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QUARTERLY PROGRESS REPORT OCTOBER 1 - DECEMBER 31, 1972

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LARAMIE ENERGY RESEARCH CENTER
Laramie, Wyoming
G.U. Dinneen, Research Director

MARCH 3, 1849

# QUARTERLY PROGRESS REPORT
## October 1—December 31, 1972

United States Department of the Interior
Bureau of Mines

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# SUMMARY OF MAJOR ACCOMPLISHMENTS

Laramie Energy Research Center — October 1 - December 31, 1972

Delay in the Utah Geological Survey's coring project until spring will not affect the analyses of Utah tar sands because of the availability of 14 cores from three Utah deposits given to the Bureau by Texaco, Inc. Also, the experimental investigation of the feasibility of using in situ combustion in Utah tar sands was furthered with completion of a fire-flood-pot apparatus.

Continuing the characterization of nonhydrocarbons in high-boiling petroleum fractions, the acid fractions of two cuts were analyzed by a recently developed technique. A study of dewaxing as an aid to separation of heavy hydrocarbons gave negative results.

Asphalt absorbed on bauxite at a rate that correlated with the energy released in the interaction. An electric dipole field was observed. Both phenomena are important to the control of asphalt properties such as viscosity and adhesiveness.

A hydrogasification experiment with in situ crude shale oil was completed with the aid of recently acquired chromatographic equipment for analysis of the products.

A 10-day hydrogenation run with shale oil produced in the 150-ton retort reduced nitrogen content to less than 0.1 percent. The results indicate a long life expectancy for the catalyst.

The proposed Prototype Leasing Program continues to have an impact. Nine cores, five from Colorado and four from Utah, were received and assayed to provide data on potential lease sites.

A hydraulic fracturing treatment of the oil shale at Rock Springs site 9 was only partly successful. Communication was established between wells, but the fractures were not wide enough to accept sand proppant.

The instrumentation for NMR assay of oil shales has been installed and the technique is expected to be used to contribute to output of data during the remainder of the year. A series of unforeseen events has delayed application of the technique about 3 months.

Three coreholes were completed in the northern Green River Basin of Wyoming to extend the known oil-shale areas to the north and west of the Eden-Farson area.

A site was selected near Hanna, Wyoming for the conduct of an underground coal gasification experiment. Site preparation included surface installations, drilling of four operating boreholes, and preparations for permeability tests. Inclement weather postponed permeability testing of the coal bed.

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# ADVANCING PETROLEUM AND NATURAL GAS CONSERVATION TECHNOLOGY TO MEET INCREASING ENERGY NEEDS

## Project 1. - IN SITU OIL RECOVERY FROM TAR SAND DEPOSITS

Submitted by: C. Q. Cupps, Supv. Pet. Eng. (Research Supervisor)

### Subproject 1. Characterization of Tar Sand Deposits

Began: FY 1973 Expected Completion: FY 1975

Personnel: L. C. Marchant, Petroleum Engineer (Project Leader)
L. A. Johnson, Petroleum Engineer

## SUMMARY

Analysis of one core from Utah's Sunnyside tar sand deposit was completed. This core is one of three from Sunnyside, four from Asphalt Ridge, and seven from PR Spring that were obtained from Texaco, Inc. Analyses of these 14 cores and 23 others to be obtained from the Utah Geological Survey in the fourth quarter will provide data for a tar sand classification system and for the design of in situ recovery experiments.

## DISCUSSION

One core from the Sunnyside, Utah, tar sand deposit was analyzed. The analytical data for 44 samples from this core were summarized with those from 150 samples from 9 other cores and 18 outcrops, previously analyzed. Average values for some of the 16 physical properties analyzed are: Porosity, 24 percent; permeability before oil extraction, 415 md; permeability after oil extraction, 1440 md; oil saturation, 50 percent of pore volume and 5.7 percent of weight; and oil specific gravity, 1.003.

The Utah Geological Survey tar sand coring project, which was to have provided cores for this research during this quarter, has been delayed by the U.S. Bureau of Land Management, U.S. Geological Survey, the Ute Indian Tribe, and unseasonable weather. As it looks now, this coring probably will not be done until the fourth quarter. As a result, the planned work has been changed, and the Utah tar sand cores obtained from Texaco, Inc., are being analyzed instead of the Utah Geological Survey project cores.

By request from Mr. Budge T. Porritt, Soilsystems, Phoenix, Ariz., 10 pounds of tar sand sample from the Asphalt Ridge deposit near Vernal, Utah, was sent to him. His need concerned preliminary experiments in the removal of oil from tar sands. Later correspondence described his process as involving petroleum solvent and high-speed mechanical agitation, with flotation separation of oil-solvent and sand in water.

Following efforts to revise the manuscript, "Acoustic Travel Times for the Madison Limestone in the Williston Basin," in accordance with reviewers' suggestions, it became apparent that the results are too limited to provide a reasonable solution to this problem. Therefore, it is now proposed to place this report on open file rather than to seek publication.

Subproject 2. - Experimental Evaluation and Engineering Design of In Situ Recovery Methods for Tar Sands

Began: FY 1973 Expected Completion: FY 1975

Personnel: C. S. Land, Petroleum Engineer (Project Leader)
F. M. Carlson, Petroleum Engineer

## SUMMARY

Laboratory investigation of in situ recovery of oil from tar sands has continued with the completion of a flood-pot apparatus for the study of combustion of tar sands. Data obtained with this apparatus will be used to determine the feasibility of using a combustion process on a larger scale. In addition, numerical simulation of reverse combustion has been accomplished with two computer programs. The numerical models will be a useful complement to the laboratory investigation.

## DISCUSSION

The construction of a fire-flood-pot apparatus has been completed. Collection of data on the effect of temperature on the rate of oxidation of the bitumen in consolidated tar sand is beginning. Information on fuel availability and the thermal stability of bitumen will be obtained with this apparatus.

Reverse combustion was simulated with two numerical models, and reasonable results were obtained from the computer. One model uses finite differences to obtain a solution, while the other employs a variational method using smooth cubic polynomials. These computer programs will be used in conjunction with laboratory data in evaluating the process and in designing and modifying the laboratory experiments.

Next quarter the work will proceed as planned, to initiate the laboratory combustion experiments.

# ADVANCING PETROLEUM AND NATURAL GAS CONSERVATION TECHNOLOGY TO MEET INCREASING ENERGY NEEDS

## Project 2. - CHARACTERIZATION OF HEAVY PETROLEUM OILS

Submitted by: W. E. Haines, Supv. Res. Chemist (Research Supervisor)

Began: July1, 1966 Expected completion: July 1, 1974

Personnel:

| | |
|---|---|
| D. R. Latham, Research Chemist (Project Leader) | T. E. Cogswell, Chemist |
| | J. F. McKay, Research Chemist |
| J. W. Bunger, Chemist | J. H. Weber, Research Chemist |
| | Paris Amend, Phys. Sci. Aid eod 11/20/72 |

## SUMMARY

Definitive characterization of the troublesome nonhydrocarbons in high-boiling petroleum cuts was the main thrust of the heavy ends studies. The acid fractions of two cuts were analyzed by the recently developed scheme. A preliminary scheme for the analysis of the neutral nitrogen fraction was tested on three samples. Initial work was done on a procedure for analyzing the base fraction.

A study of dewaxing as an aid to the separation of heavy hydrocarbons produced negative results. A paper on polyaromatic hydrocarbons was presented and accepted for publication.

One tar sand sample was extracted and submitted for testing. A crude oil from Alaska was received for analysis.

## DISCUSSION

Separation of Heavy-End Distillates and Residues. - The neutral nitrogen fraction was separated from the Wilmington 535-675°C distillate by ferric chloride treatment. Because the fraction is smaller than expected, based on experience with other Wilmington distillates, the hydrocarbon material must be further analyzed to determine if nitrogen removal was complete.

The effect of dewaxing on the separation of hydrocarbon material into saturate and aromatic fractions was investigated. A sample of hydrocarbons from the Recluse residue was treated with a mixture of methyl ethyl ketone and methyl isobutyl ketone, giving a wax fraction of 7.5 percent. Silica gel chromatography on the dewaxed hydrocarbons gave a poor separation and poor material recovery.

Added to the work plans for the third quarter is the removal of acid, base, and neutral nitrogen fractions from the Wilmington 370-535°C distillate.

Investigation of Acid Fractions. - The acid fractions from the Gato Ridge and Recluse 500-650°C cuts were separated using gel permeation and adsorption chromatography to obtain the amounts of carboxylic acids, phenols, carbazoles, and amides.

A paper entitled "Polyaromatic Hydrocarbons in High-Boiling Petroleum Distillates" was presented by Dr. John McKay at the Pacific Conference on Chemistry and Spectroscopy in San Francisco. This paper has been accepted for publication in Analytical Chemistry.

Investigation of Neutral Nitrogen Fractions. - Swan Hills, Gach Saran, and Wilmington 370-535°C fractions were separated on basic alumina into carbazole- and amide-compound-type concentrates which were further separated by GPC. Selected subfractions were analyzed by infrared and NMR spectroscopy. Data indicate that the carbazoles are more aromatic and lower in molecular weight than the amides. Several GPC subfractions from the Gach Saran carbazole concentrate were separated by TLC in an attempt to identify polyaromatic compound types. Fluorescence analysis of TLC samples is now in progress.

Investigation of Base Fractions. - Investigation of the composition of base fractions was initiated. Three separation techniques--chromatography on acidic alumina, chemical reaction with dry HCL, and ion exchange chromatography--were applied to establish an optimum separation procedure. Although an optimum procedure has not been established, preliminary results show that all three techniques separate the bases into weak and strong subfractions. Infrared analysis indicates that the weak bases are amides and the strong bases are pyridine benzologs.

Spectroscopy. - High-resolution mass spectra (HRMS) were obtained on mono-, di-, and polyaromatic fractions from the 370-535°C Swan Hills distillate; elemental maps were obtained on each mass unit. HRMS were run on three ester samples and eight basic nitrogen samples. Low-resolution mass spectra were run on saturate, mono-, di-, and polyaromatic fractions from Gach Saran and Swan Hills distillates.

Tar Sand Bitumen and Crude Oil Analyses. - A sample of Asphalt Ridge tar sand was benzene-extracted to give a bitumen fraction amounting to 11.3 percent of the sample. The bitumen was submitted for distillation and physical property data.

A sample from the Katalla field in Alaska was submitted for crude oil analysis; results of this analysis have not been received.

# ADVANCING PETROLEUM AND NATURAL GAS CONSERVATION TECHNOLOGY TO MEET INCREASING ENERGY NEEDS

## Project 3. - STUDIES OF ASPHALT AND ASPHALTIC MATERIALS

**Submitted by:** W. E. Haines, Supv. Res. Chemist (Research Supervisor)

**Date begun:** July 1963 **Expected completion:** Continuous

**Project personnel:**

J. C. Petersen, Research Chemist
(Project Leader)
F. A. Barbour, Chemist
R. V. Barbour, Research Chemist
S. M. Dorrence, Research Chemist
E. K. Ensley, Research Chemist
H. Plancher, Research Chemist
J. H. Weber, Research Chemist
J. Lorenz, Phys. Sci. Aid.

## SUMMARY

Asphalt molecules adsorbed on a porous plug of bauxite at a rate about 100 times greater than on natural aggregates. This correlates with the large amounts of energy released in the asphalt-bauxite interaction. An electric dipole field was observed in an asphalt; this field apparently is caused by molecular orientation promoted by a mineral surface. These phenomena are important to the control of many important asphalt properties including adhesiveness and viscosity.

A commonly used road aggregate, quartzite, was more effective in catalyzing asphalt oxidation than limestone aggregate. Carboxylic acids and 2-quinolones were the compound types most strongly adsorbed on four study aggregates.

Tar sand bitumens contained naturally occurring carboxylic acids in concentrations much higher than normal petroleum asphalts. These acids could impart surface-active properties to the bitumen which are important to recovery processes.

Samples of asphalt are being evaluated for use in the Boulder City, Nev., sulfur-asphalt work.

## DISCUSSION

The interaction energy of asphalt B-3036 with bauxite, an aluminum oxide, was about 100 times greater than that of typical aggregates such as quartzite or limestone. That the extremely large interaction energy reflects multilayer adsorption on the bauxite surface was supported by flow-through-porous-media experiments in which 90 percent of the void space in a bauxite porous plug was closed after five hours of flow at 150°C. This short time is in contrast to other aggregates which take weeks to close. The calculated rate of buildup of asphalt molecules on the bauxite surface was 3000 Å per minute.

The postulate of multilayer adsorption, which is important to the understanding of the asphalt-aggregate bond, suggests that the adsorbed molecules are oriented to produce a dipole field. The postulate was further supported by the observation of such a field. Asphalt was contacted with a mica surface for several days at 130°C, cooled, and cut into sections. The asphalt surface that had been in contact with the mica was attracted toward a negative electric field, indicating that the positive ends of the asphalt molecules had been oriented toward the mica surface.

Chromatographic fractions from Wilmington asphalt were oxidized in IGLC columns on a quartzite support. Quartzite was a much better oxidation catalyst than limestone. This was particularly apparent for the saturate fraction in which over one-third of the carbonyl oxidation products were acidic. Because acidic oxidation products adhere strongly to aggregate surfaces and because asphalt and aggregate are in intimate contact at high temperatures during the production of roads, these findings indicate that the catalytic effect of the aggregate is critical to the asphalt-aggregate bond and to the durability of the road.

Four aggregates (two limestones, quartzite, and granite) were used as the adsorbent to extract polar materials from a benzene solution of asphalt. Carboxylic acids and 2-quinolones were the most prevalent functional types adsorbed. Riverton limestone showed the greatest affinity for 2-quinolones.

Several tar sand samples have been extracted in preliminary experiments. The bitumen extracts showed much higher concentrations of carboxylic acids than did petroleum asphalts. Analysis of core samples indicates that these acids are naturally occurring rather than the result of oxidative weathering. These surface-active acids have important implications in the recovery of tar sand.

Samples of asphalts in current production and which are believed to have properties desirable for the Boulder City, Nev., sulfur-asphalt project have been collected. These samples are being studied so that we can make recommendations to the Boulder group. Analytical methods are being developed for analysis of the asphalt-sulfur mixes.

## MANUSCRIPTS

### Published

| Title | Authors | Citation |
|---|---|---|
| Fluorescence Spectrometry in the Characterization of High-Boiling Petroleum Distillates | J. F. McKay<br>D. R. Latham | Anal. Chem. v. 44, pp. 2132-2137 (1972) |
| Oilfields and Crude Oil Characteristics--Cook Inlet Basin, Alaska | D. P. Blasko<br>W. J. Wenger<br>J. C. Morris | Rept. of Inv. 7688, 43 pp. (1972) |

### In Progress

| Title | Authors | Form | Est. Date Submission to W. O. |
|---|---|---|---|
| Acoustic Travel Times for the Madison Limestone in the Williston Basin | L.C. Marchant | Open file[1] | Third quarter FY 1973 |
| Numerical Waterflood Calculations with Compressible Fluids | C.S. Land<br>F.M. Carlson | Journal article | Sept. 6, 1972 (to SPE Oct. 25, 1972) |
| The Error in Gas Drive Calculations Caused by Ignoring Compressibility and Solution Effects | F.M. Carlson<br>C.S. Land | Journal article | Sept. 6, 1972 (to SPE Dec. 15, 1972) |
| Polyaromatic Hydrocarbons in High-Boiling Distillates. Isolation by Gel Permeation Chromatography and Identification by Fluorescence Spectroscopy | J.F. McKay<br>D.R. Latham | Presentation and journal article | Approved Sept. 1972 |
| Analytical Review of Nonmetal Elements and Compounds in Petroleum | W.E. Haines<br>D.R. Latham | Journal article | Dec. 1972 |

See end of "Manuscript Section" for footnotes

| Title | Authors | Form | Est. Date Submission to W. O. |
|---|---|---|---|
| Computerized Calculation of Crude Oil Composition from Bureau of Mines Analytical Data | M. V. Kirk[2]<br>J. C. Morris | R. I. | FY 1973 |
| Composition of Acidic Compound Types in High-Boiling Petroleum Distillates | J. F. McKay<br>J. H. Weber<br>T. E. Cogswell<br>D. R. Latham | Presentation and journal article | April 1973 |
| Composition of Neutral Nitrogen Compound Types in High-Boiling Petroleum Distillates | T. E. Cogswell<br>J. F. McKay<br>D. R. Latham | Presentation and journal article | Oct. 1973 |
| Inverse Gas-Liquid Chromatography--Mass Spectrometry. Mass Spectral Results Obtained After Silylation and/or Oxidation of Asphalts in IGLC Columns | S. M. Dorrence<br>F. A. Barbour<br>J. H. Weber | Journal article | Feb. 1973[3] |
| Molecular Interactions of Asphalts. An Infrared Study of the Hydrogen-Bonding Basicity of Asphalts | R. V. Barbour<br>J. C. Petersen | Presentation and journal article | Approved Dec. 1972 |
| A Study of Asphalt-Aggregate Interactions by Heat of Immersion--Evidence for Multilayer Adsorption[4]<br>A Study of Asphalt-Aggregate Interactions and Asphalt Molecular Interaction by Microcalorimetric Methods[4] | Keith Ensley | Presentation and journal article | Jan. 1973[3] |

| Title | Authors | Form | Est. Date Submission to W. O. |
|---|---|---|---|
| A Study of Asphalt-Aggregate Interactions Using Inverse Gas-Liquid Chromatography | F. A. Barbour<br>R. V. Barbour<br>J. C. Petersen | Presentation by title and publication in AAPT Proc. | Jan. 1973[3] |

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[1] Change in publication form and submission date (see Subproject 1, Project 1)
[2] Shell Oil Co., Denver, Colo.
[3] Change in submission date
[4] These two papers have been combined and will henceforth be carried as one entry.

## PERSONAL MENTION

John McKay attended the 1972 Pacific Conference on Chemistry and Spectroscopy held October 16-18 in San Francisco, Calif. Dr. McKay presented a paper on the separation and identification of polyaromatic hydrocarbons in high-boiling petroleum distillates at the conference.

DeWitt Latham, Center Safety Committee Chairman for 1973, attended the National Safety Congress meeting in Chicago, Oct. 30-Nov. 2, 1972.

Dr. Dieter Severin, a physicist from University of Clausthal-Zellerfeld, Germany, arrived in Laramie, November 2 to spend a year in post-doctoral research under a Max Kade Foundation fellowship. Dr. Severin, a student of Prof. H. H. Oelert who spent a year at the Laramie Center under a similar fellowship, will be working with the mass spectroscopy and heavy ends groups.

Paris Amend, a student at the University of Wyoming majoring in geology, was hired as a part-time physical science aid in the Characterization of Heavy Ends group and started work November 20.

C. Q. Cupps, Secretary of the IOCC Tar Sand Subcommittee, attended a meeting of the Subcommittee and the Annual Meeting of the Interstate Oil Compact Commission in Houston, Texas, Dec. 3-5, 1972. He reported on the status of tar sands research at LERC to the Subcommittee.

F. M. Carlson passed his oral examination Dec 6, 1972, and has now completed requirements for a Master of Science degree in Petroleum Engineering from the University of Wyoming.

John McKay and S. M. Dorrence attended a leadership training session held at the Laramie Center, December 11-14.

J. C. Petersen met at Boulder City, Nevada, in a project advisory meeting of the Bureau of Mines Boulder City sulfur project. In addition to the Boulder City project staff, Washington management and advisory personnel from Bureau of Mines facilities in Salt Lake City and Spokane were also in attendance. The sulfur project is aimed at finding new uses for the surplus sulfur removed from sulfur-bearing fuels.

## ADVANCING OIL SHALE TECHNOLOGY

### Project 1 GASIFICATION OF SHALE OIL

Submitted by: H. W. Sohns, Research Supervisor

Began: 1972 Expected completion: Continuing

Personnel:
- P. L. Cottingham, Chemical Research Engineer (Project Leader)
- L. K. Barker, Chemical Engineer

### SUMMARY

The chromatographic equipment for analyses of product gases was recently received and installed. One hydrogasification experiment with in situ crude shale oil was made for familiarization with the equipment.

Two proposed Reports of Investigations and one journal article covering previous research are about ready to be submitted for publication.

### DISCUSSION

The chromatographic equipment for analysis of gases from hydrogasification of in situ shale oil has recently been received and installed. For familiarization of personnel with this equipment, the first hydrogasification experiment with in situ crude oil was made. The experiment was run at 1,200° F, 1,000 psig, 1.0 LHSV, and 12,000 scf/bbl hydrogen feed rate. Chromatographic analysis of the gas found it to consist of components in the volume percentages of 54.60 hydrogen, 32.38 methane, 12.14 ethane, 0.76 propane, and 0.12 isobutane. Calculated gross heating values were 746 Btu/ft$^3$ raw, and 1,254 Btu/ft$^3$ with the hydrogen removed. These compare favorably with natural gas at, usually, about 1,000 Btu/ft$^3$.

A proposed Report of Investigations entitled, "Refining Improvement of Shale Oil Naphtha," was reviewed locally and was sent to the Washington Office.

The galley proofs of the paper, "Catalytic Reforming of Hydrogenated Shale Oil Naphtha," were received from I&EC Product Research & Development Quarterly, were proofread and returned. Publication is scheduled for December 1972.

A rough draft of a proposed Report of Investigations on hydrogenation of crude shale oils from the 150-ton simulated in situ retort is being further revised.

Trouble with the detector cell of the new chromatographic equipment has caused what is hoped will be only a short delay in further gasification experiments.

# ADVANCING OIL-SHALE TECHNOLOGY

## Project 2 CHARACTERISTICS OF SHALE OILS

### Subproject a. Development and Application of Analytical Techniques

Submitted by: G. L. Cook, Research Supervisor

Began: 1963 Expected completion: Continuing

Personnel:
H. B. Jensen, Research Chemist (Project Leader)
C. S. Allbright, Research Chemist
J. J. Duvall, Research Chemist
J. R. Morandi, Research Chemist
R. E. Poulson, Research Chemist

## SUMMARY

This project develops and applies techniques to obtain characterizations of products relevant to the evaluation of retorting and refining processes for oil shales and shale oils. Continued difficulties have been experienced with deuteration of olefins to obtain standards of acceptable isotopic purity. The standards are necessary in the development of the technique for characterizing the important olefin fraction in shale oils. The difficultly reduced olefins in a shale-oil naphtha fraction have been characterized by type. Saturates from a naphtha fraction are ready for distribution for testing by an ASTM method. A new type of nitrogen base appeared in a syncrude prepared from Rock Springs in situ crude oil. The final report for the third extension of Grant PET-20 on hydrogenation of shale oil was received from the Grantee. The project is a little behind the projected schedule.

## DISCUSSION

Deuteration of n-Olefins.--This research continues to be plagued with unforeseen troubles. In an effort to prepare deuterated standards with acceptable isotopic purity, a preparative GC step was added to the synthesis of normal olefins. Deuteration of the internal normal olefins thus prepared did not result in dideuterioalkanes of greater isotopic purity than resulted from deuteration of olefins which had not been purified by GC before deuteration. In fact, the GC-purified olefins required longer to deuterate and resulted in a lesser isotopic purity than did deuteration of the nonpurified olefins. No explanation is apparent.

Additional synthesis has brought the total number of reference dideuterioalkanes which have been synthesized to 32 of the possible 80 in the $C_{10}$ to $C_{20}$ range. This should be sufficient to prepare the MS matrix for the proposed method.

Due to the unforeseen difficulties, the deuteration of fractions from the four middle distillates will again be deferred to the next quarter.

MS Analyses of Shale-Oil Naphthas.--The prep-scale preparation of a sample of naphtha hydrocarbon concentrate was deferred in favor of examining the nature of the naphtha olefins that are difficult to hydrogenate with the homogeneous rhodium catalyst. These difficultly reduced olefins (in the case of the shale-oil naphtha olefins they are nonreduced) comprise some 22 percent of the total naphtha olefins. Their spectrum was obtained as the quantitative difference between the spectrum of the total product from the homogeneous hydrogenation and the spectrum of the raffinate from the $H_2SO_4 \cdot P_2O_5$ extraction of that product. Tentatively the olefin-type distribution is 5 percent chain monoolefins, 70 percent monocyclo monoolefins or chain diolefins, and 25 percent dicyclo monoolefins or monocyclo diolefins. The cyclic olefins with at least one substituent on the olefinic carbons and tetrasubstituted ethylenes have been shown by a companion project to be the most difficult of the olefins to hydrogenate with either homogeneous or heterogeneous catalysis.

The mass spectrum of the saturated olefins (78 percent of the total naphtha olefins) indicates that hydrogenation of the naphtha olefins produced about 35 percent chain paraffins, 35 percent monocyclo paraffins, and the remaining 30 percent are dicyclo and tricyclo paraffins.

A 1.2-gram sample of the product from naphtha olefin hydrogenation was separated into its saturate and olefin portions using elution chromatography on silver nitrate coated silica gel. Recovery of the naphtha hydrocarbons from the eluted solutions is underway.

The distribution list to receive ASTM MS calibration mixtures was not received during the quarter; this distribution will be made when the list is received.

Light Distillate Nonbasic Nitrogen.--A nonbasic nitrogen concentrate was prepared by removing all of the titratable bases using a cation-exchange resin. The nonbasic nitrogen compounds were then separated from the shale-oil hydrocarbons by adsorption on florisil. Characterization was not completed and will be continued next quarter. Installation of sulfur module on microcoulometer will be done as soon as the lab benches are received and installed.

Syncrude Characterization.--This new research was initiated by cooperating with the personnel under Project 3 in selecting the Rock Springs in situ crude oil to be studied and in monitoring the preparation of the fractions to be hydrotreated in production of the syncrude. In addition, a sample of jet fuel distillate from a syncrude was examined by nonaqueous titration. The nitrogen level in this jet fuel was 0.1 percent and two-thirds of the nitrogen appears in bases stronger than quinoline. This is a new class of nitrogen bases in shale oils and undoubtedly results from the hydrogenation reactions that occur in syncrude production.

Grant PET-20.--The final report for the third extension of Grant PET-20 was completed. Nitrogen-type analyses were started on the products from the hydrogenations completed during the 1972 summer quarter.

# ADVANCING OIL-SHALE TECHNOLOGY

## Project 2 CHARACTERISTICS OF SHALE OILS

### Subproject b. Beneficiation of Shale Oil by Oxidation

Submitted by: G. L. Cook, Research Supervisor

Began: 1967 Expected completion: 1975

Personnel:
A. W. Decora, Research Chemist (Project Leader)
E. B. Smith, Research Chemist

## SUMMARY

This subproject is to determine if shale oil can be denitrogenated using oxygen to lead to an economical feedstock for hydrogenators. Experiments this quarter continue to show that a substantial reduction of nitrogen in whole shale-oil naphthas can be achieved by mild oxidation. Arrangements were made to have an economic analysis performed by the economic analysis group at the Morgantown Research Center to determine the economic benefits to shale-oil processing that might be possible from this basic research study.

## DISCUSSION

A sample of heavy naphtha (100° to 207° C) was oxidized at 25° C and a pressure of 580 torr for a period of 7 days. After an initial induction period of 5 minutes, the oxidation reaction proceeded rapidly reaching a specified level of 0.31 mole of absorbed oxygen per liter of naphtha in 7 days. A major portion of the oxidized naphtha was further subjected to a second oxidation at the same temperature and pressure. Unlike the first oxidation, this reaction proceeded at a much slower rate having an induction period of 6 hours and reaching a level of 0.08 mole of absorbed oxygen per liter of naphtha in 22 days. Tests performed during both oxidation runs indicated that peroxides or hydroperoxides are present in the reaction mixture. This was especially true for the gums formed during the oxidation reactions. No peroxides were detected in the vapor-transferred naphtha samples. Analyses of the starting naphtha and the gum-free oxidized naphtha showed that oxidation causes a substantial reduction in the nitrogen content of the naphtha. The experiments showed that the nitrogen content was reduced from 1.55 weight percent to 1.03 weight percent.

Thin-layer chromatographic techniques were applied in an effort to fractionate further the strongly basic fraction of the gum. Four subfractions were removed from the TLC plates and submitted for IR and MS analyses. Using the KBr "wick-stick" technique, for concentration, IR spectra were obtained; but detailed interpretations have not been made. Efforts to obtain mass spectra of these four subfractions were unsuccessful because of an insufficient amount of sample for probe work. Similar TLC techniques were applied to the weakly basic fraction which yielded six subfractions that will be submitted for spectral analyses.

The work performed this quarter diverted somewhat from the programmed work plans. More effort was devoted to the oxidation of a heavy naphtha and less effort to the characterization of gums. These changes were necessitated because more oxidation runs were needed on the heavy naphtha and whole naphtha than had been originally planned, and because of delays encountered in laboratory remodeling. The major emphasis next quarter will be placed on naphtha oxidation.

# ADVANCING OIL SHALE TECHNOLOGY

## Project 3 MODIFICATION OF SHALE OIL FOR THE PRODUCTION OF FUELS AND CHEMICALS

Submitted by: H. W. Sohns, Research Supervisor

Began: 1967 Expected completion: Continuing

Personnel:
P. L. Cottingham, Chemical Research Engineer (Project Leader)
C. M. Frost, Chemical Research Engineer
F. A. Birkholz, Research Chemist

## SUMMARY

A 10-day hydrogenation run with crude shale oil from Run 9 of the 150-ton retort reduced the nitrogen content to below 0.1 percent; results indicate a long catalyst life expectancy.

Crude shale oil from the Rock Springs in situ retorting experiment is being processed to prepare "Syncrude" by the method proposed by the NPC.

Steam distillations of the individual $C_{12}$ to $C_{18}$ fractions from in situ light gas oil were started. Compounds tentatively identified as anthracene, carbazole, and n-nonadecane were separated from the pot residue left after distillation of the $C_{12}$ to $C_{18}$ fractions; the nonadecane has a purity of 98 percent.

A proposed R.I. concerned with hydrogenation research is ready for publication. A paper discussing hydrodenitrification of crude shale oil is to be presented at the Spring American Chemical Society meeting. Another paper dealing with use of depleted uranium as a hydrocracking catalyst is to be published as a journal article. A proposed R.I. on chemicals from thermally cracked shale oil naphtha is being prepared.

## DISCUSSION

One 10-day hydrogenation run was completed on crude shale oil produced in the 150-ton retort during Run 9 in which the maximum oil yield to date was attained. Nitrogen content of the hydrogenated oil was reduced to less than 0.1 wt pct and results indicated a long catalyst life expectancy.

Crude shale oil from the Rock Springs, Wyo., in situ combustion retorting experiment is now being processed to prepare "Syncrude" by the methods suggested by the National Petroleum Council.

Continued distillation of the in situ light gas oil after the removal of the $C_{12}$ to $C_{16}$ hydrocarbons has permitted the separation of fractions corresponding to $C_{17}$ and $C_{18}$ distillate fractions. By refractionation of all distillate fractions, samples with distinct refractive-index and specific-gravity plateaus in the curves of these properties versus temperature were obtained. These samples are being steam-distilled for further separation of products.

Three solid compounds were isolated from the pot residue left after distillation of the $C_{18}$ fraction. One of these is a sample of 98-percent pure nonadecane containing 2 percent eicosane and heneicosane. The other two compounds are anthracene and carbazole with slightly lower purity than that of the nonadecane.

Steam distillation of the $C_{12}$ fraction has shown that an undesirably long period of time is consumed in this operation because of the high water/oil ratio obtained as distillate. Therefore, only half of the quantity of each of the $C_{13}$ to $C_{18}$ fractions will be steam distilled. This will save considerable time and, because the quantities of these fractions range from 14 to 21 liters, should provide sufficient steam-distilled oil for the following planned work.

A proposed Report of Investigations entitled, "Hydrogenating Shale Oil at Low Space Velocity," has been approved by the Office of Mineral Information. A paper entitled, "Hydrodenitrification of Crude Shale Oil," was approved for presentation at the Spring meeting of the ACS and has been submitted to the program chairman. The paper, "Depleted Uranium as a Catalyst for Hydrocracking Shale Oil," was accepted for publication in I&EC Product Research & Development Quarterly; the galley proofs have been received, proofread, and returned to the publisher. A proposed R.I. on chemicals from thermally-cracked shale oil naphtha is being further revised.

# ADVANCING OIL-SHALE TECHNOLOGY

## Project 4 SPECTROSCOPIC METHODS RESEARCH

### Subproject a. Developmental Research

**Submitted by:** G. L. Cook, Research Supervisor

**Began:** 1947 **Expected completion:** Continuing

**Personnel:**

A. W. Decora, Research Chemist (Project Leader)
F. G. Doolittle, Research Chemist
D. G. Earnshaw, Research Physicist
F. R. McDonald, Research Chemist
G. Miyake, Chemist
S. C. Banks, Mathematician (Intermittent, E.O.D. 10/1/72)
F. D. Guffey, Chemist (Intermittent)
R. E. Ellefson, Mathematician (temporary appointment expired 10/20/72)

## SUMMARY

This subproject develops and applies instrumental techniques to provide the input to the Center's research for effective evaluation of a process or a product. Detailed analysis of the mathematical model used for analysis of deuterium labeled paraffins for the shale-oil characteristics group has led to improved analytical results. Progress continued on making techniques developed for older instruments compatible with current instrumentation. A "wick-stick" technique was developed for analyzing by infrared spectroscopy gum fractions. A method has been developed for obtaining intensity data from the microdensitometer used in high-resolution mass spectroscopy.

## DISCUSSION

Efforts this quarter have been devoted to investigating the mathematical model used for shale-oil olefin analyses and in obtaining and evaluating the spectra of 11 dideuterated standards. Analyses of the mathematical model have led to improved analytical results. The spectra of the dideuterated standards were disappointing in that isotopic purity ran from 19.6 percent to 95.3 percent with seven of the eleven samples having an isotopic purity less than 70 percent.

Progress continued in collecting and evaluating mass spectral data from different types of mass spectrometers. Next quarter's effort will be to incorporate this material into a report that will indicate what instrumental conditions are necessary to obviate or lessen the recalibration of the various types of mass spectrometers.

No progress was made on the ASTM shale-oil analysis work. The delay was due to the absence of the project leader on a special Washington office assignment. Research will resume next quarter.

No progress was made on the mathematical hydrocarbon-type analyses this quarter because the mathematician worked on the detailed analyses of the mathematical model used for analyzing dideuterated paraffins.

Shale-oil gum samples (TLC fractions) were analyzed by infrared spectroscopy using the "wick-stick" technique. This technique was developed without using lyophilization, formerly thought to be necessary. Further work to adopt the technique for use in mass spectrometry is in progress. Mass and infrared spectral data should permit component identification of these microsize samples.

A very simple method has been developed for obtaining intensity data from the microdensitometer. This method will be implemented during the next quarter.

Examination of experimental results indicated that further laboratory work is necessary before finishing the manuscript on dimethylnaphthalenes.

A manuscript entitled "Spectral Characterization of Heteroatom Compounds in Oil Shale" by F. G. Doolittle, D. E. Anders, and W. E. Robinson has been prepared for presentation at the Pittsburgh Conference on Applied Spectroscopy. This paper describes the techniques and instrumental methods developed in our laboratory for the characterization of heteroatom compounds isolated from oil shale.

# ADVANCING OIL-SHALE TECHNOLOGY

## Project 4 SPECTROSCOPIC METHODS RESEARCH

### Subproject b. Nonroutine Support Spectroscopy

**Submitted by:** G. L. Cook, Research Supervisor

**Began:** 1947 **Expected completion:** Continuing

**Personnel:**
A. W. Decora, Research Chemist (Project Leader)
F. G. Doolittle, Research Chemist
D. G. Earnshaw, Research Physicist
F. R. McDonald, Research Chemist
G. Miyake, Chemist
F. D. Guffey, Chemist (Intermittent)

## SUMMARY

This group supplies spectroscopists to participate in the planning and execution of other research projects at the Center so that the projects may fully utilize instrumental information in the evaluation of their products or engineering processes. Specific accomplishments were reported to a petroleum heavy ends group on the analyses of concentrates obtained from various petroleums; to a shale group on the analyses of olefins, naphthas, and pyrroles; to a shale-oil group on the analyses of fractions obtained from retort waste waters; and to another shale-oil group on the analyses of solid residues obtained from a naphtha.

## DISCUSSION

This subproject under spectroscopic research provides project-analyst assistance to other research projects at the Laramie Center. Most of the project-analyst results are discussed under the project for which they provide spectroscopic liaison. Specific programmed work is discussed here.

High-resolution mass spectral data were obtained on several concentrates from various petroleum distillates. The samples were three aromatic concentrates, four ester concentrates, and eight basic nitrogen conentrates. Low-resolution data were obtained on the aromatic concentrates and a saturate concentrate. Progress on this work was communicated to the petroleum heavy ends group.

The dideuterated olefin mass spectral method, at the present state of development, was applied to a known mixture of dideuterioalkanes. The results obtained were very good when using the latest modification of the method. Progress on this work was communicated to the shale-oil characterization group.

Mass spectral data for application to the analyses of shale-oil naphthas were obtained on a limited number of samples. Progress in these analyses was delayed by the absence of the project leader on a special Washington office assignment.

A report on the compounds identified by spectral techniques was submitted to the waste water retort group.

Continued success was obtained on the analyses of compounds isolated from fractions of a thermally-cracked heavy shale-oil naphtha (174-255). The following compounds were shown to be present in the solid residue from a vacuum distillation: Anthracene, carbazole, nonadecane, eicosane, heneicosane. A detailed report on the spectral identification of these compounds was submitted to a shale-oil group.

Spectral data were also obtained on saturate fractions and on heterocyclic fractions isolated from Green River oil shale. Workup of these data is in progress.

Nonroutine spectroscopic services supplied to other research projects at the Laramie Center included 394 mass spectra, 22 NMR spectra, 43 infrared spectra and 4 ultraviolet spectra.

# PROTECTING THE PUBLIC OIL-SHALE INTERESTS

## Project 5 OIL-SHALE CHARACTERISTICS

### Subproject a. Continuing Operations

**Submitted by:** G. L. Cook, Research Supervisor

**Began:** 1944 **Expected completion:** Continuing

**Personnel:**

J. W. Smith, Research Chemist (Project Leader)
L. G. Trudell, Geologist
W. A. Robb, Research Chemist
G. F. Dana, Geologist

## SUMMARY

The proposed oil-shale lease program continues to have an impact on oil-shale acquisitions. Nine cores, five from Colorado and four from Utah, were received and assays completed. An additional core from Colorado was assayed in conjunction with a proposed federal land exchange. Three cores and six sets of drill cuttings (three from Wyoming, one from Utah, and two from Colorado) were also received. Average oil-yield computations were completed from data on two long cores from Colorado and four Mahogany zone cores from Utah. Data tapes for computer access were prepared for 174 cores from Colorado. Work was resumed on the examination of a Bureau of Mines' core from Wyoming, and X-ray diffraction data were obtained for shale from a Colorado core. It has been necessary to defer work on cores from Bureau of Mines drilling to obtain data pertinent to the Interior leasing program on a timely basis.

## DISCUSSION

Core drilling by private companies to extend their evaluations of federal oil-shale tracts to be offered for lease produced five coreholes in Colorado and four coreholes in Utah. To provide oil-yield data on these tracts to federal agencies and to potential oil-shale bidders, the Bureau of Mines completed assay of these cores. Approximately 3,700 assay runs were performed in the program. The samples represent a previously uncored area in Utah and an area in Colorado where oil-shale richness in the Green River Formation is variable over short distances. In addition, the prompt assay of a core involved in a proposed federal land exchange produced oil-yield data for the oil shale in the area of the Colony

Development Company Mine. Previously, this area has been closed to sampling, and no oil-yield information from it has been available to us.

Three cores from Wyoming's Green River oil shales were received. In addition, six sets of drill-cutting samples were obtained. Three of these came from Wyoming, one from Utah, and one from Colorado's Piceance Creek Basin, and one from Colorado's Sand Wash Basin. Qualitative oil-yield determinations by the test-tube method were completed on eight sample sets. Six sets of drill cuttings were assayed in addition to the lease tract cores. Crushed samples from all assayed cores were added to the Bureau's oil-shale sample library.

Computations of average oil yields for selected sections were completed on two long cores from Colorado and four Mahogany zone cores from Utah. One of the Colorado cores calculated is the richest sample set from the nine holes drilled in the lease tract in which the formation is changing rapidly.

To provide a permanent computer access to oil-yield assay data and to facilitate oil-yield comparison calculations, data tapes containing the complete oil-yield assay results have been prepared for 174 cores in Colorado. This set does not yet contain all Colorado core data. It will be added to gradually as time, facilities, and data availability permit. Assay data tapes for core samples from Utah and Wyoming are planned.

Lithologic description and sampling of a Bureau of Mines core from Wyoming are about 50 percent complete. A mineral survey by X-ray diffraction was completed on samples from a long core from Colorado. Information on Phosphoria Formation oil shales and sample availability was provided the Geology Department of McMaster University in Ontario, Canada.

# PROTECTING THE PUBLIC OIL-SHALE INTERESTS

## Project 5 OIL-SHALE CHARACTERISTICS

### Subproject b. Oil-Shale Properties

Submitted by: G. L. Cook, Research Supervisor

Began: 1944 Expected completion: Continuing

Personnel:

J. W. Smith, Research Chemist (Project Leader)
D. R. Johnson, Research Chemist
N. B. Young, Research Chemist
W. A. Robb, Research Chemist

## SUMMARY

Correlation of laboratory and field data on oil shales is proceeding through the cooperation of TCMRC. Physical property data obtained by them on an oil-shale core will be combined with data from the Laramie Center to provide a measure of the oil shale in place in the formation. The thermal analysis technique in use on oil shales is being advanced by results obtained using various atmospheres within the instrument. Techniques in development for important minerals in oil shales and for a direct determination of organic hydrogen are on schedule. A technique for estimating nahcolite and dawsonite was described in a Report of Investigations. The research projected for this year is on schedule.

## DISCUSSION

Arrangements were completed with the Minneapolis Mining Research Center for determination of assorted physical properties on oil-shale samples. Minneapolis has developed and has equipment for testing techniques which appear particularly suitable for oil shale. After completion of these tests, the residual samples will be examined here to determine the three properties which may influence physical characteristics of the samples. These properties are organic content, mineral composition, and stratigraphic arrangement. When the determinations are complete, Minneapolis personnel will cooperate in interpreting and evaluating the relationships.

Testing of a special core is in progress. This 7-inch core was cut for the Bureau of Mines during drilling of a large diameter hole in the northern part of Piceance Creek Basin. The cored section was also logged by a borehole technique designed to measure physical parameters of the rock in place. Hopefully the interpreted core data can be used to calibrate and interpret the special logs.

Preparation of a paper presenting a technique for testing atmospheric effects in thermal analysis was begun. Using a Bureau of Standards dolomite as a demonstration material, this paper will show how the course of a thermal reaction can change with changing atmospheres. Supporting data from a coauthor in Switzerland has been received to enlarge the range of instruments covered by the study. A recently described low-temperature analog of dolomite--$CdCO_3 \cdot MgCO_3$--may permit use of this technique at temperatures 200K lower than those available with dolomite.

Study of the thermal behavior of shortite, a mineral unique to and widespread in Green River oil shales of Wyoming and Utah, has been begun. A core offering samples over a range of richness suitable for thermal expansion studies has been obtained. Preparation of the paper reporting on thermal behavior of gaylussite was completed. A paper reporting development of a method for estimating nahcolite and dawsonite from oil-yield assay data was published.

Equipment to modernize the 22-year-old X-ray diffraction apparatus has been ordered.

Analysis for extractable cations of 219 Green River Formation samples, each representing approximately 10 feet of the formation, has been completed. From these analyses each sample's content of the carbonate minerals--nahcolite, dawsonite, calcite, dolomite, and ferroan--were calculated. The $CO_2$ content computed from these mineral amounts was compared with the analytically determined $CO_2$ obtained from acid treatment of the samples. The correlation between these values is over 99 percent. Final checking of the analyses is in progress. Statistical comparison of X-ray diffraction peak heights specific for each mineral shows a highly significant correspondence between the two measures. This verifies that the mineral amounts being computed from the analyses represent the actual amounts present.

Simplification of operation techniques involved in the method being tested for direct determination of organic hydrogen in oil shale produced results checking closely with known values. Obtaining enough runs for statistical evaluation is in progress.

# PROTECTING THE PUBLIC OIL-SHALE INTERESTS

## Project 5 OIL-SHALE CHARACTERISTICS

### Subproject c. Deposit Evaluation

Submitted by: G. L. Cook, Research Supervisor

Began: 1944 Expected completion: Continuing

Personnel:
J. W. Smith, Research Chemist (Project Leader)
L. G. Trudell, Geologist
G. F. Dana, Geologist
W. A. Robb, Research Chemist

## SUMMARY

Three coreholes were completed in the northern Green River Basin of Wyoming to extend the known oil-shale areas to the north and west of the Eden-Farson area. Reports of Investigations described oil shales at a Wyoming location and at a Utah location. An RI on Kinney Rim oil shales has been prepared. The oil shales described are on two tracts in the proposed leasing program. Mineral survey histograms for depth and oil-yield correlation are in progress. The evaluation of data from Subprojects a and b is on schedule.

## DISCUSSION

Drilling of three coreholes in the northern Green River Basin was completed. These coreholes--named Wyoming Coreholes 6, 7, and 8--extended sampling of oil shales in the Farson-Eden area to the north and west. The three-hole program cut nearly 1,200 feet of core with about 95 percent core recovery. Preliminary examination of the cores shows persistence of the variegated oil shales into the sampled area with some minor lithologic modifications in the beds.

Each of these coreholes reached the artesian aquifer underlying the oil shale, and each was equipped with a valve left running slowly to prevent freeze-up. Preparations for periodic sampling and analysis of the water from these coreholes have been made. The first set of semimonthly water samples were collected and analyzed.

Correlation of the nahcolite-dawsonite estimates from oil-yield assay data was more or less completed. Permission to release the data was obtained for all pertinent cores, save one. Because this occupied a key position, a substitute has been sought. An appropriate corehole drilled by Superior Oil was found and release of the data requested.

Two Reports of Investigations presenting oil yields and characteristics of the oil shales at a location in Wyoming and a cored site in Utah were published. Tables prepared and typed for inclusion in a U.S. Geological Survey Professional Paper on Wyoming's Green River Basin oil shales need to be retyped to meet U.S.G.S. specifications. In the process the tables will be reorganized to include data from Bureau of Mines Wyoming Corehole No. 2 and from a Union Pacific corehole. Negotiations to agree on the specifications are in progress.

The proposed RI, "Geology and Oil-Shale Resources of Kinney Rim, Washakie Basin, Sweetwater County, Wyoming," was prepared for station review. This manuscript presents the only oil-shale data available for evaluation of the two Wyoming tracts proposed for federal leasing. Hopefully it can be released early enough to aid evaluation of these tracts. "Aragonite and the Genesis of Carbonates in Mahogany Zone Oil Shales of Colorado's Green River Formation," a proposed RI, was completed; the manuscript has reached the printer.

Two mineral survey plots were prepared. By plotting peak heights with depth, these plots present histograms of relative amounts of the component minerals through the oil-shale formation. The final plot relates peak heights for dawsonite, quartz, nahcolite, dolomite, calcite, analcite, soda feldspar, and potash feldspar to depth and to oil yield. Although it was initially planned to report the mineral data correlated across the Piceance Creek Basin, it appears more practical to begin by interpreting geochemically the mineral profiles of just one core. The plot for Colorado Corehole No. 1 has been selected for this interpretation. It is currently being computer plotted.

# PROTECTING THE PUBLIC OIL-SHALE INTERESTS

## Project 5 OIL-SHALE CHARACTERISTICS

### Subproject d. Development of Instrumental Oil-Shale Assay Methods

Submitted by: G. L. Cook, Research Supervisor

Began: 1971 Expected completion: 1975

Personnel:
A. W. Decora, Research Chemist (Project Leader)
F. P. Miknis, Research Chemist
A. B. Denison, Intermittent Faculty Member

## SUMMARY

The application of the nuclear magnetic resonance technique for assaying oil shales was delayed this quarter owing to the incompatibility between the three-phase, 220v line voltage in our building and that required for correct operation of the magnet power supply. The instrument is now working and the major emphasis for the succeeding quarters will be the use of the NMR instrument to reduce the backlog of oil-yield assays.

## DISCUSSION

The research schedule for this quarter was delayed because of problems arising during the installation of the spectrometer. A magnet, to replace the one damaged last quarter, arrived in mid-October and was successfully unloaded and placed in our laboratory. However, additional problems arose because of an incompatibility between the three-phase, 220v line voltage in our building and that required for the correct operation of the magnet power supply. The 220v, three-phase system in our building is in the form of a Delta hookup, whereas the form required by the magnet power supply is a Wye hookup. This was not specified by the manufacturer. As a result of this power mismatch, some damage was done to the receiver section of the spectrometer console. This required the receiver section to be shipped to the Bruker laboratory for repair. A month's delay occurred in repairing the receiver because an operational amplifier had to be sent from Germany. The receiver section has been rebuilt and is now installed in the spectrometer. The instrument is now working, and a company representative will arrive shortly to give final instructions on the operation of the instrument as well as to check it to insure that the original specifications are met. Once this is done, the yearly work plan will be implemented as rapidly as possible.

Preliminary success was obtained in observing free-induction decay signals for protons in such varied substances as oil shale, a kerogen concentrate, Gato Ridge petroleum asphaltenes, asphalt, and sucrose. In addition, free-induction decay signals were observed for copper, fluorine, and sodium in special test samples. Application of the instrument to potential oil-yield assay of oil-shale samples should now be possible by the first of January.

An undergraduate physics student at the University of Wyoming has written a program for calculating spin-lattice relaxation times, $T_1$, for oil-shale samples. His program, written as part of a research course at the University, will assist us in our applications of NMR to oil-shale assay work.

# PROTECTING THE PUBLIC OIL-SHALE INTERESTS

## Project 6 CHARACTERISTICS OF OIL-SHALE ORGANIC MATERIALS

**Submitted by:** G. L. Cook, Research Supervisor

**Began:** July 1968 **Expected completion:** Continuing

**Personnel:**
W. E. Robinson, Research Chemist (Project Leader)
D. E. Anders, Research Chemist
J. J. Cummins, Research Chemist
D. L. Lawlor, Research Chemist

## SUMMARY

The organic materials in oil shales are examined in this research for properties that may be exploitable in processing to obtain shale oils. Development of a dehydrogenation technique for determining cycloalkanes was continued. Progress in setting experimental conditions indicates potential for aromatizing the ring systems either with or without removing alkyl groups from them. Application of a successful technique to shale-oil processing is indicated. Most of the analytical work has been completed to describe variations in the organic material in an oil-shale core from Utah. Analytical work on the products from heating shale at 150°-350° C for varying periods of time, a potential in situ operating condition, was continued. The analyses are somewhat behind schedule, but the work projection may have been over optimistic. Polymerization tests on known mixtures indicated that some of the desired products were obtained. Reports are being completed on the projected schedule.

## DISCUSSION

Development of a microcatalytic dehydrogenation method for distinguishing the type of ring structures in 1- to 6-ring cycloalkane compounds was continued. Parameters affecting dehydrogenation such as catalyst concentration, temperature of reaction, catalyst type, catalyst support, and stability of the catalysts were studied.

Dehydrogenation of the saturated rings of 18 different alkyl and cycloalkyl substituted indanes and tetralins without affecting the alkyl groups was attempted. Best results were accomplished in a 1/8-inch I.D. by 14-inch column using platinum catalyst supported on pyrex glass (ratio 1 to 500) at 300° C. Using this column, twenty 2-microliter samples could be dehydrogenated before exhausting the catalyst. The resulting products were analyzed gas chromatographically and mass spectrographically. Dehydrogenation tests using palladium catalyst on pyrex glass (ratio 2.5 to 100) at 375° to 400° C removed the side chains from several alkyl substituted indanes and tetralins and dehydrogenated the ring systems.

Most of the analytical work on the WOSCO EX-1 core samples (Utah) has been completed. Work to be done consists of 20 volatile material determinations and 75 carbon and hydrogen determinations. Progress on this work was slowed because of the resignation of one student aid and the training of another.

Mass spectra have been completed for the 21 branched plus cyclic alkane fractions obtained from the low-temperature heating of oil shale at 150° to 350° C. The spectra have all been read, and the resulting data have been processed for ring analysis by the "Hood-O'Neal" method. The method provided information about the amount of branched alkanes, the 1- to 6-ring alkanes, and the 1-ring aromatic compounds in the various fractions. No mass spectral data have been obtained for the 21 aromatic fractions or for the 150° C alkanes (MS-GC analysis) from the low-temperature products. These analyses will have to be rescheduled for next quarter.

Two tests of the water-gas reaction were made on bitumen and carbonate-free oil shale. The conditions used were as follows: 40 grams of oil shale, 120 milliliters of water, and 1000 psig of carbon monoxide held at 250° C for 8 hours. In one test, 5 percent by weight of sodium carbonate was added to the sample. The results showed that in the carbonate-free test 9 percent of the kerogen was converted to gases and soluble product, while the 5 percent carbonate test converted 13 percent of the kerogen to gases and soluble product. Comparable tests with oil shale containing its natural carbonates converted 8.6 percent of the kerogen. These results show a significant increase in product yield due to the presence of sodium carbonate. The yields are considerably lower than published results for cellulose conversion under similar conditions; however, heating oil-shale kerogen at 250° C at atmospheric pressure required 12 days of heating at this temperature for 9.8 percent conversion of the kerogen.

Heating known materials at 150° C in a closed system for periods of time of 1 month in an attempt to affect polymerization was continued. Two additional sets of seven mixtures were investigated. In the one set, the mixtures were as follows: Clay (montmorillonite)-oil shale bitumen-water; clay-bitumen-glycine-water; clay-bitumen-adenine-water; clay-adenine-water; clay-bitumen-water; clay-bitumen-galactose-water; and clay-bitumen-adenine-guanine-cytosine-thymine-water. In all cases, except the clay-adenine-water mixture, there was evidence of darkening of the mixture, suggesting that some form of polymerization had taken place. The same sequence of mixtures were repeated in similar tests except that the montmorillonite clay was replaced by illite clay, a clay more characteristic of the Green River Formation.

The resulting products from the first set of seven mixtures reported upon last quarter were extracted with chloroform to remove chloroform-soluble material. The insoluble residues were subjected to total nitrogen and X-ray diffraction analyses. The amounts of chloroform-soluble extract ranged from a trace to 12 percent and contained from a trace to 6 percent nitrogen. In all cases X-ray diffraction showed an expanded crystal lattice for the montmorillonite clay, suggesting that some material--either water or organic material--had entered the crystal lattice causing expansion. Other analyses of products are progressing.

The paper, "Analysis of Some Aromatic Hydrocarbons in a Benzene-Soluble Bitumen from Green River Shale," was accepted for publication in Geochimica et Cosmochimica Acta.

## CONTROLLING POLLUTION AND MANAGING WASTES IN AN OIL SHALE INDUSTRY

### Project 7 IN SITU OIL SHALE PROCESSING: FIELD STUDIES

Submitted by: H. W. Sohns, Research Supervisor

Began: 1971 Expected completion: Continuing

Personnel:

H. C. Carpenter, Chemical Research Engineer (Project Leader)
E. L. Burwell, Chemical Research Engineer
G. G. Campbell, Petroleum Engineer
R. E. Cummings, Physical Science Technician
L. Dockter, Chemical Research Engineer
A. E. Harak, Chemical Research Engineer
A. Long, Chemist
T. E. Sterner, Petroleum Engineering Technician
R. L. Wise, Chemical Engineer

### SUMMARY

A hydraulic fracturing treatment performed at Rock Springs Site 9 was partially successful. Communication between wells was established, but fractures were not opened wide enough to accept sand proppant. Two additional wells have been drilled and Site 9 is being dewatered in preparation for evaluation. A series of tests in the pressure retort using nitrogen as the carrier gas was completed. A few of these experiments will have to be repeated to check questionable data. No progress was made on the study of surface area or on the study of oil shale gasification. Delays were caused by reduced travel allotments and by temporary assignment of personnel to the Coal Gasification Project.

### DISCUSSION

An impression packer was oriented in Well 1, Site 9 on October 4. Inspection of the impression element indicated either natural fractures or soft tuff zones, 1/8-inch thick on horizontal planes at 175.2, 175.8, 178.2, and 178.4 feet.

The first of three planned treatments to hydraulically fracture oil shale at Rock Springs Site 9 was performed in the center well of an inverted five-spot pattern. The treatment, which was at a depth of 174-177 feet, was to consist of pumping 70 barrels of fresh water at 8 bpm to achieve breakdown and initiate a fracture. This was to be followed by 200 barrels of super-viscous gel carrying 6,825 pounds of 6-8 mesh sand pumped at 10 bpm. The job went well and communication was established to the surrounding wells; however, when the gel-sand mixture was started, the well screened out. The packers were moved up hole to 172-175 feet, and the treatment was tried again. Again, when the gel-sand mixture was started, the well screened out. It is thought the natural permeability in the oil shale at this depth was bleeding off enough fluid so that a fracture could not be opened wide enough at the injection rate established to accept the 6- to 8-mesh sand proppant. Another treatment is being planned that will use a higher injection rate and smaller sand.

Two additional wells, Nos. 6 and 8, Site 9, were completed. Site 9 is now being dewatered by swabbing all wells and injecting air into the center well. This is being done in preparation for the post-fracture flow log evaluation work. The dewatering is being done by the drilling contractor.

Additional work planned for Site 9 has been delayed by the reduction in travel funds and by the temporary assignment of personnel to the coal gasification project at Hanna, Wyo.

A manuscript entitled, "Evaluation of Shale Oil Recovery by In Situ Retorting," was completed. This paper is proposed for publication as a Report of Investigations.

No work was done on the study of surface area or on gasification of oil shale. Most of the equipment for the gasification study was received, but construction in the laboratory has delayed installation of the equipment.

The series of tests in the pressure retort using nitrogen as a carrier gas was completed this quarter. However, there are approximately four tests that will be re-run to check data. Analytical results are available through Run 27 only, which leaves six runs to be calculated. It is possible that some of these runs will have to be re-run depending on the results of the balance calculations.

Construction was started on a new room for locating the instrumentation for the project. The construction has caused a temporary shutdown. When the room is more nearly complete the re-runs will be resumed. Meanwhile, the balance calculations will be brought up to date as the chemical analyses become available.

## CONTROLLING POLLUTION AND MANAGING WASTES IN AN OIL SHALE INDUSTRY

## Project 8 IN SITU OIL SHALE PROCESSING: PILOT PLANT STUDIES

**Submitted by**: H. W. Sohns, Research Supervisor

**Began**: 1964 **Expected completion**: Continuing

**Personnel**:

H. C. Carpenter, Chemical Research Engineer (Project Leader)
L. Dockter, Chemical Research Engineer
A. E. Harak, Chemical Research Engineer
A. Long, Chemist
R. A. Martel, Chemical Engineer
R. A. Minster, Chemical Engineer

### SUMMARY

The aboveground retorting equipment is being operated to obtain data for designing future in situ retorting experiments and to study the mechanisms of heating and retorting large blocks of oil shale. During the quarter, two runs were made with the 10-ton unit and one run with the ½-ton retort. Work on the mathematical model was continued. Changes in work plans are not required at this time.

### DISCUSSION

Two runs, S-17 and S-18, were completed with the 10-ton retort this past quarter. For the first run the retorting gas contained 17.1 percent oxygen at a superficial gas velocity of 3.6 $ft^3$ gas/$ft^2$ bed/min. These conditions were nearly identical to those used in S-16, the previous run in the 10-ton unit. The purpose of Run S-17 was to check reproducibility in the 10-ton retort when retorting Colorado oil shale assaying about 25 gallons of oil per ton. Good reproducibility was demonstrated in that an oil recovery of 47.6 volume percent of Fischer assay was obtained for Run S-17 compared to a value of 45.5 volume percent for Run S-16.

The second run, S-18, was run at nearly identical conditions as Run 5 with the 150-ton retort to obtain additional data on scale-up factors between the two units. For Run 5 with the large retort, an oil recovery of 54.5 volume percent of Fischer assay was realized compared to a value of about 50 volume percent for the 10-ton unit. As in a previous test, this run indicates that the 150-ton retort is somewhat more efficient than the smaller 10-ton unit.

Run 5 using the ½-ton retort was completed this past quarter. An oil shale block weighing about 400 pounds was successfully retorted in this unit which is designed to determine retorting characteristics of large, solid blocks of oil shale. The vessel is also designed to visually observe retorting mechanisms through portholes in the retort wall, and a study of part of one face of the 400-pound block was permissible for about 4 hours during the 30-hour test. Bright flames resulting from the combustion of gases and shale-oil mist could be seen plainly during the run. The color of the block face changed from natural to soot black to ash gray to a deep, cherry red. Photographs were taken of these phenomena for future reference. A 2-hour lag in retorting time between the large block and the surrounding shale bed was noted. Maximum bed temperatures surrounding the block were about 1,600° F, but maximum block internal temperatures reached only 1,130° F.

No runs were completed with the 150-ton retort this quarter due to adverse winter weather conditions, lack of personnel due to a recently activated field project, and the length of time required to charge the retort for the next run. The next shale charge is time consuming because about 15 to 20 large blocks of oil shale, some weighing as much as 5 tons, are being instrumented with thermocouples and loaded into the retort to be included in the next shale charge.

To continue the development of a mathematical model, the literature was reviewed in an attempt to find treatments of problems which are related to the oil shale retorting problem. Several such results were found; those results include a cement kiln model, a three-phase flow model of an in situ oil combustion process, models of solid fuel rocket propellant burning, and various descriptions of the combustion and pyrolysis phenomena.

Equations are being sought to describe the combustion process in the oil shale retort and the propagation of a combustion zone through a burning solid (in the presence of several complicated chemical reactions). A system of nonlinear partial differential equations is being formulated, along with a system of ordinary differential equations which should represent major effects.

A computer program has been developed to calculate values for the rate constants in a system of chemical reactions. A system of reactions is assumed, then the model is specified by least squares. This program is intended to help identify the chemical reactions taking place in the pyrolysis of oil shale.

## CONTROLLING POLLUTION AND MANAGING WASTES IN AN OIL SHALE INDUSTRY

Project 9 IN SITU OIL SHALE PROCESSING
LABORATORY STUDIES

Submitted by: H. W. Sohns, Research Supervisor

Began: 1968 Expected completion: Continuing

Personnel:
P. R. Tisot, Research Chemist
G. G. Campbell, Petroleum Engineer

### SUMMARY

A series of tests was made to determine whether propped fractures in triaxially confined specimens of 29-gallon-per-ton oil shale could be maintained during heating. In all tests the proppant was either partially or completely embedded in the shale thereby seriously impairing or completely eliminating the fracture's flow capacity. No work was done on the determination of directional physical properties of oil shale during the quarter

### DISCUSSION

A series of tests was conducted to determine if propped fractures in triaxially confined specimens from a 29-gal/ton oil shale would collapse as the result of internal pressure generated during heating and whether or not the specimens' induced fracture flow capacity, in turn, would be seriously impaired.

In all tests, pressure generated within the specimen was sufficient to either seriously or completely embed the proppant followed by serious or complete loss of the specimen's induced fracture flow capacity provided by the propped fracture.

Internal pressure generated during heating was sufficient to extrude a portion of the specimen (both carbonaceous and mineral matter) between the walls (3/16-inch thick) of the two half cylinders which formed the test cell. Clearance between the half cylinders was approximately 0.003 inch. Under a load of 800 psi the internal pressure also overcame the applied stress on the test cell and forced a portion of the specimen from the top of the test cell. Under a load of 1,000 psi, the specimen was contained at the capped end; however, extrusion occurred between the two half cylinders.

In one test, under a load of 1,000 psi, a sudden explosive reaction occurred at 792° F and considerable vapor emerged from the apparatus. This event indicated that the pressure generated within the confined specimen forced most of the extruded material from the test cell within a fraction of a second.

Because of travel limitations, a proposed trip to Twin Cities Mining Research Center to discuss the work they had done on directional physical properties of the oriented cores which were sent to them last quarter was cancelled. Therefore, no results became available this quarter. No laboratory work on physical properties was done during the quarter because personnel were devoting their time to the Hanna underground coal gasification project.

# CONTROLLING POLLUTION AND MANAGING WASTES IN AN OIL-SHALE INDUSTRY

## Project 10 IN SITU PROCESSES: APPLIED KINETICS

### Subproject a. Kinetics and Mechanistics of Oil Production and Transport

**Submitted by:** G. L. Cook, Research Supervisor

**Began:** July 1971 **Expected completion:** June 1974

**Personnel:**

H. B. Jensen, Research Chemist (Project Leader)
J. J. Duvall, Research Chemist
R. E. Poulson, Research Chemist

## SUMMARY

This research is to develop input to engineering studies of in situ retorting of oil shale by obtaining and interpreting data from the operation of a controlled laboratory-scale retort. Nine runs have been completed on the retort. Changes in analytical techniques were found to be necessary so analysis and interpretation of results were deferred. Two additional retorting runs are planned. After they are completed, the results of all runs will be digested prior to making additional runs. These latter items represent changes in schedule, but they should give a better basis for designing later experiments.

## DISCUSSION

The tentative analytical technique for determining the desired data on runs made in the controlled-state retort (CSR) fell short of its expected goals and has required changes in its simulated-distillation portion. These changes were dictated partly by the attempt to use a newly acquired, fully automatic instrument for simulated distillation and partly by the failure of ion-exchange resins to remove quantitatively the tar acids and tar bases from the products from the CSR.

Three runs were completed in the CSR, but they were not the three planned runs. The following table gives the operating parameters for each of these three runs:

| Run No. | Temp. rise, °F/min | Heated zone rate, in/hr | Sweep nitrogen rate, ft$^3$/hr | Amount of shale retorted, % |
|---|---|---|---|---|
| 7 | 2 | 3 | 1.5 | 50 |
| 8 | 2 | 3 | 1.5 | 50 |
| 9 | 4 | 6 | 14 | 50 |

All three runs were nonoxidative runs, and the maximum temperature was supposed to be 1,000° F; however, the temperature in run 7 went above to an unknown high. The reason for not knowing the maximum temperature was that the temperature was being monitored by a borrowed recorder (top temperature 1,000° F) while the unit's regular recorder was being repaired. A second, borrowed recorder was used for run 8 (a duplicate of 7) and run 9.

Use of the fully automated gas chromatograph for the analysis of the products will greatly facilitate the data acquisition for the CSR project. However, to take full advantage of this system, which has a teletype tape output, a programmable calculator is needed.

Changes in work plans for the third quarter of FY 1973 include: (1) Making only the two nonoxidative, 1,600° F runs originally scheduled for the second quarter; (2) develop and apply changes in the analytical technique to the products of the nine runs made thus far; (3) apply these changes to the extracts of the cores from Rock Springs site 4; and (4) defer future planned runs until the analytical results of the first nine runs are obtained.

# CONTROLLING POLLUTION AND MANAGING WASTES IN AN OIL-SHALE INDUSTRY

## Project 10 IN SITU PROCESSES: APPLIED KINETICS

### Subproject b. Rates and Mechanisms of Oil-Shale Retorting Reactions

**Submitted by:** G. L. Cook, Research Supervisor

**Began:** 1967 **Expected completion:** 1976

**Personnel:**
A. W. Decora, Research Chemist (Project Leader)
C. F. Brandenburg, Research Chemist
I. A. Jacobson, Jr., Research Chemist

## SUMMARY

This subproject is to determine the effect on subsequent retorting of oxygen contact with shale at subretorting temperatures and to develop techniques for estimating retorting conditions during an in situ processing operation. Oxidation experiments on Hanna, Wyoming coal show that the rate of oxidation of this coal is approximately the same as the rate for oil shale at 318° C. Oil-shale oxidation experiments showed that rich shales are not as accessible to oxidation as are lean shales. Retorting temperatures were calculated from the ethylene/ethane ratios of the retort gas using various amounts of oxygen in the sweep gas. These runs were in accord with those using only nitrogen. However, when steam was used in the sweep gas, the calculated retorting temperatures were 75° F lower as compared to the nitrogen and nitrogen plus oxygen runs. The work plans are on schedule.

## DISCUSSION

Eight oxidation runs on Hanna (Wyoming) coal were made at four temperatures--150°, 225°, 240°, and 260° C. Rate of oxidation data from the literature on Indian and Australian coals indicate that the rate of oxidation of coal at 150° C should be similar to the rate for oil shale at 300° C. Our data show that the rate of oxidation of shale and coal of the same particle size is approximately the same when the coal is oxidized at 260° C and the shale at 318° C.

The hypothesis proposed last quarter, that rich shales do not allow as much oxygen diffusion as lean shales, was borne out by data gained this quarter. Rich shale (64 gpt) was found to consume oxygen for a longer time than lean shale

(22 gpt). The total oxygen consumption for the rich shale is only twice that of the lean shale. Thus, approximately two-thirds of the organic matter in rich shale is accessible to aerial oxidation while virtually all of the organic matter in lean shale is accessible to aerial oxidation.

Using the remodeled bench size retort, several oil-shale retorting runs were made at 1,187° F using various amounts of oxygen in the sweep gas ($N_2$). The oxygen content of the sweep gas used varied from 3 to 21 percent, and those runs with the higher percentages of $O_2$ showed burning of the spent shale. The ethylene/ethane ratios from the retorting runs using oxygen in the sweep gas fell within the range of values when only nitrogen was used as sweep gas. This indicates that retorting temperatures can be calculated from the ethylene/ethane using air as the sweep gas. Several retorting runs at 1,187° F using steam in the sweep gas were made. Retorting temperatures calculated from the ethylene/ethane ratio were 75° F too low for these runs. Results obtained from laboratory work using $O_2$ and steam in the sweep gas are being incorporated into the revision of the ethylene/ethane ratio--retorting-temperature calculation manuscript.

About 20 grams of a 23.8 gpt oil shale has been leached with HCl to remove carbonates. This leached shale will be retorted in the bench unit to determine how much of the carbon dioxide and possibly carbon monoxide found in the retorting products are from organic sources. Data from this work will be used in the gas formation kinetics study.

No further work has been done on the isoprenoid paper. We are awaiting the GC-MS results from Finnigan Corporation.

# CONTROLLING POLLUTION AND MANAGING WASTES IN AN OIL-SHALE INDUSTRY

## Project 11 ENVIRONMENTAL PROBLEMS ASSOCIATED WITH OIL-SHALE UTILIZATION

**Submitted by:** G. L. Cook and H. W. Sohns, Research Supervisors

**Began:** 1968 **Expected completion:** Continuing

**Personnel:**

S. S. Tihen, Research Chemist
J. R. Ruark, Chemical Research Engineer
W. J. Lanum, Research Chemist
J. R. Dryden, Chemist

## SUMMARY

The grasses which were planted in treated spent shale matured and produced a few seeds. Distillation of filtered water from the 150-ton retort produced 35 to 40 gallons of bottoms having a reduced ammonia content. The bottoms will be used as charge material to the bioxidation unit and other laboratory work. Whole retort water is being treated in the electrooxidation unit, but results to date have been inconclusive. Ethyl sorbate and γ-valerolactone were identified in water from operation of the 150-ton retort. Selected samples of shale from the Bureau's Colorado Corehole No. 3 were analyzed for mercury.

## DISCUSSION

After the grasses which were planted in treated spent shale had matured and produced a few seeds, the shale and matured grasses were thoroughly mixed and moistened to induce decay of the organic material. Following partial decay of the matured grasses, the mixture will be replanted. Continued treatment of the spent shale has improved its ability to maintain plant growth.

Completion of work with the electrooxidation unit was delayed because of a shortage of retort water from the 150-ton retort. This work is now continuing and should be completed during the first half of next quarter. Results of work with the unit have been inconclusive to date.

The mass, infrared, NMR, and ultraviolet spectra have been completed on two organic acid group samples recovered from the counter-current extraction of a 5-gallon sample of 150-ton retort water, completed in March.

Compounds identified were ethyl sorbate and γ-valerolactone. The lactone identification was verified by comparison with spectra run on a sample from Aldrich Chemical Company. Work is continuing on three additional GLC fractions from this organic acid group.

Work was continued on a manuscript, "Creating Retorting Channels Through Oil Shale by Use of Electricity." A patent was granted on the technique during the quarter.

Selected samples of oil shale from Colorado Corehole No. 3 were analyzed for mercury. An instrument, purchased during the quarter, should expedite the application of analytical techniques for mercury and other trace metals of environmental significance.

## MANUSCRIPTS

### Published

| Title | Authors | Citation |
|---|---|---|
| Oil Shale and the Energy Crisis | G. U. Dinneen<br>G. L. Cook | Preprints, Fuels Div., ASME Winter Ann. Meet., New York, N. Y., Nov. 26-30, 1972, 9 pp.[1] |
| Oil Shale--An Impending Energy Source | G. L. Cook | J. Petrol. Technol., Nov. 1972, pp. 1325-1330. |
| Oil Yields and Stratigraphy of the Green River Formation's Tipton Member at Bureau of Mines Sites Near Green River, Wyoming | George F. Dana<br>John Ward Smith | BuMines Rept. of Inv. 7681, Nov. 1972, 46 pp. |
| Estimating Nahcolite and Dawsonite Content of Colorado Oil Shale from Oil-Yield Assay Data | John Ward Smith<br>Thomas N. Beard[2]<br>Paul M. Wade[2] | BuMines Rept. of Inv. 7689, Nov. 1972, 24 pp. |
| Oil Yields and Characteristics of Green River Formation Oil Shales at WOSCO EX-1, Uintah County, Utah | John Ward Smith<br>Laurence G. Trudell<br>William A. Robb | BuMines Rept. of Inv. 7693, Nov. 1972, 145 pp. |
| Method for Producing Retorting Channels in Shale Deposits | J. R. Dryden | U.S. Patent No. 3,696,866 granted October 10, 1972 |

[1] Copies available to Sept. 1, 1973, ASME, United Engineering Center, 345 E. 47th Street, New York, N. Y., 10017.

[2] Shell Oil Company, 1700 Broadway, Denver, Colo., 80202.

## In Progress

| Title | Authors | Form | Est. date submission to W.O. |
|---|---|---|---|
| Hydrogasifying Colorado Shale Oil | P. L. Cottingham<br>C. M. Frost | R.I. | Mar. 1973 |
| Prehydrogenation and Hydrocracking Crude Shale Oil | P. L. Cottingham<br>C. M. Frost | R.I. | Apr. 1973 |
| Some Effects of Hydrocracking Shale Oil Over Different Catalysts | P. L. Cottingham<br>C. M. Frost | R.I. | July 1973 |
| Reforming of Naphtha from Hydrogenated Shale Oil | P. L. Cottingham<br>C. M. Frost<br>H. C. Carpenter | R.I. | May 1973 |
| Hydrogenating Shale Oil at Low Space Velocity | C. M. Frost<br>P. L. Cottingham | R.I. | Submitted |
| Catalytic Cracking of Shale-Oil Gas Oils | P. L. Cottingham | R.I. | July 1973 |
| Effects of Pressure on the Hydrofining of Crude Shale Oil | C. M. Frost<br>P. L. Cottingham | R.I. | Dec. 1972 |
| Refining Improvement of Shale Oil Naphtha | L. K. Barker<br>P. L. Cottingham | R.I. | Submitted |
| Hydrodenitrification of Crude Shale Oil | C. M. Frost<br>H. B. Jensen | Presentation Preprinting | Submitted |
| Reactions in the Cobalt-60 Irradiation of Pyrrole and Methylpyrroles | J. J. Duvall<br>H. B. Jensen | J.A. | Jan. 1973 |
| Reactions in the Cobalt-60 Irradiation of Butylbenzenes | J. J. Duvall<br>H. B. Jensen | J.A. | Mar. 1973 |

| Title | Authors | Form | Est. date submission to W.O. |
|---|---|---|---|
| Simulated Distillation of Shale Oil | R. E. Poulson<br>H. B. Jensen<br>J. J. Duvall | R.I. | Sep. 1973 |
| Characterization of a Shale Oil Produced by In Situ Retorting | H. B. Jensen<br>R. E. Poulson<br>G. L. Cook | J.A. | Apr. 1973 |
| Determination of Location of Double Bonds in n-Olefins by Deuterium Labeling | J. R. Morandi<br>H. B. Jensen | J.A. | Feb. 1973 |
| Beneficiation of Shale-Oil Naphtha by Mild Oxidation | E. B. Smith<br>A. W. Decora<br>G. L. Cook | J.A.<br>Presented Apr. 1972 | Mar. 1973 |
| Hydrocarbon-Type Analysis of Shale-Oil Naphthas by Mass Spectrometry | A. W. Decora<br>G. Miyake<br>and others | Presentation<br>J.A. | Sep. 1973 |
| A Study of Mass Spectral Patterns of Hydrocarbons Using a Sector Instrument | A. W. Decora<br>G. Miyake<br>and others | Presentation<br>J.A. | Oct. 1973 |
| Mass Spectral Characterization of Dimethylnaphthalenes | F. G. Doolittle<br>D. G. Earnshaw | J.A.<br>Preliminary work presented Aug. 1971 | Jan. 1973 |
| The NMR Spectra of Organic Sulfur Compounds | F. R. McDonald<br>W. J. Lanum | R.I. | June 1973 |
| Resolution of Fine Structure in the Ionization Efficiency Curves of $H_2S^+$, $C_2H_2^+$, $C_6H_6^+$, and $C_6D_6^+$ | J. H. Weber<br>R. E. Ellefson<br>A. B. Denison[1] | J.A.<br>Presented June 1972. Rough draft prepared | June 1973 |

[1] Physics Dept., Univ. of Wyo., and Bureau of Mines Faculty Member.

| Title | Authors | Form | Est. date submission to W.O. |
|---|---|---|---|
| A Study of the Excited Ionic States of $CO_2^+$, $H_2S^+$, and $n\text{-}C_5H_{12}^+$ by Optically Modified Mass Spectrometry | R. E. Ellefson<br>A. B. Denison[1]<br>J. H. Weber | J.A. Presented June 1972. Accepted by J. Chem. Phys. Resubmitted this quarter | Submitted |
| Analysis of Some Aromatic Hydrocarbons in a Benzene-Soluble Bitumen from Green River Oil Shale | D. E. Anders<br>F. G. Doolittle<br>W. E. Robinson | J.A. | Submitted |
| Aragonite and the Genesis of Carbonates in Mahogany Zone Oil Shales of Colorado's Green River Formation | John Ward Smith<br>William A. Robb | R.I. | Submitted |
| Oil-Shale Resources and Geology of the Green River Formation in the Green River Basin, Wyoming | W. C. Culbertson[2]<br>John Ward Smith<br>Laurence G. Trudell | USGS P.P. | Mar. 1973 |
| Thermal Analysis in Earth Science: Experience and Expectations | John Ward Smith | J.A. | Submitted |
| Geology and Oil-Shale Resources of Kinney Rim, Washakie Basin, Sweetwater County, Wyoming | Laurence G. Trudell<br>Henry W. Roehler[2]<br>John Ward Smith | R.I. | Jan. 1973 |
| Gaylussite: Thermal Properties by Simultaneous Thermal Analysis | Donald R. Johnson<br>William A. Robb | J.A. | Submitted |

[1] Physics Dept., Univ. of Wyo., and Bureau of Mines Faculty Member.

[2] Branch of Organic Fuels, U.S. Geological Survey, Bldg. 25, Federal Center, Denver, Colo., 80225.

| Title | Authors | Form | Est. date submission to W.O. |
|---|---|---|---|
| Simple NMR Lineshapes from the Fourier Transformation | F. P. Miknis<br>J. D. Noble[1] | J.A.<br>Submitted to J. Chem. Ed. and rejected. To be resubmitted to more appropriate journal | Submitted |
| Parameters Affecting the Analysis of Oil Shales Using Wide-Line and Pulsed NMR Spectrometry | F. P. Miknis<br>A. B. Denison[2]<br>A. W. Decora<br>G. L. Cook | J.A. | Mar. 1973 |
| Temperature Effects on the NMR Line Shapes of Oil Shales | A. B. Denison[2]<br>F. P. Miknis<br>A. W. Decora | J.A. | June 1973 |
| Geochemical Aspects of the Alkane Constituents of Colorado No. 1 Core | D. E. Anders<br>W. E. Robinson | R.I. | Submitted |
| Compositional Variations of the Organic Material of Green River Oil Shale - Wyoming No. 1 Core | W. E. Robinson<br>G. L. Cook | R.I. | May 1973 |
| Low-Molecular-Weight Hetero Compounds of Green River Shale | D. E. Anders<br>F. G. Doolittle<br>W. E. Robinson | J.A. | Feb. 1973 |
| Evaluation of In Situ Oil Shale Experiments by Hot-Film Flow Logging | T. E. Sterner<br>H. E. Thomas<br>H. C. Carpenter | R.I. | Mar. 1973 |
| In Situ Retorting of Oil Shale--Results of Two Field Experiments | E. L. Burwell<br>T. E. Sterner<br>H. C. Carpenter | R.I. | Submitted |

[1] Physics Dept., Univ. of Wyo.

[2] Physics Dept., Univ. of Wyo., and Bureau of Mines Faculty Member.

| Title | Authors | Form | Est. date submission to W.O. |
|---|---|---|---|
| Pilot Plant Studies of Retorting Ungraded Oil Shale | A. Long, Jr.<br>A. E. Harak<br>L. Dockter | R.I. | Mar. 1973 |
| Retorting Random-Sized Lean Oil Shale in a Batch-Type Retort--An Engineering Analysis | L. Dockter<br>A. E. Harak<br>H. W. Sohns | Presentation<br>J.A. | Submitted |
| Feasibility of In Situ Retorting of Green River Oil Shale Utilizing Nuclear Explosives for Fracturing | H. W. Sohns | Presentation<br>Publication | Submitted |
| Compaction of Broken Shale During Retorting | S. S. Tihen<br>H. C. Carpenter<br>H. W. Sohns | R.I. | June 1973 |
| Thermal Reactions of Three Isoprenoid Compounds | I.A.Jacobson, Jr.<br>A. W. Decora<br>G. L. Cook | Presentation<br>J.A. | Mar. 1973 |
| Temperature History of Oil-Shale Retorting from Ethylene-Ethane Ratios | I.A.Jacobson, Jr. | R.I. | Aug. 1973 |
| Oxygen Demands of Oil Shale at Sub-Retorting Temperatures | C. F. Brandenburg<br>A. W. Decora<br>G. L. Cook | Presentation<br>R.I. | Feb. 1973 |
| Oxygen Diffusion During Oil-Shale Retorting | C. F. Brandenburg<br>A. W. Decora<br>G. L. Cook | Presentation<br>R.I. | June 1973 |
| Study of Waste Water from Oil-Shale Processing | A. B. Hubbard<br>W. J. Lanum<br>G. L. Cook | Presentation<br>J.A. | June 1973 |

| Title | Authors | Form | Est. date submission to W.O. |
|---|---|---|---|
| Method of Reclaiming Waste Water from Oil-Shale Processing | A. B. Hubbard<br>G. L. Cook | J.A. | June 1973 |

# PERSONAL MENTION

Dr. Andrew W. Decora was on special assignment to Washington, D.C. to assist in preparation of the Final Environmental Statement for the Prototype Oil-Shale Leasing Program. He spent the period of October 31 to December 10 on that assignment during the quarter. In addition, Dr. Decora was a member of the Department's Public Hearings Panel that heard testimony in Denver, Colo.; Cheyenne, Wyo., and Salt Lake City, Utah during the week of October 10-13, 1972.

W. E. Robinson attended the 17th Annual Meeting of the Geochemical Society in Minneapolis, Minn., Nov. 13-15, 1972. At this meeting he was installed as the Chairman-Elect of the Organic Geochemical Division.

Leroy Dockter presented a paper entitled, "Retorting Random-Sized Lean Oil Shale in a Batch-Type Retort--An Engineering Analysis," at the 65th Annual AIChE meeting in New York, November 27, 1972.

Arnold Harak presented an informal talk entitled, "Some Experimental Results of Operating a 150-Ton Retort," at the weekly meeting of the Laramie Lions Club, December 13.

H. W. Sohns presented an informal talk entitled, "Oil Shale: What It Is, What It Means to the Nation, and the Environmental Problems It Presents," to a graduate Environmental Science Education class at the University of Wyoming, December 13.

Dr. Robert E. Ellefson completed his Bureau of Mines Pre-doctoral Physics Fellowship this quarter. Dr. Ellefson is presently employed with the Monsanto Company near Dayton, Ohio.

Frank G. Doolittle was asked to review a manuscript entitled, "Identification of Phenylcycloparaffin Alkanes and Other Monoaromatics in Green River Oil Shale by GC-MS." The manuscript was authored by E. J. Gallegos of Chevron Research. The request for the review came from the editor of Analytical Chemistry to whom the author had submitted the manuscript for publication.

Mr. Arnaldo Faro, Jr., Process Engineer from the Petrobras Research Center, Rio de Janeiro, Brazil, spent a period of about 4 weeks in the spectroscopy group acquiring experience in mass spectroscopy for application in his laboratory. Mr. Faro proved to be an exceptional scientist and indicated that he learned much from the Laramie group for his applications to shale-oil analyses.

## Training

E. L. Burwell, Leroy Dockter, D. E. Anders, and C. F. Brandenburg completed a Leadership Systems Training course at the Laramie Center, December 11-14.

## EFFECTING POLLUTION ABATEMENT THROUGH CONVERSION PROCESSES

### Project 1 UNDERGROUND GASIFICATION OF COAL

Submitted by: James L. Elder, Chief, Grand Forks Energy Research Laboratory

Began: FY 1973 Expected completion: Continuing

Personnel (as assigned):

A. The In Situ Coal Gasification Task Force which held meetings in Denver, Colo., on June 20 and July 6, 1972, and at Laramie, Wyo., October 18, 1972
B. Mr. Gerald U. Dinneen and various members of the staff of the Laramie Energy Research Center
C. Messrs. J. L. Elder and R. C. Ellman of the Grand Forks Energy Research Laboratory

## SUMMARY

The coal gasification experiment will be conducted to determine the technologic, economic, and environmental feasibility of gasifying western subbituminous coals in situ. This small scale experiment is expected to provide preliminary data on the degree of energy conversion that is possible in situ, the potential environmental impacts associated with in situ operations and their control, and the potential for underground coal gasification as an economical and convenient source of clean energy. The successful completion of the experiment will lead the way to future, larger-scale research and development with the goal of commercial application of in situ coal gasification processes.

The site for the field scale experiment was selected approximately 1.5 miles south and a little west of the town of Hanna in Carbon County, Wyoming. An access road has been constructed; the major drilling contract let; and four operating boreholes have been drilled to the coal bed, cased, cemented, cleaned, and completed. A power line has been constructed to the site; a coal core was taken, analyzed, and submitted to various laboratory tests; and an oriented core was obtained at the site location. Inclement weather postponed permeability tests of the coal bed.

A "Draft Environmental Assessment" was prepared and submitted for the underground coal gasification experiment. Currently, a long range program is in process of preparation.

## DISCUSSION

The site for the underground gasification experiment was selected during the week of August 20. It is approximately 70 miles west of Laramie, Wyoming in T 22 N, R 81 W, with the actual site in the SW1/4 of sec 29. The mineral and surface rights are owned by the Union Pacific Railroad and the administration is by their subsidiary, the Rocky Mountain Energy Company. The site has been made available to the Bureau at no cost for land acquisition.

An access road was constructed from U.S. Route 30 to the actual site of the experiment in the SW1/4 of sec 29. At the site of borehole No. 1, the overburden was drilled and a coal core taken. The top of the coal bed was found 400.8 feet below the surface (surface elevation 6,993.96). The coal bed was found to be 29.45 feet thick with the top 26.2 feet having an average ash content of 12.1 percent and the bottom 3.25 feet of 59.9 percent. The coal is of subbituminous A rank and has a free swelling index of zero which indicates no caking properties on carbonization. A composite sample of the coal was carbonized in the precision laboratory carbonization assay and carbonization yields were determined on moisture and ash free basis. The dry tar yield during 900° C carbonization was found to be 16.2 percent by weight. This relatively high yield was not unexpected since the ultimate analysis of the coal indicated a relatively high hydrogen content. This dry tar yield is approximately three times the quantity that would be expected from a high volatile A bituminous coal such as previously tested in underground gasification at Gorgas, Alabama.

Borehole No. 2 was drilled and an oriented coal core was obtained from the coal bed. At this point the thickness of the bed was 30.1 feet and 100 percent of the core was recovered. The oriented core was taken for the purpose of determining the direction of the face and butt cleats within the coal bed. Final results of the examination are not yet available.

After obtaining the cores from boreholes 1 and 2, the holes were reamed to size and boreholes 3 and 4 were drilled. All of these holes have been fitted with 4-inch I.D. casing, the casing cemented, and in the case of boreholes 1 and 3, higher strength casing was used so that either of these holes could be used for a hydrafrac application. In boreholes 1 and 3 the bottom of the casing was set at a point to permit application of hydrafrac on approximately 5 feet of coal immediately above the high ash portion at the bottom of the coal bed. As a result of drilling boreholes, it was determined that the dip of the bed was 7.1° in the direction N 61° E.

After cementing and casing of the four boreholes were completed, an attempt was made to remove accumulated water and begin permeability testing of the coal bed. Inclement weather intervened and all that could be accomplished was to obtain a qualitative indication that the coal bed had some degree of permeability and that there was a degree of interconnection between the boreholes.

A power line has been installed to the project site, an instrument trailer has been set up, and two other trailers are available for personnel protection and storage of supplies. Insofar as possible, work will be conducted on site preparation, and permeability testing will be resumed shortly after the first of the year.

A "Draft Environmental Assessment" for the underground gasification experiment has been prepared and submitted. Currently, a long range program is in the process of preparation. This program will describe planned work during FY 1974 and somewhat beyond.

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