaldehyde in the exhaust exists. The use of methanol blends as a motor fuel has, in many cases, been shown to decrease the hydrocarbon emissions slightly as compared to the use of gasoline. This effect is caused by the leaner operation afforded by the use of methanol blends in the unmodified automobile. The beneficial effect is not as pronounced or reproducible as the decrease in carbon monoxide emissions when methanol blends are used. The levels of HC emissions were not lowered enough to meet the 1977 Federal Standards and the use of a catalytic converter will be necessary to meet these standards.

#### Oxides of Nitrogen Emissions (2,5,6,14,21,25,30)

The effect of the use of methanol blends upon the emission of oxides of nitrogen ( $\text{NO}_x$ ) from a motor vehicle is pronounced, although not uniform from vehicle to vehicle. Nitrogen oxide emissions are maximized for the operation of a motor vehicle engine under conditions near stoichiometric combustion. Therefore, if the vehicle is originally adjusted to operate at or near an equivalence ratio of unity on gasoline and not modified when a methanol blend is substituted, the

leaning effect of the blend should reduce the  $\text{NO}_x$  emissions. If the vehicle originally operated fuel rich, however, this same leaning effect should increase the  $\text{NO}_x$  emissions.

When used in an unmodified vehicle, methanol blends have been shown to decrease nitrogen oxide emissions when the vehicle was of recent vintage, operating at or near stoichiometric conditions on gasoline. Tests on vehicles as old as 1970 showed such an effect; however, tests on a 1967 vehicle which originally operated fuel rich showed an increase in  $\text{NO}_x$  emissions. The blending of methanol into motor fuel has not reduced  $\text{NO}_x$  emissions below the 1977 Federal Standard, and the use of emission control devices will be necessary.

## II. Pure Methanol as a Motor Vehicle Fuel

The use of either analytic or commercial grade methanol or methyl-fuel alone as a fuel for motor vehicles has also been suggested. As described in the preceding section, there are many problems associated with the use of blends of methanol and gasoline as a motor fuel, principally in the area of phase separation caused by the presence of water and the attendant alterations necessitated in the fuel distribution system. The separation problem is eliminated when pure methanol is used as a vehicle fuel; however, when this is done certain modifications to the vehicle itself become necessary. These modifications are considered to be more feasible particularly in the case where pure methanol is considered as the fuel for fleets of vehicles.

### Economy (5,8,11,14,17,18,20,22,24,25,27,32,33,34,35,36,37)

Methanol possesses the lowest heating value of all the alcohols because it contains a higher percentage of oxygen by weight. Its heating value per gallon and per pound is approximately one-half that of gasoline. Theoretically, for the same performance, it should require twice as much methanol as gasoline per mile in the same vehicle. However, the high octane number, low volatility, high heat of vaporization and low heat of combustion of methanol can be put to good use in raising the thermal efficiency of engines. Because of the greater thermal efficiency afforded with the use of methanol, the number of miles travelled per BTU can be greater for methanol than for gasoline. As a result, the cost per mile can be lower for methanol fuel than for gasoline.

The use of methanol as a motor fuel has been shown to increase the thermal efficiency of internal combustion engines normally fuelled with gasoline. This increase is due to the possibility of using methanol at much leaner equivalence ratios and the possibility of utilizing higher compression ratios, as well as the elimination of certain emission controls that are deleterious to fuel economy. This increase in efficiency has been shown to be approximately 20 percent. Assuming that methanol is priced on an equal cost per BTU basis as gasoline, these savings will be reflected in the costs per mile to operate an equivalent vehicle.

### Power (11,14,17,20,24,27,32,34,35,36,37,38)

For a stoichiometrically correct air to fuel ratio (6.45 for methanol, 15.3 for gasoline) the energy densities of the fuels are very nearly equal (94.5 BTU/ft<sup>3</sup> for methanol, 95.5 BTU/ft<sup>3</sup> for gasoline) indicating that equal power can be extracted from comparable engines using these fuels. Methanol will extract more brake-mean-effective pressure from an engine than will gasoline because of the increased volumetric efficiency afforded by the cooler methanol charge.

Equal power output has been achieved with methanol in an engine usually operated on gasoline when stoichiometric mixtures were used. Power

output has been raised significantly above that for gasoline when richer mixtures were used; however, to gain the benefits in economy afforded by the lower lean misfire limit of methanol, this excess in power will have to be forfeited and possibly a slight loss in power sustained. For equivalent exhaust emissions, the methanol fueled engine has been shown to exhibit significantly higher power than the emission control equipped gasoline engine.

#### Driveability

Several of the driveability problems associated with the use of blends of methanol and gasoline are eliminated when pure methanol is used as a fuel; however, there remain problems associated with the vaporization properties of pure methanol as compared with those of gasoline.

#### Vapor Pressure (17,18,19,20,27,36,37)

The vaporization characteristics of pure methanol have caused some problems when it is used as a motor fuel. Its high heat of vaporization requires an enhanced supply of heat to the intake manifold in order to assure adequate mixture distribution to the cylinders. Its lower vapor pressure has made cold starting difficult and may necessitate the use of high volatility additives during this phase of the vehicle operation. Its low boiling point requires careful attention to keeping the fuel lines and carburetor shielded from excess heat. All of these problems have been encountered and several solutions developed.

#### Driveability (1,15,17,24,27,36)

The power output of a vehicle fueled with pure methanol can be equivalent to a comparable gasoline fueled vehicle, and the solubility and separability problems of blends do not exist for pure methanol fuels. Most of the subjective evaluations of the driveability of vehicles fueled with pure methanol have focused on the problems associated with cold starting of such vehicles.

The higher heat of vaporization of methanol together with the requirement of over twice as much methanol as gasoline for the same amount of air to form a stoichiometric mixture require that much more heat be supplied to the intake manifold to avoid cold starting and acceleration problems. Several solutions to these problems have been proposed. It is possible to add high vapor pressure liquids or gases such as butane either generally or preferably only during cold start situations. Either gasoline or LPG could be injected at cold starts to accomplish the same effect. Aside from the cold start problem, the performance of the methanol fueled vehicle has been shown to be equivalent to a gasoline fueled vehicle.

#### Pure Fuel-Corrosion and Compatibility (1,6,14,17,26)

Several corrosion and compatibility problems associated with the use of methanol in blends with gasoline as a motor fuel have been described. There has been much less experience reported concerning the use of pure methanol as a motor fuel. Many of the problems encountered with the use of blends may also appear during pure fuel use, but this has not been proven by experience. Significant corrosion occurs after water causes separation of gasoline and methanol-water phases in blends. Much of this corrosion may be caused by the water in the lower phase. This separation does not take place when pure methanol is utilized as a motor fuel. Water is highly soluble in pure methanol and any traces found in the fuel system will be taken into the solution. The compatibility

problems associated with the use of pure methanol as a motor fuel have been more extensively investigated. It may be expected that compatibility problems between pure methanol and Viton fuel system elements, metacrylate fuel filters and possibly certain types of fuel pump diaphragms and gaskets may exist.

The limited experience with the use of pure methanol as a motor fuel has uncovered some compatibility problems with certain fuel system components. Some test vehicles have suffered no corrosion or compatibility problems, and others have required alterations to avoid them. There is a need for further fleet testing in which the problems of corrosion and materials compatibility with pure methanol motor fuel are more completely investigated. It will only be through the experience gained during such fleet tests that all of these problems can be uncovered.

Pure Fuel-Performance-Reliability and Conversions (1,5, 8,12,13,14,15,17,20,27,31,36,37,39,40)

The reliability of motor vehicles that have been converted to operation on pure methanol fuel has proven to be as high as that of comparable gasoline fueled vehicles in several cases. The conversions necessary to enable a vehicle to operate with pure methanol as a fuel can be divided into two phases. Because the energy per cubic foot of stoichiometric mixtures of methanol and gasoline fuels is very similar, the modifications necessary to convert a conventional gasoline engine to pure methanol fuel are relatively simple. These conversions, to enable the use of pure methanol fuel in conventional engines will be called first phase conversions. Such conversions involve changes to the carburetor, intake manifold, fuel system, and spark advance curve and do not require major engine modifications. This phase of engine modification may be easily carried out on a fleet of automobiles and has been done in several cases. In addition, major engine modifications such as an increase in the compression ratio may be made in order to take advantage of the higher octane number of methanol in order to produce better thermal efficiency and an increase in fuel mileage. These modifications constitute a second phase of possible engine conversions. No full scale tests of such conversions have been reported.

Some modifications will be necessary to convert a conventional engine from gasoline to methanol fuel. Larger carburetor jets will be needed to provide the richer mixtures necessary, and larger fuel tanks will be needed to provide the same range of operation. It is also anticipated that some elastomeric seals in the fuel system may have to be changed depending upon their compatibility with methanol. Viton is the only material that has specifically caused problems in this area. Evaporative control cannisters and metacrylate fuel filters will have to be changed. Carburetor or fuel tank substitutions may be necessary on certain vehicles because of corrosion problems. The possible corrosion and compatibility problems are not well defined and require an enlarged fleet test program to uncover them. Some means of assuring fuel vaporization and even distribution to the cylinders will have to be provided. This can be accomplished by placing heat exchangers in the intake manifold or by the adoption of a fuel injection system. Provisions will be necessary to assist in cold starting engines at ambient temperatures below 55 °F. This can be accomplished by the injection of butane, propane, acetone, ethyl ether, gasoline, or LPG during the starting procedure. The adoption of fuel injection would benefit in this area as well. Depending upon the particular vehicle and its fuel system layout there may be problems with vapor lock

during hot operation. The installation of an electric fuel pump should eliminate these.

Carbon Monoxide Emissions (1,5,17,20,25,27,31,32,  
35,36,40,41,42)

Since the methanol molecule has no carbon to carbon bonds and already contains one oxygen atom, the reaction kinetics for complete oxidation of this fuel are theoretically less complex than those for gasoline and the intermediate reaction products that form exhaust emissions are more readily eliminated from the exhaust system. In addition, it has been shown earlier that methanol fuelled vehicles will operate satisfactorily at much leaner mixture ratios. Therefore, it may be expected that vehicles fueled by pure methanol, especially those equipped with catalytic muffler will emit less carbon monoxide than comparable gasoline fuelled vehicles. This reduction has been measured except in those cases in which operation was fuel-rich. The extended fuel-rich warm-up period necessary with methanol fuelled vehicles appreciably raises their CO emissions. The installation of a catalytic converter has been shown to reduce CO emissions below the 1977 Federal Standard.

Hydrocarbon Emissions (1,5,14,15,17,18,20,27,32,  
34,35,36,38,40,41)

Several tests have been performed on methanol fuelled vehicles from which the emissions of hydrocarbons and unburned fuel have been reported. Some hydrocarbons emitted in the exhaust of methanol fuelled vehicles are different than those emitted by gasoline fuelled vehicles and adequate provisions must be made to insure that the recording equipment accurately measures their presence. The major component of unburned fuel in the exhaust has been found to be methanol which is technically not a hydrocarbon at all; however, the emissions of unburned fuel are generally reported under the heading of hydrocarbon emissions.

The leaner operation afforded by the use of methanol fuel should lead to lower hydrocarbon (HC) emissions. The emissions of hydrocarbons and unburned fuel from engines fuelled by methanol have been shown to be lower than those fuelled by gasoline during hot start emissions tests. Because of the longer warm-up period under fuel rich operation which is necessary with methanol fuel, the HC emissions from methanol fuel were higher than those from gasoline during cold start tests. The use of a catalytic muffler was found to be necessary in order to meet the 1977 Federal HC Standard. There are no aromatics emitted among the hydrocarbons in the exhaust of a methanol fuelled vehicle, and there is correspondingly less carcinogenic risk from these emissions. It is also expected that the total reactivity caused by the unburned fuel for the formation of photochemical air pollution is much lower for a methanol fuelled vehicle than for gasoline.

Oxides of Nitrogen Emissions (1,5,14,15,17,18,20,27,32,33,  
34,35,36,37,38,40,41,42)

The emissions of oxides of nitrogen ( $\text{NO}_x$ ) in the exhausts of methanol fuelled vehicles have been demonstrated to be very low; lower than the  $\text{NO}_x$  emissions of comparable gasoline fuelled vehicles. Emission levels below the 1977 Federal  $\text{NO}_x$  standard have been demonstrated with methanol fuelled vehicles without the use of emission control equipment. Results have shown no increase in  $\text{NO}_x$  emissions during cold start tests. Calculations have shown that the peak Otto cycle temperature of methanol fuel is lower than that of iso-octane. The lower combustion temperature of methanol contributes to the depression of  $\text{NO}_x$  emissions from methanol fueled vehicles. The higher flame velocity

exhibited by methanol as compared to that of gasoline allows the use of later spark timing which also results in lower NO<sub>x</sub> emissions. Since emissions of NO<sub>x</sub> peak at stoichiometric conditions of operation, the lower lean misfire limit exhibited by methanol permits lower NO<sub>x</sub> emissions by allowing operation at much leaner mixture ratios than gasoline.

#### Aldehyde Emissions (1,18,27,32,35,36,38,41)

Aldehydes form a class of potential air pollutants that are not presently covered by Federal Standards. The presence of certain aldehydes, principally formaldehyde and acetaldehyde has been measured in the exhaust of methanol fuelled engines. Aldehyde emissions from automobiles have not been measured as extensively as those of other air pollutants. There exists no Federal Standard for aldehyde emissions. The level of aldehyde emissions from methanol fuelled vehicles seems to be a sensitive function of the air to fuel mixture ratios. Some tests have shown that the aldehyde emission level from methanol fuelled vehicles is no higher than the level from comparable gasoline fuelled vehicles. Others have shown increased aldehyde emissions when methanol is substituted for gasoline as a fuel. There is a need for further testing of both methanol fuelled vehicles and gasoline fuelled vehicles, however, before any definite conclusions can be drawn. The use of a catalytic muffler has been shown to considerably reduce the aldehyde emissions of methanol fuelled automobiles.

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PERFORMANCE OF AN ETHANOL-GASOLINE BLEND  
IN AUTOMOBILES AND LIGHT TRUCKS

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INTRODUCTION

The proposal that ethanol be used as a blending component in automotive fuel is almost as old as the automobile itself. In 1907 the U.S. Department of Agriculture published a report entitled "Use of Alcohol and Gasoline in Farm Engines" (5). Over the intervening years many laboratories tests on the performance of stationary automobile engines operating on ethanol-gasoline mixtures have been reported in the literature. In 1964 a series of papers on the use of ethanol and hydrocarbon motor fuels were published (4) by the SAE. In 1971 the American Petroleum Institute prepared a review of alcohol fuel studies (1). The most recent comprehensive laboratory study was that work done by Dr. H.B. Mathur in connection with his Ph.D. thesis in New Delhi, India (2). Mitre Corp. prepared a new survey (3) of alcohol fuel technology in 1974 including both ethanol and methanol.

To date no statistically designed fleet test of ethanol-gasoline mixtures have been reported in the literature. Contact with automotive and petroleum companies indicate that they too know of no such comprehensive test. Because of the knowledge to be gained from a well designed program, a two million mile road test using a mixture of 10% ethanol-90% unleaded gasoline was designed by the authors and is now in progress.

TEST PROGRAM

The Nebraska two million mile ethanol-gasoline road test program is being conducted with 36 vehicles supplied by the Nebraska Department of Roads and is being financed by the Nebraska Agriculture Products Industrial Utilization Committee. The fuel being tested is a mixture of 10% anhydrous ethanol and 90% unleaded regular grade gasoline. This blend is known by the name GASOHOL. The gasohol is being blended for the test program by the Cooperative Refiners Assoc. in Phillipsburg, Kansas. The no-lead base gasoline used in the preparation of the gasohol is the same no-lead which they market through their normal outlets.

The objectives of the two million mile road test are to obtain the following information:

1. The quantitative effect on fuel consumption of the addition of sufficient anhydrous ethanol to produce a 10% solution by volume with unleaded gasoline meeting specifications for sale after 30 June, 1974.
2. The quantitative effect of this ethanol addition on cylinder wear.
3. The quantitative effect of this ethanol addition on exhaust gas composition.

4. The qualitative effect of this ethanol addition on engine valves.
5. The qualitative effect of this ethanol addition on spark plugs.
6. The qualitative effect of this ethanol addition on the exhaust system.
7. The drivers comments on the effect of this ethanol addition on general vehicle performance.

The quantitative information is being gathered in sufficient quantity and in such a way as to allow statistical analysis of the reliability and significance of the data. The test is to extend over a period of 10-15 months. The qualitative observations are being made sufficiently often to establish any visible trends.

The road test program is making use of a total of 36 vehicles; 10 half-ton pickup trucks and 26 passenger cars. These vehicles are located in three different parts of the state of Nebraska i.e. Lincoln, North Platte, and Sidney. The reason for including vehicles in these three cities is to incorporate into the test an effect for altitude. Lincoln has an altitude of 1160 feet above sea level, North Platte is 3000 feet and Sidney is 4300 feet. Table I summarizes information on the year, make, and model of vehicles included in the test program. As the Department of Roads acquires additional 1974 and 1975 vehicles, some of these will be added to the test program.

The vehicles have been divided into three groups; those vehicles which will run on gasohol only for the entire life of the test program, those vehicles which will run on unleaded fuel only during the entire program and those which will be changed from one fuel to the other about midway through the test program. Table I includes the fuel assignment of each of these vehicles.

Those vehicles running on gasohol fuel will obtain their fuel from new storage tanks which have been buried at state service stations in Lincoln, North Platte and Sidney. Special care has been taken to insure that the tanks remain dry through the initial cleaning and by continued observation of the contents. To date no special driers have been needed on the vents. The drivers of those vehicles running on no-lead gasoline buy their fuel at local commercial outlets since the state service stations do not have facilities for storing and dispensing an additional no-lead grade. Data on the number of gallons of gasoline added to each vehicle and the corresponding odometer reading is maintained by each driver and sent weekly on a standard form to the authors for processing.

#### VEHICLE MAINTENANCE AND INSPECTION

All normal vehicles maintenance such as oil change, lubrication, etc. is carried out on the test vehicles in the same fashion as other vehicles belonging to the Department of Roads. In addition, each 90 days (+ 5 days) from the beginning of the test program a visual inspection is made of the exhaust system on each vehicle. Spark plugs are checked and the compression on all vehicles is also measured. On straight six cylinder engines cylinders two and four are checked while on eight-cylinder engines, three and six are checked. Any V-6

engines in the program have the middle cylinder of each bank checked.

On 10 of the Lincoln vehicles there will be additional inspections made. These include the visual inspection of valves and seats on all cylinders and the measurement of the diameter on all cylinders. In this case six micrometer readings are made at approximately equal spacings on the circumference of the cylinder and at approximately the center of the piston travel. The vehicles undergoing these inspections have been indicated in Table I. One of the objectives of this test is to obtain quantitative information on the exhaust gas composition of vehicles powered with gasohol and with no-lead gasoline. An analytical procedure for obtaining detailed component analyses of exhaust gases using a high resolution mass spectrometer has been developed for the authors by Dr. Michael L. Gross in the Analytical Section of the Department of Chemistry at the University of Nebraska. All exhaust gas samples in this program are being obtained from Lincoln based cars. A fitting has been installed on 10 of the test cars to permit attaching a vacuum gauge to the engine manifold while the exhaust samples are being gathered. The samples themselves are taken from the exhaust pipe and lead through a stainless steel pipe and plastic hose to a set of sample bags in the rear seat of the car. In this way the exhaust samples can be gathered over an extended period of time (typically five minutes) while the car is being driven at a constant speed and a constant load as indicated by the vacuum gauge. Earlier tests with small samples which were gathered in a matter of seconds showed too much variability and uncertainty about the exact speed and vacuum when the sample was caught. The vehicles from which exhaust gas samples are being taken are indicated in Table I.

It is also planned to include standard EPA emissions tests in this test program. These will be obtained through an outside laboratory and will include the usual schedule of warm up and driving in a climate controlled dynamometer.

#### DATA PROCESSING

Based on the results of preliminary testing of about 250,000 miles, a computer program has been developed to process the fuel consumption and mileage data. Through the use of linear regression it has been found that the significant factors in the fuel consumption are the driver, the vehicles, average daily temperature, average relative humidity and maintenance schedule. Tire pressure while known to be significant cannot be accounted for. Normal fluctuations in atmospheric pressure, precipitation, and visibility were not found to be significant. When the significant factors have been accounted for in the fuel consumption the significance of the residuals will be tested for the unleaded gasoline and gasohol fuel. With the data available from the vehicles it is expected that we will have results with a confidence limit of 99+% for a fuel consumption of + 0.1 miles per gallon. Data are processed weekly and quarterly reports are issued to the Nebraska Agricultural Products Industrial Utilization Committee.

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TABLE I

Vehicles, Fuels and Tests in  
2 Million Mile Gasohol Road Test Program

<u>Model Year</u>	<u>Vehicle Make and Type</u>	<u>Location</u>	<u>Fuel (Note)</u>	<u>Valve &amp; Cylinder Inspections</u>	<u>Exhaust Gas Analyses</u>
1973	IHC ½T Pickup	Lincoln	A	Yes	Yes
1973	IHC ½T Pickup	Lincoln	U	Yes	Yes
1973	IHC ½T Pickup	No Platte	U/A	No	No
1973	IHC ½T Pickup	Sidney	A	No	No
1974	Dodge ½T Pickup	Lincoln	A	No	Yes
1974	Dodge ½T Pickup	Lincoln	U	No	No
1974	Dodge ½T Pickup	Lincoln	A/U	Yes	No
1974	Dodge ½T Pickup	Lincoln	U/A	Yes	No
1974	Dodge ½T Pickup	No Platte	A/U	No	No
1974	Dodge ½T Pickup	Sidney	A	No	No
1974	Dodge Coronet	Lincoln	A	Yes	No
1974	Dodge Coronet	Lincoln	A	No	Yes
1974	Dodge Coronet	Lincoln	U	Yes	Yes
1974	Dodge Coronet	Lincoln	A/U	No	Yes
1974	Dodge Coronet	Lincoln	A/U	No	No
1974	Dodge Coronet	Lincoln	U/A	No	Yes
1974	Dodge Coronet	Lincoln	U/A	No	No
1974	Dodge Coronet	No Platte	A/U	No	No
1973	AM Ambassador	Lincoln	A	Yes	No
1973	AM Ambassador	Lincoln	U	Yes	No
1973	AM Ambassador	Lincoln	A/U	Yes	Yes
1973	AM Ambassador	Lincoln	U/A	Yes	Yes
1973	AM Ambassador	No Platte	U/A	No	No
1973	AM Ambassador	Sidney	A	No	No
1972	AM Ambassador	Lincoln	A	No	No

TABLE I (Con't)

<u>Model Year</u>	<u>Vehicle Make and Type</u>	<u>Location</u>	<u>Fuel (Note)</u>	<u>Valve &amp; Cylinder Inspections</u>	<u>Exhaust Gas Analyses</u>
1972	AM Ambassador	Lincoln	U	No	No
1972	AM Matador	Lincoln	A	No	Yes
1972	AM Matador	Lincoln	A	No	No
1972	AM Matador	Lincoln	U	No	No
1972	AM Matador	Lincoln	A/U	No	No
1972	AM Matador	Lincoln	U/A	No	No
1972	AM Matador	No Platte	U/A	No	No
1972	AM Matador	Sidney	A	No	No
1973	Plymouth Fury III	No Platte	A/U	No	No
1974	Passenger Car (To be Rec'd)	No Platte	A	No	No
1974	Passenger Car (To be Rec'd)	Sidney	A	No	No

Note: A - Vehicle to be run on alcohol blended fuel only  
 U - Vehicle to be run on unleaded fuel only  
 A/U - Vehicle to be run initially on alcohol blended fuel and then unleaded fuel  
 U/A - Vehicle to be run initially on unleaded fuel and then alcohol blended fuel

## BIOLOGICAL OXIDATION AND REDUCTION OF INORGANIC COMPOUNDS OF SULFUR

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The biological processes involved in the oxidation and reduction of inorganic compounds of sulfur are generally represented by the idealized "biological sulfur cycle" shown in Figure 1 (18). Sulfate and sulfide are pivotal compounds in the scheme as they represent both the most common forms of inorganic sulfur found in nature and are the most common forms of sulfur incorporated into biological materials. At the top of the scheme, the biosynthetic reactions involving the incorporation of sulfate as ester linkages into carbohydrates, lipids, phenol, steroids, etc. (14) are indicated as sulfation reactions. Sulfation reactions are extensively involved in the biosynthesis of structural components in plants and animals but sulfate esters have only rarely been reported to occur in bacteria. All three groups of organisms do have sulfatases which specifically hydrolyze the various esters. On the right hand portion of the scheme, the eight electron reduction of  $\text{SO}_4^{2-}$  to  $\text{S}^{-2}$  is represented and, at the bottom of the scheme, the biosynthesis of amino acids and cofactors (or vitamins) from  $\text{S}^{-2}$  is shown. On the left hand portion of the scheme, the oxidation of reduced sulfur compounds is indicated (shown here as sulfide but other common substrates include  $\text{S}_2\text{O}_3^{2-}$  and elemental sulfur). The biological aspects of inorganic sulfur metabolism thus provide the essential transformations for the incorporation of sulfur into biological materials and a link between the appropriate geological and biological phenomena.

The oxidative and reductive process have been further classified depending on the organisms and the physiological significance of the process in their metabolism. Two physiological types of sulfate reduction are recognized (21). The first is assimilatory or biosynthetic sulfate reduction in which organisms reduce only enough sulfate to meet their nutritional requirements for sulfur. This pathway is considered to be in the pathway for the biosynthesis of cysteine and is usually under both coarse and fine metabolic regulation (29). Animals do not classically reduce sulfate and must depend upon plants and bacteria for their metabolites containing reduced sulfur. This pathway occurs in most plants and bacteria, including aerobes and anaerobes, and, because of its wide occurrence, is probably the largest biological process for the reduction of sulfate; however, only indirectly during the digestion and hydrolysis of biological materials does this pathway produce sulfide in nature. The second sequence involved in the reduction of sulfate is the dissimilatory or respiratory pathway of sulfate reduction in which sulfate in the absence of oxygen serves as a terminal electron acceptor for anaerobic respiration (13). This pathway of sulfate reduction occurs only in the sulfate-reducing bacteria, species of Desulfovibrio (25) and Desulfotomaculum (4), and results in the formation of very large amounts of  $\text{S}^{-2}$ . Respiratory sulfate reduction is the process responsible for the formation and accumulation of most  $\text{S}^{-2}$  in nature and is believed to be involved in many geochemical phenomena. The enzymes of the respiratory pathway are constitutive, i.e. not effected by growth conditions, and the intermediates and enzymes responsible for respiratory sulfate reduction are quite different from those involved in biosynthetic sulfate reduction. Members of the genus, Desulfovibrio are the most extensively studied of the sulfate-reducing bacteria. These bacteria have only a limited capability for oxidizing substrates ( $\text{H}_2$ , formate, pyruvate, lactate, ethanol, fumarate) and are the first non-photosynthetic anaerobes in which c-type cytochrome were discovered (24). They also produce many low molecular weight electron carriers (13) and oxidative phosphorylation has been demonstrated to be coupled to electron transfer (19).

Most plants, bacteria and animals are capable of oxidizing reduced inorganic and organic compounds of sulfur to sulfate. Thus, a specific requirement of sulfate for growth has never been reported although it is extensively involved in essential biosynthetic reactions in plants and animals. Reduced sulfur compounds can also be utilized by microorganisms as electron donors for both aerobic and anaerobic growth, as well as photosynthetic growth with the formation of sulfate. Members of the genus, *Thiobacillus*, oxidize  $S^{-2}$ ,  $S_2O_3^{2-}$  and  $S^0$  to  $SO_4^{2-}$  in the presence of oxygen and gain energy for growth in the form of adenosine triphosphate (ATP) by means of oxidative phosphorylation (32). One species, *T. denitrificans* can utilize either oxygen or nitrate with the formation of  $N_2$  as terminal electron acceptor. Photosynthetic bacteria, members of the *Chromatiaceae* (purple sulfur bacteria) and *Chlorobiaceae* (green sulfur bacteria) can use reduced sulfur compounds as electron donors for photosynthetic growth first with the formation of  $S^0$  and subsequently  $SO_4^{2-}$ . Although the biological sulfur cycle generally involves a large number of diverse organisms, it is possible to construct a simple, light-driven sulfur cycle by means of a sulfate-reducing bacterium and a photosynthetic bacterium. This is not a primary producing system, as water can not serve as a source of electrons, but it provides a model system for the study of the interactions required for the biological sulfur cycle. In addition, this simple form of the cycle may represent a primitive system for the conversion of solar energy into biologically useable energy.

In most soils and natural environments, there is a continuous flux of sulfur through the biological sulfur cycle without the accumulation of intermediates or significant changes in the concentrations of sulfate and sulfide. This situation can then be regarded as an uninterrupted or continuous sulfur cycle. Under certain conditions, one or more steps in this sulfur cycle can become inhibited with the result that the concentrations of sulfate and sulfide are drastically altered, often with dramatic effects on a specific environment. This can be considered to be an interrupted or discontinuous sulfur cycle and its consequences will be briefly considered. Under anaerobic conditions, the oxidation of reduced sulfur compounds is inhibited (except in the presence of  $NO_3^{-1}$ ) and, with  $SO_4^{2-}$ , organic electron donors or  $H_2$  and an environmental pH above 4.5, copious amounts of  $S^{-2}$  can be produced by the sulfate reducing bacteria. The consequences of this microbial reduction of sulfate to an environment are complex but can be largely analyzed in terms of the chemical properties of  $H_2S$ . Sulfide is an inhibitor of cytochrome oxidase which is essential for aerobic respiration, reacts with molecular oxygen and generates a reducing environment because of its low  $E_u$  value of about -300 mV. Thus, its formation in any environment can result in the formation of anaerobic conditions and the inhibition of aerobic flora. Sulfide also combines with heavy metals present in an environment to form insoluble sulfides and there is some evidence to indicate that most pyrite ores are formed from biologically produced sulfide. The black color of anaerobic environments is due to this reaction and the Black Sea is claimed to derive its name from the fact that in areas it appears to be black due to the abundance of  $FeS$ . As indicated previously, sulfide and elemental sulfur can serve as substrates for the growth of many microorganisms and on the periphery of an environment in which there is extensive sulfate reduction (termed a "sulfuretum") one can often find high concentrations of *Thiobacilli* and/or photosynthetic bacteria. For example, in very shallow marine environments, it is common to observe red and green photosynthetic bacteria growing on the surface of sediments that are producing  $S^{-2}$ . This phenomenon is made possible in part because at physiological pH values,  $H_2S$  is volatile and a sulfuretum can usually be detected by our olfactory senses. The volatility of  $H_2S$  formed by sulfate reduction can also result in an environment becoming extremely alkaline and it has been postulated to be the cause of the formation of certain deposits of  $Na_2CO_3$  by the absorption of  $CO_2$  from the atmosphere. The concentration of sulfate can be decreased in natural waters to the point that respiratory sulfate reduction ceases and interactions with methanogenic bacteria become important as will be discussed later. The sulfate-reducing bacteria have high levels of the enzyme hydrogenase concentrated around the periphery of their cells (18) and the enzyme

appears to be important both in the production and utilization of molecular hydrogen which is commonly found in anaerobic environments. The ability to utilize extremely low concentrations of  $H_2$  has been postulated to be the role of the organisms in the rapid anaerobic corrosion of iron (9). The various environmental aspects of respiratory sulfate reduction are summarized in Table 1 and most of these environmental

TABLE 1: Environmental Effects of Respiratory Sulfate Reduction

1. Formation of Sulfide
2. Change of pH
3. Removal of Heavy Metals
4. Removal of Hydrogen
5. Removal of Sulfate
6. Changes in Microflora
7. Fractionation of Sulfur Isotopes

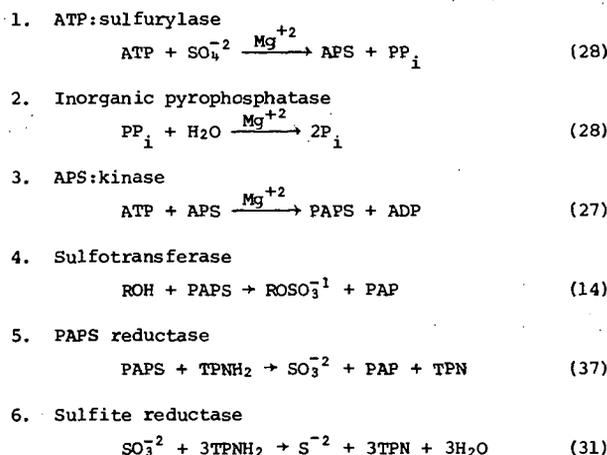
effects of respiratory sulfate reduction can be interpreted in terms of the chemical, biological and physical properties of  $H_2S$ . Postgate (23) has presented a more detailed and extensive discussion of these environmental effects of sulfate reduction. A related aspect of these bacteria is the fractionation of sulfur isotopes occurring during the reduction of sulfate which allows determination as to whether a given deposit of reduced sulfur was formed by geological phenomena or biological agents (34).

Under aerobic conditions, the absence of organic electron donors and/or acidic pH values (below 4.5) respiratory sulfate reduction is inhibited and a second type of imbalance in the biological sulfur cycle created which leads to the formation of very acidic environments (to pH 1.0). For this situation to occur, the presence of reduced sulfur compounds, such as  $H_2S$ ,  $S^0$  or  $S_2O_3^{2-}$ , which can be oxidized by the Thiobacilli to sulfate as  $H_2SO_4$ , is required. In contrast to the sulfate-reducing bacteria which require fixed carbon, these organisms can utilize  $CO_2$  as their sole source of carbon (35). This acidic environment occurs particularly where there is poor drainage and its formation can inhibit the growth of a wide variety of soil bacteria. From an economic point of view, these microorganisms can be important agents in the erosion of various types of stone and this aspect is emphasized by one isolate of these bacteria being named T. concretivorus (17). In general, the various physiological types of microorganisms responsible for the oxidation and reduction of inorganic sulfur compounds have been isolated in pure culture and their physiology studied sufficiently to predict and control the accumulation of sulfide and sulfate in a given environmental situation.

The biochemistry of the reactions of inorganic sulfur compounds has been only sporadically studied but although not all of the enzyme and reactions have been completely characterized, the reactions involved can at least be reasonably well outlined. Sulfate is first transported across the membrane of the cell by means of an active process involving sulfate-binding proteins (16) and once inside the cell universally reacts with ATP to form adenylyl sulfate (APS) and inorganic pyrophosphate ( $PP_i$ ) as shown in Table 2, reaction 1. The equilibrium of the reaction lies in the direction of ATP and  $SO_4^{2-}$  and, for significant formation of APS, the reaction must be coupled to either or both pyrophosphate hydrolysis, Table 2, reaction 2, or phosphorylation in the 3'-position to form 3'-phosphoadenylyl sulfate (PAPS), Table 2, reaction 3. PAPS serves as the substrate for all sulfation reactions, Table 2, reaction 4, and forms a sulfate ester and 3',5'-diphosphoadenosine (PAP), but specific enzymes, termed sulfotransferases, are required for the various acceptors such as alcohols, phenols, steroids, etc. PAPS is also believed to be the form in which  $SO_4^{2-}$  is reduced to  $SO_3^{2-}$  by the reduced triphosphopyridine nucleotide (TPNH<sub>2</sub>) specific PAPS reductase Table 2, reaction 5; but, the role of this enzyme and that of the TPNH<sub>2</sub>: sulfite reductase, Table 2, reaction 6, which catalyzes the 6 electron of  $SO_3^{2-}$  to  $S^{-2}$  in the biosynthetic pathway has recently been questioned (30). However,

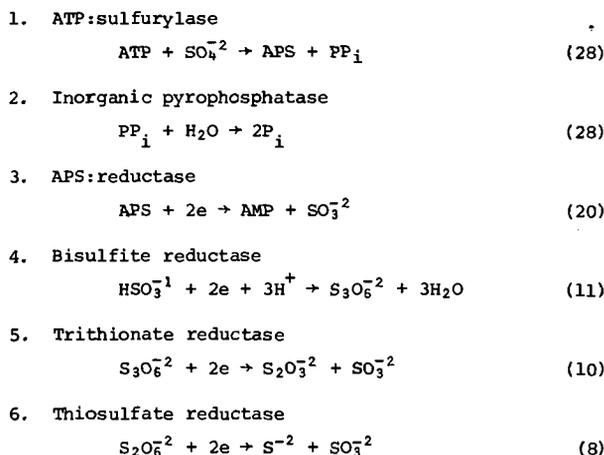
it remains clear that the biosynthetic pathway is biochemically distinct from the respiratory pathway.

TABLE 2: The Enzymes of Biosynthetic Sulfate Reduction



The initial step in the respiratory pathway of sulfate reduction is the same as that in the biosynthetic pathway, that is, the formation of APS from ATP and  $\text{SO}_4^{-2}$  by ATP sulfurylase and its formation is coupled only to the hydrolysis of inorganic pyrophosphate, Table 2 and 3, reactions 1 and 2. APS rather than PAPS is the form

TABLE 3: The Enzymes of Respiratory Sulfate Reduction



in which  $\text{SO}_4^{-2}$  is reduced to  $\text{SO}_3^{-2}$  with the formation of AMP, Table 3, reaction 3, by APS reductase in a reversible oxidation-reduction reaction. Sulfite (or bisulfite) is not directly reduced to  $\text{S}^{-2}$  by a single enzyme as in the biosynthetic pathway but rather three separate reductive steps are involved. In a complex reaction involving

three molecules of sulfite,  $\text{SO}_3^{2-}$  is reduced to trithionate ( $\text{S}_3\text{O}_6^{2-}$ ) by a hemoprotein, bisulfite reductase, of which there are three different types, desulfoviridin, desulforubidin (12) and P582 (1), Table 3, reaction 4. Trithionate is next reduced to thiosulfate with the concomitant formation of sulfite by trithionate reductase, Table 3, reaction 5. The thiosulfate is then reductively cleaved to yield  $\text{S}^{-2}$  and a second molecule of  $\text{SO}_3^{2-}$ , Table 3, reaction 6. The electron donors for these reductions have not been definitively established but they appear to be low-molecular weight electron transfer proteins. In both pathways, the result is identical in that  $\text{SO}_4^{2-}$  is reduced to  $\text{S}^{-2}$ ; however, the respiratory pathway requires one less ATP and four discrete reductive steps rather than the two involved in the biosynthetic pathway. These differences probably reflect the different physiological roles of the pathways.

The respiratory pathways involved in the oxidation of reduced sulfur compounds to  $\text{SO}_4^{2-}$  are less well defined than those in the reduction of sulfate. The key reaction is the oxidation of a cofactor or enzyme-bound polysulfide (15) to sulfite in an oxygen requiring oxidation, Table 4, reaction 1 (33). Elemental sulfur and

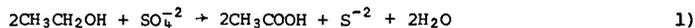
TABLE 4: The Reactions of Respiratory Sulfur Oxidation

1. Polysulfide oxidase	
	$\text{H}_2\text{O} + \text{RS}_n\text{SS}^- + \text{O}_2 \rightarrow \text{RS}_n\text{S}^{-1} + \text{SO}_3^{2-} + 2\text{H}^+$ (33)
2. Thiosulfate formation	
	$\text{S}^0 + \text{SO}_3^{2-} \rightarrow \text{S}_2\text{O}_3^{2-}$ (33)
3. Thiosulfate reductase	
	$2\text{e} + \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_3^{2-} + 2\text{S}^{-2}$ (22)
4. Sulfite oxidase	
	$\text{SO}_3^{2-} + 1/2 \text{O}_2 \rightarrow \text{SO}_4^{2-}$ (6)
5. APS reductase	
	$\text{AMP} + \text{SO}_3^{2-} + 2 \text{cyto } c_{\text{ox}} \rightarrow \text{APS} + 2 \text{cyto } c_{\text{red}}$ (22)
6. ADP sulfurylase	
	$\text{APS} + \text{P}_i \rightarrow \text{ADP} + \text{SO}_4^{2-}$ (22)

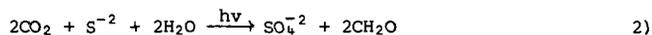
sulfide can form this "bound polysulfide" (R) and thus enter the reaction sequence; however, little is known about the details of these interactions. Sulfite is a highly reactive molecule and non-enzymatically combines with elemental sulfur to form thio-sulfate, Table 4, reaction 2. Thiosulfate is returned to the main respiratory pathway by reductive cleavage to sulfide and sulfite by thiosulfate reductase, Table 4, reaction 3. The final step is the oxidation of  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$  and is accomplished by two enzymatic pathways. The first is the simple oxidation of  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$  by the enzyme, sulfite oxidase, in certain of the Thiobacilli, Table 4, reaction 4. This oxidase has been reported to be absent in the photosynthetic bacteria (36). The second pathway, found in the photosynthetic bacteria and some of the Thiobacilli, involves the oxidation of  $\text{SO}_3^{2-}$  in the presence of AMP to the level of sulfate as APS by APS reductase, Table 4, reaction 5. The high energy sulfate can then be exchanged for a phosphate group to yield ADP by the enzyme, ADP:sulfurylase to produce biologically utilizable energy, Table 4, reaction 6. Thus, microorganisms utilizing the APS pathway are able to obtain energy by means of a substrate phosphorylation in addition to either oxidative phosphorylation or photophosphorylation. In all considerations of the biological sulfur cycle, it must be borne in mind that the

oxidation of reduced sulfur compounds yields energy and that the reduction of sulfate requires energy although the reduction of sulfate can be coupled with an oxidative reaction which produces more energy than the reduction of  $\text{SO}_4^{2-}$  requires and thereby produce energy for growth.

An important aspect of the biological sulfur cycle is the ability of certain of these anaerobic microorganisms to link and thereby modify their fermentative respiratory pathways by means of the intracellular transport or transfer of molecular hydrogen. This linking of fermentations allows these anaerobic bacteria to grow under some unexpected and surprising conditions in an almost symbiotic relationship. There are now several well documented examples of this biological phenomenon. Methanobacillus omelianskii has been demonstrated to be a mixed culture growing in this type of relationship and forming acetate and  $\text{CH}_4$  from  $\text{CO}_2$  and ethanol (3). One of the organisms, the S organism, oxidizes ethanol to acetate and  $\text{H}_2$  but grows poorly. The second organism, the H organism, reduces  $\text{CO}_2$  to  $\text{CH}_4$  with  $\text{H}_2$  and appears to "pull" the oxidation of ethanol to acetate by the oxidation of  $\text{H}_2$  as growth is greater in the mixture than in pure culture (26). Chloropseudomonas ethylica has been demonstrated to be a mixed culture which photosynthetically oxidizes ethanol to acetate (7). The culture consists of a sulfate-reducing bacterium which oxidizes ethanol to acetate with the reduction of  $\text{SO}_4^{2-}$  to  $\text{S}^{-2}$  as shown in Eq. 1.



and a green sulfur bacterium which photosynthetically oxidizes  $\text{S}^{-2}$  to  $\text{SO}_4^{2-}$  as shown in Eq. 2.

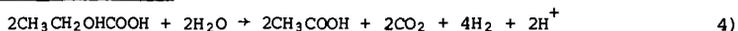


The possible involvement of intercellular  $\text{H}_2$  transfer in this relationship has not yet been resolved. A third example involves an obligatory relationship between a sulfate-reducing bacterium and a methanogenic bacterium. Sulfate (or fumarate) is obligatory for the growth of species of Desulfovibrio on lactate as shown in Eq. 3.



Recently, it has been demonstrated that the sulfate-reducing bacteria can oxidize lactate to ethanol when grown in the presence of methanogenic bacteria and the electrons (as  $\text{H}_2$ ) utilized for the reduction of  $\text{CO}_2$  to  $\text{CH}_4$  rather than the reduction of  $\text{SO}_4^{2-}$  to  $\text{S}^{-2}$  (2). This relationship involving intercellular  $\text{H}_2$  transfer is shown in Eqs. 4, 5 and 6.

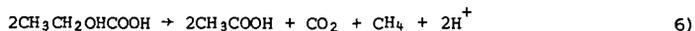
Sulfate reducing bacterium



Methanogenic bacterium



Sum:



In essence,  $\text{CO}_2$  is functioning as electron acceptor for the fermentation of lactate (and probably other electron donors) and  $\text{H}_2$  is transferred between these two anaerobic but physiologically different types of bacteria. The mechanism of this relationship has been postulated to be the "pulling" of lactate oxidation by the utilization of  $\text{H}_2$  for  $\text{CH}_4$  formation. This concept is also supported by the observation that hydrogenase is concentrated around the outside of the sulfate-reducing bacteria. Thus,

methane formation is operating as an "electron sink" or terminal oxidase and could conceivably be "pulling" the complex series of fermentative reactions occurring in the cellulose breakdown.

The observations offer a new theoretical basis for the interpretation of a portion of the microbiology and biochemistry in anaerobic sediments of fresh and marine waters. Intercellular H<sub>2</sub> transfer appears to be a specific adaptation of anaerobic bacteria which allows them to greatly extend their growth potential. Thus, the number of physiological types of microorganisms involved in the transformation of organic materials may be far fewer than previously anticipated. The ideas also suggest that a specific environment may have unexpected potential for microbial activities such as sulfate reduction, hydrogen utilization or nitrate reduction. It has also recently been established that anaerobic sediments are stable enough so that classical biochemical and physiological experiments can be performed with sediments by treating them as bacterial cultures (5). Investigations utilizing these two concepts should lead to a much greater understanding of the reactions occurring in organic deposits and indicate the ways in which these complex fermentations can be applied to specific problems of economic concern.

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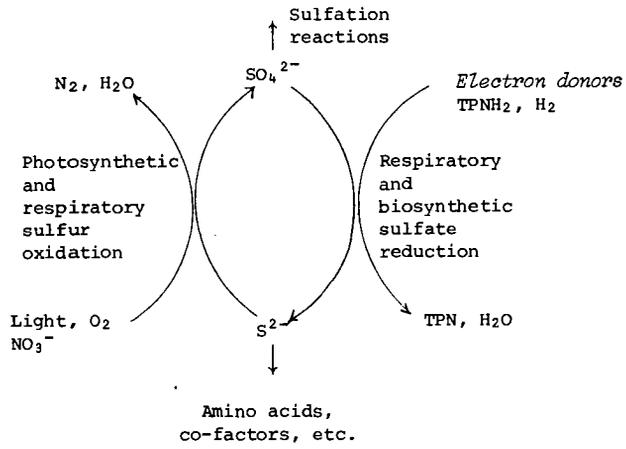


Fig. 1. A simple representation of the biological sulfur cycle.

## THE GENESIS AND STABILITY OF NITROGEN IN PEAT AND COAL

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Coal consists of the fossilized remains of bog and swamp-shore vegetation, which, following diagenesis, was preserved by water and modified by heat and pressure. Geochemists generally accept as valid the concept of a coalification series: vegetation-peat-brown coal-lignite-bituminous coal-anthracite.

Coal commonly contains 1-2% N in fixed forms which are highly resistant to biodegradation. The woody tissues of the originating vegetation--predominately tree-ferns--probably averaged about 1% N, which was of a biodegradable nature. Assuming them to be similar in structure to present-day woody tissues, about 20% of tree-fern cells contained proteinaceous material. Humic substances derived from woody and more succulent tissues as a result of microbial activities and oxidative polymerization reactions probably contained 2-5% N, although the average N content of the peat resulting from plant tissue deposition and decay remained at about 1%. The N content of bituminous coal generally is slightly higher than that of peat and lignite--about 1.5 to 1.75%--but decreases to less than 1% in anthracite.

The C/N ratio typically increases from about 50/1 in wood to 65/1 in peat and lignite. However, the C/N ratio decreases in low-rank bituminous coals, then increases with increase in rank (55/1 in high-rank bituminous coals to 100/1 or greater in anthracite). It is evident that N was gained relative to C (or C was lost) during the latter stages of diagenesis.

The accretion of N by peat may continue after its formation and subsequent submergence in waters through deposition of microbial (microflora and microfauna) protein. The total amino acid content of peat is considerably higher than in the original plant material; at least 5-10% of peat organic matter is considered to be derived from microbial tissue (1). For example, the weight of bacterial tissue per acre foot of peat might range between 35-700 pounds at any given time, corresponding to about 5-115 pounds of N. This range is calculated by assuming 35-700 million bacteria per gram of moist peat (2, 3), a volume of 1 cubic micron per organism, and a cell density of 1.04. Soil bacteria usually outnumber actinomycetes by 10:1, and fungi by 100:1, but the weight of bacteria is about equal to and half that of the actinomycetes and fungi, respectively. As can be seen, the total living and newly deceased biomass in peat could be substantial. Obviously, N accretion through deposition of microbial tissue implies the presence of sufficient fixed N to sustain microbial growth. Such N could be obtained from *in situ* biological fixation of atmospheric N<sub>2</sub> or from the transport of fixed N in sediments and aquatic life to peat beds.

Determining how and in what forms the N was preserved may be more instructive in understanding the genesis of N in coal than speculating on the primary sources of N in a coalification series. The time, manner, and circumstances of nitrogen accretion during or shortly after diagenesis is of lesser importance if one accepts the concept of a coalification series progressing from peat to anthracite rather than the concept advanced by Fuchs (4), which holds that lignites are formed under aerobic conditions and bituminous and anthracite coals are formed under anaerobiosis. More importantly, a question central to understanding the presence of fixed N in coal is how nitrogenous products of microbial activity acquire stability against further microbial and chemical decomposition over geological times.

#### SOIL HUMUS FORMATION

Humus, as used here, refers to the debris of higher plants, microflora, and microfauna in various stages of biochemical and chemical alteration. Early work on soil humus formation was much influenced by chemical studies of humus in peats and coals. Granting that the factors influencing humus formation in soils, marshes, peat bogs, etc., may be very different, one nevertheless may be justified in seeking common mechanisms for humus formation under widely different conditions because of the known gross similarities of certain humic substances (alkali-extractable, acid-precipitable substances) in soils and in lake and marine sediments.

Recent N tracer ( $^{15}\text{N}$ ) studies support the postulate of Jansson (5) that there exists in soil a large pool of relatively passive organic N, all or part of which is in equilibrium with a much smaller pool of labile organic N. Usually, when N is added to soil, some becomes immobilized through microbial activity, entering first a pool of labile organic matter, then being redistributed among progressively more refractory, bioresistant substances in the passive pool (6-10). Current knowledge of the organic forms of N in these pools is based largely on the chemical analysis of organic N compounds released by hydrolysis of soils with hot acids [for reviews, see Bremner (11, 12)]. Such hydrolysis studies indicate that the labile organic N pool consists largely of bound amino acids and amino sugars (mainly glucosamine and galactosamine), existing perhaps as mucopeptides (amino acid--amino sugar complexes), teichoic acids (ester-linked alanine-organophosphate polymers), and chitinous substances. Amino acids and hexosamines normally comprise 20-50% and 5-10%, respectively, of the total organic N of soils. Purines, pyrimidines, ethanolamine, and other N compounds also have been identified in soils, but the chemical nature of about half of soil organic N is not well understood. It is this unidentified, relatively stable fraction that is of geochemical interest.

In soils, peat bogs, and like environments, labile forms of N are assimilated by microorganisms. The microorganisms die and decay, the tissues of one generation being food for succeeding ones. With each cycle of generation and decay, waste products of metabolism are released to the microenvironment. Ammonium N and amino acids can be considered

such wastes. As long as these waste products re-enter vital processes, and then recycle as part of new living tissue, there is no mechanism for acquiring stability. However, the recycling processes may be interrupted by chemically binding labile nitrogenous substances to other intracellular or extracellular constituents to form biochemically resistant and chemically inert materials, or by decreasing their physical accessibility to enzymatic and nonenzymatic attack.

The "physical inaccessibility" concept is supported by the finding that destruction of physically stable microaggregates in soil consisting of clay mineral-organic matter complexes renders the organic matter more susceptible to chemical and microbial attack (13). Also, the entrapment of ammonia within clay lattices is another protective mechanism for soil N. Clay-protected N could survive the coalification processes and appear in coal as part of clay mineral contaminants in low-rank coals.

Much work has been reported in support of the view that stable N complexes in soil are produced by reactions of lignin- and cellulose-derived phenols or quinones with amino acids [e.g., see (11-20)] and the reactions of oxidized lignins with ammonia (21). The dark-colored substances produced by such reactions have chemical properties similar to the humic substances found in soils, peats, and sediments. A detailed analysis of the extensive work on the role of lignin in humification processes is beyond the scope of this paper.

Chemical fractions of humic substances (e.g., humic, fulvic, and hylatomelonic acids) are probably not simple chemical entities, but more likely are mixtures of components of heterogeneous structure. They are noncrystalline, which suggests that they are not formed through enzymatic activity. Although the dark humic substances exhibit the properties of oxidized lignins, it is reasonable to assume that lignins must be drastically altered before entering oxidative polymerization or polycondensation reactions with ammonia and amino acids (22, 23). Natural and unaltered lignins are too chemically inert to form complex, biologically stable polymers with amino acids. Also, formation of such polymers extracellularly in soil from lignin residues may not be extensive because only small amounts of lignin degradation products are found in soils and peats. For example, alkaline-nitrobenzene oxidation of soil organic matter yielded syringyl, guaiacyl, and p-hydroxyphenyl residues amounting to less than 1% of the total soil C; for peat, the yield was 1 to 4% (24).

The proximity of reactants to each other, their concentrations, the reaction site microenvironment, and the time that each reactant is released to the microenvironment are factors which may determine the extent of formation of dark humic substances and their nature. These factors themselves are influenced by the type of vegetation undergoing diagenesis (e.g., woody tissues are characterized by relatively high protein and lignin contents as compared to sphagnum moss). As plant tissue decays, loosely bound proteins and carbohydrates are attacked first, followed by peptides and methylated polysaccharides. Lignins are relatively resistant to biodegradation. It appears, therefore, that

ammonia and amino acids would be released from plant residues to the soil at a particular microsite, and then transformed or assimilated before lignin- or cellulose-derived phenols and quinones are produced at the microsite. Even though amino acids may persist unmodified in soils for many years, there is evidence that a considerable portion of soil amino acids is not bound to lignin (11) and may form stable complexes with transition series metals (25).

The intact cell is a potential reaction chamber in which chemically active substances may be intimately associated at high concentrations in a microenvironment favorable for reaction. Recently, considerable attention has been given to the possibility that humic substances are formed by autolysis of microorganisms (23). The presumption that stable organic N polymers can be formed intracellularly is supported by evidence that dark humic substances are formed by chemical reactions of biochemically produced reactants, that the sequence of reactant production in soil may not be conducive to extensive extracellular formation of humic substances, and that the dark humic substances formed in different media and at different geological times are similar.

#### POSSIBLE INTRACELLULAR FORMATION OF HUMIC SUBSTANCES

Living cells contain the enzymes needed for degrading their autogenous substances (e.g., proteins, peptides, and cellulose) and for the further reaction of the degradation products (e.g., the oxidation of phenols to quinones and polyphenols by phenolases). However, ligninase has not been isolated from higher plant or microbial tissue, notwithstanding the specific evidence of ligninase activity in fungal cells. In woody cells, lignin is deposited in the interstices between the micellar strands and microfibrils of cellulose and other microcrystalline components of the cell wall. After the cell or tissue dies, removal of the lignin leaves the cell wall morphologically intact. Within the protection of a relatively bioresistant cell wall, high concentrations of monomeric substances can accumulate as autolysis proceeds.

Quinones can condense with  $\alpha$ -amino acids through the amino group, leaving the acidic carboxyl groups free. Cross-linking with adjacent quinones could occur through diamino-amino acids (e.g., lysine) or thiol-containing amino acids (e.g., cysteine). Polycondensation would result from intermolecular interactions between compounds possessing at least two functional groups capable of esterification. The order and pattern of polycondensation would be irregular, resulting in a 3-dimensional amorphous substance (a heteropolycondensate co-polymer with side chains) composed of many phenolic-quinolic-amino acid units. It has been postulated that such polymeric substances, by virtue of their isolated resonance groups, would absorb light of all wavelengths and appear dark in color, be soluble in alkalis because of their free carboxyls, be slightly soluble in organic solvents because of their predominantly condensed aromatic nature, and be precipitated from alkaline solution by acids and heavy metals (26). Such co-polymers would be resistant to chemical and microbial attack because of their high molecular weight, their cross-linked, covalent bonding, and their heterogeneous, predominately nonlinear structure of nonrepeating units.

The humic substances formed within the cell would be released by extracellular microbial and chemical attack on the cell wall. Since their overall mode of formation is similar, dark humic substances found in different environments (e.g., soils, peats, and sediments) would be expected to have similar gross properties. In time, and depending on environmental factors, the linear side chains of the large, irregularly spherical co-polymer would be degraded, leaving a substance that would require the fortuitous, unlikely association of several enzymes to effect its further degradation.

#### NITROGEN FORMS IN COAL

Little is known with certainty about the N forms in coal and it appears premature to speculate about the metamorphic conversion of humic substances whose structures are only grossly identified. There is evidence that N occurs largely as heterocyclic structures (27, 28), such as nicotinic acid (29). A presumptive analysis of coal extracts after physical and chemical treatment yielded the following hypothetical distribution of nitrogen structures: Water phase--purine bases and structures with urea, amino acid, and peptide units (35%), carbazole structures yielding ammonia (10%), low-molecular weight cyclic bases and phenylamines (3%); Chloroform phase--hydrophilic bases, nonbasic N compounds, and fatty amines (23%); Residual coal--high-molecular weight N compounds (3%). Upon pyrolysis, 26% of the N compounds yielded N<sub>2</sub> (30).

Among the amino acids found in peat were glycine, aspartic and glutamic acids, alanine, leucine, threonine, and valine (31). Monoamino and diamino acids have been identified in peat, lignite, and subbituminous coal, but no diamino acids have been found in bituminous and anthracite coals (28). Glycine and aspartic and glutamic acids were found in hydrolysates of anthracite estimated to be over 200 million years old (32).

Free porphyrins have been identified in polar solvent (e.g., ether or pyridine) extracts of bituminous coal (33). Metal-porphyrin complexes may be present in concentrations as high as 7000 ppm, about 100 times those of free porphyrins. Nickel and vanadium complexes are especially stable. Porphyrins in coal originate in the chlorophyll and respiratory pigments of green plant tissue and have been preserved in water-logged peat because of their greater stability in anaerobic biological environments. Their presence lends support to the hypothesis that pressure and moderate heat are the agents of peat metamorphosis because porphyrin stability increases with pressure and decreases with heat. Also, studies of porphyrins in bitumens give support to the hypothesis that petroleum is formed in brackish environments from asphaltic constituents resulting from the alteration of marine and terrestrial plant and animal organic matter (34).

### TRACER STUDIES

Use of the N tracer,  $^{15}\text{N}$ , has contributed greatly to an understanding of the turnover of N in biological mineralization-immobilization reactions, processes which proceed simultaneously and in opposite directions [for an extensive bibliography, see Hauck and Bystrom, (35)]. However, N tracer techniques have not been used effectively to clarify the chemical nature of humic materials, largely because experiments have not been devised to make maximum use of  $^{15}\text{N}$  for this purpose. It would be instructive to follow the detailed, sequential decay of higher plant and microbial tissue labeled with  $^{13}\text{C}$  and  $^{15}\text{N}$ , and to attempt to isolate labeled polycondensation products from cell populations in various stages of autolysis. Comparisons should be made of the distribution of tracers in different humic fractions, as affected by the precursor tissue. For example, woody tissue may produce more highly aromatic, humic substances, such as those found in coals, while the corresponding humic fraction from proteinaceous tissue may be more aliphatic in character. However, such comparisons might be valid only if care is taken to separate extracellular from intracellular formation of humic substances, should such a distinction exist.

Carbon isotope studies show no correlation between isotopic composition, degree of coalification, and geological age of coals (36). From this one may infer that the C in coal was derived largely from land plants which absorbed carbon dioxide of uniform C isotopic composition and that no measurable C isotope fractionation occurred during diagenesis.

Slight but significant variations have been observed in the N isotopic composition of different peats and coals (37-39). The N in coal tends to have a slightly higher  $^{15}\text{N}$  concentration than vegetation in the vicinity of the coal seam (38), but definite conclusions are not justified from the limited data available. In another study (39) C isotope analyses indicate that some Dutch natural gas deposits originated from recoalification of coal seams 3000 and 5000 meters below sea level. Nitrogen in gases obtained from these deposits was enriched in  $^{15}\text{N}$ , while ammonia obtained from the coal (coke-oven gas) was depleted in  $^{15}\text{N}$  (relative to atmospheric  $\text{N}_2$ ), leading to the speculation that the N in natural gases was not derived from the coal. Measurements of N isotope ratios in natural gases have also been used to explain the parallel increase in He and  $\text{N}_2$  in gases with increase in age of reservoir rock (40) and to elucidate the origin of N in gases associated with crude oils and sedimentary materials (41).

The limited number and scope of the studies referred to above make it difficult to assess whether further studies of this kind will prove useful in clarifying the genesis of coal, kerogen, petroleum, and natural gases. Obviously, if the N isotope ratio of N occluded in methane, for example, is similar to but slightly lower than that of a nearby deposit of organic material, then one has reason to assume that the methane was derived from that deposit. Also, a slightly lower N isotope ratio for N in methane suggests the occurrence of isotope fractionation as C-N bonds are ruptured during gas formation.

There is a time gap of about 200 million years separating current studies of humification processes and the events which converted vegetation to coal. Because the isotope ratio reflects the cumulative effects of nitrogen cycle processes, in-depth studies of the N isotopic composition of peats, coals, and their associated materials may prove helpful in separating events that occurred during different geological times.

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## INTRODUCTION

Sulfur is a necessary element for the sustenance of all living systems. It is therefore not at all surprising that sulfur is found in abundance in coal, a rock composed primarily of organic detritus.

The forms of sulfur in coal as reported by chemical analyses (ASTM 1974) are: organic sulfur, pyritic or sulfide sulfur, and sulfate sulfur. The last two are inorganically combined within the coal and will be discussed here. Other analytical techniques have been used to identify native or elemental sulfur in coals (Yurovski, 1940; Berteloot, 1947) and also in modern peats (Casagrande, *in* Spackman et al., 1974, p. 63, 219). The amounts of elemental sulfur that have been reported are small and would not be significant in coal utilization.

Sulfate sulfur is also generally of only minor importance in fresh coal samples and except in rare instances occurs in significant amounts only as the coals oxidize (weather). Organic and pyritic sulfur comprise essentially all of the sulfur found in most coals. Yancey and Geer (1968) list analyses of these two forms of sulfur in various coals of the world and these range from a low of 0.44 percent to a high of 9.01 percent total sulfur. Only rarely would one expect to find coals in which the percentage of sulfur would not be included in that range. The organic sulfur content of the coals listed by Yancey and Geer ranged from 11.4 percent to 97.1 percent of the total sulfur. Gluskoter and Simon (1968) reported a mean value of 1.56 for the ratio of pyritic to organic sulfur in 473 face-channel samples of Illinois coals.

## SULFUR BEARING MINERALS IN COAL

Iron Sulfides—Pyrite is the dominant sulfide mineral found in coals. Marcasite has also been found in many coals and may be the dominant form in some coals of lower rank (Kemežys and Taylor, 1964). Pyrite and marcasite are dimorphs, minerals that are identical in chemical composition but differ in crystalline form. Pyrite is cubic and marcasite is orthorhombic. The two minerals cannot generally be differentiated in coals except by determining their crystalline structures, usually by X-ray diffraction methods. The term "pyrite" is often used to refer to the undifferentiated iron disulfide minerals in coals.

Rather extreme variations in morphology, size, and mode of occurrence characterize the iron sulfide minerals in coals. These variations arise because of the different geochemical environments in which the minerals were formed and the time of their genesis. Some sulfides were formed contemporaneously with the coal in a peat swamp and are therefore syngenetic. The syngenetic pyrite includes sub-micrometer-sized particles and also some nodules with diameters as large as a meter. These syngenetic sulfides are the response to the geochemical environment during or immediately following the peat formation, which was approximately 300 million years ago for the coals of carboniferous age. Other of the sulfides are epigenetic; they formed within the coal seam subsequent to the first stages of coalification. The most common form of epigenetic iron sulfide in coal is pyrite deposited along vertical fractures (cleat). I am not aware of any report of marcasite as an epigenetic mineral in bituminous coals of North America, but a mixed marcasite-pyrite cleat filling in a subbituminous coal from Wyoming is shown in Plate 1. Other epigenetic and syngenetic sulfides are shown in scanning electron photomicrographs in Plate 1.

Other Sulfide Minerals—A number of sulfide minerals other than iron sulfides have been reported in coals, including galena (PbS), chalcopyrite (CuFeS<sub>2</sub>), arsenopyrite (FeAsS), and sphalerite (ZnS). These generally occur only in small amounts. However, coals from northwestern Illinois that contain as much as 5350 ppm zinc and up to 1 percent sphalerite have recently been described by Ruch et al. (1974) and Miller (1974). The sphalerite occurs as a cleat filling up to 10 mm in width (Plate 2).

Sulfate Minerals—Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and barite (BaSO<sub>4</sub>) have both been identified as cleat-filling minerals or in nodules in unweathered coals (Plate 2). However, their occurrences are rare and sulfate minerals do not generally comprise a significant portion of the total sulfur in coal.

Because pyrite and marcasite oxidize rapidly when exposed to moist air, a number of different phases of ferrous and ferric sulfates may form. The following have been identified as oxidation products of iron sulfides in Illinois coals (Gluskoter and Simon, 1968): Szomolnokite (FeSO<sub>4</sub>·H<sub>2</sub>O), rozenite (FeSO<sub>4</sub>·4H<sub>2</sub>O), melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O), coquimbite (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O), roemerite (FeSO<sub>4</sub>·Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·12H<sub>2</sub>O), and natrojarosite ((Na<sub>2</sub>K)Fe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>). Although these are not present in fresh coals they can become abundant in weathered, oxidized coal samples. The amount of sulfate sulfur reported in the chemical analyses of many coals is a function of the length of time since the fresh sample was collected and of the manner in which it was sorted. Several iron sulfates are shown in Plate 2.

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## ILLUSTRATIONS

## Plate 1. Pyrite in Coals: Scanning Electron Photomicrographs

- A. Framboids in low-temperature ash of a sample from the DeKoven Coal Member (bituminous), southern Illinois
- B. Octahedra in low-temperature ash of a sample from the DeKoven Coal Member (bituminous), southern Illinois
- C. Epigenetic cleat filling in a sample of the Opdyke Coal Member (bituminous), southern Illinois
- D. Cast of plant cells from the low-temperature ash of a sample from the Colchester (No. 2) Coal Member (bituminous), northern Illinois
- E. Epigenetic pyrite along inclined shear surface in a sample of lignite, North Dakota
- F. Epigenetic cleat filling in a sample from the Colchester (No. 2) Coal Member (bituminous), northern Illinois

## Plate 2. Sulfide and Sulfate Minerals in Coals: Scanning Electron Photomicrographs

- A. Marcasite, epigenetic, along cleat in a sample from a sub-bituminous coal, Wyoming
- B. Sphalerite (ZnS), along cleat in a sample from the Herrin (No. 6) Coal Member (bituminous), northwestern Illinois
- C. Barite (BaSO<sub>4</sub>) with marcasite and pyrite in a sample from a sub-bituminous coal, Wyoming
- D, E, and F. Iron sulfates which formed on bituminous coal samples subsequent to their having been collected from fresh exposures. X-ray diffraction analyses of these samples identified melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O) and coquimbite (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O).

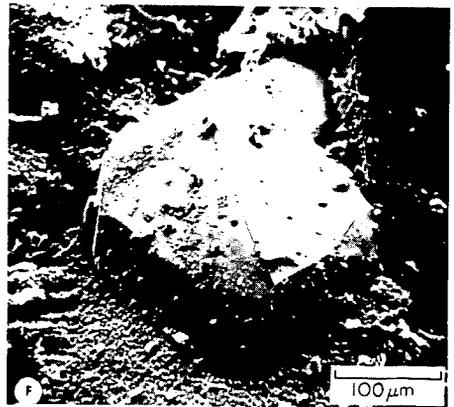
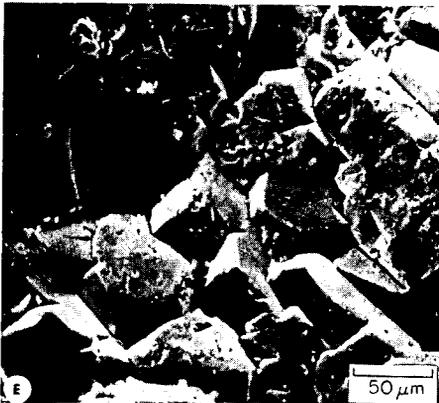
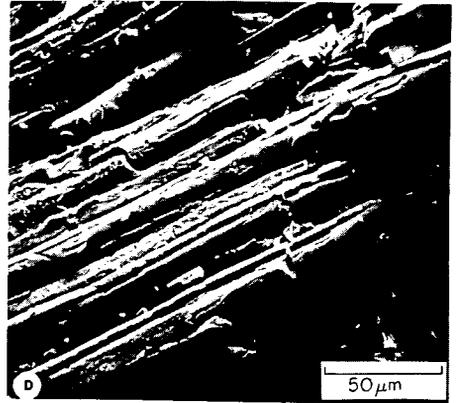
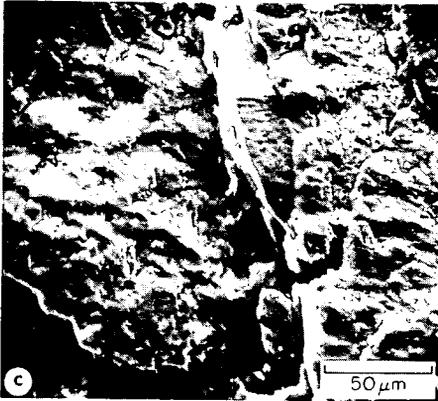
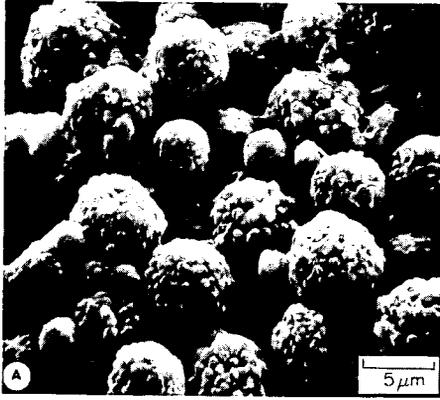


Plate 1. Pyrite in Coals

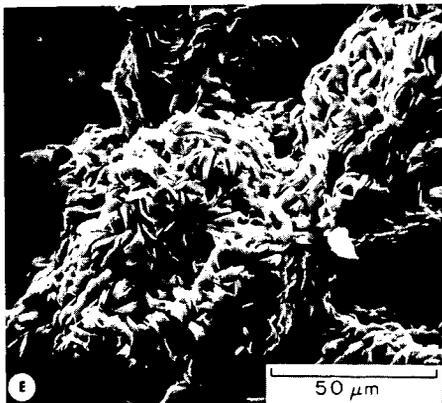
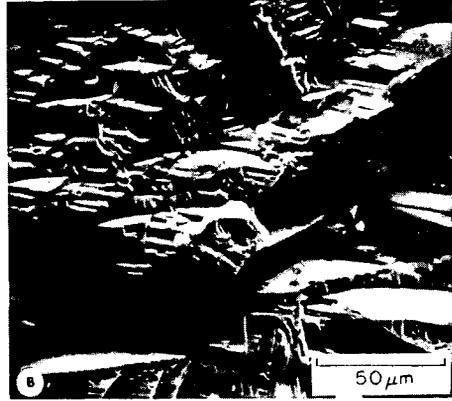
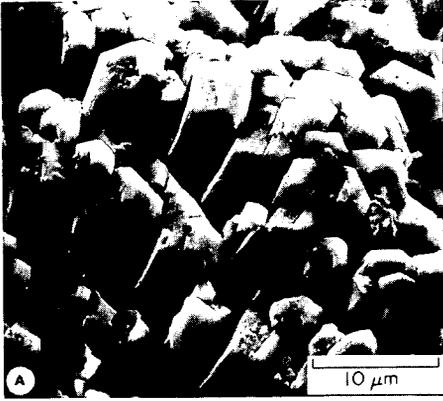


Plate 2. Sulfide and Sulfate Minerals in Coals

## Determination of Forms of Sulfur in Coal

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## INTRODUCTION

The need for low-sulfur coal has assumed major proportions. Shortages of other fossil fuels, restrictions on sulfur oxide emissions, and technical problems associated with the use of high-sulfur coals in newly proposed coal conversion processes are contributing to the crisis. It is now apparent not only to coal specialists but also to others that the emission standards and technical problems associated with high sulfur content of bituminous coals are contributing greatly to the severity of the fuel shortages in the United States. Consequently, it is appropriate to discuss old and new methods of evaluating the sulfur status of coal and to reexamine some of the problems associated with their application.

Free sulfur as such does not occur in coal to any significant extent. Sulfur is present in coal in organically bound combinations, in inorganic compounds mainly as pyrite ( $\text{FeS}_2$ ), and especially in weathered coals as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and as ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). In a few coals, significant amounts of other inorganic sulfates and sulfides, e.g. barite ( $\text{BaSO}_4$ ) and sphalerite ( $\text{ZnS}$ ), (1,2) which normally occur only in trace concentrations, may be present.

The three forms of sulfur commonly measured in coal are sulfate, pyritic, and organic. Although less frequently determined than total sulfur, they are, perhaps, the most significant in terms of coal utilization. Of the two predominant sulfur forms, pyritic and organic, the former can be partially removed by conventional gravity coal cleaning procedures prior to combustion, but the latter cannot. The amount of pyritic sulfur in Illinois coals and the percentages of it that can be removed with reasonable coal recovery (80%) were recently reported by Helfinstine et al. (3,4). For 64 coals, they found that the total sulfur removed as pyrite in laboratory washing studies varied from about 10 to 65%. The pyritic sulfur that was removed with 80% coal recovery varied from about 10 to 90% and averaged about 60%.

Although significant amounts of pyritic sulfur can usually be removed by physical means, very finely divided or framboidal pyrite is not amenable to reduction by such treatment. For complete removal of pyritic sulfur, a combination of physical and chemical extraction methods is usually required. Methods of this type are currently being developed, but these have not been employed on an industrial scale (5).

Similar methods for the reduction of organic sulfur, without destruction of the coal molecule itself, have not been developed. Even if 100% of the pyritic sulfur were removed from all the Illinois coals produced, only about 15% would meet current environmental standards without supplementary controls (3,4).

Because the degree to which sulfur can be reduced in coal is primarily a function of the forms of sulfur contained in the coal, analytical methods for their accurate determination are essential.

## ASTM FORMS OF SULFUR INVESTIGATION

Committee D-5 on Coal and Coke, of the American Society for Testing and Materials (ASTM), began a study of methods for the determination of forms of sulfur in coal in 1957. This study eventually led to the current Standard Method D-2492,

Forms of Sulfur in Coal (6). In this procedure, total sulfur and only two of its three forms - sulfate and pyritic - are determined. The third form, organic sulfur, is calculated by difference:

$$\text{Organic S} = \text{Total S} - (\text{sulfate S} + \text{pyritic S}).$$

For this method, it is not only essential to obtain accurate values for sulfate and pyritic sulfur forms, it is also necessary to obtain accurate total sulfur values. Any errors made in total, pyritic, or sulfate sulfur determinations will be cumulative in the organic sulfur calculation. Unfortunately, there are no published methods for the direct determination of organic sulfur that will permit the sum of independently determined values for the three forms of sulfur to be checked against an independently determined total sulfur value. This has led to a number of problems, which will be discussed in more detail later.

A flow sheet for ASTM Standard Method D-2492, Forms of Sulfur in Coal, is given in Figure 1. The method is based on the different solubilities of sulfate and pyritic sulfur in HCl and HNO<sub>3</sub>. Sulfate sulfur is soluble in dilute HCl, both sulfate and pyritic forms of sulfur are soluble in HNO<sub>3</sub>, and organic sulfur is insoluble in the acids. Pyritic sulfur is generally determined by extracting the coal residue from the sulfate sulfur determination (Figure 1), although it may also be determined on a separate coal sample if corrections for the sulfate sulfur or iron are made. Pyrite is oxidized by HNO<sub>3</sub> to ferric iron and sulfate, but it is the ferric iron associated with the pyrite that is usually determined rather than the sulfur (Figure 1). The HNO<sub>3</sub> extraction may oxidize small amounts of organic matter that contains sulfur. This would be erroneously determined as part of the pyritic sulfur. Organic sulfur is calculated by difference as previously described.

During the ASTM round-robin testing of this method, large amounts of data were generated and subsequently compiled by Krumin (7,8,9,10) for Committee D-5. The results and conclusions of this study are unavailable in published form, but a brief summary of its nature and the conclusions drawn are as follows\*.

1) Five coal samples containing from 1.6 to 24% sulfur, each ground to pass a -60 mesh and -200 mesh-sieve, and analyzed by five different laboratories gave essentially the same results for forms of sulfur. Thus, the use of -60 mesh coal was recommended.

2) Further studies using methods originally developed by Powell and Parr (11) and Powell (12) were conducted by 24 laboratories, each analyzing two coals in triplicate and using the coal extraction and method variations given in Table I. In all cases, organic sulfur was determined by differences. Results of this study are summarized in Table I. Table II presents the results of the t-test of means, and Table III presents results of the F-test of variances as performed on the data determined by the various methods for sulfate and pyritic sulfur in coal samples designated S-1 and S-2. Conclusions were drawn by Krumin (10) and presented at the meeting of ASTM Committee D-5, January 30, 1961:

Total Sulfur-Eschka Method (ASTM D-3177). Deviations in the data reported by the various laboratories were within, or exceeded by only a small amount (0.01 to 0.05%), ASTM limits for maximum deviations of results.

Sulfate Sulfur (ASTM D-2492). The results determined by the two methods Sulfate Sulfur, Short Extraction and Sulfate Sulfur, Long Extraction are in close agreement, and are characterized by almost identical values for the standard deviation, repeatability and reproducibility. The great advantages of the 30-minute extraction procedure over the 40-hour technique make the method Sulfate Sulfur, Short Extraction the more suitable method for use in the routine analysis of coal.

\* Permission to summarize this work was granted by the Executive Committee of ASTM Committee D-5 on Coal and Coke.

TABLE I. STATISTICAL EVALUATION\*

Experimental procedure	Sample	Meant data (%)	Standard deviation	Repeat-ability	Reproduc-ibility
Total Sulfur	S-1	2.93	0.0945	0.0610	0.2514
	S-2	2.94	0.0846	0.0928	0.2142
Sulfate Sulfur,	S-1	0.08	0.0131	0.0196	0.0311
HCl Short Extraction (30 min.)	S-2	0.16	0.0124	0.0214	0.0322
Sulfate Sulfur	S-1	0.08	0.0115	0.0196	0.0339
HCl Long Extraction (40 hrs., 60° C)	S-2	0.15	0.0124	0.0191	0.0316
Pyritic Sulfur, Short	S-1	1.75	0.1799	0.1412	0.4412
HNO <sub>3</sub> Extraction (reflux, 30 min.), Gravimetric Determination	S-2	1.62	0.1637	0.14555	0.4069
Pyritic Sulfur, Long	S-1	1.74	0.1952	0.1614	0.5085
HNO <sub>3</sub> Extraction (24 hrs., room temp.), Gravimetric Determination	S-2	1.59	0.1228	0.1460	0.3359
Pyritic Sulfur, Short	S-1	1.74	0.1553	0.1198	0.4119
HNO <sub>3</sub> Extraction (reflux, 30 min.), Titrimetric Determination of Iron	S-2	1.58	0.0943	0.1213	0.2516
Pyritic Sulfur, Long	S-1	1.85	0.1027	0.0922	0.2815
HNO <sub>3</sub> Extraction (24 hrs., room temp.), Titrimetric Determination of Iron	S-2	1.59	0.0974	0.0998	0.2553

\*After a thesis by E. Fasig, Jr., Engineering and Experiment Station, Ohio State University, Columbus, OH.

†Moisture-free.

TABLE II. RESULTS OF THE T-TEST OF MEANS\*

Method of determination	Sample	Degrees of freedom	Calculated value of t	Critical value or range of t
Sulfate Sulfur, Long vs. Short Extractions	S-1	102	0.790	2.000 to 1.980
	S-2	100	4.475	2.000 to 1.980
Pyritic Sulfur, Short Extraction, Gravimetric vs. Titrimetric Determinations	S-1	70	0.106	2.000 to 1.980
	S-2	70	1.505	2.000 to 1.980
Pyritic Sulfur, Long Extraction, Gravimetric vs. Titrimetric Determinations	S-1	76	3.371	2.000 to 1.980
	S-2	72	0.007	2.000 to 1.980
Pyritic Sulfur, Short vs. Long Extractions, Gravimetric Determination	S-1	86	0.126	2.000 to 1.980
	S-2	83	0.953	2.000 to 1.980
Pyritic Sulfur Short vs. Long Extractions, Titrimetric Determination	S-1	60	3.768	2.000
	S-2	59	0.552	2.008 to 2.000

\*After a thesis by E. Fasig, Jr., Engineering Experiment Station, Ohio State University, Columbus, OH.

TABLE III. RESULTS OF THE F-TEST OF VARIANCES\*

Method of determination	Sample	Degrees of Freedom		Calculated value of F	Critical range, F
		numerator	denominator		
Sulfate Sulfur, Long vs. Short Extractions	S-1	1	102	1.73	4.00 to 3.92
	S-2	1	100	26.97	4.00 to 3.92
Pyritic Sulfur, Long and Short Extractions	S-1	3	146	6.87	2.68 to 2.60
	Gravimetric and Titrimetric Determinations	S-2	3	142	2.96

\*After a thesis by E. Fasig, Jr., Engineering Experiment Station, Ohio State University, Columbus, OH.

Pyritic Sulfur (ASTM D-2492). Data determined by four methods (Table 1), were, for all cases except one, in close agreement with each other and were characterized by values of standard deviation, repeatability, and reproducibility, all of which were very similar. The precision of the titrimetric technique was better than that of the gravimetric procedure as shown by the values of standard deviation and reproducibility shown in Table I. Since the precision and results of the various methods are so similar, the advantages of the short, 30-minute extraction procedure over the long, 40-hour technique, and the greater ease and speed of the titrimetric determination in comparison with the gravimetric procedure make the method Pyritic Sulfur, Short Extraction, Titrimetric Determination the most suitable for use in the routine analysis of coal.

#### TOTAL SULFUR

The need for accurate methods of determining total sulfur in coal was previously noted. The Eschka and bomb washing procedures are the two most commonly used methods in the United States, both of which are given in ASTM D-3177 (6).

The Eschka procedure consists of thoroughly mixing coal with Eschka mixture (2 parts calcined MgO and 1 part anhydrous Na<sub>2</sub>CO<sub>3</sub>) and ashing it in a muffle furnace at 800° C. The ashed coal is leached with hot water, filtered, and the sulfur is determined gravimetrically in the filtrate. This method is rapid when carried out on large batches of samples; it is most accurate when used for coals containing no more than 6 or 7% sulfur.

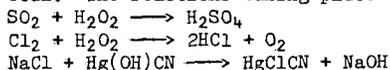
The bomb washing procedure is convenient for laboratories that make frequent coal calorimetric determinations as described in ASTM D-2015 (6). After cooling and careful venting, the bomb used for a calorific determination is thoroughly washed with water, and the sulfur is then gravimetrically determined in the bomb washings. This method gives excellent results when used for the analysis of coals containing no more than 4% sulfur.

A third method in common use, but which was dropped as an ASTM standard in 1974, is the peroxide bomb method (13). In this method, coal is fused with Na<sub>2</sub>O<sub>2</sub> in a special bomb. Following dissolution of the melt, sulfur is usually determined gravimetrically. This procedure is especially useful for the determination of high sulfur concentrations up to 30 or 40%. The difficulties and precautions required for the correct use of these three methods have been described by Selvig and Fieldner (14) and Rees (15).

There are at least three other less frequently used procedures: The high-temperature combustion method (16), which has been approved by ASTM Committee D-5 and will probably be published in 1975; the Leco or induction furnace method, which was tested by ASTM Committee D-5 with unsatisfactory results (17); and X-ray fluorescence methods.

The high-temperature combustion procedure is most useful for the rapid (30 min. per sample) determination of total sulfur in a small batch of less than 8 or 10 samples. Under these conditions, it is much more rapid than the Eschka method; however, when samples are analyzed in larger groups (20 to 30 samples), the Eschka procedure is preferred over the high-temperature combustion method.

The high-temperature combustion method for determining total sulfur in coal is based on the procedure of Mott and Wilkinson (18) in which a weighed coal sample is burned in a tube furnace in a stream of oxygen at a temperature of 1350° C. The sulfur oxides and chlorine formed are absorbed in H<sub>2</sub>O<sub>2</sub> solution yielding HCl and H<sub>2</sub>SO<sub>4</sub>. The total acid content is determined by titration with NaOH, and the amount of NaCl resulting from the titration of the HCl is converted to NaOH with a solution of mercuric oxycyanide (Hg(OH)CN). This NaOH is determined titrimetrically and used to correct the sulfur value, which is equivalent to the amount of H<sub>2</sub>SO<sub>4</sub> formed during combustion of the coal. The reactions taking place are as follows:



The method is accurate for both low and high sulfur concentrations.

Finally, X-ray fluorescence has been used for determining total sulfur in coal (19,20,21). Ruch et al. (1) have recently described a method of preparing pressed coal samples, which may be used for the determination of a variety of major, minor, and trace elements, including sulfur, in whole coal. Their sulfur values for more than 100 coals showed good agreement with those determined by the ASTM standard Eschka procedure (Ruch, p. 15). The economy and speed of such X-ray fluorescence methods, when used for multiple determinations (e.g. Al, Si, Ca, Mg, Fe, K, Ti, P, and S) in the same prepared coal sample, are probably unsurpassed by any other method. The relative standard deviation for sulfur, as determined by the X-ray fluorescence method of Ruch et al. (1) is 0.5%.

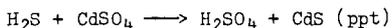
#### INSTRUMENTAL METHODS FOR DETERMINING PYRITIC SULFUR

The HNO<sub>3</sub> extraction of pyrite (FeS<sub>2</sub>) from coal yields a solution ideal for the atomic absorption determination of iron as a measure of pyritic sulfur. Current studies of this method by ASTM Committee D-5, the U. S. Bureau of Mines, Pittsburgh, PA, and the TVA Central Chemical Laboratories, Chattanooga, TN, show good agreement between pyritic iron values determined using an atomic absorption procedure with those determined by the titrimetric methods described for pyritic iron in ASTM D-2492 (6). The method is simple and rapid, and it may soon replace currently specified ASTM standards. Care must be taken to avoid interferences from variable amounts of H<sub>2</sub>SO<sub>4</sub> formed when pyrite is oxidized during extraction of the coal with HNO<sub>3</sub>. Compensation for this matrix change can be made by adjustment of the sample size and addition of H<sub>2</sub>SO<sub>4</sub> to standards, by addition of a flame buffer such as LaCl<sub>3</sub> to samples and standards, or both.

The determination of crystalline pyrite in coal by an X-ray diffraction method has been described by Schehl and Friedel (22). Finely ground coal samples of known pyrite concentration were used as standards in a technique that takes advantage of digital computers for measurement of the diffraction patterns, as well as for the calculation of the percentage of pyrite present in the coal sample. Background corrections due to carbon are made and quantitative results achieved by comparing the integrated intensity of a given pyrite reflection with the integrated intensity of a particular reflection from an internal standard (nickel). Acceptable precision within current ASTM tolerances was obtained for the coals studied, but interferences from reflections due to high concentrations of kaolin in coal were noted.

## CHEMICAL REDUCTION METHOD FOR DETERMINING PYRITIC SULFUR

Methods involving reduction of pyrite to  $H_2S$  have also been employed for the determination of forms of sulfur (23,24,25). A reduction method (24) was recently studied by Kuhn et al. (26). This method uses lithium aluminum hydride to reduce pyritic sulfur to  $H_2S$ , which is then reacted with  $CdSO_4$ . The  $H_2SO_4$  formed from the reaction



is titrated with standard base. Both sulfate and organic sulfur were determined by ASTM D-2492 procedures (6).

Major advantages of this method are that pyritic sulfur can be directly determined without danger of oxidation of the sulfur containing organic constituents, and that it can be determined without prior removal of sulfate sulfur. Further, it is extremely useful as an independent check on the accuracy of values for the forms of sulfur determined by the ASTM oxidation method.

## ACCURACY OF FORMS OF SULFUR METHODS

Questions concerning the accuracy of either oxidation or reduction methods for the determination of forms of sulfur in coal generally stem from the difficulties associated with the incomplete extraction of finely-dispersed pyrite (25,27,28,29). Results of these studies have been at variance. In some cases, fine grinding of coal (-200 mesh) tended to increase the amount of pyrite extracted by  $HNO_3$ , especially in high rank British coals (>85% carbon content). However, for U. S. coals, grinding to the usual -60 mesh particle size has been successful (7,8,9,10). Burns (30) also found fine grinding to be unnecessary for Australian coals when pyritic sulfur was extracted from the coal residue following the sulfate sulfur extraction rather than from a fresh coal sample.

These and other questions regarding the reliability of determinations of forms of sulfur were the subject of a recent investigation (26). For this study, results from the ASTM oxidative method were compared with those of a reductive method (24) to determine whether or not extraction of pyrite is complete, whether or not organic matter is significantly affected by  $HNO_3$  extraction, and whether or not organic sulfur can be obtained either by computation or by Eschka determination of residual sulfur following  $HNO_3$  extraction of pyritic sulfur. The influence of coal particle sizes (-60, -200, and -400 mesh) on the values determined by both methods was also studied.

Results for two coals, which are representative of the nine coals studied in this investigation, are given in Table IV. The principal conclusions are summarized as follows:

- 1) Coal particle size had no significant effect on total sulfur determined by the Eschka method (Table IV, column four).
- 2) X-ray fluorescence values for total sulfur agree well with Eschka values (Table IV, columns four and five).
- 3) Pyritic sulfur values determined by the ASTM method are not significantly influenced by coal particle size (Table IV, column seven).
- 4) For the reduction method, pyritic sulfur values in agreement with those from the ASTM procedure were obtained only when the coal was ground to -400 mesh (Table IV, columns seven and eight).
- 5) Agreement of total iron in the coals, as determined by X-ray fluorescence, with the sum of the iron determined in the ASTM HCl and  $HNO_3$  extracts was excellent (Table IV, columns two and three). This indicates that all of the pyritic iron (sulfur) was extracted by the  $HNO_3$ .
- 6) It was concluded that no pyritic iron remained in the residues of the nine coals studied after they were subjected to either the ASTM oxidation method or the reduction method (on -400 mesh coals only). Therefore, organic sulfur values calculated by subtracting the sum of sulfate sulfur plus pyritic sulfur from total sulfur were deemed accurate (Table IV, columns nine and ten).

TABLE IV. CONCENTRATION OF IRON AND VARIETIES OF SULFUR IN TWO ILLINOIS COALS

Sample and size	Total iron (%)		Total Sulfur (%)				Sulfur (%)				
	X-ray fluorescence		X-ray fluorescence		SO <sub>4</sub> ASTM	Pyritic		Calculated organic		Determined organic	
	ASTM	ASTM	ASTM	ASTM		ASTM	Reduc.	ASTM	LAH	ASTM	Reduc.
<u>C-18067</u>											
-60	4.28	3.80	7.48	7.25	0.02	4.82	4.08	2.64	3.38	2.50	2.24
-200	4.26	4.28	7.53	7.45	0.02	4.76	4.44	2.75	3.07	2.48	2.21
-400	4.30	4.52	7.52	7.63	0.02	4.79	4.60	2.71	2.90	2.54	2.51
<u>C-17167</u>											
-60	1.24	1.23	2.91	3.05	0.40	0.94	0.77	1.57	1.74	1.37	1.45
-200	1.29	1.31	2.95	3.09	0.39	0.92	0.88	1.75	1.68	1.26	1.25
-400	1.30	1.31	2.93	3.07	0.39	0.93	0.93	1.61	1.61	1.19	1.31

## ORGANIC SULFUR

Research on the nature and removal of organic sulfur compounds from coal has been extensive (31,32,33,34,35,36). Unfortunately, none of these investigations has led to useful methods for determining varieties of organic sulfur in coal. Indeed, as previously mentioned, no methods have as yet been developed for the direct determination of total organic sulfur in the presence of inorganic sulfates and sulfides. When organic sulfur has been "determined" rather than calculated by difference, the coal was first demineralized using methods similar to those described in the International Standards Organization Recommended Method R-602 (37), or by Kuhn et al. (26) and Smith and Batts (38). In these, sulfate and pyritic sulfur are first removed by acid dissolution, oxidation and/or reduction reactions. The total sulfur determined in the coal residue is then considered to be organic sulfur. This method was found to be fairly reliable by Kuhn et al. (26), although small losses of organic sulfur were unavoidable (Table IV, columns nine through twelve). The most accurate results for organic sulfur seemed to be those which were calculated.

An interesting new approach to the purported determination of organic sulfur in coal is that of Hurley and White (39). They employed a X-ray fluorescence method to first determine total sulfur from the K $\beta$  line intensity and then a line ratio technique to find the proportion of sulfate sulfur (K $\beta'$  line intensity) in the total sulfur:

$$\%S_{SO_4} = \% \text{ Total } S \times (SK\beta' / SK\beta) \times M_1$$

where  $M_1$  is the slope of a standard straight line calibration curve of the ratio (SK $\beta'$ /SK $\beta$ ) vs. concentration. The peak shift of sulfur K $\beta$  was used to determine amounts of sulfide and organic sulfur:

$$\%S_{org} = \% \text{ Total } S \times \left( \frac{\Delta SK\beta - B}{M_2} \right)$$

$$\%S_{pyr} = \% \text{ Total } S \times \left( 100 - \frac{\Delta SK\beta - B}{M_2} \right)$$

where the calibration constants,  $M_2$  and B are obtained from a straight line calibration curve of the form  $Y = MX + B$ . It should be noted that pyritic sulfur is a calculated difference figure, i.e., the sum of the three forms of sulfur must equal 100%. Therefore, the sulfur values are not independently determined.

## NONPYRITIC SULFIDES

Studies have shown that some coals contain significant quantities of nonpyritic sulfide (1,2), and that it usually occurs in conjunction with high zinc concentrations (up to 5000 ppm). In the reduction method the pyrite (FeS<sub>2</sub>) is first reduced to sulfide (FeS). Any nonpyritic sulfide present in the coal will contribute to the pyritic sulfur value when the chemical reduction of pyrite is carried out prior to

sulfate removal\*. This is true only when the reduction step is done first, as some nonpyritic sulfide is lost in the HCl digestion for sulfate sulfur (ASTM). The ASTM method for pyritic sulfur measures only the pyritic iron. Consequently, a pyritic sulfur value determined by the reduction method that is higher than one determined by the ASTM method would be a measure of the amount of nonpyritic sulfide present in the coal. In such a case, Zn concentration is also a useful measure of nonpyritic sulfide.

The loss of nonpyritic sulfides as hydrogen sulfide in the hydrochloric acid digestion of sulfate sulfur (ASTM) would result in this sulfide's being determined as neither sulfate nor pyritic sulfur. The organic sulfur value, calculated as the difference between the total sulfur and the sulfate + pyritic sulfur values, would then be erroneously high.

#### ANALYSIS OF COAL-RELATED MATERIALS

Coal preparation and float-sink studies frequently require the determination of forms of sulfur in coal gravity fractions. Because these commonly contain 10 to 20% sulfur, care must be taken when applying methods developed for the analysis of whole coal to them. Helfinstine et al. (3,4) determined forms of sulfur in 64 Illinois coals, in their float fractions (five for each coal), and in the material that sank at a specific gravity of 1.60. These data were then used to calculate sulfur in the "raw coal" by proportionally combining the individual float-sink fractions to give values that should be equivalent to values given in the original raw coal analysis. The average difference in percent between analyzed raw coal sulfur values and those calculated from the individual analyses of float-sink fractions are -0.15, -0.05, and -0.11 for total sulfur, pyritic sulfur, and organic sulfur respectively. Although the means (as well as their standard deviations) are small and indicate good agreement, examination of all of the data shows notable exceptions for some high sulfur samples. In one coal, percent differences between analyzed and calculated values for total sulfur, pyritic sulfur, and organic sulfur were -0.56, -0.49, and -0.10, respectively. Careful resampling and analysis has shown that differences of this magnitude are not due to poor sampling or analytical techniques, but rather to small errors in the analysis of high sulfur materials using the ASTM method of determining forms of sulfur. Such errors may be magnified by factors of 10 or 20 in making the calculations.

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\* For the reduction method, it was shown by Kuhn et al. (26) that pyritic sulfur can be determined in the presence of sulfate sulfur.

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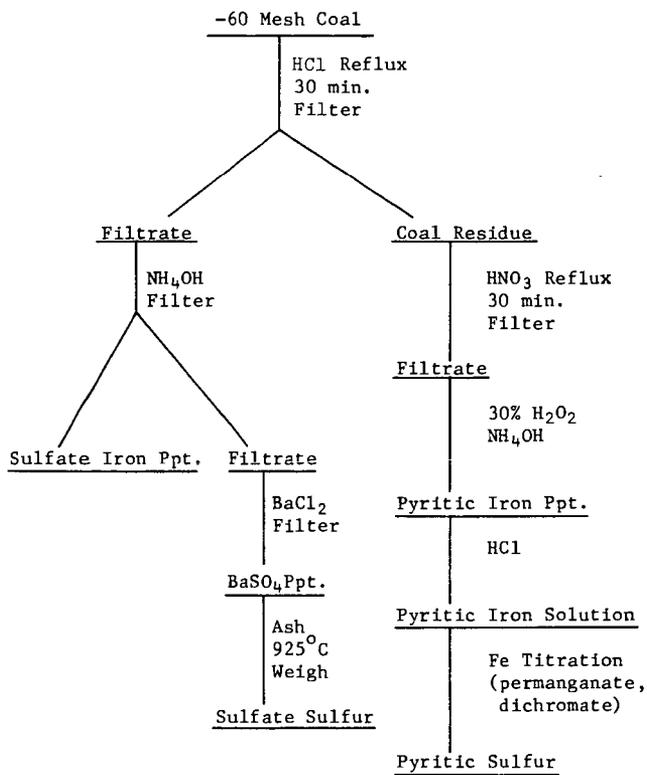


Figure 1. Flow diagram for ASTM determination of forms of sulfur in coal.

## FATE OF ATMOSPHERIC SULFUR AND NITROGEN FROM FOSSIL FUELS

CHARLES HAKKARINEN\*

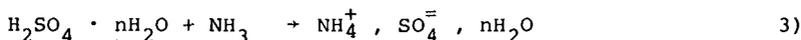
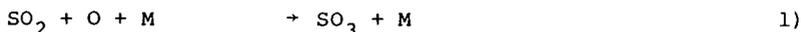
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Sulfur and nitrogen are emitted to the atmosphere during the combustion of coal and other fossil fuels principally as the gases sulfur dioxide ( $\text{SO}_2$ ) and nitric oxide ( $\text{NO}$ ). In uncontrolled systems, approximately 90% of the sulfur in the fuel is converted to  $\text{SO}_2$  and 5% to  $\text{SO}_3$ . The balance is emitted in flyash or collected in the bottom slag. (1) Coal combustion accounts for about 60% of the man-made sulfur oxide emissions (2,3), which represent 1/3 of the total global sulfur emissions to the atmosphere, i.e.  $300 \times 10^6$  tons  $\text{SO}_2/\text{yr}$ . (3) Nitrogen oxide emissions during fossil fuel combustion result from high temperature reaction of atmospheric nitrogen and oxygen, as well as partial combustion of nitrogenous compounds in the fuel. Important factors that affect  $\text{NO}$  production include: Flame and furnace temperature, residence time of combustion gases, rate of cooling, and presence of excess air. (1) Coal combustion accounts for 20% of the man-made  $\text{NO}$  emissions, which represent 1/10 of the  $500 \times 10^6$  tons/yr produced by natural sources. (4)

The atmospheric transport, conversion, and fate of sulfur dioxide and nitric oxide is quite complex. While qualitative descriptions of some conversion and deposition mechanisms are available, quantitative estimates of the importance of each mechanism remain crude.

Sulfur dioxide emitted into the atmosphere is advected and dispersed by the general air flow and smaller scale turbulence. Direct adsorption may occur on vegetation and soil surfaces (5).  $\text{SO}_2$  may also be "washed out" in precipitation (6). However, it is generally believed that most  $\text{SO}_2$  is chemically converted to sulfuric acid or a particulate, sulfate before removal from the atmosphere.

In the presence of sunlight,  $\text{SO}_2$  may be oxidized in a three body reaction by photochemically produced monatomic oxygen. (7) Rapid hydration would follow to form a sulfuric acid mist. The presence of ammonia may buffer the reaction and increase production of sulfates. (8)



Other investigators (9, 10, 11) have recently proposed  $\text{SO}_2$  reaction with either  $\text{OH}$  or  $\text{HO}_2$  as an important homogeneous gas-phase conversion mechanism.



This mechanism has been purportedly demonstrated in laboratory experiments (11), but remains to be verified under actual field conditions. The development of a remote monitoring instrument for OH (9) should provide more information on its relative significance.

Direct photo-oxidation of  $\text{SO}_2$  is considered to be negligible. (12)

Heterogenous reactions on solid or liquid surfaces represent a second important class of  $\text{SO}_2$  oxidation mechanism. The presence of heavy metal ions, such as iron or manganese have been observed to catalyze the conversion of  $\text{SO}_2$  to acid sulfates. (13) Oxidation rates are highly dependent on temperature and relative humidity.

Catalytic oxidation may also occur on dry surfaces. Novakor, et al. (14) have demonstrated catalytic formation of sulfate on carbon soot in the laboratory and have identified several sulfur compounds on the surface of carbon particulates collected in urban atmospheres.

Sulfur compounds emitted during combustion and converted to sulfates are ultimately removed from the atmosphere by dry deposition and precipitation. Although the removal rates are not well quantified, the atmospheric residence time is estimated to range between one and seven days. (3) Long range transport of sulfates may therefore extend to hundreds of kilometers from the  $\text{SO}_2$  source. (15, 16, 17,18)

"Ballpark" estimates of net  $\text{SO}_2$  to sulfate conversion rates for several mechanisms are listed below.

Table 1SO<sub>2</sub> to SO<sub>4</sub> Conversion Rates

<u>Mechanism</u>	<u>SO<sub>2</sub> Consumption Rate</u>
Direct photo-oxidation	0.5 %/hr
Indirect photo-oxidation	1-3 %/hr
Air oxidation in liquid droplets	1-20 %/hr
Catalyzed oxidation in liquid droplets	1-20 %/hr
Catalyzed oxidation on dry surface	1-13 %/hr
Observed SO <sub>2</sub> consumption in a coal- fired power plant plume	
70% relative humidity	0.1 %/min
100% relative humidity	0.5 %/min

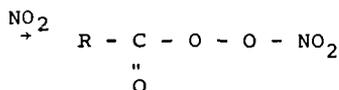
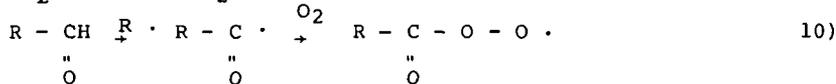
(Table adapted from 19, 20)

Nitrogen compounds are emitted during fossil fuel combustion principally as NO. Oxidation to NO<sub>2</sub> occurs very rapidly, however. Equilibrium values of NO and NO<sub>2</sub> are determined by the following reactions:



The NO/NO+NO<sub>2</sub> ratio is approximately .5 during daylight and .1 at night. (9)

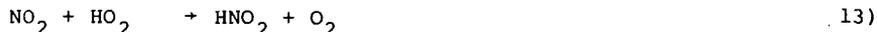
NO may undergo a series of complex chain reactions (typically 100 times slower than the NO + NO<sub>2</sub> reaction) with olefinic hydrocarbons and hydroxyl radicals to form nitrate compounds. A typical sequence might be:



Measurements of nitrate ions in rain (21) suggest that NO<sub>2</sub> is transformed to nitrates in precipitation. However, the direct reaction



has not been shown to be significant in the atmosphere. (4) Two other mechanisms have been suggested recently (9) for nitrous and nitric acid formation during daylight:



Both mechanisms remain to be verified by field measurements of hydroxyls.

Heterogeneous surface catalysis of NO and NH<sub>3</sub> on carbon soot has been proposed by Chang and Novakov (22). In laboratory experiments they have generated volatile ammonium salts at ambient temperatures and reduced nitrogen compounds at elevated temperatures, in qualitative agreement with field observation at urban California sites.

Little information is available on the consumption rate of  $\text{NO}_2$  by the mechanisms described. However, Robinson and Robbins have estimated the residence time of  $\text{NO}_2$  to be three days, based on the total atmospheric nitrogen cycle. (23)

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REVIEW OF DESULFURIZATION AND  
DENITROGENATION IN COAL LIQUEFACTION

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INTRODUCTION

With ever increasing demands on fossil fuels as a source of energy and ever decreasing supplies of crude petroleum within the United States, the nation must turn more and more to the use of coal. Yet the people of this country have mandated through their representatives that they do not want the anticipated use of coal to degrade their environment.

The air pollutants of particular concern are nitrogen oxides, sulfur oxides and particulates. Nitrogen oxides are formed from nitrogen in air as well as organic nitrogen in the fuel, and their concentration is primarily a function of combustion parameters. Sulfur oxides and particulates are a function of the chemical composition of the fuel used.

In response to public demand, the Environmental Protection Agency, EPA, has established air quality standards which define maximum allowable concentrations of pollutants in the atmosphere. Individual states have established emission standards for existing sources which meet the EPA's Air Quality Standards while the EPA has established emission standards for new sources. The current Federal Standards for emissions for new fossil fuel fired steam generators larger than 250 million BTU/hr are presented in Table I.

Because nitrogen oxides are so dependent upon furnace operating parameters such as burner configuration, excess air used, air and fuel distribution, etc., it is difficult to predict the level of nitrogen oxides to be expected from a given fuel. On the other hand, reasonable predictions can be made of the expected  $\text{SO}_2$  emissions from coal since the only source of  $\text{SO}_2$  is the sulfur in the coal. Thus, we would expect that in order to meet the  $\text{SO}_2$  emission standard for solid fuels of 1.2 lbs per million BTU's while burning 10,000 BTU/lb coal, the coal must contain 0.6 wt.% sulfur or less. Unfortunately, the sulfur content of coals ranges from 0.2 to over 10 wt.% while the typical coal contains 0.5 to 4 wt.% sulfur.

Sulfur in coal exists in three distinct forms; (a) as organic sulfur, (b) as pyrite or marcasite (two common crystal forms of  $\text{FeS}_2$ ), and (c) as sulfates. The amount of organic sulfur is normally not over 3 wt.%. The sulfates, mainly calcium and iron, rarely exceed a few hundredths percent except in highly weathered or oxidized samples. Because pyrite and marcasite are difficult to distinguish, these forms of sulfur in the coal are called pyrite. Nitrogen in coal exists in organic form, and is generally in the range of 1.0 to 1.5 wt.%. A hypothesized structure which shows possible forms of organic sulfur and organic nitrogen in coal is shown in Figure 1.

COAL LIQUEFACTION

Process Description

One method that is being seriously considered to reduce sulfur and nitrogen contents of coal to acceptable limits is liquefaction in the presence of hydrogen. A conceptual flow diagram of such a process is shown in Figure 2. Coal mixed with a solvent and hydrogen reacts at elevated temperatures and pressure either in the absence or presence of a catalyst to form a mixture of liquid products. If hydrogen consumption is maintained at low levels, 1.5 - 3 wt.% of the coal fed, most of the product is a high boiling, heavy liquid with a heating value in the order of 16,000 BTU/lb. This

product is solid at room temperature and may be used directly as fuel if its sulfur content is less than 0.96 wt.% or further processed to form either gasoline or chemicals. Higher hydrogen consumption in the liquefaction reactor produces lower boiling products with lower levels of sulfur and nitrogen.

Organic sulfur and nitrogen are removed when coal is liquefied mainly by reactions which form  $H_2S$  and  $NH_3$ . The ammonia can be recovered by conventional purification methods.

Hydrogen sulfide is normally recovered, concentrated, and then converted to sulfur in the Claus process. The effluent gas from the Claus unit must be further processed in a Claus tail gas cleanup unit to reduce sulfur compounds to an environmentally acceptable level. Hydrogen sulfide produced by gasification of coal or of unliquefied coal to produce hydrogen would normally be processed in that same equipment. Organic nitrogen compounds are converted almost completely to molecular nitrogen in high temperature gasification processes such as the Koppers-Totzek or Texaco.

In the liquefaction process, pyritic sulfur is reduced to  $FeS_x$ , where  $x$  is about 1.0.  $FeS_x$  is then removed mechanically by filtration or by solvent precipitation along with heavy liquid-like product and unconverted coal.

#### Desulfurization Results

Published data on the desulfurization of coal as a function of hydrogen consumption from the catalytic H-Coal, Gulf CCL, and Synthoil processes are presented for Illinois, Kentucky, Kaiparowits, Pittsburgh, Big Horn, Wyodak, and Middle Kittanning coals in Figure 3 (1,2,3,4,5). Analyses of these coals are presented in Table II. Published data from non-catalytic (SRC) processes are also presented in Figure 3 for Kentucky, Kaiparowits, and Illinois coals(5,6).

In general, the data plotted in Figure 3 show that as the total amount of hydrogen consumed increases, the sulfur content of the fuel oil product decreases. A band has been used to indicate the trend of all the catalytic data since this data has been taken over widely different combinations of reactor temperatures and pressures, coal space velocities, catalyst types, catalyst ages and activity levels with resulting wide differences in fuel oil yields. Consequently, no alleged superiority for hydrogen selectivity for sulfur removal of one catalytic system over another can be inferred from this particular collection of data.

Interestingly, the data plotted in Figure 3 show that the amount of hydrogen required to reach a moderate sulfur level of about 0.9 wt.% in large scale non-catalytic reactors corresponds reasonably well with the amount of hydrogen required to reach that same level of sulfur in catalytic systems. However, there may be larger differences in hydrogen consumption requirements between large-scale non-catalytic and catalytic processes at fuel oil product sulfur levels below about 0.5 wt.%. It should also be pointed out that the reactor residence times in non-catalytic systems corresponding to a given hydrogen consumption are much higher than the reactor residence times in catalytic systems at the same hydrogen consumption levels.

As hydrogen consumption will have a large effect on the economics of coal liquefaction processes, it would be advantageous if the process consumed hydrogen only in the formation of  $H_2S$  and  $NH_3$ . Material balance calculations show that a hydrogen consumption equivalent to only 0.16 wt.% of the coal is required to convert 2.5 wt.% sulfur in the coal completely to  $H_2S$  and a hydrogen consumption equivalent to only 0.11 wt.% of the coal is required to convert 0.5 wt.% nitrogen in coal completely to  $NH_3$ . However, as shown in Figure 3, the amount of hydrogen required to desulfurize coal to products containing sulfur levels of 0.5 - 1.0 wt.% is equivalent to 1.5 to 6.0 wt.% of the coal. A relatively larger amount of hydrogen is required to produce low sulfur fuel oil products from low sulfur subbituminous coals than from bituminous coals because subbituminous coals contain a much larger concentration of oxygen, 15 - 20 wt.%,

than bituminous coals which contain 7 - 12 wt.% oxygen. However, most of the hydrogen consumption shown in Figure 3 goes to the production of gaseous and liquid hydrocarbons with a hydrogen content of about 6 to 12 wt.% from coal with a hydrogen content of about 5 wt.%. Methane, for example, contains 25 wt.% hydrogen.

Although most of the data obtained from both catalytic and non-catalytic coal liquefaction falls within the band shown in Figure 3, a separate line has been drawn through data obtained from a bench scale non-catalytic flow reactor. The observed difference in the results obtained from the bench scale reactor and other reactors is not entirely due to differences in the coal processed. For example, there is a significant difference in the results obtained on the fraction of organic sulfur removed during the processing of a mixture of Kentucky No. 9 and No. 14 coals in the Wilsonville, Alabama six ton per day SRC plant and in the bench scale reactor, as shown below.

#### DESULFURIZATION RESULTS

	<u>Wilsonville (7)</u>	<u>Bench Scale</u>
Coal Processed	Kentucky No. 9 & No. 14	Kentucky No. 9 & No. 14
T, °F	830	825
P, psig	2400	2500
Space Time, hrs.	0.7	0.7
Fraction of organic sulfur removed, x	0.62	0.82

In order to explain the large observed differences in the fraction of organic sulfur removed in the two different reactor systems, the effect of mixing in the reactor was evaluated. Flow considerations indicated that the Wilsonville reactor may have acted essentially as a backmix reactor while the bench scale reactor may have acted essentially as a perfect plug flow reactor. However, neither a first order nor a second order kinetic rate plot fit the bench scale data.

In similar work, Lessley (8) suggested that the first order cracking rate coefficient in a non-catalytic system is a function of conversion. Applying a simplified form of the Lessley equation to the desulfurization bench scale data, a first order rate coefficient was assumed to have the following dependence on the fraction of organic sulfur removed, x;

$$k = k_0 e^{-ax}$$

where  $k_0$  is an initial rate coefficient  
and  $a$  is a constant

Assuming a first order reaction mechanism, values of " $k_0$ " and " $a$ " were obtained which would fit the experimental bench scale data. These results were then used to predict that if the reaction in the bench scale reactor had been carried out in a perfectly backmixed reactor, the fraction of organic sulfur removed under the reaction conditions specified in the preceding table would have been 0.58 rather than 0.62 actually observed. The fact that the Wilsonville reactor only approaches perfect backmixing was confirmed by the existence of a small temperature gradient in the reactor. The results of this analysis, based on limited data, suggest that the flow pattern of the fluid in the reactor may be an important variable.

After pyrite removal, overall reductions of up to 90% of the total sulfur in the original coal are possible. The sulfur levels of the various product fractions generally increase with boiling range. This is shown in Figure 4 for non-catalytic operation and Figure 5 for catalytic operations. Most of the sulfur is contained in the non-distillable ash free residual fraction to which an arbitrary mid-boiling point of 1100 or 1200°F has been assigned depending on the source of the data. These high boiling fractions may contain up to 1.2 wt.% sulfur when obtained from high sulfur bituminous coals.

Slurry oils produced during the non-catalytic liquefaction of high sulfur bituminous coals and boiling in the range of 450° to 600°F normally contain 0.2 - 0.4 wt.% sulfur. The sulfur content in the slurry oil produced from low sulfur subbituminous coals is normally less than 0.05 wt.%. An interesting, but unexplained anomaly, is indicated for narrow product fractions with a mid-boiling point between 350° and 450°F. These materials have sulfur contents higher than both lighter products and higher boiling products.

#### Denitrogenation Results

The amount of hydrogen required to obtain fuel oil products with a specific nitrogen content is indicated in Figure 6. There is a differentiation indicated on this figure between catalytic and non-catalytic processing results with higher nitrogen removal obtained catalytically. However, more hydrogen is required to obtain these lower product nitrogen levels. Even in the case of catalytic systems, the nitrogen content of the fuel oil fraction is seldom less than one half the nitrogen content of the feed coal. If higher levels of denitrogenation are required, additional hydrogen processing of the primary products using nitrogen specific catalysts will be necessary.

Figures 7 and 8 show nitrogen content as a function of the average boiling points of product fractions. These results show that there is a steady increase in nitrogen content as average boiling point increases. Surprisingly little difference is evident between the nitrogen contents of particular product fractions from catalytic and non-catalytic systems. However, as the yield of low boiling liquids is much larger from catalytic systems than from non-catalytic systems, the total nitrogen in all products from the catalytic systems is lower than the total nitrogen in all products from the non-catalytic systems.

#### CONCLUSIONS

Coal liquefaction can provide a low sulfur, environmentally acceptable fuel from high sulfur, environmentally unacceptable coal. However, current coal liquefaction processes require substantial amounts of hydrogen.

There is little difference in the amount of hydrogen consumed to reach a moderate sulfur level of about 0.9 wt.% in the fuel oil products from catalytic processes and in the fuel oil products from large scale SRC processes. There are indications that the hydrogen consumption requirements for desulfurization are significantly affected by the extent of mixing within the reactor.

A significantly larger amount of nitrogen is removed from coal processed in catalytic systems than from coal processed in non-catalytic systems. At the same time, the hydrogen consumptions and yields of low boiling liquids from catalytic systems are substantially larger than the hydrogen consumptions and yields of low boiling liquids from non-catalytic systems.

Finally, analyses of liquefied coal products indicates that the highest nitrogen and sulfur levels are contained in the highest boiling product fractions.

TABLE INEW STATIONARY SOURCE EMISSION STANDARDSFor Fossil Fuel Fired Steam Generators larger than  $250 \times 10^6$  Btu/Hr.

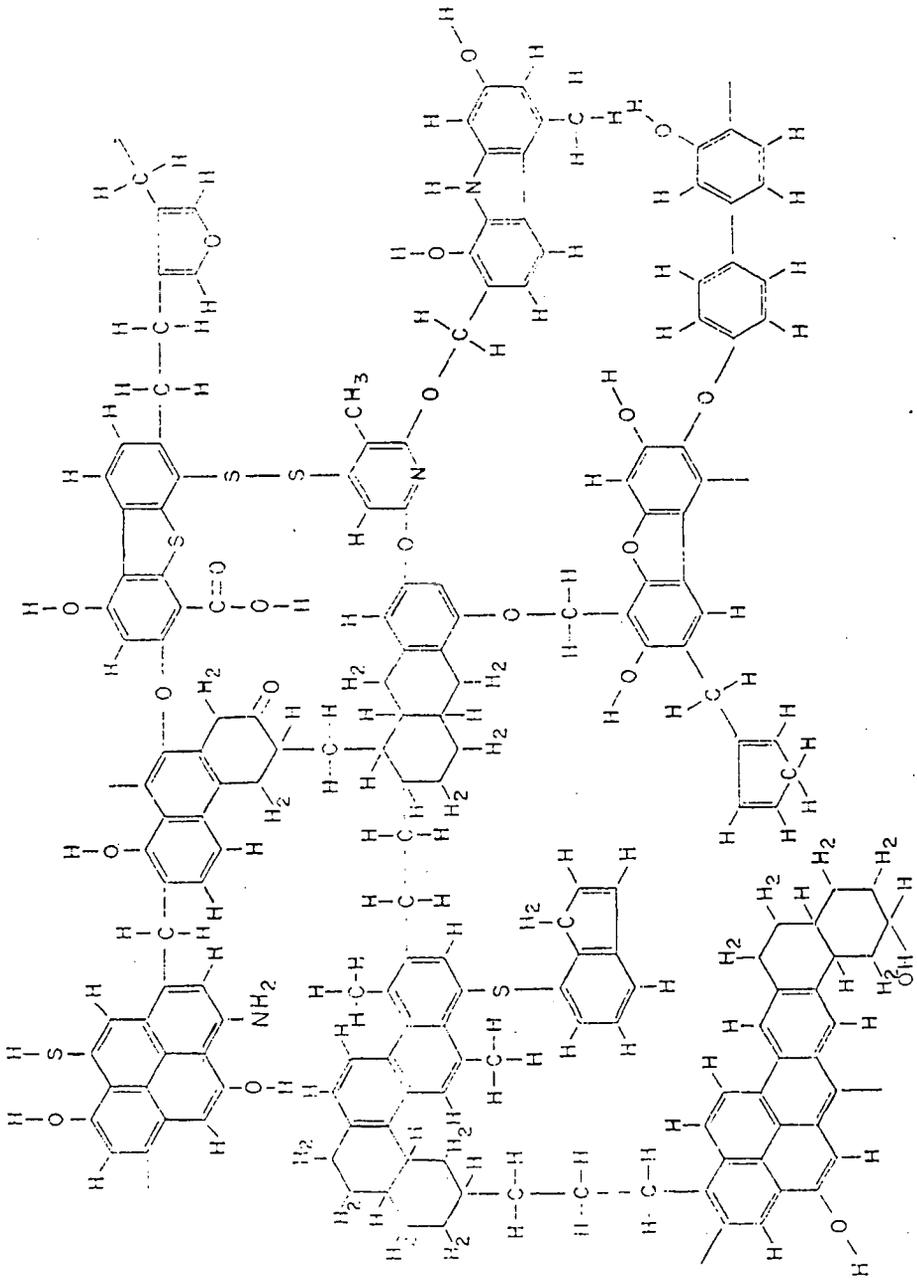
<u>Species</u>	<u>Standard</u>
Particulates	a) $0.1 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. b) 20% opacity. 40% opacity not more than 2 min/hr. c) Excludes $\text{H}_2\text{O}$
$\text{SO}_2$	a) Liquid Fuel: $0.8 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. b) Solid Fuel: $1.2 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave.
$\text{NO}_x$	a) Gas Fuel: $0.2 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. b) Liquid: $0.3 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. c) Solid: $0.7 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave.

TABLE 2

## COAL PROPERTIES

	-----Bituminous-----						-----Subbituminous-----		
	Kentucky #4	Illinois #9,11, 12,13	Pittsburgh #6	Pittsburgh #8	Middle #8	Middle Kittaning	Kaiparowits	Big Horn	Wyodak
<u>Proximate Analysis</u>									
<u>Wt. %</u>									
Ash	8.5	17.2	11.6	8.3	8.3	9.7	6.3	4.4	7.3
Volatile Mater	39.2	37.8	42.0	34.1	42.8	40.3	43.9	42.5	46.4
Fixed Carbon	52.3	45.0	46.4	57.6	48.9	50.0	49.8	53.1	46.3
<u>Ultimate Analysis</u>									
<u>Wt. %</u>									
Hydrogen	5.1	4.8	4.8	5.1	5.1	5.3	5.1	4.6	4.8
Carbon	73.0	60.7	70.2	76.8	73.9	72.8	72.5	69.4	66.0
Nitrogen	1.3	1.2	1.4	1.6	1.2	1.3	1.0	1.2	1.1
Oxygen	9.0	11.3	9.3	6.7	7.5	7.5	14.7	19.9	20.4
Sulfur	3.1	5.5	3.2	1.5	4.0	3.1	0.4	0.5	0.4
Ash	8.5	16.5	11.1	8.3	8.3	10.0	6.3	4.4	7.3
<u>Forms of Sulfur</u>									
<u>Wt. %</u>									
Sulfate	0.26	0.47		[.66	0.00	0.01	0.02		[.14
Pyritic	1.42	3.08			2.1	1.32	0.00		
Organic	1.35	1.95		.83	1.9	1.77	0.38		.40

Figure 1 A REPRESENTATION OF BITUMINOUS COAL STRUCTURE



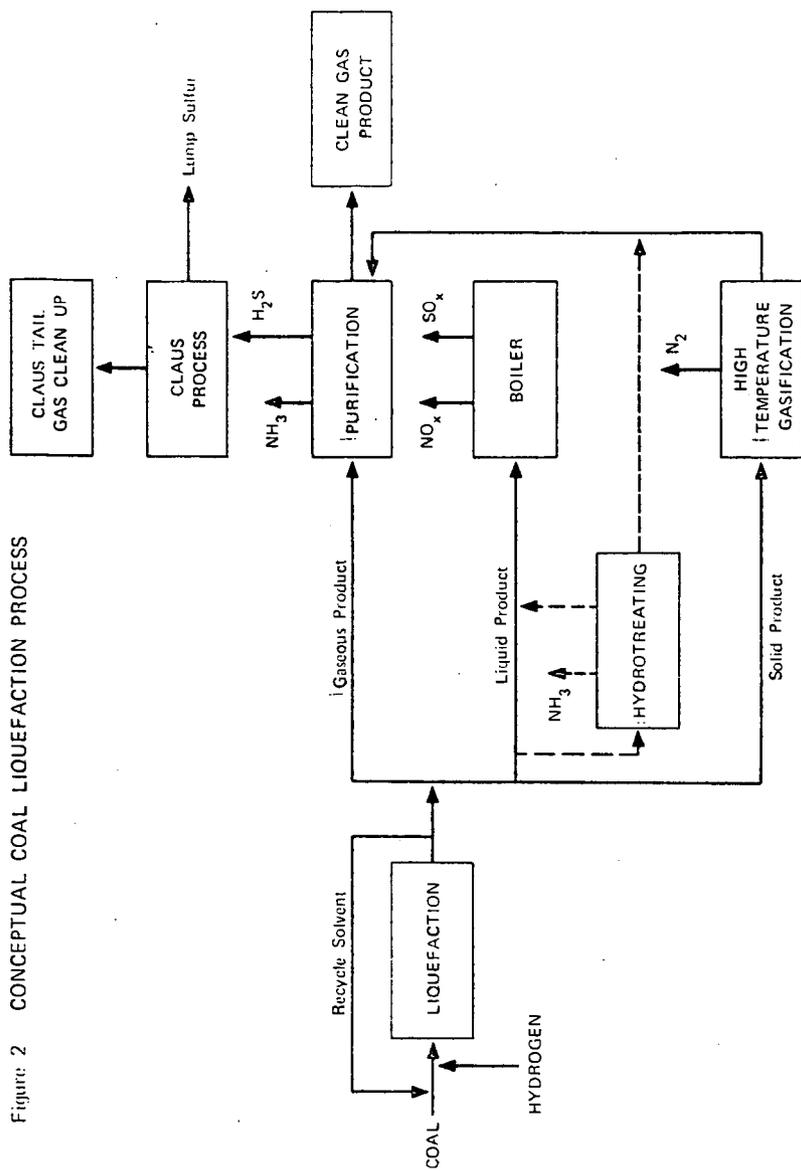


Figure 3 HYDROGEN REQUIRED TO PRODUCE LOW SULFUR FUEL OIL

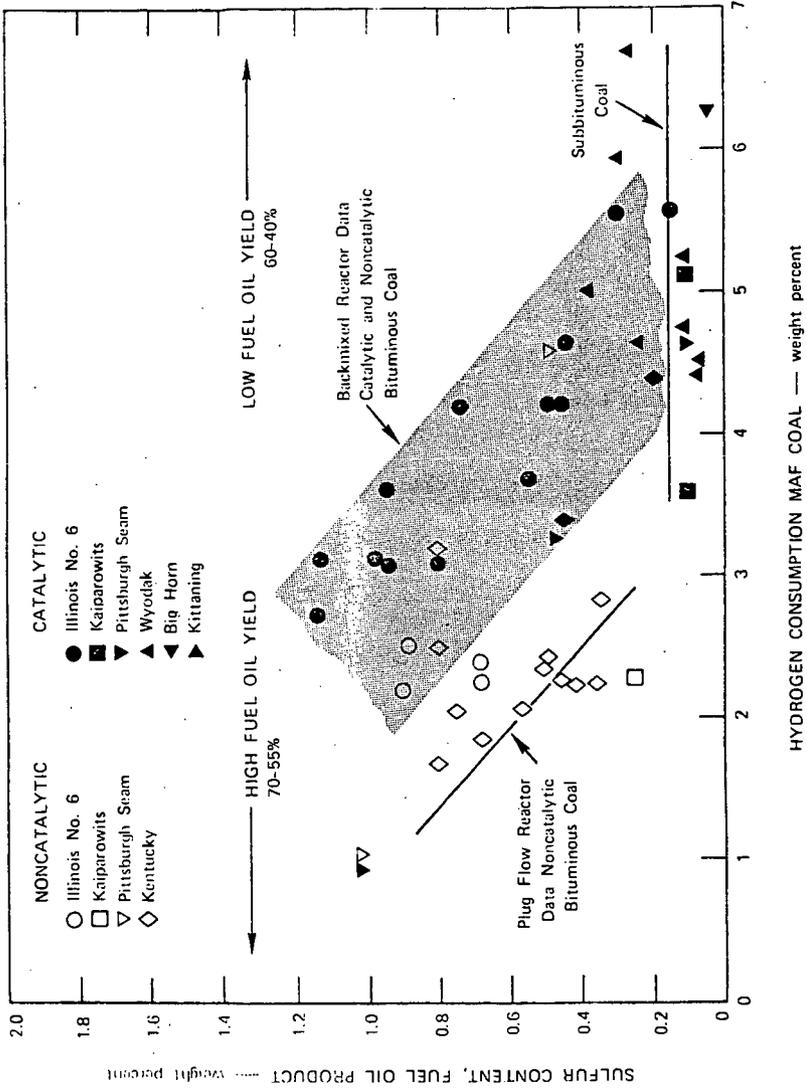


Figure 4 SULFUR CONTENT OF COAL LIQUIDS FROM NONCATALYTIC OPERATIONS

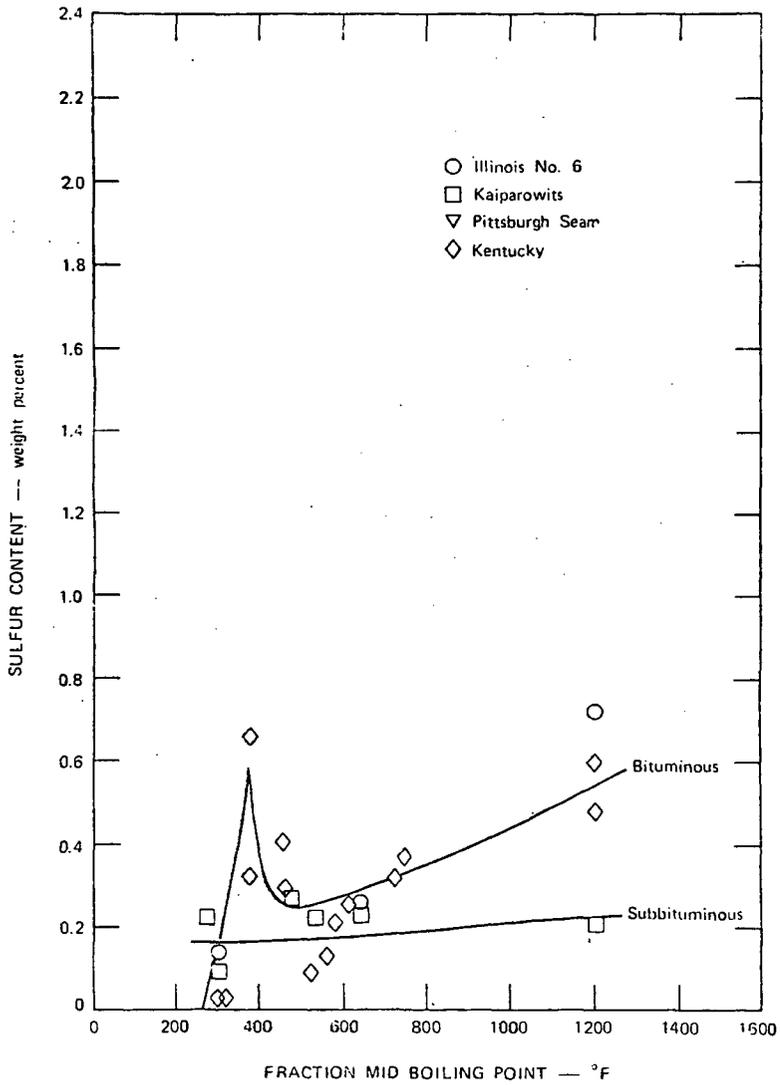
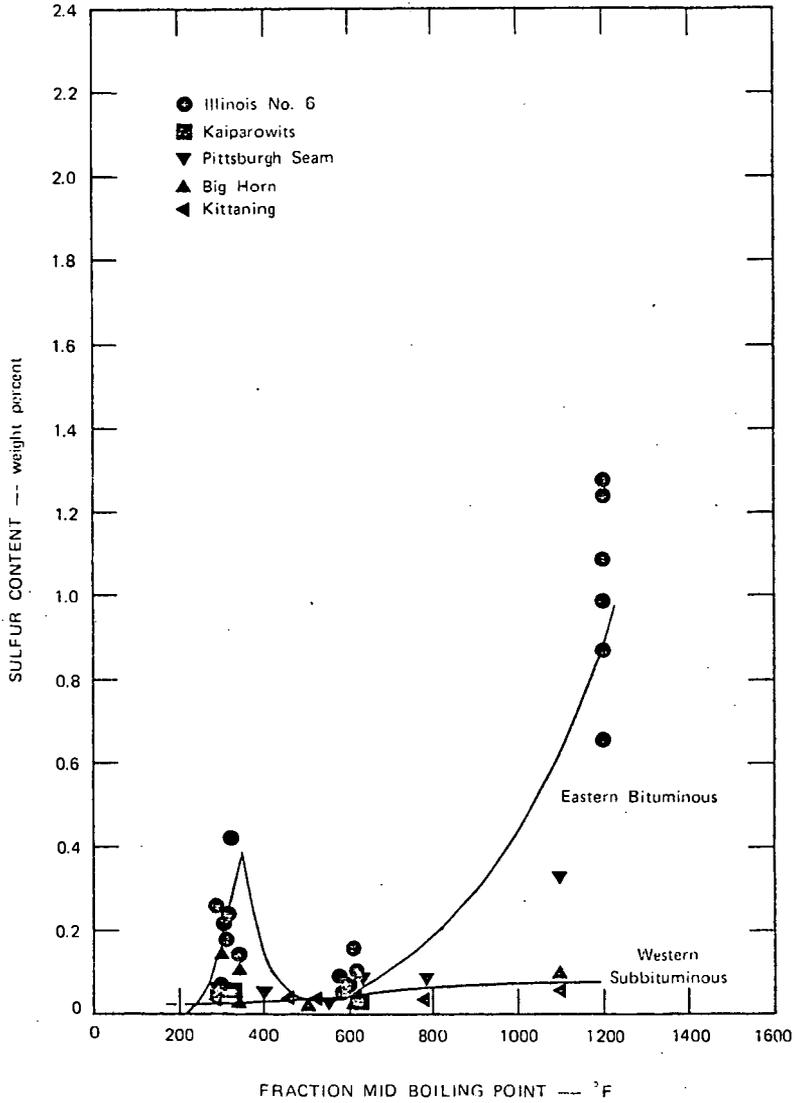


Figure 5 SULFUR CONTENT OF COAL LIQUIDS FROM CATALYTIC OPERATIONS



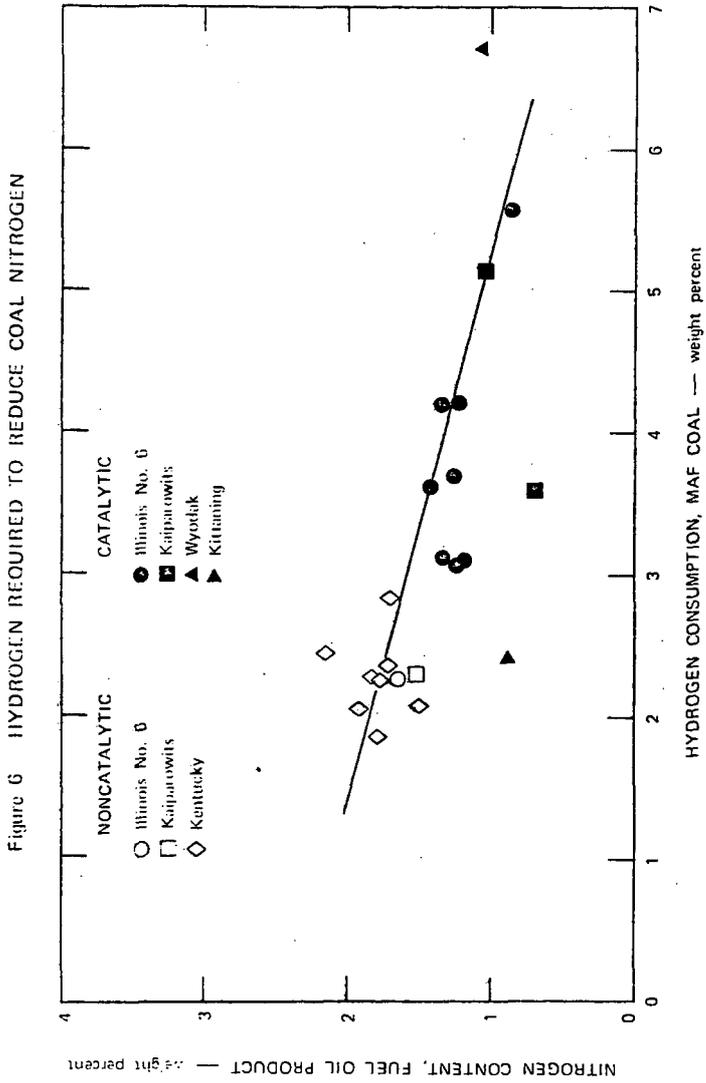


Figure 7 NITROGEN CONTENT OF COAL LIQUIDS FROM NONCATALYTIC OPERATIONS

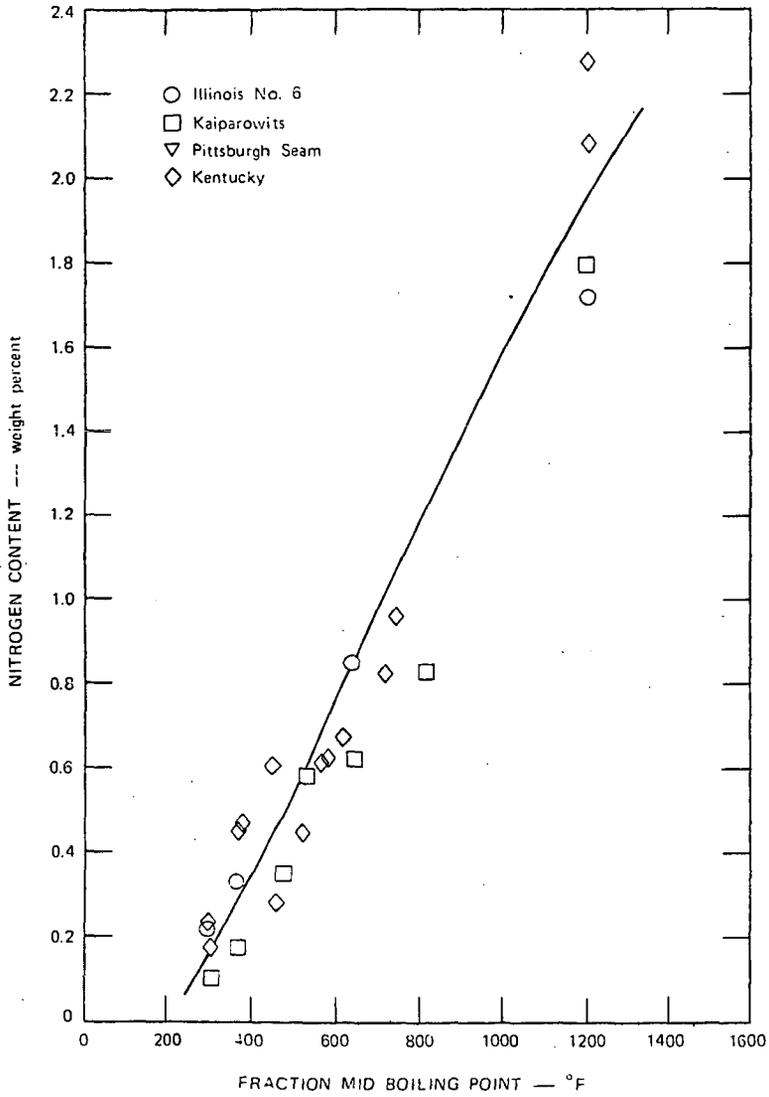
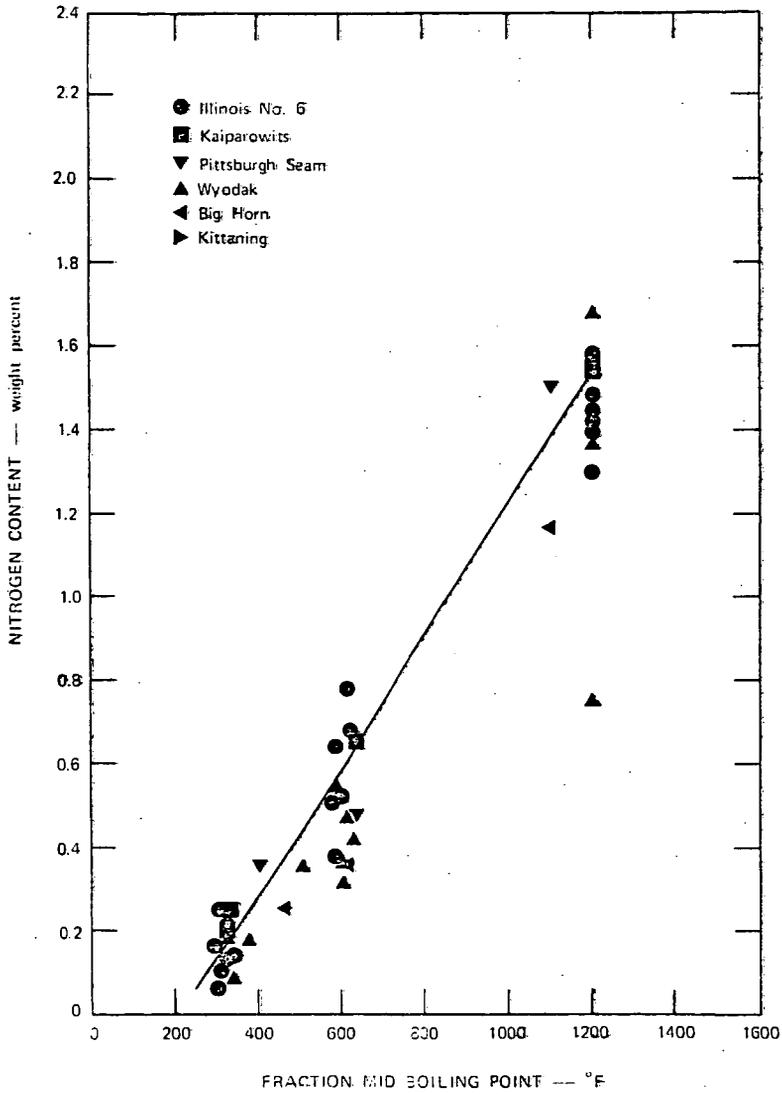


Figure 8 NITROGEN CONTENT OF COAL LIQUIDS FROM CATALYTIC OPERATIONS



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CHARACTERIZATION OF NITROGEN COMPOUNDS IN TAR  
PRODUCED FROM UNDERGROUND COAL GASIFICATION

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## INTRODUCTION

In the fall of 1972, the Laramie Energy Research Center of the Bureau of Mines (now the Energy Research and Development Administration) initiated an in situ coal gasification experiment in Hanna, Wyoming. The objective was to ascertain if a low-Btu gas which would be competitive with other energy sources could be produced using present technology. If such a process were feasible it could provide an alternative to the hazards, costly transportation, and environmental objections of current coal mining technology.

The idea of underground coal gasification is over a hundred years old and has been tried in several different countries, with the largest experiments in the USSR, Great Britain and the U. S. These experiments showed that gasification was possible and a combustible fuel could be produced, yet the British and U. S. trials were determined to be economically impractical at the time they were conducted. Although information is sketchy, the USSR is presently generating electricity from low-Btu gas generated via in situ gasification. It is claimed that this power is generated at costs competitive with coal fired power plants.

## DESCRIPTION OF THE UNDERGROUND GASIFICATION EXPERIMENT

The Hanna, Wyoming, experiment (I-3) was conducted in a subbituminous coal seam thirty feet thick at a depth of four hundred feet. A pattern of sixteen wells was drilled into the seam to take advantage of the natural fractures and permeability of the coal. In March 1973 the coal was ignited and air was supplied as the gasification agent. After initial start-up a steady-state system was obtained which lasted from September 1973 through February 1974. During this six-month period, gas analyses were taken along with other operating data. A low-Btu gas averaging approximately 130 Btu/scf was produced and the production was controlled to some degree by varying pressure and flow rates of the air injected and the gases produced.

In conjunction with low-Btu gas production, a liquid product was condensed from the gas stream. The major part was water but approximately 10% was an organic layer or coal tar. This coal tar has been estimated to contain 5% of the total energy produced from the in situ system. This coal tar raised three questions. What was its value as a petroleum substitute, either as a fuel or as a petrochemical feedstock? What information could be derived from this coal tar concerning reaction conditions occurring in the coal seam? Did the coal tar contain compounds which may lead to environmental damage? Characterization of these coal tars was therefore undertaken in an attempt to answer these questions.

During the period of gas production coal tar samples were collected from the produced gas stream. The liquid condensate, composed of coal tars and water, was separated in an air cooled condenser and a portion was drawn off as a sample. Two of these samples which represented distinctly different operating conditions during the life of the in situ coal gasification experiment were chosen for characterization.

The dry gas production rate over an eight-month period is shown in Figure 1 with the collection dates for samples 1 and 2 shown. As can be seen, Sample 1 was taken during a period of low gas production, which is associated with carbonization rather than gasification. Sample 2 was taken during a period of high gas production when the contribution of gasification was greater. A further indication of the relative contributions of carbonization and gasification can be seen from the gas analyses shown in Table 1 for the dates of coal tar sample collection. The carbonization of coal produces a large amount of methane compared to the amount of carbon monoxide. Upon reaching the conditions required for gasification, the carbon monoxide produced will increase due to the reactions shown by Equations 1 and 2.



TABLE 1. - Gas Analyses on Collection Dates

	Sample 1 August 4, 1973	Sample 2 December 10, 1973
Hydrogen	9.5 <sup>a</sup>	16.14
Argon	1.17	1.01
Nitrogen	55.62	53.84
Methane	9.62	3.74
Carbon Monoxide	0.80	6.94
Ethane	0.81	0.28
Carbon Dioxide	21.90	17.91
Propane	0.16	0.08
Propene	0.12	0
n-Butane	0.01	0
iso-Butane	0.05	0
Hydrogen Sulfide	0.23	0.05
Heating Value	154 Btu/scf	119 Btu/scf

<sup>a</sup>Values are expressed in mole %

The high ratio of methane to carbon monoxide in the product gas on the collection date for Sample 1 indicates that carbonization is the primary reaction mode. Conversely, the low ratio of methane to carbon monoxide on the collection date for Sample 2 indicates that gasification was occurring to a greater degree.

#### Experimental

Nonaqueous titration of nitrogen was performed in acetic anhydride and benzene with  $HClO_4$  as described by Buell (4). GLC analyses of tar bases were done on a 15' x .18" 15% TRITON X-305 on a Gaschrom P column. With a helium carrier gas, a flow rate of 46 ml/min STP, isothermally at 100°C for 16 min, then a 2°C/min

increase to 220°C, a useable separation of components resulted. NMR spectra were recorded on a Varian HA-100 instrument with the use of a Varian C1024 (CAT) console for one specific sample. UV spectra were recorded on a Beckman DB-G spectrometer with cyclohexane as solvent. Mass spectra were obtained on an AEI MS-12 instrument. Simulated distillations were performed with use of gas chromatography with residue defined as any material that does not boil below 1000°F. Fractionalization into tar acid, tar base and neutral fractions was accomplished by mineral acid and sodium hydroxide extraction and then regeneration through pH adjustment.

Coulometric nitrogen determination was performed on a Dohrmann instrument by reductive pyrolysis and subsequent ammonia titration in a microcoulometer. Coulometric sulfur determination was obtained using a Dohrmann instrument by oxidative pyrolysis to sulfur dioxide and titration of the sulfur dioxide in a microcoulometer.

### COAL TAR CHARACTERIZATION

Each sample was subjected to analyses by simulated distillation, nonaqueous titration, and elemental analysis, plus determination of some physical properties. Upon separation of both samples into tar base, tar acid and neutral fractions, each fraction was then subjected to nonaqueous titration and coulometric determination of nitrogen and sulfur. The tar base fractions from both samples were separated by GLC where compound types have been assigned to separated components with specific structures identified in some cases.

#### Simulated Distillations

Simulated distillations showed Sample 1 to have a boiling range of 100-600°F with no residue. Sample 2 had a boiling range of 100-950°F with no residue. The percentage of the coal tar within a specified boiling range is shown in Table 2. As Table 2 shows, over 50% of sample 2 has a boiling distribution between 500°F and 700°F, while sample 1 has almost 50% of the boiling range distribution between 400°F and 500°F. This shows that sample 1 was a lighter coal tar than sample 2 and that the average molecular weight of sample 1 was less than sample 2.

TABLE 2. - Boiling Range Distribution

Sample	100 - 400°F	400 - 500°F	500 - 600°F	600 - 700°F	700 - 800°F	800 - 900°F	900 - 1000°F	Residue
1	30.0%	46.7%	22.0%	1.3%	0%	0%	0%	0%
2	6.2	16.9	25.6	28.2	16.0	5.3	1.8	0
Carbonized	0	11.3	16.3	13.1	15.2	12.4	7.5	24.2

For comparison, the boiling range distribution for the coal tar produced by laboratory carbonization of a Hanna coal sample at 500°C is presented. In comparing the distribution of material depicted in Table 2 the relative amount of residue becomes evident. Samples 1 and 2 show no residue while nearly a fourth of the carbonized sample is residue or material boiling above 1000°F. This demonstrates a unique fact concerning these coal tars. While the underground gasification may be similar to aboveground gasification, the coal tars produced in underground gasification are carried to the surface as a steam distillate. Since very little heavy tar will reach the surface, under these conditions, very little if any residue is expected, and the coal tar will not be entirely representative of the total tar generated in the combustion zone.

Nonaqueous Titrations

Nonaqueous titrations of samples 1 and 2 are shown in Table 3.

TABLE 3. - Nonaqueous Titrations of Samples 1 and 2

Sample 1	0.665% WB <sup>a</sup>	0.129% VWB <sup>a</sup>
Sample 2	0.524% WB	0.186% VWB

<sup>a</sup>WB and VWB refer to weak and very weak base

Strong, weak, and very weak bases are defined by their half neutralization potentials (HNP), with strong bases having an HNP less than 150 mV, weak bases between 150 and 350 mV, and very weak base greater than 350 mV. Examples of weak bases would be pyridines or quinolines while amides would be titrated as very weak bases. Primary and secondary anilines titrate as very weak bases since they will acetylate and then titrate as amides. It should be understood that not all nitrogen compounds will titrate. Conversely not only nitrogen containing compounds will titrate, as an example, some sulfoxides titrate as very weak bases.

Physical Properties

Some of the physical properties of samples 1 and 2 are shown in Table 4. As expected from the conclusions of the simulated distillations, sample 2 is a heavier sample. The higher specific gravity, viscosity and heat of combustion all indicate that Sample 2 does indeed represent a higher average molecular weight coal tar.

TABLE 4. - Physical Properties

	Sample 1	Sample 2
Specific gravity at 60°F	0.962	0.977
Viscosity at 100°F	3.55 centistokes	13.16 centistokes
Heat of Combustion	16,073 Btu/lb	17,256 Btu/lb

Elemental Analyses

The elemental analyses of samples 1 and 2 indicate a marked difference in oxygen content as shown in Table 5.

TABLE 5. - Elemental Analyses

	Sample 1	Sample 2
Carbon	77.80	86.33
Hydrogen	10.22	10.43
Nitrogen	0.74	0.79
Sulfur	0.23	0.18
Oxygen	11.04 <sup>a</sup>	2.27 <sup>a</sup>

<sup>a</sup>Oxygen percentage is determined by difference

This change in oxygen content is attributed to the relative amounts of tar acids in each sample. This is shown in Table 6, where the composition of samples 1 and 2 vary noticeably with respect to the relative amounts of tar acids. Preliminary mass spectral analysis of the tar acid fraction from Sample 1 showed the majority of the fraction to be substituted phenols which would help explain the higher oxygen content in sample 1 compared to sample 2.

TABLE 6. - Composition of Coal Tar, by Weight Percent

	Sample 1 <sup>a</sup>	Sample 2 <sup>b</sup>
Tar Base	4.0	8.7
Tar Acid	42.1	14.5
Neutral	53.9	76.8

<sup>a</sup>90.9% recovery of sample 1

<sup>b</sup>96.4% recovery of sample 2

The difference in tar acid content between the two samples is proposed to be due to some basic change in the conditions producing the two samples. At the time Sample 1 was produced, the air injection rate into the combustion zone was considerably less than at the time Sample 2 was formed. Higher air injection rates are associated with higher coal utilization, higher gas production rate, and higher exit temperature of the produced gas. This would suggest that the coal tars collected in Sample 2 either were being formed at higher temperatures or were passing through a higher temperature flame front (combustion zone). Fieldner and Davis (5) have reported a change in composition of coal tar with increasing carbonization temperature. They stated that increasing temperature causes a decrease in tar acid content which agrees with the comparison of Samples 1 and 2 (Table 6). With the increase in boiling range and other parameters measured during the experiment, this evidence indicates that Sample 2 was indeed produced at a higher temperature than Sample 1.

Total Nitrogen, Total Sulfur and Nonaqueous Titration  
of Base, Acid and Neutral Fractions

The results of coulometric determination of nitrogen and sulfur plus the nonaqueous titrations of the tar base, tar acid and neutral fractions of samples 1 and 2 are shown in Table 7.

TABLE 7. - Total Nitrogen, Total Sulfur, and Titratable Nitrogen for Acid, Base and Neutral Fractions

	Total Sulfur	Total Nitrogen	Titratable Nitrogen <sup>a</sup>
Sample 1			
Tar Base	0.00%	9.64%	8.10% WB, 1.36% VWB
Tar Acid	0.33	0.35	0.264% WB, 0.081% VWB
Neutral	0.02	0.08	0.035% VWB
Sample 2			
Tar Base	0.23	4.82	4.45% WB, 0.36% VWB
Tar Acid	0.14	0.09	0.058% VWB
Neutral	0.20	0.37	0.037% WB, 0.145% VWB

<sup>a</sup>WB and VWB refer to weak and very weak base

As can be seen from Table 7, the distribution of sulfur in the separate fractions seems to be random and therefore no conclusions have been drawn as to their compound types or explain their distribution. An interesting point about the nitrogen values is the fact that while sample 2 contains approximately twice the weight percent tar base that sample 1 contains, the total nitrogen of sample 2's tar base fraction is about half that of sample 1's tar base fraction. This would suggest that the tar bases in sample 2 have a higher average molecular weight than those of sample 1.

The nonaqueous titrations of the two different tar base fractions indicate the possibility of pyridines and quinolines as weak bases with the added possibility of anilines titrated as very weak base.

#### Identification of Selected Components in the Tar Base Fraction

Twelve different components were fractionated by GLC from Sample 1 and spectral data were obtained on each. These twelve peaks constituted 69% of the base fraction of Sample 1. Compound types have been assigned to all separated components and specific structures in some cases. Assignments were accomplished with the combined aid of NMR, MS, UV and GLC data. The results are tabulated in Table 8.

TABLE 8. - Tabulated Spectra on Separated Components From Tar Base Fraction of Sample 1

Component	$t_R^a$	% Total of Base Fraction	NMR Predominant Peaks	UV	MS	Compound Type or Compound
1	8.9	1.18%	Triplet- $\delta$ 7.10; Triplet- $\delta$ 7.50; Doublet- $\delta$ 8.45	$\lambda_{max}$ at 262 nm	100% m/e 79	pyridine
2	11.0	6.40	Singlet- $\delta$ 2.41; Quartet- $\delta$ 6.95; Triplet- $\delta$ 7.36; Doublet- $\delta$ 8.33	$\lambda_{max}$ at 257 nm	100% m/e 93	2-picoline
3	13.1	6.20	Singlet- $\delta$ 2.37; Doublet- $\delta$ 6.74; Triplet- $\delta$ 7.24	$\lambda_{max}$ at 260 nm	100% m/e 107	2,6-lutidine
4	14.9	9.61	Triplet- $\delta$ 1.24; Singlet- $\delta$ 2.24; Quartet- $\delta$ 2.72; Multiplet- $\delta$ 6.98; Multiplet- $\delta$ 7.35; Singlet- $\delta$ 8.30	$\lambda_{max}$ at 255 nm	90% m/e 93 10% m/e 107	3-picoline, 4-picoline and 2-ethyl pyridine
5	17.3	12.90	Triplet- $\delta$ 1.21; Singlet- $\delta$ 2.17; Singlet- $\delta$ 2.36; Quartet- $\delta$ 2.65; Multiplet- $\delta$ 6.77; Multiplet- $\delta$ 7.22; Doublet- $\delta$ 8.17	$\lambda_{max}$ at 258 nm	90% m/e 107 8% m/e 121	2,4-lutidine, 2,5-lutidine plus some methyl ethyl pyridine
6	18.3	3.22	Singlet- $\delta$ 2.18; Singlet- $\delta$ 2.36; Multiplet- $\delta$ 6.81; Doublet- $\delta$ 7.19; Singlet- $\delta$ 8.15	$\lambda_{max}$ at 263 nm	90% m/e 107	2,3-lutidine

TABLE 8. - Tabulated Spectra on Separated Components From Tar Base Fraction of Sample 1 (Continued)

Component	t <sub>R</sub> <sup>a</sup>	% Total of Base Fraction	NMR Predominant Peaks	UV	MS	Compound Type or Compound
7	19.2	7.11	Triplet- $\delta$ 1.21; Singlet- $\delta$ 2.14; Singlet- $\delta$ 2.32; Quartet- $\delta$ 2.59; Singlet- $\delta$ 6.58; Doublet- $\delta$ 7.34	$\lambda_{\max}$ at 262 nm	15% m/e 107 79% m/e 121	trimethyl pyridine and an ethyl pyridine
8	31.1	5.98	Broad Singlet- $\delta$ 3.36; Quartet- $\delta$ 6.52, Triplet- $\delta$ 6.96	$\lambda_{\max}$ at 283 nm $\lambda_{\max}$ at 231 nm	93% m/e 93	aniline
9	34.7	4.88	Singlet- $\delta$ 2.15; Broad Singlet- $\delta$ 3.28; Multiplet- $\delta$ 6.32; Triplet- $\delta$ 6.84	$\lambda_{\max}$ at 285 nm $\lambda_{\max}$ at 235 nm	97% m/e 107	2-methylaniline
10	38.1	2.54	Triplet- $\delta$ 1.15; Singlet- $\delta$ 2.10; Quartet- $\delta$ 2.45; Broad Singlet- $\delta$ 3.32; Multiplet- $\delta$ 6.25; Triplet- $\delta$ 6.86	$\lambda_{\max}$ at 286 nm $\lambda_{\max}$ at 235 nm	92% m/e 121	a dimethyl aniline and an ethylaniline
11	39.1	4.08	Doublet- $\delta$ 1.15; Singlet- $\delta$ 2.05; Multiplet- $\delta$ 6.10 to $\delta$ 8.10; Singlet- $\delta$ 8.80	$\lambda_{\max}$ at 313 nm $\lambda_{\max}$ at 270 nm	63% m/e 129; 16% m/e 121; 9% m/e 135; 8% m/e 94	quinoline, a dimethyl aniline and a trimethyl aniline
12	40.5	5.02	Triplet- $\delta$ 1.12; Quartet- $\delta$ 2.40; Singlet- $\delta$ 2.62; Doublet- $\delta$ 2.75; Multiplet- $\delta$ 7.04 to $\delta$ 8.00; Singlet- $\delta$ 8.78	$\lambda_{\max}$ at 315 nm; $\lambda_{\max}$ at 265 nm	45% m/e 143; 22% m/e 135; 17% m/e 129; 12% m/e 157	a methyl quinoline, a C <sub>3</sub> aniline; quinoline, a dimethylquinoline

<sup>a</sup>GLC retention times are relative to air

As can be seen from the data presented, all the components separated were not pure compounds, but a compound type can be determined from the spectrographic data. The resolution of the GLC tended to drop off as the heavier components were eluted. Due to the more complex nature of their spectra and the greater number of possible structures, specific structures have not been assigned to some of these heavier components.

46.6% of the base fraction was substituted pyridines, 13.4% anilines, and 9.1% quinolines. The majority of the remainder is probably substituted pyridines since

they are eluted after component #7 and before #8 which is aniline. Comparing this analysis with the work of Karr, et.al. (5), who found the majority of the tar base fraction of a low temperature coal tar to be quinolines, indicates that this coal tar was produced under conditions other than those producing low temperature coals.

The base fraction from Sample 2 was also subjected to identical GLC analysis as the base fraction from Sample 1. This sample also showed a wide distribution of components except that the majority of the fraction was much heavier than that from Sample 1. The GLC trace indicated six resolved peaks with retention times from 39.5 to 46.6 constituting approximately 45% of the base fraction. Comparing these retention times with those in Sample 1 suggests that these components are alkylated anilines or quinolines.

NMR spectra of five of these six peaks indicate these components to be substituted quinolines. As yet, no specific structures have been assigned to any of the peaks. This would agree with Karr's work and would suggest that the coal tars are formed under low temperature conditions. However, with other evidence already presented, such as boiling range, production rates, gas exit temperatures and tar acid content, it is believed that Sample 2 could not have been produced at lower temperatures than Sample 1.

#### CONCLUSIONS

In summary, the composition of the coal tar, particularly the basic fraction, is reasonably well known. A decision on its use as a petrochemical feedstock might be made from this information. However, the conditions under which the coal tar is produced are still unknown. Improved monitoring of the combustion zone, especially temperatures, will be included in future experimentation at Hanna. Data from this additional monitoring should allow more definite conclusions to be drawn. Possible herbicidal properties of components identified would require precautions against spillage to minimize environmental impacts. Monitoring underground migration of these organic fluids to determine what effect they may have on water supplies is being studied.

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NOTE: Any reference to specific brand names does not imply endorsement by the Bureau of Mines.

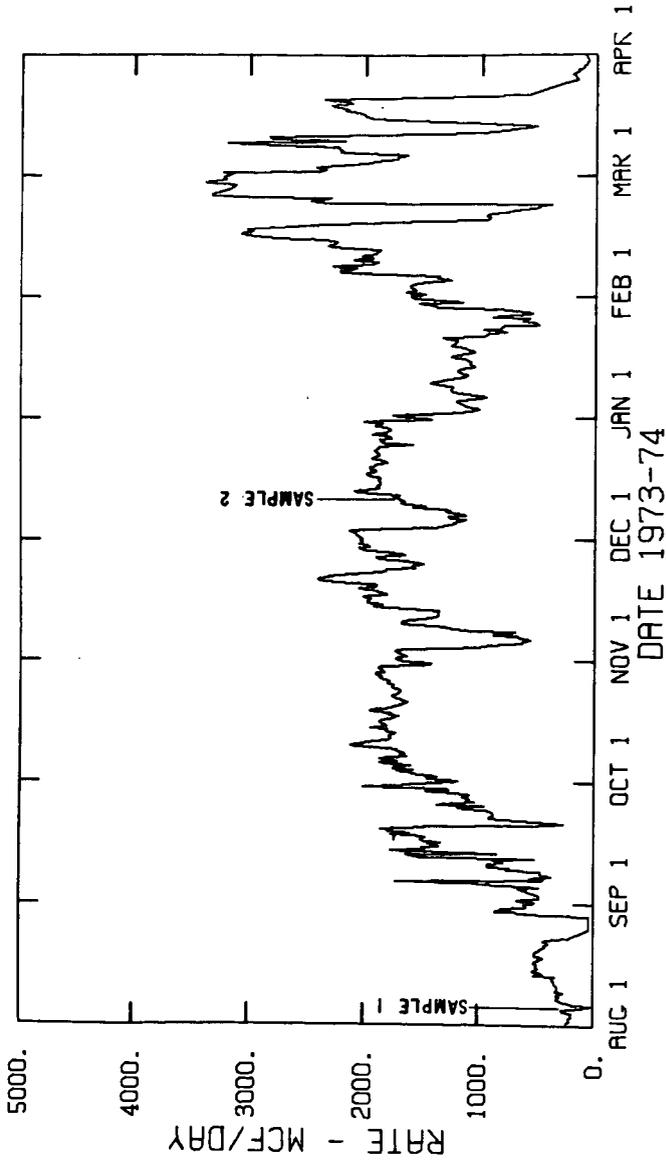


FIGURE 1. - DRY GAS PRODUCTION RATE, UNDERGROUND COAL GASIFICATION EXPERIMENT, HANNA, WYOMING

LOWERING THE SULFUR AND ASH CONTENTS OF HIGH-SULFUR COALS  
BY PEROXIDE-ACID TREATMENT

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## INTRODUCTION

Considerable effort has been devoted in recent years to upgrading high-sulfur coals by both physical and chemical methods. Some methods are mild, selectively removing mineral components without significantly altering the organic matter. The more drastic methods break down the coal structure, separating it into an inorganic sludge and an organic product essentially not coal. As a recently publicized example, high-gradient magnetic separation has been proposed as a technique for removing pyrite and other weakly paramagnetic minerals from slurried coal.<sup>1</sup> The Bureau of Mines' froth flotation process<sup>2</sup> removes pyrite and other minerals by taking advantage of differences in density and wettability of these undesirable substances and organic material. A method known as Meyer's Process<sup>3</sup> involves up to six leaches of pulverized coal with ferric salt solution at about 100° C, converting pyrite to sulfate and elemental sulfur. A more vigorous chemical method<sup>4</sup> requires leaching finely pulverized coal with aqueous alkali at about 225° C in a closed system under an inert atmosphere, followed by treatment with strong acid and leaching with water. The still more vigorous PAMCO process<sup>5</sup> involves dissolution of coal in solvent at elevated temperature, hydrogen treatment, physical separation of undissolved matter, and vacuum distillation of the dissolved products.

Our laboratory is investigating methods for upgrading shale oil and high-sulfur coal by mild oxidation. Currently, experiments are being conducted with two types of oxidation systems--one using oxygen, which shows promise as a method for upgrading shale-oil distillates,<sup>6</sup> and the other using mixtures of H<sub>2</sub>O<sub>2</sub> and acid, which may be useful for upgrading both shale oil and coal. This report describes results of treating several high-sulfur coals with solutions of H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub> or with H<sub>2</sub>SO<sub>4</sub> alone. Acid concentrations ranged from 0.1 N to 0.5 N, H<sub>2</sub>O<sub>2</sub> concentrations ranged from 7 to 17 percent, and treating periods ranged from 1 to 72 hours. Most of the tests were conducted at ambient temperature, but in one test series, the solutions were warmed to speed up the reaction.

## EXPERIMENTAL PROCEDURES

Coals and Sample Preparation

Five different high-sulfur, high-volatile bituminous coals, representing a wide range of sulfur contents, sulfur types, and ash contents, were obtained from the Pittsburgh Energy Research Center. These were (A) Pittsburgh Seam, St. Clairsville, Ohio; (B) Pittsburgh Seam, Pittsburgh, Pennsylvania; (C) Illinois No. 5 Bed; (D) Hastie, Iowa Bed; and (E) Ft. Scott, Oklahoma Bed. Each coal as received was first screened through a 32-mesh screen to separate fine and coarse material. The plus 32-mesh material was crushed in a ceramic mill jar with Burundum cylinders; that which passed through the 32-mesh screen was combined with the initially separated fine material, and the plus 32-mesh material was returned to the mill jar for further crushing. This process was repeated until the entire sample was reduced to minus 32 mesh.

## Reagents and Analytical Procedures

### Reagents

$\text{H}_2\text{O}_2$  (30 percent),  $\text{H}_2\text{SO}_4$ , and  $\text{HCl}$  were ACS reagent grade.  $\text{Ce}(\text{SO}_4)_2$  was certified 0.1000 N solution standardized against primary standard iron wire. Treating solutions were prepared by dilution based on label values.

### Coal Analyses

Proximate and ultimate composition and heating values were determined by standard methods<sup>7</sup> at the Bureau of Mines Coal Analysis Laboratory, Pittsburgh Energy Research Center.

### Determination of Extracted Iron

An aliquot of filtered spent treating solution was transferred to a 125-ml Erlenmeyer flask, 2-ml 6 N  $\text{H}_2\text{SO}_4$  was added, the mixture was heated to boiling, and 0.5 N  $\text{KMnO}_4$  solution was added dropwise until the pink color persisted for at least 2 minutes. After addition of 10-ml of 6 N  $\text{HCl}$ , the solution was again brought to a boil, reduced by the Zimmerman-Reinhardt method, and titrated with 0.1 N cerate solution using Ferroin indicator. A blank titer was determined on the reagents, subtracted from the sample titers, and the net titers calculated as Fe.

### Treating Procedures

#### Varying the Treating Time

Ten-gram samples of coal A were shaken at ambient temperature in 500-ml Pyrex Erlenmeyer flasks with 100-ml portions of solution, which were 17 weight-percent  $\text{H}_2\text{O}_2$  and 0.3 N  $\text{H}_2\text{SO}_4$ . Treating times were 2, 4, 19, 24, 48, and 72 hours. One sample was treated with 0.5 N  $\text{H}_2\text{SO}_4$  alone for 72 hours. After treating, each mixture was filtered with the aid of vacuum through a fine-porosity fitted glass funnel, and the coal was washed several times with water until a small portion of wash showed little or no sulfate content. Each treated coal and a portion of the untreated coal were dried for 2 hours in a vacuum dessicator at 80° C and analyzed for proximate and ultimate composition and heating value. The combined filtrates and washes from each coal sample were analyzed for iron content.

#### Varying Hydrogen Peroxide Concentration

Thirty-gram samples of coal A were treated for 2 hours in the manner previously described with 100-ml portions of solution, each 0.1 N in  $\text{H}_2\text{SO}_4$  but with different concentrations of  $\text{H}_2\text{O}_2$  in each. Hydrogen peroxide concentrations were 7, 9, 11, 13, 15, and 17 percent. After filtering and washing, the coals were dried and analyzed, and the extracted iron was determined in each filtrate.

#### Treating Coals Containing Different Proportions of Inorganic and Organic Sulfur

Coals B, C, D, and E, ranging in pyrite sulfur content from less than 1 percent to more than 4 percent and ranging in organic sulfur content from 1 percent to 3 percent, were treated for 1 hour with 15 percent  $\text{H}_2\text{O}_2$  solutions that were 0.3 N  $\text{H}_2\text{SO}_4$  and with 0.3 N  $\text{H}_2\text{SO}_4$  alone. The volume of treating solution was 250-ml and the sample weight was 50 grams in each test. The treating and workup procedures were the same as previously described.

### Repetitive Treating

Coals B and C were treated with 250-ml portions of 0.3 N  $H_2SO_4$ -10 percent hydrogen peroxide as follows: Three 50-gram samples of each coal were first treated as previously described for 1 hour at ambient temperature. After filtering the three mixtures, one sample was worked up for analysis, and the other two were retreated with fresh solution for 3 hours at 55° C. After filtering the remaining two, one was worked up for analysis; the last sample was treated a third time with fresh solution for 7 hours at 85° C., filtered, and worked up for analysis.

### RESULTS AND DISCUSSION

Analyses of samples of coal A before and after treating for 2 to 72 hours are shown in table 1. Acid-peroxide treatment caused a 49-percent decrease in sulfur content and a 32-percent

TABLE 1. - Results<sup>1</sup> of treating high-sulfur coal A with  $H_2O_2$ - $H_2SO_4$  or with  $H_2SO_4$  alone

Treating time, hr	Treating solution <sup>2</sup>		C	H	N	S	O	Ash	Heating value, Btu/lb	Extracted Fe, wt-pct of coal
	$H_2O_2$ , wt-pct	$H_2SO_4$ , N								
	Untreated coal		68.9	4.8	1.1	4.5	7.9	12.8	12,460	0
2	17	0.3	74.8	5.0	1.3	2.3	7.8	8.7	---	1.92
4	17	.3	75.2	5.0	1.3	2.0	7.9	8.6	---	2.27
19	17	.3	75.4	5.0	1.3	1.9	8.4	8.0	13,310	2.32
24	17	.3	75.1	4.9	1.3	2.0	8.3	8.4	---	2.33
48	17	.3	75.0	5.0	1.3	2.0	8.5	8.2	---	2.39
72	17	.3	74.8	5.0	1.3	2.0	9.0	7.9	13,380	2.45
72	0	.5	72.3	4.8	1.2	3.9	7.5	10.8	12,890	.31

<sup>1</sup> Ultimate analyses and heating values on a dry basis.

<sup>2</sup> 100-ml solution per 10 grams of minus 32-mesh coal, ambient temperature.

decrease in ash content in 2 hours; thereafter, sulfur and ash contents decreased slowly to minimums of 44 and 62 percent, respectively, of original values. Values of iron extracted followed a similar trend, which indicated that most improvements in composition were substantially accomplished in 2 to 4 hours. Heating values of the treated samples were about 7 percent higher than that of the untreated coal. The sample treated for 72 hours with 0.5 N  $H_2SO_4$  alone showed a modest increase of 3.5 percent in heating value and decreases of only 13 percent in sulfur and 16 percent in ash. It is apparent that this treatment for 72 hours had less effect on the coal than 2 hours of treatment with acid-peroxide, which demonstrates the importance of  $H_2O_2$  in the solution.

Another series of tests on the same coal indicates the importance of sulfuric acid in the treating solution. In these tests conducted for 2 hours at ambient temperature, the initial concentrations of hydrogen peroxide were varied from 7 to 17 percent; initial sulfuric acid concentration was 0.1 N in each solution. The results, shown in table 2, show that at peroxide concentrations greater than 7 percent, very little further change in coal composition was achieved. At 17 percent peroxide concentration, comparison of these results with the results of 2 hours treating shown in table 1 indicate that the solution with the higher acid concentration was more effective in removing iron and sulfur and in lowering ash content. The analyses of sulfur forms show that only mineral sulfur was affected by acid-peroxide under these conditions. Neither organic sulfur nor nitrogen contents were appreciably affected by these treatments, and the increased heating values indicate there was little or no attack on organic components.

TABLE 2. - Composition<sup>1</sup> of high-sulfur coal A before and after treating with H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> solution

Treating H <sub>2</sub> O <sub>2</sub> , wt-pct	Solution <sup>2</sup> H <sub>2</sub> SO <sub>4</sub> N	Ultimate analysis, wt-pct						Sulfur forms, wt-pct			Heating value, Btu/lb	Extracted Fe, wt-pct of coal
		C	H	N	S	O	Ash	SO <sub>4</sub>	Pyr.	Org.		
Untreated coal		68.9	4.8	1.1	4.5	7.9	12.8	0.41	2.30	1.79	12,460	0
7	0.1	73.0	5.0	1.2	3.3	8.0	9.5	.06	1.44	1.80	13,150	1.15
9	.1	73.0	5.0	1.2	3.1	8.4	9.4	.06	1.22	1.82	13,160	1.37
11	.1	72.9	5.0	1.2	3.1	8.5	9.3	.01	1.31	1.78	13,130	1.31
13	.1	73.3	5.0	1.2	2.9	8.6	9.0	.05	1.12	1.73	13,180	1.39
15	.1	73.3	5.1	1.2	2.8	8.3	9.3	.08	.94	1.78	13,170	1.41
17	.1	73.3	5.0	1.2	2.9	8.4	9.2	.09	1.04	1.77	13,200	1.50

<sup>1</sup> Ultimate analyses and heating values on a dry basis.

<sup>2</sup> 200-ml solution per 30 grams of minus 32-mesh coal, 2 hours at ambient temperature.

To test the effectiveness of acid-peroxide treatment on coals having widely different proportions of sulfur types, 50-gram samples of four coals were treated for 1 hour at ambient temperature with 250-ml volumes of either 15 percent H<sub>2</sub>O<sub>2</sub>-0.3 N H<sub>2</sub>SO<sub>4</sub> or 0.3 N H<sub>2</sub>SO<sub>4</sub> alone. Results are shown in table 3. In all cases acid-peroxide treatment was more effective than treatment with acid alone in terms of reducing sulfur and ash contents and increasing heating values. As previously observed, only the sulfate and pyrite sulfur were removed. Treatment of coal C with 0.3 N H<sub>2</sub>SO<sub>4</sub> removed iron equivalent to 2 weight-percent of the sample, the source of which was not pyrite. Calculated as iron oxide, this amount of iron would account for the difference in ash content in this acid-washed sample and the untreated coal. In general, dilute sulfuric acid treating removed varying amounts of mineral matter, including sulfates and nonpyrite iron, but had no apparent effect on pyrite. In every case, acid-peroxide solution removed more mineral than acid alone and removed most of the pyrite but had no apparent effect on organic matter under these mild conditions.

To test the effects of multiple treatments, 50-gram samples of coals B and C were treated with one, two, or three 250-ml portions of a solution which was 10 weight-percent H<sub>2</sub>O<sub>2</sub> in 0.3 N H<sub>2</sub>SO<sub>4</sub>. Reactions in second and third treatments were quite slow at ambient temperature, and the flasks were warmed to expedite peroxide decomposition. Analyses of the treated samples and of the untreated coals are shown in table 4 and show that these coals suffered some loss in quality when treated for a second and third time, characterized by a trend toward lower carbon contents and heating values accompanied by rising oxygen and ash contents. Even though the pyrite contents of the coals had decreased after the third treatment to less than 10 percent of the original contents, the amounts removed by repeated treatment were relatively small. Both coals show a modest decrease in organic sulfur content after treating a second and third time. The change in coal C is more significant, amounting to a decline of 11 percent of the organic sulfur present in the coal after the first treatment. The results indicate that continued exposure to acid-peroxide after pyrite or other reactive minerals are removed leads to oxidative attack on the organic matter.

Although the main object of these experiments was to gauge the potential of a strongly oxidizing system for demineralizing coal, rather than to examine the chemistry in detail, some observations of mainly chemical interest emerged. Treatment of the coals used in this work with 10 to 15 percent H<sub>2</sub>O<sub>2</sub> solution for 1 to 2 hours at ambient temperature had very little effect on coal composition. The foregoing experiments demonstrate that in the concentrations employed, only the mixture of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>, but neither reagent alone, is capable of attacking pyrite or

TABLE 3. - Analyses<sup>1</sup> of coals before and after treating with  $H_2O_2$ - $H_2SO_4$  or with  $H_2SO_4$  alone

Coal	Treating solution <sup>2</sup>		Ultimate analysis, wt-pct						Sulfur forms, wt-pct			Heating value, Btu/lb	Extracted Fe, wt-pct of coal
	$H_2O_2$ , wt-pct	$H_2SO_4$ , N	C	H	N	S	O	Ash	$SO_4$	Pyr.	Org.		
B	Untreated coal		71.8	5.1	1.4	1.8	8.2	11.7	0.06	0.74	1.00	12,990	0
	0	0.3	72.3	5.0	1.4	1.8	8.0	11.5	.04	.79	.97	12,960	0.04
	15	.3	73.5	5.0	1.4	1.1	8.2	10.8	.02	.08	1.00	13,060	.63
C	Untreated coal		69.8	4.7	1.3	3.6	11.0	9.6	.08	1.06	2.46	12,590	0
	0	.3	71.5	4.9	1.3	3.6	10.1	8.6	.01	1.11	2.48	12,800	.08
	15	.3	72.0	5.0	1.3	2.7	11.5	7.5	.06	.09	2.55	12,860	1.02
D	Untreated coal		58.7	4.6	1.0	8.7	9.9	17.1	2.00	3.93	2.77	10,700	0
	0	.3	65.7	4.9	1.1	7.9	6.5	13.9	.51	4.45	2.94	11,900	2.06
	15	.3	68.9	5.1	1.2	4.4	10.8	9.6	.29	1.15	2.96	12,360	4.38
E	Untreated coal		73.7	5.3	1.6	4.1	6.7	8.6	.48	2.05	1.57	13,300	0
	0	.3	75.9	5.5	1.6	3.8	6.4	6.8	.07	1.94	1.79	13,770	.46
	15	.3	77.0	5.6	1.7	2.5	8.0	5.2	.04	.58	1.88	14,040	1.56

<sup>1</sup> Ultimate analyses and heating values on a dry basis.<sup>2</sup> 250-ml solution per 50 grams minus 32-mesh coal, ambient temperature for 1 hour.TABLE 4. - Effects of repeated treatment with 10-percent  $H_2O_2$ -0.3 N  $H_2SO_4$  on the composition<sup>1</sup> of two high-sulfur coals

Coal	Total treatments <sup>2</sup>	Ultimate analysis, wt-pct						Sulfur forms, wt-pct			Heating value, Btu/lb	Extracted Fe, wt-pct of coal
		C	H	N	S	O	Ash	$SO_4$	Pyr.	Org.		
B	Untreated	71.8	5.1	1.4	1.8	8.3	11.6	0.06	0.74	1.00	12,990	0
	1	73.3	5.1	1.4	1.2	8.2	10.8	.01	.11	1.08	13,090	0.60
	2	72.5	5.0	1.4	1.0	9.3	10.8	.0	.04	.96	12,980	.72
	3	71.5	5.0	1.4	1.0	9.9	11.2	.0	.03	.97	12,630	.74
A	Untreated	69.8	4.7	1.3	3.6	11.0	9.6	.08	1.06	2.46	12,600	0
	1	72.9	5.1	1.3	2.8	10.3	7.6	.06	.16	2.58	12,900	.84
	2	72.7	5.0	1.4	2.6	11.3	7.0	.08	.08	2.44	12,840	1.22
	3	70.1	4.6	1.3	2.5	14.3	7.2	.11	.10	2.29	12,240	1.14

<sup>1</sup> Ultimate analyses and heating values on a dry basis.<sup>2</sup> Each treatment 250-ml solution per 50 grams minus 32-mesh coal. First treatment, 1 hour at ambient temperature; second treatment, additional 3 hours at 55° C; third treatment, additional 7 hours at 85° C.

demineralizing coal to the extent observed. It is therefore reasonable to postulate that peroxysulfuric acid,  $H_2SO_5$ , is formed in equilibrium quantity in the mixture and plays an important role in the reaction. However, the expected initial  $H_2SO_5$  concentration would be extremely low in the solution employed in this work because of the low  $H_2SO_4$  concentration and the low value of the equilibrium constant measured by Monger and Redlich.<sup>8</sup> Further, in view of the rapid decomposition of  $H_2O_2$  in contact with high-sulfur coal and the apparent low rate of  $H_2SO_5$  formation,<sup>8</sup> it is difficult to reconcile the amount of peroxyacid expected in the treating solutions with the amounts of pyrite and other minerals removed unless it is assumed that substances in coal catalyze peroxyacid formation. This catalytic effect has been observed for a number of metal ions and for sulfates,<sup>8</sup> and so could be expected in mixtures of  $H_2O_2$ ,  $H_2SO_4$ , and coal. The principle reactions are therefore visualized as catalytic formation of  $H_2SO_5$  and oxidation of pyrite with competing peroxide decomposition by metal ions. After removal of most of the active metals and sulfates from coal, oxidative attack on the organic matter becomes significant as indicated by analyses of coal subjected to repeated acid-peroxide treatment (table 4).

Evolution of small amounts of hydrogen sulfide was detected when coals were treated with acid-peroxide, although none was detected when using  $H_2SO_4$  or  $H_2O_2$  alone. Its presence in the strongly oxidizing media was surprising. Acid concentrations were apparently too low to produce  $H_2S$  from pyrite, in view of the selective extraction of sulfate from coal with  $\sim 3$  N HCl, which is not expected to attack pyrite.<sup>7</sup> Nalwalk and coworkers<sup>9</sup> report that decomposition of coal with 30 percent  $H_2O_2$  slowly oxidized pyrite to sulfate, but no evolution of  $H_2S$  was mentioned either in this work or that of Ward.<sup>10</sup> The formation of  $H_2S$  cannot be conveniently explained as a result of  $H_2SO_5$  formation because it is apparently a weaker acid than sulfuric acid.<sup>8</sup> However, the formation of  $H_2S$  in minute quantities, whatever the reaction path, is not expected to be important in the overall reaction.

Further experimentation is in progress to determine the most effective concentrations of peroxide and sulfuric acid for coal demineralization. On the premise that peroxysulfuric acid is the most effective reagent and in order to increase its initial concentration, the concentration of sulfuric acid must be considerably higher than used in the initial experiments described in this work.

## CONCLUSIONS

Treatment of high-sulfur coals with  $H_2SO_4$ - $H_2O_2$  solution lowers the sulfur and ash contents of the coals by removing pyrite, iron, and other minerals, leading to fuels of higher heating value. No significant attack on organic constituents occurs at ambient temperature before minerals susceptible to oxidation have been removed. Acid-peroxide treatment apparently has potential as a method for demineralizing high-sulfur coals.

## ACKNOWLEDGMENTS

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Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

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## KEROGEN CONSTITUENTS: REDUCED CHLOROPHYLLIN AS A MODEL FOR THE PRECURSORS OF NITROGENOUS COMPOUNDS IN SHALE OIL

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### INTRODUCTION

In evaluating and developing the resource potential of the Nation's vast oil-shale reserves, the U.S. Bureau of Mines has been conducting research in the origins and chemistry of shale oil. As part of this work, the role of plant pigments and their decomposition products as possible precursors of the nitrogenous compounds found in shale oil was investigated. An accurate picture of the origin of the compounds and their compound types may be an aid in analyzing the character of the oil, its suitability as a refinery feedstock, or perhaps its importance as a source of commercially valuable chemical compounds.

The idea that plant pigments may be the origin of nitrogen-containing compounds in shale oil is not new. Mapstone has proposed that the pyrroles found in shale oil result from the pyrolysis of the porphyrins in chlorophyll.<sup>1</sup> It has been shown that kerogen, the organic phase of oil shale, is 45 to 60 percent heterocyclic material.<sup>2</sup> This work was undertaken to substantiate Mapstone's proposal and to see if plant pigments could be the origin of the heterocyclic material in kerogen.

Experimentally, a comparison between the nitrogen compounds in a shale-oil light distillate and the nitrogenous compounds found in the pyrolysates of chlorophyll derivatives was made. The similarity of the compounds found in both the shale oil and chlorophyllin pyrolysate indicates that reduced chlorophyllin derivatives are a good model for the portion of kerogen that produces nitrogen compounds upon pyrolysis of oil shale. The present paper describes the preparation and characteristics of the kerogen model and shows that pyrolysis of this model yields pyrroles and products which are comparable to the nitrogenous products of shale oil.

### EXPERIMENTAL PROCEDURE

#### Description of Materials

##### Commercial Chlorophyllin

Chlorophyllin is commercially available as the trisodium-copper salt with the empirical formula  $C_{31}H_{31}N_4Cu(CO_2Na)_3$ . Most processes for commercial production of chlorophyllin involve saponification of plant material, and the resulting product frequently contains fatty acid salts as impurities.<sup>3</sup> A commercial sample of chlorophyllin with a nitrogen content of 4.83 percent was used in this study. This compares with the theoretical value of 7.73 for the pure salt, indicating that the commercial sample is 63 percent pure. The remaining material is assumed to be fatty acid salts.

##### Shale-Oil Light Distillate

Samples for mass spectral analysis were obtained as follows. A 110-g sample of an in situ shale-oil light distillate was separated on 880 g of Florisil. Each fraction was monitored by infrared spectroscopy as a 2-percent solution in carbon tetrachloride. The fraction richest in pyrrolic

N-H (as indicated by the intense band at  $3,480\text{ cm}^{-1}$ ) was further fractionated into six subfractions, A<sub>0</sub>-A<sub>5</sub>, using the method of Snyder and Buell for separations on alumina.<sup>4</sup> Three of the subfractions--A<sub>2</sub>, A<sub>3</sub>, and A<sub>5</sub>--were sufficiently different in the IR to be examined individually by mass spectroscopy, along with two later fractions which gave indications in the infrared of meriting further study.

### Reduction and Pyrolysis of Chlorophyllin

#### Reduction

The reduction of chlorophyllin with PtO<sub>2</sub> in glacial acetic acid with the resultant uptake of three moles of hydrogen to give hexahydrochlorophyllin is reported in the literature<sup>5</sup> as a straightforward reaction, but this was not found to be so during the course of this study. Using a PtO<sub>2</sub>-to-chlorophyllin ratio of 2:25, H<sub>2</sub> pressure of 275 psig (at 25° C), and heating to 150° C for 72 hours resulted in only partial reduction. At no time during this study was the success of the reaction predictable. In each case the reduced platinum was removed by filtration, and the acetic acid was removed with mild heat and vacuum on a rotary evaporator. The resulting dark brown material was the synthetic kerogen which was pyrolyzed to yield the oils which were compared with shale oil. For additional comparison, a sample of commercial chlorophyllin was dissolved in acetic acid and then recovered by the above technique to yield chlorophyllin acetate for pyrolysis.

#### Pyrolysis of Reduced Chlorophyllin

Samples to be pyrolyzed (~10 g) were placed in a 300-ml flask which was connected to a trap cooled with liquid nitrogen. The system was evacuated to  $\sim 10^{-2}$  mm for at least 30 minutes; then the pressure was reduced to  $\sim 10^{-5}$  mm, and heat was applied to the sample container with a hot air bath. Heat was applied slowly, and as it approached 200° C a clear distillate began to collect in the trap. This was believed to be excess acetic acid and perhaps some water. The pressure in the system also took a rapid jump to  $\sim 10^{-2}$  mm Hg as CO<sub>2</sub> was eliminated from the acids present. After the pressure began to drop, additional heat was applied until the temperature in the air bath reached 375° C to 425° C. The temperature was maintained at this level until no more distillate, a dark red-brown liquid, was observed coming from the sample. At this point the pressure had risen to  $10^{-2}$  mm Hg and remained fairly constant. The heating was discontinued, the system was allowed to cool to room temperature, and the pressure was returned to normal. The frozen distillate was dissolved in ethyl ether and washed with saturated NaHCO<sub>3</sub> until the wash water was basic. The sample was dried over anhydrous K<sub>2</sub>CO<sub>3</sub>, and the ether was removed at room temperature under a slight negative pressure. If the acetic acid and water were not removed immediately, the sample tended to polymerize and form heavy precipitates. The samples were stored under a nitrogen atmosphere at 0° C.

### Characterization Procedures

#### Chromatographic Separation and Analysis

The pyrolysates from chlorophyllin and a reduced chlorophyllin were treated with an ion-exchange resin to separate the basic from the neutral material in the following manner. Two ml of a 5-percent solution of the pyrolysate in cyclohexane were passed through a column containing 1.0 g of activated Rohm and Haas Amberlyst 15 cation-exchange resin with cyclohexane as the solvent. The first 2 ml of eluent were collected and used in the subsequent analysis. GC analysis by simulated distillation of aliquots of the solution before and after treatment and comparison of the sample areas gave percent basic nitrogen in the total sample. Breakdown of the GC output in terms of 50° C increments gives the relative distribution of compounds according to boiling range and, by inference, according to molecular weight.

### Titrimetric Analysis

Titration of the bases in the pyrolysates was done in acetic anhydride and in acetonitrile using an autotitrator. The titrations were performed on samples containing about 0.1 milliequivalent of nitrogen, using 0.1 N perchloric acid in dioxane based on the methods of Wimer<sup>6</sup> and Buell.<sup>7</sup> The electrode system was glass versus calomel reference, and the electrolyte in the calomel electrode was methanolic KCl.

### Infrared Analysis

Qualitative spectra of all fractions were run as 2-percent solutions in carbon tetrachloride with 0.5-mm NaCl cells. Quantitative pyrrolic N-H was determined by the method of Koros, et al.<sup>8</sup>

### Mass Spectral Analysis

Low-ionizing voltage mass spectrometry at 14 to 16 nominal volts was used to obtain the molecular weights of the various homologous series in various samples. High-resolution spectra were run at 70 eV to confirm the empirical formulas of the various ions.

## RESULTS AND DISCUSSION

Table 1 lists the elemental composition of the starting materials as well as the distillates

TABLE 1. - Elemental composition of the starting materials, distillates, and residues from the pyrolysis of some samples of chlorophyllin and its related products

Sample	Carbon, wt-pct	Hydrogen, wt-pct	Nitrogen, wt-pct	Carbon/hydrogen
Chlorophyllin	59.46	5.82	4.83	0.85
Distillate	85.31	9.31	5.18	.76
Residue	59.50	4.16	5.41	
Chlorophyllin acetate	58.45	6.14	4.26	.79
Distillate	85.31	9.78	4.49	.73
Residue	59.67	4.08	5.29	
Reduced chlorophyllin A <sup>1</sup>	60.07	6.53	2.88	.77
Distillate	85.21	10.90	2.96	.65
Residue	59.49	3.82	5.04	
Reduced chlorophyllin B <sup>1</sup>	46.24	6.03	2.19	.64
Distillate	80.85	10.00	4.78	.67
Residue	38.45	2.73	2.99	

<sup>1</sup> Reduced chlorophyllin A and B are products of two separate reductions of commercial chlorophyllin with PtO<sub>2</sub>.

and residues from the pyrolysis of some samples of chlorophyllin and related products. The reduction caused some hydrodenitritification, as shown by the lowered nitrogen percentages. Upon pyrolysis, the two reduced materials gave the products with the lowest carbon-hydrogen ratio as would be expected.

Figure 1 shows the distribution of basic and neutral compounds as defined by their affinity for adsorption on Amberlyst 15 resin. Pyrolysis of reduced chlorophyllin produces 50 percent more basic material than does pyrolysis of the nonreduced material, and it is noteworthy that most of this additional material is fairly low boiling, falling in the 200 to 300° C range.

Titration of the pyrolysates in nonaqueous solvents gives information concerning the strength of the various bases present. These data are presented in table 2. There appears to be no correla-

TABLE 2. - Nitrogen composition of distillates

Distillate source	Titrateable N, total	Wt-pct strongly basic	Wt-pct weakly basic	Wt-pct very weakly basic
Chlorophyllin	1.52	0	0.78	0.74
Chlorophyllin acetate	1.68	0	1.22	.46
Reduced sample A	1.57	0	.76	.81
Reduced sample B	3.08	0	.82	2.25

tion between the amount of hydrogen in the starting material and the types of bases formed, but the presence of bound acetic acid does favor the production of weak bases at the expense of the very weak bases.

Tables 3 and 4 list the homologous series of nitrogen compounds found in the low-ionizing-voltage mass spectrum of the reduced chlorophyllin pyrolysate having the highest pyrrolic N-H content, 2.02 percent, and the five fractions of the shale-oil light distillate, respectively. High-resolution mass spectra on reduced chlorophyllin pyrolysates confirm the presence of all the mono-nitrogen series of compounds listed in table 3. In the shale-oil light distillate, the  $Z = -3$  series is missing from the high-resolution mass spectrum. Its absence is unusual because pyrroles have been isolated from shale oil.<sup>9</sup> The absence of the  $Z = +1$  series in the mass spectrum of the pyrolysate is not too surprising; few materials in such a reduced state would be expected from the thermal decomposition of what is basically a hydrogen-poor substrate. The absence of the  $Z = -7$  series in the reduced chlorophyllin pyrolysate cannot be explained at this time, but it has been found in other reduced chlorophyllin pyrolysates.

For the  $Z$  series (-3, -5, -7, -11) found in various chlorophyllin pyrolysates by mass spectrometry, the following compound types are probably represented: Pyrroles (-3); cycloalkylpyrroles, pyridines (-5); cycloalkylpyridines (-7); indoles (-9); and azanaphthalene derivatives (-11). These represent materials whose presence has been reported in shale oil before<sup>9,10</sup> or that were found in this work. It is felt, therefore, that chlorophyllin derivatives, especially the reduced materials, represent a reasonable model for the portion of kerogen that produces nitrogen-containing compounds upon pyrolysis.

#### SUMMARY

The reduction and pyrolysis of a commercially available plant pigment extract, chlorophyllin, is described. The amounts of bases formed and their boiling-range distribution are related to the hydrogen content of the starting materials. Mass spectral studies are given which show that many of the same types of bases are found in the pyrolysate and in an in situ light distillate. These results indicate that reduced chlorophyllin may be used as a model for the nitrogen-containing constituents in kerogen.

TABLE 3. - Mononitrogen-containing molecular ions in the low-ionizing voltage mass spectrum of reduced chlorophyllin pyrolysate

Series	General formula	Carbon No. range	Rings plus double bonds
I-a	$C_nH_{2n-3}N$	6-14	3
I-b	$C_nH_{2n-5}N$	7-15	4
I-c	$C_nH_{2n-9}N$	10-15	6
I-d	$C_nH_{2n-11}N$	14-18	7

TABLE 4. - Nonnitrogen-containing molecular ions from the low-ionizing voltage mass spectra of chromatographic fractions of shale-oil light distillate

Series	General formula	Carbon No. range	Rings plus double bonds
<u>Fraction A<sub>2</sub></u>			
II-a	$C_nH_{2n+1}N$	8-14	1
II-b	$C_nH_{2n-11}N$	10-13	7
II-c	$C_nH_{2n-9}N$	10-14	6
<u>Fraction A<sub>3</sub></u>			
II-d	$C_nH_{2n-11}N$	9-14	7
<u>Fraction A<sub>5</sub></u>			
II-f	$C_nH_{2n-7}N$	8-12	5
II-g	$C_nH_{2n-9}N$	12-15	7
<u>Fraction 42</u>			
II-h	$C_nH_{2n-9}N$	8-12	6
II-i	$C_nH_{2n-11}N$	11-15	7
II-j	$C_nH_{2n-13}N$	13-15	8
<u>Fraction 58</u>			
II-k	$C_nH_{2n-5}N$	8-15	4
II-l	$C_nH_{2n-11}N$	9-14	7

#### ACKNOWLEDGMENTS

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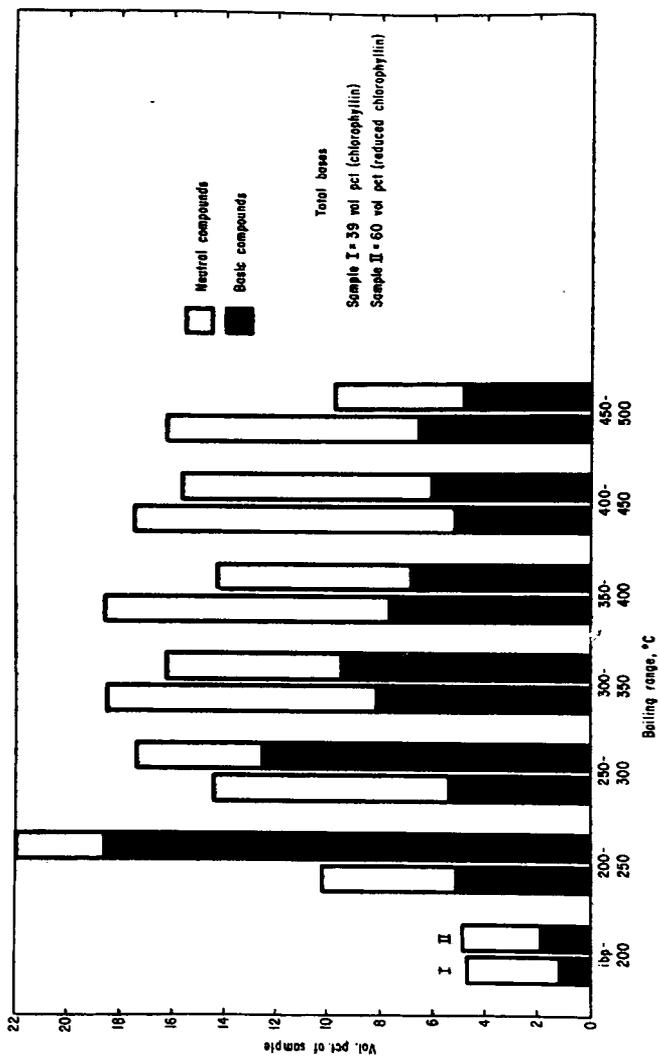


FIGURE 1. - Distribution of compounds in distillates.

## NITROGEN COMPOUND TYPES IN GREEN RIVER OIL SHALE AND ITS KEROGEN DEGRADATION PRODUCTS

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### INTRODUCTION

Information about the nitrogen compounds in oil shale and oil-shale degradation products is needed in order to provide more efficient processes for converting oil shale to useful energy with minimum environmental contamination. At present very little is known about the types of nitrogen compounds present in the soluble extracts that can be obtained from oil shale or the types of nitrogen compounds that are formed when previously extracted oil-shale samples are heated for prolonged periods at temperatures below those usually employed in retorting.

Some research has been done on the nitrogen compounds in shale oil and oil shale. Smith and coworkers<sup>4</sup> separated a shale-oil distillate boiling above 400° F on Florisil into hydrocarbon and nonhydrocarbon nitrogen-containing fractions. Haines and coworkers<sup>5</sup> published techniques for separating and identifying nitrogen compounds in petroleum and shale oil. Decora and Dinneen<sup>4</sup> developed a gas-liquid chromatography method, based on using detergent as the solid phase, for separating basic nitrogen compounds in shale oil. Dinneen<sup>5</sup> identified pyridines, indoles, quinolines, and tetrahydroquinolines in shale oil. Moore and Dunning<sup>6</sup> isolated the porphyrins from oil-shale extracts and determined that they were complexed with iron and nickel. Anders and Robinson<sup>1</sup> studied the polar constituents isolated from Green River oil shale and found that alkoxy-pyrrolines, alkylmaleimides, tetrahydroquinolines, and quinolines were present in the polar material. Morandi and Jensen<sup>7</sup> compared the porphyrins from a shale-oil fraction, oil-shale extract, and a petroleum fraction. They found that the porphyrins in oil shale are a complex mixture of etio-type porphyrins in the 366 to 522 molecular-weight range. Simoniet and coworkers<sup>3</sup> studied nitrogenous compounds of the Green River Formation and found quinoline, indole or pyridine, and tetrahydroquinoline present in their oil-shale extracts.

The object of this research was to increase our knowledge about the effect of depth of burial on the nitrogen compounds present in Green River oil shale and to determine what types of nitrogen compounds are formed when oil shale is heated at temperatures in the range of 150° to 350° C for periods from 0.5 to 360 days. The present paper describes the results obtained for nitrogen compound-type analysis of fractions of the complex high-molecular-weight oil-shale products. In the study of extracts from the oil-shale core samples, an attempt was made to relate the analytical data to depth of burial and to determine if depth of burial affects the type of nitrogen compounds present in the extracts. In addition, the effect on oil-shale nitrogen structures due to long-time heating at low temperatures similar to that experienced peripherally to in situ retorting operations was determined.

### EXPERIMENTAL PROCEDURES

The samples used in this study were obtained from two previous oil-shale studies. The extracts (soluble bitumen) obtained from a core of the Green River Formation are the same as described in a report by Robinson and Cook<sup>12</sup> on the 2,300-foot Colorado No. 1 core. The low-temperature thermal products (pyrolytic bitumen) are the same as those described by Cummins and Robinson<sup>3</sup> where previously extracted 66-gpt oil shale from the Bureau of Mines' demonstration

mine at Rifle, Colorado was heated at temperatures ranging from 150° to 350° C for periods ranging from 0.5 to 360 days. The samples were fractionated into acid, bases, neutral-nitrogen, aromatic, and saturate compounds by a fractionation scheme. Each of the various fractions were analyzed for strong bases, weak bases, very weak bases, and nontitratable nitrogen by potentiometric titration. No attempt was made to distinguish between titratable nitrogen compounds and titratable nonnitrogen compounds; however, the latter type has been found by Poulson<sup>11</sup> to be insignificant in shale-oil products.

#### Product Fractionation

The samples used in this study are high-molecular-weight complex materials; however, they are amenable to a fractionation and separation scheme devised by Jewell, et al.<sup>7</sup> Figure 1 shows the fractionation scheme used and the fractions that resulted.

The acid and base fractions are removed with Amberlyst A-29 anion- and Amberlyst 15 cation-exchange resins, while the neutral nitrogen fraction is removed by coordination-complex formation with ferric chloride supported on Attapulug clay. Most of the nitrogen compounds are removed as acid, base, and neutral nitrogen fractions. The remaining hydrocarbon material was separated into aromatic and saturate fractions by adsorption chromatography on a column of Davison grade 12 silica gel.

#### Analyses of Fractions

The concentration of nitrogen present in the original samples and in the acid, base, neutral nitrogen, aromatic, and saturate fractions of these samples was determined using a system consisting of a reductive-nickel pyrolysis tube which directed the pyrolyzed product to an ammonia micro-coulometer. Samples were introduced through a boat inlet into the pyrolysis tube. Types of nitrogen compounds present in the fractions were determined using published methods by Streuli<sup>5</sup> and Nicksic.<sup>10</sup> No attempt was made to identify individual nitrogen compounds in this research. Nitrogen compounds referred to in this report are based on Buell's<sup>2</sup> published classification results.

### RESULTS AND DISCUSSION

The nitrogen content was determined for samples obtained either by extracting portions of Colorado No. 1 core or by thermally degrading oil-shale kerogen. The nitrogen content of the oil-shale core extracts range from 0.11 to 0.82 percent, and the thermal degradation products ranged from 1.36 to 2.22 percent. On an average basis, the thermal product contains 2.7 times more nitrogen than the core extracts.

The distribution of the fractions obtained from Colorado No. 1 core extracts is shown in table 1. All the fractions contain more hydrocarbon (aromatic plus saturated) material than polar (acid, base, and neutral nitrogen) material except sample No. 7. The base-to-acid ratio remains at about one except for samples Nos. 24, 58, and 59. The base-to-neutral nitrogen ratio remains at about one except for samples Nos. 7, 24, and 58. The highest ratio of base-to-acid or base-to-neutral occurs in sample No. 58. The most hydrocarbons appear in the two samples at the bottom of the core. This generalization agrees with the results published by Robinson and Cook.<sup>12</sup> The average percents show that the polar materials are equally divided between the acid, base, and neutral nitrogen fractions. The various amounts of loss are probably complex high-molecular-weight materials generally insoluble in the solvents used in the fractionation scheme.

The distribution of fractions of kerogen thermal degradation products appears in table 2. The amount of aromatic and saturate fractions range from 37.7 to 60.0 percent of the total thermal

TABLE 1. - Distribution of the fractions obtained from Colorado No. 1 core extracts

Sample No.	Depth of burial, ft	Fraction, weight percent of total product						Loss
		Acid	Base	Neutral-N	Aromatic	Saturate		
5	943.7- 947.4	12.0	12.0	13.2	22.0	33.2	7.6	
6	989.5- 990.5	11.7	10.5	9.3	22.1	30.7	15.7	
7	995.4- 998.1	21.1	16.9	10.3	19.4	23.6	8.7	
9	1,076.3-1,079.9	13.2	12.6	10.2	24.4	30.3	9.3	
17	1,399.8-1,401.3	11.3	11.1	10.4	29.3	27.7	10.2	
20	1,539.5-1,541.0	14.9	11.6	11.1	26.2	36.1	.1	
24	1,696.1-1,697.1	6.0	10.8	23.1	29.3	23.2	7.6	
58	3,039.0-3,040.3	4.2	12.8	7.0	20.2	40.6	15.2	
59	3,065.1-3,071.2	2.3	4.8	5.8	17.9	66.8	2.4	
Average		10.7	11.5	11.2	23.4	34.7	8.5	

TABLE 2. - Distribution of fractions of kerogen thermal degradation products

Heating time, days	Temperature °C	Fraction, weight percent of total product						Loss
		Acid	Base	Neutral-N	Aromatic	Saturate		
360	150	12.4	15.4	17.0	21.2	16.5	17.5	
90	200	7.9	11.3	10.6	25.5	27.9	16.8	
12	250	17.2	21.2	7.1	24.3	19.6	10.6	
4	300	8.3	23.2	6.3	34.0	26.0	2.2	
0.5	350	9.1	25.3	15.7	34.4	7.5	8.0	
Average		11.0	19.3	11.3	27.9	19.5	11.0	

product. Three fractions contain less than 50 percent hydrocarbon material (aromatic and saturate). All the thermal products contain higher proportions of base than acid material. On an average basis, about the same amounts of acid and neutral material are present. The amount of aromatic material generally increases with temperature from 150° to 350° C and on an average is about 1.4 times the amount of either the saturate or base material. The percent loss tends to decrease with increased temperature as the complex materials are thermally degraded to lower-molecular-weight and more soluble materials.

The nitrogen content of fractions of the core extracts appears in table 3. As expected, most of the nitrogen is concentrated in the polar fractions, and the largest amount of nitrogen always appears in the base fraction. Samples Nos. 58 and 59 have base-to-acid nitrogen ratios ranging from 7 to 9.5 compared to an average of about 1.9 for samples 5 through 24. Also, samples Nos. 58 and 59 have base-to-neutral nitrogen ratios of 7 to 15 compared to an average of about 3 for samples Nos. 5 through 24. These results suggest some form of diagenetic process at the bottom of the core similar to that expected by thermal alteration.

Nitrogen content of fractions of the kerogen thermal degradation products appears in table 4. Most of the nitrogen appears in the base fractions as it did in the oil-shale core extracts. On an average basis, aromatic fractions contain about 2.5 times more nitrogen than the comparable core fraction while the saturate fractions are approximately equal. The ratios of nitrogen in the base fractions relative to the acid and neutral nitrogen for thermal products prepared at 200° C and above are high. They range from about 5 to 10 in regard to base-to-acid nitrogen ratio and

TABLE 3. - Nitrogen content of fractions of the core extracts

Sample No.	Nitrogen content, weight percent of total nitrogen					
	Acid	Base	Neutral-N	Aromatic	Saturate	Loss
5	25.8	42.8	15.0	4.5	3.4	8.5
6	23.2	39.7	13.9	2.9	3.2	17.1
7	19.8	40.6	10.9	1.9	1.2	25.6
9	24.7	55.8	11.1	3.4	3.1	1.9
17	22.1	42.8	20.0	5.0	3.5	6.6
20	24.8	29.7	19.2	6.6	4.6	15.1
24	12.4	38.7	8.5	5.6	5.6	29.2
58	5.1	48.7	3.3	9.6	13.9	19.4
59	9.0	63.6	9.0	9.0	9.0	.4
Average	18.5	44.7	12.3	5.4	5.3	13.8

TABLE 4. - Nitrogen content of fractions of the kerogen thermal degradation products

Heating time, days	Temperature °C	Nitrogen content, weight percent of total nitrogen					
		Acid	Base	Neutral-N	Aromatic	Saturate	Loss
360	150	14.9	26.7	6.2	4.3	2.5	45.4
90	200	7.0	33.6	9.9	9.6	5.5	34.4
12	250	15.4	46.0	7.1	10.2	5.4	15.9
4	300	2.7	26.7	4.1	12.2	7.2	47.1
0.5	350	5.6	38.0	9.8	25.4	3.6	17.6
Average		9.1	34.2	7.4	12.3	4.8	32.2

from about 3 to more than 6 for the base-to-neutral nitrogen ratio. These results are roughly similar to the results obtained on samples Nos. 58 and 59 of the core fractions (table 3) showing the change expected by thermal alteration.

The distribution of nitrogen-compound types present in fractions of the core extracts appears in table 5. Four different nitrogen-compound types were determined and are as follows: Strong bases, weak bases, very weak bases, and nontitratable nitrogen compounds. Contrary to what one would expect, strong base compounds appeared in the neutral nitrogen fractions. The separation method used should have retained any strong bases on the cation resins. One possible reason for the presence of strong bases in this fraction may be steric hindrance and molecular shape. Nitrogen compounds such as highly alkylated substituted pyridines could pass through the cation resin. No strong bases appear in any of the other fractions. All of the acid and base fractions contain both weak and very weak base type nitrogen compounds. Quinolines, hindered pyridines, and phenanthridines may be present in the weak-base type of nitrogen compounds. Weak bases are present in both the neutral nitrogen samples Nos. 6 and 17 and in saturate sample No. 9. All of the fractions except aromatic fraction No. 17 and saturate fractions Nos. 7 and 9 contain very weak base type nitrogen compounds. Very weak base type compounds could be anilines and certain acridines which acetylate and titrate as amides in acetic anhydride. All of the acid and aromatic fractions, three of the base fractions, one of the neutral nitrogen fractions, and two of the saturate fractions contain nontitratable nitrogen compounds. Nontitratable nitrogen-type compounds could be certain multiring pyrrolic nitrogen compounds, amides, or diamides that are partially or completely insoluble in acetic anhydride. Also, other high-molecular-weight insoluble materials in these fractions of the extracts could account for some of the titratable nitrogen type.

TABLE 5. - Distribution of nitrogen-compound types present in fractions of the core extracts

Sample No.	Nitrogen content, relative weight percent of total nitrogen			
	Strong base	Weak base	Very weak base	Nontitratable nitrogen
		<u>Acid fraction</u>		
5	<1	4	6	90
6	<1	4	5	91
7	<1	4	5	91
9	<1	29	57	14
17	<1	46	46	8
		<u>Base fraction</u>		
5	<1	6	6	88
6	<1	6	5	89
7	<1	5	4	91
9	<1	39	61	<1
17	<1	56	44	<1
		<u>Neutral nitrogen fraction</u>		
5	33	<1	67	<1
6	<1	26	74	<1
7	14	<1	86	<1
9	32	<1	68	<1
17	<1	10	23	67
		<u>Aromatic fraction</u>		
5	<1	<1	9	91
6	<1	<1	21	79
7	<1	<1	11	89
9	<1	<1	9	91
17	<1	<1	<1	100
		<u>Saturate fraction</u>		
5	<1	<1	100	<1
6	<1	<1	100	<1
7	<1	<1	<1	100
9	<1	100	<1	<1
17	<1	<1	26	74

In general, the results show that most of the nitrogen compounds in the various fractions of the extracts from Colorado No. 1 core consisted of very weak bases or nontitratable nitrogen compounds. Some fractions contained weak bases and there was some evidence of strong bases in the neutral nitrogen fraction but generally the nitrogen components were of the less basic forms.

The distribution of nitrogen-compound types present in the kerogen thermal degradation products shown in table 6 are similar to that obtained for the core extracts in that most of the nitrogen-type compounds in the acid and base fractions appear in the weak base and very weak base class. Only the 360-day, 150° C saturate fraction contained strong base nitrogen compounds. This material must consist of high-molecular-weight hindered nitrogen compounds that did not react with the resins or with the silica-gel during the separation. Most of the nitrogen-type compounds in the neutral nitrogen fractions appear as nontitratable nitrogen; however, about half of the nitrogen in the 90-day, 200° C sample is very weak base type nitrogen as would be expected

TABLE 6. - Distribution of nitrogen-compound types present in fractions of the kerogen thermal degradation products

Heating time, days	Temperature, °C	Nitrogen content, relative weight percent of total nitrogen			
		Strong base	Weak base	Very weak base	Nontitratable nitrogen
<u>Acid fraction</u>					
360	150	<1	35	65	<1
90	200	<1	51	29	20
<u>Base fraction</u>					
360	150	<1	44	56	<1
90	200	<1	71	29	<1
<u>Neutral nitrogen fraction</u>					
360	150	<1	16	<1	84
90	200	<1	<1	46	54
<u>Aromatic fraction</u>					
360	150	<1	<1	5	95
90	200	<1	<1	80	20
<u>Saturate fraction</u>					
360	150	62	<1	<1	38
90	200	<1	<1	9	91

by our separation scheme. One aromatic fraction contained 80 percent very weak base nitrogen compounds and two aromatic fractions contained more than 90 percent nontitratable nitrogen-type compounds.

In general, the results for the kerogen thermal degradation product were about the same as those obtained for the extracts from the oil-shale core samples. Most of the nitrogen compounds consisted of very weak bases or nontitratable nitrogen compounds; however, weak bases predominate in two of the fractions. One saturate fraction contained predominantly strong base; but, in general, most nitrogen compounds were of the less basic forms.

#### SUMMARY

Most of the nitrogen compounds in the extracts from oil-shale core samples and in the kerogen thermal degradation products consisted of very weak bases or nontitratable nitrogen. There was some evidence of strong bases and weak bases in some of the fractions, but generally the nitrogen-compound types consisted of the less basic forms. Basic nitrogen components were the most extensive at the greatest depth of burial for the core extracts, suggesting alteration to more basic forms of nitrogen compounds similar to those found in shale-oil products. The results of nitrogen-compound type analysis for the kerogen thermal degradation products prepared at 150° and 200° C were about the same as those obtained from extracts from the oil-shale core samples. Additional analyses will have to be made in order to determine the effect of increased temperature upon the nitrogen compound-type distribution.

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Reference to specific trade names does not imply endorsement by the Bureau of Mines.

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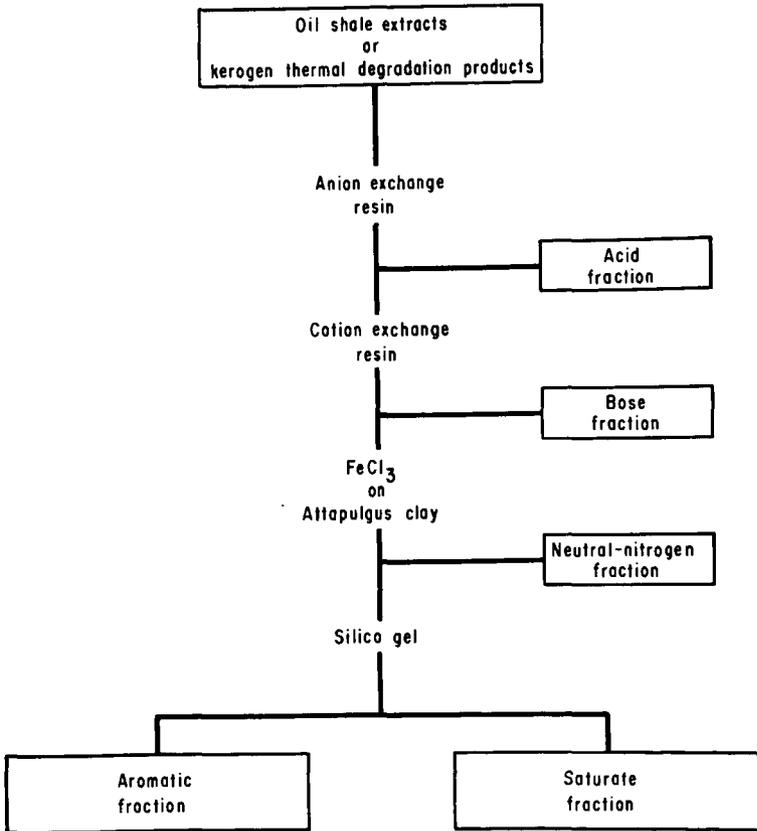


FIGURE I.-Fractionation scheme.

NITROGEN TYPES IN LIGHT DISTILLATES FROM ABOVEGROUND AND IN SITU  
COMBUSTION PRODUCED SHALE OILS

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## INTRODUCTION

There is some evidence that in situ retorted shale oils may have generally lower heteroatom and polar compound concentrations than aboveground retorted oils.<sup>1,2</sup> This could make in situ oils more attractive as refinery feedstock or as fuel sources than aboveground produced oils. To help determine if differences in heterocompound composition might exist between oils produced in these different ways, light distillate fractions (400° to 600° F nominal boiling range) from two different types of internal combustion retorting processes, one aboveground and one in situ, were compared in analyses. Both oils were produced in forward-burn type processes in which the exiting oil had the opportunity for contacting raw oil shale or included minerals.

The main difference in the two retorting processes was the time-temperature history of the oils produced. The aboveground process using crushed shale was a rapid-heat, high temperature process whereas the in situ process was apparently a slow-heat, low temperature process.<sup>1</sup> Direct gas-to-solids heat exchange occurs in both processes. Other imponderables such as the contact of the product oil with raw shale or air in either case, or raw or spent shale in situ could, of course, affect the character of the oil also.

The aboveground retorted oil (AGRO) was made from a shale oil produced from Colorado Green River Formation oil shale by the Union Oil Retort A<sup>3</sup> and its nitrogen bases have been studied before.<sup>4</sup>

Additional compound-type information is available from early work with a shale-oil naphtha<sup>5</sup> and a heavy gas oil<sup>6</sup> from a different aboveground combustion retort-produced crude (a Nevada-Texas-Utah type retort). Much of this compound-type information has been drawn upon in the following discussion when specific compound types are postulated as relating to a nitrogen- or oxygen-type value determined.

The in situ retorted oil (ISRO) studied here was made from a shale oil produced in the Northern Green River Formation near Rock Springs, Wyoming.<sup>7</sup> The shale used in the aboveground retort came from the Mahogany zone of the Piceance Basin in Colorado. Although the oil shales used were far apart, they were both of the Green River Formation. The Wyoming shale appears to be very similar in composition and properties to the extensively studied Mahogany zone oil shales.<sup>8</sup> Therefore, it was assumed that if both shales had been retorted in the same way, the oils produced would have been similar.

The light distillate from the aboveground retorted oil (AGRO) represents 15 percent of the crude, but the light distillate from the in situ retorted oil (ISRO) represents 50 percent of the crude. A larger proportion of light products appears to be characteristic of in situ-produced shale oils.<sup>1</sup> In table 1 the heteroatomic concentrations are shown for the two distillates. Both oils have similar nitrogen levels, but sulfur and oxygen are much lower in the ISRO. The nature of sulfur and oxygen compounds in shale oils has been summarized earlier<sup>9</sup> and in this symposium.<sup>2</sup> For production of refined products, sulfur and oxygen compound types apparently disappear with

hydrodenitrogenation before nitrogen types so that the nitrogen-type assessment seems of primary importance. For other contemplated uses of the resource, such as low grade burner fuel or as a source of specific chemical compounds, other heteroatomic compounds could be of comparable importance.

TABLE 1. - Heteroatoms in the shale-oil light distillates (400° to 600° F)

Element	Aboveground retorted oil	In situ retorted oil
Total nitrogen	<u>1.34</u>	<u>1.34</u>
Sulfur	.90	.53
Oxygen (by difference in ultimate analysis)	1.24	.35

The weight-average molecular weight for the oils corresponds to  $C_{14.3}$  or 200 based on simulated distillation. Using this value and assuming, for illustration, a maximum of heterocompounds with one nitrogen atom per molecule, the nitrogen levels shown in table 1 would represent 20 percent nitrogen-type compounds in either distillate. With similar assumptions for oxygen and sulfur, the AGRO would contain about 16 percent oxygen compounds and 6 percent sulfur compounds. The ISRO distillate would contain about 4 percent oxygen compounds and 3 percent sulfur compounds. Over 80 percent of the nitrogen in either of these oils is titratable as basic compounds.

This paper reports a comparison of some observed nitrogen types in these two oils (distillates). In addition, some oxygen types have been estimated because they appear to relate closely to the chemistry of the nitrogen types and there is a large difference in the elemental oxygen contents of the oils. Techniques for nitrogen-type characterization of shale oils developed and applied previously<sup>9,10</sup> have been used. Some techniques in a state of development for phenolic and carboxylic acid-type characterization of shale oils have been applied also.

## EXPERIMENTAL WORK

### Separation Procedure

The fractionation scheme used is depicted in detail in figure 1 and summarized in table 2. The procedure<sup>11</sup> involved anion-exchange fractionation followed by cation-exchange fractionation to prepare three acid fractions ( $A_1, A_2, A_3$ ) and three base fractions ( $B_1, B_2, B_3$ ). The raffinate from this procedure was further fractionated on a ferric chloride-Attapulugus clay column<sup>11</sup> into three fractions ( $N_0, N_1, N_2$ ). The first of these neutral fractions,  $N_0$ , is referred to also as the HC (hydrocarbon) fraction. Approximately 50 g of each distillate was fractionated using 50 g of each ion-exchange resin. Twenty grams of the raffinate from the ion-exchange resins was separated on 140 g of the ferric chloride-Attapulugus clay mixture.

The solvents were percolated at 20° C through the column removing most of the material in the fraction. The remaining amount of material was removed by percolating fresh solvent through the column and recirculating by distillation the solvent from the receiver back to the top of the column. Percolation was continued until there was no evidence of sample being desorbed from the column. Solvents were removed at reduced pressure, with slight rectification, and the recovered fractions were stored under an inert atmosphere at 0° C.

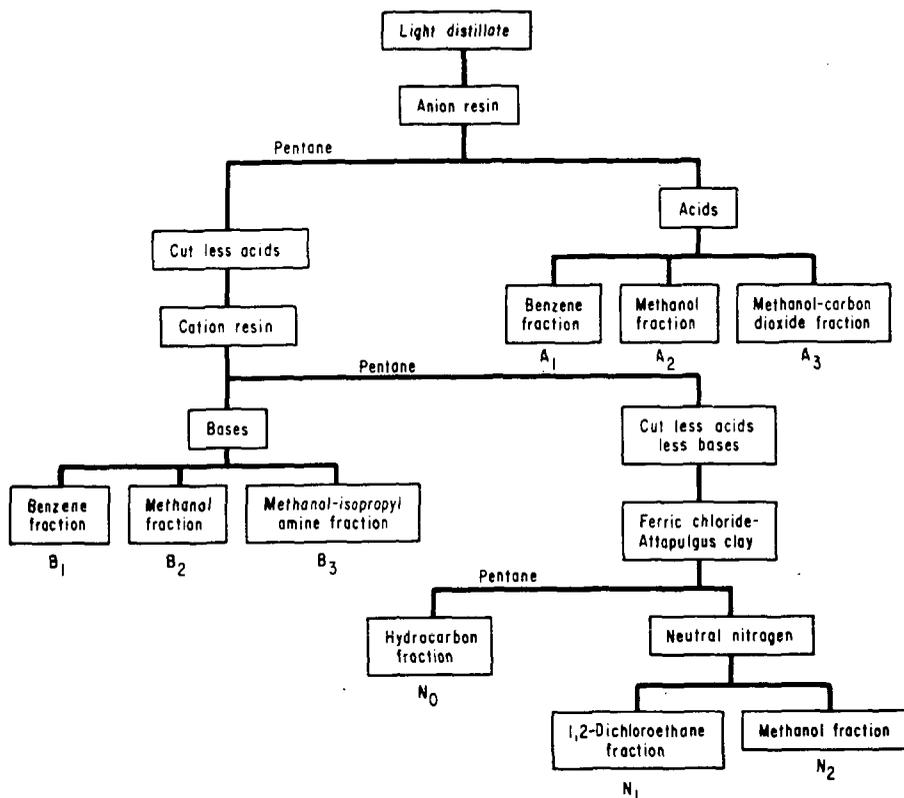


FIGURE 1. - Separation scheme.

### Reagents

#### Adsorbents

The anion- and cation-exchange resins were Rohm and Haas Amberlyst A-29 and Amberlyst A-15, respectively. The resins and ferric chloride supported on clay were prepared, activated, and extracted as described by Jewell.<sup>11</sup>

#### Solvents

N-pentane (99 percent, Phillips Petroleum) was purified by percolation through activated silica gel and by flash distillation. Benzene and methanol (reagent grade, J. T. Baker) were flash distilled as was 1,2-dichloroethane (Eastman Chemical Co.). The isopropyl amine (reagent grade, Eastman) was used as received. Acetonitrile and dioxane used in the titrations were purified by passing through activated alumina.

TABLE 2. - Anion-, cation-exchange, and ferric chloride-Attapulgus clay fractionation sequence

Fraction name	Desorbing solvent	Amount, wt-pct of distillate	
		Aboveground combustion retorted oil <sup>a</sup>	In situ combustion retorted oil <sup>b</sup>
<u>Acids From Anion-Exchange</u>			
<u>Resin Column</u>			
A <sub>1</sub> , very weak	Benzene	1.65	1.32
A <sub>2</sub> , very weak	Methanol	1.60	1.87
A <sub>3</sub> , weak	Methanol-carbon dioxide	1.32	.76
<u>Bases From Cation-Exchange</u>			
<u>Resin Column</u>			
B <sub>1</sub> , very weak	Benzene	.48	.57
B <sub>2</sub> , very weak	Methanol	.11	.08
B <sub>3</sub> , weak	Methanol-isopropylamine	8.45	10.12
<u>Neutrals From Ferric Chloride</u>			
<u>Clay Column</u>			
N <sub>0</sub> hydrocarbon	Pentane	79.44	81.85
N <sub>1</sub> first neutral	1,2-Dichloroethane	4.75	2.84
N <sub>2</sub> second neutral	Methanol	2.20	.63

<sup>a</sup> 2.6 Percent loss apportioned throughout.

<sup>b</sup> 1.6 Percent loss apportioned throughout.

#### Characterization Procedures

Procedures applied to shale oil previously have been described earlier<sup>4,10,12-19</sup> but will be summarized here along with procedures for oxygen types being developed. The sequence in the separation scheme is a potent characterization tool in itself and is used to supplement information obtained from more direct determinations described below. The various fractions have been given letter symbols and also names shown in table 2 to aid in discussion. Most of the fractions are actually heterogenous with respect to acid-base character.

#### Nitrogen Types

Total nitrogen value, N<sub>T</sub>, was determined with a reductive, hydrogen-nickel pyrolysis tube followed by an ammonia microcoulometer cell. A cool boat inlet system was used. Nonaqueous potentiometric titration was used to classify the nitrogen compounds<sup>12,13</sup> into strong base nitrogen, N<sub>SB</sub> (pKa > 8); weak base nitrogen, N<sub>WB</sub> (pKa 8 to 2); very weak base nitrogen, N<sub>VWB</sub> (pKa 2 to -2); and nonbasic nitrogen N<sub>N</sub> (pKa < -2). Examples of the various nitrogen compounds which fall in these basic types are: Strong base type (alkylamines), weak base type (pyridines, quinolines, anilines, highly ring alkylated pyrroles, N-methyl indoles, etc.), very weak base type [pyrroles, indoles, amides (including cyclic amides)], and nonbasic types (nitriles, carbazoles, second nitrogen atom in some diazo-compounds, etc.). Because some pyrroles and indoles titrate only about 70 percent, they contribute to the nonbasic nitrogen also. Infrared spectrometry of dilute solution absorption near 3,480 cm<sup>-1</sup> was used to determine pyrrolic NH type, nitrogen

$N_{N-H}$ .<sup>14,15</sup> Colorimetry<sup>16,17</sup> was used to determine  $\alpha$ - or  $\beta$ -unsubstituted pyrrolic-type nitrogen  $N_{pyr}$  (excludes carbazoles).

### Oxygen Types

Infrared spectrometry of dilute solutions in the free -OH region was used to classify oxygen types based on the frequency of the absorption supplemented by the fractionation sequence information. In acid fractions  $3,610\text{ cm}^{-1}$  was assumed specific for phenols and  $3,530\text{ cm}^{-1}$  was assumed specific for carboxylic acids.<sup>20,21</sup> In fractions generated below  $A_3$  in the sequence, the  $3,610\text{ cm}^{-1}$  absorption was assumed to represent sterically hindered phenolic types which were not taken up by the anion-exchange resin. The  $3,530\text{ cm}^{-1}$  region absorption for the post-acidic fractions was attributed to sterically hindered carboxylic-type compounds. Alcoholic OH, bridged phenolic OH, or some amide N-H absorptions would have been indistinguishable from that assigned to sterically hindered carboxylic OH. Spectra of the fractions were run at such dilution that Beer's law applied for the absorptions considered. Calibrations were made based on measured molar absorptivity values for the specific type compounds: Phenol and alkylated phenols, and octanoic and benzoic acids. The molar absorptivity for the sterically hindered OH-type calculations was assumed equal to that of the corresponding unhindered free OH.

## RESULTS AND DISCUSSION

### Distribution of Organic Material in Fractions

In table 2 the gravimetric recoveries of various fractions are compared for the two oils. The  $A_1$  and  $A_2$  acid fractions together represent about 3.2 percent of either oil. The AGRO fractionates equally between the two, but the ISRO is split with  $A_2:A_1$  equal to 1.5. In the last acid fractions,  $A_3$ , the AGRO:ISRO ratio is 1.7. The quantities of base fractions are similar, as are those of the hydrocarbon fractions ( $N_0$ ). The  $N_1$ , AGRO:ISRO ratio is 1.67 and the  $N_2$  ratio is 3.5. Based on the data in table 2, the distillates show some differentiation in distribution of the very weak acid fractions. The AGRO distillate shows considerably more weak acid present than the ISRO distillate. The neutral fractions adsorbed by ferric chloride represent twice as much material in the AGRO as in the ISRO distillate. Basic and neutral hydrocarbon fractions are comparable in quantity for the two distillates.

### Titration

#### Distillates

The titration data for the two distillates and fractions as weight percent of the distillates are shown in table 3. Total nitrogen concentrations for the two oils are the same. The AGRO titration shows 0.79 percent  $N_{VWB}$  compared to 0.90 percent  $N_{VWB}$  for the ISRO. The  $N_{VWB}$  value in the AGRO is 0.42 percent compared to 0.22 percent in the ISRO. The AGRO oil shows slightly less  $N_N$  than the ISRO. In summary the titratable bases are similar in amount for the two distillates. The ratio AGRO:ISRO for  $N_{VWB}$  is 0.88 and for  $N_N$  1.9 indicating lower basicity--i.e., fewer weak bases and more very weak bases--for the AGRO although there is a slightly higher  $N_N$  value for the ISRO.

#### Acidic Fractions

The very weak acid fractions  $A_1$  plus  $A_2$  AGRO:ISRO,  $N_{VWB}$  ratio is 1.8 which is in the same direction as the similar ratio for the whole distillates. In the  $A_2$  fractions the AGRO:ISRO,  $N_{VWB}$  ratio is 10 although the amount of base represented is small. Bases in the  $A_3$  fractions are low in quantity and comparable.

TABLE 3. - Distribution of weakly basic, very weakly basic, and nonbasic nitrogen in fractions and distillates

Fraction	Nitrogen, wt-pct of light distillate					
	Aboveground			In situ		
	$N_{WB}$	$N_{VWB}$	$N_N$	$N_{WB}$	$N_{VWB}$	$N_N$
Distillate	0.79	0.42	0.13	0.90	0.22	0.22
A <sub>1</sub>	.010	.056	.017	.009	.045	.023
A <sub>2</sub>	.013	.031	.004	.015	.003	.007
A <sub>3</sub>	.005	0	.005	.004	.001	.006
B <sub>1</sub>	.016	.012	.005	.026	.006	.005
B <sub>2</sub>	---	.009 <sup>a</sup>	---	---	.005 <sup>a</sup>	---
B <sub>3</sub>	.59	0	.033	.72	0	.023
N <sub>1</sub>	.014	.130	.056	.010 <sup>b</sup>	.085	.034
N <sub>2</sub>	.041	.057	.054	.013 <sup>b</sup>	.019	.004
N <sub>0</sub>	.001 <sup>b</sup>	.074	.038	.002	.015	.070
	Recoveries					
Total in fractions <sup>c</sup>	.69	.37	.21	.80	.18	.17
Change in type	-.10	-.05	+.08	-.10	-.04	-.05

<sup>a</sup> Too small to titrate; this figure is based on the total nitrogen.

<sup>b</sup> Approaches strong-base titration characteristic potential.

<sup>c</sup> Total nitrogen recovery AGRO = 94 percent; ISRO = 86 percent.

### Basic Fractions

In the two very weak base fractions, B<sub>1</sub> and B<sub>2</sub>, the overall basicity of the bases titrated is less for the AGRO fractions as in the original distillates. The weak base fractions for both oils titrate almost completely as weak bases with an AGRO:ISRO  $N_{WB}$  ratio of 0.82. A small amount of nonbasic nitrogen is present.

### Neutral Fractions

The amount of nitrogen in the three neutral fractions which titrate as weak base or very weak base is remarkable. The total nitrogen,  $N_T$ , in these fractions is 0.465 weight-percent of the AGRO and 0.252 percent of the ISRO. Based on an assumption of one nitrogen atom per molecule and a molecular weight in this distillate of about 200, these figures would represent 7 weight percent of the distillate as nitrogen-containing compounds retained by the ion-exchange resins for the AGRO and about 4 percent for the ISRO distillate. The potential for polymerization of pyrroles, and more slowly indoles, in acid media<sup>22</sup> and for their loss to cation-exchange resins<sup>23</sup> is well known so that the question of artifact formation of neutrals through polymerization was considered. Previous work<sup>4</sup> showed less than 0.5 weight percent polymer in neutrals from cation-exchange fractionation of the AGRO. Weak base titrations in this paper approaching strong base character were observed for the AGRO-N<sub>0</sub> fraction and for the ISRO-N<sub>0</sub> and N<sub>2</sub> fractions. Because no strong base titration is observed for the original distillates, this suggests possible pyrrole trimer formation which would have a strongly basic nitrogen atom in addition to two pyrrolic-type nitrogen atoms. The nitrogen and oxygen types observed in the neutral fractions are treated in the following discussion as the monomeric entities the functional parts would represent.

The summation of titrations on the AGRO fractions  $N_0$ ,  $N_1$ , and  $N_2$  indicates them to contain about twice the basic nitrogen concentration of the ISRO neutrals. These levels represent about 26 percent of the basic nitrogen and 114 percent of the neutral nitrogen for the AGRO and about 13 percent of the basic and 49 percent of the neutral nitrogen for the ISRO.

The overall nitrogen recovery from table 3 was 94 percent for the AGRO, which is probably within the experimental error involved, but only 86 percent for the ISRO, which probably indicates a real loss of nitrogen-containing compounds to the columns. The oils showed similar decreases in  $N_{WB}$  and  $N_{VWB}$  as shown at the bottom of table 3, but the AGRO showed an apparent increase in  $N_N$  compared to a loss in the ISRO  $N_N$ . The increase in  $N_N$  for the AGRO could represent a shift in more basic nitrogen to nonbasic nitrogen. Since the shift is toward formation of neutral nitrogen, oxidation might be a suspected cause. Care was taken to prevent this by nitrogen purging. Another possible explanation is that titration characteristic potentials depend to some extent on the matrix as shown by Buell.<sup>18</sup> We assume the latter to be the case and that the net decrease in basic nitrogen and increase in  $N_N$  in the AGRO occurred for this reason.

In summary the distillates and fractions indicate that the AGRO has lower basicity in general than the ISRO. This is consistent with a picture of a more oxidized oil since, for example, oxidation of most amines produces weaker bases or nonbasic compounds. There was appreciable loss of nitrogen in the fractionation of the ISRO, but this was not so for the AGRO. Questions of artifacts possibly introduced by the separation scheme have not been thoroughly assessed but have been discounted in the following discussions.

#### Pyrrolic-Type Nitrogen

Table 4 shows the distribution of pyrrolic-type nitrogen in the oils and their fractions. The notable differences here are the larger  $N_{N-H}$  in the AGRO and the large loss from this category in the fractionation.

The loss of  $N_{N-H}$  is interpreted as follows. Because the initial values of pyrrolic-type nitrogen in the AGRO distillate are  $N_{NH} = 0.21$  and  $N_{pyr} = 0.11$ , the latter value does not include 0.10 weight percent of the distillate which represents closely the loss of  $N_{N-H}$  through the fractionation sequence. All the other pyrrolic nitrogen values in the original oils are preserved in the fractions within experimental error. The observed loss of 0.10 weight-percent of the AGRO distillate as  $N_{N-H}$  represents a real difference between these oils. One type of material this could represent is carbazoles, but these are believed to be excluded by the distillate cut points.<sup>4</sup> Pyrroles or indoles with  $\alpha$  and  $\beta$  substituents are an alternative interpretation fitting this boiling range.<sup>4</sup> Pyrroles are known to be lost rapidly to cation-exchange resins while indoles react at a much slower rate.<sup>23</sup> Based on these facts, the  $N_{N-H} = 0.11$  weight-percent of the oil is postulated to represent  $\alpha$ - and  $\beta$ -substituted pyrroles. Using this assumption that pyrroles have been lost to the cation-exchange resin and that the pyrrolic nitrogen remaining is indole type, the ratio of N-H pyrrole nitrogen to indole nitrogen in the AGRO would be about unity but for the ISRO the ratio would be about 0.23. The  $N_{pyr}$  values are largely recovered in the fraction and probably represent mostly indole-type nitrogen assumed shown by the  $N_{N-H}$  values in the recovered fractions.

It might be expected that the higher temperature oil, the AGRO, would show  $N_{N-H}$  predominantly because as shown by Jacobson<sup>24,25</sup> N-alkyl pyrroles and indoles rearrange thermally to C-alkyl isomers. Other unknowns such as the contact of the in situ oil with minerals in the post-retorting region could account for differences however. That highly substituted N-H type pyrroles appear to be lost preferentially to the columns in this work is surprising because these types are the more stable with respect to polymerization in acidic media.<sup>22</sup> This subject requires further investigation.

TABLE 4. - Distribution of pyrrolic-type nitrogen

Fraction	Nitrogen, wt-pct of light distillate			
	Aboveground		In situ	
	N <sub>N-H</sub>	N <sub>pyr</sub>	N <sub>N-H</sub>	N <sub>pyr</sub>
Original light distillate	0.21	0.11	0.16	0.11
A <sub>1</sub>	.013	.017	.042	.046
A <sub>2</sub>	.0022	.0008	.0023	.0016
A <sub>3</sub>	.0016	.0002	.0003	.0001
B <sub>1</sub>	.0018	.0016	.0028	.0026
B <sub>2</sub>	.0005	.0003	.0002	.0002
B <sub>3</sub>	.0027	.0017	.0028	.0008
N <sub>1</sub>	.078	.043	.056	.035
N <sub>2</sub>	.0077	.0042	.0032	.0011
N <sub>0</sub>	.0016	.014	.024	.0023
<u>Recoveries</u>				
Total in fractions	.11	.083	.13	.090
Change in type	-.10	-.03	-.03	-.02

In the first acidic fractions, A<sub>1</sub>, the AGRO shows about one-fourth of the N<sub>N-H</sub> and one-third of the N<sub>pyr</sub> that the ISRO fraction does. Both oils show concentration of N<sub>N-H</sub> and N<sub>pyr</sub> in the first neutral fraction. The AGRO N<sub>0</sub> fraction shows 6 times the N<sub>pyr</sub> of the other oil, but the N<sub>N-H</sub> values are reversed with the ISRO showing 15 times the AGRO N<sub>N-H</sub> value.

#### Oxygen-Containing Types

##### Heteroatoms Per Molecule

Tables 5 and 6 show summaries of nitrogen types and hydroxylic types for the AGRO fractions and the ISRO fractions, respectively. The results are tabulated in milliequivalents per gram in the fraction. These numbers should be compared with a molal concentration of organic material of approximately 5 millimoles per gram for a distillate of M.W. 200 like the distillates we are discussing. The polar compounds in these distillates may be heavier than this but will not change the interpretation much. The total of nitrogen and oxygen atomic concentrations observed runs as high as 6.36 in the fractions indicating an average of as much as 1.3 heteroatoms per molecule in some cases. The oils appear similar in respect to the heteroatom-per-molecule values based only on nitrogen and hydroxylic oxygen.

##### Acid Fractions

The oils differ markedly in their hydroxylic composition in the acid fractions. It was expected from the character of the anion-exchange resin that most of the phenols would be desorbed in the first two fractions, A<sub>1</sub> and A<sub>2</sub>, and any carboxylic acids would appear in A<sub>3</sub>. For the AGRO this appears true. Except for a minor amount of phenolic type in A<sub>3</sub>, the fraction is carboxylic acid types. On the other hand for the ISRO, A<sub>3</sub> contains largely phenolic types with a minor amount of carboxylic types. The appearance of major amounts of phenolic types in A<sub>3</sub> for the ISRO suggests these phenolic types have electron-withdrawing substituents present to enhance their acidity. Substituents<sup>20</sup> which could produce considerable enhancement of the acidity of phenols are for example formyl-, cyano-, or nitro- although no identification of these types of

TABLE 5. - Nitrogen and oxygen types in an aboveground, combustion retorted light distillate

Fraction	Wt-pct of oil	Heteroatomic type, milliequivalents per gram of fraction									
		N <sub>WB</sub>	N <sub>VWB</sub>	N <sub>N</sub>	N <sub>T</sub>	N <sub>N-H</sub>	N <sub>pyr</sub>	Phenolic -OH	Carboxylic -OH	Total -OH <sub>T</sub>	Total N <sub>T</sub> + OH <sub>T</sub>
A <sub>1</sub>	1.65	0.42	2.42	0.73	3.57	0.58	0.77	2.50	0.13	2.63	6.20
A <sub>2</sub>	1.60	.60	1.39	.20	2.19	.10	.037	3.99	.19	4.18	6.36
A <sub>3</sub>	1.32	.29	0	.28	.57	.091	.013	.91	2.42	3.33	3.90
B <sub>1</sub>	.48	2.35	1.82	.69	4.86	.28	.25	.04	.06	.10	4.96
B <sub>2</sub>	.11	-	5.52 <sup>b</sup>	-	5.52	.31	.19	.03	0	.03	5.55
B <sub>3</sub>	8.45	4.98	0	.28	5.26	.024	.015	.01	0	.01	5.27
N <sub>1</sub>	4.75	.21	1.99	.84	3.04	1.21	.66	.57	.02	.59	3.63
N <sub>2</sub>	2.20	1.32	1.84	1.74	3.99	.26	.14	.04	.07	.11	4.10
N <sub>0</sub>	79.44	.0007	.065	.034	.10	.001	.013	0	0	0	.10

<sup>a</sup>Partially soluble. <sup>b</sup>Not titrated because of small size of fraction.

TABLE 6. - Nitrogen and oxygen types in an in situ combustion retorted light distillate

Fraction	Wt-pct of oil	Heteroatomic type, milliequivalents per gram of fraction									
		N <sub>WB</sub>	N <sub>VWB</sub>	N <sub>N</sub>	N <sub>T</sub>	N <sub>N-H</sub>	N <sub>pyr</sub>	Phenolic -OH	Carboxylic -OH	Total -OH <sub>T</sub>	Total N <sub>T</sub> + OH <sub>T</sub>
A <sub>1</sub>	1.32	0.50	2.43	1.26	4.19	2.29	2.51	1.45	0.058	1.51	5.70
A <sub>2</sub>	1.87	.56	.13	.25	.944	.089	.061	4.89	.109	5.00	5.94
A <sub>3</sub>	.76	.34	.084	.006	.430	.031	.014	5.02	.715	5.74	6.17
B <sub>1</sub>	.57	3.31	.72	.69	4.72	.36	.33	.08	.02	.10	4.82
B <sub>2</sub>	.08	-	4.21 <sup>b</sup>	-	4.21	.21	.19	.86	.05	.91	5.12
B <sub>3</sub>	10.12	5.11	0	.16	5.27	.020	.006	.01	0	.01	5.28
N <sub>1</sub>	2.84	.26	2.15	.86	3.27	1.43	.89	.09	.03	.12	3.39
N <sub>2</sub>	.63	1.46	2.14	.48	4.08	.37	.12	.08	.02	.10	4.18
N <sub>0</sub>	81.85	.002	.013	.061	.076	.021	.002	0	0	0	.08

<sup>a</sup>Partially soluble. <sup>b</sup>Not titrated because of small size of fraction.

materials has been made in shale oils. The phenolic:carboxylic molal ratios are about 4 for the AGRO and about 16 for the ISRO. The  $A_3$  fractions were of limited solubility in carbon tetrachloride so that the actual acid concentrations may have been larger than observed. If fraction AGRO,  $A_3$  were presumed to be 100 percent carboxylic acids plus phenols, the phenolic:carboxylic ratio could be as low as 3. Higher  $N_N$  in the ISRO- $A_1$  fraction correlates with the greater pyrrolic nitrogen-type values observed in table 4. The  $N_{VWB}$  for the AGRO- $A_2$  fractions is 10 times that for the other oil. It does not correlate with N-H so this material may be amide type, including cyclic amide (pyridone, quinolone, etc.) types which have been indicated before.<sup>4</sup> Additional neutral nitrogen in the AGRO- $A_3$  fraction could also be placed in this category for the same reasons.

#### Base Fractions

Small amounts of hydroxyl appear in the base fractions and are comparable for the oils except in the  $B_2$  fractions. This fraction of either oil is such a small amount of the oil it will not be discussed further.

#### Neutral Fractions

No hydroxyl absorption appeared in the  $N_0$  (hydrocarbon) fractions. The AGRO- $N_1$  fraction shows six times the hydroxyl absorption that the ISRO- $N_1$  fraction does. In addition, the AGRO- $N_1$  fraction is 4.75 weight-percent of the oil whereas the ISRO- $N_1$  fraction is 2.84 weight-percent of its oil. The AGRO- $N_1$  fraction represents a much larger hydroxyl concentration in the oil than the ISRO- $N_1$  fraction. The AGRO- $N_2$  fraction is 2.20 weight-percent of its oil and the ISRO- $N_2$  fraction is only 0.63 percent of its oil although it has slightly higher -OH concentration. The summation of hydroxyl types in the neutral fractions gives a molar ratio AGRO:ISRO of 9 in the oils with the concentration of these hydroxylic neutral types in the AGRO being only 0.03 milliequivalent/gram oil.

In the neutral fractions, nitrogen-containing types appear much more abundant than hydroxyl types. From the AGRO neutral fractions the summation of nitrogen concentrations is 0.31 meq/g oil and from the ISRO neutral fractions the nitrogen concentration is 0.18 meq/g oil either of which is over an order of magnitude above the hydroxyl-type concentrations found in either.

#### Nonhydroxylic Oxygen Types

The comparison of the concentrations in the distillates of each of the heteroatoms S, N, and O is shown in table 7 along with O-phenolic, O-carboxylic, and  $N_{VWB}$  found in this work. The value of phenolic plus carboxylic oxygen in the AGRO = 0.23 and in the ISRO = 0.17. This is about 77 percent of the ISRO distillate total oxygen but only about 30 percent of the AGRO distillate oxygen. Assuming  $N_{VWB}$  to contain one oxygen atom per molecule and including it in the summation of oxygen types would account for 150 percent of the ISRO distillate oxygen but only 70 percent of the AGRO distillate oxygen. This suggests a large portion of the oxygen in the AGRO occurs in other forms than we have considered. Dinneen<sup>5</sup> has shown the presence of benzofuran in an AGRO-type naphtha and perhaps these types occur in this distillate also. Combinations of oxygen with sulfur could also account for the rest of the oxygen. Previous examination<sup>4</sup> of the AGRO showed sulfoxides absent but other forms were not determined.

### CONCLUSIONS

This paper shows that there can be considerable variation in the distribution of some nitrogen and oxygen types in two combustion retorted shale oils. It is not presently possible to infer

TABLE 7. - Comparison of heteroatomic types in 400 to 600° F distillate fractions

Species	Concentration in distillate, meq/g	
	Aboveground	In situ
S <sub>T</sub>	0.28	0.17
N <sub>T</sub>	.96	.96
O <sub>T</sub>	.78	.22
<u>Oxygen Accounted For</u>		
<u>O<sub>T</sub></u>		
O-phenolic	.15	.15
O-carboxylic	.08	.02
N <sub>VWB</sub>	.30	.16
Total	.53	.33

much about retorting mechanism from these data because of the many unknowns in the post-retorting regions in the production of the oils. The analyses of these two oils show many qualitative differences in polar fractions which could form the basis for a retorting index or parameter for comparative evaluation of shale oils.

#### SUMMARY

The differences in observed chemical types for the AGRO and ISRO could be interpreted largely in terms of a greater oxygen content in the AGRO. Part of this oxygen in the AGRO may be showing up as higher very weak base content (probably amides) compared to the ISRO distillate. The molal ratio of weak bases AGRO:ISRO is 0.88 and the ratio of very weak bases AGRO:ISRO is 1.9. The AGRO pyrrole:indole ratio calculated is unity, but the ISRO pyrrole:indole ratio is 0.23. The molal ratio of phenolic:carboxylic acids is about 5 for the AGRO but about 16 for the ISRO. Small amounts of hydroxyl occur in the neutral nitrogen fractions of the oils but are dwarfed by the nitrogen content. The nonhydrocarbon neutral fractions of the AGRO represent twice the concentration in the oil that the similar ISRO neutral fractions do. Hydrocarbon fractions from both oils show appreciable (0.3 to 0.5 percent) pyrrolic nitrogen concentrations. To account for the oxygen level in the AGRO, oxygen types other than hydroxylic, carboxylic, and amidic must be considered to account for 30 percent of the AGRO oxygen, but the ISRO oxygen could be accounted for this way. Although marked differences in the oils can be observed, conclusions about differences in retorting based on the heterocompound types found are tenuous because of the many questions involved in the post-retorting history of the oils.

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ABSTRACT

Crude shale oil from in situ retorting of Wyoming oil shale by the underground combustion method was hydrocracked over a nickel-molybdena catalyst in a single-pass operation at 800°F, 1,500 psig pressure, and 0.5 volume of oil per volume of catalyst per hour. The liquid product was fractionally distilled into naphtha and heavier oil. The fractions distilling above naphtha were collected at 5°F intervals and nitrogen percentages were determined on these. The distribution of nitrogen in 54 distillate fractions is reported.

## NITROGEN TYPES IN SYNCRUDES FROM IN SITU CRUDE SHALE OIL

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## INTRODUCTION

Crude shale oils produced by in situ combustion retorting of Green River oil shale contain more than twice as much nitrogen as high-nitrogen petroleum crudes. Because existing refineries would not be able to cope with the high nitrogen content of shale oil if it were a substantial part of the refinery feed, the National Petroleum Council (NPC) has suggested (1) that crude shale oil be upgraded at the retorting site by a process of catalytic hydrogenation to produce a premium feedstock called "syncrude."

We have already shown (2) that a premium refinery feedstock can be produced from in situ crude shale using methods suggested by the NPC. We have also determined (3) the nitrogen-compound types remaining in the finished syncrude since it would be these compounds with which a refiner would have to deal if he used a similar crude in his refinery feed.

In the NPC process, the crude shale oil is distilled to produce naphtha, light oil, heavy oil, and residuum. The residuum is processed in a delayed-coking unit to produce petroleum coke and a vapor stream. The vapor stream from the coking unit flows back to the crude distillation unit for separation into various fractions. The naphtha, light oil, and heavy oil are subsequently hydrogenated to remove nitrogen and sulfur and to reduce the viscosity and pour point of the finished syncrude.

One alternate method of preparing syncrude from crude shale oil would be to hydrogenate the total crude shale oil in a one-step process. This would not only reduce the number of processing units required at the retorting site, but could result in higher yields of liquid and gaseous products since the coking step would be eliminated.

The purpose of the present work was to prepare a syncrude of total nitrogen content comparable to that of an NPC-type syncrude produced earlier (2-3) by catalytically hydrogenating the total in situ crude shale oil in one step, and to determine the amounts and types of nitrogen compounds remaining in the finished syncrude. Yields of products, properties of the finished syncrude, and amounts and types of nitrogen compounds remaining in the one-step syncrude are compared with those of a multistep syncrude prepared by an NPC-type process.

## PROPERTIES OF IN SITU CRUDE SHALE OIL

The crude shale oil used in this work, the same as that used in our previous studies (2-3), was obtained from an in situ combustion retorting experiment near Rock Springs, Wyo., during the last week of the experiment. It is considered to be a representative "steady state" oil. Properties of the in situ crude shale oil are shown in table 1.

## ANALYTICAL METHODS

Standard ASTM procedures were used wherever practicable. Catalyst deposit percentages were calculated from the weights of carbon dioxide collected on ascarite when the deposits were burned with a stream of air passed through the reactor at the end of a run. Hydrogen consumption was calculated from precise measurements of the amount of hydrogen fed to the unit and that collected in the product gas. Total nitrogen values in the oils were determined with a reductive, hydrogen-nickel

TABLE 1. - Properties of in situ crude shale oil

Gravity, ° API	28.4
Nitrogen, weight-percent	1.41
Sulfur, weight-percent	0.72
Pour point, ° F	40
Viscosity, SUS at 100° F	78
Carbon residue, weight-percent	1.7
Ash, weight-percent	0.06

pyrolysis tube and an ammonia microcoulometer. Sulfur values were determined with an oxygen combustion tube and a sulfur dioxide microcoulometer. Samples were water washed. Samples for sulfur analysis were also extracted with mercury and filtered.

Nonaqueous potentiometric titration (4-7) was used to classify the nitrogen types into weak-base (pKa + 2 to + 8), very weak-base (pKa - 2 to + 2), and neutral types (nontitratable). Infrared spectrometry (6-8) was used to determine the concentration of pyrrolic N-H type nitrogen (which includes carbazoles). Colorimetry (with p-dimethylaminobenzaldehyde) (6, 9-10) was used to determine pyrroles and indoles with an unsubstituted  $\alpha$  or  $\beta$  position which are termed here pyrrolic nitrogen (excludes carbazoles).

#### EXPERIMENTAL

The total in situ crude shale oil was hydrogenated over a presulfided, nickel-molybdenum catalyst in a fixed-bed, bench-scale unit. The crude oil was mixed with 5,000 scf of hydrogen per barrel and passed downflow over the catalyst bed at a rate of 0.7 weight of oil per weight of catalyst per hour ( $W_o/W_c/hr$ ). The catalyst was contained in a stainless steel reactor. The temperature of the reactor was maintained at 815° F by means of a four-zone electric furnace, each zone of which was independently controlled. Pressure in the reactor was maintained at 1,500 psig by means of a backpressure regulator, and liquid products were collected in a separator maintained at 200 psig. Tail gas from the separator was metered and sampled. The hydrogenation was accomplished in a continuous 10-day run.

Liquid products were drained from the separator after each 24-hour period of operation and washed with water to remove ammonia and hydrogen sulfide before a sample was taken for analysis. Aliquot portions of the daily liquid products were combined to form the finished syncrude. A portion of the syncrude was then fractionated to obtain a C<sub>5</sub> - 175° F light naphtha, a 175°-350° F heavy naphtha, a 350°-550° F light oil, and a 550° F+ heavy oil. Preparation of the multistep syncrude was described in detail earlier (2) but consists basically of a distillation unit, a delayed coker, and three catalytic units for hydrogenations of heavy oil, light oil, and naphtha separately.

#### RESULTS AND DISCUSSION

In table 2, the yields of products from hydrogenation of the total in situ crude shale oil (one-step) are compared with yields of products from separate hydrogenation of various distillate fractions (multistep) (2). The yield of C<sub>4</sub>+ liquid product was 104.5 volume-percent for the one-step process and 103 volume-percent for the multistep process. The yield of C<sub>5</sub>+ liquid product was only slightly higher for the one-step process, but there was a substantial decrease in the yield of heavy oil with a corresponding increase in the yields of gas, naphtha, and light oil. Hydrogen consumption was somewhat higher for the one-step process (1,475 scf/bbl versus 1,280 scf/bbl) as the result of the increased depth of conversion.

TABLE 2. - Comparison of product yields from multistep and one-step hydrogenation of in situ crude shale oil

Product, percent of crude	Multistep		One-step	
	Weight	Volume	Weight	Volume
C <sub>4</sub> + liquid product	93.81	102.99	95.27	104.54
C <sub>5</sub> + liquid product	92.66	101.24	93.42	101.67
C <sub>5</sub> - 175° F light naphtha	2.34	2.96	2.62	3.33
175°-350° F heavy naphtha	19.60	22.65	21.14	24.20
350°-550° F light oil	45.68	49.45	51.44	55.03
550°-850° F heavy oil	25.04	26.18	18.22	19.11
Coke (catalyst deposit)	<sup>1/</sup> 3.24			0.13
Hydrogen	<sup>2/</sup> -2.19		<sup>3/</sup> -2.53	
Methane	0.69		1.31	
Ethane	0.68		1.37	
Ethylene	0.03		-	
Propane	0.72		1.41	
Propylene	0.09		-	
Isobutane	0.26	0.41	0.46	0.76
Butane	0.79	1.20	1.39	2.11
Butenes	0.10	0.14	-	
Ammonia	1.57		1.69	
Hydrogen sulfide	0.62		0.75	

<sup>1/</sup> Multistep process includes a coking step.

<sup>2/</sup> 1,280 scf/bbl.

<sup>3/</sup> 1,475 scf/bbl.

Table 3 shows the effect of operating time on the nitrogen contents and gravi-

TABLE 3. - Effect of operating time on nitrogen contents, denitrification rate constants and gravities of liquid product

Days on stream	Nitrogen content of liquid product, ppm	Denitrification rate constant $\ln N_0/N_t (.7)$	Gravity, ° API
1	51	5.26	44.2
2	83	4.79	43.8
3	148	4.20	43.8
4	177	4.00	43.3
5	195	3.92	43.2
6	207	3.86	43.2
7	238	3.72	43.2
8	306	3.47	43.1
9	316	3.44	43.1
10	338	3.37	43.0

ties of the liquid products. Under the conditions used in this experiment there was a significant decrease in the activity of the catalyst during the course of the run. This indicates that crude shale oil could not be processed under these severe conditions in a fixed-bed unit without frequent regeneration of the catalyst.

Properties of the syncrudes and their various distillate fractions are shown in table 4. Sulfur contents of both of the syncrudes discussed was near the lower

TABLE 4. - Comparison of syncrudes and distillate fractions from multistep and one-step hydrogenation of in situ crude shale oil

	Multistep	One-step
Syncrude, volume-percent of in situ crude	102.99	104.50
Gravity, ° API	43.9	44.6
Nitrogen, ppm	250	225
Sulfur, ppm	5	6
Butanes and butenes, volume-percent of syncrude	1.7	2.7
C5-350° F naphtha, volume-percent of syncrude	24.8	26.3
Gravity, ° API	54.7	53.4
Nitrogen, ppm	1	83
Sulfur, ppm	8	3
350°-550° F light oil, volume-percent of syncrude	48.1	52.7
Gravity, ° API	41.5	38.5
Nitrogen, ppm	79	200
Sulfur, ppm	1	5
550° F+ heavy oil, volume-percent of syncrude	25.4	18.3
Gravity, ° API	35.6	36.2
Nitrogen, ppm	935	513
Sulfur, ppm	9	5

level of experimental uncertainty. Although sulfur could be detected down to 0.5 ppm, the significance of a few parts per million is doubtful because of difficulty in removing hydrogen sulfide and colloidal sulfur. The total nitrogen contents of the syncrudes were essentially equal; however, there were substantial differences in the distribution of nitrogen in the distillate fractions.

In table 5, the distribution of nitrogen in the two syncrudes and their distillates is shown. Although total nitrogen in the two syncrudes is comparable, it is seen that the nitrogen in the one-step syncrude occurs in significantly higher concentrations in the heavy naphtha and light oil fractions and in lower concentration in the heavy oil fraction in comparison with the multistep syncrude.

In table 6 the nitrogen distributions as percent of total nitrogen in the syncrudes and their distillates is summarized according to basic and neutral types. Almost all (86.5 percent) of the nitrogen in the multistep syncrude appears in the heavy oil, but for the one-step syncrude only about half (49.7 percent) appears in the corresponding distillate. The neutral nitrogen in these heavy oils is about 40 percent of the total nitrogen in the syncrude. This neutral nitrogen appears to be largely carbazole type in either oil. This can be inferred from table 5 by the large values for N-H type nitrogen and small values for ( $\alpha$  or  $\beta$  unsaturated) pyrrolic-type nitrogen. A predominance of carbazole structures was indicated by mass spectrometry in the characterization of the multistep heavy oil (3), but mass spectrometry was not used in characterization of the one-step syncrude. The fate of the neutral nitrogen then appears similar in either multistep or one-step processing; the neutral type concentrating in the heavy oil while other, more readily hydrogenated types react.

As shown in table 6 the amounts of basic nitrogen (weakly basic plus very weakly basic nitrogen) relative to the total nitrogen is similar for the two syncrudes, but differs markedly for the corresponding distillate fractions in the two oils as does the occurrence of primary and secondary amines. In the multistep



TABLE 6. - Basic and neutral nitrogen distribution in syncrudes and their fractions

	Nitrogen, percent of total in syncrude			
	Total	Basic	Neutral	I°, II° amines <sup>1/</sup>
Syncrude <sup>2/</sup>	100	60.0	40.0	0
Syncrude <sup>3/</sup>	100	64.4	35.6	3.5
Light naphtha <sup>2/</sup>	0	0	0	0
Light naphtha <sup>3/</sup>	0	0	0	0
Heavy naphtha <sup>2/</sup>	0	0	0	0
Heavy naphtha <sup>3/</sup>	10.6	10.5	0.1	2.2
Light oil <sup>2/</sup>	13.5	13.5	0	0
Light oil <sup>3/</sup>	39.7	34.9	4.8	2.0
Heavy oil <sup>2/</sup>	86.5	42.9	43.6	0
Heavy oil <sup>3/</sup>	49.7	12.9	36.8	0

<sup>1/</sup> I° and II° amines included in basic nitrogen.

<sup>2/</sup> Multistep.

<sup>3/</sup> One-step.

syncrude, the weakly basic nitrogen compound types were shown to be largely pyridines, and the very weakly basic nitrogen compound types were shown to be largely pyrroles and indoles by a combination of techniques including mass spectrometry. Although mass spectrometry was not used in characterization of the one-step syncrude, the compound types are probably similar.

Presence of large amounts of nitrogen in the light oil and heavy naphtha of the one-step syncrude can be attributed to hydrocracking and thermal cracking reactions in the heavy oil and residual portions of the crude. Buildup of nitrogen compounds in the lighter oil products from heavy oil hydrogenation in the multistep syncrude production was observed in earlier work (3). This lighter oil produced from the heavy oil hydrogenation is then hydrogenated in the various lighter oil reactors in the multistep process (2). The basic types are readily converted to ammonia as found by others (4, 12) and as evidenced by the relatively mild conditions required to reduce the nitrogen content in the fractions boiling below 550° F to the low values in table 6 (2).

The occurrence of small amounts of primary and secondary amines in both the heavy naphtha and light oil fractions from the one-step syncrude is consistent with the work of Brown (11) who found anilines made up nearly one-third of the tar bases from a recycle, hydrocracked shale-oil naphtha. None of these amines were found in the multistep syncrude product although anilines were identified in intermediate fractions (light oil products from the heavy oil hydrogenation unit). In the multistep process these amines are removed readily in the lighter oil reactors as part of the basic types which were discussed in general earlier.

#### SUMMARY

Total crude shale oil produced by underground combustion retorting was hydrogenated in one step over a nickel-molybdenum catalyst at an operation temperature of 815° F, an operating pressure of 1,500 psig, and a space velocity of 0.7  $W_o/W_c$ /hr. A high yield (104.5 volume-percent) of synthetic crude oil, called a one-step syncrude, containing 225 ppm total nitrogen was attained. Hydrogen

consumption was 1,475 scf/bbl. A combination of microcoulometry, nonaqueous potentiometric titration, colorimetry, and infrared spectroscopy was used to determine the amounts and types of nitrogen compounds present in the syncrude and its various distillate fractions.

Light naphtha comprised 3.2 percent of the syncrude and contained no nitrogen. Heavy naphtha comprised 23 percent of the syncrude and contained 83 ppm nitrogen. The light oil comprised 53 percent of the syncrude and contained 200 ppm nitrogen, and the heavy oil comprised 18 percent of the syncrude and contained 513 ppm nitrogen.

The nitrogen compounds in the naphtha were shown to be 95 percent weak base of which 6 percent were primary and secondary amine types, 4 percent very weak base, and 1 percent neutral compounds. Nitrogen compounds in the light oil were shown to be 80 percent weak base of which 5 percent were primary and secondary amine types, 8 percent very weak base, and 12 percent neutral compounds. The nitrogen compounds in the heavy oil were shown to be 14 percent weak base, 12 percent very weak base, and 74 percent neutral compounds. More than 80 percent of the neutral compounds were largely carbazole types.

The one-step syncrude produced in this work was compared with a multistep syncrude of comparable total nitrogen content and basic and neutral nitrogen compound-type content produced earlier by a process suggested by the NPC. These syncrudes contained comparable amounts of neutral nitrogen-type compounds in their heavy oil fractions. Basic nitrogen-type compounds in the one-step syncrude were distributed in much larger amounts in the light oil and heavy naphtha fractions than in the corresponding multistep syncrude fractions. There was no nitrogen in either of the light naphtha fractions. The distribution of basic nitrogen into the lower boiling syncrude fractions is interpreted as a consequence of cracking of the heavy oil and residual portions of the crude oil subjected to the one-step process. The basic cracking products are readily denitrified in the lighter oil reactors in the multistep process.

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## NITROGEN AND SULFUR IN RAW AND REFINED SHALE OILS

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## INTRODUCTION

Raw Green River Formation shale oils contain significantly higher concentrations of some heteroatoms than most petroleum fractions of a similar distillate range. The nitrogen content of shale oils often runs twice that in a petroleum and therefore may require special refining methods. Removal of heteroatoms from shale oil is important because of (1) the potential for air pollution from their combustion products and (2) the susceptibility of modern refining catalysts to degradation, especially by nitrogen compounds. In addition to high heteroatom content, shale oils by and large have pour points too high for pipelining. In a shale-oil industrial process some sort of upgrading or partial refining is usually planned for reducing heteroatom content and improving fluidity to attempt to make shale oil compatible with existing petroleum processing facilities.

This paper reviews and discusses the work since the first Synthetic Liquid Fuels Act (1944) relating to heteroatom and heterocompound content of shale oils produced from Green River Formation of Colorado, Utah, and Wyoming oil shales. The work includes heteroatomic composition data for raw shale oils (crudes and distillates from various retorting processes) and their products in various stages of refining. Refining methods to be discussed include early upgrading processes involving distillation, delayed-recycle coking, thermal visbreaking, and acid and base or solvent extraction. Finally, modern hydrodenitrogenation (HDN) work with shale oil and related materials will be presented and heterocompound-type data for some refined and partially refined products will be discussed along with related analytical techniques.

It is apparent in reviewing the refining of shale oil that the nitrogen level has been the primary index of refining with respect to heteroatom content. This is not only because of the severe nitrogen effect in catalyst degradation<sup>1</sup> but also because of the persistence of nitrogen relative to sulfur and oxygen in the course of modern refining. For this reason data on sulfur and oxygen heterocompounds in shale oils are lacking in most cases.

## DISCUSSION

Effect of Retorting Process on Heteroatom Content

One advantage in use of shale oil as a feed is that once a set of retorting parameters is found giving a desired and stable retorting operation the feed produced could be quite constant in its properties. All shale oils are not alike, however. Jensen<sup>2</sup> has shown that retorting processes in which the oil shale is more slowly heated in general correlate with oil products having increased amounts of naphtha plus light distillate fractions. In these fractions the aromatic content remains constant, but the saturate-olefin ratio increases. An approximate index to these effects is the specific gravity or pour point of the oil. In table 1 we see properties of crude shale oils produced by various retorting methods arranged from top to bottom in order of decreasing specific gravity or pour point. We see that the nitrogen level decreases in the same order but that the sulfur level only decreases appreciably in the lower half of the table.

As pointed out by Jensen<sup>2</sup> the retorting parameters that control the character of shale oils, largely, are shale size, combustion zone velocity, and effective retorting temperature. If this is

TABLE 1. - Properties<sup>a</sup> of crude shale oils

Retort type	Retorting Index or T °F	Specific gravity, 60/60° F	Pour point, °F	Nitrogen, wt-pct	Sulfur, wt-pct
Gas combustion <sup>3</sup>	1,200 <sup>b</sup>	0.943	85	2.13	0.69
Fischer assay <sup>3</sup>	900 <sup>b</sup>	.918	70	1.95	.64
150-Ton batch <sup>2</sup>	---	.909	60	1.59	.94
USBM in situ-4 <sup>2</sup>	---	.885 <sup>d</sup>	40	1.36	.72
Equity Oil in situ <sup>4</sup>	750 <sup>c</sup>	.825 <sup>d</sup>	-20 <sup>d</sup>	.53	.49

<sup>a</sup> - References in table refer to properties of oils. <sup>b</sup> - Retorting index. <sup>c</sup> - Temperature of injected fluid. <sup>d</sup> - Properties of oil produced in laboratory simulation of process.<sup>4</sup>

carried a step further, it can be pointed out that these are not independent parameters and that effective retorting temperature itself may suffice to classify retorting methods.

Jacobson<sup>5,6</sup> has defined a retorting index with dimensions of temperature which relates to the severity of oil-shale pyrolysis. The index is derived from the ethylene:ethane ratio in the retort product gas. The retorting index is listed in table 1 for the gas combustion retort and the Fischer assay retort along with the measured temperature of the injected fluid used in the Equity Oil in situ process. We see at least qualitatively that these temperatures are in a systematic order.

To see that the oils with unknown retorting temperatures or indexes also probably fall in a logical order based on particle size, let us consider each process very briefly. The gas combustion retort,<sup>7-11</sup> heated by internal combustion is fed crushed-screened shale of about 3-inch dimensions. The Fischer assay retort,<sup>12</sup> uses small sized shale crushed to pass 8 mesh screen but is externally heated at a controlled moderately low rate. The 150-ton batch retort,<sup>13-15</sup> uses mine-run shale with blocks as large as 3 ft x 4 ft x 5 ft and is heated by internal combustion. The USBM in situ oil<sup>16-18</sup> was a combustion-retorted oil produced in fractured shale between injection and recovery wells. The Equity Oil in situ oil<sup>4,19</sup> was produced by recycling of hot natural gas, at a controlled temperature, into an oil-shale formation. All of the combustion-type retorts were of the forward burning type where gas plus oil moves countercurrently to oil shale. Except for the Fischer assay retort which is a controlled temperature retort, the increase in particle size is down table 1 corresponding with decreasing heating rate. It is probable that the USBM in situ experiment with poorly controlled combustion had a higher effective temperature than the controlled nonoxidative Equity Oil process. Very high temperature retorted oils<sup>20-25</sup> which by their very high aromatic content indicate a high degree of pyrolysis of the oil itself do not fit the above oversimplified pattern.

In summary, nitrogen and sulfur levels are both affected by the retorting method. Nitrogen level varies over a wider range than sulfur level and follows the specific gravity, pour point, and probably effective retorting temperature down for these oils. There is then potential for control of the nitrogen level in a crude shale oil through retorting. Whether the method of retorting adopted might be an economic approach to denitrogenation will not be pursued in this review. It depends undoubtedly on many factors, chief of these being probably the desired end use of the oil, whether for petroleum-type feedstock, direct fuel production or for chemicals, and the efficiency of resource recovery sought.

### Composition of Raw Shale Oils

Much of the early shale-oil characterization work was on a shale oil from an NTU (Nevada-Texas-Utah) retort which was an aboveground internal combustion batch-type retort.<sup>26</sup> Cady and Seelig<sup>27</sup> have shown that an NTU crude may contain as much as 61 percent heterocompounds of which about 60 percent are nitrogen compounds, 10 percent sulfur compounds, and 30 percent oxygen compounds. Thus only 39 percent of this oil is hydrocarbons. These proportions will vary some depending on the retorting scheme; but in any case, the heterocompounds form a significant part of the potential source of hydrocarbons. The work in identification of specific heterocompound types and heterocompounds in an NTU shale-oil naphtha<sup>28</sup> and in a heavy gas oil<sup>29</sup> has been summarized by Dinneen and others.<sup>30-40</sup> Others studying light gas oil fractions and other distillates have supplemented this work.<sup>41-43</sup> The naphtha and heavy gas oil represent the extremes of molecular weight in the distillates. Having nitrogen compound-type analyses for these extreme fractions with supplementary information on light distillate fractions allows interpolation to aid in compound-type assessment throughout the shale-oil distillate range. Sulfur and oxygen compound-type analyses have been done only for the naphtha distillate region.

In the following generalized discussion, the description of a compound type will be construed to include also homologous and benzologous series members depending on boiling range--e.g., pyridinic-type N includes pyridine, quinoline, acridine, alkylpyridines, etc.

#### Sulfur

In table 2<sup>44</sup> we see that for a crude shale oil the sulfur distribution is rather uniform throughout the boiling ranges but that nitrogen is more concentrated as the fractions get heavier. We have already seen in table 1 that the type of retorting seems to have only a second-order effect on sulfur level in the crude. The refractory nature of the sulfur<sup>45</sup> may be accounted for by the fact that most of the sulfur is in thiophene types<sup>28,44</sup> as shown in table 3 for a naphtha fraction.

#### Oxygen

The oxygen in a shale-oil crude may run 0.5 to 2 percent. Much of the oxygen in a naphtha,<sup>28</sup> light distillate,<sup>43</sup> and gas oil<sup>29</sup> appears as phenols with minor amounts of carboxylic acids. Benzofuran was found in small amounts in the nonacidic portion of the naphtha.<sup>28</sup> It was shown

TABLE 2. - Sulfur and nitrogen contents of distillates from a Green River Formation crude shale oil<sup>44</sup>

Fraction	Nominal boiling range, °F	Nitrogen, percent by wt	Sulfur, percent by wt
Naphtha	<400	1.17	0.77
Light distillate	400-600	1.24	.83
Heavy distillate	600-800	1.60	.79
Residuum	>800	2.04	.70

that light distillates from different retorting processes can vary in their oxygen content and its distribution.<sup>43</sup> For one in situ produced oil, oxygen appears to be accounted for largely in the tar acids. For one aboveground retorted oil it appeared that two-thirds of the oxygen was unaccounted for by tar acids implying the presence of other forms of oxygen possibly amidic type,<sup>41,43</sup> or other as yet unclassified types.

TABLE 3. - Type sulfur in Green River Formation shale-oil naphtha<sup>44</sup>

Sulfur type	Percent of total sulfur
Elemental	0
Thiol	4
Disulfide	2
Sulfide (includes cyclics)	19
Residual (includes thiophene type)	75

### Nitrogen

The principal nitrogen-containing species in shale oils are pyridine types and pyrrole types. In pyridinic types the single aromatic ring type appears to predominate over multiple ring types through wide distillate ranges. In pyrrolic types multiaromatic rings tend to predominate as boiling range increases.<sup>29,41</sup> Small amounts of amides,<sup>41</sup> arylamines,<sup>46-48</sup> and nitriles<sup>28,35</sup> have been detected. Much of the nitrogen in shale-oil distillates is basic enough to titrate in acetic anhydride ( $pK_a > -2$ )<sup>28,41-43</sup> and be extracted by acidic agents as shown in table 4.<sup>42</sup> In addition appreciable acidic material containing oxygen or nitrogen is titratable in pyridine ( $pK_a < 12$ ) and is extractable from the lighter distillates by basic reagents as shown. The relative amounts of various nitrogen types and their basicities observed for a shale-oil light distillate are shown in table 5.<sup>41</sup>

TABLE 4. - Polar materials by different methods for a 150-ton batch retort shale oil<sup>42</sup>

Method	Nominal distillate cut		
	Naphtha IBP to 400° F	Lt. distillate 400° F to 600° F	Gas oil 600° F to 1,000° F
	Bases, wt-pct		
Titration: Weak, <sup>a</sup> very weak <sup>b</sup>	7.1, 3.6	13.1, 2.4	27.9, 0.0
Ion-exchange extraction	10.2	12.8	24.3
Aqueous extraction	11.2	11.5	12.0
	Acids, wt-pct		
Titration: Weak, <sup>c</sup> very weak <sup>d</sup>	1.0, 3.9	0.8, 5.6	0.3, 8.0
Ion-exchange extraction	4.2	3.3	1.1
Aqueous extraction	5.0	3.7	1.2

<sup>a</sup>  $pK_a = +8$  to  $+2$ . <sup>b</sup>  $pK_a = +2$  to  $-2$ . <sup>c</sup>  $pK_a = +3$  to  $+10$ . <sup>d</sup>  $pK_a = +10$  to  $+12$ .

### Products from Early Refining Processes

Because of the waxy, viscous nature of shale oils from conventional retorting processes and the high pour point and heteroatom content along with the low light-end content, it was apparent from the outset that some sort of hydrocarbon-conversion process was required for shale-oil utilization. Early work centered on thermal processing (visbreaking, recycle cracking, and coking) along with chemical treatment to remove objectionable compounds in an attempt to improve gasoline and distillate fuel content and stability of shale oil.<sup>49-54</sup> These methods were chosen because of the

TABLE 5. - Summary of nitrogen-type analysis of a shale-oil light distillate (400° to 600° F)<sup>41</sup>

Nitrogen type	Percent of total nitrogen
Weak bases (pKa = +8 to +2)	
Alkylpyridines	43
Alkylquinolines	22
Very weak bases (pKa = +2 to -2)	
Alkylpyrroles (N-H)	10
Alkylindoles (N-H)	9
Cyclicamides (pyridones, quinolones)	3
Anilides	2
Unclassified	7
Nonbasic (pKa < -2) corrected for pyrroles and indoles	4

availability of these processing facilities in all refineries, because of the poor economic aspect of hydrogenation at the time, and the lack of suitable catalysts which could stand up to the high nitrogen concentrations encountered in shale oil.

#### Thermal Methods

Visbreaking of shale oil or cracking with recycle can produce a low pour point shale oil with increased light end content. Recycle delayed coking can further increase the light end content as shown in table 6 but does not affect the nitrogen and sulfur concentrations appreciably.<sup>54</sup>

TABLE 6. - Recycle delayed coking of crude shale oil to various endpoints<sup>54</sup>

	Crude feed	Nominal distillate endpoint		
		650° F	750° F	850° F
Yields, vol-pct	--	77	87	89
Sulfur, wt-pct	0.74	0.63	0.61	0.63
Nitrogen, wt-pct	2.01	1.65	1.90	1.95
		<u>Light end yields</u>		
IBP-350° F, vol-pct	1.5	5.5	9.0	19
350-550° F	18	87	36	36

#### Chemical Methods

Chemical treatment of shale oils can be very effective in nitrogen removal. One such treatment consisting of successive contacting at 100° F with 15 weight-percent NaOH, 20 weight-percent H<sub>2</sub>SO<sub>4</sub>, 100 percent H<sub>2</sub>SO<sub>4</sub>, and then neutralization with 3 volume percent NaOH produced a diesel fuel from a shale-oil light gas oil as shown in table 7.<sup>50</sup> The sulfur level, however, is nearly unaffected. Although similar treatment of naphtha fractions may produce very low

TABLE 7. - Result of chemical treatment<sup>a</sup> of shale-oil recycle delayed-coker distillate light gas oil (400° to 670° F)<sup>50</sup>

	Raw oil	Treated oil (diesel fuel)
Yield, vol-pct	100	67.0
Sulfur, wt-pct	0.84	0.74
Nitrogen, wt-pct	1.66	.085
Tar acids, vol-pct	3.4	.3
Tar bases, vol-pct	13.0	0

<sup>a</sup> Treatment consists of 15 percent by weight NaOH, 20 percent by weight H<sub>2</sub>SO<sub>4</sub>, 100 percent H<sub>2</sub>SO<sub>4</sub> (22.8 lb/bbl), and 3 volume percent NaOH to neutralize, then redistill to restore end-point. Treating temperature about 100° F.

nitrogen gasolines, these may still have a few tenths percent sulfur present. Diesel fuels from various solvent extractions of light oils showed greatly improved nitrogen levels with little effect on sulfur levels much the same as acid base treated oil in table 7.

The loss of distillate shown in table 7 illustrates a problem with chemical refining of shale oil. Undoubtedly quite effective nitrogen and oxygen compound removal could be achieved with various reactants or solvents, but it is unlikely that improvement in sulfur level would be obtained because of the chemical similarity of thiophene-type compounds to the hydrocarbon matrix. If all heterocompounds were removed from a crude shale oil, as much as 60 percent of the oil might be removed.<sup>27</sup>

### Summary

It was shown by the Bureau of Mines in 1949<sup>51</sup> that adequate gasolines and diesel fuels could be produced from shale oil by methods like those just discussed. However, there were at least three good reasons for continuing research in refining of shale oil. First, the losses in raw material involved in extraction of heterocompounds represent great waste unless a ready use exists for the extracted materials. Secondly, the demand for very low nitrogen stocks for refining to high octane fuels was increasing. Finally, the pressure from an environmental standpoint for extremely low sulfur fuels was increasing steadily.

### Products from Modern Refining Processes

Fortunately a by-product of the demand for higher octane fuels was hydrogen from petroleum catalytic reforming processes. The economics of hydrogen utilization began to look favorable as a means of improving the quality of shale oils and the research emphasis swung to hydrogenation. In 1947 Union Oil was successful, on a pilot plant basis, in catalytic hydrosulfurization of high thiophenic sulfur-type coker distillates from Santa Maria Valley crude petroleum.<sup>55</sup> Since then, aided by the increasing availability of hydrogen, much work has been done in refining shale oil via hydrogenation one way or another.<sup>56-75</sup> Shale-oil crude was analogous to this petroleum crude in that sulfur was present largely as thiophenes and distributed uniformly throughout the distillate ranges.<sup>55</sup> As it turned out, both sulfur and nitrogen could be removed from shale oil effectively by catalytic hydrogenation. Production of potentially high quality fuels and refinery feedstocks has been achieved in many cases.

The question of which method of HDN is best of course depends on the individual case-- i.e., what is the feed and what are the desired products. Knowledge of the types and kinetics in

HDN of heterocompounds remaining in refined and partially refined shale oils could be of value in optimizing refining processes. Nitrogen level alone is only a partial criterion of the degree of hydrogenation that has taken place. Various deleterious heterocompounds appear to be removed at different rates for a given set of conditions as discussed below. To date little data concerning the nature and reactivity of the heterocompounds in refined shale oils have appeared in the literature of shale-oil refining.

### Sulfur and Oxygen

In the hydrodesulfurization of Santa Maria Valley petroleum crude by Union Oil, all types of sulfur present (mercaptan, sulfide, and thiophenic) appeared to be removed at the same rate.<sup>55</sup> Little compound-type information relating to hydrodesulfurization or hydrodeoxygenation has been reported in shale-oil refining studies however. This is probably because it has been found in refining of shale oils by catalytic hydrogenation that both sulfur and oxygen are removed before desired nitrogen levels are attained. In cases where results suggest otherwise, it is not always apparent whether analytical interference from elemental sulfur might not have been a factor. Elemental sulfur is formed readily as an interference by air oxidation of hydrogen sulfide. Inadvertent air contact with hydrogenated distillates before thorough washing has been accomplished may complicate evaluation of low organic sulfur levels. (Elemental sulfur may be removed from oils by extraction with metallic mercury<sup>76-77</sup> or in some cases with aqueous sulfite solution.<sup>78</sup>) In addition, direct low-level oxygen analyses are not readily available in most laboratories. From these properties of sulfur and oxygen, it can be understood why nitrogen level has been the index usually used in shale-oil heterocompound removal studies.

### Nitrogen

In an attempt to work out some of the HDN reaction kinetics, several shale-oil HDN studies have been made in which nitrogen-type analyses were presented.<sup>46-48,73,75,79-81</sup> Studies have been made on pure nitrogen compounds occurring in shale oils and also on low-level nitrogen oils "spiked" with some of these nitrogen compounds.<sup>82-85</sup> Work in this area has been aided by the simple nitrogen-type analysis described by Koros, et al.,<sup>46</sup> extended by Silver, et al.<sup>47,48</sup> and by Poulson, et al.<sup>41,81</sup>

This analytical method for nitrogen types uses elemental analysis, nonaqueous titrimetry, infrared spectrophotometry, and visible colorimetry to define several nitrogen types: 1° and 2° alkylamine, 3° amine (pyridine and other), arylamine, pyrrolic N-H,  $\alpha$ - or  $\beta$ -unsubstituted pyrrolic (excluding carbazoles), amide, and miscellaneous very weak base and nonbasic nitrogen types. Further subdivisions are possible depending on which groups are represented in a given sample. As hydrogenation progresses, oxygenated types disappear so rapidly that specific compound-type assignments become simpler. Some examples of uses of this analysis and the nature of hydrodenitrogenated shale oils are shown below followed finally by a summary of the principal nitrogen types in a premium shale-oil syn crude having 0.025 percent nitrogen.

### Pyridines Versus Pyrroles

This analysis has been used to resolve a fundamental conflict in shale-oil refining literature; which is easier to hydrodenitrogenate, pyridinic types or pyrrolic types? Researchers were split about equally on each side of this question. Using an analytical scheme similar to the one just described, Frost and Jensen<sup>73</sup> were able to rationalize the conflicting reports. Working with crude shale oil over a wide range of temperature and hydrogen pressure, they showed denitrogenation of pyridinic types was faster than for pyrrolic types at low temperature and pressure, but the other way round for more severe conditions of temperature and pressure.

## Anilines in Shale Oils

The reaction sequence for denitrogenation of indoles and carbazoles proposed by Flinn, et al.<sup>83,84</sup> contains approximately a dozen competing or consecutive reactions. Reactants, intermediates, and products run the gamut from nonbasic to strongly basic nitrogen types. Anilines are postulated as intermediates as they are also in a denitrogenation sequence proposed for quinolines by Doelman and Vlugter<sup>85</sup> and Koros, et al.<sup>46</sup> Anilines would arise from saturation of the heteroring in a fused ring compound followed by rupture of the bond between nitrogen and the aliphatic carbon.

### One-Step HDN

Although anilines themselves have been shown to be readily hydrodenitrogenated,<sup>83-85</sup> they have been observed in severely hydrodenitrogenated shale oils. Brown<sup>79</sup> found that 33 percent of the tar bases in a hydrocracked recycle shale-oil naphtha were anilines at 95 percent denitrogenation. Koros, et al.,<sup>46</sup> Silver, et al.,<sup>47,48</sup> and Frost<sup>75</sup> found a few percent aniline-type nitrogen in shale oils which had up to 98 percent denitrogenation levels. All these results were based on one-step HDN processes whereby anilines formed by the processes just described above would appear directly in the products, probably as lighter boiling compounds as a result of hydrocracking.

### Multistep HDN

In addition to the one-step syncrude described above, Frost, using a multistep HDN process with the same crude shale-oil feed and denitrogenating to a similar level, produced a syncrude with a different nitrogen-type distribution.<sup>74,81</sup> The multistep process, based on an NPC proposed scheme,<sup>86</sup> involves continuous catalytic hydrogenation of three individual distillate fractions from a crude shale oil with the inclusion of products from delayed coking of the residuum in the distillate fractions. Anilines were completely absent from this syncrude product but did show up in intermediate products.

In table 8 the heteroatom composition of these two syncrudes is reviewed, as discussed by

TABLE 8. - Nitrogen and sulfur in shale-oil syncrudes and distillate fractions<sup>75</sup>

	Nitrogen, ppm		Sulfur, ppm	
	Multistep	One-step	Multistep	One-step
Syncrude	250	225	5	6
Naphtha	1	83	8	3
Light oil	79	200	1	5
Heavy oil	935	513	9	5

Frost<sup>75</sup> in this symposium, and is compared through the distillate ranges. Light nitrogen compounds are virtually absent from the multistep syncrude illustrating the difference of a multistep process compared to a single-step process.

### Premium Syncrude

Residual nitrogen types in a shale-oil premium syncrude (multistep syncrude above) heavy oil (550° to 850° F) were determined by Poulson, Frost, and Jensen<sup>81</sup> using the above-described classification scheme supplemented by mass spectrometry. This heavy oil contained 935 ppm nitrogen which was 90 percent of the total nitrogen in the syncrude. The total nitrogen concentration

in the whole syncrude was 250 ppm and resulted from over 98 percent nitrogen removal from the crude shale-oil feed. The general nitrogen-type analyses are shown in table 9. In pyrrolic types,

TABLE 9. - Summary of nitrogen types in a heavy oil (550° to 850° F)<sup>a</sup> from a multistep shale-oil syncrude<sup>b</sup> 81

	N, pct of total in oil
<u>Pyrrolic-type nitrogen</u>	
Three aromatic rings	30
One or two aromatic rings	25
<u>Pyridinic-type nitrogen</u>	
Two aromatic rings	15
One aromatic ring	30

<sup>a</sup> Total N = 935 ppm.    <sup>b</sup> Total N = 250 ppm.

three aromatic ring compounds (carbazoles) predominate and in pyridinic types one aromatic ring compounds (pyridines) predominate, much as in a raw shale-oil heavy gas oil.<sup>29</sup> A slight olefin interference makes the exact pyridine:quinoline ratio somewhat uncertain in table 9, however.

In table 10 the neutral and very weak-base nitrogen types are summarized for this heavy oil which represents 90 percent of the nitrogen in the syncrude. Pyrroles and indoles appear to be N-unsubstituted and highly ring-alkyl substituted. Carbazoles in this oil are about evenly split between N-substituted and N-unsubstituted types.

TABLE 10. - Summary of neutral and very weak base nitrogen types in the heavy oil (550° to 850° F)<sup>a</sup> from a multistep shale-oil syncrude<sup>b</sup> 81

Nitrogen-type compounds	N, pct of total in fraction
<u>N-unsubstituted pyrroles (or indoles)</u>	29.0
$\alpha$ - or $\beta$ -unsubstituted	6.8
$\alpha$ - or $\beta$ -substituted	22.2
<u>Carbazoles</u>	71.0
N-unsubstituted	34.4
N-substituted	36.6

<sup>a</sup> Total N = 935 ppm.    <sup>b</sup> Total N = 250 ppm.

In summary HDN is effective in heteroatom removal from shale oils and its use has been and is being studied widely. Optimum processing conditions for denitrogenation of shale oils depend on the individual case but probably have not been determined for many situations. Little information on nitrogen types in refined or partially refined shale oils has been reported. A relatively simple analytical scheme can produce nitrogen-type compound data of aid in mechanistic interpretations of denitrogenation reactions in shale oils.

## SUMMARY

Crude Green River Formation shale oils contain large amounts of heterocompounds containing nitrogen, sulfur and/or oxygen. Shale oils produced in low temperature retorting processes seem to have lower nitrogen levels paralleling lower specific gravities and pour points. The effect of retorting on sulfur level is not as clear. Sulfur occurs principally as thiophenic-type compounds. Oxygen occurs mainly as phenols with minor amounts as carboxylic acids, amides, ethers, or other unidentified types. Nitrogen occurs principally as pyridinic type and pyrrolic type with small amounts of amide types, nitriles, and other unidentified types. Refining of shale oil by thermal methods and chemical or solvent extraction processes reduces nitrogen levels appreciably, but sulfur level is not affected much. Refining of shale oil by processes involving hydrogenation can be effective in producing extremely low level nitrogen, sulfur, and presumably oxygen fuels and feedstocks.

The susceptibility of oils to HDN depends on the nature of the nitrogen compound types present and the hydrogenation scheme employed. The nature of the nitrogen compound types remaining at low levels after upgrading of shale oil gives evidence of the reaction mechanisms involved. Some available analytical techniques can give nitrogen compound-type information relating to mechanisms of hydrodenitrogenation.

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HAZARDOUS AND TOXIC AIR POLLUTANTS, Max Sanfield, Environmental Protection Agency, Research Triangle Park, North Carolina 27711

Background and current state of knowledge with regard to hazardous and toxic air pollutants are reviewed. Secondary pollutants formed from the interaction of primary pollutants are likely to be the major hazard. Their formation and biological effects are discussed. The need for a uniform strategy and a realistic cost/risk/benefit analysis of the problem is pointed out.

A LOOK AT THE ENVIRONMENTAL ASPECTS OF COAL CONVERSION, R. R. Bertrand,  
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Several processes, either currently in operation or in the development stage, offer significant prospects for conversion of coal into relatively clean gaseous or liquid fuels. The scale of these processes needed for economic viability, likewise suggest a potential for significant environmental degradations in the immediate neighborhood of the conversion facility. The magnitude of the environmental aspects of coal conversion facilities will be assessed not only in terms of absolute potential but also in terms of likely effluent discharges based on application of demonstrated control technology. These assessments will draw heavily on an on-going study being conducted for the Environmental Protection Agency; a study that has involved discussion with process developers, plant visits and a detailed analysis of the probable environmental effluents from several coal conversion processes. A comparison will also be made of the probable magnitude of effluent discharges to be expected from coal conversion processes relative to those from alternate processes using coal and other fossil fuels for production of equivalent quantities of clean energy.

POTENTIALLY VOLATILE TRACE ELEMENTS IN COAL.\* R. R. Ruch, J. K. Kuhn, G. B. Dreher, J. Thomas Jr., Joyce K. Frost, and R. A. Cahill, Illinois State Geological Survey, Urbana, IL 61801.

Most of the following trace and minor elements have been determined in over 100 U. S. whole coals and 34 specific gravity fractions of coal: As, Ag, Au, B, Ba, Be, Bi, Br, Cd, Cl, Co, Cr, Cu, F, Ga, Ge, In, Pb, Mn, Mo, Ni, Hg, Hf, P, Rb, Ru, Sb, Se, Sn, Sr, Ta, Te, Th, Tl, U, V, W, Zn, Zr, and some rare earths. A combination of analytical techniques, including atomic absorption, X-ray fluorescence, optical emission, neutron activation, and ion-selective electrode, have been adopted, compared, and utilized. A summary of the sampling, sample pretreatment, and analyses procedures employed with preliminary results and interpretation, will be presented.

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POLLUTANTS IN GASIFICATION, A. Attari, Institute of Gas Technology,  
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INTERACTIONS BETWEEN HYDRODESULFURIZATION  
AND HYDRODENITROGENATION REACTIONS

by

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ABSTRACT

Interactions between the hydrodesulfurization (HDS) of thiophene and the hydrodenitrogenation (HDN) of pyridine on commercial CoMo, NiMo and NiW sulfided catalysts were studied using a flow microreactor at pressures up to 11.1 atm and temperatures up to 425°C.

Pyridine HDN is more difficult than thiophene HDS, and above 350°C there is a thermodynamic limitation on the first step of the HDN reaction mechanism, in which the pyridine ring is saturated to piperidine. Sulfur compounds have a dual effect on HDN. At low temperatures, thiophene inhibits the reaction, which is postulated to occur by competition with pyridine for hydrogenation sites on the catalyst, retarding the hydrogenation of pyridine to piperidine, and thus reducing the overall reaction rate. At high temperatures sulfur compounds enhance HDN. It is suggested that the dominant effect here is interaction of hydrogen sulfide, an HDS reaction product, with the catalyst to improve its activity for rupture of the C-N bond. This increases the rate of reaction of piperidine, which is rate-determining at the latter conditions, and enhances the overall rate of HDN.