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APRIL-JUNE 1982 DOE/BETC/QPR-82/2

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Liquid Fossil-Fuel Technology

BARTLESVILLE ENERGY TECHNOLOGY CENTER
U.S. Department of Energy
Quarterly Technical Progress Report

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DOE/BETC/QPR--82/2
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Director's Comments

Since I began my duties at the Bartlesville Energy Technology Center only in mid-July, I still have much to learn about the Center, its programs and staff. However, in my previous positions within DOE Headquarters in Washington, D.C., I often worked closely with BETC's administrators and scientists and followed the progress of much of the research. It was always apparent to me that BETC had some of the finest people and programs anywhere.

Since arriving at the Center, I have become even more impressed with the breadth and depth of the research programs, and I am pleased to be a part of such programs.

My predecessor, Harry R. Johnson, did a great deal in his four years at BETC to mold individual research projects into an overall mission-oriented research system built around the concept of the liquid fossil fuel cycle. This system allows periodic adjustments and refinements in our research programs in response to changing national energy priorities and changing budgets.

As the current administration attempts to redefine energy priorities and research needs, the Bartlesville Energy Technology Center and many other government research facilities are in a transition period. Both our form and our programs could change considerably. In the meantime, we will work toward our established research goals and to maintain continuing services to our audiences.

Edward J. Lievens Jr.

EDWARD J. LIEVENS, JR.
Acting Director, BETC

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QUID FOSSIL-FUEL TECHNOLOGY

**JARTERLY TECHNICAL
ɩOGRESS REPORT**
ɔril-June 1982

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TABLE OF CONTENTS

FEATURES

MASTER

DISCLAIMER

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Date Published—October 1982

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BETC Highlights

BARTLESVILLE ENERGY TECHNOLOGY CENTER

April-June 1982

- The Third Joint Symposium on Enhanced Oil Recovery sponsored [illegible] DOE
  BETC and the Society of Petroleum Engineers was held in Tulsa [illegible] 14-
  This largest of the symposia attracted more than 2,300 registrants, includir
  160 persons from 15 foreign countries. An exhibit sponsored by BETC di
  tributed about 8,500 reports dealing with enhanced oil recovery. Gener
  chairman for the symposium was Harry R. Johnson, then director of BETC
  Other BETC participants were Bill Linville, publicity co-chairman; Do
  Ward, program committee; and Rex Thomas and Erle C. Donaldson, pape
  presenters. (Extraction Research).
- An early assignment to BETC when it was a part of the Bureau of Mines wa
  to survey the fuels being sold and report on their properties. The gasolin
  survey was started in 1916 and was made semi-annual in 1920. From 1935 t
  1948 the surveys were made in cooperation with the Coordinating Researc
  Council; since then they have been done in cooperation with the America
  Petroleum Institute. Aviation fuels have been surveyed annually since 194
  diesel fuel oils since 1950, and burner fuel oils since 1955. During the pas
  quarter, the summer 1981 gasoline survey and the 1981 survey on aviatio
  turbine fuels were issued. A report (DOE/BETC/RI-82/4) on "Trends i
  Motor Gasoline: 1942-1981" was published by Ella Mae Shelton, M. L. Whis
  man, and Paul W. Woodward. (Processing and Thermodynamics Researcl
- In order to obtain quantitative results for analyses of hydrocarbons by fiel
  ionization mass spectrometry, reliable values of sensitivity must be availabl
  Because the presence of acetone was known to have an effect on sensitivit
  the sensitivities of 37 saturated hydrocarbons were determined in the pres
  ence of acetone. Results indicated that the acetone effect was negligibl
  above C_{26}. Analyses on hydrotreated shale oil showed that the results by fiel
  ionization mass spectrometry compared favorably with results by electro
  impact mass spectrometry and by gas chromatography. (Processing an
  Thermodynamics Research).
- A project to assess the capability for using solid particles of coal in a slurry a
  a fuel in diesel engines has been started at BETC. The work will screen 20
  slurry fuels through use of a specially designed fuel combustion assessmen
  rig. The rig allows the turbulence to be varied, the wall temperature to b
  controlled up to 500°F, the selective use of pilot injection, the selective use c
  a heat source within the chamber, combustion to occur with either air c
  oxygen at initial pressures up to 30 atmospheres, different main injectors an
  the use of a prechamber and direct injection. From the initial slate of 20
  fuels, 20 will be selected for further examination in a single-cylinder researc
  engine. Finally, four fuels will be selected for extensive testing. (Utilizatio
  Research).
- The work of the BETC Resource Assessment Branch generally is aimed a
  discovering and evaluating good prospects for enhanced oil recovery pro
  ects. A data base describing the oil reservoirs of the nation is under deve
  opment for this purpose, and various data files are being integrated into th
  data base. Special attention has been given by the Reservoir Characteriza
  tion Section to the preparation of lists of abandoned oilfields and tl [illegible] cha
  acteristics. The Reservoir Evaluation Section is developing improved meth
  ods for analyzing reservoirs and for measurement of residual oil. Th
  Recovery Projections Section has custody of the computer operations and
  obtaining predictive models for the various processes for enhanced o
  recovery. A thermal recovery predictive model is being tested, and the CO
  miscible predictive model is to be delivered soon. (Extraction Rese[illegible]

Executive Summary

LIQUID FOSSIL FUEL CYCLE

The Liquid Fossil Fuel Cycle (LFFC) is a planning framework that follows fossil fuel from extraction through processing to utilization as liquid fuel. This framework is used for planning at BETC, forms the basis for the organization of BETC, and furnishes the outline for this quarterly report. This report, *Liquid Fossil Fuel Technology,* reports on in-house work concerned with the LFFC and on contracted work not reported elsewhere. A companion quarterly, *Enhanced Oil Recovery and Improved Drilling Technology,* reports on contracted work involved with EOR and drilling research.

EXTRACTION

RESOURCE ASSESSMENT

Reservoir Characterization

Four computerized files containing data relevant to enhanced oil recovery reservoirs were entered into Data Base Management System 2000. A program to validate and correct faults in the files was partially developed. Reports on injection waters for EOR and strontium sulfate solubility were published, a third on abandoned oilfields was submitted for publication, and a fourth on hydrogeochemical investigations of Uinta Basin formations is nearing completion. A new standard practice for calculation of $BaSO_4$, $SrSO_4$, and $CaSO_4$ in oilfield waters was approved by the American Society for Testing and Materials.

Reservoir Evaluation

Surface chemical analysis of sedimentary rocks and clays is now being done by a combination of the scanning electron microscope and X-ray analytic equipment. A mathematical model for subsidence is under development. A study of Prudhoe Bay (Alaska) oil and gas cores is being made to determine the effect of gas withdrawal on residual oil saturation. Modification of extraction procedures for polar organic compounds will allow processing of larger samples in less time.

Recovery Projections

Data base demonstrations were made to representatives of the Independent Petroleum Association of America, the Society of Petroleum Engineers, and Venezuelan oil companies. A magnetic tape system and additional core memory have been added to the PE 732 computer. A thermal recovery predictive model has been delivered, and a CO_2 miscible predictive model is scheduled for delivery in July. A cost estimate of the EOR incentives program projects is nearing completion.

PRODUCTION

Reservoir Access

Polycrystalline diamond compact drill bits were shipped to Venezuela for a drilling test. The final report on improving drilling capability of PDC cutters was submitted. A proceedings of a workshop designed to identify needed research in Arctic, offshore, and drilling technologies was published.

Recovery Processes

Two disulfonate products used as cosurfactants were found to impart some calcium tolerance. A diphenyl ether sulfonate was more effective than a diphenyl alkylate, but had an unfavorable effect in the absence of calcium. Temperature effects were mapped out for polyacrylamide in the lower Newtonian and power-law regions. Differences in alcohol partitioning for aromatic and aliphatic hydrocarbons were correlated with deviations from the equivalent alkane carbon number concept. The Bureau of Mines method for measuring wettability gives a linear correlation on sands of mixed wettability.

A report titled "Silica Gel as a Model Surface for Adsorption Calorimetry of Enhanced Oil Recovery Systems" was published. The enthalpy of immersion of silica gel activated at 400°C in a series of alcohols of increasing chain length shows that the interaction of neat alcohol with a hydrophilic oxide surface is, to a first approximation, independent of chain length. A completely hydrophobic surface has been prepared by attaching octadecyl silane to the polar sites of silica gel. For the hydrophobic material, the enthalpies of immersion are completely reversed, being numerically the largest for immersion in heptane and smallest for water. Considerable effort was expended to discover the source of a precipitate in studies of aqueous solutions of sodium 4-(1-pentylheptyl)benzene sulfonate.

Values of critical micelle concentration, partial molal volume at infinite dilution and the partial molal volume of the micelle were obtained for the system sodium octanoate/water. Isopiestic distillation experiments were completed on the system NaOct/3.0 m NaCl(aq). A paper was accepted by the *Journal of Applied Crystallography* on the small-angle X-ray scattering studies of association of clay particles into aggregates.

Continuation of studies to determine the effect of flow rate on oil recoveries by CO_2 flooding showed that there was a definite decrease in oil recoveries at 100°F, while at lower temperatures there was very little change with temperature. At any given temperature, a change in flow rate results in no significant change in oil recoveries.

Process Implementation

A second well is being added to the cooperative solar-augmented chemical recovery project. This will enable the comparison of different times of soaking for the hot water/chemical solution. A project to study the recovery of oil through the injection of sulfur trioxide has been initiated. A huff-and-puff carbon dioxide injection-production experiment was carried through four cycles. Using a Berea core and a 17° API gravity oil, recovery measurements were made after 7, 14, 7 and 8 days of soaking in the respective cycles. Laboratory studies on the Noone oil/carbon dioxide system were completed. It was compared with the Wilmington, Calif., oil and dissolved more carbon dioxide than the California oil. Contacts were maintained with proposed oil mining projects in California, Wyoming, Louisiana, and Kansas.

Extraction Technology

A repeat experiment was conducted to monitor fracture width in a propped fracture with passage of time under *in situ* conditions of temperature and pressure. The influence of temperature was found to be minimal on the fracture width, and gas permeability decreased slightly (if at all). A "non-damaging" brine such as 2 percent KCl causes a reduction in fracture width that is probably insignificant with respect to loss of productivity.

Further experiments were made to determine the molecular weight distribution (MWD) of broken uring fluid polymers. Time decr d th amount of polymer with a molecula weight of more than 2×10^6, up to 2 hours; increasing the strength of th oxidant had a similar effect.

PROCESSING

LIQUID PROCESSING

Characterization

A method for sulfide removal wa developed, which oxidizes the sulfide with sodium periodate. A liquid chro matographic method for thiophen removal shows promise. In separatio of Cerro Negro distillates, carboxyli acids appear to dominate the aci concentrates. Difficulties have ap peared in the preparative scale sepa ration of neutral hydrocarbon frac tions. Several column packings hav been evaluated for separation eff ciency. Methods for determination c water in vapor-liquid-equilibrium sam ples have been modified to improv quantitative recovery.

A nonaqueous titration techniqu was developed for acidic (oxyger containing compounds) material i synthetic fuels and petroleum. comparison of ion exchange an extraction procedures for acid-base neutral separations was complete Generally, extraction procedure proved inadequate for materials boi ing above 350°C.

Sensitivity data for field ionizatio mass spectrometry studies of satu rates were investigated. Papers wer presented at the annual meeting c the American Society for Mass Spec trometry. The mass spectrometr equipment was moved into a ne laboratory, but inadequate idit control caused delays in its operation

Reports on the summer 1981 gaso line survey and the 1981 aviation tu bine fuel survey were published. Fou crude oils were analyzed. nica assistance was given to the teg Petroleum Reserve Office.

Thermodynamics

The two-phase heat capacities of the low-molecular-weight alcohols are being measured with a differential scanning calorimeter. The studies are exploratory to determine if composition dependence can be used to obtain vital thermodynamic information on vapor-liquid-equilibria of mixtures. Vapor pressure measurements on 2,2′-dimethylbiphenyl can now be made with a newly modified apparatus.

A new calorimetric cryostat for operation at temperatures between 4 and 550 K was completed. Various determinations are underway on 4-methylphenanthrene. The comprehensive vibrational studies of the methylbenzenes have been completed.

The experimental information to calculate the comprehensive thermophysical properties of 3-methylpyrrolidine has been obtained. The heat capacity for the liquid state shows an anomalous behavior that has also been found in other amines. A study suggests that a universal correlation of the thermodynamic properties can be made for a class of amines.

A series of combustion calorimetry experiments on experimental ram-jet fuels is in progress for the Air Force.

Processing Technology

A sample of SRC-II middle distillate was hydrotreated to determine effects of mild upgrading on combustion properties and pollutants. Experiments at Lawrence Berkeley Laboratory have identified methyl and phenylarsonic acids, as well as arsenate in shale oil and shale oil waters. The occurrence of vanadium in four crude oils has been shown to be associated primarily with the asphaltenes. Very high concentrations were shown in the asphaltene fraction with molecular weights above 900. Samples of shale oil have been hydrogenated by Gulf Research and Develop-

LIEVENS IS ACTING DIRECTOR OF BETC

Edward J. Lievens, Jr.

Edward J. Lievens, Jr. was named acting director of the Bartlesville Energy Technology Center in mid-July.

Previously acting director of the Oil, Gas and Shale Office in DOE Headquarters, Lievens replaced former BETC Director Harry R. Johnson who joined a private engineering firm. Johnson served as director of the Bartlesville center for 3½ years.

Since its establishment in 1918 as the government's primary petroleum research facility, the Bartlesville Energy Technology Center has been operated and staffed by federal personnel. One of Lievens' primary responsibilities as acting director is to ensure an orderly transition of the Center to a facility operated by a private firm by mid-1983.

Current plans call for the BETC to remain government owned, but operated by a private firm under a cost-sharing cooperative agreement. The operating firm will be selected as a result of competitive proposals to the Department of Energy.

In addition to his duties at BETC, Lievens also is serving as director of the Special Projects Division in the Office of Oil, Gas, Shale and Coal Liquids, part of the Energy Department's Fossil Energy Office.

Lievens has been involved in the government's energy research program since he joined a predecessor agency of the department, Energy Research and Development Administration, in 1976. From 1970 to 1976, he served as the director of the Office of Program Planning for the National Highway Traffic Safety Administration, and from 1962 to 1970, he served in several posts at the National Aeronautics and Space Administration.

He was born in South Bend, Ind., graduated from the University of Notre Dame with a BS degree in aeronautical engineering, and holds IS in industrial management from the Massachusetts Institute of nology.

ment Corporation and are being subjected to ion exchange experiments to remove the nitrogen.

Two new commercial waste oil recycling plants are being started, and full reports on problems and procedures will be contained in reports to DOE. A project on the fate of hazardous wastes found in waste lubricating oils will be part of the basis for Environmental Protection Agency regulation of used oil operations.

Assessment of engineering designs for innovative upgrading processes prepared by UOP and Hydrocarbon Research will be assessed both for engineering aspects and for a commercial operation.

Stability studies at the Naval Research Laboratory have shown that the peroxide number is not a suitable test for predicting stability. Work is proceeding to increase the temperature of aging in order to decrease the time required for a stability test.

A crude oil stratification study for the Strategic Petroleum Reserve Office is being enlarged to provide additional analyses of samples. The original gravity and viscosity tests do not account for different diffusion rates of various classes of compounds, and analyses for sulfur and vanadium will be added.

UTILIZATION

ADAPTIVE ENGINEERING

Advanced Processing Technology—Fuels Utilization

Tests with nitrogen compounds added to diesel fuel have shown conversion to NO_x of 20 to 35 percent. Octyl nitrate and quinoline had higher conversions than octyl amine, pyridine, and aniline. For the most part, fuel economy and regulated emissions were unaffected by the additives.

Diesel Particulate Emissions

The diesel particulate extract has been separated by chromatography into 22 fractions. Five of these contain 90 percent of the biological activity. Two of the fractions are known to contain nitro and dinitro polycyclic aromatic hydrocarbons.

COMBUSTION SYSTEMS ASSESSMENT

Alternate Fuels Data Bank

The Alternative Fuels Data Bank is accessed from remote locations by approximately 100 users a month. Of the three files, the publications file is now maintained by a contractor, but the ongoing research and topics sections are maintained by BETC personnel.

Evaluation of Ethanol Use in Diesel Engines for Farming Applications

An engine durability program is underway at Southwest Research Institute to investigate the effect of using 25 percent ethanol (160-proof) in diesel fuel on engine life expectancy. Preliminary results suggest that premature engine failure occurs when mechanically emulsified fuels are used. A fumigation system, however, results in normal wear rates.

HEAT ENGINES/HEAT RECOVERY

Coal Liquid Fuel/Diesel Engine Operating Compatibility

A fuel combustion assessment rig has been developed to assess the capability for using solid particles of coal in a slurry as a fuel in diesel engines. Approximately 200 unique slurry fuels will be appraised for their combustion potential. Second and third step experiments will involve 20 and 4 fuels respectively in more extensive examinations.

Work is concluding on t[illegible]se three coal liquids (SRC-II middle distillate, H-Coal, and Exxon Dono Solvent) in mixtures with diesel fuels

PROJECT INTEGRATION AND TECHNOLOGY TRANSFE

PLANNING AND ENVIRONMENTAL INTEGRATION

International Activities

A meeting of Venezuelan and DO participants in the U.S./Venezuel cooperative projects was held a BETC on June 16.

Environmental Integration

Studies to identify and assess wate issues as they relate to enhanced o recovery are being conducted by Gu Universities Research Consortium.

TECHNOLOGY TRANSFER

Almost 300 visitors used the Oklahoma well log file and copied mor than 5,000 logs. More than 4,000 we logs were added to the file. A total c 408 acquisitions were made by th library. Interlibrary loans (183) an bibliographic searches (22) using 1 data bases were made.

Nearly 38,500 technical report were distributed during the quarte and 131 reports were reviewed, edite and prepared for publication or distribution. Quarterly reports on enhanced oil recovery and improve drilling technology, liquid fossil fu technology, and western gas sand were prepared and published.

The Third Joint SPE/DO[illegible]mposium on Enhanced Oil Rec[illegible] wa held in Tulsa April 4-7. The International Conference on Microbi Enhancement of Oil Recovery wit BETC as a co-sponsor was held a Afton, Okla., May 16–21.

iquid Fossil uel Cycle

ECTION A

The Liquid Fossil Fuel Cycle (LFFC) has been established as the planning basis for research, development, and demonstration efforts on liquid fossil fuels. It traces.the operation of the cycle from resource assessment to ultimate use and, in an expanded form, provides a framework to assess proposed research projects as to their impact on the supply of liquid fuels.

The BETC is organized around the programs shown to be most important by the LFFC. As shown in Fig. A1, the BETC organization has major research activities of Extraction, Processing, and Utilization. In addition, the Divisions of Project Management, Project Integration and Technology Transfer, Operations, and Administrative Services perform necessary research support roles.

The Center operates on a matrix management system. Projects with a number of contracts may be administered by a project manager in the Division of Project Management, but each contract is monitored by a technical project officer (TPO) who, generally, is a part of one of the three research divisions and has research responsibilities in fields related to the contract. Most project managers and TPO's are located at BETC, but others are located at the Morgantown Energy Technology Center and at Operations Offices at Las Vegas and San Francisco.

This report primarily covers in-house oil, gas, and synfuel research and lists the contracted research. A more complete report of the contracted research on enhanced oil recovery and drilling is given in a companion quarterly report, *Enhanced Oil Recovery and Improved Drilling Technology*. Progress Review No. 31 of that series covers the same period as this report.[1a] Results from these contracts are not given in this report, but results from other contracts are included.

[1a] *Contracts and Grants for Cooperative Research on Enhanced Oil Recovery and Improved Drilling Technology*. Progress Review No. 31, edited by Bill Linville, DOE/BETC-82/3, October 1982. Available from Bartlesville Energy Technology Center, P.O. Box 1398, Bartlesville, OK 74005.

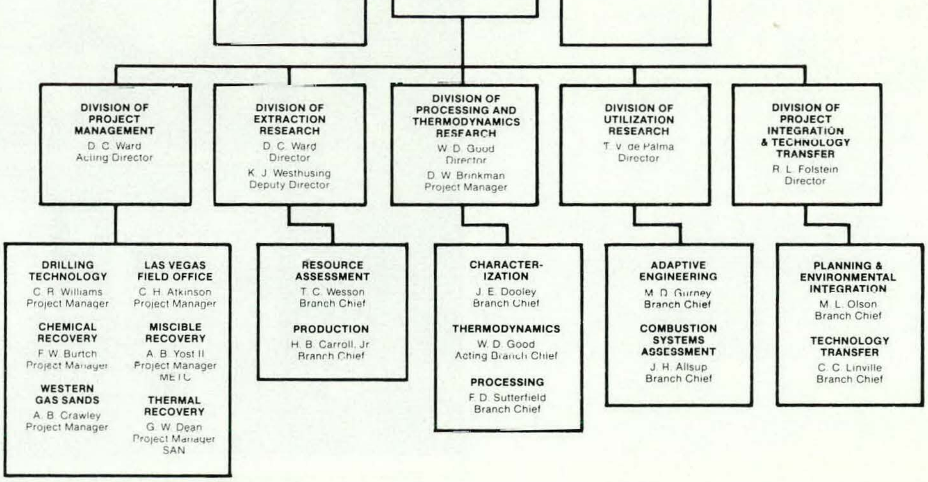


FIGURE A1. *Organizational chart of BETC and associated groups, July 1, 1982.*

Extraction

Division Director: D. C. Waro

SECTION B

RESOURCE ASSESSMENT

The Liquid Fossil Fuel Cycle starts with an assessment of the resources available. This consists of Reservoir Characterization, Reservoir Evaluation, and Recovery Projections. Each is concerned with building a data base for assessment of U.S. petroleum resources that might be recovered through enhanced oil recovery (EOR) technology.

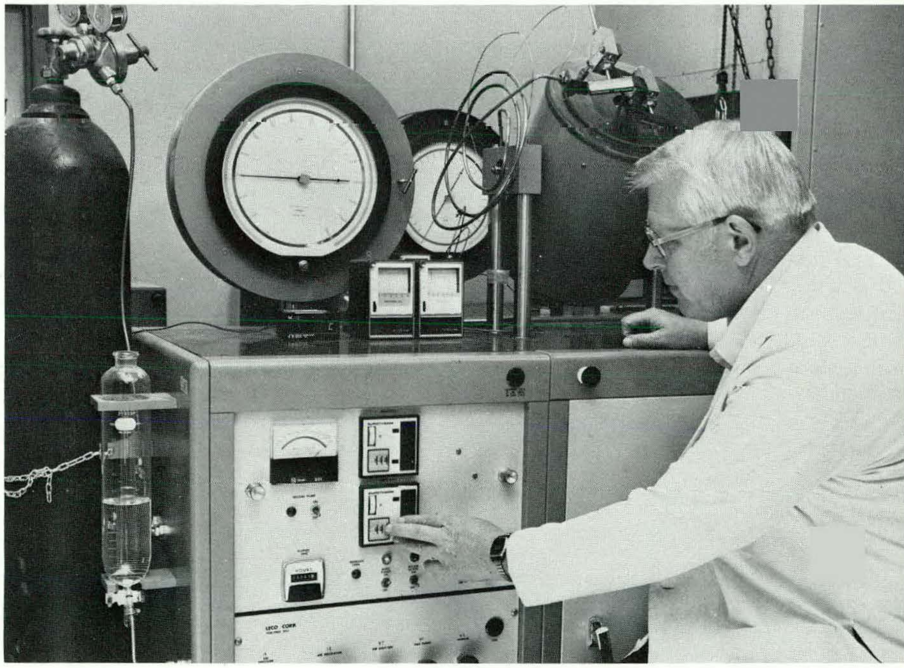
RESERVOIR CHARACTERIZATION[1b]

The objectives of this project are to compile comprehensive, validated, integrated, computer processible, continuously maintained and updated data files, containing information on all domestic oil resources (except tar sands) and the Western Gas Sands Project (WGSP).

Relevant data include oil reserves, gas reserves, water reserves, oil analyses, gas analyses, water analyses, geologic analyses, rock analys ggir records and analyses, drilling anal ses, enhanced oil recovery (EO chemical data, fracturing data, inje tion water compatibility data, et These data will be used to calculat the total EOR and WGSP resourc and to project the resources for sp cific EOR and WGSP techniques.

Four computerized files containir data relevant to EOR reservoirs wer entered into Data Base Managemer System 2000. A program to validat and correct faults in the files wa partially developed. Two reports wer published, a third was submitted fc publication, and a fourth is nearir completion. A new standard practic for calculation of $BaSO_4$, $SrSO_4$, an $CaSO_4$ in oilfield waters was approve by the American Society for Testir and Materials.

[1b] Project: Reservoir Characterization. B& No. AC-15-10-20. Staff: Branch Chief, T. Wesson; Section Chief, A. G. Collins; Petr leum Engineer, J. W. Chism; Researc Chemists, G. E. Fletcher and T. R. Frenc Geologist, M. Szpakiewicz.



Gordon Fletcher, research chemist, makes an adjustment on the hydrotherma reactor, used to study the solubility of barium and strontium sulfate line waters under simulated reservoir conditions. These data are used t sigr treatment specifications for waters to be used in enhanced oil recover operations.

ese Data Base Development

The Science Applications, Inc., SAI) file of reservoirs amenable to hermal recovery methods was en- ered into Data Base Management ystem 2000 (S2K). This is the system hat will be used in the BETC EOR Data System. The SAI file contains in- ormation on type of project, volume f fluid injected, cumulative produc- on, and recovery factor. It is divided to three parts: steam drive at depths ss than 2,500 ft, steam drive at epths below 2,500 ft, and *in situ* ombustion. It covers 247 fields, 264 econdary recovery projects, and 152 rtiary projects.

Most of the Gruy Federal, Inc., file as entered into S2K. This file con- ains information such as field loca- ons, production data, formation, ap, depth, acreage, net pay, number nd type of wells, lithology, recovery actors, primary and secondary pro- uction, porosity, permeability, oil nd water saturations, temperature, as-oil ratio, and API oil gravity. Major reas covered are the Permian, Wil- ston, and Paradox Basins. There is ome minor coverage of the Sweet- rass Arch, Big Horn, Wind River, nd Green River Basins.

The Gary-Intercomp file containing ata on reservoirs amenable to micel- r flooding in the Mid-Continent and alifornia was entered into S2K. This e contains information on 1,930 lid-Continent and 604 California eservoirs.

An Outer Continental Shelf (OCS) ase sale data file was assembled and ntered into S2K.

Conversion routines are being de- eloped to enter the Lewin OCS EOR e, the Lewin on-shore 800 EOR field e, the Gulf Universities Research ons[illegible]m EOR file, and the AGAT ay mineral file.

Progress was made in developing a rogram to validate the data and cor- ct faults in the EOR reservoir data es. This program will be applied to ach [illegible] in the BETC EOR Data ystem.

A subsurface temperature gradient map was produced for the domestic United States. It will be used on a county basis to validate bottom hole temperature of wells in the BETC EOR Data System.

New Methods for Reservoir Data Collection and Interpretation

Information on abandoned oilfields in Oklahoma, Kansas, Arkansas, Louisiana, Mississippi, and New Mexico was obtained from the various state agencies. The information was validated by use of the correct files. **A report, "Abandoned Oilfields in Arkansas, Louisiana, Mississippi, and New Mexico," was drafted and submitted for publication.**

Experiments were performed to determine the composition of the interstitial water in core samples obtained from the No. 2 well in the Western Tight Gas Sands Multi-Well Experiment. Details of the experiments and the results will be reported later if they are successful.

Two reports were published: "Enhanced Oil Recovery Injection Waters," DOE/BETC/RI-82/5; and "A Method for Calculating Strontium Sulfate Solubility," published in *Well Servicing,* v. 22, No. 3, pp. 49–54.

Additional experiments were performed to determine the solubilities of barium and strontium in saline waters under simulated reservoir conditions. This information is needed to better predict potential scaling problems in the oilfield.

An American Society for Testing and Materials (ASTM) meeting was chaired. A new standard practice for calculation of $BaSO_4$, $SrSO_4$, and $CaSO_4$ in saline water was approved and will be published as an ASTM standard practice.

A paper, "A Preliminary Hydrogeochemical Investigation of Upper Cretaceous and Lower Tertiary Formations in the Uinta Basin," was presented at a Petroleum Data System (PDS) Houston Users' Group Meeting and at a PDS Advisory Council Meeting. Progress was made in drafting the paper and associated maps into a formal report for consideration for publication.

Contracts. Two research contracts are monitored and are reported in Progress Review No. 31.[1a]

University of Oklahoma (DE-AC19-79BC10115). Oilfield Water Analysis Data Bank. Technical Project Officer: A. G. Collins.

Lewin and Associates, Inc. (DE-AC19-79ET14010). Identify Outer Continental Shelf Fields and Project Abandonment. Technical Project Officer: J. W. Chism.

RESERVOIR EVALUATION[2b]

The objectives of the Reservoir Evaluation Section are to assess petroleum reservoirs amenable to enhanced oil recovery processes and to correlate those reservoirs with potential hydrocarbon production.

These objectives will be achieved through improved geochemical and geophysical methods and applications, which include modifications to existing instrumentation and procedures for determining fundamental fluid/rock interactions, improving residual oil determinations, development of improved coring and core analysis tools, development of improved well-logging tools and analysis procedures, improving techniques for measuring reservoir properties in the inter-well area, and improving modeling applications.

[2b] Project: Reservoir Evaluation. B&R No. AC-15-10-20. Staff: Branch Chief, T. C. Wesson; Section Chief, E. C. Donaldson; Research Chemists, M. E. Crocker and L. M. Marchin; Petroleum Engineer, M. B. Kayser; Physical Science Technician, R. L. Masias.

Computer Programming

Equations for a mathematical model of subsidence due to fluid withdrawal have been developed and programming is anticipated by the end of September. This is in preparation for the DOE/INTEVEP-Venezuela Forum on subsidence scheduled for November 1982.

Scanning Electron Microscopy

X-ray analytic equipment has been installed and personnel have been trained in its operation. This is being used for surface chemical analysis of sedimentary rocks and clays. A visual, qualitative analysis is obtained with the scanning electron microscope (SEM), Figure B1, and this is followed by an X-ray scan of the surface to determine the elements present. Figure B1 is an SEM picture of Berea sandstone showing a surface composed principally of SiO_2; however, the presence of small amounts of various clays (total less than 5 percent) are detectable with the X-ray. Figure B2 is the X-ray scan of the surface showing a dot-pattern of the location of 11 percent aluminum, which is most likely a constituent in the clays that are not obvious in the picture.

This type of analysis, coupled with a total cation analysis with the emission spectrograph, is being used to define the chemical reactivity of the sandstones to develop a better understanding of the adhesion of oil to the sand body, creating a non-recoverable residual oil saturation. Ion exchange and gas/liquid catalytic experiments also will be conducted during the course of this research. Comparative analyses between the total chemical composition, which is derived from

FIGURE B1. *Scanning electron micrograph of Berea sandstone. Note pores an clay minerals on and between sand grains.*

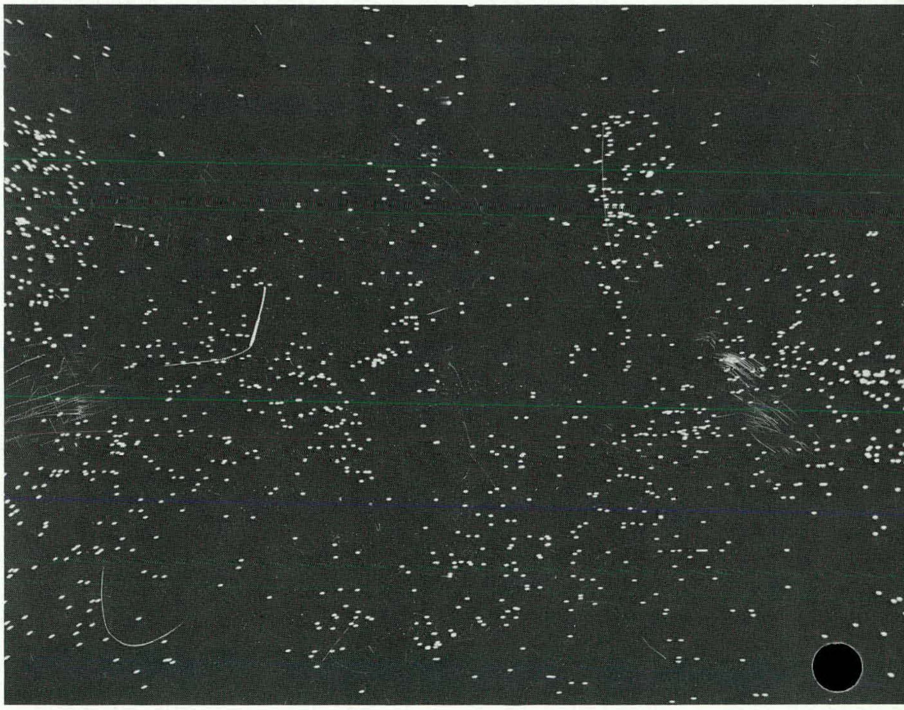


FIGURE B2. *X-ray scan of aluminum on the surface of Berea sandstone shown i figure B1.*

he sion spectrograph, and the urfa hemical composition of the ame clay mineral or sandstone also re being conducted. Table B1 shows n example of such comparative nalysis.

TABLE B1. *Comparison of the mission spectrographic analysis of Kaolinite clay and the X-ray ispersive analysis (note the close correspondence)*

ompound	Emission, percent	X-ray, percent
iO_2	43.6	42.5
l_2O_3	39.6	36.8
iO_2	1.3	2.1
lgO	0.2	0.9
aO	0.2	0.9
e_2O_3	0.2	1.9

esidual Oil Saturation

Samples of Prudhoe Bay oil, gas nd cores are being secured from the laska Office of Conservation for esting to determine the effect that epletion of the gas cap (by extraction nd sale of the gas) will have on the esidual oil saturation. Gas-drive and vater-drive tests will be conducted at eservoir conditions. Van Poollen and ssociates, consultants to the State f Alaska, will assist in the evaluation f the data using a mathematical nodel of the Prudhoe Bay oilfield.

olar Organic Compounds

Procedures for the extraction of olar organic compounds were modied to allow processing of larger amples in less time. The polar comounds are being extracted to acumulate samples for total chemical nalysis. This is part of the research o develop a complete understanding f the nature of crude oil adhesion to edir ary rocks and thus to disove y there is a high residual oil aturation.

Contracts. Contracts monitored are listed below. Results are reported in Progress Review No. 31.[1a]

City of Long Beach (EF-77-C-03-1395). Residual Oil Saturation Technology Evaluation in an Unconsolidated Sandstone Reservoir. Technical Project Officer: E. C. Donaldson.

Oklahoma State University (DE-AS19-80BC10302). Isolation and Screening of Anaerobic Clostridia for Characteristics Useful in EOR. Technical Project Officer: E. C. Donaldson.

Oklahoma State University (DE-AS19-80BC10304). Microbial Degradation of EOR Compounds. Technical Project Officer: E. C. Donaldson.

University of Oklahoma (DE-AC19-80BC10169). *In Situ* Methods of Biopolymer and Biosurfactant Formation for EOR. Technical Project Officer: E. C. Donaldson.

Science Applications, Inc. (DE-AC19-80BC10301). Development of a Procedure for the Microbiological Evaluation of a Petroleum Reservoir. Technical Project Officer: E. C. Donaldson.

University of Georgia (DE-AS19-81BC10507). The Application of Microbial Processes for the Reduction of Viscosity of Heavy Crude Petroleum. Technical Project Officer: E. C. Donaldson.

University of Southern California (DE-AS19-81BC19508). Bacteria Transport Through Porous Media. Technical Project Officer: E. C. Donaldson.

GeoChem Research, Inc. (DE-AC19-79BC10100). Development of a Rapid and Accurate Method for Determining Partition Coefficients of Chemical Tracers Between Oils and Brines. Technical Project Officer: M. E. Crocker.

Petroleum Recovery Research Center of New Mexico Institute of Mining and Technology (DE-AS01-78ET12077). Measurement and Correlation of Conditions for Entrapment and Mobilization of Residual Oil. Technical Project Officer: M. E. Crocker.

Illinois Institute of Technology (DE-AC19-80BC10222). Effect of Chemical Environment on Mechanical Behavior of Oil-Bearing Rocks. Technical Project Officer: L. M. Marchin.

Lawrence Livermore Laboratory (DE-AT19-79BC10062). Cross-Borehole Seismic Probing for Petroleum Reservoir Assessment. Technical Project Officer: M. B. Kayser.

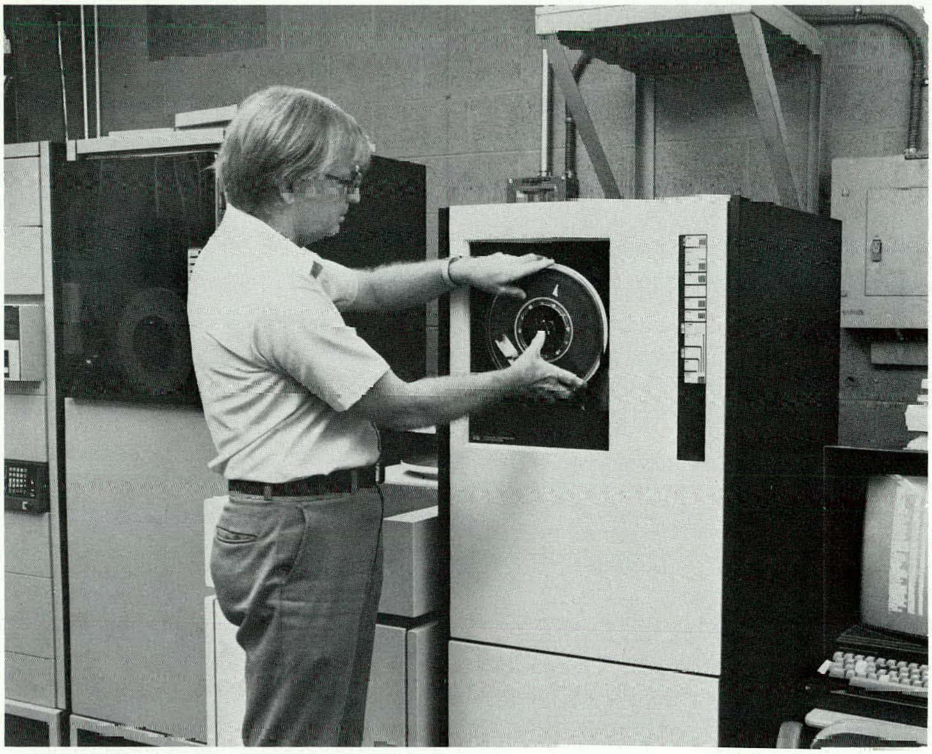
GeoChem Research, Inc. (DE-AC19-80BC10309). Development of an Improved Method for the Analysis of Pressure Core Samples. Technical Project Officer: M. B. Kayser.

Argonne National Laboratory (DE-AC19-80BC10308). Investigation of Pulsed Neutron Techniques for Oil Well Logging. Technical Project Officer: M. B. Kayser.

RECOVERY PROJECTIONS[3b]

The objectives of the Recovery Projections Section are to determine economically and technologically recoverable oil reserves suitable for EOR process technology, to prioritize these reservoirs by economic and/or technological benefits to the EOR program, and to provide administrative and technical support to the operation and maintenance of the EOR data base.

[3b] Project: Recovery Projections. B&R No. AC-15-10-20. Staff: Branch Chief, T. C. Wesson; Section Chief, R. M. Ray; Research Chemists, R. J. Heemstra and J. W. McGhee.



BETC's recovery projections section acquired a new tridensity magnetic tape unit during May. Here, John McGhee, research chemist, loads a computer tape containing reservoir information for the chemical flood predictive model into the unit, which can be set to read 800, 1,600, or 6,250 bits per inch.

These objectives will be achieved through development of economic and process-analog models to estimate technically and economically recoverable reserves, installation and operation of an EOR data base containing reservoir data sufficient in detail to be used as input to the economic and process-analog models, and development of a computer architecture to define communication between the various satellite facilities and the data base. Research efforts include three sub-projects and two contracted activities.

Reservoir Data Base Support and Operation

Data base demonstrations were given to representatives of the Independent Petroleum Association of America (IPAA) at the IPAA mid-year convention, the Society of Petroleum Engineers (SPE) at the Tulsa SPE/DOE EOR Symposium, and to the representatives of Venezuela oil companies. The demonstrations show the sources and types of data in the data base, the manner in which the data base is organized, and various examples of retrieval schemes that demonstrate the usefulness of the data bases to different segments of the industry.

An 800/1600/6250 bytes-per-inch (BPI) magnetic tape system and 552 kilobytes of core memory have been added to the Perkin-Elmer (PE) 7/32 computer facility. The memory is now at maximum (1.0 megabyte) configuration and will satisfy current data processing requirements. The magnetic tape system allows complete compatibility with satellite computer facilities. In the past, this lack of compatibility has been a detriment to transfers of information. Due to funding reductions in our rese program, the Recovery Projec Section will have the responsibility fo complete data base management an operation. An appropriate trainin schedule has been designed to allo training in data loading and retrieva data base back-up and restoratio and data base management function

Reservoir Process Model/ Screening Model Development

Development of the simplified predictive models by Intercomp Resourc Development and Engineering, Inc is continuing. Considerable work ha been accomplished on evaluating th chemical flood predictive model an this work is expected to continue fo about 60 more days. **The therma recovery predictive model (TRPM has been delivered to BETC an installed on the PE 7/32.** The TRP is undergoing extensive evaluativ testing, which should continue fo about 60–90 days. The CO_2 miscibl predictive model is expected to b delivered in mid-July.

Development and Maintenance of Resource Projections

A previous attempt to develop cost estimate of the EOR Incentive Program projects by normalizing cos elements to acre-feet-pore volum had difficulties related to insufficie data provided by program partic pants. Contracted support for acqu sition of missing data has been in tiated and should be complete soon.

Contracts. The following contract were monitored, and reports are give in Progress Review No. 31.[1a]

Texas Tech University (DE-AC1 80BC10257). Mathematical hod ology for Evaluating Flow i rou Media. Technical Project Office J. W. McGhee.

Intercomp Resource Developme and Engineering, Inc. (D 19 80BC10327). Development Ver fication of Simplified Predictio

Mod or Enhanced Oil Recovery Applications. Technical Project Officer: R. M. Ray.

PRODUCTION

The Liquid Fossil Fuel Cycle LFFC) activities included under Production are Reservoir Access, Recovery Processes, Process Implementation, and Extraction Technology. In essence, these refer to drilling echnology, development of processes o recover oil, application of the processes to field operations, and diagnostics of the reservoir.

Reservoir Access is conducted prinipally by contract from BETC. Recovery Processes includes work from he Production and Thermodynamics Branches of BETC, from METC, and rom DOE's San Francisco Operaions Office (SAN). Process Implementation includes laboratory and ield work from BETC. Extraction Technology describes work commisioned by the Western Gas Sands Project, a project of the Unconvenional Gas Recovery Program, adminstered from the Morgantown Energy Technology Center (METC) through BETC and with contract monitorship t DOE's Nevada Operations Office t Las Vegas.

RESERVOIR ACCESS[4b]

The objective of this research is o accelerate the development of domestic oil and gas resources, espeially in frontier areas. Future reearch efforts will attack problems inhibiting drilling and producing operations in Arctic areas, deep offshore areas, and hostile, ultradeep drilling environments. Some concurrent goals hat assist in accomplishing this objective are to increase the annual drilling footage per rig while reducing he cost per foot, to examine innovative concepts, and to improve the data quality while drilling and coring. The work is done mostly through contracts or National Laboratories.

Three 5⅝-inch Polycrystalline Diamond Compact (PDC) drill bits were fabricated by Pressure Concepts, Inc., and shipped to the Venezuelan Petroleum Institute (INTEVEP) at Caracas. They will be used in an August 1982 drilling test.

The final report for the Diamond Oil Well Drilling Co. (DOWDCO) contract was submitted for publication. The report number is DOE/BC/10364-24, and it is entitled "Improvement of Drilling Capabilities of PDC Cutters in Hard Formation."

A report was published covering the results of a January 1981 workshop that identified frontier area research projects. The report is numbered DOE/BETC/SP-81/12 and is entitled, "Research Projects Needed for Expediting Development of Domestic Oil and Gas Resources Through Arctic, Offshore, and Drilling Technology."

Contracts. The following contracts were monitored, and reports are given in Progress Review No. 31.[1a]

DOWDCO (DE-AC19-80BC10364). Improve Drilling Capabilities of PDC Cutters. Technical Project Officer: C. R. Williams.

University of Tulsa (DE-AC19-79BC10079). Drill Cuttings Transport in Vertical Annuli by Air, Mist and Foam in Aerated Drilling Operations. Technical Project Officer: C. R. Williams.

University of Tulsa (DE-AC19-80BC10361). Corrosion Fatigue Studies of Drill Pipe Immersed in H_2S Drilling Mud. Technical Project Officer: C. R. Williams.

GEOLOGIC PARAMETERS WORKSHOP REPORT AVAILABLE

The results of a Department of Energy-sponsored workshop on the importance of geologic parameters to enhanced oil recovery have been published by BETC.

The 44-page report, "The Impact of Geologic Parameters on Enhanced Oil Recovery—Workshop Proceedings" (report No. CONF-8110160), is available free from BETC, Attention Bill Linville, P.O. Box 1398, Bartlesville, OK 74005.

The workshop, held last fall in Tulsa, brought together industry, government, and academic representatives to discuss the interactions between enhanced oil recovery (EOR) fluids and oil reservoirs.

Four workshop subgroups met to determine research needed in the areas of rock-fluid interactions, reservoir heterogeneity, reservoir description, and geologic input into EOR simulation studies.

One finding was the need for expanded geological studies of reservoir characteristics and parameters, including efforts to improve data-collection systems and improve models used for predicting reservoir parameters and EOR results.

Summaries prepared by the subgroups and an outline of research areas to be explored are in the report. Chairman for the workshop was Herbert B. Carroll, Jr., chief of the BETC petroleum production branch.

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[b] Pr Improved Drilling Technology. B&R N -10-05. Staff: Director, Division of Project Management, D. C. Ward; Project Manager, C. R. Williams.

RECOVERY PROCESSES[5b]

The three recovery processes under study are chemical flooding, gas miscible displacement, and thermal recovery. Research on chemical flooding includes laboratory research, field projects, thermodynamics studies, and investigations of properties of micelles. Much of this work is conducted by or monitored by BETC personnel. As part of the gas miscible displacement efforts, Morgantown Energy Technology Center researchers are studying carbon dioxide flooding and mobility control in the laboratory and, through contracts, in the field. Thermal recovery research is performed through contracts monitored by the San Francisco Operations Office.

Chemical Flooding Research

Two disulfonate products used as cosurfactants were found to impart some calcium tolerance. A diphenyl ether sulfonate was more effective than a diphenyl alkylate, but had an unfavorable effect in the absence of calcium. Temperature effects were mapped out for polyacrylamide in the lower Newtonian and power-law regions. Differences in alcohol partitioning for aromatic and aliphatic hydrocarbons were correlated with deviations from the equivalent alkane carbon number (EACN) concept. The Bureau of Mines method for measuring wettability gives a linear correlation on sands of mixed wettability.

In an extension of the work on disulfonates presented last quarter, phase volume measurements were made on systems of TRS 10-410 (3 weight-percent active), octane (WOR = 1), and "cosurfactant" (3 weight-percent total) in blends of the following proportions:

IBA (isobutyl alcohol)	3.0	2.5	2.0	1.5	1.0
DPA (diphenyl alkylate) as active disulfonate	0	0.5	1.0	1.5	2.0

The DPA is a product supplied by Conoco, 46 percent active in constituents having a sulfonate on each of two benzene rings attached to a carbon chain of average length C_{12}. The active equivalent weight [illegible] 58.

The electrolyte was $CaCl_2/NaCl$ with various equivalent fractions o calcium. The purpose of these experiments was to test the calciu tolerance of disulfonate-containin mixtures.

Figure B3 shows the effect of replacing IBA by DPA in the absence o calcium. Plotted are optimal salinit and solubilization parameter V/V (volume of oil = volume of water solubilized per unit volume of surfactant, at optimal salinity). For comparison, the same two parameters ar

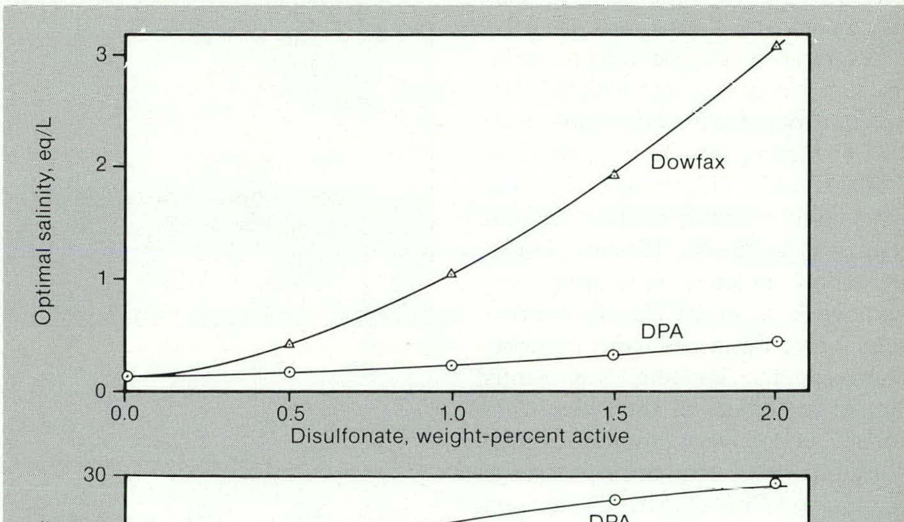

FIGURE B3. *Effect of replacing isobutyl alcohol by disulfonates as cosurfactan in the TRS 10-410/octane system.*

[5b] Project: Recovery Processes. B&R No. AB-15-10-10-4. Staff: Branch Chief, H. B. Carroll, Jr.; Section Chief, P. B. Lorenz; Chemical Engineer, M. K. Tham; Petroleum Engineers, R. D. Thomas and A. F. Bayazeed; Research Chemist, S. Brock.

Fred Burtch (right), project manager for chemical recovery, reviews quarterly results of a DOE cost-shared project with Don Ward, director of the Division of Extraction. This micellar-polymer flooding project, being performed by Marathon Oil Co., is showing successful oil recovery rates. Detailed information on the program is contained in Marathon's latest annual report that was published in May, report no. DOE/ET/13077-63, "Commercial Scale Demonstration—Enhanced Oil Recovery by Micellar-Polymer Flood," which covers the period of October 1980 to September 1981 and is available from BETC.

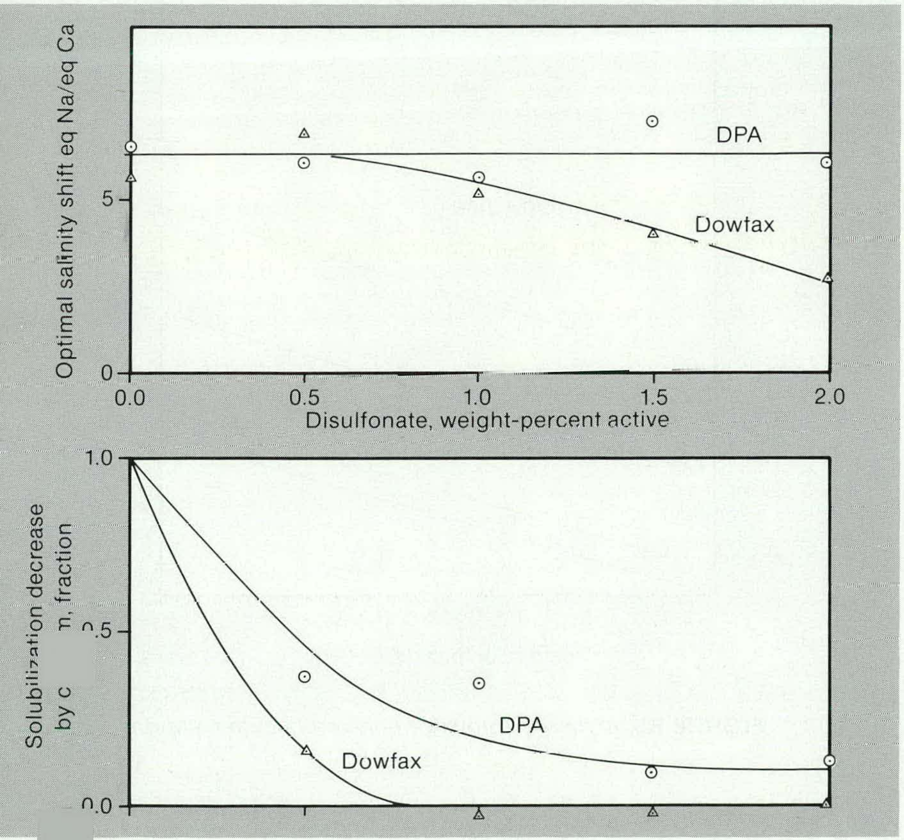

FIGURE B4. *Effect of disulfonate on calcium sensitivity. Lower curves are xpressed as fraction of the decrease in the absence of disulfonates.*

presented as a function of the content of Dowfax 2A1 (a diphenyl ether disulfonate, *cf.* Ref. 6b), and as a function of calcium without disulfonate. As before,[6b] calcium sensitivity is assessed in terms of optimal salinity shift, $\Delta[Na]/\Delta[Ca]$, and solubilization changes, $\Delta(V/V_s)/\Delta[Ca]$. Values are plotted in Figure B4 for 0.04 equivalent fraction calcium. The results are not very sensitive to calcium concentration.

In contrast to Dowfax, DPA itself does not reduce solubilization and has a minor influence in shifting optimal salinity. However, DPA appears to be less effective than Dowfax in reducing calcium sensitivity, although the results are very uncertain, depending on small differences between large quantities. Another comparison is the range of salinities over which Type III behavior is observed, shown in Table B2.

TABLE B2. *Range of salinities over which Type III behavior is observed*

Wt-pct disulfonate	0	0.5	1.0	1.5	2.0
Eq/L of NaCl for					
Dowfax	0.01	0.07	0.16	0.4	0.3
DPA	0.01	0.01	0.01	0.01	0.02

The conclusions are: (1) both disulfonates impart some calcium tolerance, (2) the system is more salt-tolerant (wider range of Type III) and perhaps more calcium tolerant with the ether linkage than with a hydrocarbon chain, and (3) the intrinsic effect of the disulfonate is unfavorable (reduces solubilization) when there is an ether linkage.

It is still undetermined whether the effect of these disulfonates is simply a low equivalent weight and high water solubility, or a sequestering action on the calcium ion.

[6b] *Liquid Fossil Fuel Technology,* DOE/BETC/QPR-82/1, July 1982.

Last quarter, preliminary measurements were reported on the temperature variation of solutions of Nalco polyacrylamide. The power-law exponent, b, appeared to be insensitive to temperature. The viscosity activation energy calculated from Arrhenius plots was about 15 J/mol.

Measurements were repeated this quarter with improved temperature control. Two sets of viscosity values were examined. High shear-rate behavior (70–130 sec^{1}) was represented by the coefficient of the power-law equation (i.e., an extrapolated unit-shear-rate viscosity). Low-shear-rate values (0.1–7.0 sec^{-1}) were the actual Newtonian viscosities. For both sets, as before, reduced viscosity, μ_r gave linear plots against polymer concentration, C_p:

$$\mu_r = (\mu - \mu_w)/\mu_w C_p = [\mu] + \mu' C_p$$

where μ_w is viscosity of water at the same temperature and $[\mu]$ is intrinsic viscosity. The intrinsic viscosities gave reasonable Arrhenius plots (Figure B5). Within the accuracy of the measurements, it is plausible to assign the same slope at all salinities. The high-shear-rate values gave an activation energy of 31 ± 5 J/mol. Unexpectedly, low-shear-rate values appeared to be significantly different, with activation energy 33 ± 4 J/mol. As before, the coefficients μ' from high-shear-rate data were larger than those from low-shear-rate data. However, the two sets of slopes displayed the same temperature dependence,

$$\frac{d \log \mu'}{d\,(1/T)} \approx 900°\text{K}$$

The present measurements revealed a dependence of power-law exponent on temperature, as well as other parameters. For a variation of any single one of the quantities—salinity, polymer concentration, or temperature—a majority of the data could be fitted to the correlation

$$b = 1 - c(\mu - \mu_m)^d$$

The values of c and d depended on which experimental parameter was varied. Representative results, calculated from smoothed values of c and d, are presented in Figure B6. These results tell us:

(1) When solutions [illegible] iffe ent polymer concentration ar brought to the same viscosity b adjustment of salinity, lowe polymer concentration is assoc ated with more non-Newtonia behavior,

(2) When viscosity is altered b changes in polymer concentra tion, the solution is more nor Newtonian at low salinity, and

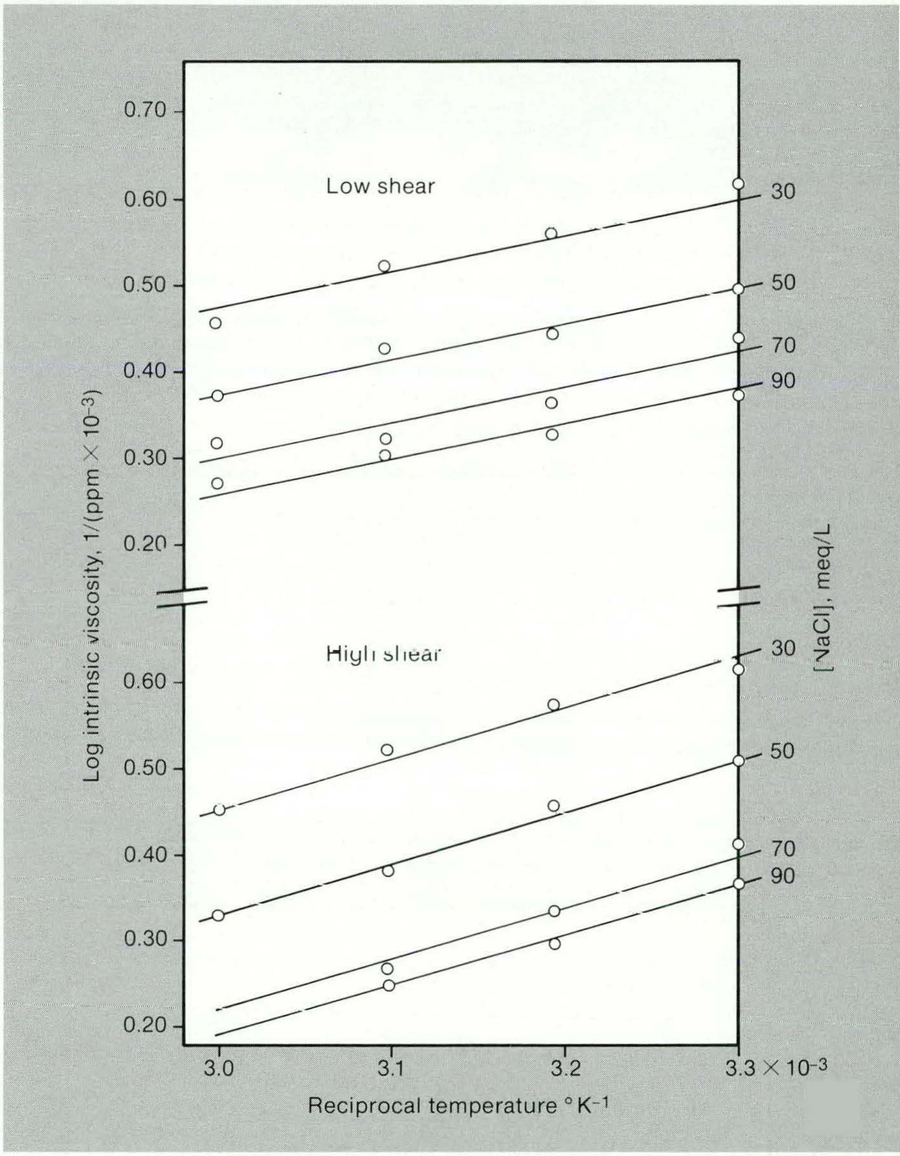

FIGURE B5. *Arrhenius plots for polyacrylamide solutions.*

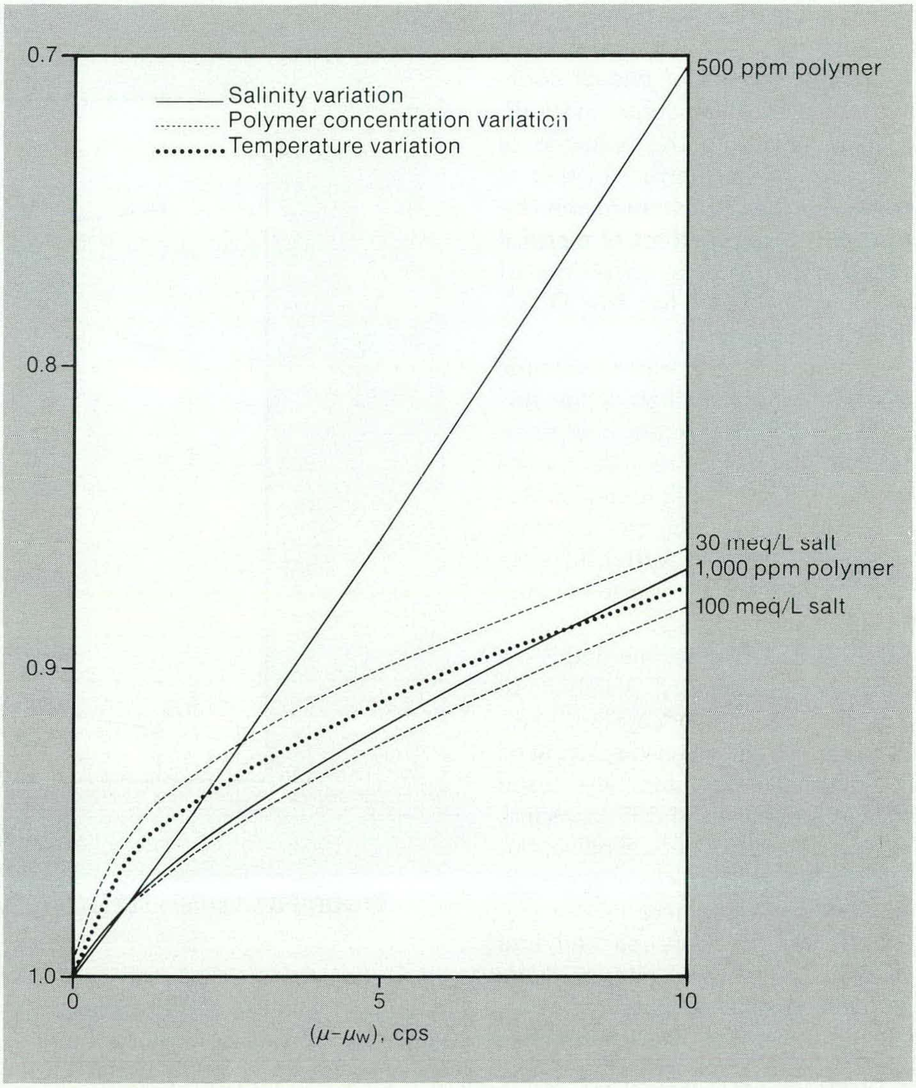

FIGURE B6. *Correlations between viscosity and power-law exponent.*

(3 [illegible]en viscosity is altered by tem[illegible]ture, the non-Newtonian haracter is not significantly altered by polymer concentration or salinity.

In an earlier work,[7b] it was shown hat the optimal salinity of Delaware-Childers (D. C.) oil decreased with ncrease in water-oil ratio (WOR), in contrast to that of octane. This result ndicates that the equivalent alkane carbon number (EACN) of D. C. oil ncreases with increase in WOR, in violation of the EACN concept.[8b] The EACN of the phenyl alkanes also does not follow this concept. In particular, the EACN of phenyl dodecane was 9.0 with the Witco TRS 10-410 isobutyl alcohol system, and 6.3 with the Floodaid 141 system (FA 141), although its EACN should be 12.[8b] In agreement with our findings, the results of Puerto and Reed[9b] also show deviation of the EACN of the phenyl alkanes from the EACN concept. Our investigation indicated that the differences in the partitioning of the co-solvent, Amoco 122, in FA 141 is one of the causes for the deviation in that system. For example, the partition coefficient of Amoco 122 in phenyl dodecane is about eight times more than that in octane.

Moreover, the heavy components of Amoco 122 tend to partition preferentially in the oleic phase for the phenyl dodecane system. Since D. C. oil is high in aromatic compounds, it is logical to assume that the abnormal value of the EACN of D. C. oil is due to this partitioning property. Confirmation of this postulate is difficult, because the multicomponent nature of the crude oil inhibits the analysis of the alcohol components in crude oil. An indirect indication of the correctness of the postulate would be a similarity between phenyl dodecane and D. C. oil in their behavior with changes in WOR.

A set of experiments was performed to measure the optimal salinity of phenyl dodecane with FA 141 as

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[7b] M. K. Tham and P. B. Lorenz. 1981 European Symposium on Enhanced Oil Recovery Proceedings. Burnemouth, England. pp. 123–134.

[3b] R. L. Cash, J. L. Cayias, G. Fournier, D. J. MacAllister, T. Schares, R. S. Schechter, and W. H. Wade. *J. Colloid Interface Sci.* (1977) 59, 39.

[9b] M[illegible]uerto and R. L. Reed. Paper 10678 pr[illegible]ed at the Third Joint Symposium on Enhanced Oil Recovery, April 4–7, 1982 in Tulsa, Oklahoma.

the WOR was changed from 1 to 2. It is gratifying to note in Figure B7 that the optimal salinity of phenyl dodecane increases with increase in WOR, which is similar to the behavior of D. C. oil, and in contrast to that of octane. **The results strengthen the argument for the effect of alcohol partitioning on the variation of EACN with WOR for the D. C. oil-FA 141 system.**

A project has been started to study the effects of distribution of the surfaces with different wetting characteristics on capillary pressure curves and wettability. The first step in this project was to compare capillary pressure curves and wettabilities for mixtures of strongly water-wet and strongly oil-wet sands.

The Bureau of Mines method[10b] for determining wettability, which compares the area under capillary pressure curves for water-displacing-oil and oil-displacing-water, was used with 140–200 mesh (74–105 μm) sand. The results are not yet definitive, but some data and advances in the technique are presented here.

Sand samples were packed into cylindrical cups ¾ in. interior diameter, and internal height with ⅛ in. walls and bottom. The bottom had five 340 μm drainage holes, and sand loss was impeded by a thin layer of 35–65 mesh sand (230–500 μm). Another very small layer was placed on top to keep the finer sand from floating away.

Oil-wet sands were prepared by treating clean (water-wet) sand with DCDMS (dichlorodimethylsilane) and Syl-Off (Syl-Off 1107, a silicone release product of Dow Corning). Both treatments were found to be stable (reproducible capillary pressure/saturation data) over 4 weeks and 10 cycles with water and n-dodecane. Since the Syl-Off was easier to apply and slightly more oil-wet, it was used for all later studies.

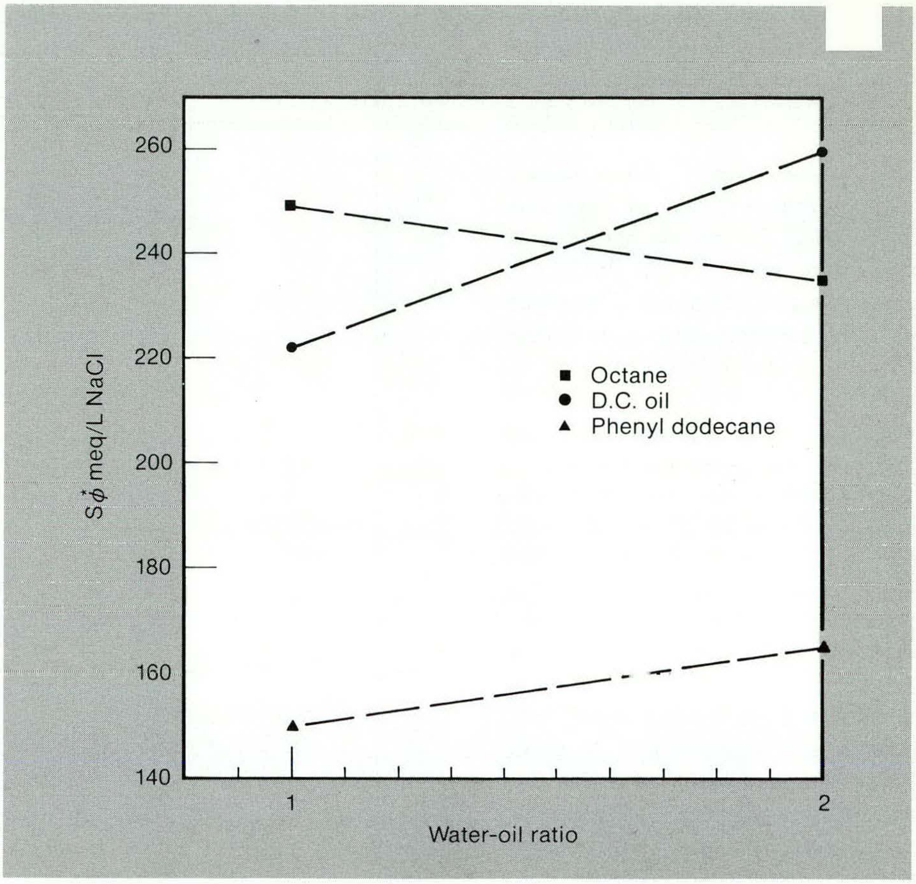

FIGURE B7. *Variation of FA141 optimal salinity S^*_ϕ, with water-oil ratio.*

Samples of randomly mixed water-wet (clean) and oil-wet (Syl-Off) sands were prepared and their wettability determined. The usual calculation procedure for wettability (capillary pressure curves cut off at 8 psi) was found to give large errors for data from these sands. The problem was found to be caused by the large pores and narrow pore size distribution of these sands. This resulted in the area under the capillary pressure curves being influenced more by the small pores that make up 5 to 10 percent of the pore space than the much more important large pores.

These errors were eliminated by calculating only with data over a 0.7 pore volume saturation range, to eliminate the small pores. Wettabilities so calculated are plotted against fraction of oil wet sand in Figure B8. For comparison, the figure also shows Amott's data on similarly mixed sands.[11b] The dashed line is as drawn by Amott. **The solid line shows that the present method gives a reasonable linear correlation.**

Figure B9 shows individual capillary pressure curves. It would be premature to look for systematic dif-

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[10b] E. C. Donaldson, R. D. Thomas, and P. B. Lorenz. *Soc. Petrol. Eng. J. 9*, pp. 13–20 (March 1969).

[11b] E. Amott, *Trans AIME, 216*, pp. [illegible] 162 (1959).

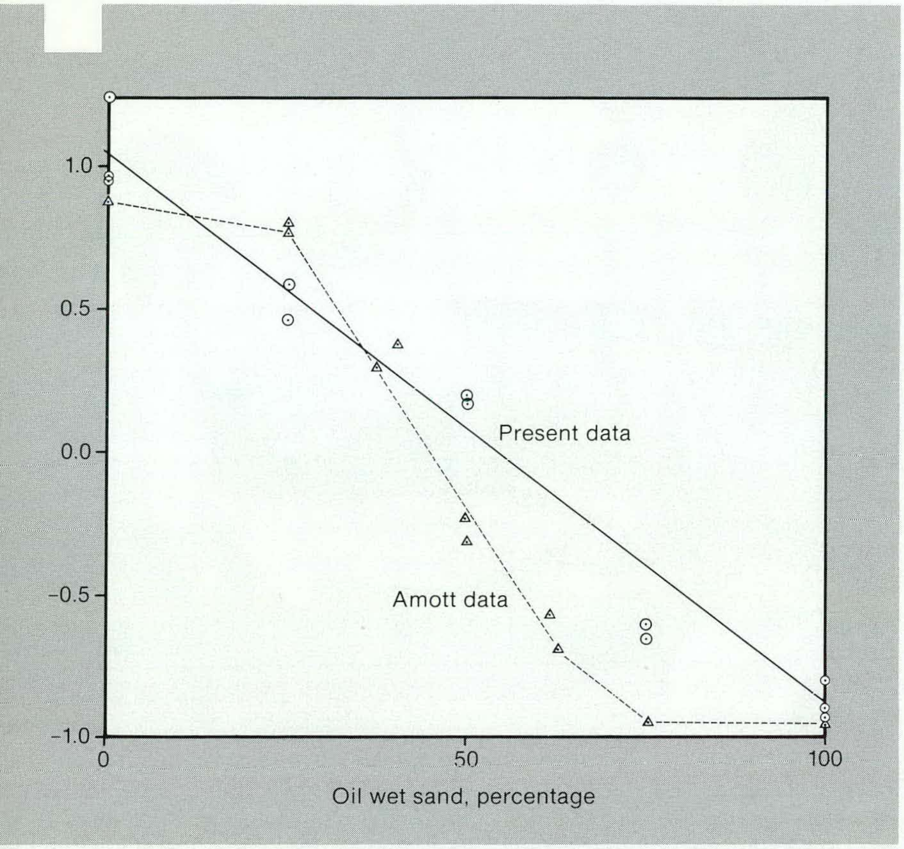
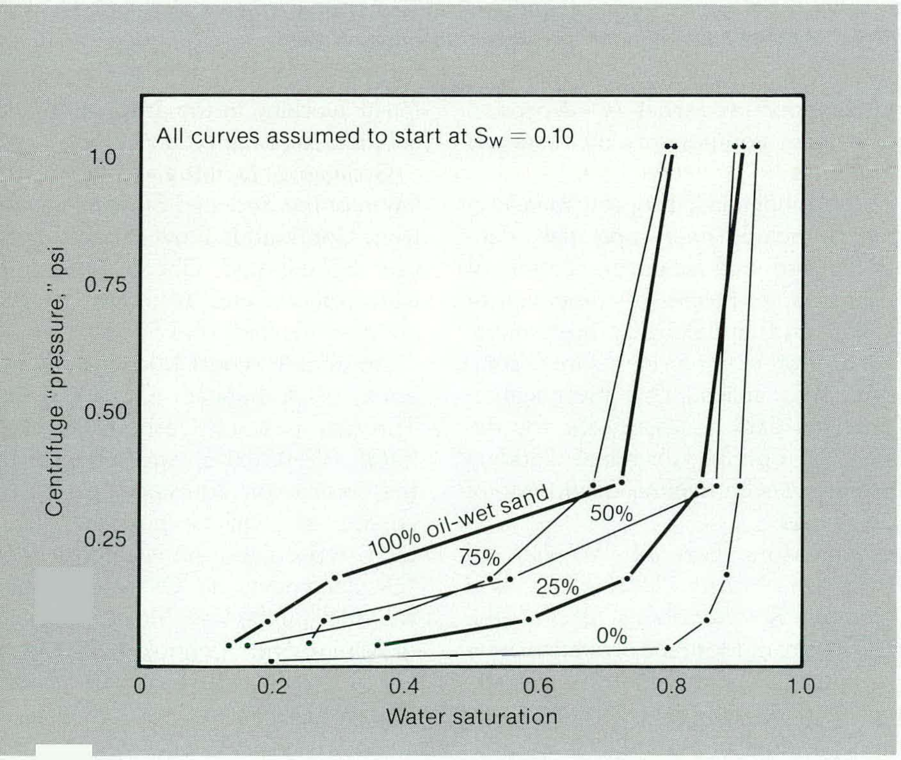


FIGURE B8. *Bureau of Mines and Amott wettabilities of sand mixtures.*



IGl B9. *Effect of random-mixed oil-wet sand concentration on capillary ressure curves.*

ferences between uniform and mixed wettability.[12b]

Contracts. Both field tests and supporting research for Chemical Flooding are contracted. These projects are reported in Progress Review No. 31.[1a] They are supervised jointly by the Divisions of Extraction Research and Project Management.

Chemical Flooding Field Demonstration Contracts. The following field demonstration contracts were monitored:

Cities Service Co. (DE-AC03-78ET13070). Improved Oil Recovery by Micellar-Polymer Flooding, El Dorado, Kansas, Field. Technical Project Officer: R. E. Porter.

Conoco, Inc. (DE-AC03-78SF01-424). Big Muddy Field Wyoming Multipattern Low-Tension Flood. Technical Project Officer: R. D. Thomas.

Energy Resources Co., Inc. (DE-AC19-78ET12065). Enhanced Oil Recovery by Improved Waterflooding, Storms Pool, Illinois. Technical Project Officer: F. W. Burtch.

Marathon Oil Co. (DE-AC19-78-ET13077). Commercial-Scale Demonstration Enhanced Oil Recovery By Micellar-Polymer Flooding. Technical Project Officer: R. E. Porter.

Chemical Flooding Supporting Research Contracts. Supporting research to the chemical flooding program is monitored in the following institutions:

Columbia University (DE-AC19-79BC10082). Adsorption from Flooding Solutions in Porous Media. Technical Project Officer: P. B. Lorenz.

Illinois Institute of Technology (DE-AC19-80BC10069). The Mechanism of Oil-Bank Formation and Coalescence in Porous Media. Technical Project Officer: P. B. Lorenz.

[12b] J. P. Batycky, F. G. McCaffery, P. K. Hodgins, and D. B. Fisher. *Soc. Petrol. Eng. J. 22*, pp. 296–308 (June 1981).

Oak Ridge National Laboratory (W-7405-eng-26). Enhanced Oil Recovery Research. Technical Project Officer: F. W. Burtch.

State University of New York (DE-AS19-80BC10326). Effects of Pressure, Time, and Composition on Oil. Technical Project Officer: P. B. Lorenz.

University of Kansas (DE-AS19-80BC10354). Evaluate Methods of Reducing Permeability in Rocks by *In Situ* Polymer Treatments. Technical Project Officer: R. D. Thomas.

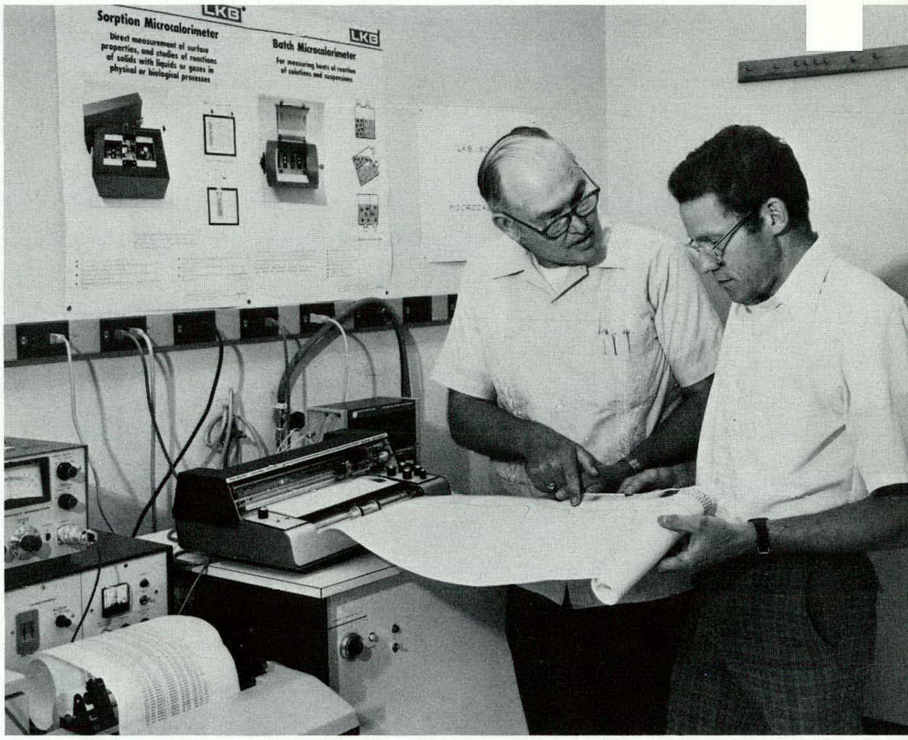
University of Minnesota (DE-AC19-79BC10116). Flow in Porous Media, Phase Behavior, and Ultralow Interfacial Tensions. Technical Project Officer: L. J. Volk.

University of Southern Mississippi (DE-AS19-80BC10321). Improved Polymers for Enhanced Oil Recovery Synthesis and Rheology. Technical Project Officer: B. L. Gall.

University of Texas (DE-AC19-79BC10095). Mobility Control and Scaleup for Chemical Flooding. Technical Project Officer: M. K. Tham.

University of Texas (DE-AS19-80BC10345). Study of Enhanced Oil Recovery Processes. Technical Project Officer: P. B. Lorenz.

Thermodynamic Characterization of Tertiary Recovery Systems.[13b] The objective of BETC's research on the thermodynamic properties of tertiary recovery systems is to provide data on the solution thermodynamic properties of chemical systems that are similar to those used in chemical flooding and on the thermodynamic properties of adsorption of system components on reservoir materials.



Reviewing results from an experiment to determine the heat of adsorption of ar alcohol surfactant on silica gel, performed with the adsorption calorimeter, are Leo A. Noll (left), research chemist, and Earl M. Woolley, DOE/Associated Western Universities faculty participant. These studies determine how the surfactan slug injected into a reservoir adsorbs onto solid surfaces, such as reservoir rock Woolley, a member of the faculty at Brigham Young University, began work a BETC in June and will continue here through July 1983.

Thermodynamic property measurements include heat capacities, densities, and enthalpies of dilution of solutions; enthalpies of immersion of solids; and enthalpies of preferential adsorption of components from solution onto solids. This investigation provides data necessary for the design of optimal chemical flooding processes with minimal adsorption of chemicals.

Professors Earl M. Woolley of Brigham Young University and George W. Woodbury, Jr., of the University of Montana arrived in June to spend 15 and 3 months, respectively, working in the adsorption anc solution calorimetry laboratory.

Galley proofs of the article “Calculation of the Reduced Surface Excess from Continuous Flow Frontal Analysis Solid-Liquid Chromatography” were edited and returned to the editor of *Colloids and Surfaces*.

An annual report titled “Investigations of Enhanced Oil Recovery Through Use of Carbon Dioxide” (DOE/BC/03103-6) was revised b the contractor, Louisiana State University, and will be published as a DOE report. An annual report titlec “Displacement of Oil by Carbon Dioxide” by the New Mexico Institute of Mining and Technology has beer published as report number DOE/BC/10331-4.

[13b] Project: Thermodynamic Characterization of Tertiary Recovery Systems. B&R No. AC-15-10-10. Division Director, W. D. Good; Acting Chief, Thermodynamics Branch, W. D. Good; Research Chemists, N. K. Smith, T. E. Burchfield, and L. A. Noll.

Two papers are being prepared for pres[illegible]ion at the 37th Annual Calorimetry Conference. A report titled "Silica Gel as a Model Surface for Adsorption Calorimetry of Enhanced Oil Recovery Systems" has been published as DOE/BETC/RI-82/7.

Further heat capacity and density measurements were made on aqueous solutions of sodium 4-(1-pentylheptyl)benzene sulfonate ($6\text{-}\emptyset C_{12}SO_3\text{-}Na$). At the higher concentrations studied, a small amount of precipitation was noted in some of the solutions. Since the presence of a precipitate influences heat capacity and density measurements, an investigation into the origin of the precipitate was initiated.

In order to investigate the solubility behavior of the $6\text{-}\emptyset C_{12}SO_3Na$ compound in water, an attempt was made to measure the clear point of a 0.143 molal (4.75 weight-percent) solution. The solution was cooled to 11.2°C and then slowly warmed at the rate of approximately 5°C per hour and agitated periodically. At 11°C the solution was turbid, but at approximately 22°C the solution appeared to clear significantly. A small amount of precipitate did persist even after maintaining the solution at 59°C for 30 minutes.

The sample of surfactant was dried again at reduced pressure and a 0.0443 molal (1.52 weight-percent) solution was prepared. At ambient temperature (28–29°C) this solution also exhibited a small amount of precipitate. Both of the above-mentioned solutions were warmed to 78°C in a water bath and were found to be turbid at that temperature. A 0.044 molal solution of the compound was prepared. The compound as received had [illegible]n stored in a desiccator, but had [illegible]een dried in the drying oven. This solution appeared also to exhibit a trace of precipitate, but the amount was less than that observed for a solution of similar concentration prepare[illegible]th the dried compound.

Several explanations seem possible for the formation of a precipitate by aqueous solutions of the $6\text{-}\emptyset C_{12}SO_3\text{-}Na$. There always is the chance that a precipitate can be due to an impurity initially present in the compound or resulting from decomposition during drying or storage. Elemental analysis of a sample of the compound that had been dried at 100°C at reduced pressure for 48 hours is as follows (theoretical values in parentheses): C, 61.70 percent (62.04 percent); H, 8.48 percent (8.39 percent); S, 9.28 percent (9.20 percent); and Na, 6.54 percent (6.60 percent). The uncertainty in the numbers is approximately ± 0.3 percent.

The agreement between the theoretical and experimental elemental composition of the compound tends to preclude the presence of a significant impurity other than an isomer of the compound. However, it is known[14b] that the ortho- and para-isomers of octyl- and dodecyl-benzene sulfonate differ considerably in their solubility in water. Another possibility is that the precipitate is a liquid crystalline phase. Further experiments are being conducted to establish the composition of the precipitate.

Precipitation of the $6\text{-}\emptyset C_{12}SO_3Na$ compound from water at ambient temperatures was expected somewhat. Magid, et al.[15b] have reported densities of aqueous solutions of this compound at concentrations as high as 0.04 molal (1.37 weight-percent) at 25°C. No mention was made of precipitation of surfactant from the solutions.

Schechter and Wade[16b] have reported a phase diagram for isomeric dodecylbenzene sulfonates in a 1 percent aqueous sodium chloride solution. Their phase diagram indicates that a 0.1 weight-percent solution of the $6\text{-}\emptyset C_{12}SO_3Na$ compound containing 1 percent sodium chloride exists as a solid hydrate in equilibrium with a cloudy solution at temperatures below 18°C and as a cloudy solution with gel-like formations between 18° and 72°C. They indicate that the clear point of the solution is approximately 72°C.

Surfactants with mid-chain attachment of the ionic group (i.e., double-tailed surfactants) are known to form liquid crystalline phases. For some compounds, the first aggregate formed can be a liquid crystalline phase rather than a normal micelle.

Recently there has been conflicting evidence in this regard for the compound sodium 4-(1-heptylnonyl) benzene sulfonate ($8\text{-}\emptyset C_{16}SO_3Na$). Franses, et al.[17b] concluded that this compound (Texas No. 1) does not form normal micelles in water, but instead at saturation the equilibrium phase is a lamellar liquid crystal. Magid, et al.[18b] have asserted that their evidence confirms the formation of small normal micelles of the $8\text{-}\emptyset C_{16}\text{-}SO_3Na$ compound in water.

[14b] F. W. Gray, J. F. Gerecht, and I. J. Krems, *J. Org. Chem., 20,* 511 (1955).

[15b] L. J. Magid, R. J. Shaver, E. Gulari, B. Bedwell, and S. Alkhafaji, Preprints, Div. Petrol. Chem., *Am. Chem. Soc., 26,* 93 (1981).

[16b] R. S. Schechter and W. H. Wade, "Tertiary Oil Recovery Processes Research at the University of Texas," Annual Report for the period Oct. 1977–Sept. 1978, BETC-0001-1, Bartlesville Energy Technology Center, April 1978, p. 46.

[17b] E. I. Franses, J. E. Puig, Y. Talmon, W. G. Miller, L. E. Scriven, and H. T. Davis, *J. Phys. Chem., 84,* 1547 (1978).

[18b] L. J. Magid, R. Triolo, J. S. Johnson, and W. C. Koehler, *J. Phys. Chem., 86,* 164 (1982).

Progress also was made this quarter on interpretation of the concentration dependence of the enthalpies of dilution of surfactant systems. Enthalpy of dilution data obtained from researchers at the University of Oklahoma on the enthalpy of dilution of sodium octyl sulfate in water at 298.15 K were analyzed. Relative apparent molal enthalpies, partial molal enthalpies, and the enthalpy of micellization have been calculated from the data. These results were compared with earlier data on sodium dodecyl sulfate.

The adsorption work has progressed in studying the interaction of cosurfactants with silica gel. An investigation of the properties of octadecyl sylanized silica gel, a hydrophobic surface, was initiated.

Table B3 lists the data for immersion of silica gel activated at 400°C (t400) in toluene, water, and a series of alcohols of increasing chain length.

TABLE B3. *Enthalpy of Immersion of t400 in Various Liquids*

Substance	$\Delta_{imm}H$, J/g
n-Heptane	-16.1
Toluene	-28.0
Water	-44.6
n-Propyl alcohol	-44.0
n-Butyl alcohol	-42.5
n-Pentyl alcohol	-41.6
n-Octyl alcohol	-41.2
n-Dodecyl alcohol	-43.0

There is increasing evidence that the alcohol (cosurfactant) plays a greater role in the formulation of EOR slugs than was earlier believed. **The present results show that the interaction of neat alcohol with a hydrophilic oxide surface is to a first approximation, independent of chain length.** Earlier we conducted experiments in which the replacement of toluene by alcohol on t400 is studied; these results will be incorporated with the present data into a report and will be made available.

The second item to report for this quarter is a study of D62 silica gel activated at 300°C, t300. This material has been immersed in toluene, water and normal butyl alcohol, with the results given in Table B4.

TABLE B4. *Enthalpy of Immersion of t300 in Various Liquids*

Substance	$\Delta_{imm}H$, J/g
Toluene	-31.4
n-Butyl alcohol	-45.1
Water	-50.8

These results indicate that material activated at 300°C is not much different from t200; it is more active toward alcohol, water and toluene than t400 (Table B3).

Surface excess and enthalpies of replacement of water and toluene by n-butyl alcohol on t300 have been measured and will be incorporated into a journal article in preparation.

A sample of D62 has been modified by attaching octadecyl silane (C_{18}) groups to the polar sites; any nonreacted sites have been "end capped" with methyl groups. We refer to this material as "C18D62." It is a completely hydrophobic surface.

Preliminary results for immersion of this material are given in Table B5.

TABLE B5. *Enthalpy of Immersion of C18D62 in Various Liquids*

Substance	$\Delta_{imm}H$, J/g
Toluene	- 6.7
n-Heptane	-11.9
n-Butyl alcohol	- 9.0
Water	- 1.2

There is a possibility that the process of bonding octadecyl groups to the surface can reduce the area available to other molecules. **It is interesting to note that, for the hydrophobic material, the enthalpies of immersion are completely reversed, being numerically the largest for immersion in n-heptane and smallest for water.** It also is interesting that the interaction of the hydrophobic surface with n-l alcohol is much larger than with water.

The surface excesses and enthalpies for replacement of water an toluene have been tested, and th results are being calculated. Result to date show that the calorimetri technique demonstrates a large difference for hydrophobic and hydrophilic surfaces.

Significant progress has been mad this quarter in improving the laboratory instrumentation. A Fluke 8502 digital multimeter was received t replace the Dana 5000 digital multimeter as the analog-to-digital converter for the digital data acquisitio system. A precision constant curren supply was received and will be use as part of the calibration system fo the LKB flow mixing microcalorimeter. Previously, one calibration uni was used for both the LKB sorptio and flow mixing microcalorimeters Now both calorimeters are capable o independent operation.

A Bascom-Turner data acquisitio system for the sorption microcalorimeter also was received this quarter. The Bascom-Turner system wi handle the acquisition and processing of data from both the sorptio calorimeter and the differentia refractometer. This will result in a improvement in data precision fro the differential refractometer and i the ease of data reduction. The sorption calorimeter is now capable o completely independent operation The digital data acquisition syste can now be used primarily for acquiring and processing data from th mixing and heat capacity microcalorimeters.

The Picker specific heat microcalorimeter has been received th manufacturer after being red The operation of the calorimeter wa checked by determining the hea capacities and densities of aqueou solutions of sodium chloride at 298.1 K. Values of the apparent m hea capacity and volume of sodium chlo rid eed well with those of other inv ators.

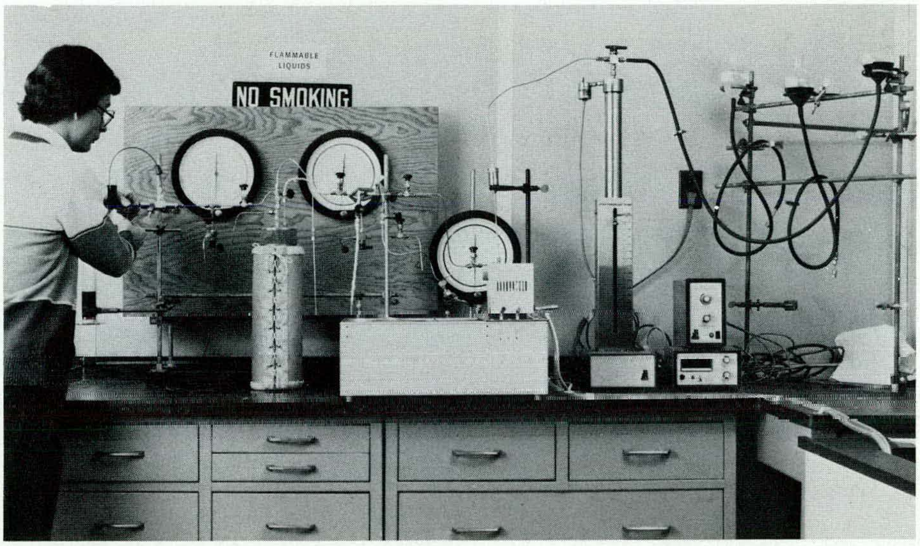
Micellar Properties of Oil and Additives.[19b] The objectives are to determine how colloidal physical properties, such as size and shape of oil micelles, are influenced by additives and physical changes used to increase production and to determine how properties of colloidal solutions, such as detergents and polymers, are changed by contact with crude oil and by changes in their chemical composition and physical treatment.

A paper concerning small-angle X-ray scattering studies of association of clay particles into aggregates was revised and accepted for publication by the *Journal of Applied Crystallography*. **The data presented in the paper show that many clays form aggregates in sediments obtained from water, even in the presence of a deflocculant.**

The automated Bonse-Hart small-angle X-ray scattering instrument was modified to improve accuracy of angular measurements. A stepping motor is connected to a precision gear reduction box that drives the micrometer of the instrument. A metal bellows between the stepping motor and gear box was difficult to align and developed cracks with extended use. A new type of thin-disc coupler was used to replace the metal bellows. It is easy to align, does not crack, and gives sufficient isolation between the stepping motor and the gear box.

Small-angle X-ray scattering was used to study aggregation of clay particles in sediments and to study colloidal silica.

The new printer, a Hewlett-Packard model 2673A, ordered for use with the 5S control computer used to operate the photographic plate scanner, was received this quarter. Some time was spent this quarter in connecting the printer into the system and checking out its operation. The printer has considerable graphics capability, and a computer program was written to plot graphs of experimental data together with fitted curves.



During carbon dioxide displacement testing being performed at the Morgantown Energy Technology Center, Anthony M. Zammerilli, METC chemist, adjusts the carbon dioxide pressure through a release valve. The work will determine the amount of oil recovered by carbon dioxide in the Berea sandstone core sample under study.

A 30-g sample of sodium octanoate (NaOct) was prepared by titrating n-octanoic acid (Aldrich Gold label, 99.5 percent) with 1 M NaOH(aq). Precision density measurements were made on the system NaOct/H_2O. The following values were obtained respectively for the critical micelle concentration (CMC), partial molal volume at infinite dilution ($\bar{V}^{\infty}$), and the partial molal volume of the micelle ($\bar{V}^{m}$): 0.412 m, 132.5 cm^3 mol^{-1}, and 143.3 cm^3 mol^{-1}. These values compare favorably with published data.

Isopiestic distillation experiments were completed on the system NaOct/3.0 m NaCl(aq). Preliminary analysis of the results indicates that the preferential interaction parameter, $(\partial g_3/\partial g_2)_{\mu 1}$, is negative as obtained for other anionic surfactants. Some researchers have postulated that this parameter would be positive in these high NaCl(aq) concentrations.

The manuscript "Effect of Co-Ion on the Preferential Interaction Parameter and Micelle Aggregation Number. Sodium Dodecyl Sulfate in Aqueous Sodium Halide" by Daryl A. Doughty was approved locally for publication and was submitted to the *Journal of Physical Chemistry*.

Gas Miscible Displacement Research[20b]

The activities of the Gas Miscible Displacement (carbon dioxide flooding) EOR project at the Morgantown Energy Technology Center (METC) include in-house research and contracts for field and supporting research.

The injection of carbon dioxide

[19b] Project: Micellar Properties of Oil and Additives. B&R No. AC-15-10-10. Division Director, W. D. Good; Acting Chief, Ther- namics Branch, W. D. Good; Re- h Chemist, C. W. Dwiggins, Jr.; Research Physicist, D. A. Doughty.

[20b] Project: Gas Miscible Displacement. B&R No. AC-15-10-10-1. Staff: Division Director, D. C. Ward; Project Manager, A. B. Yost II (METC); Petroleum Engineer, K. I. Kamath (METC); Research Chemist, J. R. Comberiati (METC); Research Chemist, A. M. Zammerilli (METC).

(CO_2) in pressure-depleted oil reservoirs has been studied by a number of researchers. Its unique ability to solubilize oil, to cause the oil to swell, and to lower the viscosity of oil makes it a good possible method for recovering additional oil.

The overall purpose of this program is to determine what effect, if any, that the various reservoir conditions (temperature, pressure, flow rate, oil hydrocarbon composition, etc.) have on the recovery of oil by CO_2 flooding. The program includes research for the development of novel methods of CO_2 flooding to recover additional oil.

Past studies have provided data on the effects of temperature, pressure, and CO_2 injection slug size and have shown the importance of the use of liquid CO_2 for recovering oil.

A study is being made to determine the effect of flow rate on oil recoveries from 1.5-in. by 8-in. Berea sandstone cores by CO_2 flooding. A 15 percent pore volume (PV) CO_2 slug (adjusted according to temperature and pressure) was injected into oil- and brine-saturated cores while varying the flow rate from 5 to 40 cc/hr (1.6 to 12.4 ft/day) followed by 1 PV of 2 percent brine (sodium chloride in water) at 75°F and a pressure of 1,150 psi. Other tests at 86° and 100°F and at a pressure of 1,500 psi were also made.

Fifteen more tests were made this quarter at a pressure of 1,150 psi and temperatures of 75°, 86° and 100°F with flow rates of 5, 10, 20, and 40 ml/hr. The results from these tests are presented in Table B6. They appear to indicate that oil recoveries decrease a small amount with an increase in flow rate and in temperature, and the overall change is not very significant.

When these values are averaged with previous tests, the trends appear to be a little more definite. These results are presented in Table B7. **The values at 100°F show a definite decrease in oil recoveries, while the values at 75° and 86°F show very little change with temperature.** Also, at all temperatures there is a trend of decreasing oil recoveries with increasing flow rates, but these changes are very small.

TABLE B6. *Oil Recoveries from CO_2 Flooding at Different Flow Rates and Temperatures*

Core Test	Temperature, Degrees F	Flow Rate, ml/hr	Oil Recovered, Percent Pore Volume
L-27-22	75	5	50.4
L-27-17	75	20	50.0
L-27-15	75	40	49.1
L-27-26	75	40	47.4
L-27-18	86	5	50.8
L-27-27	86	5	47.8
L-27-12	86	10	48.3
L-27-23	86	10	48.7
L-27-19	86	40	47.8
L-27-14	100	5	49.1
L-27-24	100	5	49.6
L-27-16	100	10	47.8
L-27-25	100	10	49.1
L-27-13	100	20	49.5
L-27-21	100	40	48.7

TABLE B7. *Average Oil Recoveries by CO_2 Flooding According to Temperature and Flow Rates*

Temperature	5 ml/hr	10 ml/hr	20 ml/	40 l/hr
75° F	49.3	49.1	48.9	48.8
86° F	49.0	48.4	49.8	47.6
100° F	47.1	46.9	46.1	46.5

FUNDAMENTAL CARBON DIOXIDE EOR REPORT AVAILABLE

Research on the use of carbon dioxide in enhanced oil recovery, with emphasis on the fundamental features of displacement and recovery efficiency, is the focus of an annual report published by DOE.

The 118-page report, "Displacement of Oil by Carbon Dioxide" (DOE/BC/10331-4), was prepared by the New Mexico Institute of Mining and Technology under contract to DOE. Single copies are available free from the Bartlesville Energy Technology Center, Attention Bill Linville, P.O. Box 1398, Bartlesville, Okla. 74005.

The study centers on measuring the extent to which carbon dioxide mixes with and recovers oil under conditions imposed by several factors of displacement, such as phase behavior and fluid properties of the carbon dioxide-oil mixture.

Because miscible displacement of oil by carbon dioxide is essential to effective recovery, tests were conducted to determine how the phase behavior of carbon dioxide and oil mixtures is affected by variants such as temperature and pressure. The effects of pore structure of reservoir rock on recovery efficiency also are addressed.

Technical project officer for the contract work is L. A. Noll of the BETC.

The [illegible] tentative conclusions are:

(1 [illegible] effect at all four flow rates is only significant when the temperature is raised to about the critical temperature of CO_2 (87.8°F), thus, changing the CO_2 from a liquid to a gas. This, in turn, results in a decrease in oil recoveries.

(2) At a given temperature, the change in flow rate shows no significant change in oil recoveries.

The second conclusion is probably a contradiction to the theory that slow flow rates provide better contact with the oil droplets and, thus, increase oil recovery. It is believed that solubility of the CO_2 in the oil is one of the main factors in increasing oil recovery. **This indicates that oils containing hydrocarbon components, which increase the solubility of CO_2, will increase oil recoveries.** This will be discussed in a report now in preparation.

A second study being made will determine the effect of oil viscosity on oil recovery by CO_2 flooding. Using a 15 percent CO_2 slug (corrected for temperature), oils with viscosities ranging from 3.7 to 69 cps were displaced from 8-in. Berea sandstone cores at a pressure of 1,150 psi and at temperatures of 75°, 86°, and 100°F. In each test, the CO_2 was followed by 1 PV of 2 percent brine, and then the pressure was lowered to atmospheric.

The experimental portion of this study has been completed, and the results are being evaluated for a formal report.

Mobility Control Studies. METC in-house research on mobility control studies is concentrating on the following tasks: (1) determine research requirements for mobility control, (2) determine the state of the art for mobility control, (3) design a mobility control test of foams, polymers, and thickeners, (4) initiate a mini-test of mobility control, and (5) review DOE/industry contract research on mobility control.

The preliminary planning, design, and a review of the state of the art for the Pennzoil mobility control test have been completed. Work continues into how to apply mobility control in a liquid CO_2 environment. The chemicals to be tested have not been chosen. The start of the mobility control field test was delayed by a labor strike. Work is expected to resume during the third quarter of 1982.

Evaluation of the surfactant injection studies conducted at the Columbia Gas Granny's Creek CO_2 project indicates a significant pressure response due to injection of surfactant foaming agent. The results are encouraging that surfactant injection using the *in situ* foaming concept might provide a new approach to CO_2 mobility control.

Contracts for Field Projects. The following field tests were monitored, and reports are given in Progress Review No. 31.^{1a}

Columbia Gas Transmission Corporation (EF-76-C-05-5302). Oil Recovery by Carbon Dioxide Injection, Granny's Creek Field, West Virginia. Technical Project Officer: R. J. Watts, METC.

Pennzoil Company (DE-AC21-76ET12002). Oil Recovery by Carbon Dioxide Injection, Rock Creek Field, Roane County, West Virginia. Technical Project Officer: R. J. Watts, METC.

Shell Oil Company (EF-77-C-05-5232). Weeks Island "S" Sand Reservoir B Gravity Stable Miscible CO_2 Displacement, Iberia Parish, Louisiana. Technical Project Officer: R. J. Watts, METC.

See also Gulf Oil project under Process Implementation section.

Contracts for Supporting Research. The supporting research projects are:

Gruy Federal, Inc. (DE-AC21-79MC08341). Target Reservoirs for Carbon Dioxide Miscible Flooding. Technical Project Officer: R. J. Watts, METC.

Louisiana State University (DE-AS19-80BC10344). Investigation of Enhanced Oil Recovery Through Use of Carbon Dioxide. Technical Project Officer: T. E. Burchfield, BETC.

New Mexico Institute of Mining and Technology (DE-AC21-79MC-10689). Methods for Mobility Control in CO_2 EOR Processes. Technical Project Officer: A. B. Yost II, METC.

New Mexico Institute of Mining & Technology (DE-AS19-80BC10331). Displacement of Oil by Carbon Dioxide. Technical Project Officer: L. A. Noll, BETC.

New Mexico State University (DE-AC21-79MC10865). CO_2 Formation Damage Study. Technical Project Officer: R. J. Watts, METC.

University of Kansas (DE-AC19-79BC10122). Development of a Method for Evaluating Carbon Dioxide Miscible Flooding Prospects. Technical Project Officer: B. E. Gammon, BETC.

West Virginia University (DE-AT21-79MC11284). Phase Behavior of Appalachian Crudes with Carbon Dioxide—Single and Multiple Contacted Mixtures. Technical Project Officer: A. M. Zammerilli, METC.

University of Alabama (DE-AC21-81MC16140). Determination of Miscibility Pressure by Direct Observation Method. Technical Project Officer: A.B. Yost II, METC.

New Mexico Institute of Mining and Technology (DE-AC21-81MC16426). Mobility Control for CO_2 Injection. Technical Project Officer: A. B. Yost II, METC.

Thermal Recovery[21b]

Six field projects and two supporting contracts comprise the heavy oil/thermal recovery program, which is managed by the San Francisco Operations Office (SAN). More detailed information is given in Progress Review No. 31.[1a] Other thermal recovery work is reported in the Process Implementation Section.

Contracts for Field Projects

Cities Service Co. (DE-AC03-76ET-12057). Improved Oil Recovery by *In Situ* Combustion, Bellevue Field, Louisiana. Technical Project Officer: A. J. Leighton, SAN.

CLD Group, Inc. (DE-FC03-79SF-10761). Oil Recovery by Steam Drive with Ancillary Materials. Technical Project Officer: H. J. Lechtenberg, SAN.

Getty Oil Co. (DE-AC03-76ET-12058). Improved Oil Recovery by Steamflooding, Cat Canyon Field, California. Technical Project Officer: A. J. Leighton, SAN.

Petro-Lewis Corp.–CORCO (DE-FC03-79SF10762). Kern Front Field Steam Drive with Ancillary Material. Technical Project Officer: H. J. Lechtenberg, SAN.

Santa Fe Energy Co. (DE-AC03-79-ET12059). Enhanced Oil Recovery by Steamflooding, Midway-Sunset Field, California. Technical Project Officer: H. J. Lechtenberg, SAN.

Stanford University Petroleum Research Institute (DE-AC03-80SF-11445). Field Pilot of Steam Drive with *In Situ* Foaming. Technical Project Officer: H. J. Lechtenberg, SAN.

Contracts for Supporting Research

Stanford University Petroleum Research Institute (DE-AC03-81SF-11564). Secondary Recovery by Thermal Methods. Technical Project Officer: H. J. Lechtenberg, SAN.

University of Southern California (DE-AS03-76SF00113). Chemical Additives with Steam to Increase Oil Recovery. Technical Project Officer: H. J. Lechtenberg, SAN.

RESULTS ON FOAM ADDITIVES RESEARCH PUBLISHED

A study aimed at improving the efficiency of carbon dioxide in enhanced oil recovery by using foams to control high gas mobility is summarized in a new report published by the U.S. Department of Energy.

The 144-page report, entitled "Enhanced Oil Recovery By CO_2 Foam Flooding" (DOE/MC/03259-15), was prepared as a result of a DOE research contract with New Mexico State University. Single copies are available from the Bartlesville Energy Technology Center, Attention: Bill Linville, P.O. Box 1398, Bartlesville, OK 74005.

High gas mobility of carbon dioxide in enhanced oil recovery can result in severe gas channeling, causing the gas to bypass some or most of the oil reservoir. However, findings in this study confirm previous research which indicated that the use of foam with injected carbon dioxide reduces high gas mobility and eliminates channeling, thus increasing recovery efficiency.

Results of extensive testing to determine which foam additives are most effective in reducing the mobility of carbon dioxide are described and depicted in numerous graphs and tables.

Principal investigator for New Mexico State University was John T. Patton. DOE technical project officer was Kenneth Spence of BETC.

PROCESS IMPLEMENTATION[22b]

The purpose of this project is to study, through field experimentation, the methods by which both heavy and light oil can be efficiently and economically recovered from petroleum reservoirs. Several advanced recovery processes are being investigated for efficient, cost-effective application to various reservoir environments. Field applications of these processes are being monitored, data plotted and analyzed for ultimate recovery efficiency. Laboratory experiments are being conducted to determine characteristics of heavy oils and to develop a CO_2 injection method, in conjunction with computer modeling, to produce heavy oil fluids. A laboratory is being prepared and equipment assembled to study the use of additives in the application of steam drive in light- and heavy-oil reservoirs. A literature search and laboratory work are being performed to investigate the technical feasibility of using sulfur trioxide to recover heavy oils. The overall goal is to increase available petroleum reserves at minimum cost to the consumer, without damaging the environment, and through proper analysis to increase the process predictability.

[21b] Project: Heavy Oil Recovery. B&R No. AC-15-05. Managed by the Fossil Energy Division, San Francisco Operations Office. Division Director, Gordon Dean.

[22b] Project: Process Implementation. B&R No. AC-15-10-10-4. Staff: Branch Chief, H. B. Carroll, Jr.; Section Chief, J. S. Miller; Petroleum Engineers, K. L. Spence and R. E. Porter; Petroleum Engineering Technician, R. A. Jones.

In S[illegible] Combustion

A field experiment was conducted near Bartlett, Kans. to test the technical feasibility of recovery of crude oil by *in situ* combustion from shallow reservoirs. Laboratory and available field data were used to calculate oil recovery and to predict production time for a 1.25-acre inverted five-spot at the Bartlett lease. The final paper on the field experiment will be completed and made available soon. Results of evaluation work conducted by Sandia Laboratories have been received and will be incorporated into the report.

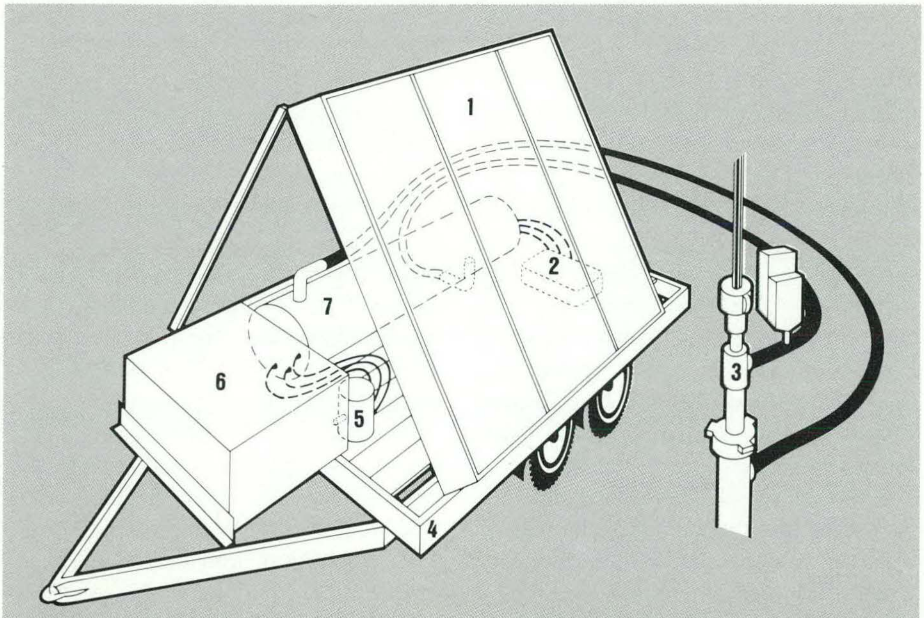
Solar-Augmented Chemical Recovery

A concept developed by Bill Estep, Inc., is under study that recovers heavy oil deposits with hot water chemical solution heated by a solar panel system.

A formation preheater, shown in Figure B10, is used to heat water which in turn is injected into the formation. The preheater includes two heat exchangers, solar panels, a tank and a heat pump mounted on a mobile trailer so that the unit can be moved from well to well. One heat exchanger works on air to a minimum temperature of 32°F which can be used for daytime or nighttime operation. The other heat exchanger works in conjunction with the solar panels and can only be used for daytime operation. Both heat exchangers work independently of each other.

The heated water is injected through the annulus and circulated back through the tubing until the temperature of the recovered water equals the temperature of the injected wa[illegible] The preheater, once the forma[illegible] has reached the injection temperature, is then moved to another well and the existing well is turned into the system where the water is heated by the main solar pa[illegible] operation.

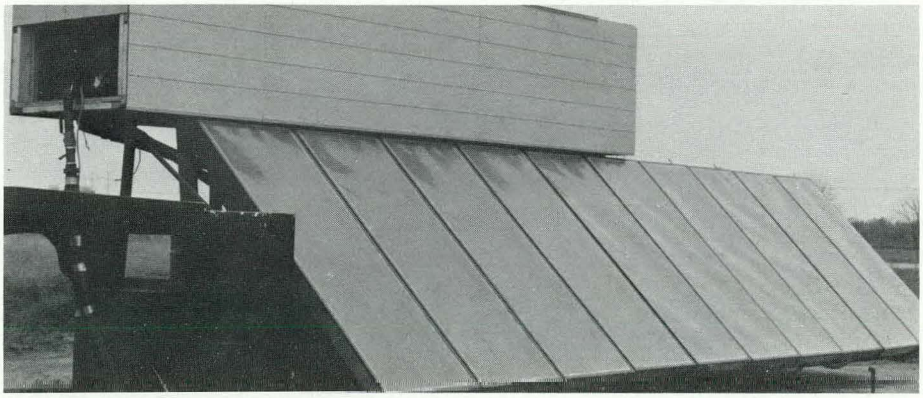
The fluid is injected into a well, which is soaked for a time before



1. Solar panels—daytime use only.
2. Heat exchanger solar panel; only used in daytime.
3. Well hook-up.
4. Mobile trailer.
5. Heat exchanger to minimum temperature of 32°F—nighttime or daytime use.
6. Heat pump.
7. Heat tank to store hot water.

FIGURE B10. *Schematic of water preheater.*

Trailer-mounted preheater includes two heat exchangers, solar panels, a tank, and a heat pump.



The main solar panel is used after the preheater has raised the temperature of the recovered water to that of the injected water.

being produced. Operation of the Link 1 well has continued using the solar-chemical treatment. The treatment consists of 14 bbl of hot water (heated by solar unit) combined with 0.5 gal of chemical. The treating fluid is injected and then "chased" by 10 bbl of cold formation water to clear the treatment from the casing to the formation. The soak time for the treating fluid in the formation is 1 hour, and then the well is produced. **A slight show of oil has been noted in the production of fluid from the well.**

The Link 5 well is ready to undergo the same treatment with the same amount of treating fluid and chase water. This will be done every other day, with a soak period of 8 hours. This will give a comparison between different treating times in wells on the same lease.

A Netzsch pump will be installed and in operation on a newly drilled well with open hole completion scheduled for July 19, 1982.

Laboratory Studies

CO_2 and Noone Oil. Tests at 200, 400, 600, 800, 1,000, 1,500, 2,000, and 3,000 psi were completed in the characterization study of the CO_2-Noone oil at 200°F. Noone oil is a Kansas oil with a suitable gravity for these experiments. The viscosity, density, solubility, and swelling factor data have been plotted and analyzed.

The viscosity at atmospheric conditions with no CO_2 is 37.65 cp and 55.08 cp at 3,000 psi. **The viscosity drops with the addition of CO_2 from 27.65 cp to 4.7 cp at 3,000 psi.** This is a ten-fold drop in viscosity from atmospheric conditions to 3,000 psi with CO_2 in solution. This is similar to viscosity curves on other heavy-oil samples. The density of the oil compared with the CO_2-oil mixture at 200°F is similar to other oils run in that the CO_2-oil curve was below the oil curve. The densities of the Noone oil with no CO_2 at 200 and 3,000 psi are 0.8875 and 0.8985, respectively; by comparison, the Wilmington oil has densities of 0.9175 and 0.9281.

The densities of the Noone oil with CO_2 in solution at 200 and 3,000 psi are 0.8855 and 0.8915, respectively, while the corresponding Wilmington densities are 0.9035 and 0.9281.

The ability of CO_2 to go into solution with the Noone oil at 200°F is greater than with Wilmington oil—500 scf/bbl to 544 scf/bbl. The swelling factors of the two oils at 3,000 psi are similar—1.203 for the Noone oil and 1.193 for the Wilmington oil.

A complete four-cycle injection-production experiment was performed using the huff-and-puff technique to produce heavy oil from a consolidated core, using CO_2 as the enhanced oil recovery system.

A 2-in. diameter by 12-in. long Berea core was tested for physical properties. The core properties were as follows: porosity, 24 percent; permeability, 700 md; pore volume, 140 cc; oil saturation, 86 percent; and water saturation, 14 percent.

The core was then mounted in a Hassler-type holder and saturated with water and a 17° API gravity oil with a viscosity of 800 cp at 75°F. The oil saturation and water saturation in volume terms were 120.4 cc and 19.6 cc, respectively. The core was placed in a vertical position, and for the first experiment, all injection and production cycles were accomplished at the top end of the core holder.

For the first cycle, 74.55 cc of CO_2 was injected at 300 psig to the system. The system was soaked for 7 days and was then produced with the following results: oil production, 16.7 cc; water production, 11.5 cc; and CO_2 (gas) production, 424 cc at atmospheric pressure and room temperature.

For the second cycle, 154.9 cc of CO_2 was injected at 300 psig at room temperature to the system. The system was soaked for 15 days. The system pressure had decreas 46 psig, and an attempt to proc the core was made, but not enough system energy was available for production. A total of 206 cc of CO_2 was produced at atmosphere and 75°F, with no fluid production. The system was then injected with 141.5 cc of CO_2 at 300 psig at 75°F. The system was soaked overnight, and production was started at 260 psig and 74°F. The production results for cycle 2 are as follows: oil production, 30.9 cc; water production, 0.1 cc; and gas production, 1,520 cc at atmospheric pressure at 75°F.

For the third cycle, 157.8 cc of CO_2 was injected at 300 psig and 75°F. The system was soaked for 7 days; the system pressure was 94 psig when production commenced. The production results for cycle 3 are as follows: oil production, 8.8 cc; water production, none; and gas production, 1,447 cc at atmospheric pressure at 75°F.

For the fourth cycle, 164.9 cc of CO_2 was injected at 300 psig and 75°F. The system was soaked for 8 days, and the system pressure was 109 psig when production was started. The production results for cycle 4 are as follows: oil production, none; water production, none; and 1,382 cc of CO_2 at atmospheric pressure and 75°F.

A laboratory is being prepared to determine the effectiveness of additives in steam-drive experiments using both light and heavy oils. Several pieces of equipment have been received and are being installed.

SO_3 Thermal-Chemical Drive Process. The general objective of this project is to investigate the technical feasibility of using sulfur trioxide (SO_3) to recover heavy oils. A series of experiments was planned i ich a number of cores containing oil and water were to be exposed to liquid SO_3 in a reaction chamber. The heat produced from the reaction between the SO_3 and H_2O would cause ge reduction in the viscosity of th

In addition, exothermic sulfonation reactions between SO_3 and several hydrocarbon fractions will occur. Further, the SO_3 and H_2SO_4 will react with formation inorganic compounds to produce CO_2 and other products. Both CO_2 and SO_3 are miscible in hydrocarbons. This combination of reactions and energy production suggests that SO_3 may offer a viable thermal-chemical system to enhance the recovery of oils especially the heavier oils. Analysis of both liquid and gas samples will be performed, in addition to a mass balance on the reaction chamber.

Work on the project began in May 1982 with the arrival of Dr. Charles W. Terrell, a visiting professor from the University of Oklahoma. The research is divided into two phases. The first is the theoretical/analytical phase, which is ongoing and which has two components: (1) definition of an *in situ* model in which SO_3 is pumped into a formation through one or more production wells, and (2) definitions and calculations in support of laboratory experiments. A literature search is an ongoing effort.

The second phase is experimental. A series of laboratory experiments is planned. Facilities for the experiments have been designed and are in final assembly.

Laboratory equipment has been assembled and tested, and the liquid SO_3 has been received.

Oil Mining

The objective of the oil mining program is to identify, classify, evaluate, and improve oil mining methods that might have the greatest potential for recovering oil that cannot be recovered through conventional methods in light or heavy-oil reservoirs.

Contact is being maintained with five companies who have either active or developing oil mining programs. The companies with active programs are: Cornell Oil Company, Getty Oil Company (both of Bakersfield, Calif.) and Conoco Oil Company in Wyoming. The McCarthy Oil Mining Company in Louisiana and Tetra Systems in Kansas are in the planning and development stages of their projects.

Contacts were made during the quarter with the McCarthy and Cornell companies to review the status of their projects.

Contracts. Three field tests and four supporting research projects are monitored and are reported in Progress Review No. 31.[1a]

Gulf Oil Exploration and Production Company (DE-AC21-79MC08383). Enhanced Oil Recovery by CO_2 Miscible Displacement in the Little Knife Field, Billings County, North Dakota. Technical Project Officer: J. S. Miller.

Marathon Oil Co. (DE-AC19-78ET13077). Commercial-Scale Demonstration Enhanced Oil Recovery by Micellar-Polymer Flooding. Technical Project Officer: R. E. Porter.

Cities Service Co. (DE-AC03-78ET13070). Improved Oil Recovery by Micellar-Polymer Flooding, El Dorado, Kansas, Field. Technical Project Officer: R. E. Porter.

New Mexico State University (DE-AC21-79MC03259). Enhanced Oil Recovery by CO_2 Foam Flooding. Technical Project Officer: K. L. Spence.

Texas A&M Research Foundation (DE-AC21-79MC10509). Enhanced Recovery of Oil from Subsurface Reservoirs with CO_2. Technical Project Officer: J. S. Miller.

Petroleum Training and Technical Services (DE-AC19-80BC10316). Maximizing Steam Drive Recovery in Light Oil Systems. Technical Project Officer: J. S. Miller.

Colorado State University (DE-AS19-81BC10640). Computer Simulation of Recovery of Heavy Crude Oil Using Carbon Dioxide Drive or Huff-n-Puff. Technical Project Officer: J. S. Miller.

Fuel and Mineral Resources, Inc. (DE-AC19-82BC10704). Detailed Technical and Economic Feasibility of Light Oil Mining in the United States. Technical Project Officer: H. B. Carroll.

EXTRACTION TECHNOLOGY[23b]

The general objective of this research effort is to determine and define experimental parameters critical to successful application of stimulation technology for hydrocarbon production from marginal reservoirs. This includes evaluation of potential productivity of low-permeability and low-porosity formations by applying new or innovative logging techniques and interpretations. The project also examines the degree of formation damage due to presence of hydraulic fracture fluids and proppants.

Hydraulic Fracturing and Fracture Conductivity

Long-Term Fracture Closure and Proppant-Induced Formation Damage. A technique for examining long-term fracture closure and proppant-induced formation damage was described in a previous report. An initial experiment was described that used a 2-in. diameter Berea core and a monolayer of 12–20 mesh sintered bauxite proppant. This experiment was terminated when the core seal developed a slow leak.

The apparatus was modified and a second experiment run as before. The apparatus is schematically repre-

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[23b] Project: Extraction Technology. B&R No. AB-05-10. Staff: Branch Chief, H. B. Carroll, Jr.; Section Chief, C. J. Raible; Petroleum Engineer, B. A. Baker; Research Chemists, B. L. Gall and L. J. Volk; Physical Science Aide, T. Rovenstine.

sented in Figure B11. The results of the experiment are summarized in Figure B12. For convenience, the experiment was divided into three parts, referred to as regions in Figure B12. These regions are discussed below.

Region I. The cell containing the dry Berea core and proppant was pressurized hydrostatically to 120 psi at ambient temperature. The micrometer reading under these conditions was considered to be the "zero point" of the experiment. Pressure was increased at approximately 500 psi intervals until 4,000 psi confining pressure was attained. As in experiment 1, this curve was similar to those observed previously. The gas permeability dropped from about 350 md at 120 psi confining pressure to 150 md at 4,000 psi (corrected for gas slippage). Difficulty with the flow-measuring apparatus is believed to be responsible for the scatter observed in the permeability data. The pressurization process required 1¾ hours to complete.

Region II. Since very little change was observed in either the gas permeability or fracture closure with time for the dry core at 4,000 psi overburden (experiment 1), this step was omitted in experiment 2. In experiment 2, the core was heated to 70°C and maintained at this temperature for 25 days. During this time, there was some variation in the fracture width, but the net change was essentially zero. The gas permeability dropped slightly, to approximately 120 md. Better permeability data will be needed to verify this decrease. The jump in percentage fracture closure upon heating is due to the coefficient of thermal expansion of the stainless steel rod epoxied in the lower core-piece and extending up to the micrometer (see Figure B11).

Region III. Hot (70°C) 2 percent KCl was introduced (vacuum saturation) into the core and proppant. A

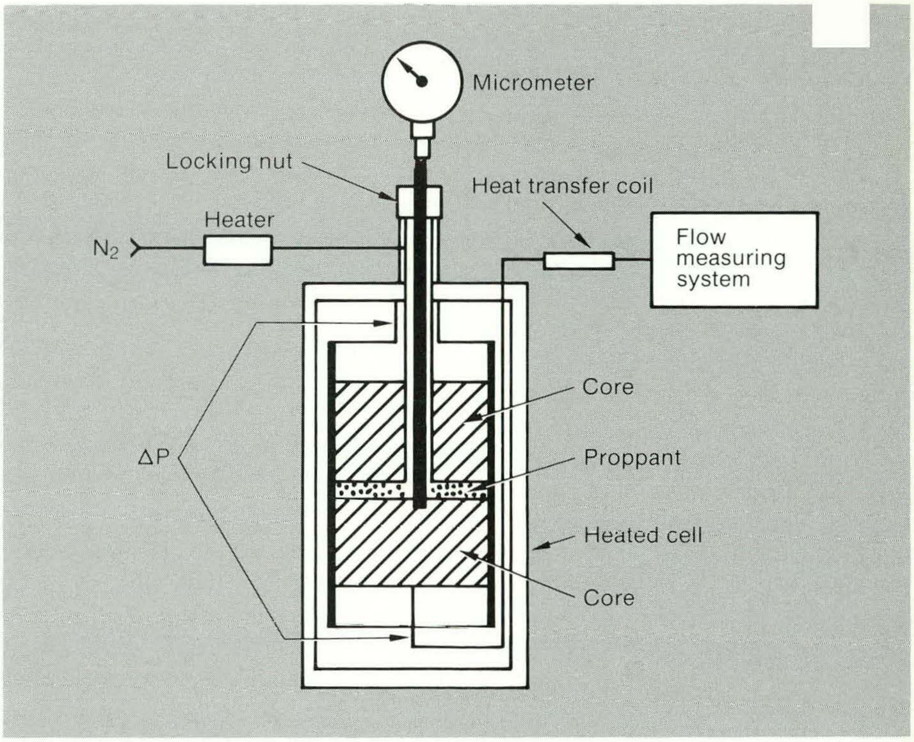
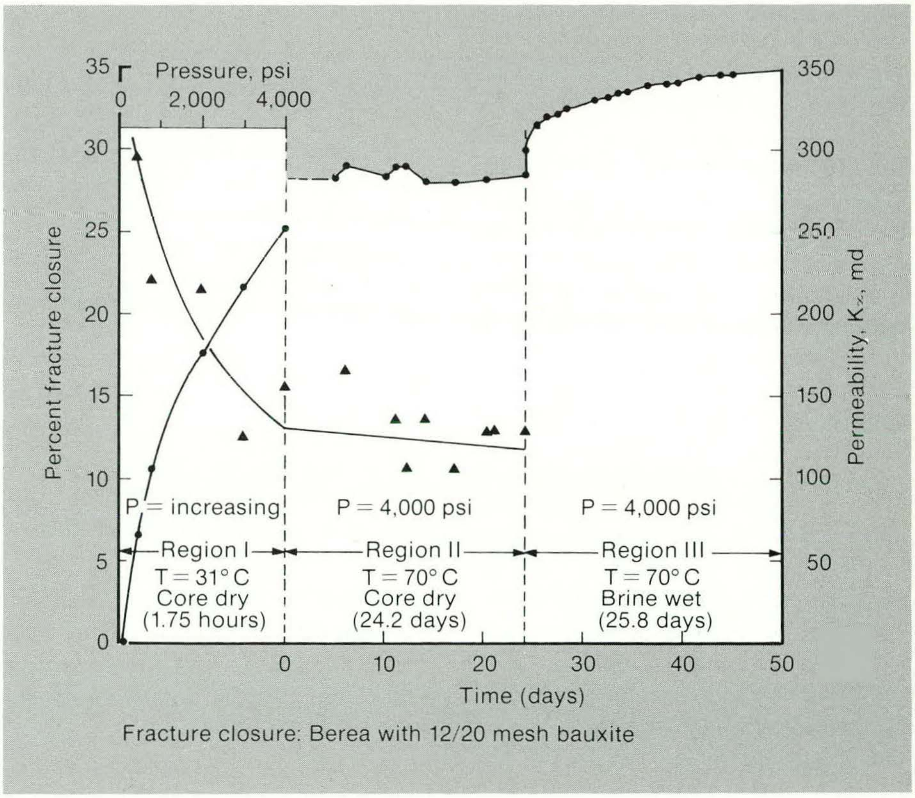


FIGURE B11. *Apparatus for measuring long-term fracture closure and proppant-induced formation damage.*



Fracture closure: Berea with 12/20 mesh bauxite

FIGURE B12. *Percent fracture closure (solid circles) and gas permeabili olid triangles) versus elapsed time.*

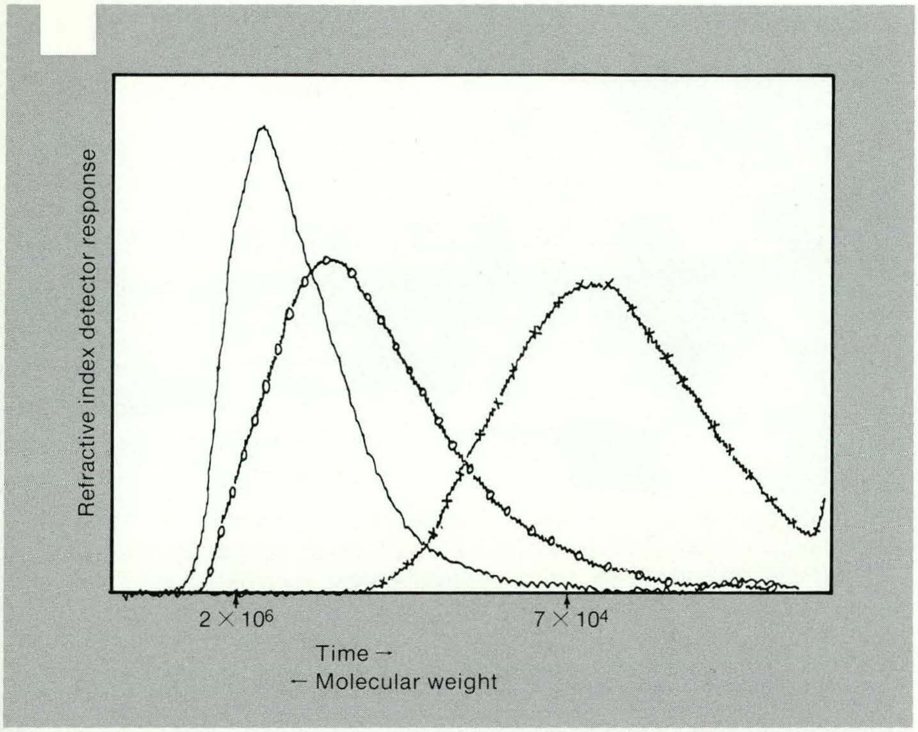


FIGURE B13. *Molecular weight distribution of high residue guar broken with ammonium persulfate after 3 hours at 70° C.* — 0.05% $(NH_4)_2S_2O_8$; —o— 0.10% $(NH_4)_2S_2O_8$; —x— 0.20% $(NH_4)_2S_2O_8$.

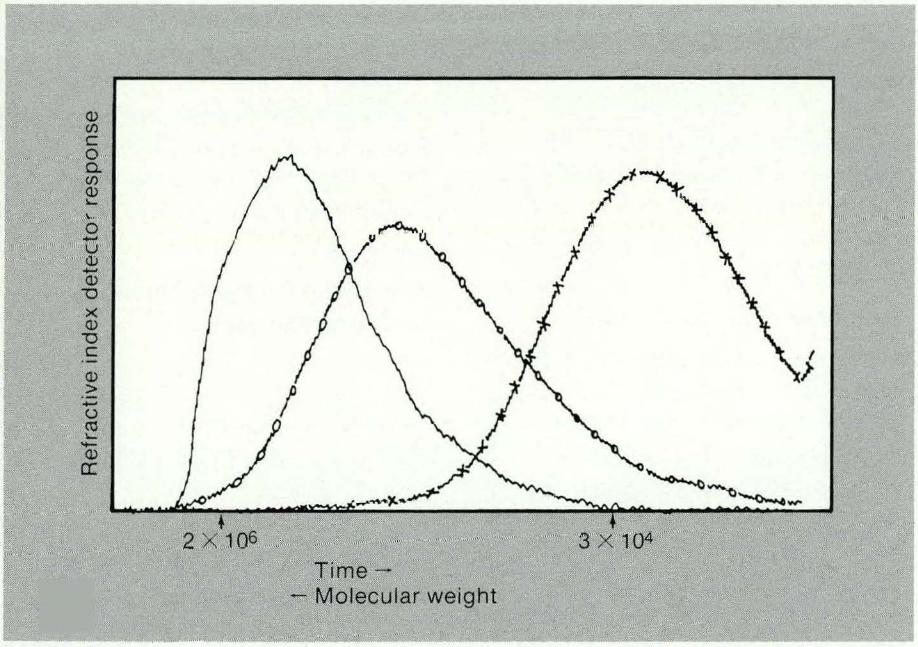


FIGURE B14. *Molecular weight distribution of high residue guar broken with ammonium persulfate after 24 hours at 70° C.* — 0.05% $(NH_4)_2S_2O_8$; —o — 0.10% $(NH_4)_2S_2O_8$; —x — 0.20% $(NH_4)_2S_2O_8$.

rapid increase in fracture closure was observed. The rate of closure gradually decreased. It is estimated that by the 55th day, the fracture closure would have ceased. The introduction of brine caused a 6 percent decrease (0.6 mm) in fracture width.

As in experiment 1, the influence of temperature on the fracture width is minimal. The corresponding gas permeability decreased slightly (if at all). A "nondamaging" brine, such as 2 percent KCl, causes a reduction in fracture width that probably is not significant with respect to loss of productivity of the propped fracture. The next core to be studied will be from DOE's Multi-Well Experiment well number 1 in Garfield Co., Colo., in the Piceance Basin.

Fracture Fluid Induced Formation Damage. Incomplete breaking of fracturing fluid polymers might result in fracture and formation damage. Large molecules of polymer might block capillaries and pores of tight gas sands and result in impeded gas flow. For the tight gas sands, molecules with a molecular weight approximately 1 × 10^6 might cause formation damage.

Studies have been made to determine the effects of time and breaker concentration on the ability of various breakers to degrade fracturing fluid polymers. Molecular weight distributions (MWD) of high residue guar (HRG) and low residue guar (LRG) were determined using gel permeation chromatography on Toyo Soda, Inc., columns with a molecular weight exclusion limit of approximately 5 × 10^6.

Figure B13 shows the MWD of HRG broken with a strong oxidant breaker, ammonium persulfate, after 3 hours at 70°C. Three different breaker concentrations are shown. Figure B14 shows the MWD of the same polymer solutions after 24 hours at 70°C. Measurement of the MWD after 48 hours at 70°C showed little change from the 24-hour curves. At low oxidant concentration (0.05 percent), approximately 20 percent of the polymer had a molecular weight greater than 2×10^6 after 3 hours at 70°C. After 24 hours at 70°C, however, only 6 percent of the polymer had a molecular weight greater than 2 million. At high oxidant concentration (0.20 percent), all of the polymer was well below 2 million, even after only 3 hours.

The apparent viscosities of all the solutions were less than 3 cp as measured on the Fann 35 viscometer, however. The reduced viscosity, therefore, could not be used as an indication of the size of the polymer fragments after degradation.

A series of experiments using LRG and ammonium persulfate breaker showed similar results. An enzyme breaker, however, efficiently broke only the HRG. The LRG solutions remained viscous with most of the polymer eluting at the exclusion limit of the chromatographic system. Further experiments are planned using a weak oxidant breaker, t-butyl peroxide.

Contracts. The following contracts support Extraction Technology and its subprojects as shown. They are reported in Progress Review 31.[1a]

Hydraulic Fracturing and Fracture Conductivity Activities

Terra Tek, Inc. (DE-AC19-79BC-10038). Determine Feasibility of Fabricating Light Weight Proppants for Application in Gas and Oil Well Stimulation. Technical Project Officer: L. J. Volk.

University of Tulsa (DE-AC19-80BC10197). Proppant Transport in Massive Hydraulic Fracturing. Technical Project Officer: B. L. Gall.

Oral Roberts University (DE-AC19-80BC10215). Stochastic Model of Massive Hydraulic Fracture. Technical Project Officer: H. B. Carroll, Jr.

Edward J. Lievens, Jr., new acting director of BETC, familiarizes himself with BETC laboratory work by reviewing results of molecular weight determinations with Bonnie Gall, research chemist. These determinations for a high-residue-guar fracturing fluid gel were made by size occlusion chromatographic equipment (foreground) as part of the Western Gas Sands Project studies. Fracturing fluid gels are being examined to determine (1) how much damage they cause to sandstone formations and hydraulic fractures, and (2) how easily they can be removed from a fracture once the fracture has been propped open.

Sandia National Laboratories. Stimulation Instrumentation and Diagnostics. Technical Project Officer: L. J. Volk.

Sandia National Laboratories. Stimulation Research. Technical Project Officer: L. J. Volk.

Lawrence Livermore Laboratories. Theoretical Rock and Fluid Mechanics Modeling and Laboratory Rock Mechanics. Technical Project Officer: C. J. Raible.

Reservoir Simulator Studies

University of Oklahoma (DE-AC19-80BC10253). Reservoir/Well Simulator Development for Hydraulically Fractured Gas Wells in Non-Continuous Lenticular Formations. Technical Project Officer: H. B. Carroll, Jr.

Formation Evaluation Studies

Institute of Gas Technology (DE-AC19-78BC00042). Measurement of Formation Characteristics for Western Tight Sands. Technical Project Officer: C. J. Raible.

New Mexico Institute of Mining and Technology, Petroleum Recovery Research Center (DE-AS19-80BC10216). Relationship of Pore Structure to Fluid Behavior in Low-Permeability Gas Sands. Technical Project Officer: L. J. Volk.

Improved Logging Techniques and Studies

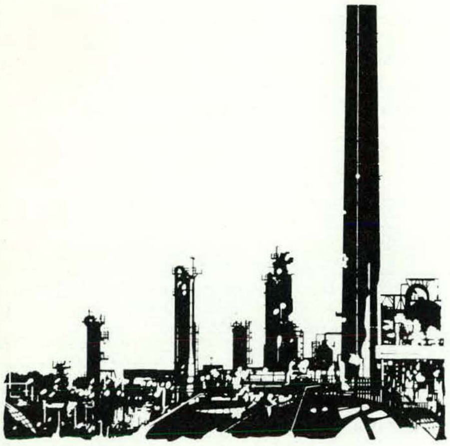
Texas A&M Petroleum Engineering Department (DE-AC19-79BC10086). Mapping and Contouring Water Resistivities in the Tight Sands. Technical Project Officer: C. J. Raible.

Advanced Logging Techniques and Interpretations

Sandia Laboratories (DE-AT19-79BC10208). Electromagnetic Impedance Sonde for Evaluation of Tight Gas Reservoirs. Technical Project Officer: L. J. Volk.

Lawrence Livermore Laboratories (DE-AT19-79BC10108). Use of Sonic Techniques to Measure *In Sit*[illegible]ess. Technical Project Officer: C. J. Raible.

Los Alamos Scientific Laboratory (DE-AC19-79BC10018). Remote Characterization of Fluid Sa[illegible]ion in Western Sands. Technical [illegible]ect Officer: L. J. Volk.



Processing

Division Director: W. D. Good

SECTION C

LIQUID PROCESSING

Basic information on the composition and energy relationships of the various materials entering into the Liquid Fossil Fuel Cycle (LFFC) is necessary for the scientific development of conversion processes and the evaluation of those processes. The Liquid Processing organization involves Characterization, Thermodynamics, and Process Technology. In addition, the analytical and physical/thermodynamic property capabilities are needed and utilized by all parts of the LFFC.

CHARACTERIZATION

Characterization of materials that may be feedstocks in the refining of liquid fossil fuels or products for end use applications includes liquids from petroleum, coal, shale, and other alternate sources. The projects that comprise the BETC characterization efforts include characterization of heavy ends and syncrudes, quality of crude oils, fuel surveys, brine analyses, Strategic Petroleum Reserve support, analytical services, instrumental, and separation support. The objectives of these efforts are to provide: (1) analytical research to develop and modify techniques for characterizing heavy oils, heavy ends, and syncrudes, (2) detailed compositional analyses and data for liquid fossil fuel materials, (3) crude oil data bases, (4) analytical support services for the Center, and (5) other research and support functions as designated by DOE Headquarters.

Heavy Ends[1c]

Some of the chemical and chromatographic separations that might be applied to mixtures of sulfides, thiophenes and hydrocarbons have been reexamined. The major problem remains the separation of thiophenes from hydrocarbons contained in a class concentrate that might be obtained from adsorption chromatography. Removal of sulfides is a more manageable problem.

Sulfide removal by ligand exchange chromatography is reasonably satisfactory, but the columns become deactivated in use and on aging more easily than had been noted in the past. This method requires that the oil sample be separated to class concentrates before sulfide removal can be done. A more general and rapid sulfide removal procedure is needed; some chemical methods for sulfoxide formations were examined. Oxidation by sodium periodate supported on alumina proved to be the most satisfactory approach because of the rapid and specific action on sulfides and lack of action on thiophenes.

Several liquid chromatographic procedures have been studied in the separation of model triaromatic hydrocarbons and thiophenes. The relative retention values have ranged from 1.0 to 1.5. Although this is a relatively narrow range, attempts will be made to prepare narrow cuts in the chromatographic system that demonstrated the high relative retention, followed by isolation of thiophenes from these cuts by use of the chromatographic system that showed the extreme low relative retention.

Methods for determination of water in vapor-liquid-equilibrium samples have been modified to improve quantitative accuracy.

Subfractionation of Cerro Negro acid concentrates continued this quarter. As reported last quarter, the tetramethylammonium-based separation of acids on silica has been scaled up to gram quantities and applied to Cerro Negro (Venezuelan heavy petroleum) and Wilmington (California) petroleum acid concentrates. This

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[1c] Project: Characterization Studies: Heavy Ends. B&R No. AC-05-10. Staff: Branch Chief, J. E. Dooley; Section Chief, Instrumental Methods, S. E. Scheppele; Research Chemists, J. B. Green, J. W. Vogh, R. D. Grigsby, K. Chung, and J. L. Lacina; Chemist, J. Thomson.

quarter, separation of the 200–425°C and 550–700°C Cerro Negro acids was completed, and the results are shown in Table C1. Obviously, the weight distributions in all three boiling ranges are quite similar. Fraction 5, predominantly carboxylic acids, obviously is the major fraction in every distillate. Fraction 2, largely pyrrolic benzologs, is the second largest fraction in all boiling ranges. Fraction 4, which is much larger in the 550–700°C acids, is the only fraction in significant quantity in the Cerro Negro acids. It should contain predominantly phenolic type compounds, but, based on infrared spectral data, appears to be contaminated with amides and carboxylic acids.

Acids from another Venezuelan crude, Zuata, also were fractionated. It was found that 61 percent of the 200–425°C distillate acids (2.11 percent total acids in distillate) were carboxylic acids in that crude. Thus, a high percentage of carboxylic acids might be typical of Venezuelan heavy petroleums.

Elemental analyses of two sets of acid subfractions are shown in Table C2. As can be seen from inspection of the data: (1) the H/C ratio minimizes at fraction 2 and climbs slowly with increasing fraction number, (2) nitrogen maximizes at fraction 2 and decreases sharply after fraction 3, (3) oxygen increases steadily with fraction number, and (4) no significant pattern of sulfur variation exists, thus indicating that sulfur plays no significant role in the acidity of any acid subclass.

TABLE C1. *Results from Subfractionation of Cerro Negro Heavy Petroleum Acids**

Distillation Range	200–425°C	425–550°C	550–700°C
Wt.-Pct. Acids in Distillate	3.18	5.6	8.7
Wt.-Pct. Subfractions:			
1	1.0	0.8	1.0
2	20.7	15.0	17.7
3	2.7	1.7	3.8
4	7.7	6.3	15.3
5	63.9	75.7	62.9
6	3.5	0.1	0
Total	99.5	99.6	100.7

*Work performed by Lante Carbognani—visiting scientist from INTEVEP, the Venezuelan Petroleum Institute.

TABLE C2. *Elemental Analysis of Cerro Negro Acid Subfractions**

	Weight-Percent					
Fraction No.	C	H	N	S	O	Total
425–550°C acids						
Whole	79.52	9.81	0.72	2.61	7.34	100.0
1	ND	ND	ND	ND	ND	—
2	81.03	8.34	2.89	2.03	2.42	96.71
3	78.70	7.86	ND	ND	ND	—
4	77.88	8.56	0.49	2.08	10.70	99.71
5	76.82	10.03	0.13	2.62	7.78	97.38
6	ND	ND	ND	ND	ND	—
550–700°C acids						
Whole	78.86	9.84	0.80	3.81	6.46	99.77
1	78.66	10.08	ND	ND	ND	—
2	79.24	7.80	2.51	3.86	2.77	96.18
3	79.60	8.47	2.31	3.52	4.33	98.23
4	76.93	9.32	1.21	2.58	5.13	95.17
5	76.52	9.90	0.30	3.54	6.96	97.22
6	ND	ND	ND	ND	ND	—

ND = not determined.

*Galbraith Laboratories, Knoxville, Tenn.

Preparative-scale separation of Cerro Negro hydrocarbon neutrals (boiling 425–550°C) was completed and fractions were shipped to the Venezuelan Petroleum Institute (INTEVEP). Problems with this separation scheme brought about a reevaluation of the technique, and a subsequent generation of new fractions will be undertaken based on a saturate, aromatic, acid, and base split. Reproducibility was found to be questionable with the present fractionation techniques, and improvements are being sought. A new set of fractions will be generated next quarter for the 200–425°C and 425–550°C distillates of Cerro Negro crude oil for evaluation by mass spectrometry (MS) and nuclear magnetic resonance (NMR) techniques.

A number of column packings were synthesized this quarter. These include 2,7-dinitro-; 2,4,7-trinitro-; 2,4,5,7-tetranitro-9-fluoreniminopropylsilicas; 4,4′-dichlorobenzophenoneimineopropylsilica; the 2,4-dinitrobenzene derivative of "diamine" column packing material; and trinitroanilinopropylsilica (TNAP). The tetranitro-9-fluoreniminopropylsilica had shown promise as a charge-transfer complexing agent, but proved to be unstable toward the solvents used. Attempts to modify the weak imino bond by reduction with sodium cyanoborohydride failed to produce a stable packing material, so this compound along with the weaker di- and trinitrofluorene derivatives were abandoned.

[illegible] o-derivatives of 4,4′dichlorobe[illegible]phenone and pentafluorobenzophenone produced packings that were far superior to NH_2-silica for separation by ring number, but these were not deemed to be an improvement over DNAP-silica. The TNAP-silica appears to be an improvement over the currently used DNAP. A detailed evaluation is underway. Several analytical columns and one large preparative column have been packed with this material.

Syncrudes[2c]

A nonaqueous titration technique for acidic (oxygen-containing compounds) material in synthetic fuels and petroleum was developed. Tetrabutyl ammonium hydroxide, potassium tertbutoxide, and potassium dimsyl (prepared by reacting potassium hydride with dimethyl sulfoxide) were evaluated as titrants; potassium dimsyl in dimethyl sulfoxide was determined to give the best results.

Samples were dissolved in a mixture of DMSO/benzene (29/1) containing 1 percent H_2O. The performance of the measuring electrode (glass pH electrode) was found to degrade fairly rapidly when an anhydrous solvent mixture was used. The aqueous electrolyte of the reference electrode was replaced with a 0.1 N solution of lithium perchlorate in DMSO. To prevent possible formation of potassium salts of titrated acids, an excess of 18-crown-6 ether was added to the titrant to complex the potassium ion. Several model compounds were titrated (~0.02 N titrant) to determine their half neutralization potentials and titration efficiencies.

Previously, the separation of six hydrotreated coal liquids into strong a[illegible] weak acids, strong and weak bases, and hydrocarbons was described. These acidic and basic fractions were titrated using the nonaqueous titration techniques that have been developed. Also, digestion procedures were begun in preparation for trace-metal analysis of all fractions by atomic absorption spectroscopy.

A comparison was made of ion exchange and extraction methods for acid-base-neutral separations. Table C3 shows results from separation of several different fuels into acid, base, and neutral fractions by nonaqueous ion exchange chromatography and aqueous-alcoholic extraction techniques.[3c] Generally, the data in Table C3 demonstrate the inapplicability of the extraction procedure to distillates or residues boiling higher than 350°C. The difficulty in extracting the larger-molecular-weight acids and bases present in high boiling samples arises from (1) the greater hydrophobicity of large molecules, and (2) the weaker acidity or basicity of many of the polar molecules in high boiling fractions. The results from the two methods are often fairly close for samples or distillates boiling below 350°C. However, the ion exchange method will give higher results even for low boiling samples if significant quantities of weak acids or bases (e.g., carbazoles or indoles) are present. The results in Table C3 were accumulated over the past 4 years.

TABLE C3. *Comparison of Mass Balance Data from Ion Exchange vs Extraction of Various Fuels*

Dist., °C	Method	Weight Percent			
		Acids	Bases	Neutral	Total
Wilmington (Calif.) Petroleum					
<370	IE	1.40	1.48	97.6	100.5
<370	EX	1.32	0.82	95.5	97.6
370-535	IE	6.5±0.5	6.0±0.5	88±1	100±1
370-535	EX	1.9±0.3	2.5±0.5	95±1	100±1
535-675	IE	5.54	10.8	85.1	101.4
535-675	EX	1.25	1.53	—	—
675+	IE	4.24(s) 4.48(w)	41.27(s) 9.33(w)	42.9	102.2
675+	EX	0.24	0.09	100.8	101.1
Shale Oil OSCR 76-552 (LETC)					
<200	IE	3.93(s) 5.19(w)	18.92(s) 1.17(w)	68.1	97.3
<200	EX	2.86	11.4	81.6	95.9
SRC-II Coal Liquid					
325-425	IE	22.1(s) 2.9(w)	10.8	65.6	101.5
325-425	EX	15.8	10.5	72.1	98.4
Coed Coal Liquid					
200-370	IE	4.96	2.37	88.1	95.4
200-370	EX	4.86	2.33	90.5	97.72
370+	IE	3.18	2.58	94.7	100.4
370+	EX	0.94	2.36	96.8	100.1
Synthoil Coal Liquid					
200-370	IE	29.12	6.20	68.5	103.8
200-370	EX	20.58	7.01	69.13	96.7
370+	IE	15.0(s) 6.4(w)	25.8(s) 2.5(w)	51.3	101.0
370+	EX	11.59	18.22	73.70	103.5

[2c] Project: Characterization of Syncrudes, B&R No. AA-25-15-15. Staff: Branch Chief, [illegible] E. Dooley; Research Chemists, J. B. [illegible]en, J. W. Vogh, J. L. Lacina, and G. P. Sturm, Jr.; Graduate Research Participant, J. G. Green.

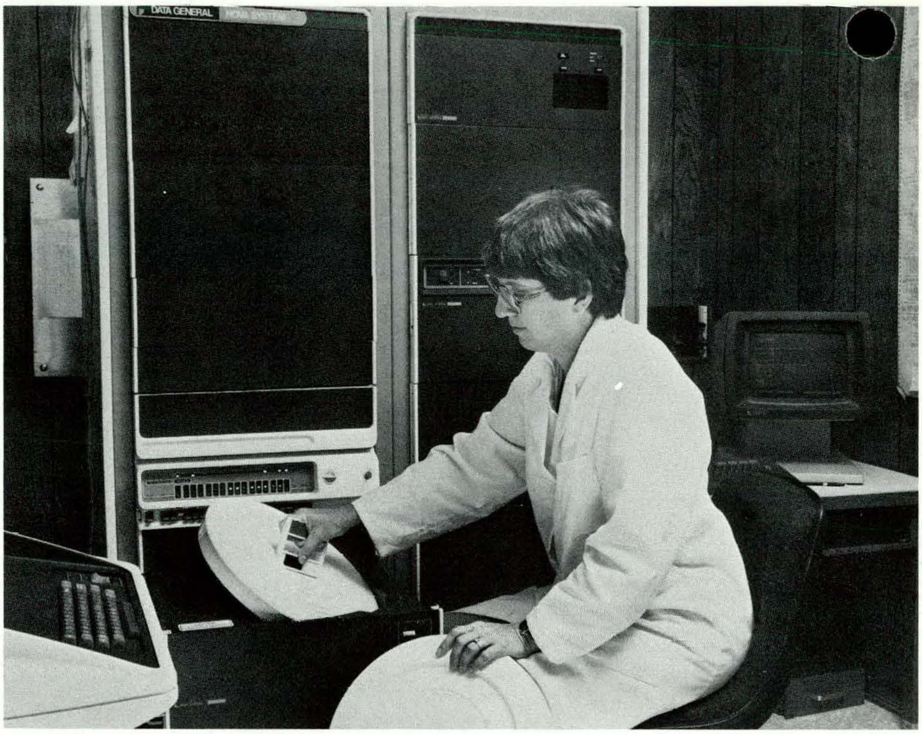
[3c] J. B. Green and R. J. Hoff, *J. Chromatogr.*, *209* (1981) 231–50.

A meeting regarding progress on the RCRA Multilab Waste Leachate Trace Organic study was attended in April at the Pittsburgh Energy Technology Center (PETC). The goals of the study include developing a quantitative method for organics in waste water, measuring the precision and accuracy of the methods and measuring the difference in the efficiency of the American Society for Testing and Materials (ASTM) proposed leaching method A and the current EP method.

The participants at the meeting have finished precision and accuracy studies, and plan to finish efficiency studies during the coming quarter. An SRC-II still-bottom sample was used in preliminary leaching studies. It contained only three leachable organics of the compounds of interest in amounts greater than 1 ppb. The six laboratories participating in the study agreed to change to an H-Coal scrubber sludge for further extraction experiments. Samples of the H-Coal raw sludge and leachate prepared by the two extraction methods have been received, and may be analyzed when some equipment problems are resolved.

A Perkin Elmer 900 Model gas chromatograph (GC) was reconditioned and added to the lab for use in routine analyses. Routine samples run this quarter include ongoing analysis by capillary GC of high-purity compounds prepared by Oklahoma State University for the thermodynamics group, and "fingerprinting" of Strategic Petroleum Reserve Office (SPRO) oils, brines, and sludge samples. Simulated distillations of the SPRO samples were also done.

One report was published this quarter, "Liquid Chromatographic Separation of Aromatic Hydrocarbons with Chemically Bonded 2,4-Dinitroanilinopropylsilica," by P. L. Grizzle and J. S. Thomson, *Analytical Chemistry, 54* (1982) 1071–1076.



Loading a computer disk into the Nova 3 Data General computer, Jane Thomson, chemist, prepares to run a computer-simulated distillation analysis of a crude oil. This program is used in chromatography studies of Strategic Petroleum Reserve crudes and in solvent distillation of low boiling cuts of Cerro Negro crude oils.

Instrumental Operations[4c]

The Instrumental Section completed moving laboratory equipment and offices to new facilities at BETC. Installation of the MS-50 mass spectrometer was initiated, but inadequate humidity control in the new space necessitated termination of MS-50 installation. In addition, the MS-30, MS-80, and CEC 21-103 mass spectrometers were not activated. However, both new data acquisition systems were assembled. Plans were developed and implemented for achieving adequate humidity control and for correcting a number of defects in the closed loop water system that supplies chilled water to the mass spectrometers.

Extensive use of the prototype dual-beam FI/EI source revealed a totally inadequate pumping capacity for the MS-30 vacuum system resulting in rapid contamination of the FI source ceramics. In order to rectify this problem, the Instrumental Section initiated activities to replace both the existing housing with one possessing high-speed pumping and the oil diffusion pumps with high-speed turbomolecular pumps. This modification will also significantly reduce the rate of contamination of the ceramics in EI sources.

Q. G. Grindstaff, R. D. Grigsby, and S. E. Scheppele attende[illegible]e 30th annual conference on Mass Spectrometry and Allied Topics sponsored by the American Society of Mass Spectrometry (ASMS) in Honolulu, Hawaii, June 6–11. An i[illegible]d paper entitled "Field Ionization MS Analysis of Saturates in Shale Oil" au-

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[4c] Project: Instrumental Operations. B&R No. AC-05-10. Staff: Branch Chief, J. E. Dooley; Section Chief, S. E. Scheppele; Research Chemists, G. P. Sturm, Jr., Q. Grindstaff, K. Chung, and R. D. Grigsby; Electronics Technician, R. P. Vrana.

th~~d by Scheppele and Grindstaff wa esented by Scheppele in the Symposium on the Characterization of Shale Oils. At the technical meeting preceding the ASMS meeting, Grindstaff presented a paper, “The MS-30 Dual FI/EI Ion Source—A Deal or Flawed Gem,” and Scheppele presented a paper entitled “The Next Step Beyond DS 55.”

The final checking was completed of program FZM, which assigns formulas and specific Z values to masses, and of program DBG, which generates data bases for program FZM.

Two papers were submitted for publication: (1) “Computer Processing of Mass Spectra Data I. Assignment of Formulas to Experimental Masses. Chemical and Mathematical Principles,” authored by Scheppele, K. C. Chung, and C. S. Hwang, and (2) “Computer Processing of Mass Spectral Data II. Assignment of Formulas to Experimental Masses Illustrating Program FZM. Effects of the Electron Mass and the Functional Form of the Exponential Scan Law on the Accuracy of Mass Measurement,” authored by Scheppele, Grindstaff, Grigsby, S. R. McDonald, and Hwang.

These are the first two papers in a set of five that describe in detail our method for the computer assignment of formulas to experimental masses. One paper was published this quarter, “Evaluation of Fast Atom-Bombardment Mass Spectrometry for Identification of Nitrogen-Containing Compounds in Fossil Fuels,” by Grigsby, Scheppele, Grindstaff, G. P. Sturm, Jr., L. C. E. Taylor, H. Tudge, C. Wakefield, and S. Evans. *Anal. Chem., 54* (1982) 1108–1113.

In other activities, determination of field ionization (FI) mass spectrometı ensitivities for saturates was ir igated. Unlike ASTM 2786,[5c] field-ionization mass spectrometry should be capable of providing carbon-number distributions for saturated hydrocarbons. The sensitivities for saturates are dependent upon hydrocarbon structure[6c] and are altered by the addition of acetone.[7c] Consequently, sensitivities were determined for FI of 37 saturated hydrocarbons in the 2(H;H), O(H;H), -2(H;H), and -4(H;H) Z series in the presence of acetone. The FI sensitivities used in quantitative analysis were determined at acetone concentrations resulting in relative sensitivities independent of the partial pressure of acetone.

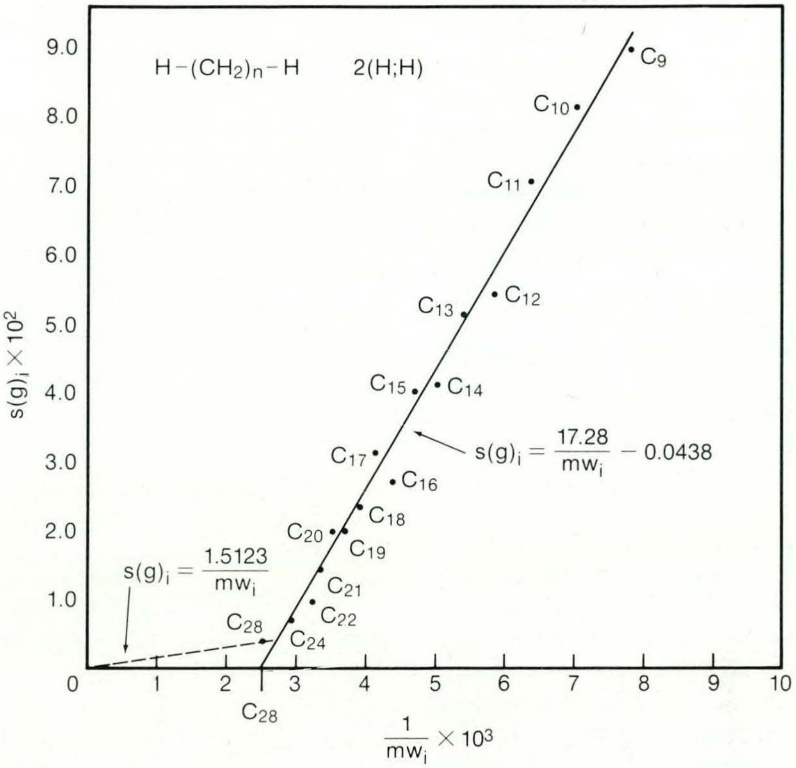

FIGURE C1. *Gram sensitivities for field ionization—alkanes relative to decalin vs. MW.*$^{-1}$

Let *p* and *r* represent the first homolog in a specific-Z series and the reference compound, respectively, and $(\Delta/C_i)_p$ be the variation of the relative FI mole sensitivity on carbon number in a specific-Z series.[6c] The variation in the relative gram sensitivity in a given Z series has a slope, M, equal to

$$M = MW_p \left(1 - \frac{(\Delta/C_i)_p(MW)_p}{14}\right).$$

If the relative mole sensitivity is carbon-number independent, i.e., $\Delta/C_i = 0$, then $M = MW_p$. If $\Delta/C_i > 0$ or $\Delta/C_i < 0$, then M will be less than or greater than MW_p, respectively.

A plot of the gram sensitivities for FI of alkanes relative to the gram sensitivity for FI of decalin versus MW^{-1} is shown in Figure C1. The least-squares fit of $s(g)_i$ to MW^{-1} is excel-

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[5] ual Book of ASTM Standards, Petroleum Products and Lubricants, II, *24*, 700 (1977).

[6c] S. E. Scheppele, C. S. Hsu, T. D. Marriott, P. A. Benson, K. N. Detwiler, and N. B. Perreira, *Int. J. Mass Spectrom., 28*, 335, (1978).

[7c] Unpublished results of Q. G. Grindstaff and S. E. Scheppele.

lent. Since the FI sensitivities must be greater than zero, the functional form of $s(g)_i$ on MW^{-1} must change at a carbon number less than 28. Preliminary results suggest that this phenomenon occurs at a carbon number of *ca.* 26 as indicated in the figure. Acetone enhances the sensitivity for carbon numbers less than this value, but appears to have a much smaller effect on the sensitivity for alkanes possessing in excess of *ca.* 28 carbons. For present purposes, (Δ/C_i) for the 2(H;H) series was assumed to be zero above C_{28}.

Table C4 summarizes the results obtained for other compounds. Acetone induces a significantly greater falloff in relative gram sensitivity in the 0(H;H) and -2(H;H) series than would be predicted for the normal assumption that $\Delta/C_i = 0$. In contrast, the decrease in the relative gram sensitivity in the -4(H;H) series is less than predicted by a slope of 192. The x-axis intercept for 0(H;H) and -2(H;H) compounds occurs at carbon numbers of 30 and 32, respectively. For predictive purposes, Δ/C_i was taken as 0 at carbon numbers equal to or greater than 26 and 30 in these series, respectively.

Tables C5 and C6 present compositional results obtained from FI/MS, 70-eV EI/MS, and GC analysis of the saturates obtained from a hydrotreated shale oil. Direct comparison of the FI and ASTM 2786 results requires that the densities are not varying significantly. Thus, the agreement in the two MS analyses for the 200–325°C saturates shown in Table C5 is satisfactory although the 70-eV EI/MS analysis did not reveal compounds in the -8 and -10 Z (H;H) series. Likewise, the carbon-number distributions for and the total weight percents of 2(H;H) compounds by FI and by GC, shown in Table C6, are in good agreement. The value 34.4 by GC is a lower limit to the percentage 2(H;H)

TABLE C4. *Carbon-Number Dependence of Relative Mole Sensitivities for FI of Saturates on Reciprocal of Molecular Weight in Presence of Acetone*

Compounds	Z(H;H)	$\langle(\Delta/C_i)_p\rangle$	$M(L.S.)_p$[a]	$M(MW)_p$[b]	$\frac{M(L.S.)_p}{M(MW)_p}$
Alkanes	2	−0.058[c]	213[c]	142[c]	1.5
Cyclohexanes	0	−0.018	111	84	1.3
Decalins	−2	−0.050	195	138	1.4
Perhydrophenanthrenes	−4	0.021	126	192	0.7

[a] Least-squares slope of relative gram sensitivity versus MW^{-1}.

[b] Slope of relative gram sensitivity versus MW^{-1} for $\Delta/C_i = 0$.

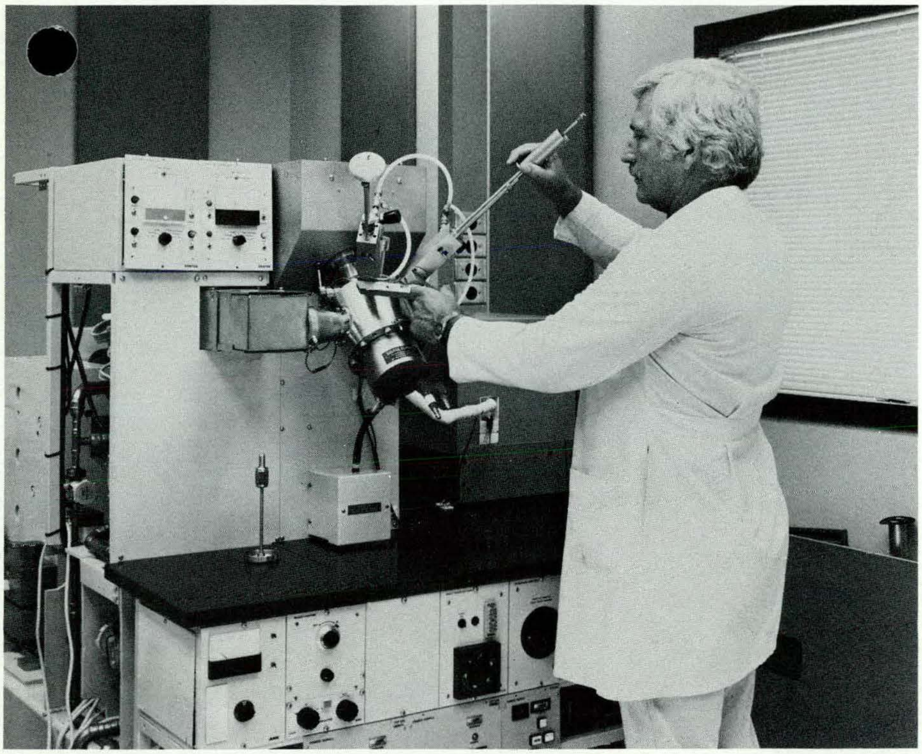
[c] Calculated relative to decane rather than methane.

TABLE C5. *Compositional Data for Saturate Fractions from Hydrotreated Shale Oil Distillates*

	200–325°C Distillate		325–425°C Distillate		>425°C Distillate	
Z(H;H)	Wt-Pct FI	Vol-Pct ASTM 2786	Wt-Pct FI	Vol-Pct ASTM 2786	Wt-Pct FI	Vol-Pct ASTM 2786
2	37.0	42.0	70.2	38.9	59.5	35.9
0	33.0	24.3	15.8	24.1	20.2	23.2
− 2	19.5	21.0	6.1	15.2	7.2	11.4
− 4	5.9	7.9	3.0	8.8	2.2	18.0
− 6	3.1	3.1	2.8	6.9	3.6	6.5
− 8	1.3	—	1.4	5.4	6.6	2.6
−10	0.2	—	0.7	—	0.7	2.1

TABLE C6. *Carbon-Number Distributions for 2(H;H) Compounds in Saturate Fractions from Hydrotreated Shale-Oil Distillates*

200–325°C Distillate			325–425°C Distillate			>425°C Distillate		
	Wt-Pct			Wt-Pct			Wt-Pct	
Carbon No.	FI	GC	Carbon No.	FI	GC	Carbon No.	FI	GC
11	0.9	—	19	2.5	8.7	27	4.6	5.6
12	7.9	9.6	20	3.6	8.5	28	8.1	15.0
13	7.1	7.0	21	3.8	6.6	29	6.8	15.1
14	5.0	5.0	22	4.2	6.3	30	5.9	8.0
15	4.5	4.0	23	5.8	5.6	31	6.6	6.6
16	3.7	3.3	24	7.1	5.4	32	5.5	2.6
17	3.2	3.1	25	9.7	5.5	33	4.7	1.6
18	3.0	2.4	26	12.1	4.6	34	4.8	0.7
19	0.9	—	27	8.2	2.6	35	4.5	[illegible]
20	0.8	—	28	6.8	0.2	36	5.2	[illegible]
			29	4.0	—	37	2.8	—
			30	2.5	—			
Total	37.0	34.4		70.3	54.0		59.5	55.6



After the relocation of the mass spectrometric equipment to the new BETC mass spectrometry laboratory, Robert Vrana, electronics technician, installs a direct insertion probe into the source of the new MS-50 mass spectrometer. A characterization analysis will then be made of one of the Venezuelan Cerro Negro crude oil samples as part of studies performed under the joint U.S.-Venezuela scientific exchange agreement.

compounds because the analysis does not explicitly consider branched alkanes.

In contrast, the results in Table C5 reveal that FI and ASTM 2786 yield significantly different results from the 325–425°C and >425°C distillates. The disagreement appears to be inconsistent with density effects. Although the GC results in Table C6 show the presence of significant amounts of n-alkanes in both distillates, the carbon-number distributions are not in good agreement with those obtained by FI. Realization of agreement between the two analyses would require the presence of significant amounts of branched alkanes having the higher carbon numbers.

In summary, sensitivities for FI of saturates are influenced in a complex manner, presently not understood, by addition of acetone. Three different analytical methods yielded reproducible results for three saturate fractions having different boiling ranges. The agreement between the methods is quite good for the lowest-boiling fraction but very poor for the two higher-boiling samples.

Quality of Crude Oils and Products[8c]

Most of the activity in this area was devoted to continued technical consultation and analytical services to the Strategic Petroleum Reserve Office (SPRO). Extensive special analytical testing of SPRO oils is being conducted in the BETC laboratories and at contract laboratories, and results will be compiled in a special report for the SPRO. Other special studies for the SPRO include simulated storage in bench-top experiments to determine the physical and chemical changes associated with mixing different crudes in storage.

Four crude oils were analyzed for inclusion in the BETC crude oil analysis data bank. This data bank is being enhanced by the efforts of two contract programmers that began work at BETC this quarter. They have reviewed several versions of the operating programs and consolidated the best features of all into one working system for enhancements. The data bank now contains more than 9,000 crude oil analyses from fields around the world. Additional crude oil samples are analyzed for inclusion as resources permit. Many written and telephone requests are responded to weekly with information about crude oils and their products. Crude oils in BETC storage, both tested and awaiting testing, have been transferred from cans to glass bottles and placed in a better organized storage and retrieval system

BETC has a cooperative agreement with the American Petroleum Institute to provide regularly published data defining the quality of motor gasolines, aviation turbine fuels, heating oils, and diesel fuels marketed throughout the United States. The summer 1981 Motor Gasoline report (DOE/BETC/PPS-82/1), was published this quarter, and about 1,200 copies were distributed. The 1981 aviation turbine fuels report (DOE/BETC/PPS-82/2) was published, and about 1,200 copies were distributed.

A special report (DOE/BETC/RI-82/4) was prepared from fuel survey data and is being distributed to interested parties. A condensed version of this report has been accepted for

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[8c] Project: Quality of Crude Oils and Products and Brine Analyses. B&R No. AC-05-10, AC-15-10-20. Staff: Branch Chief, J. E. Dooley; Section Chief, P. W. Woodward; Statistical Assistants, E. M. Shelton and C. L. Dickson; Physical Science Technicians, F. P. Fennell and E. J. Zagula.

publication in the *Oil and Gas Journal*.

BETC has a cooperative agreement with the National Exchange Group of the American Society for Testing and Materials to provide statistical analysis and reports for fuel test-engine performance. The purpose of testing is to evaluate the combustion characteristics of motor, aviation and diesel fuels. Some 26 individual reports are prepared annually and distributed to program participants.

Contracts. Contracts supporting the BETC Characterization Branch are listed below:

American Petroleum Institute (DE-AM19-78BC30003). Collaborate in Preparation and Publication of Analytical Petroleum Products Data. Technical Project Officer: P. W. Woodward.

American Society for Testing and Materials (DE-FC19-81BC10576). Engine Test Methods Applied to Motor and Aviation Gasoline. Technical Project Officer: P. W. Woodward.

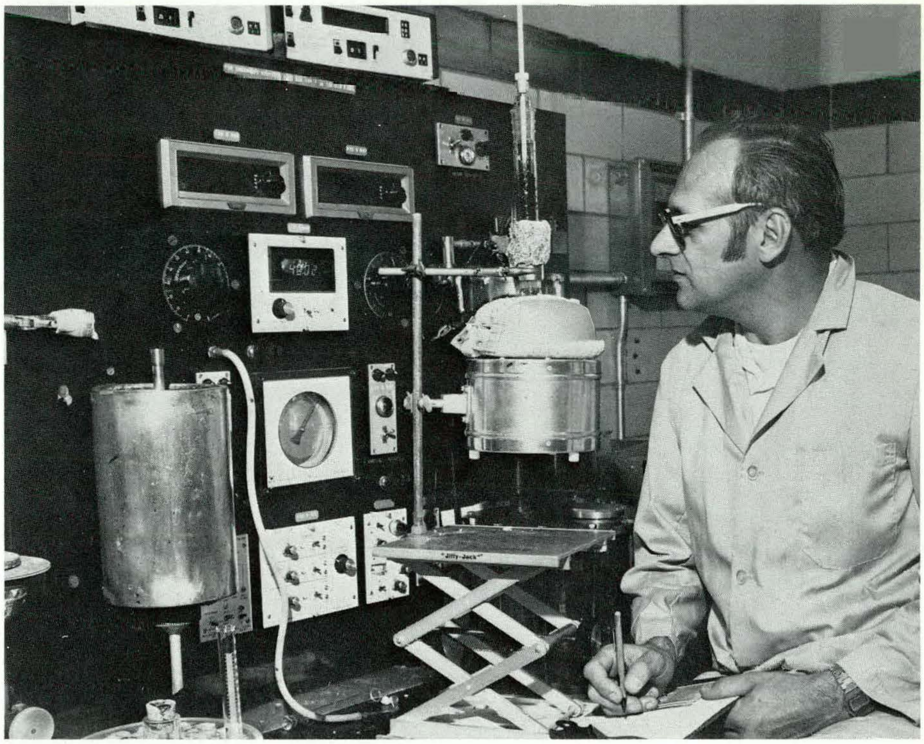
Global Geochemical (DE-AC19-80BC10370). Analyze Crude Oil Samples. Technical Project Officer: P. W. Woodward.

OAO Corporation (GS-OOC-70032). Computer Programming Assistance. Technical Project Officer: P. W. Woodward.

Oklahoma State University (DE-AS19-80BC10298). Synthesis of Hydrocarbon Standards for Mass Spectroscopy. Technical Project Officer: G. P. Sturm, Jr.

Texas A&M Research Foundation (DE-AC19-80BC10171). Analysis of Heavy Ends from Petroleum by Probe. Technical Project Officer: R. D. Grigsby.

University of Southern Florida (DE-AS19-81BC10606). Measurements of Deuterium and Stable Carbon. Technical Project Officer: J. B. Green.



As part of work being performed to characterize and safely maintain oils in the Strategic Petroleum Reserve, Ed Zagula, physical science technician, monitors the temperature controls during the distillation of a high-boiling (here, 530–650° F) fraction of a crude oil sample.

THERMODYNAMICS

Thermodynamic Studies on Coal Conversion Processes[9c]

Four subprojects are conducted as follows:

Heat Capacities and Heats of Combustion of Chars and Liquids from Coal Conversion Processes. The two-phase heat capacity of the low-molecular-weight alcohols is being measured with a differential scanning calorimeter. These studies include methanol, ethanol, n-propanol and n-butanol, and will be run to near the critical point. By making the measurements at two or more different fraction fillings of our constant volume cells, the heat capacity, c_V^{II}, at any filling fraction of the cell can be determined from the following relationship:

$$c_V^{II} = v^T \left(\frac{d^2p}{dT^2} \right)_\sigma - mT \left(\frac{d^2G}{dT^2} \right)_\sigma$$

where the derivatives of the pressure, P, and Gibbs energy, G, are along the liquid vapor saturation line, σ, and m is the mass in the cell of volume, v. **This is a rapid and convenient but previously unexploited way to provide the two derivatives which offer stringent tests to equation-of-state correlations used for such fluids in calculations for plant design.** Studies are also planned with mixtures of fluids where the equation above still applies; however, the two derivatives are dependent upon the composition and mass of the mixture, as well as the volume. **The studies are exploratory to determine if**

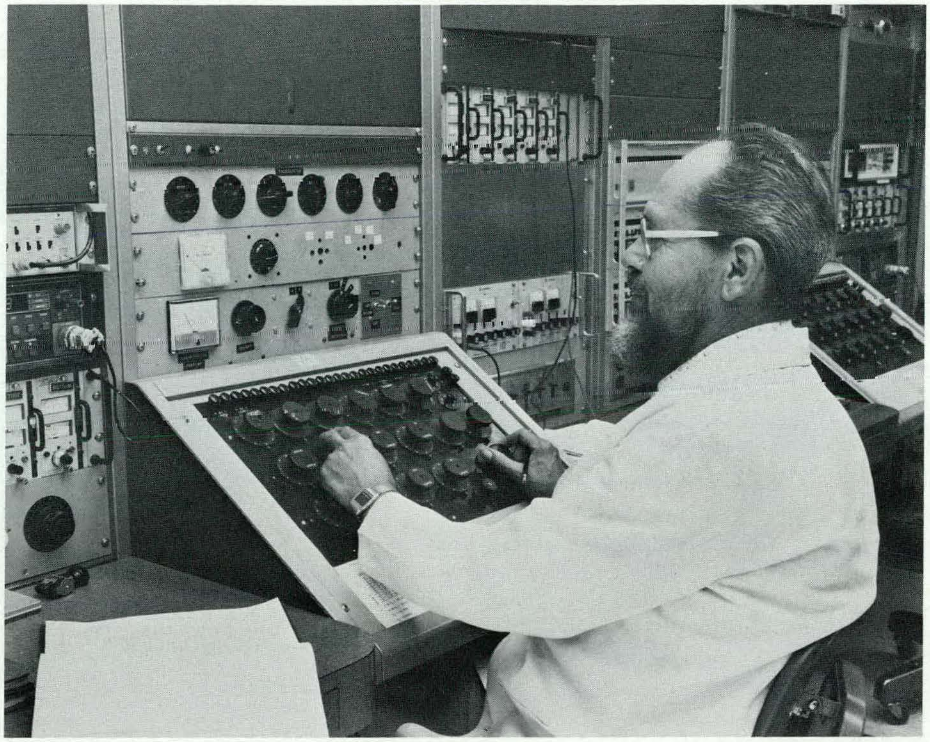
[9c] Project: Thermodynamic Studies on Coal Conversion Processes. B&R No. AA-15-15-10. Acting Chief, Thermodynamics Branch, W. D. Good; Research Chemists, B. E. Gammon, N. K. Smith, R. D. Chirico, R. H. Harrison, A. G. Osborn; Research Physicist, I. A. Hossenlopp; Instrument Mechanic, S. E. Knipmeyer.

composition dependence can be utilized to give a new, quick and convenient way to obtain vital thermodynamic information on vapor-liquid equilibria of mixtures.

Determination of ΔH_f°, ΔS, and C_p for Selected Key Compounds. Measurements for the heat capacity, entropy, and enthalpy of 4-methylphenanthrene were continued. This substance has a phase transition ~12 K below the melting point, and measurements in this region have been very slow since long times are required to prepare the equilibrium forms of the crystals. It is a major task to obtain sensible results around such transitions. The results to date are thermodynamically consistent, and when studies in this region are finished, the remaining parts of the studies on this compound should be completed with ease.

Solubility of Hydrogen (and Possibly Synthesis Gas) in Selected Process Solvents. The vapor-liquid-equilibrium apparatus has been modified to permit the study of three-phase systems that do not form emulsions. A sample of tetralin was purified for use in the next run on a multicomponent mixture. Sample bombs have been heated, evacuated, and weighed. Standard samples containing various concentrations of water are being used to select the best gas chromatographic system for the analysis of samples.

Vapor Pressure Measurements. Measurements of the vapor pressure of 2,2′-dimethylbiphenyl are now assured of completion. The apparatus used for these measurements was modified extensively, and reliable results have been obtained at the lowest pressures where problems previously arose. Final check measurements are being made. **With the completion of these studies we will be able to specify the Gibbs energy of formation of this substance in the ideal gaseous state, and thereby predict the equilibrium constant for the hydrogenation of phenanthrene to form the product 2,2′-dimethylbiphenyl.**



Seated at the control panel of the low-temperature cryostats, Alex Hossenlopp, research chemist, performs calorimetric measurements on a polynuclear-aromatic compound found in coal liquids, oil shale, and heavy petroleum ends. These measurements provide fundamental data to be used in designing processing methods for these materials.

Thermodynamic Characterization of Condensed-Ring Compounds[10c]

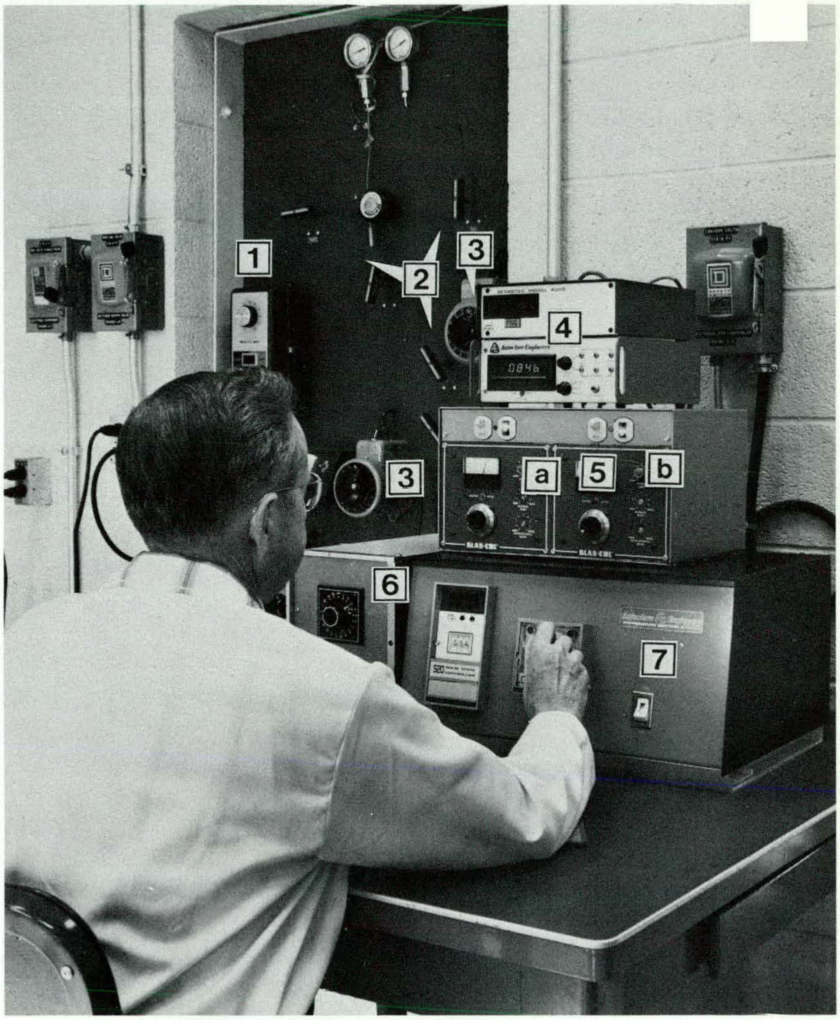
Work is reported under three headings dealing with adiabatic calorimetry, spectroscopic measurements, and vapor pressure measurements.

Adiabatic Calorimetry with Modernization and Automation. Fabrication and electroplating of the parts to modify a calorimetric cryostat for operation between temperatures from 4 to 550 K were completed. **This new instrument will extend the range of our present operation so that measurements can be made up through the melting point of high-molecular-weight polynuclear aromatic compounds found in coal, oil shale, and heavy ends of petroleum.** The ability to make measurements up into the liquid state is essential to ensure that equilibrium forms of the crystals are used in evaluation of entropies by use of the third law of thermodynamics. Severe difficulties were faced by the machinists in fabricating the new parts with a minimum of mass and with an intricate maze of fine grooves for adequate tempering of electrical leads in the system; the parts surpass expectations and should provide a very reliable instrument. The instrument will be assembled soon.

[10c] Project: Thermodynamic Characterization of Condensed-Ring Compounds. B&R No. KC-03-02-01. Acting Chief, Thermodynamics Branch, W. D. Good; Research Chemists, B. E. Gammon, N. K. Smith, R. D. Chirico, A. G. Osborn, J. A. Draeger; Research Physicist, I. A. Hossenlopp.

Performing studies on the thermodynamics of coal liquefaction is Roland Harrison, research chemist. As part of this work, he utilizes the gas solubility apparatus to perform vapor-liquid equilibrium tests on H-Coal liquids. The action of the impeller in the autoclave mixes the nine component gases and water he has added with the H-Coal liquid to obtain equilibrium. At the controls for the apparatus, Harrison adjusts the heating jacket temperature.

1. *Speed control for impeller (stir shaft).*
2. *Valves supplying the gases to the system.*
3. *Variacs for adjusting voltage fed into the heaters.*
4. *Digital readouts from pressure transducer.*
5. *Temperature control for (a) vapor sample bomb and (b) liquid sample bomb.*
6. *Thermocouple temperature indicator.*
7. *Equilibrium cell temperature control system.*



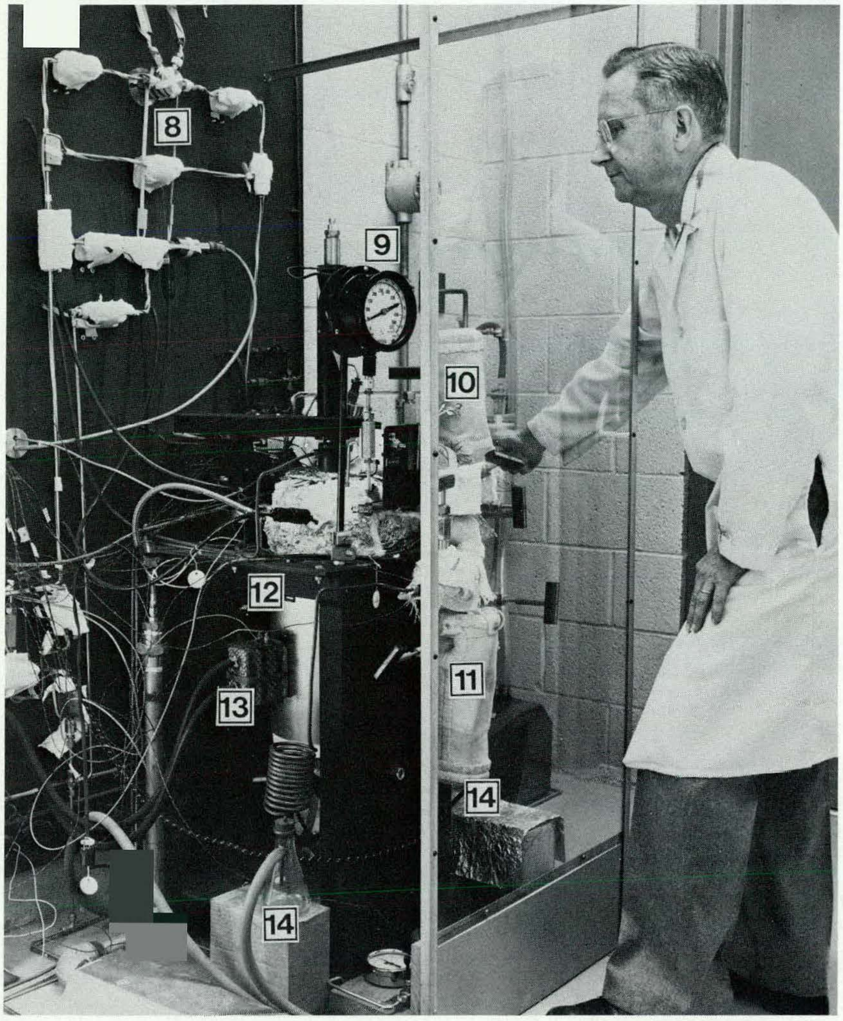
Successful efforts also were made to extend the operating range of one of the existing cryostats to higher temperatures. This was accomplished by modifying the refrigerants used in the tanks and was tested in the calibration of a newly assembled platinum calorimeter at temperatures from 10 to 450 K. The instrument materials and method of construction do not allow its operating limits to be modified further.

Experimental studies on the heat capacity, entropy, and enthalpy of quinoline are in progress. Measurements are almost complete in the region of a phase transition where the sample is slow to come to equilibrium, and preparation of the equilibrium form of the crystals requires very long times. When the studies are complete in this region, preliminary results indicate that the remaining measurements can be made rapidly.

In related studies, the heat capacity, entropy, and enthalpy are being determined on 4-methylphenanthrene, and preparations are being made for measurements on 2,6-dimethylpyridine.

In the experimental heat capacity measurements, it is essential to locate temperatures of phase transition early and quickly. To meet these needs, reliable methods were developed to locate the transition from equilibration rates at fixed times after heating the sample. This technique was shown to be useful for the compounds under study. It offers a method for locating transitions that do not give discontinuities in calorimetric results, but which nevertheless can be observed by other experimental techniques that cause problems in obtaining reliable calorimetric results because of the long times required to reach equilibrium in the region of such hidden transitions.

In the development of the new method, it was shown that the equilibration rates were independent of the prior heating rate, but were dependent upon the size of the tempe[illegible]e increment of the prior heating of the sample. These two results indicate that temperature gradients in the sample are not the source of the long equilibration times, but that th[illegible]g times arise solely from redistribution of energy within the microscopic



During the operation of the gas solubility system, Harrison takes samples for study at each 100° F boiling range. Here, he opens a valve to release a liquid sample. Liquid and vapor samples have been analyzed by J. W. Vogh, P. L. Grizzle, and J. S. Thomson for each of the nine component gases, water, and the H-Coal liquid. Harrison will present a paper, "Vapor-Liquid Equilibrium of the H-Coal Liquids, Water, and a Nine Component Gas Mixture," summarizing these studies at the American Chemical Society Annual Meeting in Kansas City September 12–17.

8. Manifolding directing gas into autoclave.

9. Impeller pressure gauge.

10. Liquid sample bomb (covered with heating jacket).

11. Vapor sample bomb (covered with heating jacket).

12. Autoclave (equilibrium cell).

13. Electrical leads controlled by variacs.

14. Vacuum bottles enabling liquid and vapor to flow freely as samples are taken.

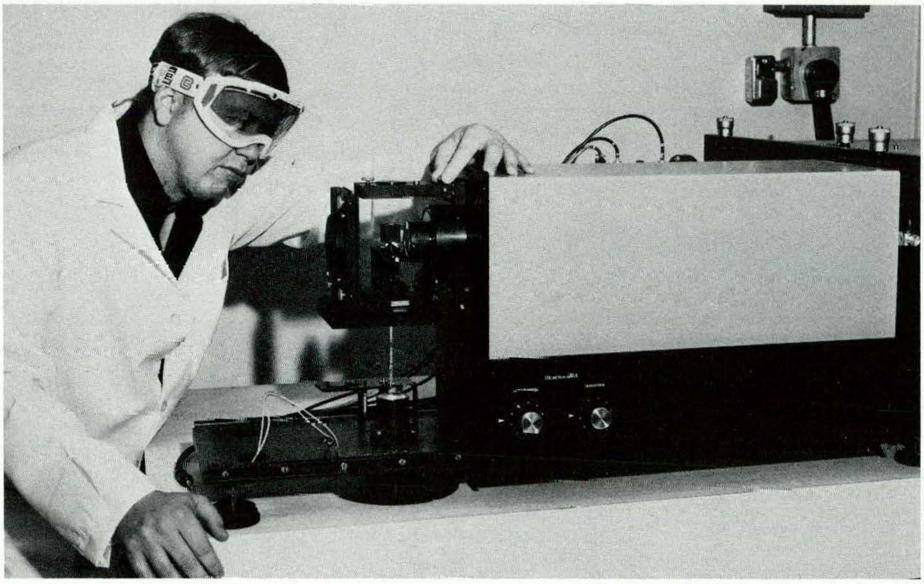
energy levels of the sample.

Thus, a new experimental design will not decrease equilibration times. The universal nature of the equilibration rates in the vicinity of the transition indicate that many workers in this field have misconceptions about reliable methods for making suitable measurements in the region of phase transitions. The new rate data show clearly how to expediently get results suitable for the evaluation of third law c[illegible]ermodynamics entropies. The data also show that many currently used methods are incorrect for obtaining fine details of the thermodynamics around solid-state phase [illegible]itions.

[illegible]utomation of the experimental data logging system was slowed because of a breakdown of an auxiliary memory unit for the computer and to troublesome electrical connections to the computer. These have been remedied, and software developments are expected in coming months. For the automatic shield controls of the calorimeter, a very low voltage amplifier from one manufacturer was tested and shown to be unsuitable for current purposes. An old electromechanical amplifier currently is being used in this element of the control system. A suitable modern solid-state electronic counterpart has not been found; custom designs are being explored.

Final literature surveys were made for data to be used in four different manuscripts describing the comprehensive thermodynamic properties of cyclic oxygen compounds, cyclic hydrocarbons, normal alkenes, and condensed-ring hydrocarbons.

Fourier Transform Infrared and Raman Spectroscopy. The two manuscripts describing the chemical thermodynamic properties of the dimethyl- and trimethylpyridines have been accepted for publication and should be published next quarter. The manuscript dealing with aniline, methylamine, cyclopropylamine, and cyclopentene is being prepared for submission. **This manuscript describes the method for calculating the thermodynamic property contributions of any asymmetric rotor with a complex hindering potential function.**



Using a laser raman spectrometer, Jon Draeger, research chemist, measures the vibrational energy levels of nitrogen components in coal liquids, shale oils, and heavy crudes. The raman spectrum of these compounds provides information on the thermodynamic properties of these compounds useful in process technology development.

The comprehensive vibrational studies of the methylbenzenes have been completed. The normal coordinate calculations have been done, and the ideal gas chemical thermodynamic functions and properties of formation have been calculated. The modified valence force field has 45 parameters, and the average error between the 662 observed and calculated frequencies is 8.9 cm^{-1} or 1.3 percent. Manuscripts discussing these compounds will be prepared soon.

The liquid and vapor-state far infrared spectra of the dimethylpyridines have been published in the Infrared Catalog of the Thermodynamics Research Center Hydrocarbon Project at Texas A&M University. The Raman spectra of the dimethyl- and trimethylpyridines should appear next quarter.

Vapor Pressure Measurements. In related work, vapor pressure measurements on 2,2′-dimethylbiphenyl and 3-methylpyrrolidine were completed. For the former measurements, a piston gage for very low pressure measurements was used, and to give more reliable results, this instrument required additional modifications over those reported previously. The source of very small, but troublesome, leaks was traced to unnecessary valves, which were removed from the system. Strong pressure-coupling between the piston gage and a diaphragm gage was removed by insertion of a ballast volume in the inert gas coupling section of the system. These two modifications improved the performance of the system considerably, and recent measurements indicate that the rate for taking data from the instrument has been increased by several times.

Thermodynamics of Organic Nitrogen Compounds[11c]

Vapor pressure measurements were completed, and the results were analyzed for 3-methylpyrrolidine. The results complete the experimental information required to calculate the comprehensive thermophysical [illegible] erties of this substance, and suc[illegible] lculations will be completed in coming months.

It was shown last quarter that the results for the heat capacity of liquid 3-methylpyrrolidine completely delineate an anomalous behavior that has been only partially shown, but not noted for other amines. From a complete review and analysis of the available heat capacity data for liquid amines, Table C7 shows which amines (excluding aromatics) do or do not give the anomalous behavior. A convenient source for showing the approximate anomalous contribution is the difference in the heat capacity of a liquid primary or secondary amine from its corresponding sulfur analog.

TABLE C7. *Behavior of the Heat Capacity, C_s, near 240 K for Liquid, Saturated Amines with Data Available*

Anomalous C_s	Normal C_s
Ammonia	Ethylenediamine
Methylamine	1,2-Propanediamine
1-Propylamine	2-Methyl-1,2-propanediamine
2-Propylamine	Cyclopropylamine
t-Butylamine	Ethylenimine
Cyclopentylamine	Trimethylamine
Dimethylamine	
Pyrrolidine	
3-Methylpyrrolidine	
Piperidine	

Figure C2 shows this difference for 3-methylpyrrolidine minus 3-methylthiolane,[12c] and pyrrolidine[13c] minus thiolane.[14c] The peaks in these curves are at temperatures surprisingly close to analogous results for the amines

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[11c] Project: Thermodynamics of Organic Nitrogen Compounds. B&R No. AC-05-05. Acting Chief, Thermodynamics Branch, W. D. Good; Research Chemists, B. E. Gammon, N. K. Smith, J. A. Draeger.

[12c] J. F. Messerly, H. L. Finke, and S. S. Todd, *J. Chem. Thermodynamics, 6,* 635 ([illegible]

[13c] J. P. McCullough, D. R. Douslin, [illegible] Hubbard, S. S. Todd, J. F. Messerly, I. A. Hossenlopp, F. R. Frow, J. P. Dawson, and Guy Waddington, *J. Am. Chem. Soc., 81,* 5884 (1959).

[14c] W. N. Hubbard, H. L. Finke, D. W. Scott, J. P. McCullough, C. Katz, M. E. ([illegible] J. F. Messerly, R. E. Pennington, an[illegible] Waddington, *J. Am. Chem. Soc., 74,* 6025 (1952).

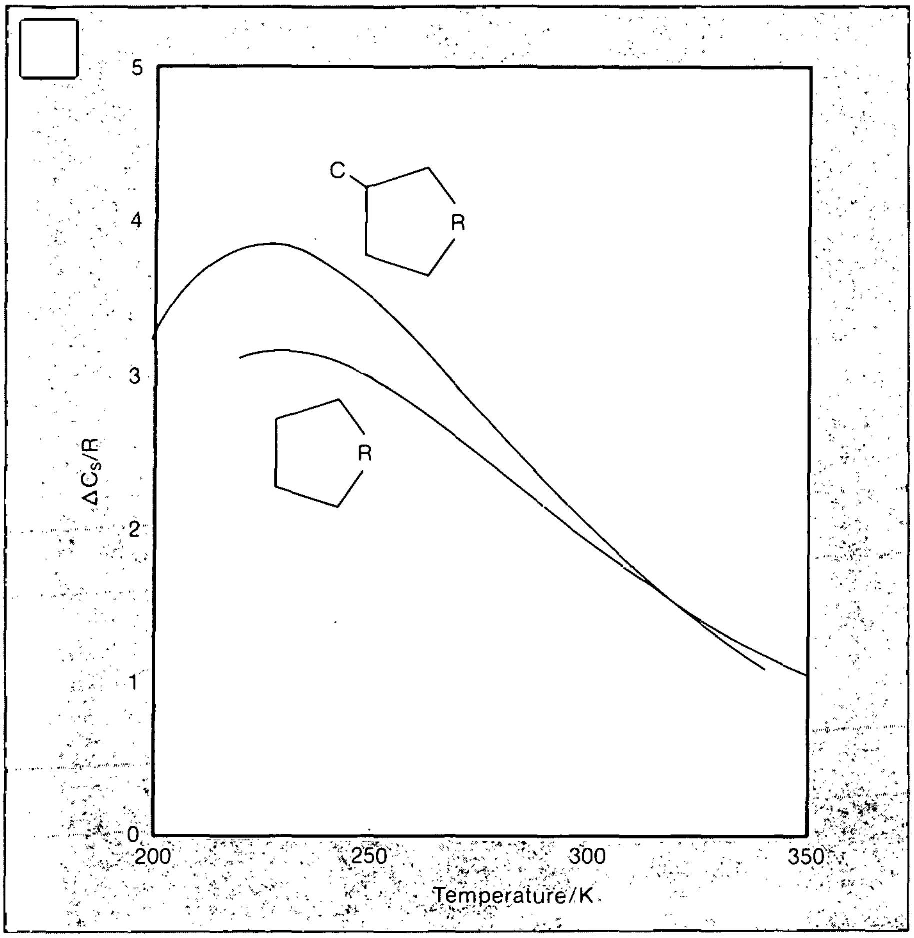

FIGURE C2. *Heat capacity anomaly for liquid pyrrolidine (lower curve) and 3-methylpyrrolidine (upper curve) derived from the differences in the heat capacity of the amines from their sulfur compound analogs, thiolane and 3-methylthiolane.*

listed in column 1 of Table C7. The relative invariance in the position of the temperature of the maximum anomalous behavior for these liquids indicates that all of the compounds form an analogous species whose Gibbs energy of formation is probably close to the same value for all of the compounds listed in column 1 of the table. **This suggests that a universal correlation of the thermodynamic properties can be made for a es of the type indicated in c nn 1**; those amines listed in column 2 of the table are exclusions for obvious reasons concerning ring strain energy, intramolecular hydrogen bonding, etc. **The indicated universal correlation for the thermodynamic properties of this broad class of primary and secondary amines provides an essential tool for unraveling the myriad problems associated with the correlation and prediction of thermodynamic properties of fluid amines found in fossil materials.**

Preparations are being made to fill a calorimeter with 2,6-dimethylpyridine; heat capacity, entropy, and enthalpy measurements will be made in coming months.

A literature survey was made on six nitrogen compounds as a part of final preparation of manuscripts describing their comprehensive thermodynamic properties.

Final results were calculated for a series of combustion calorimetry experiments on quinoline.

Thermodynamic Properties of Organic Compounds[15c]

At the request of personnel at Wright-Patterson Air Force Base, studies were started on distillate fuels derived from shale oil that has been subjected to varying degrees of hydrogenation.

A series of combustion calorimetry experiments is in progress on 14 samples of experimental ram-jet fuels. These liquids have been sealed in 87 glass ampoules. No problems have been encountered in the combustion of these materials.

PROCESSING TECHNOLOGY

Refining Process Technology[16c]

Experiments are being conducted to determine the upgrading and refining characteristics of synthetic crude oils, the type and quality of finished products potentially obtainable, and changes in refining processes required to yield the finished fuels. Correlations of upgrading requirements will be developed based on syncrude composition, biological activity, stability, and projected future use of refined liquid fuels.

A sample of SRC-II middle distillate was hydrotreated in a cooperative program with the BETC Utilization

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[15c] Project: Thermodynamic Properties of Organic Compounds. B&R No. 40-04-03. Acting Chief, Thermodynamics Branch, W. D. Good; Research Chemists, N. K. Smith, B. E. Gammon, R. D. Chirico, A. G. Osborn.

[16c] Project: Refining Process Technology. B&R No. AC-05-10. Staff: Branch Chief, F. D. Sutterfield; Project Manager, D. W. Brinkman; Research Chemist, J. W. Goetzinger; Physical Scientist, G. L. Steele; Physical Science Technician, E. J. Zagula.

Research Division to determine effects of mild upgrading on combustion properties and pollutants. The SRC-II was hydrotreated at two conditions to add approximately 1 and 2 weight-percent hydrogen. These conditions, for once-through operation, were 1.5 LHSV (volume liquid per volume catalyst per hour), 320°C, 3,500 SCF hydrogen per barrel of feed, and 2,000 psig total pressure. The second hydrotreating conditions were 1 LHSV, 335°C, 5,000 SCF hydrogen per barrel of feed, and 2,000 psig total pressure. Analytical data and results of the utilization tests are not available at this time.

Lawrence Berkeley Laboratory has identified methyl and phenylarsonic acid as well as arsenate in oil shale products—namely shale oil and oil shale retort waters.[17c] It is important to elucidate the biogeochemical origin of these compounds because they either have a biogeochemical origin in oil shale kerogen or they are formed during the pyrolysis of oil shale kerogen. Additionally, it is desirable from a processing standpoint and for environmental reasons that the origin of these compounds be established.

The total methanol extracts of a Green River oil shale kerogen sample were used in earlier experiments to identify by high performance liquid chromatography-graphite furnace atomic absorption (HPLC-GFAA) and gas chromatography-electron impact mass spectrometry (GC-EIMS) analysis phenylarsonic acid and, tentatively, arsenate. Similar experiments were done with HPLC-purified fractions of the methanol extract in which both phenylarsonic acid and, the previously unidentified, methylarsonic acid were derivatized with 3-methylcatechol, followed by GC-EIMS analysis. The known compounds from the reaction of 3-methylcatechol and either phenyl or methylarsonic acid, i.e., the five coordinate organoarsenic catecholates shown in Figure C3, were chromatographed on a 30-m fused silica capillary column interfaced to an electron impact mass spectrometer.

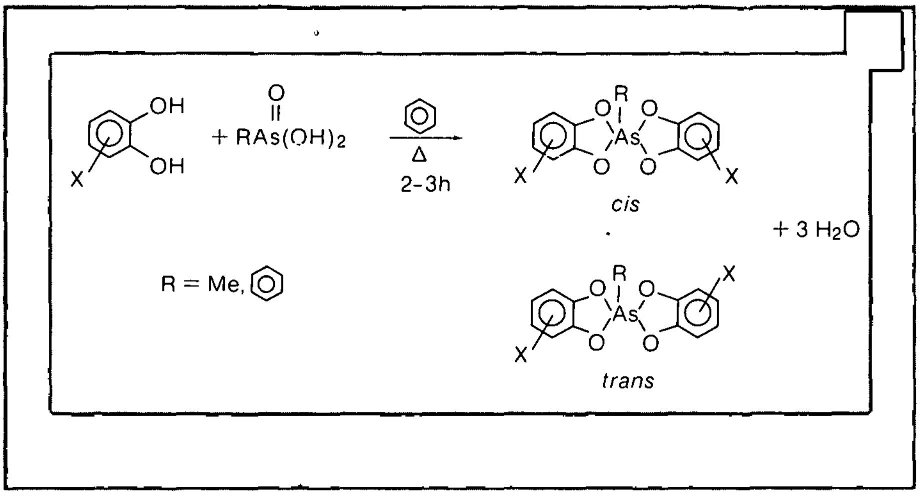


FIGURE C3. *Known compounds from reaction of 3-methylcatechol and either phenyl or methylarsonic acid.*

A similar analysis, as stated above, with the HPLC-purified factors provided unequivocal evidence for the identification of methylarsonic acid, as well as reconfirmation of the previously identified phenylarsonic acid.

These exciting discoveries open a new field that we have called organometallic geochemistry, which further enhances our original goals of providing polymeric ligands to remove inorganic and organoarsenic compounds from shale oil.

The usefulness of the HPLC-GFAA analysis has been demonstrated for "fingerprinting" heavy crude oils and utilizing these data in defining the molecular weights of various vanadyl compounds found in oils.[18c]

Heavy crude oils, extracted oils and extracts were analyzed on size-exclusion HPLC columns, which showed the molecular weight distribution for vanadyl compounds in four heavy crude oils. Recently, this study was extended to the asphaltenes of Cerro Negro, Boscan, Wilmington and Prudhoe Bay, isolated via pentane precipitation. Analysis of the vanadium content in the asphaltenes by x-ray fluorescence provided a comparison to the whole heavy crude oils previously studied (Table C8).

TABLE C8. *Whole Heavy Crudes Previously Studied*

	PPM vanadium in crude oil	PPM vanadium in asphaltene	Wt-pct of asphaltene in crude	Percent of total vanadium in asphaltene
Boscan	1,100	4,310	23.3	91.3
Cerro Negro	560	1,680	25.7	77.[illegible]
Wilmington	49	422	7.05	60.[illegible]
Prudhoe Bay	19	327	2.75	47.3

[17c] R. H. Fish, K. L. Jewett and F. E. Brinckman. *Environ. Sci. Tech.*, *16*, 174 (1982). C. W. Weiss, K. L. Jewett, F. E. Brinckman and R. H. Fish. NBS Special Publication *618*, 197 (1981).

[18c] R. H. Fish, LBID523, Quarterly Report to the Bartlesville Energy Technology Center, Jan. 1, 1982-April 1, 1982.

TABLE C9. *Vanadium Distribution in Heavy Crude Oils and Asphaltenes*

	Boscan			Cerro Negro			Wilmington			Prudhoe Bay		
	>900[a]	>400 <900	<400	>900	>400 <900	<400	>900	>400 <900	<400	>900	>400 <900	<400
Heavy Crude Oil . . .	527[b]	251	315	298	114	148	25.2	9.4	14.5	11.3	4.4	3.3
	47.9%[c]	23.4%	28.7%	53.2%	20.4%	26.4%	51.4%	19.1%	29.5%	59.7%	22.9%	17.4%
Asphaltene	2.064[b]	777	1.468	739	235	706	235	60	127	228	32	67
	47.9%[c]	18%	34.1%	44%	14%	42%	55.6%	14.2%	30.2%	69.7%	9.8%	20.5%
	91.2%[d]	70.4%	109%	63.7%	53%	123%	70%	47.9%	65.7%	55.5%	20%	55%

[a] Molecular weights [b] PPM vanadium [c] Percent of total vanadium in fraction [d] Normalized to the heavy crude oils.

REPORT AVAILABLE ON EMULSIFIED INDUSTRIAL OIL TREATMENT

A study of industrial lubricant recycling practices in industrialized countries indicates that the United States uses chemical treatments to break down used oil-water emulsions before re-refining while Japan and European countries prefer physical methods of separating the mixture.

The results have been published in a Department of Energy-sponsored report, "Emulsified Industrial Oils Recycling" (report No. DOE/BC/10183-1), by Springborn Laboratories, Inc. The report is available only from the National Technical Information Service, 5285 Port Royal Road, Springfield, Va. 22161, at a cost of $15.

The study focused on emulsion-type fluids, regardless of industrial application, as these fluids represent a high percentage by volume of the total fluids used in the U.S. industrial lubricant market.

Re-refining has now become a viable option for oil-water emulsions. Regulations stipulate that used emulsions must undergo separation of the oil and water phases, and the water must be treated before dumping. This separation is costly, but once the water is removed, re-refining the remaining oil becomes economical.

This study found that the most commonly used method to perform the separation is chemical treatment, practiced in the United States. This method produces large amounts of waste, causing secondary pollution problems. Ultrafiltration and other physical methods of separation are preferred in other industrialized countries because no byproducts are generated in these processes. Filtering methods, however, are not currently efficient enough to treat the large quantities of emulsions produced by U.S. industry—about 1.4 billion gallons each year.

Principal investigator for the project was Tibor Gabris of Springborn Laboratories, Enfield, Conn. Dennis W. Brinkman, BETC project manager for processing, was the DOE technical project officer.

As shown in Table C8, the asphaltene fraction, as previously understood, has a high concentration of vanadium. More importantly, these asphaltene fractions were examined by SEC (size-exclusion chromatography)-HPLC-GFAA analysis, and the vanadium distribution was determined with molecular weights of >900; <900, >400; <400.

Table C9 states the results and shows conclusively that vanadyl compounds incorporated into molecules with >900 mw are present in the asphaltenes in very high concentrations, as are the porphyrin and nonporphyrin vanadyl compounds. These latter results need to be examined, along with an analysis of the maltene fraction (oil remaining after pentane precipitation of asphaltenes) and extracts of the asphaltenes.

The preliminary results on the fingerprinting of asphaltenes for vanadyl compounds will help in future speciation studies for identification of these compounds in the heavy crude oils and components of the oil.

A contracted research project by the Gulf Research and Development Corporation is testing the feasibility of a novel process to denitrogenate shale oil by mild catalytic hydrodenitrogenation (HDN), followed by ion exchange treatment. Samples of shale oil from the No. 6 burn of Occidental Oil have been hydrogenated in both bench- and pilot-scale units over a range of conditions. Subsequently, bulk samples from the pilot-scale HDN runs were distilled to recover naphtha, jet fuel, heavy furnace oil, gas oil and residue.

Ion-exchange experiments in both batch and flow units are underway with the emphasis on using the jet fuel fractions. Results from the batch experiments indicate that the diffusion of nitrogen-containing compounds into the ion-exchange resin is a significant factor in the dynamics of the process. In the flow-unit runs, the concentration of nitrogen-containing compounds in the column effluent follows the typical s-shaped curve with a strong dependence on flow rate. It is interesting that the initial column effluent is water-white and contains essentially no nitrogen, with levels of 1–10 ppm versus feeds of 1,700 and 2,700 ppm. The resin is retaining sizable levels of nonbasic nitrogen, in addition to the expected basic nitrogen compounds.

Detailed analysis of several straight-run distillate fractions has been completed. Nitrogen concentrate from straight-run jet fuel was analyzed by GC-MS. The straight heavy distillate was fractionated by chromatography and the fractions were analyzed by nuclear magnetic resonance and infrared radiation. The results show that pyridines are the major components of the ion-exchanged jet fuel. Polar compounds in the heavy distillate are comprised mainly of pyridines and quinolines, but also contain some phenolics and carbonyls.

Waste Oil Recycling[19c]

Research is being conducted to develop and/or critically evaluate technology for recycling used lubricants; to obtain compositional data on new, used, and recycled lube oil; to demonstrate the technical, economic, and environmental feasibility of recycling lubricants; and to develop useful roles for any by-products from recycling processes.

A special event this quarter was the completion and start-up of the new re-refinery at Booth Oil Company in Buffalo, N.Y. As part of this project, DOE is receiving data and information from this innovative operation so that it can be published and passed along to others considering entering the used oil recycling business.

Booth Oil already has submitted a detailed report on all the environmental regulations with which they had to comply. This report alone should save considerable time and concern for others just beginning the process of putting in a new facility. Altogether there were 23 rules and regulations from federal, state, county, and local agencies with which Booth had to comply or for which a license had to be obtained. The report should be published and made available by BETC by late fall.

A similar activity is in earlier stages in Los Angeles, where Lakewood Oil Service is beginning to install a plant using the Research Technology, Inc. re-refining process. Lakewood is about 9 months behind Booth Oil, so Lakewood's first topical report is not expected before the end of 1982. Since California and New York have some of the strictest regulations, the information provided on environmental rule compliance in those states should be more than adequate for most sites.

The major research effort on the fate of hazardous wastes found in used lubricating oils is nearing completion by the GCA Corporation. In this study, a "spiked" used oil undergoes a variety of scenarios simulating actual fates of used oil, varying from dumping it down the sewer to re-refining it into quality lube oils. A recent modification of the contract will allow for additional computer model studies to verify experimental predictions and for sampling at one commercial re-refinery for additional confirmation. **This attempt to be especially careful that the research findings are accurate is due to our knowledge that the findings are going to be used by the Environmental Protection Agency as part of the basis for regulating used oil, and that the data might be challenged in court cases.**

Two reports were published this quarter and are now available from the National Technical Information Service; they are: "Banbury Oil Recycling," DOE/BC/10329-4, which discusses the recycling of lubricants from the rubber industry, and "Emulsified Industrial Oils Recycling," DOE/BC/10183-1 (see page 47).

[19c] Project: Waste Oil Recycling. B&R No. ED-01-01. Staff: Project Manager, D. W. Brinkman; Branch Chief, F. D. Sutterfield; Research Chemist, J. W. Goetzinger; Physical Scientist, G. L. Steele; Physical Science Technician, E. J. Zagula.

Heavy Oil Processing[20c]

This project is aimed at accelerating innovative designs needed for upgrading and refining heavy oil and residuum to maximize transportation fuel production and minimize gas and residue yields. The majority of upgrading and refining research is done by industry and should continue. However, there are technical risks associated with heavy oil and a need for accelerated development, which make a joint government/industry effort useful. Special emphasis can be given to rapid technology transfer and to assisting smaller refiners.

Four prime contractors are working on various parts of this effort. Two firms, UOP, Inc. and Hydrocarbon Research, Inc., are completing engineering designs of innovative upgrading processes. These generic designs are essentially complete, except for cost estimates and final internal review. During the next quarter all drawings and data will be sent to Walk, Haydel and Associates, Inc., for a detailed engineering review. Simultaneously, the data for both processes will be sent to ENTEC Research Associates, Inc., for an independent market assessment of commercial potential and the proposed product slates as they relate to the likely future demands. A combined report should be published by BETC in early 1983.

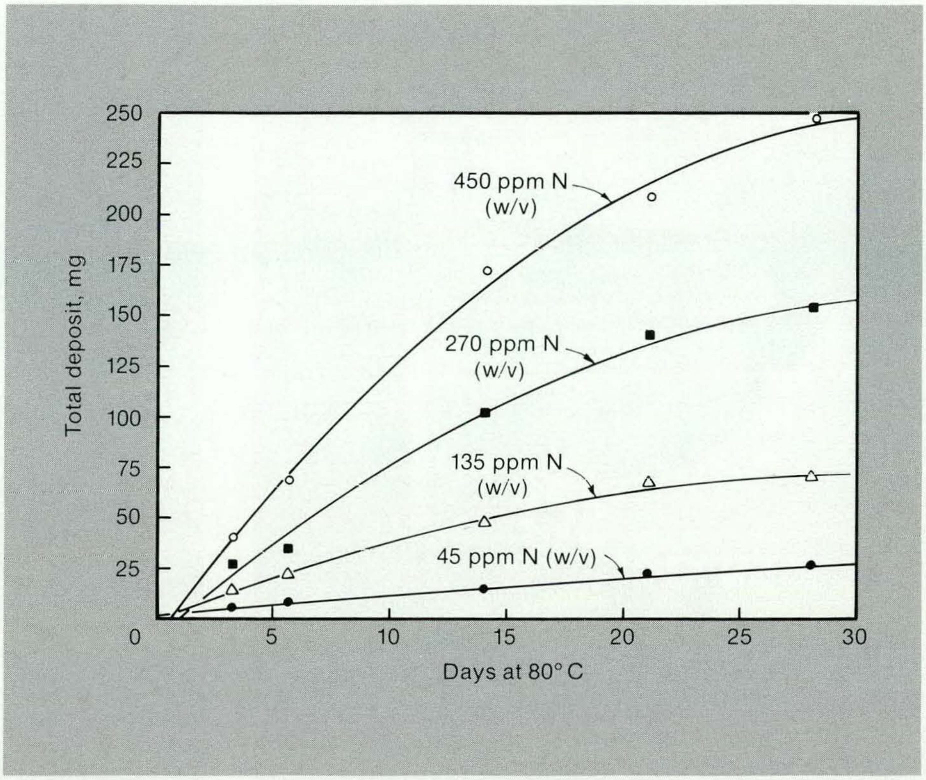


FIGURE C4. *Test results at various concentrations of 2,5-dimethylpyrrole for various aging times.*

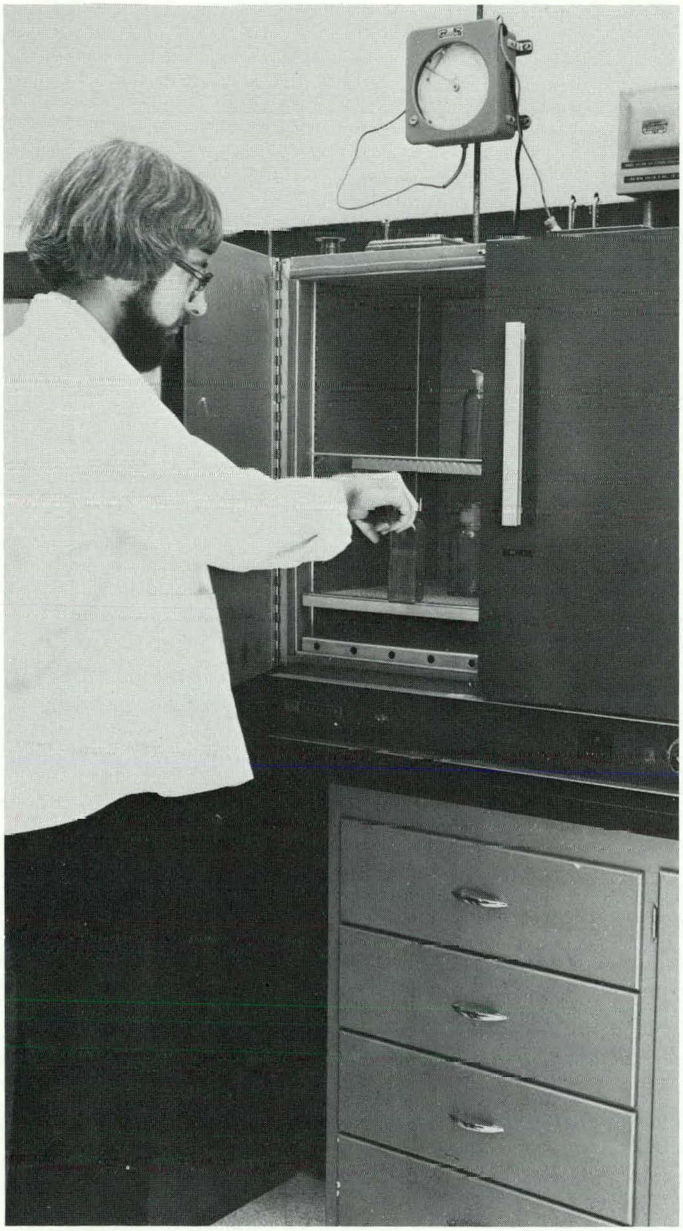
Stability Characteristics of Hydrocarbon Fuels[21c]

This project is aimed at determining the storage and thermal stability characteristics of representative liquid hydrocarbon fuels. This includes analyzing various gasolines, diesel fuels, and jet fuels for hydrocarbons and nonhydrocarbons found to be precursors of deterioration products. Ultimately, stability information is useful to refiners in selecting process conditions that will minimize deterioration through removal or inhibition of reactive compounds. It will be critical to know the trade-offs between severity of processing and stability as synthetic fuels approach commercial production.

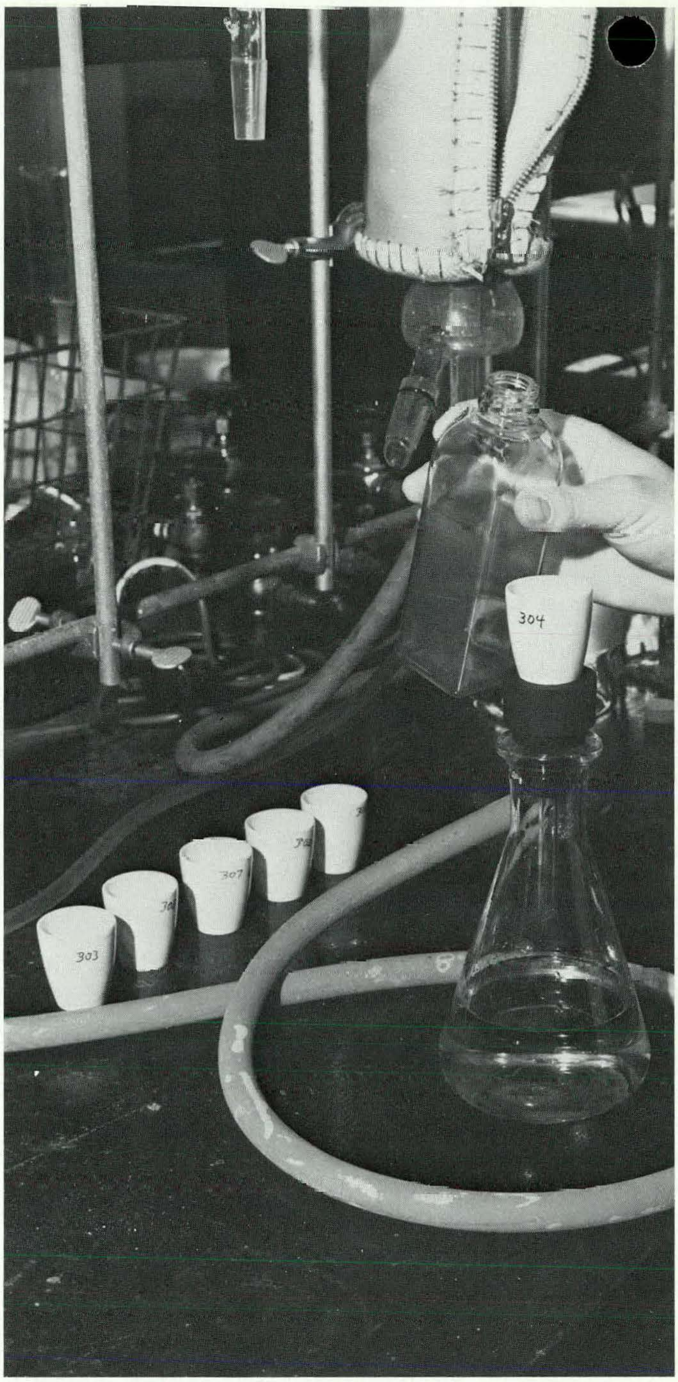
The principal effort within this project is being carried out at the Naval Research Laboratory (NRL). Its work on degradation mechanisms is building on the prior studies conducted by Exxon and funded by BETC. **One recent finding is that the peroxide number, normally thought to be very high in autoxidatively reactive mixtures, is essentially zero for all fuel samples containing 2,5-dimethyl pyrrole at concentrations as low as 45 ppm N.** This implies that the formation of any peroxide intermediates is the rate-limiting step, with all subsequent reactions very rapid. Thus, test methods being developed at other laboratories based on peroxide monitoring probably will yield false results.

[20c] Project: Heavy Oil Processing. B&R No. -05-15. Staff. Project Manager, D. W. kman; Branch Chief, F. D. Sutterfield.

[21c] Project: Stability Characteristics of Hydrocarbon Fuels. B&R No. AB-05-10. Staff: Project Manager, D. W. Brinkman; Branch Chief, F. D. Sutterfield.



Laboratory work is being performed at BETC as part of studies to develop an improved storage stability test technique for representative hydrocarbon fuels. Here, Dennis Brinkman, project manager for processing, removes a sample of 2,5-dimethylpyrrole in n-dodecane from an aging oven. This sample was aged for 14 days at 80° C in the ovens to simulate actual long-term ambient storage. Temperature monitors closely record interior oven temperature.



Aged samples are then filtered, and the material on the filters is carefully analyzed to determine the degree of fuel degradation.

One of the innovations that the NRL is working on is increasing the temperature at which aging of the fuel samples takes place in order to decrease the time required. While this has been tried in the past, only now have the experimental procedures become refined enough to permit demonstration of correlations between runs at different conditions. Thus far, we have been able to advance from the commonly accepted 43°C (110°F) to 80°C with good correlation of results. Work is beginning on a 100°C test.

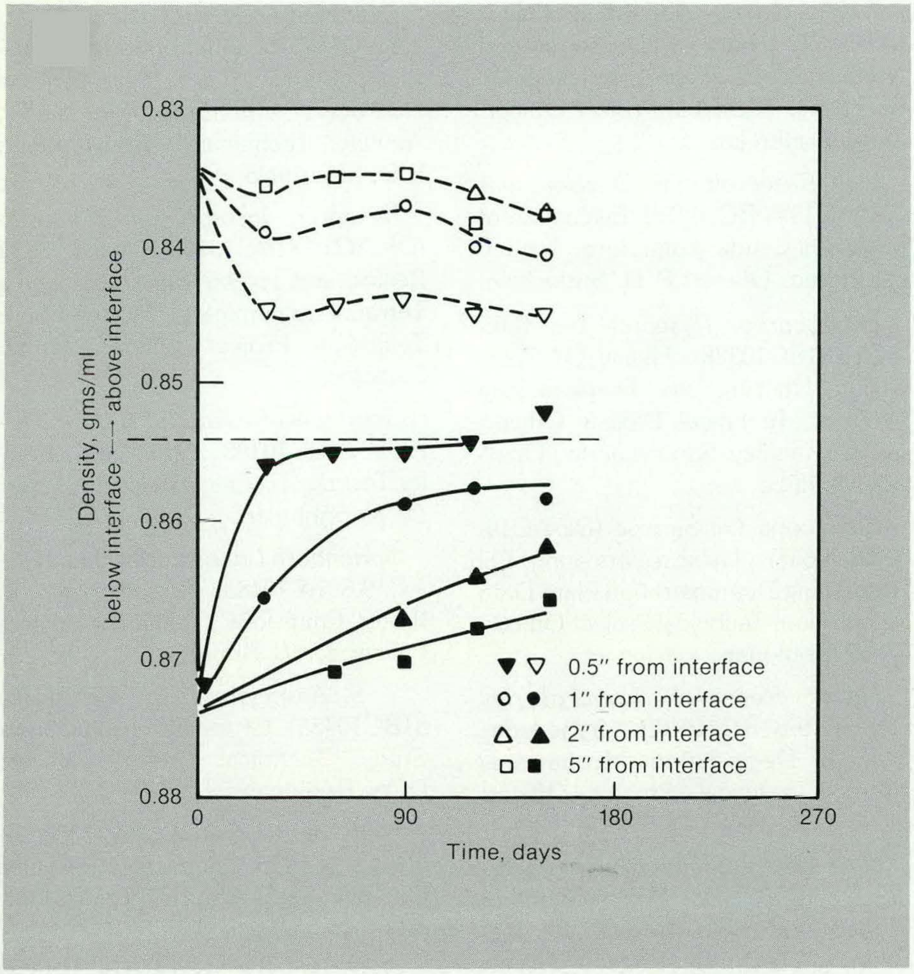


FIGURE C5. *Change in densities of two crude oils at various levels over time.*

Figure C4 shows a series of test results at various concentrations of 2,5-dimethyl pyrrole (designated as nitrogen equivalent concentration) for various aging times at 80°C. The computer-generated least-squares quadratic curves show that the rate of sedimentation begins to decrease at longer times, as would be expected due to depletion of the reactive species. The shale-derived marine diesel fuel used in this case had antioxidant present. As the figure shows, the addi[illegible] did little to prevent significant de[illegible]t formation.

Experimental work now is being focused on a series of nitrogen compounds to study further the relationship between various structural features and the tendency for gum formation. This part of the project probably will include compound synthesis, where specific combinations of features are not commercially available. In addition, attempts are being made to produce data accurate enough to permit reliable nitrogen balance calculations.

New shale liquid samples have been obtained by the Southwest Research Institute for use in its development of stability test procedures for syncrudes. The samples are intermediate materials from the Ashland Petroleum Company's Phase III refining contract with the Air Force, in which Occidental crude shale oil was upgraded. In conjunction with the various coal liquid samples available, these shale liquids will give us a good basis for evaluating the various test methods being developed.

Crude Oil Stratification Study[22c]

The DOE Strategic Petroleum Reserve Program has a goal of storing up to a billion barrels of crude oil underground over prolonged periods for potential use during unexpected supply interruptions. Since many crudes of differing properties are stored together, it is important to know how much mixing occurs and related effects. Detailed characterization of the crudes before and after mixing should provide insight into long-term storage effects.

A study looking specifically at the extent of mixing of two different crude oils is being carried out under contract by T. S. Associates, Inc. As described last quarter, the study involves two crude oils carefully introduced into a large container such that the experiment began with total stratification. Figure C5 shows how the densities have changed at various levels over time. As can be seen, the lower oil seems to be undergoing a smooth, monotonic change, while more complex actions are involved in the upper oil. It is assumed this difference is related in some way to gravity-induced factors.

[22c] Project: Strategic Petroleum Reserve Supporting Research. Staff: Project Manager, D. W. Brinkman; Section Chief, P. W. Woodward.

A recent modification of this research contract will permit the monitoring of more properties of each sample. Preliminary data support the theory that different compounds will diffuse at different rates rather than the two oils acting like two uniform liquids in a simple binary diffusion process. Detailed analyses now will be done for sulfur and vanadium, in addition to the routine density and viscosity measurements. The duration of the experiment has been increased from 180 days to 300 days to permit several sets of these additional samples to be taken at 1-month intervals. At the end of the tests, detailed diffusion-rate calculations will be performed for all types of species monitored.

Contracts. Contracts supporting Processing Technology are listed below:

Booth Oil Co. (DE-AC19-81BC10562). Used Lubricating Oil Refining Demonstration Plant Data Acquisition. Technical Project Officer: D. W. Brinkman.

ENTEC Research Associates, Inc. (DE-AC19-81BC10450). Specific Heavy Oil Processing Market Study. Technical Project Officer: D. W. Brinkman.

GCA Corp. (DE-AC19-81BC10375). The Fate of Hazardous and Nonhazardous Wastes in Used Oil Recycling. Technical Project Officer: D. W. Brinkman.

Gulf Research and Development (DE-AC19-80BC10313). Evaluation of Shale Oil-Crude Admixture. Technical Project Officer: F. D. Sutterfield.

Hydrocarbon Research, Inc. (DE-AC19-81BC10328). Heavy Oil Processing Utilizing the Dynacracking Process. Technical Project Officer: G. W. Standley, San Francisco Operations Office.

Lakewood Oil Service (DE-AC19-81BC10658). Used Lubricating Oil Re-refining Demonstration Plant Data Acquisition. Technical Project Officer: D. W. Brinkman.

Naval Research Laboratories (DE-AI19-81BC10525). Syncrude/Synfuel Degradation Mechanisms Study. Technical Project Officer: D. W. Brinkman.

New Mexico State University (DE-AS19-80BC10332). Deactivation of Hydrotreating Catalyst in Re-Refining. Technical Project Officer: D. W. Brinkman.

Oklahoma State University (DE-AS19-80BC10306). Kinetics of Hydrogenation of Alternate Crude Oil. Technical Project Officer: F. D. Sutterfield.

Oklahoma State University (DE-AS19-81BC10465). Extended Analyses of Crude and Hydrogenated Hydrocarbon Mixtures for Mutagenic Activity. Technical Project Officer: F. D. Sutterfield.

Research Institute of Colorado (DE-AC19-81BC10446). Upgrading of Resids and Heavy Ends Utilizing a Tetrachloroaluminate Molten Salt. Technical Project Officer: F. D. Sutterfield.

Southwest Research Institute (DE-AC19-80BC10188). Syncrude Stability Testing. Technical Project Officer: D. W. Brinkman.

Springborn Laboratories, Inc. (DE-AC19-80BC10183). Recycling of Oil-Water Emulsions. Technical Project Officer: D. W. Brinkman.

T. S. Associates, Inc. (DE-AC19-81BC10435). Crude Oil Stratification Study. Technical Project Officer: D. W. Brinkman.

UOP, Inc. (DE-AC19-78BC00045). Effects of EOR Chemicals on Crude Oil Refining. Technical Project Officer: F. D. Sutterfield.

UOP, Inc. (DE-AC19-81BC10453). Heavy Oil Processing Utilizing the Aurabon Process. Technical Project Officer: G. W. Standley, San Francisco Operations Office.

Walk, Haydel & Associates, Inc. (DE-AC19-81BC10349). Heavy Oil Process Engineering Review and Assessment. Technical Project Officer: D. W. Brinkman.

Utilization

Division Director: T. V. de Palma

SECTION D

ENERGY CONVERSION

The Liquid Fossil Fuel Cycle (LFFC) encompasses all of the various uses of liquid fuels; most of BETC's liquid fuels research on utilization deals with the transportation sector. Over the years, the BETC program has had two thrusts: (1) more effective use of fuels in present engines, and (2) use of synthetic fuels in present engines.

Reacting to the LFFC concept, a new approach—that of adapting processing methods and engines to give an optimal balance—has been taken. Projects investigate whether engines and processing methods can be varied to match fuels and engines to give a more efficient use of synthetic fuels, with overall energy savings.

More specific issues are also approached, usually at the request of another government agency. A study of the effects of diesel exhaust is sponsored by the Office of Energy Research. The study of the use of alcohol in farm machinery was requested by the DOE Alcohol Fuels Office.

ADAPTIVE ENGINEERING

Advanced Processing Technology Fuels Utilization[1d, 2d]

The purpose of this study is to provide information on fuels and engines interactions for use in the selection of synfuel product specifications. An evaluation is being conducted into the effects of fuel physical properties characteristic of coal- and shale-refined fuels.

Research plans for the current fiscal year include: (1) a determination of the effects of fuel-bound nitrogen on exhaust emission products, and (2) an examination of the separate effects of diesel fuel cetane number, aromaticity, and hydrogen-carbon ratio (H/C).

Efforts this quarter concentrated on the examination of fuel-bound nitrogen combustion effects.

Coal- and shale-derived products contain significant quantities of organically bound nitrogen. Tests have been made using several nitrogen-containing compounds of varying molecular structure; both tight and loose nitrogen/fuel bondings are represented. These compounds are representative of those found in fossil fuels.

In addition to earlier experiments with octyl nitrate, tests have been made with quinoline, octyl amine, pyridine, and aniline added in varying amounts to the reference No. 2D diesel fuel. Three different fuel-nitrogen levels were examined for each compound (0.04, 0.08, and 0.24 wt-pct nitrogen). Duplicate tests with each fuel are being made with an Oldsmobile 350-CID compression ignition engine coupled to a transmission and flywheel system and installed on an engine dynamometer. The system was designed for cyclic tests, in this case, hot-start Federal Test Procedure cycle.

Results indicate somewhat higher nitrogen to NO_X conversion efficiencies for octyl nitrate and quinoline than for the other compounds. Conversion efficien-

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[1d] Project: Advanced Processing Technology—Fuels Utilization. B&R No. AC-05-10-00-0. Staff: Project Leader, J. R. Allsup; Mechanical Engineer, R. N. Wares; Research Chemist, F. W. Cox. See also footnote 2d.

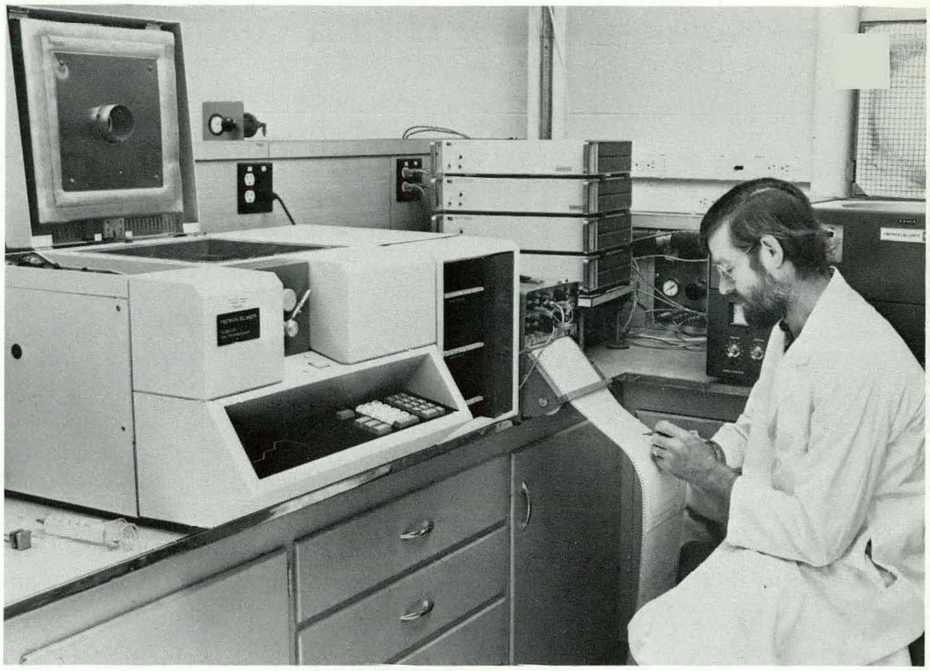
[2d] Personnel used on projects as needed: Supervisory Mechanical Engineering Technician, T. R. Owens; Mechanical Engineering Technicians, C. W. Beazer II and J. A. Tyler; Electronics Technicians, J. L. Cary, J. D. Newton; Physical Science Technician, S. J. Golemon; Physical Science Aide, T. A. Shaw; Engineering Aide, D. J. Johnson; Instrument Mechanic, J. D. Nichols.

cies range from about 20 to 35 percent. For the most part, fuel economy and regulated emissions were unaffected by the additives. Additional tests are scheduled using pyrrole and indole. Comparative experiments using constant nitrogen level blends of diesel fuel and coal-derived liquids will also be made.

Diesel Particulate Emissions[3d]

The objectives of this study are to: (1) obtain a data base of gaseous and particulate emissions and fuel economy data from current production light-duty vehicles, (2) collect particulate samples from a light-duty diesel vehicle fueled with mixtures of alcohol and diesel fuel, (3) collect particulate samples for Ames testing at Lovelace Inhalation Toxicology Research Institute, and (4) characterize particulate extractables for the purpose of identifying those species in the extract which are mutagenically active.

The characterization studies of the diesel particulate extract have concentrated on chromatographic separation of the extract into fractions which have been Ames-tested. The Ames-test data have been used to select the fractions to be used in a study to identify the species or class of species which are mutagenically active. Typically, the concentration level of the mutagenically active species ranges from less than 1 ppm to about 50 ppm; therefore, large quantities of particulate are required for characterization studies of this type.



After characterizing diesel particulate extracts with a liquid chromatograph as part of a preliminary study to determine how many different types of organic nitrogen components are found in these extractions, Frank Cox, research chemist, checks the chromatograph readout. The readout gives the results of the test, showing the retention times for organic nitrogen-containing compounds extracted from diesel emissions.

The diesel particulate extract has been separated chromatographically into 22 different fractions using successive separation techniques. About 90 percent of the samples' biological activity is concentrated in five of the samples' fractions. Two of these fractions are known to contain nitro and dinitro polycyclic aromatic hydrocarbons, such as nitro and dinitropyrenes. The identification of the remaining fractions is under investigation.

COMBUSTION SYSTEMS ASSESSMENT

Alternative Fuels Data Bank[4d]

The Alternative Fuels Data Bank continues to provide technical information about utilization of alternative fuels to the technical community. The system is currently being accessed remotely via computer telecommunications link by about 100 users a month. Users are about evenly divided among three groups—government, academic, and industry research and consulting.

Recent BETC staff cutbacks have resulted in initiation of a contract to provide technical assistance for evaluation and preparation of synopses of published information. The on-going research and topic portions of the system continue to be wholly maintained by the BETC staff.

Evaluation of Ethanol Use in Diesel Engines for Farming Applications[5d]

A program funded by DOE's Office of Alcohol Fuels is underway to evaluate the use of ethanol for farming applications.

The program has evaluated the potential of various alcohol fuel induction systems, including f[illegible]ation, chemical emulsions, mechanical emulsions, and straight alcohol with

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[3d] Project: Diesel Particulate Emissions. B&R No. GK-01 02-04-3. Staff: Project Leader, J. R. Allsup; Research Chemists, D. B. Eccleston, D. E. Seizinger. See also footnote 2d.

[4d] Project: Alternative Fuels Data Bank. B&R No. C5-01-03-01. Staff: Project Leader, J. R. Allsup; Data Transcriber, C. Morrison.

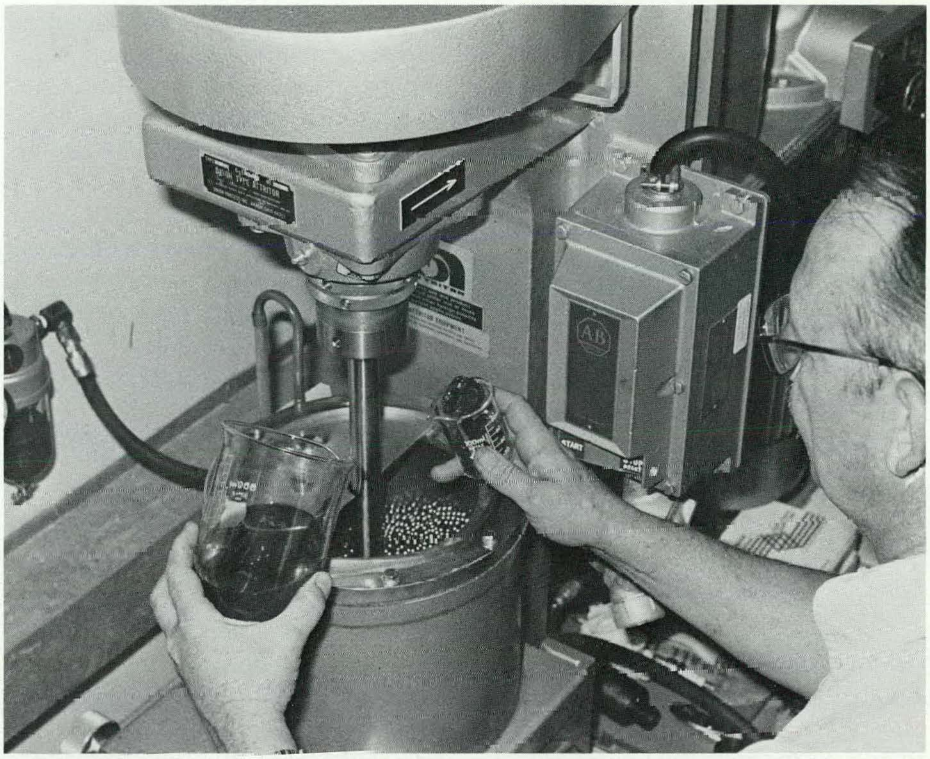
[5d] Project: Evaluation of Ethanol Use in Diesel Engines for Farming Applications. B&R No. AN-05-15. Project Leader, J. R. [illegible]p; Chemical Engineer, J. M. Clingenpeel. See also footnote 2d.

cetane and lubricity improvers. Extensive experimental data have been generated about emissions and combustion efficiency of several farm-type diesel engines using various ratios of diesel fuel in combination with 160- to 200-proof ethanol. The data suggest that 25 to 50 percent ethanol can be used with diesel fuel at essentially the same thermal efficiency as straight diesel fuel, without major emission problems.

An engine durability program is underway via contract with Southwest Research Institute, San Antonio, Texas, to investigate the effect on engine life expectancy of using 25 percent ethanol (160-proof) in diesel fuel. The program involves a 500-hr engine durability cycle using three farm engines.

Preliminary results suggest premature engine failure occurs when a mechanically emulsified fuel system is used. It appears that the injection system does not maintain adequate spray patterns—resulting in alcohol impinging upon the cylinder walls and removing the lubricant, which leads to excessive ring and cylinder wear.

Preliminary results also suggest that a fumigation system—wherein the alcohol is introduced into the intake air stream rather than through the fuel injection system—results in only normal wear rates. The three test engines are being dismantled and inspected to determine exactly the amount of wear that took place during the test cycle.



Jim Clingenpeel, chemical engineer, adds the ingredients to produce a coal slurry to be tested in BETC laboratory work to discover which coal slurry fuels might be suitable for use in diesel engines.

HEAT ENGINES/HEAT RECOVERY

Coal Liquid Fuel/Diesel Engine Operating Compatibility[6d]

The objective of this project is to assess the capability for using solid particles of coal in slurry as a fuel in diesel engines and to determine related problem areas where additional work is required.

The project approach is a three-level screening process.

First, a set of approximately 200 unique slurry fuels will be appraised for their combustion potential. Table D1 lists the variables to be considered in the selection of the fuels.

Second, a set of 20 fuels will be selected from those in the first step, and they will be examined further in a single-cylinder research engine for an approximate 2-hr test in which the effects of controlled parameters will be measured and an assessment of the degree of wear with each fuel will be made.

Third, extensive tests will be done with four fuels selected from the second step. Tests will involve detailed, precise engine experimental work—including emissions and particulate

This closeup shows details of the fuel combustion assessment rig being used in the first step of the coal slurry fuel screening process.

[6d] Project: Coal Liquid Fuel/Diesel Engine Operating Compatibility. B&R No. AA-55-10-05. Project Manager, M. D. Gurney; Chemical Engineer, J. M. Clingenpeel; Mechanical Engineer, R. N. Wares; Research Chemists, F. W. Cox, D. B. Eccleston and D. E. Seizinger. See also footnote 2d.

TABLE D1. *Key Variables of Coal Slurry Fuels*

Coal Type
- Cleaned
- Noncleaned
- Processed

Slurry Carrier
- No. 2 diesel fuel
- Methanol
- Water

Coal Sizes
- 2 to 5 microns, upper limit 7 microns
- 15 microns, upper limit 20 microns
- Blends of the two sizes

Ash Content, weight-percent
- Varies from 0.1 to 8

Coal Concentration
- Varies in periodic steps to the maximum and still has fuel-pumping characteristics.

determination, with wear quantified. Additional work on the investigation of diesel engine fuel injector response to coal slurry fuels will be performed on a maximum of four slurry fuels.

The combustion of the fuels in the first step will examine the effects of several different conditions. A fuel combustion assessment rig has been developed that will allow the turbulence to be varied, the wall temperature to be controlled up to 500°F, the selective use of pilot injection, the selective use of a heat source within the chamber, combustion to occur with either air or oxygen at initial pressures up to 30 atmospheres, different main injectors, and the use of a prechamber and direct injection.

A matrix of these parameters will be selected for each of the first-step fuels. The fuels will be burned, and the combustion pressure, flame speed, and temperature will be monitored. In addition, the gaseous combustion products will be examined to determine completeness of combustion.

The second step will determine the potential of the fuels' combustion in a single-cylinder research engine, with the fuels being generated as the test progresses. Engine parameters of power, load, and rpm will be varied with specific fuel consumption, and the gaseous emissions of NO_X, HC, CO_2, CO, O_2, and smoke will be monitored. Wear will be determined by measuring loss of material on the cylinder liner, rings, and piston for each fuel, and a tear-down and inspection will be made. In addition, special liners will be used that incorporate the wear-resistant materials representing the state of the art in coatings.

A separate noncombustion fuel-handling system is being fabricated, and the 20 fuels each will be circulated through it to examine wear on pumps, injectors, and associated components. This step is crucial since previous experimenters have reported numerous problems with fuel-system components when coal slurries were used.

The third step will use a precision research test engine representative of medium-output engines. It will be modular to allow for rapid component/design effects such as: the head, prechamber versus direct, piston design, compression ratio, and fuel system modifications. It will allow for operational changes while the engine is firing—in speed, load, timing, exhaust gas recirculation, water injection, intake air temperature, intake fuel temperature, intake air pressure, and dual fueling. It will allow for flame diagnostics, with viewing windows and probe access ports. Performance parameter effects will be analyzed along with combustion gases and particulates. An engine tear down after the use of each fuel for approximately 20 hours will provide precise wear information. A request for proposals for this work has been issued.

The injector work will consist of studies and experimental evaluation and analysis of existing or published injector/fuel system designs. Innovative approaches toward solving the problems are included and, within funding limits, new designs and component fabrication will be performed. A request for proposal is being prepared for this work and is expected to be released soon.

Coal Liquid Work. Work is concluding on the use of three coal liquids (SRC-II middle distillate, H-Coal, and Exxon Donor Solvent). The results will be distributed shortly after the final reports have been published.

Contracts.

A. D. Little, Inc. (DE-AC19-79BC-10109). Coal-Derived Liquids/Diesel Compatibility. Technical Project Officer: M. D. Gurney.

General Electric Co. (DE-AC19-79BC10110). Coal-Derived Liquids/Diesel Compatibility. Technical Project Officer: M. D. Gurney.

United Technologies Research Center (DE-AC19-81BC10495). Electronically Controlled Fuel Injection System for Alternative Diesel Fuels Program. Technical Project Officer: M. D. Gurney.

Project Integration & Technology Transfer

Division Director: R. L. Folstein

SECTION E

PLANNING AND ENVIRONMENTAL INTEGRATION[1e]

Planning

Work continued on the preparation of a summary report of the program modeling project. The first step, which basically was concerned with the development of a simple model for illustrative purposes, is completed. The model is currently being reviewed in preparation for computerization.

International Activities

On June 16, 1982, a status briefing on the United States/Venezuela cooperative projects was held at the Bartlesville Energy Technology Center. Attending from Venezuela were Evanan Romero, vice president, and Frank Ashford, manager of petroleum engineering, for INTEVEP—the Venezuelan Petroleum Institute. This meeting provided an opportunity for discussion of the cooperative program in some technical detail, a demonstration of the capability of BETC's Enhanced Oil Recovery Data Base, exploration of the capability of new BETC mass spectrometer equipment, and consideration of future cooperation in microbial EOR.

Romero made a presentation describing the INTEVEP organization, activities, and future. The six cooperative projects reviewed included: joint characterization of heavy crude oils; supporting research at universities, energy technology centers and national laboratories; EOR thermal processes; drilling, coring and telemetry; residual oil saturation; and petroleum products utilization and evaluation.

Environmental Integration

The objectives of the Environmental, Safety and Health (ES&H) unit are: consolidation and dissemination of ES&H requirement information to BETC personnel, other government agencies, industry, and the public; coordination of BETC's ES&H activities; mitigation of environmental constraints on technology development, and transfer of new ES&H technology.

The project being performed for BETC by Gulf Universities Research Consortium to identify and assess water issues as they relate to EOR is continuing. During the quarter, a study was conducted at the University of Oklahoma School of Law to examine the law as it relates to water rights and to establish procedures for obtaining water rights for each state in which EOR is expected to play a major role in future oil production. **The information being compiled will assist oil producers by providing a guide to steps required in acquiring rights for use of both surface water and ground water in EOR operations.**

TECHNOLOGY TRANSFER[2e]

Oklahoma Well Log Library

BETC maintains an open file of Oklahoma drillers' well logs; this is in cooperation with the Oklahoma Corporation Commission, which furnishes the logs. The State of Oklahoma provides funding for a library aide to maintain the file. About 350,000 logs are now on file for onsite use by the public. During the April–June quarter, the well log library performed the following functions:

Visitors using the file	296
Well logs copied	5,326
Well logs received and filed	4,037
Publications distributed	105

[1e] Project: Planning and Environmental Integration. Staff: Branch Chief, M. Olson; Physical Science Analysts, R. H. Castellano and R. F. Kendall.

[2e] Project: Technology Transfer. Staff: Branch Chief, C. C. Linville; Information Specialist, J. R. Lindley; Editorial Assistant, David Fuqua; Library Technician, M. R. Marak; Library Aide, Charlotte Stock; Records Management Officer, A. R. Silva.

Library

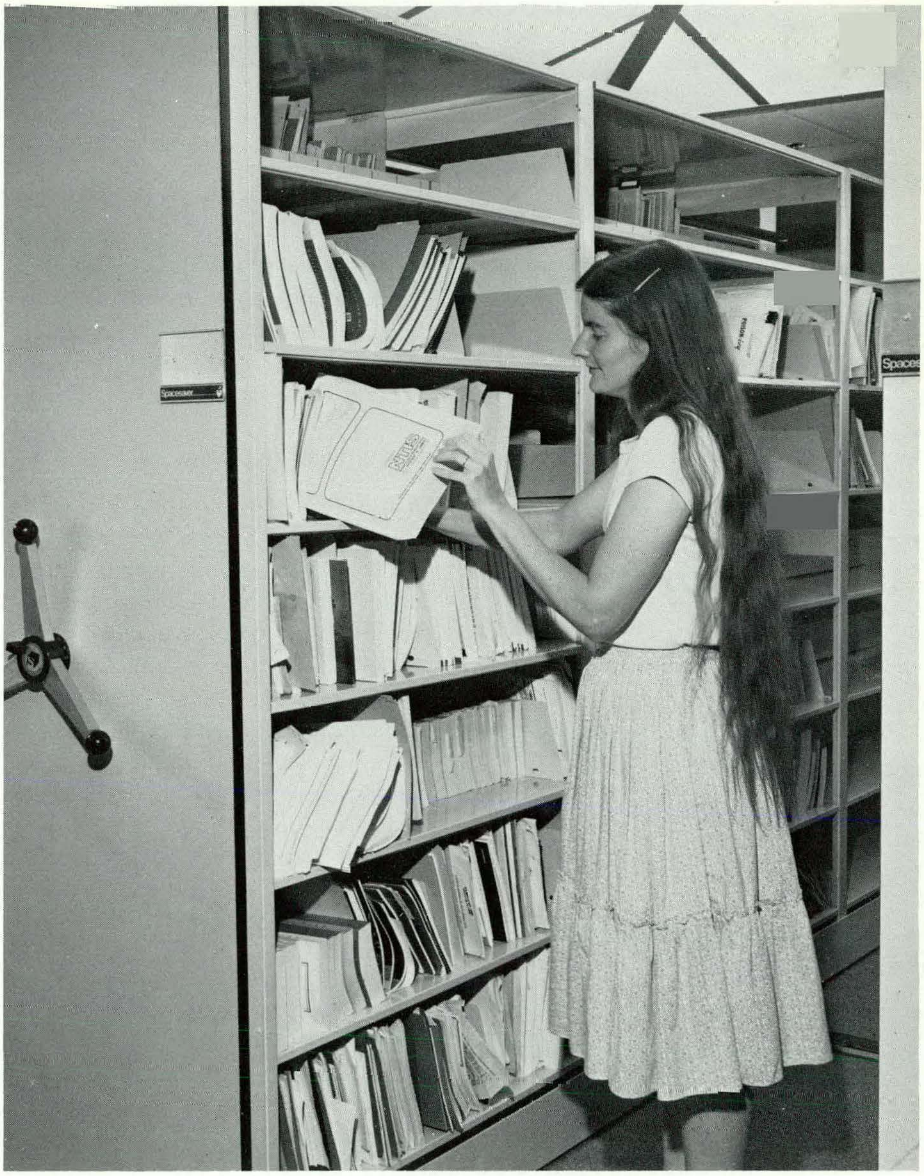
The BETC Library provides technical information to the research and administrative staff at the Center and is open to the public. Heavy use is made of the Library's 20,000 volumes and of its communications network with other libraries across the nation.

On-line bibliographic data base searching is available to the Center's staff; more than 100 data bases are available for searching, including those in the Department of Energy's RECON system. The Library is a member of OCLC, a nationwide consortium of libraries; a linkup with OCLC's computer allows the Library staff to locate and obtain material for interlibrary loans and allows speedy cataloging of new material.

Although the primary mission of the Library is to provide service to the BETC staff, Library personnel also answer information requests from outside the Center.

The Library's activities for the quarter are summarized as follows:

Acquisitions	
Books	11
BETC publications	27
Other government agency and society reports	370
Interlibrary Loans	
Requested by BETC	74
Requested of BETC	109
On-line Searching	
Search sessions	22
Data bases searched	12



The BETC library was moved this quarter to the basement of the new south wing addition to the administration building. One of the features of the new facility is the compact shelving. Here, Charlotte Stock, library aide, locates a journal in the moveable stacks, which are being stocked with reference materials.

Report Distribution

A total of 38,415 technical reports and publications were distributed during the quarter, a large increase over the previous quarter, due in part to the 8,500 reports distributed at the Society of Petroleum Engineers/Department of Energy (SPE/DOE) Joint Symposium on Enhanced Oil Recovery held in Tulsa in early April. **The number of reports distributed in fulfillment of requests received by mail and telephone increased by about 5,000 from the previous quarter.** Table E1 shows the types of distribution, and Table E2 classifies the requestors by segment of the industry.

TABLE E1. *Distribution of Reports from BETC; April–June, 1982*

Response to 3,009 mail and telephone requests	4
Distribution to mailing lists	12,535
Organizational distribution (DOE internal)	6,036
Distribution at SPE/DOE Symposium	[illegible]
Total for April–June	[illegible]

TABLE E2. *Total Reports Distributed to Various Groups of Individuals Requesting Reports by Mail or Telephone*

Consultants (engineering, geological, research and management)	2,490
Major and Integrated Oil Companies	2,377
Independent Oil Companies	1,487
Service and Supply Companies (to petroleum industry)	1,353
Academic	684
Foreign Oil Producers	487
Miscellaneous or Unidentified	2,466
Total	11,344

Report Production

Three quarterly reports were compiled and prepared for printing. *Liquid Fossil Fuel Technology* for January-March 1982, *Progress Review No. 30 on Enhanced Oil Recovery and Improved Drilling Technology,* for the same period, and *Western Gas Sands Project Status Report,* for October-December 1981. Publication Lists for March, April, and May were published and distributed. The proceedings for the 1982 Annual Heavy Oil/EOR Contractor Presentations was compiled as a bound volume from individual papers submitted by the contractors.

Abstracts of papers were compiled and published as the program for the International Conference on Oil Recovery by Microbial Technology held near Afton, Oklahoma, May 17-20.

A supplement to the Proceedings of the Joint SPE/DOE Symposium on Enhanced Oil Recovery was prepared for publication. The supplement will contain papers presented at the general-interest opening session and the evening session on advanced EOR technology.

During the quarter, 131 reports were reviewed, edited, and prepared for publication or distribution, including 10 in-house reports.

Meetings

The Third Joint Society of Petroleum Engineers/Department of Energy Symposium on Enhanced Oil Recovery was held in Tulsa April 4-7. The opening session was highlighted by a speech given by Governor George Nigh of Oklahoma. J. W. Mares, assistant secretary for Fossil Energy, DOE; E. J. Lievens, Jr., then acting director of the Office of Oil, Gas and Shale, DOE; Kye Trout, chairman of the Independent Petroleum Association of America (IPAA); and T. Don Stacy, president-elect of the Society of Petroleum Engineers, also spoke. Harry Johnson, then BETC director, was general chairman for the symposium. The record registration of more than 2,300 included 160 participants from 15 foreign countries.

The International Conference on Microbial Enhancement of Oil Recovery at Afton, Oklahoma, May 16-21, was co-sponsored by BETC, and the University of Oklahoma, and the Engineering Foundation. The attendance of 140 included 32 scientists from 12 foreign countries, most of whom gave reports on research in their countries. E. C. Donaldson of BETC and J. Bennett Clark of Phillips Petroleum Co. were co-chairmen. Another conference is planned for 1984.

Two fossil energy research seminars were given at BETC during the quarter. On April 14, Leonard C. Axilrod, vice-president for technology and engineering of the Synthetic Fuels Corporation, presented a seminar on “The Current Status of the Synthetic Liquid Fuels Corporation.” Prof. Richard K. Pefley of the mechanical engineering department of the University of Santa Clara spoke May 5 on “Alcohols as Alternative Transportation Fuels—A Status Report.”

Exhibits

An exhibit at the Third Joint SPE/DOE Symposium on Enhanced Oil Recovery in Tulsa April 4-7 featured BETC technical reports. Some 8,500 copies of BETC publications were distributed at the symposium.

Public Affairs

Radio presentations were made by Fred Burtch, Dexter Sutterfield, and Q. Grindstaff as a regular monthly feature of Bartlesville station KWON. Fifteen announcements of general interest were distributed to the media during the quarter.

BETC Publications

Bartlesville Energy Technology Center
EDWARD J. LIEVENS, JR., *Acting Director*

APRIL-JUNE, 1982

AVAILABILITY OF PUBLICATIONS

Application for free reports should be made to:

Bartlesville Energy Technology Center
Attention: Technology Transfer Branch
P.O. Box 1398
Bartlesville, OK 74005
(918) 337-4316
FTS 735-4316

With the exception of this publications list and the three quarterly research publications, Liquid Fossil Fuel Technology, Enhanced Oil Recovery and Improved Drilling Technology, *and* Western Gas Sands Project Status Report, *the Bartlesville Energy Technology Center no longer automatically distributes technical reports and publications to mailing lists. You must now select the reports of interest to you and make specific application for them. Reports will be furnished free as long as the supply lasts, but only one copy of any report and a maximum of 10 titles per order can be furnished. Please request only those publications needed, order by the report number listed at the beginning of each citation, and enclose a self-addressed mailing label.*

If you need more than one copy of an individual report or more than 10 separate titles, you can obtain these from the National Technical Information Service (NTIS). You can obtain the cost of the reports of interest by contacting NTIS, 5285 Port Royal Road, U.S. Department of Commerce, Springfield, VA 22161; telephone 703-487-4650. Give the full title of the report and the report number.

GENERAL RESEARCH

Quarterly Reports

DOE/BETC/QPR-81/4. Liquid Fossil Fuel Technology. Quarter ending December 31, 1981. Edited by Bill Linville. April 1982. 76 pp. Progress reports on research, development, and demonstration projects conducted by Bartlesville Energy Technology Center personnel and contractors are given, with emphasis on liquid fossil fuel projects. Reports are included from BETC's Divisions of Extraction Research, Processing and Thermodynamics Research, Utilization Research, and Project Integration and Technology Transfer.

Enhanced Oil Recovery—General

CONF-8110160. The Impact of Geologic Parameters on Enhanced Oil Recovery—Workshop Proceedings, Oct. 15-16, 1981, Camelot Hotel, Tulsa, Oklahoma. Bartlesville Energy Technology Center. This DOE-sponsored workshop was designed to bring together geologists and engineers from industry, academia, and government to discuss the importance of the reservoir in enhanced oil recovery operations. Recommendations were made that some research efforts be directed toward interactions between EOR fluids and the reservoirs. There is also a need for geological studies of both micro- and macro-reservoir heterogeneities, especially the lithologic, petrographic, and stratigraphic parameters. Results from the following workshop groups are included in the report: rock-fluid interactions, reservoir heterogeneity, reservoir description, and geologic input into EOR simulation techniques.

DOE/BC/10033-1. Review of Statistical Methods Used in Enhanced Oil Recovery Research and Performance Prediction. BDM Corp. June 1982. 82 pp. Recent literature in the field of enhanced oil recovery was surveyed to determine the extent to which researchers in EOR take advantage of statistical techniques in analyzing their data. This study also aimed at promoting, by example, the greater use of these tools. The results of the survey are grouped by statistical technique and include brief descriptions of each of the 21 relevant papers.

DOE/BETC-82/1. Contracts for Field Projects and Supporting Research on Enhanced Oil Recovery and Improved Drilling Technology. Progress Review No. 29, Quarter ending December 31, 1981. Edited by Bill Linville. May 1982. 160 pp. Status reports are given of various enhanced oil and gas recovery projects sponsored by the Department of Energy. The field projects and supporting research on enhanced oil recovery include chemical flooding, carbon dioxide injection, thermal/heavy oil recovery, microbial recovery,

DOE/BETC/RI-82/5. Enhanced Oil Recovery Injection Waters. A. G. Collins and C. C. Wright. April 1982. 86 pp. Oilfield waters occur with petroleum in reservoirs in sedimentary basins. This report discusses the occurrence, origin, evolution, chemical and physical properties, and sampling and analysis methods of oilfield waters with respect to importance in enhanced oil recovery technology. The discussion covers the types of injection waters used in enhanced oil recovery, plus some of the problems associated with injection waters, such as compatibility, clay sensitivity, corrosion, and bacteria.

Enhanced Oil Recovery—Chemical

DOE/BC/00047-19. Development of Improved Mobility Control Agents for Surfactant/Polymer Flooding, Final Report. New Mexico Petroleum Recovery Research Center. June 1982. 106 pp. The goal of the laboratory work in this project was to develop mobility control agents that are more effective than the polymers currently used in surfactant/polymer flooding operations. During the final year of the project, the preliminary screening tests were completed and polymers of interest were evaluated in more detail. This report contains highlights of the significant accomplishments of the project and presents conclusions regarding the development of improved mobility control agents.

DOE/BC/10068-23. Interfacial Effects in the Recover [illegible] Residual Oil by Displacement, Final Report. Northwestern University. April 1982. 32 pp. The goal of this study was to determine the relative effects of the interfacial viscosities, interfacial tension, wetting, and contact angle hysteresis on the recovery of residual oil by displacement. The first studies determined the relative effects of these factors on displacement within single pores. When the ir[illegible]ial tension is less than the critical value required for displacement [illegible]he interfacial viscosities are large, it is equally important to reduce both the interfacial tension and the interfacial viscosities. This work was then extended to permeable media. The initial tests performed on steady-state dis[illegible]nents were extended to unsteady-state displacements, where the [illegible] t of the interfacial viscosities upon capillary pressure can be seen. The third portion of the work focused on confirming the reality of the surface viscosities and developing new techniques for measuring the surface shear viscosity. A complete analysis was developed for the thin biconical bob interfacial viscometer, which was found to be consistent with other surface techniques and may be the best viscometer currently available for measuring the interfacial shear viscosity at liquid-liquid interfaces.

DOE/BC/10082-8. **Adsorption from Flooding Solution in Porous Media, A Study of Interactions of Surfactants and Polymers with Reservoir Minerals, Second Annual Report.** Columbia University. April 1982. 230 pp. Past studies on the interaction of sulfonates with dissolved inorganics showed that sulfonates precipitated by multivalent ions can undergo redissolution upon increasing either the sulfonate or NaCl concentration. Since the phenomenon of redissolution can be beneficially used for minimizing the surfactant loss due to precipitation, investigation of this phenomenon was continued during the second project year. The objectives were to develop a quantitative understanding of the molecular mechanisms involved and to formulate a model with predictive capabilities for the precipitation behavior of surfactant/inorganic ion systems. Towards this purpose, precipitation/redissolution/reprecipitation behavior of sulfonates was studied as a function of relevant variables, including surfactant and salt concentration, surfactant chain length, alcohol and oil concentration, and temperature.

DOE/BC/10321-5. **Improved Polymers for Enhanced Oil Recovery Synthesis and Rheology, Fourth Annual Report, October 1980–September 1981.** University of Southern Mississippi. June 1982. 282 pp. Studies on the fundamental mechanisms of enhanced oil recovery have been performed in order to gain a more complete understanding of the structure/property/performance interrelationships of water-soluble polymers. Improved polymers can be designed from an understanding of concepts relating macromolecular structure to performance under controlled conditions, and this can lead ultimately to commercial production of polymers that are more efficient than those currently used. Therefore, these studies have cen-

DOE/BETC/RI-82/7. **Silica Gel as a Model Surface for Adsorption Calorimetry of Enhanced Oil Recovery Systems.** L. A. Noll and T. E. Burchfield. June 1982. 52 pp. This report describes a method for studying interaction of fluids with surfaces by measuring the heat of immersion and then measuring simultaneously the surface excess and enthalpy of replacement for a series of binary solutions. The method of calculating surface excess is described. These techniques are applied to silica gel which has had different activation temperatures. Heating overnight to 400°C results in a reproducible surface. The adsorption of n-butyl alcohol from toluene and from water upon these surfaces is compared.

DOE/ET/12065-52. **Enhanced Oil Recovery by Improved Waterflooding, Fourth Annual Report, Oc[illegible]r 1980–September 1981.** Energy Resources Co., Inc. May 19[illegible] pp. A 100-acre pilot polymer flood is being conducted in the Storms Pool Field near Carmi, in White County, Ill. The Storms Pool, typical of many old fields in the Illinois Basin that are candidates for enhanced oil recovery, was once highly productive and has yielded more than 12 million barrels of oil since its discovery in 1939. This fourth annual report di[illegible]s the preflush injection and polymer injection initiated during this pe[illegible] Total polymer injection stands at 179,453 barrels (about 6 percent pore volume). Laboratory testing emphasized troubleshooting field problems and monitoring the field injection and production systems. No evidence of polymer breakthrough was detected at the production wells. Details of the interference testing program and the radiotracer study are presented in this report, along with a diagram of the injection and production facilities as they stand after design refinements.

DOE/ET/13070-79. **El Dorado Micellar-Polymer Demonstration Project, Seventh Annual Report, September 1980–August 1981.** Cities Service Co. June 1982. 588 pp. This project is aimed at determining the economic feasibility and the associated benefits and problems of improved oil recovery using the Union Oil soluble-oil-flood micellar-polymer process. During this project year, polymer solution was injected into two patterns. Produced and injected fluid analyses continued, and samples were collected from an observation well during the passage of the oil bank and analyzed. A radial flow simulator was used to match the field performance at this well, and results of the match were used to explain the observed field performance; comparisons are made to laboratory data. Documentation of the geology of the 650-ft Sand formation has continued. The information and interpretations should be useful in understanding fluid flow within the reservoir, in accurate modeling of the reservoir, and for evaluation of the project performance.

DOE/ET/13077-63. **Commercial Scale Demonstration—Enhanced Oil Recovery by Micellar-Polymer Flood, Annual Report, October 1980–September 1981.** Marathon Oil Co. May 1982. 130 pp. A commercial-scale test of enhanced oil recovery by the Maraflood^{TM} oil recovery process is located in Crawford County, Ill. It encompasses 407 acres of Robinson sand reservoir and covers portions of several waterflood projects that were approaching economic limit. The project includes 248 acres developed on a 2.5-acre five-spot pattern and 159 acres developed on a 5.0-acre five-spot pattern. Development work commenced in late 1974. Micellar solution injection was initiated in February 1977 and is now completed. After 10 percent of a pore volume of micellar slug was injected, 11 percent pore volume of Dow 700 Pusher^{TM} polymer was injected. The oil cut of the 2.5-acre pattern decreased from 11 percent in September 1980 to 7.9 percent in September 1981. The 2.5-acre pattern had been on a plateau since May 1980, and as of May 1981 appeared to be on a decline. The oil cut of the 5.0-acre pattern increased from 5.9 percent in September 1980 to 10.9 percent in September 1981. This pattern experienced a sharp increase in oil cut after 34 percent of a pore volme of total fluid was injected and appears to be continuing to increase.

Enhanced Oil Recovery—Thermal

DOE/ET/12056-32. **A Preliminary Study of *In Situ* Combustion in Diatomites.** Stanford University Petroleum Research Institute. May 1982. 32 pp. To test the feasibility of applying *in situ* combustion techniques to diatomaceous reservoirs, a laboratory test was conducted for a section of core taken in the south plunge of the anticline in the Lost Hills Field of the San Joaquin Valley in California. During the experiment, a fast steam plateau, good oxygen utilization, and an unusual front were observed. Fingering caused formation of a second front downstream. This finger stabilized and later became very hot (1,600°F). Velocity of front movement through the core almost doubled after the two fronts joined. API gravity of the oil extracted from the core ranged between 28 and 45, compared to the original value of 28° API. Tests were conducted to compare the cores before and after combustion, using scanning microscopy, powder X-ray diffraction, and extraction techniques.

Enhanced Oil Recovery—Carbon Dioxide

DOE/BC/10331-4. **Displacement of Oil by Carbon Dioxide, Annual Report, October 1980–September 1981.** New Mexico Petroleum Recovery Research Center. April 1982. 128 pp. This report describes a research program to quantify factors affecting CO_2-flood displacement efficiency. Literature reviews were conducted on the interpretation of miscible displacement in one- and two-phase systems. Results of miscible displacement experiments with fluids of matched density and viscosity are compared with results of a few displacements in which fluid properties were not matched. Investigations of the phase behavior of CO_2-crude oil mixtures provided the basis for a qualitative analysis of the effects of solution gas on CO_2 performance. Modifications were made to improve the continuous multiple contact experiment, which measures phase compositions and fluid properties,

DOE/MC/03259-15. **Enhanced Oil Recovery by CO_2 Foam Flooding, Final Report.** New Mexico State University. April 1982. 152 pp. The objective of this study is to identify commercially available additives which are economical plus effective in reducing the mobility of carbon dioxide in enhanced oil recovery processes, thereby improving efficiency in recovering tertiary oil. Experiments on gas mobility control, conducted in linear sand-pack models, show only a general correlation with the static foam test. In general, all surfactants that produce reasonable quantities of foam in that test also give some degree of mobility control to gas during two-phase flow. The best mobility control additives are only modest foam volume producers. These spontaneously produce a viscous foam under flow conditions present in a petroleum reservoir. Three basic chemical structures showing most promise for gas mobility control are: (1) ethoxylated adducts of C_8-C_{14} linear alcohols, (2) sulfate ethers of ethoxylated C_9-C_{16} linear alcohols, and (3) low molecular weight copolymers of ethylene oxide and propylene oxide. Each type is compatible with normal oilfield brines, unaffected by the presence of crude oil, and stable under conditions common in a petroleum reservoir.

DOE/MC/08341-39. **Field Project to Obtain Pressure Core, Wireline Log, and Production Test Data for Evaluation of CO_2 Flooding Potential.** Gruy Federal, Inc. May 1982. 278 pp. Pressure coring and associated logging and testing programs are planned for selected wells to provide data on *in situ* oil saturation, porosity and permeability distribution, and other data needed for resource characterization of fields and reservoirs in which CO_2 injection might have a high probability of success. This report presents detailed information on the first such project at the Bennett Ranch Unit well No. 310, Wasson (San Andres) Field, Yoakum County, Texas. Porosity and water saturation, as determined by extensive core and log analyses, agreed well in intervals where cores were successfully retrieved under pressure. Core and log data were useful in determining the residual oil saturations, and production data confirmed the validity of oil saturation determinations.

DOE/MC/12004-5. **Weeks Island "S" Sand Reservoir B Gravity Stable Miscible CO_2 Displacement, Iberia Parish, Louisiana, Fourth Annual Report, June 1980-June 1981.** Shell Oil Co. April 1982. 40 pp. A gravity stable displacement field test of the miscible CO_2 process is being conducted in the portion of a fault-sealed reservoir lying below a subsea depth of −12,750 feet. Injection of the CO_2 slug at the producing gas-oil contact commenced in October 1978. Injection of the 860 million cubic foot slug was completed in February 1980. The slug of CO_2 was moved downward through the watered out sand by production of downdip water. The leading edge of the displacement reached the producing perforations, and production of the oil column commenced on January 26, 1981.

Enhanced Oil Recovery—Microbial

DOE/BC/10301-11. **Application of ATP Measurements to the Microbiological Evaluation of a Petroleum Reservoir, Final Report.** Science Applications, Inc. June 1982. 82 pp. The objective of this work was to determine whether the bioluminescent luciferin/luciferase-based adenosine triphosphate (ATP) assay could be used as a rapid field test for determining the pres [illegible] and numbers of microorganisms in oil field fluids. The ATP-photom [illegible] chnique employed is based on the ATP-mediated bioluminescent oxidation of firefly luciferin. Light production is stoichiometrically related to ATP concentration; ATP concentration is related to numbers of living organisms present in a sample. Samples used in this study comprised reservoir fluids collected from several Southern California oilfields. Based on experimental evidence, it was concluded that the ATP assay could be profitably applied to microbially enhanced oil recovery process monitoring and control. The theoretical basis for the assay, field-usage methodologies, and fundamentals of data interpretation are presented to make this a usable field manual.

Drilling

DOE/BC/10079-47. **Rheology of Foam and Its Implications in Drilling and Cleanout Operations, Topical Report.** The University of Tulsa. June 1982. 102 pp. Experimental analysis was carried out to study the rheological properties of foam. Foam was generated by simultaneously injecting air and an aqueous solution of the foaming agent through a coiled-tubing foam generator. Results showed that flowing foam behaved as a pseudo-plastic fluid with no yield value; effective foam viscosity decreased with an increase in shear rate for a fixed quality. For shear rates in the range 500 sec^{-1} to 1000 sec^{-1}, the effective foam viscosity was independent of foam quality. This information is useful because most field applications fall in this range.

Western Gas Sands Program

CONF-8103113. **Western Tight Gas Sands Advanced Logging Workshop Proceedings, March 17-18, 1981, Tulsa, Oklahoma.** Bartlesville Energy Technology Center. April 1982. 260 pp. This workshop, designed to allow a free interchange of ideas on all aspects of the current logging research program of the Western Tight Gas Sands Project, was attended by industry, academic, and government representatives. Each of the 16 presentations was followed by an open discussion on the merits of the work, and a written survey was taken containing questions for each project. Particular interest was given the nuclear magnetic resonance tool research, neutron transport studies, and plans for the multi-well experiment. This report contains the presentations, discussions, and the results of the workshop survey.

DOE/BETC/SP-81/12. **Research Projects Needed for Expediting Development of Domestic Oil and Gas Resources through Arctic, Offshore, and Drilling Technology.** U.S. Department of Energy. April 1982. 152 pp. This report contains the results of a workshop to determine the needs of the petroleum industry as seen by oilfield professionals. The projects described support the development of advanced methods to characterize the environment and research to advance the state of the art of drilling and exploration in the Arctic and offshore frontier areas.

DOE/BC/00010-33. **Study of Sonic, Neutron and Density Logging of Low Permeability Gas [illegible] ds, Final Report.** Texas A&M University. May 1982. 70 pp. Gas a [illegible] ulations in Lower Tertiary and Upper Cretaceous formations are the object of widespread exploration in the tight western gas sands. The complex lithology of these formations has hindered the usefulness of the sonic, density, and neutron logs. Core and petrographic studies have been made on samples from Lower Tertiary and Upper Cretaceous formations in the Uinta Basin. Results indicate that a carbonate cement [illegible] ed much of the original porosity and altered the matrix density. Lower porosity samples tend to be heavily cemented and have matrix densities that approach 2.68 gm/cc. Higher porosity samples tend to be lightly ce-me[illegible] and have matrix densities that approach 2.65 gm/cc. Log analyses [illegible] Uinta Basin, supplemented by core data, reveal that the higher porosity samples have matrix travel-times that approach 55.6 microseconds/ft. The presence of the carbonate cement does not decrease the matrix travel-times as expected. Laboratory measured matrix travel-times substantiate these conclusions. Log analyses also indicate the neutron log, when calibrated for a sandstone matrix, will not accurately evaluate the higher porosity, non-shaly sandstones.

DOE/BC/00042-39. **Laboratory Measurement of Directional Permeability Trends, Topical Report.** Institute of Gas Technology. May 1982. 36 pp. A procedure is described that is suitable for measuring the maximum and minimum permeabilities of porous sediments. This procedure has been tested only on sediments characterized by a two-dimensional anisotropy. The data that confirm the theory and illustrate the application of the method are given. In ordinary methods, measurement errors are unavoidable because uncompensated end effects are introduced as it is convenient to employ arbitrary sample shapes. In the new method, the test samples are given a shape that is purposely designed to eliminate such end-effect zones. This procedure is suitable for studying the directional properties of sediments of western tight sands. For instance, preliminary data indicate that the maximum-to-minimum permeability ratios range from 1 to 2 for single-phase flow under ambient laboratory conditions. It is implied that the ratios may be considerably higher for cases in which the specific gas permeability is reduced, for example, because of the presence of connate water and/or because of the effect of overburden stress.

DOE/BC/00042-40. **Effect of Confining Pressure on Pore Volume in Tight Sandstones, Topical Report.** Institute of Gas Technology. May 1982. 12 pp. Investigations on the effect of confining pressure on the pore volume of some tight sandstones from the Uinta Basin, Utah, produced a new method to measure pore volume reduction. The new method is based on the pressure-volume relationships of gas. The results were compared with the results obtained using the method that involves the measurement of liquid expelled from a saturated core, and the results were found to be in good agreement. Pore volume compressibility of the samples studied ranges in value from 2.0×10^{-6} to 1.3×10^{-5} pv/pv/psi at a confining pressure of 5,000 psi.

DOE/BC/00042-41. **Special Core Analysis for Western Tight Sands, Annual Report, Aug. 1, 1980-July 31, 1981.** Institute of Gas Technology. May 1982. 48 pp. Results are presented of laboratory investigations on low-permeability sandstone core samples obtained from the Uinta Basin, Utah, and Sublette County, Wyo.; some experiments also used samples from the Greater Green River Basin in Wyoming. Permeability to gas was measured as a function of pore pressure, confining pressure, and partial water saturation. Porosity characteristics of the samples were also measured, and a new method was developed to measure pore volume compressibility of sandstone samples. A comprehensive theoretical analysis of anisotropy in porous media was completed, and an experimental technique was developed to characterize anisotropy in sandstone sediments. Correlations were developed to describe the dependence of permeability of tight sandstones on confining pressure and partial water saturation. A cooperative program with the U.S. Geological Survey in Denver enabled reseachers to us[illegible]lts of USGS petrographic analyses in conjunction with reservoir parameters measured at IGT to better understand the properties of tight sandstones.

DOE/BC/10038-22. **Lightweight Proppants for Deep Gas Well Stimulation, Second Annual Report, J[illegible] 1980-June 30, 1981.** Terra Tek, Inc. April 1982. 52 pp. Existing high strength proppants have desirable strength characteristics for propping deep hydraulic fractures, but also have high specific gravities and high cost when compared to sand. This study investigated low specific gravity proppants that would reduce costs and improve fracture control. Theoretical stress and strength analyses suggested that porous and hollow ceramics offer an alternative to dense proppants. Fracture conductivity as a function of closure pressure was experimentally determined for several materials. Good correlation of experimental results with theory was observed for solid and porous proppants. Fabrication methods for the production of inexpensive lightweight proppants are discussed. Spray drying into a fluidized bed appears to be a viable method for producing both porous and hollow proppants. Characterization of spray dried alumina proppants is discussed. Materials that may be effective lightweight proppants and areas of emphasis for future research are presented in the report.

PROCESSING AND THERMODYNAMICS

Processing

DOE/BC/10183-1. **Emulsified Industrial Oils Recycling.** Springborn Laboratories, Inc. April 1982. 152 pp. This study, aimed at analyzing the industrial lubricant market in the United States and other industrialized countries, emphasized current and developing recycling technology. Attention was focused on re-refining emulsion-type (soluble oil) fluids, which represent a higher percentage of the total fluids used in the U.S. than in the other countries. Recycling is being explored by the industry to extend the longevity of the emulsion to keep expenses down by using the emulsion as long as possible; recycling is also attractive as it postpones the problem of treating the emulsion as required by environmental regulations. Regulations require separating the water and oil phases for treatment, and once the emulsion is separated, re-refining the oil becomes economical. The most commonly used method to break the emulsion is chemical treatment, practiced in the United States. This method produces large amounts of waste, causing secondary pollution problems. Ultrafiltration, a physical method of separation that generates no by-products, is preferred in Japan and the European countries. Ultrafiltration, however, is not efficient enough at the present state of the art to treat the large quantities of emulsions produced by U.S. industry.

DOE/BC/10329-4. **Banbury Oil Recycling, Final Report.** Hydrocarbon Recyclers, Inc. April 1982. 40 pp. This report investigates the recovery of waste Banbury oil generated during the manufacture of tires. Approximately 1.5 to 2 million gallons of this type of oil is discarded each year. The oil could be re-refined by removing water, carbon black, sulfur, zinc oxide, and polymers and various rubber chemicals from the used Banbury or dust-stop oil. It is estimated that a simple processing plant would cost $174,000 and the same oils could be recycled at a cost of about $1 per gallon. To recover the oil as a fuel, the water and some of the other contaminants must be reduced, but the treatment would not be so severe and costs would be lower. It is recommended that the re-refiners process other types of industrial oil in the same equipment to reduce operating costs.

Characterization

DOE/BETC/PPS-82/1. **Motor Gasolines, Summer 1981.** E. M. Shelton. April 1982. 68 pp. Analytical data for 715 samples of motor gasolines were collected from service stations throughout the country and analyzed in the laboratories of various refiners, motor manufacturers, and chemical companies. The data were submitted to the Bartlesville Energy Technology Center for study, necessary calculations, and compilation under a cooperative agreement between the BETC and the American Petroleum Institute. The samples represent the products of 33 companies that manufacture and supply gasoline. These data are tabulated by groups according to brands (unlabeled) and grades for 17 marketing districts. A map included in the report shows marketing areas, districts, and sampling locations. Sixteen charts report octane distribution percentages for unleaded antiknock index below 90.0, unleaded antiknock index for 90.0 and above, leaded antiknock index below 93.0, and leaded antiknock index for 93.0 and above. The report includes charts indicating the trends of selected properties of motor fuels since 1959.

DOE/BETC/PPS-82/2. **Aviation Turbine Fuels, 1981.** E. M. Shelton. April 1982. 14 pp. Properties of some aviation turbine (jet) fuels marketed in the United States during 1981 are presented in this report. The samples are typical 1981 production and were analyzed in the laboratories of 15 manufacturers of jet fuels. The data were submitted for study, calculation, and compilation under a cooperative agreement between the BETC and the American Petroleum Institute. Results for the properties of 95 samples of jet fuels are included in the report for military grades JP-4 and JP-5 and commercial type Jet A.

DOE/BETC/RI-82/4. **Trends in Motor Gasolines: 1942-1981.** E. M. Shelton, M. L. Whisman, a [illegible] W. Woodward. June 1982. 32 pp. Trends in motor gasolines [illegible] 942 through 1981 have been evaluated based upon data contained in surveys that have been prepared and published by BETC. These surveys have been published twice annually since 1935 to describe the properties of motor gasolines sold throughout the country. Various companies obtain samples from retail outlets, analyze the samples by the American Society for Testing and Materials procedures, and report data to BETC for compilation, tabulation, calculation, analysis, and publication. From these data in 77 semiannual surveys, this summary report has been assembled to show trends in motor gasolines for this era. Physical properties including octane numbers, antiknock ratings, distillation temperatures, Reid vapor pressure, sulfur and lead content are tabulated, plotted, and discussed. Also included are trend effects of technological advances and the interactions of engine design, societal and political events, and prices on motor gasoline evolution during the 40-year period.

TECHNICAL PRESENTATIONS

Note: Presentations are listed for reference purposes only; copies are not available from BETC.

Brinkman, D. W., "**Used Oil Recycling Research at BETC.**" Association of Petroleum Re-refiners, Mid-Year Meeting, Washington, D.C., April 26.

Brinkman, D. W., "**Re-refined Oil.**" Engineers Club of Tulsa, Okla., May 10.

Burtch, F. W., "**Outlook for Enhanced Oil Recovery.**" 5th Annual Oil Industry Conference, American Marketing Association, Houston, Tex., May 7.

Donaldson, E. C., "**Introductory Statements.**" International Conference on Microbial Enhancement of Oil Recovery, Afton, Okla., May 16.

Donaldson, E. C., "**Microbial Enhancement of Oil Recovery.**" SPE/DOE Joint Symposium on Enhanced Oil Recovery, Tulsa, Okla., April 6.

Gammon, B. E., "**The Use of Velocity of Sound Measurements to Determine the State Properties of Fluids.**" Seminar, Texas A&M University, College Station, Tex., May 3.

Grindstaff, Q. G., "**The MS-30 Dual FI/EI Ion Source—A Deal or Flawed Gem.**" American Society for Mass Spectrometry, Annual Meeting, Honolulu, Hawaii, June 7.

Johnson, H. R., "**Prospects for Enhanced Oil Recovery in the United States.**" Southwest Regional Energy Council, Oklahoma City, Okla., April 10; Independent Petroleum Association of America, Reno, Nev., May 6-7; Advances in Petroleum Recovery and Upgrading Technology Conference, Calgary, Alberta, Canada, June 9-11.

Lievens, E. J., Jr., "**The Department of Energy Looks at Emerging Technologies for Enhanced Oil Recovery.**" International Conference on Microbial Enhancement of Oil Recovery, Afton, Okla., May 16.

Lievens, E. J., Jr., "**Welcoming Remarks.**" SPE/DOE Joint Symposium on Enhanced Oil Recovery, Tulsa, Okla., April 5.

Ray, M., "**Demonstration of Data Base.**" SPE/DOE Joint Symposium on Enhanced Oil Recovery, Tulsa, Okla., April 5; Independent Petroleum Association of America, Reno, Nev., May 7.

Scheppele, S. E., "**The Next Step Beyond DS-55.**" American Society for Mass Spectrometry, Annual Meeting, Honolulu, Hawaii, June 7.

Scheppele, S. E., and Q. G. Grindstaff, "**Field Ionization Analysis of Saturates in Shale Oil.**" American Society for Mass Spectrometry, Annual Meeting, Honolulu, Hawaii, June 7

Seizinger, D. E., "**Analysis of Polynuclear Aromatic Hydrocarbons in Diesel Fuels and Exhaust Particulates.**" Oklahoma State University, Seminar, Stillwater, Okla., April 27.

Seizinger, D. E., "**Diesel Particulates and Bioassay Effect of Fuels, Vehicles, and Ambient Temperature.**" Society of Automotive Engineers Passenger Car Meeting, SAE Paper 820.813, Troy, Mich., June 7-10.

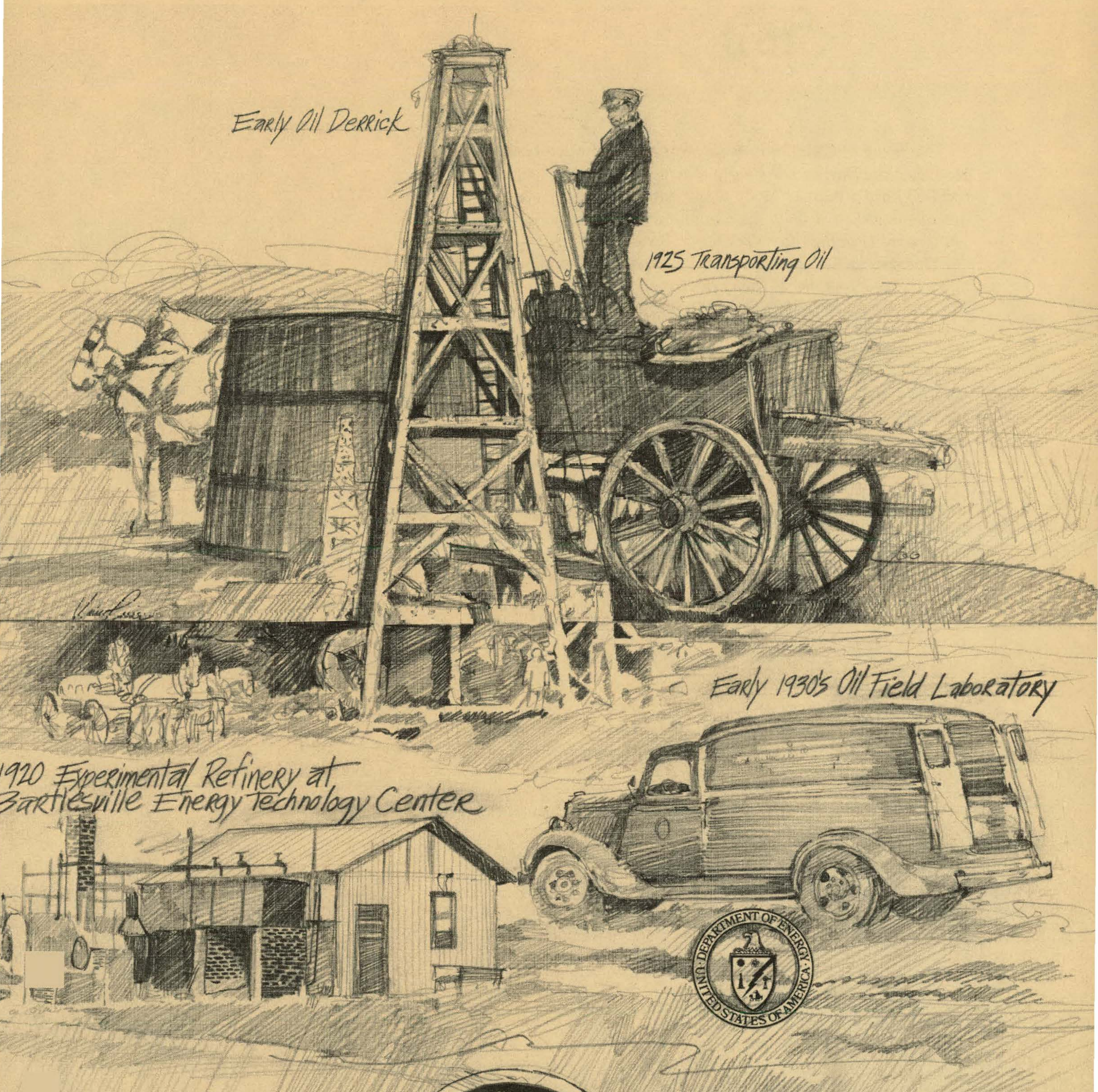
Szpakiewicz, M., "**A Preliminary Hydrogeological Investigation of Upper Cretaceous and Lower Tertiary Formations in the Uinta Basin.**" Petroleum Data System, User's Group Meeting, and PDS Advisory Council Meeting, Houston, Tex., May 19 and 20.

☆ U.S. GPO: 1982 - 569-028/70

OKLAHOMA AND BETC

PARTNERS IN PETROLEUM RESEARCH FOR 64 OF OKLAHOMA'S 75 PROUD YEARS

"A Special Section for a Special State"



United States Department of Energy You're doin' fine, Oklah 75 [redacted] 1907 Diamond [redacted] [redacted] **Bartlesville Energy Technology Center**

A Special Section for a Special State

The State of Oklahoma is 75 years old on November 16, 1982. The Bartlesville Energy Technology Center (BETC) has "grown up" with Oklahoma and the petroleum industry since the Center was established in 1918—only 11 years after Oklahoma became a state.

This special section—an official Oklahoma Diamond Jubilee Project—reflects the cooperation and mutual assistance between BETC and the State of Oklahoma and chronicles some of the accomplishments that the Bartlesville Center has made with the assistance of the State.

The Bartlesville Energy Technology Center is one of the few Federal laboratories that has enjoyed uninterrupted financial support from a state. As pointed out in an article within this special section, the State of Oklahoma support was nearly one-third of BETC's total budget during its first 20 years when it was known as the Petroleum Experiment Station of the U.S. Bureau of Mines. This early support was instrumental in helping BETC become the Nation's leader in the development of improved petroleum production technology that is non-proprietary and available for adoption by anyone in the petroleum industry.

The State of Oklahoma continues to provide financial support to the Bartlesville Energy Technology Center in support of the Oklahoma Well Log Library and other activities. We are grateful for this support and look forward to a long and successful partnership with the State.

Edward J. Lievens, Jr.
Acting Director
Bartlesville Energy Technology Center

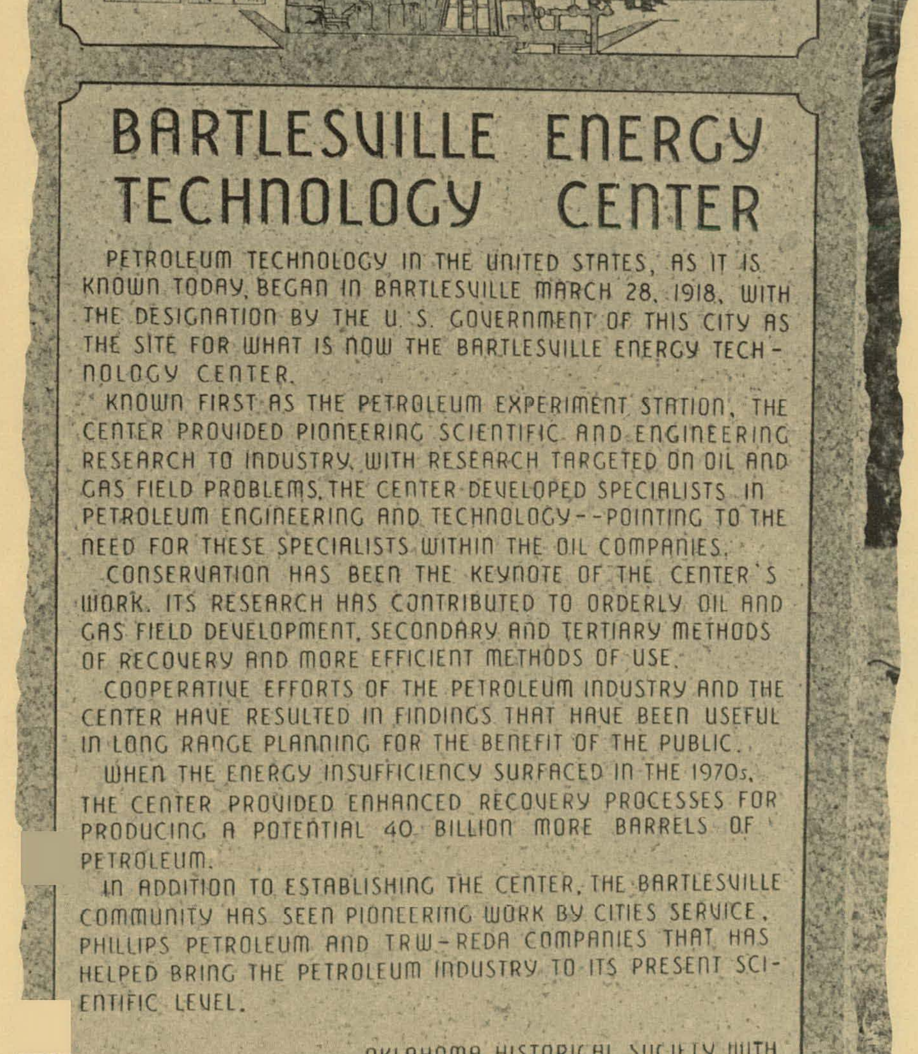
Oklahoma and BETC— A Scientific Partnership

"Petroleum technology in the United States, as it is known today, began in Bartlesville March 28, 1918, with the designation by the U.S. Government of this city as the site for what is now the Bartlesville Energy Technology Center."

So reads the inscription on the granite marker placed in front of the Bartlesville Energy Technology Center (BETC) Administration Building by the Oklahoma Petroleum Council and the Oklahoma Historical Society in 1978. It marks the close cooperation between the State of Oklahoma and the Federal government in advancing petroleum technology for almost 65 of Oklahoma's 75 years.

This long relationship is based on the primary mission of BETC—to use scientific knowledge to promote efficiency and conservation. As expressed by Joseph A. Holmes, the first director of the U.S. Bureau of Mines, "True conservation is a wiser and more efficient use of our natural resources." BETC was a part of the Bureau of Mines from 1918 to 1975.

Over the years, the Bartlesville Center has furnished scientific and technical background for the administration and regulation of petroleum and natural gas resources. The regulatory arm of state government is the Oklahoma Corporation Commission.



BARTLESVILLE ENERGY TECHNOLOGY CENTER

PETROLEUM TECHNOLOGY IN THE UNITED STATES, AS IT IS KNOWN TODAY, BEGAN IN BARTLESVILLE MARCH 28, 1918, WITH THE DESIGNATION BY THE U. S. GOVERNMENT OF THIS CITY AS THE SITE FOR WHAT IS NOW THE BARTLESVILLE ENERGY TECHNOLOGY CENTER.

KNOWN FIRST AS THE PETROLEUM EXPERIMENT STATION, THE CENTER PROVIDED PIONEERING SCIENTIFIC AND ENGINEERING RESEARCH TO INDUSTRY, WITH RESEARCH TARGETED ON OIL AND GAS FIELD PROBLEMS. THE CENTER DEVELOPED SPECIALISTS IN PETROLEUM ENGINEERING AND TECHNOLOGY--POINTING TO THE NEED FOR THESE SPECIALISTS WITHIN THE OIL COMPANIES.

CONSERVATION HAS BEEN THE KEYNOTE OF THE CENTER'S WORK. ITS RESEARCH HAS CONTRIBUTED TO ORDERLY OIL AND GAS FIELD DEVELOPMENT, SECONDARY AND TERTIARY METHODS OF RECOVERY AND MORE EFFICIENT METHODS OF USE.

COOPERATIVE EFFORTS OF THE PETROLEUM INDUSTRY AND THE CENTER HAVE RESULTED IN FINDINGS THAT HAVE BEEN USEFUL IN LONG RANGE PLANNING FOR THE BENEFIT OF THE PUBLIC.

WHEN THE ENERGY INSUFFICIENCY SURFACED IN THE 1970s, THE CENTER PROVIDED ENHANCED RECOVERY PROCESSES FOR PRODUCING A POTENTIAL 40 BILLION MORE BARRELS OF PETROLEUM.

IN ADDITION TO ESTABLISHING THE CENTER, THE BARTLESVILLE COMMUNITY HAS SEEN PIONEERING WORK BY CITIES SERVICE, PHILLIPS PETROLEUM AND TRW-REDA COMPANIES THAT HAS HELPED BRING THE PETROLEUM INDUSTRY TO ITS PRESENT SCIENTIFIC LEVEL.

OKLAHOMA HISTORICAL SOCIETY, WITH
OKLAHOMA PETROLEUM COUNCIL 1978

Placed on the grounds of the Bartlesville Energy Technology Center in 1978, this granite marker credits BETC with pioneering efforts in several areas of petroleum technology.

Some Notable Achievements

Together with some forward-looking industry leaders and a receptive legislature, Oklahoma has pioneered and led in establishing principles of petroleum conservation.

Notable among the achievements are:

- Unitization legislation
- Interstate Oil Compact Commission
- Maximum efficient rate (MER) basis for proration

Perhaps the most effective way to point out the research contributions of the State of Oklahoma and the Bartlesville Energy Technology Center is to quote from the *History of Petroleum Engineering,* published by the American Petroleum Institute (Dallas, Texas, 1981):

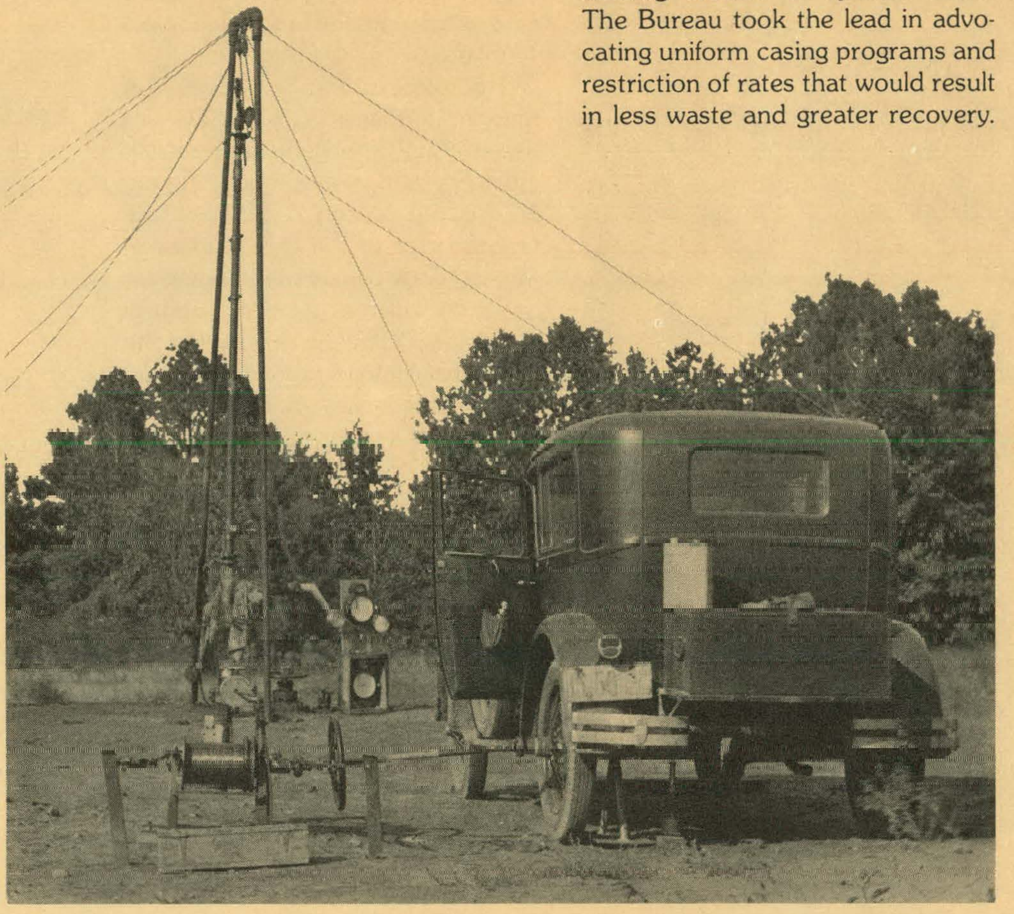
"The United States Bureau of Mines soon after its establishment in 1910 began studying means of preventing waste of oil and gas and methods of increasing the recovery of oil. Their investigations of oil-well cementing, drilling mud, and the physical properties of hydrocarbons were followed by petroleum-engineering studies of specific fields. The Bureau took the lead in advocating uniform casing programs and restriction of rates that would result in less waste and greater recovery. A. W. Ambrose, H. C. Miller and several other pioneer workers at the Bureau made important contributions in petroleum research.

"In 1920 the Bureau began experiments on underground flow of oil and water. These were followed by a wide range of studies continuing to the present including development of bottom-hole pressure bombs and samples, determination of the physical properties of hydrocarbons, estimation of reserves, correlation of oil field brines, secondary recovery experiments and fluid-flow research," (pages 1083–4).

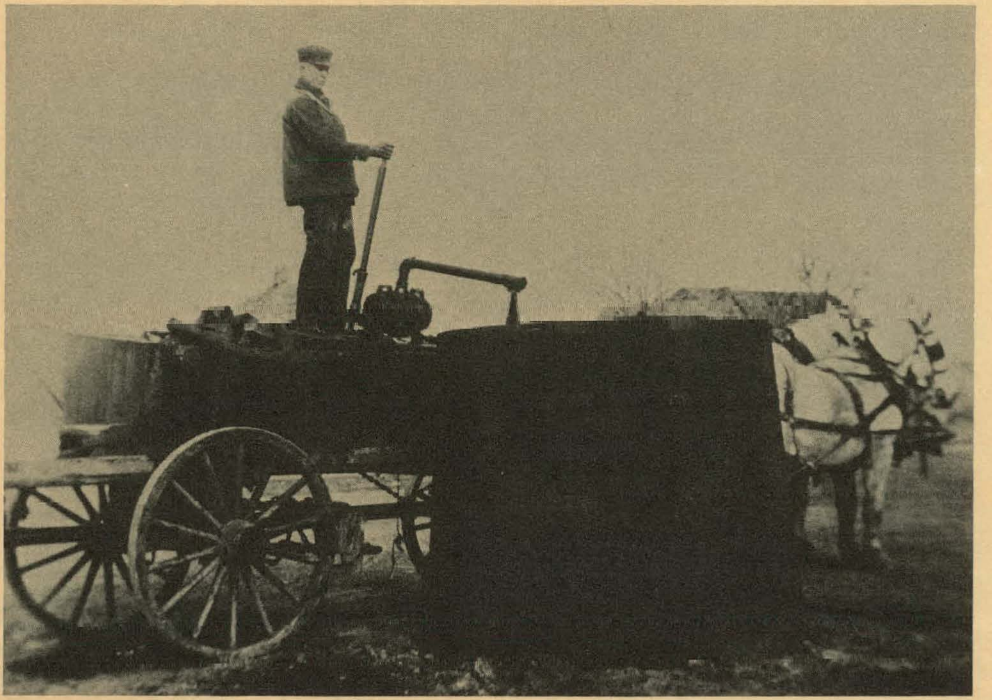
The same book, in its chapter on conservation, states:

"It is true that a number of scientists, many of them in the United States Bureau of Mines, had over many years published papers and books on the subject of underground waste, especially with respect to the function of gas in the production of oil, but this literature failed to bring about material changes," (page 1125).

"Oklahoma took the lead in comprehensive regulation in 1930, partly because of earlier experience and partly because the conservation statute that had been enacted in 1915 was not limited to individual well problems," (page 1133). "... competent technical men, including scientists in the United States Bureau of Mines had written articles between 1913 and 1930 saying capacity production usually causes



"Necessity is the mother of invention" according to legend. Perhaps that was never truer than in early field operations. Here BETC engineers us a Model A Ford for running a wire line spool for bottom-hole measurements.



Petroleum production problems weren't the only types of problems in earlier days. Transportation of crude from the field to collection points was not easy before modern times. Here a one-man, one-wagon operation unloads crude into a storage tank near Bartlesville.

dissipation of reservoir energy," (page 1135).

"Finally an agreement was reached in 1935 called the 'Interstate Compact to Conserve Oil and Gas,'" (page 1143).

IOCC Headquartered in Oklahoma

Oklahoma took a leading role in the establishment of the Interstate Oil Compact Commission (IOCC), and its headquarters are in Oklahoma City. As an information resource, it has enabled the states to pass regulations preventing waste, restricting production, establishing MER's and establishing unitization.

With regard to unitization, (pages 1182, 1183, 1185): "Unit operation became more important than ever. It was particularly attractive to the producing industry in the State of Oklahoma as a means of increasing the reserve of known fields and an opportunity to more economically recover reserves in place.... The contributions of the U.S. Bureau of Mines were received with great interest." (Footnote: The fact that the [illegible] branch of its Petroleum Experiment Station was located in Oklahoma was particularly important in creating local attention to the results of the work being done.)

Finally 1945 session passed (Oklahoma) H. B. 339 providing for compulsory unit operation under certain specified conditions. Other states followed the pattern set by the industry in Oklahoma."

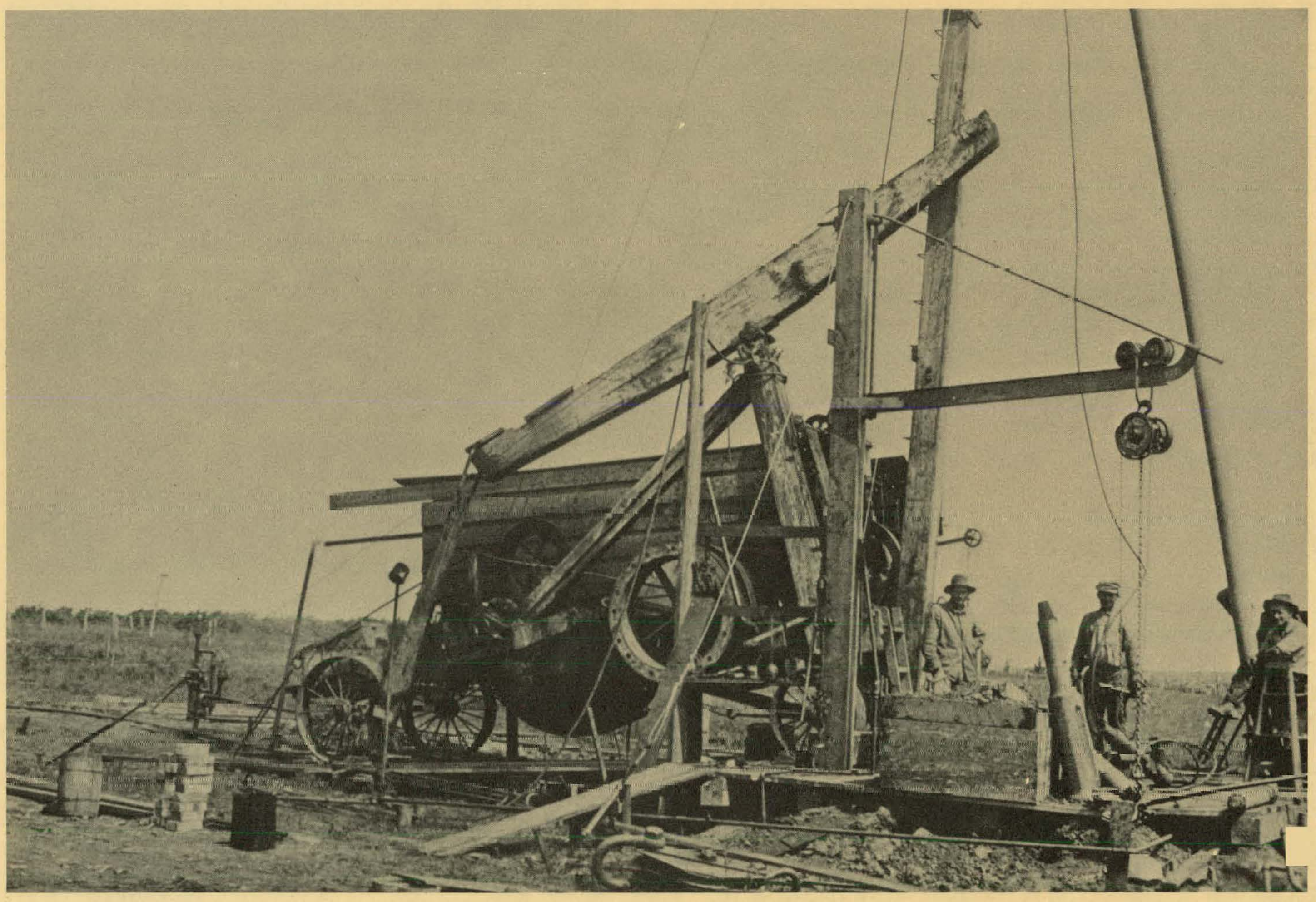
A similar relationship has been present in the protection of the environment. Not only has BETC furnished background information, but many times has assisted in specific problems where the Corporation Commission or other agency wanted scientific confirmation of the sources of various types of pollutants.

One of the problems that has faced oil producers is the disposal of salt water produced along with the oil. An early (1929) report from BETC in cooperation with the State of Oklahoma was Bureau of Mines Report of Investigations (BuMines RI) 2945, "The Disposal of Oil Field Brines," by Ludwig Schmidt and John M. Devine. This concern was continued over the years with BuMines RI 3603 in 1942, "Subsurface Disposal of Oil Field Brines in Oklahoma," by Sam S. Taylor and E. O. Owens. It is noteworthy that BETC alumni C. E. Reistle and W. S. Morris were responsible for the East Texas salt water disposal system about which the *History of Petroleum Engineering* says:

"But it was not until subsurface disposal was successfully demonstrated in the East Texas Field in the late 1930's that operators began to adopt the technique of injecting salt water into porous underground formations on a wide scale," (page 932).

Advancement of scientific knowledge about petroleum has been a continuing priority at BETC. Consequently, BETC has been a prime source of reliable, unbiased information for the State of Oklahoma, various Federal agencies, and the petroleum industry.

Cooperative Funding by State of Oklahoma Helps BETC



For years cable tool rigs were used throughout Oklahoma to drill thousands of wells. This cable tool spudder operated in southern Oklahoma in about 1919.

Soon after the U.S. Bureau of Mines established the Petroleum Experiment Station at Bartlesville in 1918, the legislature of the State of Oklahoma began cooperative funding for the station's research programs—a pattern that has continued for more than 60 years.

During the first 20 years of the station's existence, state funds provided about one-third of the total budget. State appropriations provided needed stability and were of substantial help in enabling the station to withstand the depression of the thirties (see table).

The station produced a series of engineering field reports on Oklahoma fields, which are credited with greatly increasing the production of oil from those fields. In the *Bartlesville Daily Enterprise* special edition of March 10, 1937, the value of the station's work to Oklahoma was summarized as follows:

(1) Increased revenue to the state (gross production tax) thr increased recovery and prevention of waste of oil and gas. This amount is estimated to be in excess of $500,000 per year.

(2) Increased revenue (ad valorem tax) through appreciation

FEDERAL AND STATE APPROPRIATIONS—1919-1940

Early support from the State of Oklahoma gave the new Petroleum Experiment Station stability during its first two decades and allowed the staff to work on many petroleum projects important to the State. Oklahoma has continued the annual appropriation through the present. Today the State provides about $200,000 a year to BETC.

Year	Federal Appropriation	State Appropriation	Total Budget
1919	$ 25,000	—	$ 25,000
1920	25,000	$12,500	37,500
1921	35,000	12,500	47,500
1922	35,000	37,500	72,500
1923	95,000	37,500	132,500
1924	104,000	37,500	141,500
1925	104,000	37,500	141,500
1926	104,700	37,500	142,200
1927	96,908	37,500	134,408
1928	90,840	50,000	140,840
1929	111,500	50,000	161,500
1930	101,000	62,500	163,500
1931	102,000	62,500	164,500
1932	101,300	57,500	158,800
1933	94,600	57,500	152,100
1934	62,000	40,300	102,300
1935	64,000	40,300	104,300
1936	82,400	41,800	124,200
1937	109,424	41,800	151,224
1938	106,150	47,960	154,110
1939	107,380	47,960	155,340
1940	107,380	30,385	137,765

of property values in oil-producing areas.

(3) A reduction in the number of deaths and injuries due to accidents in the petroleum industry.

) Reducing the waste incident to the utilization of an irreplaceable natural resource.

The station found it necessary many times to transfer personnel n the Federal payroll to the State Oklahoma payroll during the tight money days of the great depression. This was done by the superintendent (now called director) who was the designee of the Bureau of Mines to administer the State Cooperative Agreement.

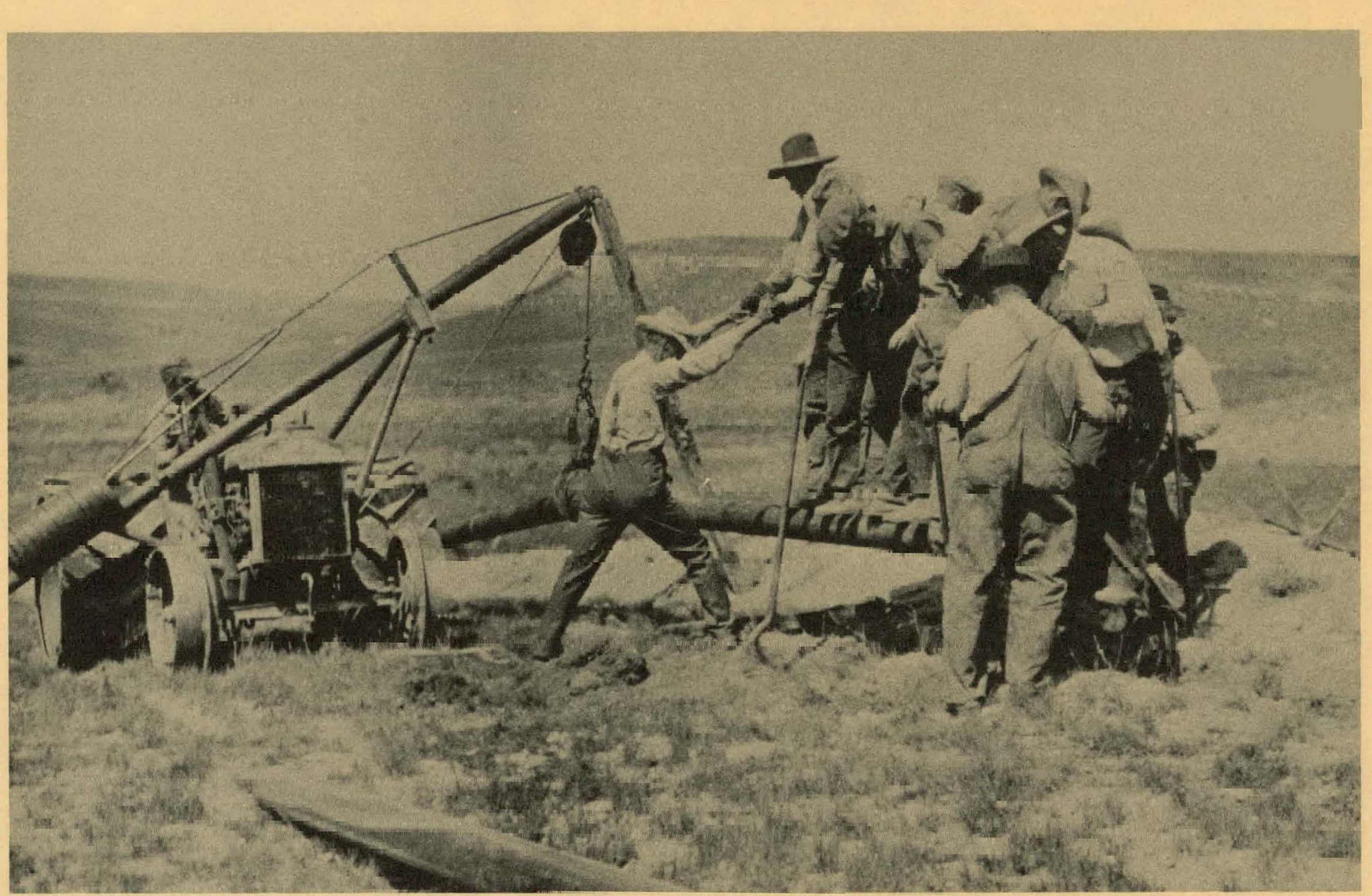
The cooperative effort by State and Federal agencies to introduce scientific methods into the oilfields was the impetus that led to a number of companies placing research laboratories in Oklahoma during this period. Major laboratories in Oklahoma now performing petroleum production research include Amoco Production Research, Tulsa; Cities Service, Tulsa; Conoco, Ponca City; Kerr-McGee, Oklahoma City; and Phillips, Bartlesville, among the oil companies, and Dowell, Tulsa; and Halliburton, Duncan, among the service companies.

1941-1960

During World War II, when effort was concentrated on war programs, the Federal support grew, and the State support remained relatively constant. In the fifties, the big thrust was on waterflooding. The waterflood program did much to maintain Oklahoma oil production when new oilfield discoveries became less frequent and primary production declined. Oklahoma crude oil production by waterflooding has climbed steadily and now accounts for more than half of the total production.

During the war, the need for additional basic data became apparent, especially in the synthetic rubber program, and led to the establishment of the thermodynamics laboratory at BETC. The search for aviation gasoline sources during the period brought out the problems associated with sulfur compounds in petroleum and the lack of knowledge concerning them.

When the war was over, the research priorities at the Bartlesville station were realigned, and basic research was again emphasized. By 1948, these programs had attained such stature that the American Petroleum Institute joined in financing and advising on problems concerning sulfur compounds in petroleum and thermodynamic properties of hydrocarbons. This gave impetus to



Early pipeliners lower pipe into a ditch near the Oklahoma panhandle in this 1938 photo. Note the counter-weighted rigging on the Fordson tractor used to assist the pipeliners.

the cooperative system of research, and the funding from such sources grew rapidly.

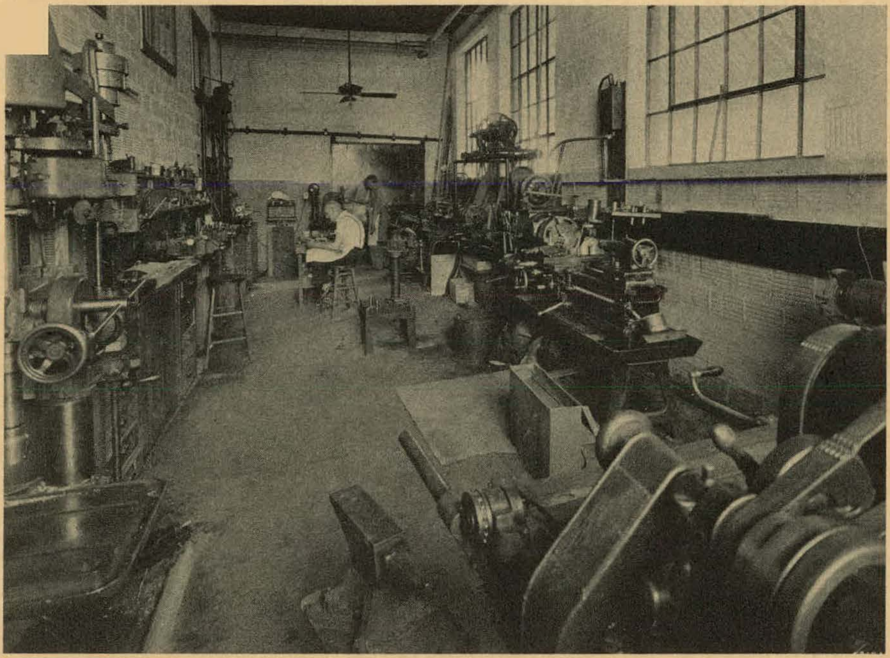
As the State of Oklahoma funding became a smaller percentage of the total funding, an effort was made to apply the State funds more selectively, and their use became a means of starting new research projects or augmenting older ones without waiting for the Federal budget process to provide funds. In addition, the State funds were used to enhance services that otherwise would have been meager. The rise in stature of the station's thermodynamics group to one of international recognition was based on the capability to design and construct custom-built equipment of advanced design in the Bartlesville shops. Also, augmentation of the Library not only provided researchers with information from the scientific literature, but also provided a specialized technical library that answered many questions for Oklahoma citizens.

1961-Present

Beginning in 1960, a designation of $12,500 (later $15,000) of Oklahoma Corporation Commission funds was appropriated annually to BETC in addition to the regular State appropriation. This was for the purpose of establishing a well-log file in northeast Oklahoma and making it available to interested people. The two appropriation measures were combined in 1971 and placed in the Department of Economic Development appropriation in 1973.

The Enhanced Oil Recovery Program and a policy of decentralization of funds in the Department of Energy accounted for a sharp rise in Federal funding starting in 1978. This, together with a rigid personnel ceiling, changed the character of operations from an "in-house" research establishment to a combination "in-house" research and contract administration agency.

Although these events have resulted in the state appropriation becoming a smaller percentage of the overall budget of BETC, the actual amount of the State appropriation has risen gradually but steadily since 1961. In the early 1960's, the annual State funding was $87,500. Tc the State of Oklahoma is investing more than $200,000 a year in the operation of the Bartlesville Center. This money is used primarily to employ administrative and maintena personnel and to operate the Ol homa Well Log Library.



Many of the instruments and devices invented and developed for petroleum technology were hand-made in this shop at BETC. This photograph was taken in 1935.

Oklahoma Well Log Library Contains 350,000 Logs

A comprehensive collection of drillers' logs furnished by the Oklahoma Corporation Commission has long been an attraction of the Bartlesville Energy Technology Center, especially for the independent oil producer. Many of these producers searched out new prospects for production by studying the logs of nearby wells that had been drilled previously. Many of these projects were stripper production, not profitable enough for the large company but worthwhile for the independent operator.

became legend at BETC that, when a prolonged rainy spell prevented the operators from getting into the field, an influx of visitors to the Well Log Library could be expected. Here they could search out data on wells in the proximity of their interests, make their own geological projections, and decide where their new ventures would take them.

Established in the late 1930's, the Oklahoma Well Log Library was long attended by the late Charley Bopp. After Bopp's second retirement—he retired from the Bureau of Mines before becoming a State of Oklahoma employee—the well logs were made part of the main BETC library, and a succession of BETC personnel operated the Well Log Library. Charlotte Stock, currently in charge of the activity, is the sixth such employee since Bopp retired.

The increase in oil prices of the 1970's made the stripper wells a more lucrative operation, and the number of operators visiting the Well Log Library increased. Over the past 3 years, the number of visitors has averaged 1,468 a year or slightly more than 5 per work day, reproducing an average of 26 logs each for further study. The well log file contains more than 350,000 logs and is receiving about 1,000 new logs a month.

Although the well log file has contributed chiefly to developing additional oil production, there have been other uses. For example, one prospective driller came in to check which formation was best for producing irrigation water. BETC personnel resorted to the file when a sensitive hydrocarbon-detection instrument revealed that gas was leaking from an abandoned well in front of the Administration Building. The file helped them locate a gas well that had been inadequately plugged years before the Center was built. A rig was brought in, and the well was plugged.

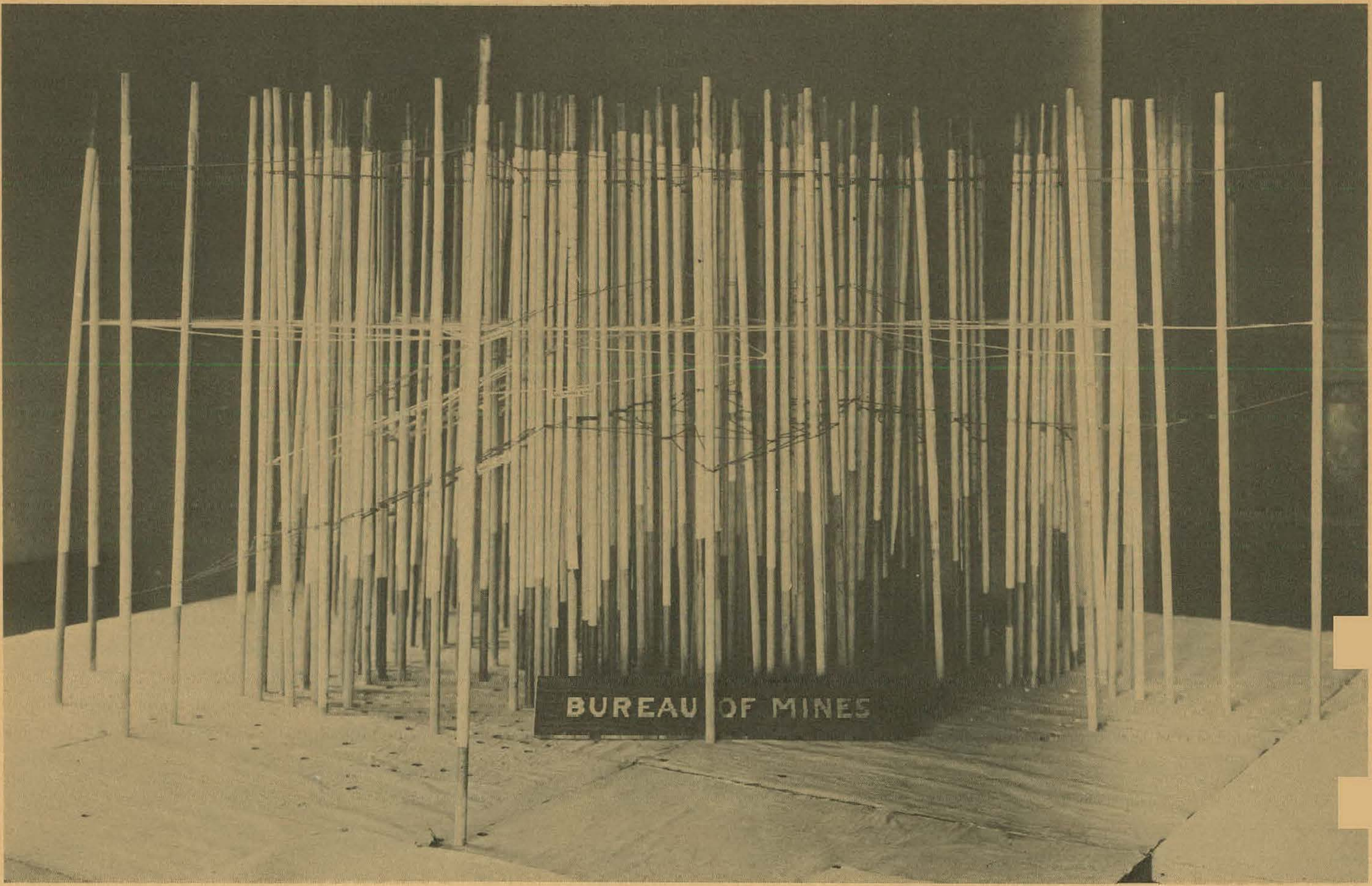
BETC Helps Early-Day Drillers

A history of the Bartlesville Energy Technology Center currently being written provides the following story:

T. E. Swigart, assisted by F. X. Schwarzenbek, both employees of the Bartlesville Center, spent 3 months of 1920 in the Hewitt field (southern Oklahoma) gathering information about every well in the field. A peg model, with a peg representing each well and labeled to show the depths of producing regions and other geologic information, was constructed at Bartlesville and shipped to Ardmore, Okla. Swigart placed the model on display in the lobby of the Hotel Ardmore, where he and Schwarzenbek set up temporary offices for consulting with drillers.

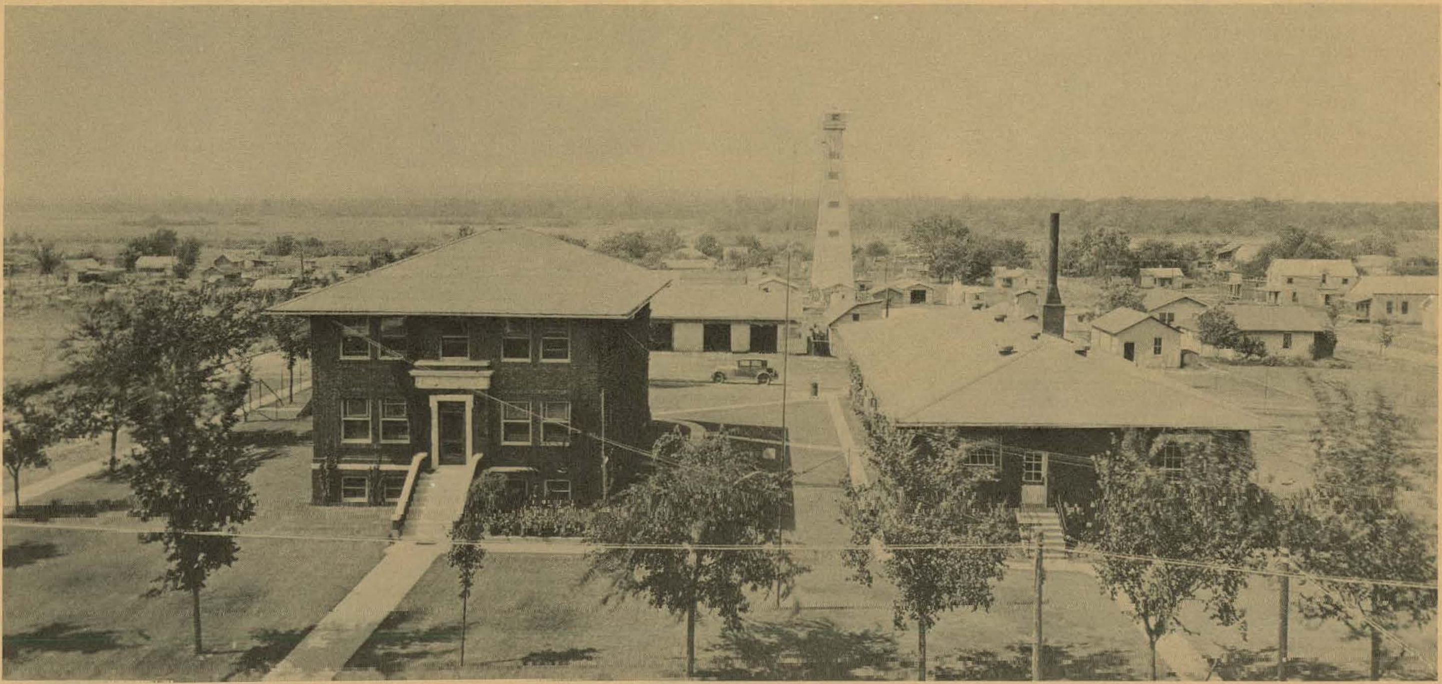
In the case of the Hewitt field, the cross sections indicated a severe dip in the producing or "pay" sands. Using this information, Swigart could tell operators when to drill deeper. A number of them followed the advice and made profitable discoveries. The Hewitt investigation lasted from April through July 1920, when the crew headed by Swigart was ordered back to Bartlesville. At that point, the Ardmore Chamber of Commerce, using $1,000 in funds provided by several local operators, funded the return of the team for an additional 2 months.

The peg model of the Hewitt field (Oklahoma) showed a severe dip in the pay sands. This information helped drillers determine how deep to drill in 1920.



BETC Physical Plant Grows To Meet Research Needs

by Kenneth J. Hughes
Director, BETC Operations Division



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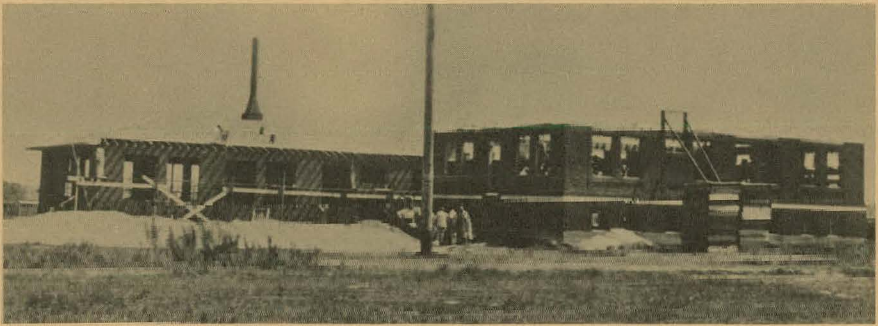
This 1928 photograph shows the two main buildings, a number of sheet metal shop buildings and laboratories added during the first 10 years, an enclosed experimental derrick that exploded and killed two people the following year, and some surrounding private houses.

The Bartlesville Energy Technology Center, first called the Petroleum Experiment Station, came into being when the Bartlesville Chamber of Commerce provided the U.S. Department of the Interior $50,000 and a block of land in north Bartlesville. The land was given by George B. Keeler, a prominent local businessman.

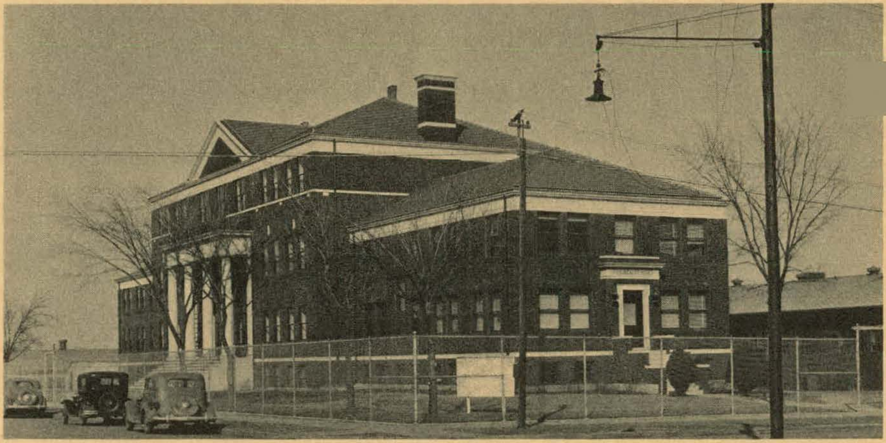
The first two buildings—a laboratory and an office building—were completed in January 1919 at a cost of $34,688. From this modest beginning, the Bartlesville Energy Technology Center has grown gradually but steadily into a major liquid fossil fuel research complex. As of the summer of 1982, BETC consisted of a 16-acre campus with 16 major buildings, including four laboratory buildings. The laboratories, shops and offices comprise about 156,000 sq ft of space. The current replacement value of the buildings and land is estimated at $33 million, and the equipment is valued at an additional $15 million.

The accompanying photographs show representative stages and buildings, beginning with the construction phase of the first two buildings in 1918 and ending with a current aerial view.

Shown during 1918 construction are the ► first two BETC buildings—a laboratory building (with the stack) and an office building. The laboratory building included a general purpose lab, a machine shop, and a storage area. The office building included a basement where the caretaker and family lived, offices, a library, and a drafting room.



A major Work Projects Administration building project was completed in 1936. The near wing was one of the original buildings completed in 1919. The central part of the building and the far (north) wing added about 29,000 sq ft of space at a cost of $350,000. This brought the total space to about 37,000 sq ft. The building is known today as the Administration and Chemistry building. ►



Completed in 1962, the 55,000 sq ft Engineering and Physical Sciences building gave BETC a big boost in area and in research capabilities. The $1.95 million building is the largest on the BETC campus. The flat-plate solar collector system partially visible on the roof was added in 1978 to provide much of the building's hot water. ►

One of the newest structures at BETC is the $750,000 Fuel Storage building, surrounded by an earth berm for safety and energy-saving purposes. The 5,000 sq ft building is used to store the experimental petroleum-based and synthetic fuels that are used in BETC's laboratory studies and is a model energy-conserving structure.

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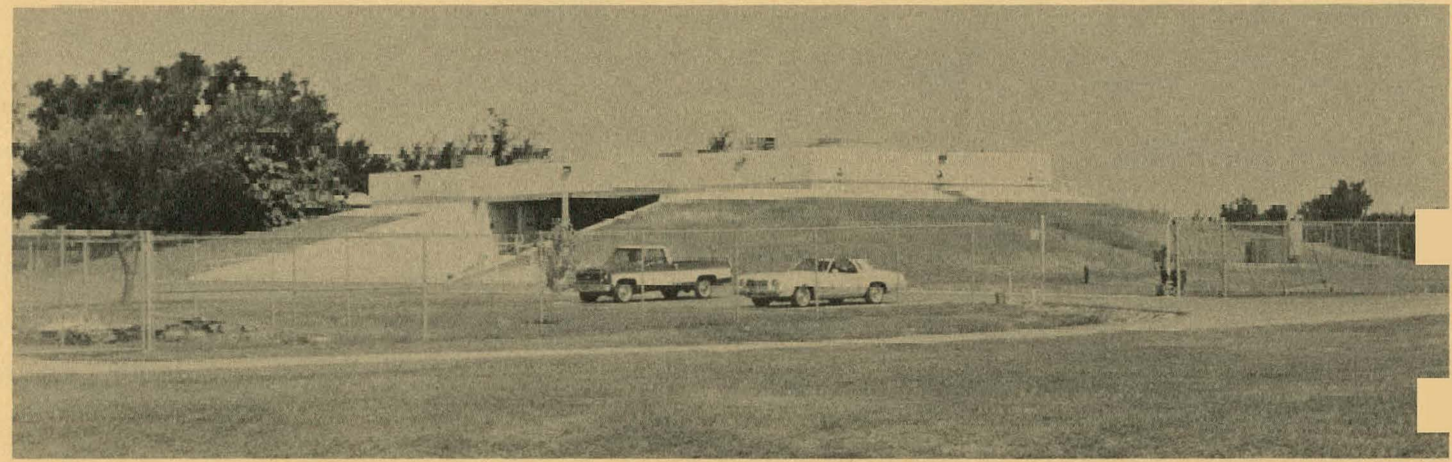

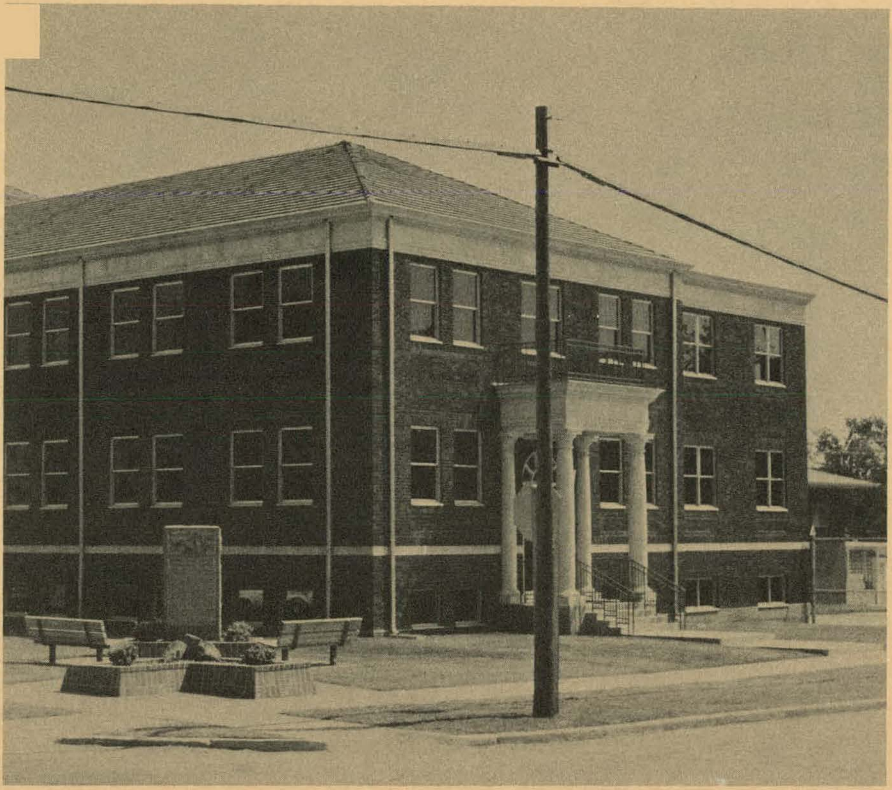

◄ This new south wing of the Administration and Chemistry building was completed in 1982 and replaced one of the two original buildings. The 15,000 sq ft wing is used primarily for offices and the BETC Library.

Recent aerial photograph of the Bartlesville Energy Technology Center campus.

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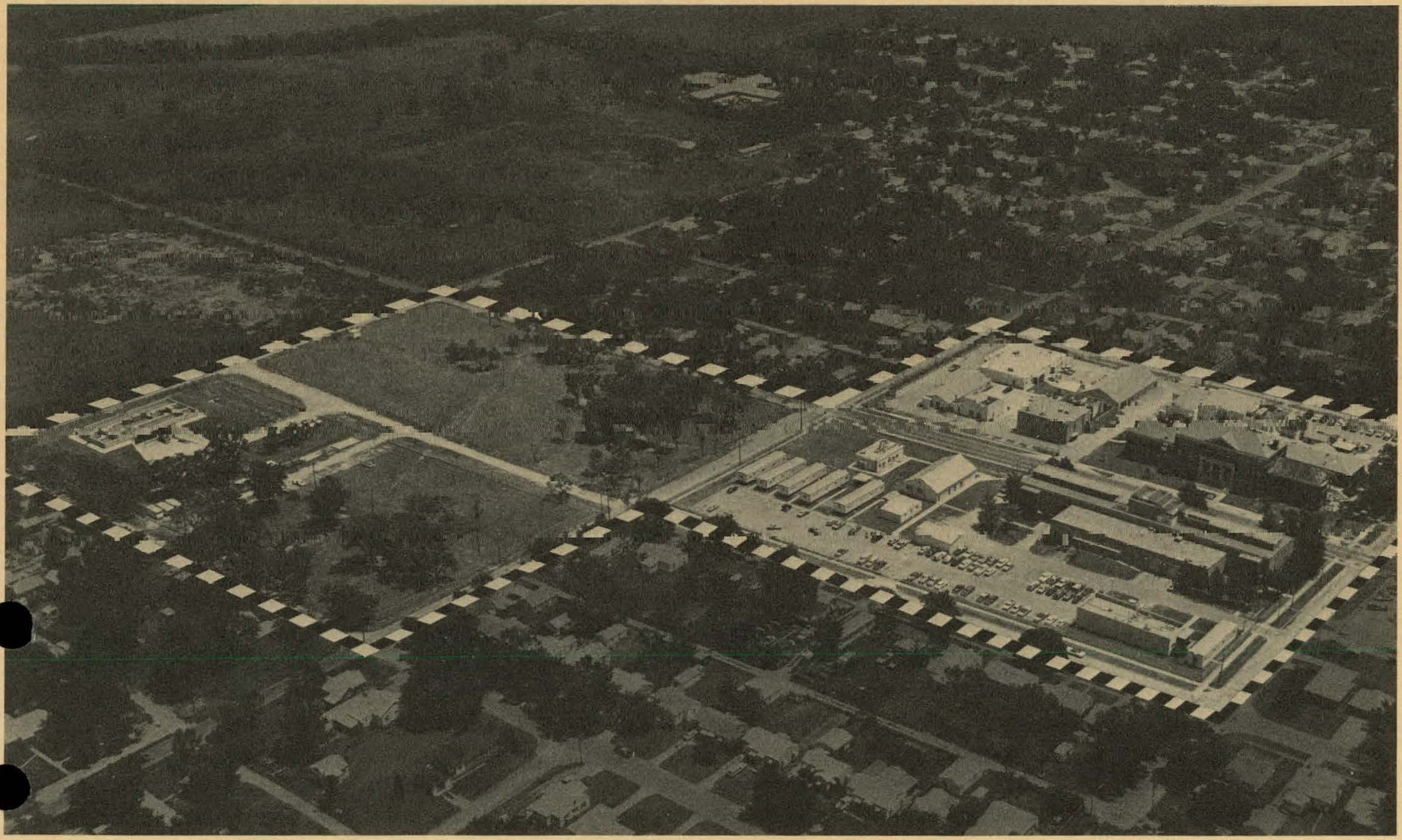


Technology for Improving Petroleum Production Developed in Oklahoma

The first drilled oil well—Drake's well in Pennsylvania in 1859—required pumping to produce the oil. However, many of the subsequent wells were brought in as "gushers," wells which spewed their oil over the top of the derrick. These flowing wells were rapidly depleted, and the wells were placed on the pump. As they were pumped, the owners found that oil seeped into the borehole at ever-decreasing rates. There was considerable interest in processes that might prolong or increase the flow of the oil.

The first superintendent of the Bartlesville Petroleum Experiment Station was J. O. Lewis. He made a study of ways to improve production from oil wells just before coming to Bartlesville, and in 1917, had published a Bureau of Mines Bulletin on "Methods for Increasing the Recovery of Oil From Oil Sands."[1] A prime consideration was the study of field conditions, and engineering field studies were an important part of his program for the new station. Among the methods discussed were vacuum, gas injection, and water displacement. Application of vacuum to oil wells, while used to a considerable extent, had the disadvantage that the maximum energy that could be exerted was 1 atmosphere, or about 15 psi. On the other hand, fluid injection pressures could go up to just below the pressure that would break the formation.

Gas injection has included use of compressed air, natural gas (methane), combustion gases, nitrogen, and carbon dioxide. These gases not only pressure the formation to push the oil out, but also, by going into solution, reduce the viscosity of the oil and lighten it so that it is easier to produce. The most accessible gases were air and natural gas, so they were the first tried. A next step was to burn the natural gas, which increased its volume and heated it—both of which were helpful.

Pressure maintenance became a keyword in petroleum production because, when the reservoir pressure is depleted, naturally occurring gas comes out of solution, resulting in a more viscous oil that is harder to produce. One result of pressure maintenance operations was a recycling process in which the gas was separated from the produced oil and returned to

A monument to Oklahoma's first waterflood was placed near Nowata by the Oklahoma Petroleum Council and the Oklahoma Historical Society in 1973. Shown from left are John Ball, then director of BETC; Kenneth Hughes, director of the BETC Operations Division; and R. C. "Chuck" Earlougher, a pioneer in waterflooding technology.

OKLAHOMA'S FIRST WATERFLOOD

INJECTION OF WATER INTO AN OIL RESERVOIR TO INCREASE RECOVERY WAS FIRST ATTEMPTED IN OKLAHOMA ON AN OIL LEASE 5.8 MILES EAST OF THIS LOCATION.

FROM THAT EFFORT, A RECOVERY METHOD PREVIOUSLY USED IN EASTERN FIELDS WAS ADAPTED TO CONDITIONS FOUND IN THIS AREA. SINCE THEN, WATERFLOODING TO OBTAIN GREATER OIL RECOVERY HAS SPREAD TO ADJOINING STATES AND AROUND THE WORLD.

THE INITIAL WATERFLOOD, EXPERIMENTAL IN NATURE, WAS DEVELOPED BY BERT COLLINS ON A SHALLOW PRODUCING PROPERTY IN ROGERS COUNTY IN MAY 1931 ON A CARTER OIL COMPANY LEASE. AS THE TEST WAS ENCOURAGING, THE METHOD WAS APPLIED TO OTHER OIL RESERVOIRS.

WATER FOR MODERN FLOODING PROJECTS IS INJECTED UNDER HIGH PRESSURE INTO OIL-BEARING FORMATIONS TO FORCE THE OIL THROUGH THE STRATA TO NEARBY PRODUCING WELLS FROM WHICH IT IS PUMPED. ON THE AVERAGE 10 BARRELS OF WATER IS INJECTED FOR EACH BARREL OF CRUDE OIL RECOVERED.

THE CITY OF NOWATA BECAME THE HUB OF WATERFLOODING FOR THE AREA WITH MOST OF THE FIELD ACTIVITY BEING IN ROGERS COUNTY WHERE VAST OIL RESERVES HAD BEEN PROVEN.

BILLIONS OF BARRELS OF CRUDE OIL HAVE BEEN RECOVERED BY WATERFLOODING TO PROVIDE MAN WITH INCREASED SUPPLIES OF ENERGY AND FUEL THAT COULD STILL BE LOCKED IN THE EARTH WITHOUT THE INDUSTRY'S CONSTANT EFFORT TO IMPROVE ITS RECOVERY METHODS.

OKLAHOMA HISTORICAL SOCIETY 1973
WITH OKLAHOMA PETROLEUM COUNCIL

the formation to produce additional oil.

Later, because of availability and low cost, water became the prime means for producing additional oil after the primary or flush flow ceased. Waterflooding is generally applied in a five-spot pattern with water-injection wells at the corners of a square and a production well in its center. In this way, the water from the outer parts of the pattern is slowly forced toward the center, pushing the oil toward the production well.

Waterflooding Once Illegal

In the early part of this century, injection of water into the formation was illegal because many people believed that harm would result. However, as the result of surreptitious work in the Bradford, Pa., oilfield, the benefits of waterflooding came to be known. So in 1921 the Pennsylvania legislature repealed the law, giving waterflooders the opportunity to proceed.

Waterflooding was first tried in Oklahoma in May 1931 on a Carter Oil Co. (now Exxon) lease south of Nowata in Rogers County. Bert Collins, under agreement with Carter Oil Co., injected water into two wells. The lease became fully developed over the decade. A 1942 report indicated that slightly more than 200,000 barrels of oil had been recovered by injection of 6½ million barrels of water, and assessed the project: "Although the project can- be considered an outstanding ncial success, it demonstrated that under favorable sand conditions the recovery of large quantities of oil by waterflooding in Oklahoma not only s practical but if the price of oil is h enough would be a lucrative oil-producing operation."[2]

Another waterflood project in Oklahoma was begun in 1934, and after 1935 waterflooding proliferated rapidly. By 1940, about 3 million barrels of oil was being produced annually by waterflooding. During World War II, waterflooding progress was slowed because of unavailability of pipe, but after the war a resurgence of effort began. By 1960, more than 50 million barrels of oil a year was being recovered in Oklahoma by waterflooding (about 25 percent of total production). More than half of Oklahoma's oil was produced by waterflooding in the 1970's.

Contributing to the rapid increase in the use of waterflooding techniques were the "waterflood tours" of the U.S. Bureau of Mines and the Kansas-Oklahoma Waterflood Association.[3] In the 1950's and early 1960's, oilmen in a caravan of cars annually visited 3 to 5 waterflood projects where new or improved techniques were used. This annual event attracted several hundred oilmen. The tours were started by R. C. (Chuck) Earlougher, petroleum consultant in Tulsa, Okla., and D. B. Taliaferro of the Bartlesville Center of the U.S. Bureau of Mines. See accompanying information about the tour reports.

The table shows the rapid increase in waterflooding during the 1955–1965 period. This method of secondary recovery permitted Oklahoma to main-

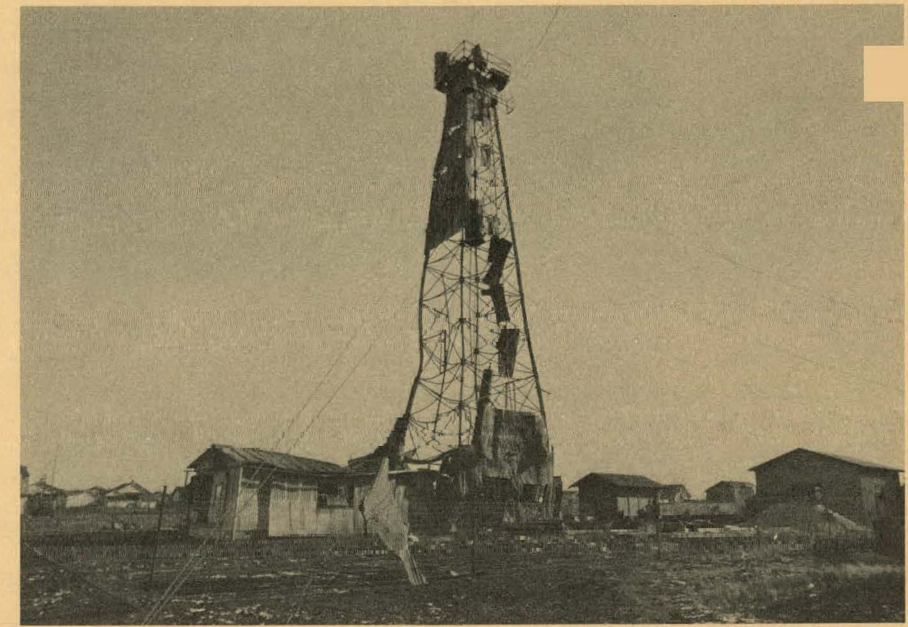
GROWTH OF WATERFLOODING IN OKLAHOMA

Year	Total Oil Production BOPD[a]	Waterflood Production BOPD[b]	Percentage of Total Production
1900	164		
1910	143,000		
1915	202,000		
1920	291,000		
1925	484,000		
1930	593,000		
1935	508,000	c	
1940	428,000	8,000	2
1945	382,000	10,000	3
1950	451,000	15,000	3
1955	556,000	27,000	5
1960	527,000	137,000	26
1965	560,000	241,000	43
1970	613,000	276,000	45
1975	447,000	274,000	61
1980	410,000	c	

[a] *Oil and Gas Journal*, January reviews.

[b] Waterflood production estimated from various Interstate Oil Compact Commission reports.

[c] No figures available.



Research pioneers in many disciplines often face unknown dangers. This certainly was true in early oil and gas research. The photo at left taken in 1928 shows an experimental derrick on the BETC grounds. The photo at right from another angle shows what was left of the setup after a natural gas explosion killed two men on Dec. 13, 1929.

tain its total production for years after the primary production curve had started downward.

Improvements in waterflood technology were relatively minor as long as economic limitations prevailed. Attention to water quality was first based on bacteriocides to prevent the growth of bacteria which might plug the formation. Oxygen was removed and inhibitors were added to help prevent corrosion. The use of STP—sodium tripolyphosphate was recommended to hold iron and other heavy metals in solution to prevent plugging and to allow faster injection rates by changing wetting properties of the formation.[4]

Acidizing and Fracturing Developed

Other techniques that contributed to improved recovery by stimulation were acidizing and hydraulic fracturing.

The use of acid for well completions instead of shooting with nitroglycerine came into vogue in the 1930's. The acid permits a more rapid recovery of oil by enlarging pores in the formation. The "hydrafrac" process was announced in 1948 by J. B. Clark of Pan American Research (now Amoco Production Co.) of Tulsa. This process used a gel under pressure to fracture the formation. It rapidly supplemented explosive fracturing or "shooting" as a means of increasing oil flow.[5]

Various techniques to enhance the recovery of oil were attempted in the 1960's.[6] Thermal methods—including steam injection and *in situ* combustion—were tried. Miscible flooding, in which injection fluids could dissolve the oil, were used in various experimental projects.

Chemical flooding is a term used for the addition of chemicals to the waterflooding process in order to recover additional oil. The first step was the addition of a polymer to the water being injected in a pattern. The polymer increases the viscosity of the water so that it has less tendency to penetrate or run past the oil bank, and consequently more oil is recovered. A second step was the use of surfactant in the water to lower the interfacial tension between the oil and water, and thus to produce additional oil from the rock pores. A third method was to add a chemical (sodium hydroxide, for example) to alter the rock surface and decrease wettability toward oil.

The relatively low price for oil and high price for the chemicals held back progress in developing the processes through field tests until the 1973 oil embargo and the resultant rise in oil prices. In 1974, the U.S. Bureau of Mines began a cooperative program with industry to demonstrate the processes and to develop data to reduce risk in designing new projects. The Bartlesville Center was given the lead role in this program.

Twenty-six Field Projects Involved

The first project was with Cities Service Co. in the El Dorado (Kansas) field using the surfacta polymer process. The program timately spread to 26 field projects throughout the United States. The projects were financed on average by one-third government funds a two-thirds industry-owner funds. return for its investment, the government required that extensive data be generated and that the data could be made available to any interested individual or company. This resulted in a completely documented history of each project and served to spur commercial EOR projects as economics allowed. The projects included micellar-polymer flooding, alkaline flooding, polymer flooding, carbon dioxide flooding, steam drive and *in situ* combustion projects.

Supporting the field demonstration program was a basic research program conducted at universities and other research institutions. These projects have performed research to explain and improve the processes being demonstrated.

Oklahoma participants in the field and laboratory projects included Cities Service Co. (El Dorado, Kans., micellar-polymer flood, and Bellevue, La., *in situ* combustion project); Phillips Petroleum Co. (Burbank, Okla., micellar-polymer flood); Gulf Oil Corp. (originally Kewanee Oil Co.) (North Stanley, Okla., polymer flood); University of Tulsa; University of Oklahoma; and Oklahoma State University.

A third program, which was begun in 1979, was the Department of Energy Tertiary Oil Recovery Incentives Program,[7] whereby a company was permitted to sell oil at world prices as partial payment for conducting an enhanced oil recovery project. Of the 416 projects, 24 were in Oklahoma, including four miscible fluid displacement projects, one conventional steam drive injection project, seven microemulsion flooding projects, 10 polymer-augmented waterflooding projects, one alkaline (caustic) flooding project, and one miscible nonhydrocarbon gas displacement project.

Altogether, DOE's Enhanced Oil Recovery Program has resulted in the world's largest accumulation of data supporting the new technologies. Individual cost-sharing and basic research projects have been

Portable laboratories such as this were used in waterflooding field tests by BETC engineers working in cooperation with industry. The first Oklahoma waterflood was about 20 miles east of BETC near Nowata.

thoroughly documented. The resulting information and data are made available through government publications, quarterly reports, symposia, and through the petroleum industry media.

REFERENCES

[1] Lewis, J. O. Methods for Increasing the Recovery of Oil From Oil Sands. *BuMines Bull. 148,* 1917, 128 pp.

[2] Taliaferro, D. B., and D. M. Logan. History of Waterflooding Oil Sands in Oklahoma. *BuMines RI 3728,* 1943, 182 pp.

[3] Liquid Fossil Fuel Technology, "How Waterfloods Popularized Secondary Recovery." DOE/BETC/QPR-81/1, January–March 1981, pp. 12–15.

[4] Johansen, R. T., and R. J. Heemstra. Effectiveness of Sodium Tripolyphosphate for Improving Injection Rates of Waterfloods. *BuMines RI 6557,* 1964, 15 pp.

[5] Carter, D. V., Editor, *History of Petroleum Engineering.* American Petroleum Institute, 1961, 1,241 pp.

[6] Poettman, F. H., D. C. Bond, and C. R. Hocott, Editors, *Secondary and Tertiary Oil Recovery Processes,* 1974, 187 pp.

[7] "DOE Enhanced Oil Recovery Incentive Program," Progress Review No. 26, DOE/BETC-81/2, January–March 1981.

WATERFLOOD TOUR REPORTS REPRINTED BY BETC

One feature of the waterflood tours co-sponsored by the U.S. Bureau of Mines and the Kansas-Oklahoma Waterflood Association was the issuance of Bureau of Mines publications describing the projects visited. The preparation of these reports was started as soon as the projects for the next waterflood tour were selected. Some of these publications were recently reprinted by BETC, and subsequent requests have shown continued interest in the technology.

Following is a partial listing of waterflood reports reprinted by the BETC. Single copies are still available free and will be mailed upon request as long as supplies last. If interested, request each report desired by the report number and title. Send your request to: Technology Transfer Branch, Bartlesville Energy Technology Center, P.O. Box 1398, Bartlesville, OK 74005.

BuMines RI 3728. "History of Waterflooding of Oil Sands in Oklahoma," by D. B. Taliaferro and D. M. Logan, 1943, 182 pp.

BuMines RI 4795. "Waterflooding of Oil Sands in Washington County, Okla.," by C. H. Riggs and W. C. Smith, 1951, 16 pp.

BuMines RI 4831. "A Survey of Oil Production in Oklahoma by Waterflooding, Pt. I. Nowata, Rogers and Craig Counties," by J. P. Powell and K. H. Johnston, 1952, 160 pp.

BuMines RI 4832. "A Survey of Oil Production in Oklahoma by Waterflooding. Pt. II. Counties other than Nowata, Rogers, and Craig," by J. P. Powell and K. H. Johnston, 1951, 142 pp.

BuMines RI 4896. "Waterflooding in Nowata County, Okla., Oil Fields," by J. P. Powell and J. L. Eakin, 1952, 49 pp.

BuMines RI 5000. "Waterflooding in Burbank Oil Field, Osage County (Okla.)," by C. H. Riggs, 1954, 19 pp. (7th Annual Waterflood Tour.)

BuMines RI 5134. "Recent Developments in Waterflooding in Nowata County, Okla., Oilfields, 1954-55," by J. L. Eakin, 1955, 49 pp. (8th Annual Waterflood Tour.)

BuMines IC 7750. "Waterflooding of Oil Sands in Butler and Greenwood Counties, Kans.," by J. P. Powell, 1956, 42 pp. (9th Annual Waterflood Tour.)

BuMines IC 7787. "Some Recent Developments in Waterflooding in Washington County, Okla., 1956-57," by J. P. Powell, 1957, 35 pp. (10th Annual Waterflood Tour.)

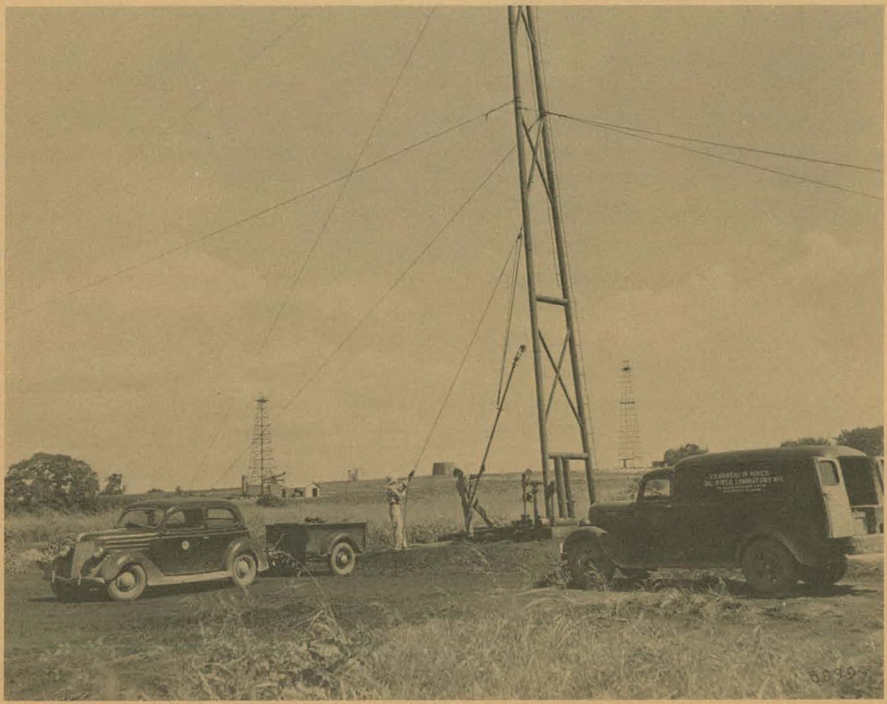
BuMines IC 7896. "Four Waterflooding Projects in Washington and Nowata Counties, Okla.," by J. P. Powell, 1959, 34 pp.

BuMines IC 7969. "Four Waterflooding Projects in Greenwood County, Kansas, 1960," by K. H. Johnston, 1960, 36 pp.

BuMines IC 8038. "Developments in Waterflooding and Pressure Maintenance in Osage County, Okla., Oilfields, 1961," by K. H. Johnston and J. L. Castagno, 1961, 38 pp.

Most of the publications were produced in cooperation with the State of Oklahoma. Many of the reports were reprinted or adapted in the *Oil and Gas Journal, Producers Monthly,* and *Interstate Oil Compact Commission Bulletin.*

Engineering Field Reports Aided Oklahoma Operators



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In the 1930's, BETC petroleum engineers tested instruments in the field for obtaining bottom-hole pressures and temperatures.

When the Petroleum Experiment Station was established in Bartlesville, oilfield practices were often haphazard. Operators came to a field, drilled wells at random, took the flush production, and moved on. In an effort to introduce conservation, Bureau of Mines engineers made studies of fields and showed operators how, by a more systematic production scheme based on engineering knowledge, the profits as well as the total oil production could be increased.

Bureau engineers used a "hands-on" approach, and the early days found them assigned to help with day-to-day operation as well as to lead producers to better practices. Resulting from their close association with a field, they produced an engineering field report designed not only to show what had been

This steam-powered pump was used in the 1930's for treating emulsions in oilfields.
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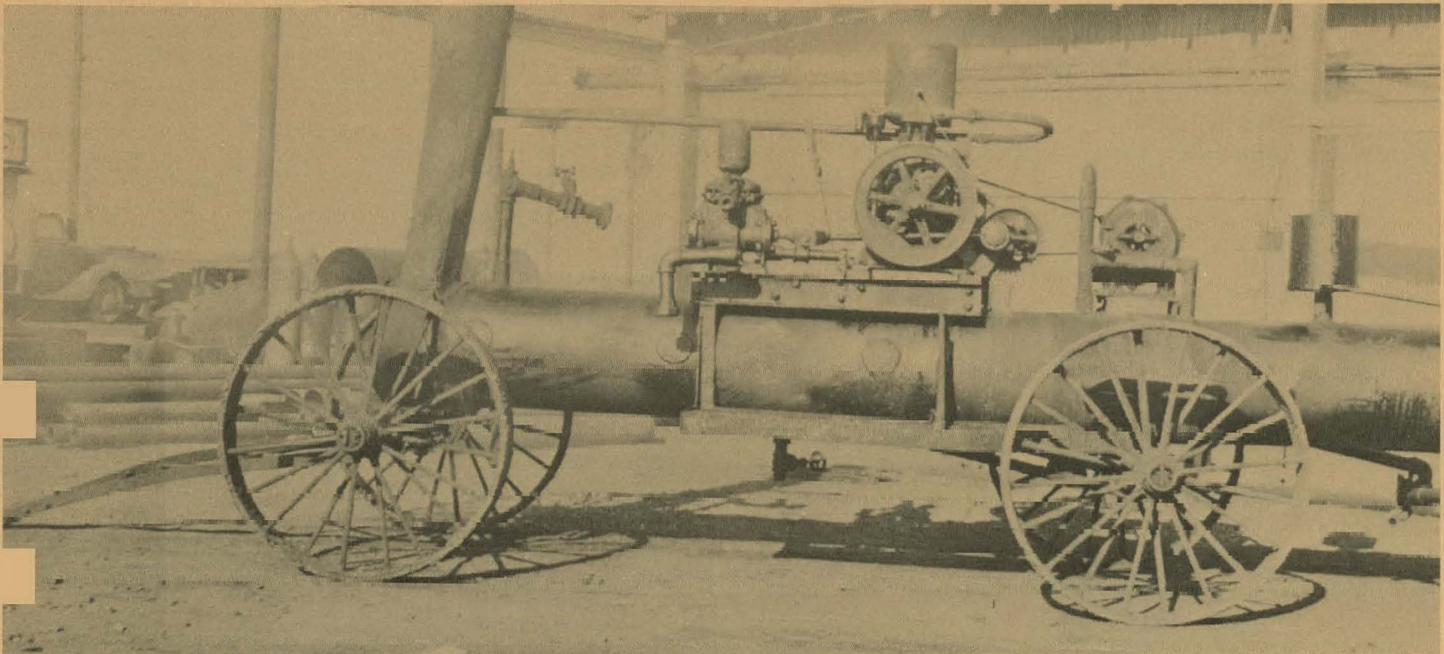


done, but also to suggest what could be done by other operators. Reports dealing with Oklahoma fields were generally in cooperation with a local or state organization, which often furnished funds for printing the report.

A series of reports in the early 1920's was labeled "Engineering Field Reports," but later these were blended into the Bureau of Mines' series of Reports of Investigations. They were phased out in the late 1930's as the oilfield operators became more engineering oriented and performed their own studies.

The following is a list of field reports dealing with Oklahoma fields. The year during which each report was published is shown before the title. These old reports are not available for distribution by the Bartlesville Energy Technology Center, but copies are available for examination in the BETC Library. Some of the old reports may be available from the Bureau of Mines; if interested, individuals should contact the U.S. Bureau of Mines, 4800 Forbes Ave., Pittsburgh, PA 15213.

1917 Geologic Structure in the Cushing Oil and Gas Field, Oklahoma and Its Relation to the Oil Gas and Water, by Carl H. Beal.

1919 Underground Problems in the Comanche Oil and Gas Field, Stephens County, Oklahoma, by T. E. Swigart (in cooperation with the State of Oklahoma).

1920 Report on the Underground Conditions in the Walters Oil and Gas Field, by T. E. Swigart (in cooperation with the State of Oklahoma).

1921 Petroleum Engineering in the Deaner Oil Field, Okfuskee County, Oklahoma, by M. J. Kirwan and F. X. Schwarzenbek (in cooperation with the State of Oklahoma and the Chamber of Commerce, Bartlesville, Okla.).

1921 Petroleum Engineering in the Hewitt Oil Field, Oklahoma, by T. E. Swigart and F. X. Schwarzenbek (in cooperation with the State of Oklahoma and the Chamber of Commerce, Ardmore, Okla.).

1922 Petroleum Engineering in the Slick Oil Field, Creek County, Oklahoma, by F. X. Schwarzenbek, J. S. Ross and J. H. Cable with a chapter on Dehydration Methods Used in the Slick Field by J. H. Cable (in cooperation with the State of Oklahoma and the Chamber of Commerce, Bartlesville, Okla.).

1923 Engineering Report of the Chickasha Gas Field, Grady County, Oklahoma, by M. J. Kirwan and T. E. Swigart (in cooperation with the State of Oklahoma and the Chamber of Commerce, Bartlesville, Okla.).

1923 Preliminary Report on Engineering in the Tonkawa Oil Field, Kay and Noble Counties, Oklahoma, by J. S. Ross (in cooperation with the State of Oklahoma).

1923 Report of Investigations 2450, Petroleum Engineering in the Skull Creek Oil Pool, Northeastern Osage County, Oklahoma, by T. E. Swigart.

1924 Petroleum Engineering in the Fox and Graham Oil and Gas Fields, Carter County, Oklahoma, by H. C. George and John R. Bunn (in cooperation with the Office of Indian Affairs, the State of Oklahoma and the Chamber of Commerce, Ardmore, Okla.).

1924 Report on the Quinn Dome in the Lyons-Quinn Oil and Gas Field, Okfuskee and Okmulgee Counties, Oklahoma, With Special Reference to the Migration of Gas Found Below the Lyons Oil Sand and the Resulting Effect on the Oil and Casinghead Gas Production of This Sand, by M. J. Kirwan, C. O. Rison, and D. P. Wardwell (in cooperation with the Office of Indian Affairs).

1924 Petroleum Engineering in the Cromwell Oil Field, Seminole and Okfuskee Counties, Oklahoma, by C. O. Rison and John R. Bunn (in cooperation with the Office of Indian Affairs and the State of Oklahoma).

1924 Report of Investigations 2612, Effects of Extraneous Gas on the Production of Oil Wells in the Lyons-Quinn Field of Oklahoma, by M. J. Kirwan.

1926 Engineering Report on the Chickasha Gas Field, Grady County, Oklahoma, by R. R. Brandenthaler and E. P. Campbell (in cooperation with the State of Oklahoma and the Chamber of Commerce, Oklahoma City, Okla.).

1926 Engineering Report on the Davenport Oil Field, Lincoln County, Oklahoma, by R. R. Brandenthaler, K. C. Sclater, and H. M. Kent (in cooperation with the State of Oklahoma and the Chamber of Commerce, Bartlesville, Okla.).

1926 Petroleum Engineering in the Papoose Oil Field, Okfuskee and Hughes Counties, Oklahoma, by John R. Bunn and Louis Roark with a chapter on the Geology of the Papoose Oil Field, by Louis Roark (Oklahoma Geological Survey Bulletin No. 36).

1926 Report of Investigations 2778, The Application of Compressed Air to the Elliott Pool, Nowata County, Okla., by B. E. Lindsly.

1927 Water Problems in the North Part of the Cushing Oil Field, Creek County, Oklahoma, by D. P. Wardwell, R. R. Brandenthaler, W. L. Williams, and John Van Dall (in cooperation with the State of Oklahoma).

1928 Preliminary Engineering Report on the Seminole Pool, Seminole County, Oklahoma, by C. R. Swarts, C. R. Bopp, and W. S. Morris (in cooperation with the State of Oklahoma).

1930 Report of Investigations 2997, Engineering Study of the Seminole Area, Seminole and Pottawatomie Counties, Oklahoma, by R. R. Brandenthaler, W. S. Morris, and C. R. Bopp (in cooperation with the State of Oklahoma).

1933 Report of Investigations 3217, Estimate of Gas Reserves of the Oklahoma City Oil Field, Oklahoma County, Oklahoma, by H. B. Hill and E. L. Rawlins (in cooperation with the State of Oklahoma and the Chamber of Commerce, Oklahoma City, Okla.).

1937 Report of Investigations 3330, E neering Report on Oklahoma City Field, Oklahoma, by H. B. Hill, E. L. Rawlins, and C. R. Bopp (in cooperation with the State of Oklahoma).

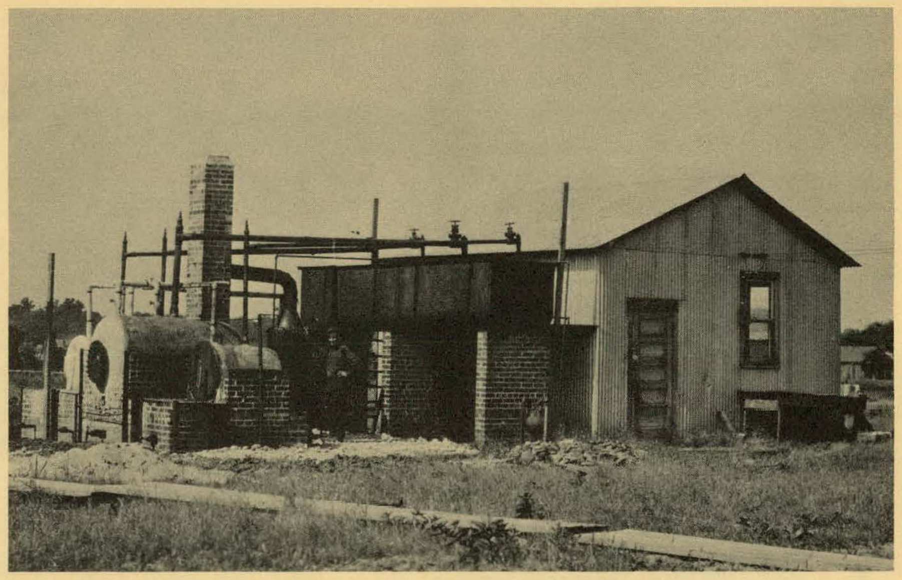
1937 Report of Investigations 3338, Estimate of Natural Gas Reserves From the L ton, Oolitic and Oswego-Prue Horiz in the Oklahoma City Oil Fields, by R. E. Heithecker (in cooperation with the State of Oklahoma).

Much Basic Petroleum Research Conducted in Oklahoma

This crude oil analysis laboratory at BETC (about 1925) was the forerunner of today's crude oil analysis data bank that contains about 12,000 analyses on oils from throughout the world. BETC employees shown are Dr. F. W. Lane, at left desk; John Devine, standing in background, and Harold Thorne.

Petroleum as it comes from the earth is a mixture of various proportions of oil, gas and brine. The oil, after separation from gas and brine, varies considerably in its appearance, texture, and suitability for the erent products to be made from Early scientists decided that, if they knew the chemical compounds comprising the oil, they could select oils for special purposes. However, complexity of the mixture made a task of overwhelming magnitude. It has been estimated that a crude oil can contain more than a million species of molecules.

Although small excursions into the identity of petroleum components had been made, it was not until 1925 that a major effort was started. Under the auspices of the American Petroleum Institute (API) and funded by contributions from John D. Rockefeller and the Universal Oil Products Co., a program of fundamental research was started.[5]



In the 1920's, this experimental refinery at the Bartlesville Energy Technology Center was the very latest in petroleum technology facilities.

One of the early projects—API Research Project 6—continued for almost 40 years, with most of its effort on the elucidation of the composition of one crude oil.

Chosen as the representative crude oil on which the project concentrated for more than 35 years was the Oklahoma oil from Well No. 6 in the South Ponca field of Kay County.[8]. This oil, furnished by Marland Oil Company in a 1,000-gallon quantity, was representative of the crudes from the burgeoning Mid-Continent oil province. It was first distilled in a commercial still by Sun Oil Company and then at the National Bureau of Standards where the project was first located (1926–1950). It was moved to Carnegie Institute of Technology for the remainder of its existence (1950–1965).

Project 6 identified 295 hydrocarbon compounds, which accounted for about 50 percent of the crude oil. About 200 scientific papers were written on the research.[13]

A chairman of the API advisory committee, Dr. S. S. Shaffer of Humble Oil Co., described the work:[9] "A worker in basic scientific research is motivated by a driving curiosity about the unknown. Discovery of truth and understanding are his objectives. His research is to do something no man ever did before or to learn something no man ever knew before. When he obtains new knowledge, he experiences the same thrill and satisfaction as does the explorer first reaching the top of a mountain. The staff of the API research Project 6 works in this vein."

New Procedures Developed

The separation proceeded by repeated distillations until the fractions could not be separated further. When this process was not sufficient to isolate a compound, new methods were developed, and some of the major contributions of the work were the new separation and identification procedures developed by the project.

A display of the samples of individual hydrocarbons isolated by Project 6 from the Ponca crude oil is in the auditorium of the Bartlesville Energy Technology Center. Some 194 hydrocarbons are sealed in glass ampoules, representing many man-years of work and more than $1 million of effort. With newer methods and exploratory results from Project 6, the identifications can be made in a fraction of the time at much less cost.

As part of the Mid-Continent activity, another manifestation was the establishment of the Petroleum Experiment Station (now Bartlesville Energy Technology Center) of the U.S. Bureau of Mines at Bartlesville. Although the primary purpose was to assist drillers and production people in becoming more efficient and to promote conservation, it became evident early that a scientific approach was needed and that basic information would have to be obtained.

Crude oil analyses and brine analyses were the first steps taken. Together, they constituted an appreciable effort over the years to learn more about the variations in petroleum found in different environments and led to the science of geochemistry.

One of the early studies of the composition of crude oil is described in H. M. Smith's 1930 report[11] on the lubricant fraction of Cabin Creek, W. Va., crude oil. Although no compounds were isolated and the chief conclusion concerned the tremendous complexity of the fraction, the application of solvent extractior the separation processes undoubtedly led to advances in lubricating-oil technology.

The early battle victories of the Japanese in World War II effecti shut off the supply of natural rub to the United States. A crash research program resulted in the rapid development of synthetic rubber processes. However, this development was slowed and was somewhat inefficient because of the lack of basic data on the hydrocarbons used. Thermodynamic properties—which govern the transformation of one molecular species to another—were particularly sparse for the butane-butadiene reaction, which is the basis for much synthetic rubber. This caused such problems as resorting to trial-and-error experimentation to discover reaction conditions that should have been calculated, and to over-design of equipment because pressures and temperatures could not be calculated.

Thermodynamics Laboratory Established

As a result, the government established at the Bartlesville Center a thermodynamics laboratory which has become internationally distinguished. Dr. H. M. Huffman, a widely-known thermodynamicist then at the California Institute of Technology, came to Bartlesville in 1943 to head the new laboratory. It was noteworthy that Huffman brought with him his calorimeter that he had designed at Cal Tech. He proceeded to build a staff of specialists in combustion calorimetry, low-temperature calorimetry, vapor flow calorimetry, pressure-volume-temperature relationships, and molecular spectroscopy. Much of the equipment used was designed and built at Bartlesville and thereafter copied in other laboratories all over the world.

After Huffman's death in 1950, he was succeeded by Dr. Guy Waddington, who received the Southwest Regional American Chemical Society Award in 1953. In 1957, he left Bartlesville for Washington to head the Office of Critical Tables in the National Academy of Sciences—National Research Council.

Dr. J. P. McCullough succeeded Dr. Waddington. He received the American Chemical Society Award in Petroleum Chemistry in 1963. McCullough left the Bureau of Mines in 1963 to head Mobil Oil Company's Basic Research Laboratory in Princeton, N.J.

Other directors of the thermodynamics laboratory have been Dr. D. R. Douslin (1963–1976) and W. D. Good (1976–1982).

During the almost 40 years that the thermodynamics laboratory has been in existence, 247 papers have been published. Properties of more than 375 compounds have been determined and published.

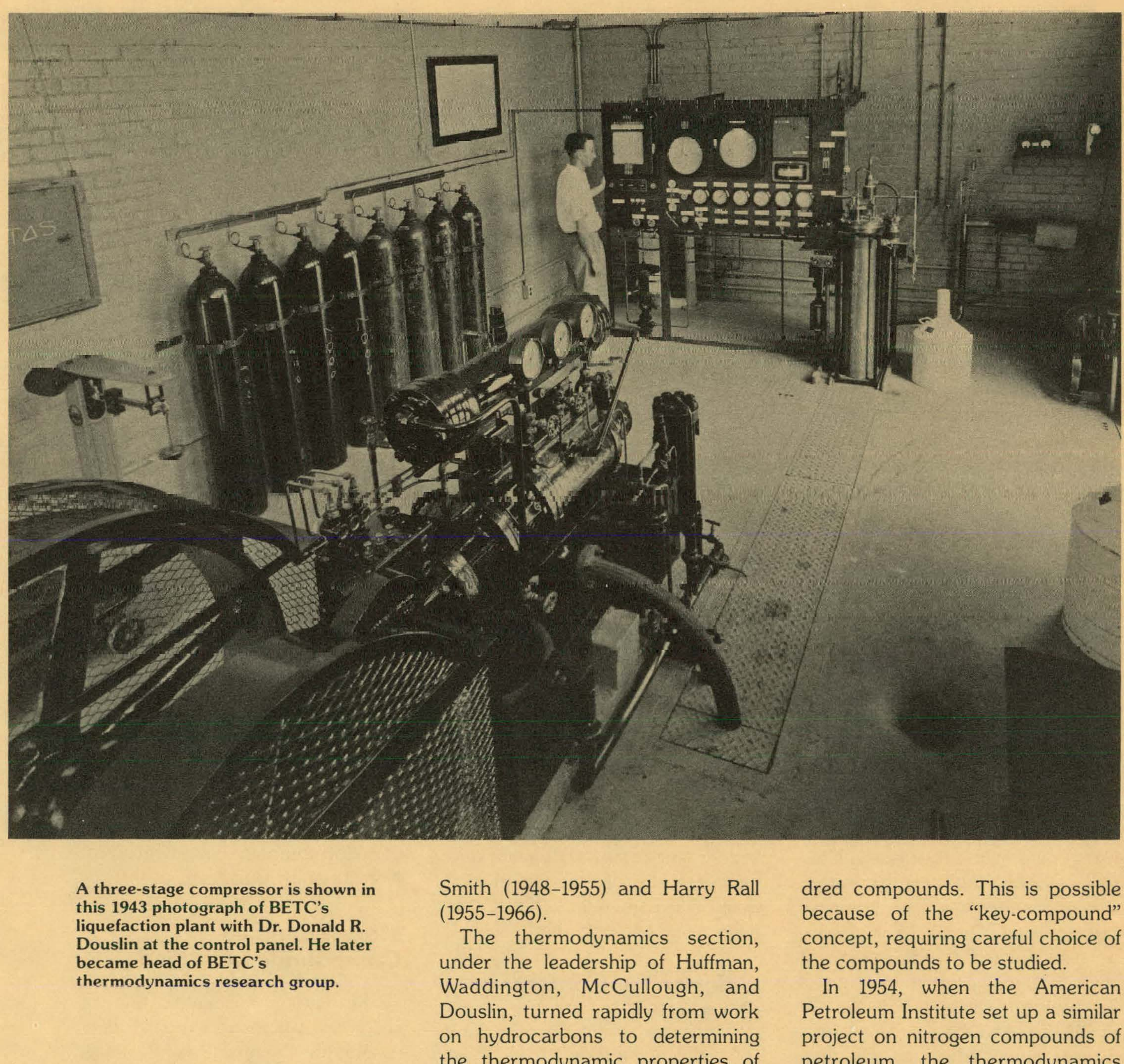
Calorimetry Conference Organized

At the suggestion of Huffman, a group of thermodynamics investigators was organized into the Calorimetry Conference in 1945 to hold annual meetings. The Huffman Memorial Award to honor outstanding thermodynamicists was established in 1954. BETC recipients have included Waddington (1954), McCullough (1963), Ward N. Hubbard at BETC with Huffman but later at Argonne National Laboratory (1969), and Good (1981).

World War II work on aviation gasoline had shown scientists at the Bartlesville Energy Technology Center the need for more information about the sulfur compounds of petroleum. By the summer of 1947, BETC and Laramie, Wyo., Petroleum Experiment Station personnel had prepared a proposal for work on sulfur compounds to be jointly sponsored by the American Petroleum Institute and the Bureau of Mines. Set up as API Project 48 in July 1948,[1] sections on the identification of sulfur compounds from petroleum and on thermodynamic properties of sulfur compounds were established at Bartlesville. A section on the preparation of highly purified sulfur compounds for reference standards and the development of analytical methods was established at Laramie, and a section on synthesis of sulfur compounds was set up at Northwestern University.

More Than 200 Compounds Identified

The work on identification of sulfur compounds was very productive, and by the time the project was terminated in 1966, more than 200 sulfur compounds from four different crude oils had been identified. The compounds represented 13 different classes of sulfur compounds, four of which—alkyl cycloalkyl sulfides, disulfides, alkyl aryl sulfides, and thiaindans—had not been identified previously in petroleum. Directors of the section were Harold



A three-stage compressor is shown in this 1943 photograph of BETC's liquefaction plant with Dr. Donald R. Douslin at the control panel. He later became head of BETC's thermodynamics research group.

Smith (1948–1955) and Harry Rall (1955–1966).

The thermodynamics section, under the leadership of Huffman, Waddington, McCullough, and Douslin, turned rapidly from work on hydrocarbons to determining the thermodynamic properties of sulfur compounds. An outstanding achievement was the development of the rotating bomb calorimeter—a necessity for obtaining meaningful data with sulfur compounds. A body of sulfur compound data was developed over the 18-year project, involving careful measurements on 40 highly purified compounds. The data can be extrapolated to several hundred compounds. This is possible because of the "key-compound" concept, requiring careful choice of the compounds to be studied.

In 1954, when the American Petroleum Institute set up a similar project on nitrogen compounds of petroleum, the thermodynamics studies were placed at Bartlesville. This project, which was active for
years, made a considerable impa
An inclined piston gage was developed at BETC for the determination of vapor pressures in extremely low ranges.

In 1966, a realignment of Ame
can Petroleum Institute Projects saw the beginning of API Project 60

on Heavy Ends of Petroleum, API Project 62 on Thermodynamics of Hydrocarbons and Related Compounds, and API Project 58 on Synthesis of Hydrocarbons. Project 58 arose from the needs of the thermodynamics work for pure compounds and a need for replenishment of a reference sample bank which the API sponsored at Carnegie Institute of Technology. Project 62 emphasized hydrocarbons, as well as sulfur and nitrogen compounds. Project 60 resulted from the cessation of work on hydrocarbons (API 6), sulfur compounds (API 48), nitrogen compounds (API 52) and metal-organic compounds (API 56). In jumping to higher-boiling fractions of petroleum, it was no longer possible to segregate the compounds into these classes because one molecule might belong to two or three of the classes.

API Project 58B was placed at Oklahoma State University with Dr. E. J. Eisenbraun as director. Its role was to prepare pure hydrocarbons for determination of properties, both physical and thermodynamic, and to furnish material for the reference standard program (API 58A). To do this required the development of new methods of synthesis and new techniques of purification. The project operated from 1966 to 1975.

eavy-Ends Work Divided

The research on heavy ends of petroleum was divided among the Bartlesville and Laramie Centers and North Dakota State University.

e Bartlesville Center was assigned the development schemes of distillation and chromatography to separate the compounds of interest from those of lower or higher molecular weight. The work was under the direction of H. T. Rall, C. C. Ward, and C. J. Thompson, successively. The development of methods and their application to six crude oils were major achievements of the 9 years.[2,3]

The thermodynamics work at BETC continued the investigation of sulfur and nitrogen compounds, and in addition reexamined the properties for several hydrocarbons. As a result, a consistent set of tables for 100 alkane hydrocarbons was prepared.[10]

The API sponsorship of such projects ceased in 1975, but BETC continued basic work, turning largely to alternate fuels under the Energy Research and Development Administration and later under the Department of Energy. The methods developed for petroleum furnished a sound foundation for extension into the more highly aromatic compounds found in coal liquids, the nitrogen compounds of shale oil, and the complex asphaltenes of tar sands.

REFERENCES

1 Barnes, K. B. Sulfur in Petroleum. *Oil & Gas Journal,* Nov. 4, 1948.

2 Dooley, J. E., D. E. Hirsch, C. J. Thompson, J. W. Vogh, and C. C. Ward. Analyzing Heavy Ends of Crude. *Hydrocarbon Processing,* v. 52, Sept. 1973, pp. 123–130; v. 53, April 1974, pp. 93–100; v. 53, July 1974, pp. 141–146; v. 53, Nov. 1974, pp. 187–197.

3 Haines, W. E., and C. J. Thompson. Separating and Characterizing High-Boiling Petroleum Distillates. The USBM-API Procedure. Energy Research and Development Administration, BERC/RI-75/2 and LERC/RI-75/5, 1975, 28 pp.

4 *Liquid Fossil Fuel Technology.* Scientific Skill Plus Advanced Equipment Equals Breakthrough. DOE/BETC/QPR-80/4, 1981, pp. 46–49.

5 Miller, A. E. Review of American Petroleum Institute Research Projects on Composition and Properties of Petroleum. *Proc., World Petroleum Congress,* 1955, Section V, pp. 27–86.

6 Petroleum Fraction Yields 21 Compounds. *Chemical and Engineering News,* March 5, 1962, pp. 54–56.

7 Rall, H. T., C. J. Thompson, H. J. Coleman, and R. L. Hopkins. Sulfur Compounds in Crude Oil. *BuMines Bull. 659,* 1972, 187 pp.

8 Rossini, F. D. The Chemical Constitution of the Gasoline Fraction of Petroleum—API Research Project 6. *Proc., American Petroleum Institute,* Midyear Meeting, 1935, pp. 47–62.

9 Rossini, F. D., and S. S. Shaffer. API Research Project 6—Analysis, Purification, and Properties of Petroleum Hydrocarbons. *Proc., American Petroleum Institute,* Annual Meeting, Section VI, 1954, pp. 14–61.

10 Scott, D. W. Correlations of the Chemical Thermodynamic Properties of Alkane Hydrocarbons. *J. Chem. Phys.,* v. 60, No. 8, April 1974, pp. 3144–3165. Also *BuMines Bull.* 666, 1974, 187 pp.

11 Smith, H. M. A Study of the Lubricant Fractions of Cabin Creek (W. Va.) Petroleum. With Chapters on the Action of Solvents on the Heavy Constituents of Petroleum by F. W. Lane, I. H. Nelson, and J. M. Devine. *BuMines Tech. Paper 477,* 1931, 48 pp.

12 Smith, H. M., H. N. Dunning, H. T. Rall, and J. S. Ball. Keys to the Mystery of Crude Oil. *Proc., American Petroleum Institute,* v. 39 (III) (1959), pp. 433–465.

13 Thompson, C. J., C. C. Ward, and J. S. Ball. Characteristics of World's Crude Oils and Results of API Research Project 60. Energy Research and Development Administration. BERC/RI-76/8, 1976, 28 pp.

BETC Utilization Research Began After World War II

There has been a conscious effort at the Bartlesville Energy Technology Center to avoid process research that is competitive with industry research. Certain areas of research that have failed to attract industrial effort have, however, been deemed appropriate for government research.

For example, the U.S. armed services have the unusual requirement of storing supplies of fuel in remote locations for long time periods. This is not a critical problem for industry because turnover times for fuel supplies in this country are short. Consequently, BETC has, with the cooperation of the Army, Navy, and Air Force, entered into research not only to determine effective-life for fuels but also to determine mechanisms for deterioration and means for extending the "life" of the fuel.

Diesel fuels, aviation gasoline, and other fuels have been the object of considerable investigation. More recently, the stability of fuels prepared from alternate fuels—tar sands, shale oil, and coal liquids—has been investigated.

Re-Refining Used Oil

With impetus from both the environmental movement and the crude oil shortage, the problem of reclamation of used lubricating oil came to the fore in the mid-1970's. The small re-refining industry was in difficulty because of its inability to dispose of wastes and a depressed price resulting from the perception that re-refined oil was not as good as oil from virgin stocks. A newly patented process from BETC, based on solvent refining, showed that re-refined oil could work as well as new oil and that the waste problem could be solved as well. The wide dissemination of the information resulting from the research brought others into the field. For example, Phillips Petroleum Co. developed its "PROP" process for re-refining oil.

Fuels Combustion Research

Following World War II when railroads and trucks became dieselized, BETC was involved in studies of the efficiency of the diesel engine. One requirement was the effective analysis of the combustion, or exhaust, gases. The development of this technique came at the time when air pollution problems were becoming serious. Almost no laboratories in the country had the background of automotive research and analytical capability necessary for investigating air pollution from automobile exhausts.

As a result, BETC was drawn into the air pollution research effort early. In cooperation with the Public Health Service, the National Air Pollution Control Authority, the American Petroleum Institute, the Coordinating Research Council, the LP-Gas Association and the Environmental Protection Agency, various projects were undertaken.

Techniques were developed for capturing, handling, and analyzing exhaust gases. That work led to an understanding of the chemical composition of the exhaust gases. With these techniques, studies could be made about how fuel composition affects exhaust gases, how engine design affects exhaust gases, and how fuels and engines could be altered to reduce contaminating emissions.

Soon it became evident that knowledge was needed about the reaction mechanism whereby exhaust gases are converted to smog. For that work, BETC constructed one of the first environmental smog chambers. Exhaust gases were placed in a temperature-controlled chamber providing irradiation by light of controlled intensity and color to reproduce the effect of the sun. Complicated analysis systems determined which components of exhaust contributed to smog and what reactions took place.

Since it was known that olefins are converted easily to smog, a proposal to ban olefins from gasoline was introduced into the California legislature. Research at BETC showed, however, that olefins in gasoline generally are completely combusted, and the olefins in exhaust gas arise from incomplete reaction of saturated compounds. The proposal was dropped.

Diesel Fuel Studies

A program of diesel fuel studies was established. An unusual feature of diesel is that the odor of diesel exhaust is probably its most objectionable property. To study this factor, BETC set up a human die exhaust odor panel. This gro mostly housewives, would meet in a specially designed odor laboratory to sniff samples of diesel exhaust and rate odor by comparison on a scale of standards. Combined w compositional analysis, this information allowed correlation of chemical

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Throughout WWII, BETC was engaged in separating fractions of selected crudes and ascertaining the worth of those crudes as base fuel for aviation gasoline. The BETC knock testing laboratory is shown here in September 1948. This configuration was in place throughout the early 1940's.

compounds with odor-producing tendency.

Chassis Dynamometer

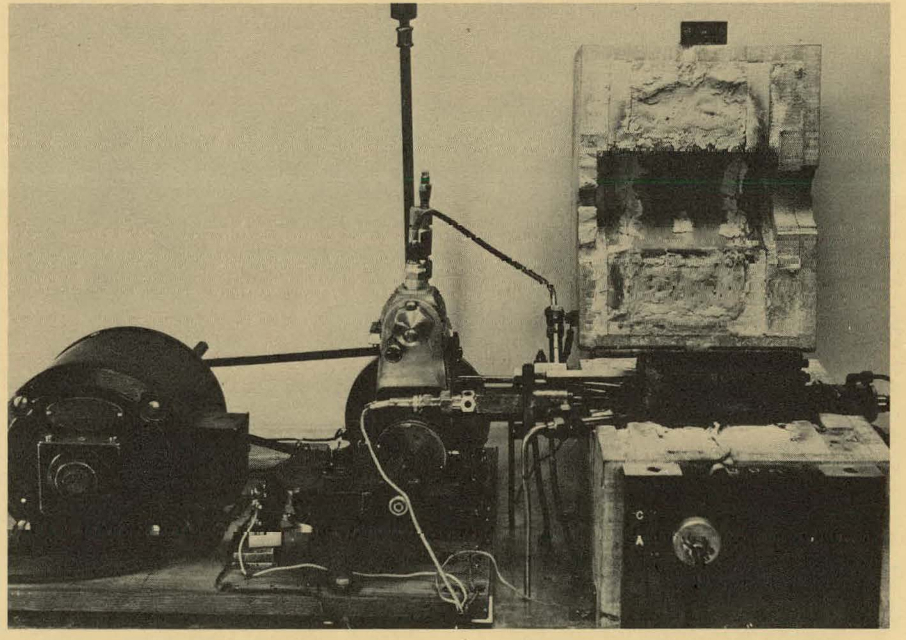
Construction of an environmentally controlled chassis dynamometer permitted an investigation of the effect of evaporation of gasoline on smog. The dynamometer permitted the testing of cars in a temperature-controlled atmosphere accompanied by an air current simulating the speed of the car. Exhaust samples were analyzed over a standard cycle of driving conditions. Measurements showed that evaporation losses were appreciable and led to techniques for returning the gasoline to the gas tank.

Gasohol Studies

Interest in blending alcohol with gasoline to extend the supply caused BETC to make exhaustive tests on driveability, efficiency, and emissions of cars using alcohol and various blends of alcohol and gasoline as fuel. These tests contributed to EPA's permission to market "gasohol"—a blend of 10 percent ethanol in gasoline. A fleet test using gasohol that was made in cooperation with Southwestern Bell Telephone Co. revealed no adverse emissions, slightly fewer miles per gallon, and an increase in road octane number.

As the focus for automotive research turned from emission control to alternate fuels to supplement a decreasing availability of petroleum, it continued to be important to determine expected emissions. BETC studies have ranged from use of natural gas under pressure to finely divided coal in diesel fuel, alcohols (both ethanol and methanol), liquids from coal hydrogenation, shale-oil gasoline, and blends with petroleum stocks.

Of growing interest is the BETC Alternative Fuels Data Bank, which includes summaries of publications, ongoing research projects, and a current topics file. This computerized data bank is available for call-in consultation by researchers throughout this country and even from Europe.



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From 1949 to 1956, BETC was engaged in developing a constant-volume bomb for static combustion studies of diesel fuels. One of the earlier bombs developed and put in use at BETC is shown here. Fuel is injected into a heated atmosphere capable of supporting combustion. The ensuing pressure rise is shown on an oscilloscope as a function of pressure and time. Although researchers elsewhere worked in this area, BETC's bomb and accessory equipment was easily the most advanced.

PROCESSING AND UTILIZATION SELECTED BIBLIOGRAPHY

Stability of Fuels

Brinkman, D. W., J. N. Bowden, John Frankenfeld, and Bill Taylor, "Synfuel Stability: Degradation Mechanisms and Actual Findings." American Chemical Society Symposium Series No. 163, 1981. pp. 297-314.

Schwartz, Frank G., M. L. Whisman, C. S. Allbright, and C. C. Ward, "Storage Stability of Gasoline Fundamentals of Gum Formation Including a Discussion of Radiotracer Techniques." BuMines Bulletin 626, 1964, 44 pp.

Whisman, M. L., F. O. Cotton, J. W. Goetzinger, and C. C. Ward, "Radiotracer Study of Turbine Aircraft Fuel Stability." BuMines Report of Investigations 7493, 1971, 30 pp.

Re-Refining of Used Lubricating Oils

Benham-Blair-Holway & Spragins, "The BERC Re-Refining Process: An Engineering Evaluation Final Report." BETC/RI-79/1, Dec. 1978, 22 pp.

Cotton, F. O., D. W. Brinkman, J. W. Reynolds, J. W. Goetzinger, and M. L. Whisman, "Pilot-Scale Used Oil Re-Refining Using a Solvent Treatment Distillation Process." BETC/RI-79/14, Jan. 1980, 40 pp.

Goetzinger, J. W., F. O. Cotton, and M. L. Whisman, "A Comparative Evaluation of New, Used, and Re-Refined Lubricating Oils." *Oil and Gas Journal,* Vol. 73, No. 9, March 1975, pp. 130-135.

Whisman, M. L., J. W. Reynolds, J. W. Goetzinger, F. O. Cotton, and D. W. Brinkman, "Re-Refining Makes Quality Oils." *Hydrocarbon Processing,* Vol. 57, No. 10, Oct. 1978, pp. 141-145.

Diesel Fuel Research

Hurn, R. W. and K. J. Hughes, "Constant-Volume Combustion of Diesel Fuels." *Proceedings,* American Petroleum Institute, Vol. 30M (III), 1950, pp. 227-237.

Hurn, R. W., J. O. Chase, C. F. Ellis, and K. J. Hughes, "Fuel Heat Gain and Release in Bomb Autoignition." Soc. Automotive Engineers *Transactions,* Vol. 64, 1956, pp. 703-711.

Hurn, R. W. and K. J. Hughes, "Ignition Accelerators and Autoignition Environment." *Ind. Eng. Chem.,* Vol. 48, 1956, pp. 1904-1908.

Techniques for Analyzing Exhaust Gases

Ferrin, C. R., J. O. Chase, and R. W. Hurn, "Analysis of Complex Hydrocarbon Mixtures Using an Unsaturate-Discriminating Gas Chromatograph." Chapter XXVII in *Gas Chromatography,* Academic Press, Inc., New York, 1962, pp. 423-429.

Hughes, K. J., and R. W. Hurn, "A Preliminary Survey of Hydrocarbon-Derived Oxygenated Material in Automotive Exhaust Gas." *Air Pollution Control Association Journal,* Vol. 5, No. 10, Oct. 1960, pp. 367-373.

Hurn, R. W., and T. C. Davis, "Gas Chromatographic Analysis Shows Influences of Fuel on Composition of Automotive Engine Exhaust." American Petroleum Institute *Proceedings,* Division of Refining, Vol. 38, 1958, pp. 353-372.

Odor From Diesel Exhaust

Dimetriades, B., and T. C. Wesson, "Reactivities of Exhaust Aldehydes." BuMines Report of Investigations 7527, 1971, 18 pp.

Marshall, W. F., and D. E. Seizinger, "Diesel Odor Measurement: Comparison of Two Methods." BETC/TPR-78/5, August 1978, 7 pp.

Vogh, J. W., "Nature of Odor Components in Diesel Exhaust." Air Pollution Control Association Journal, Vol. 19, No. 10, Oct. 1969, pp. 773-777.

Vogh, J. W., "Contribution of Some Carbonyl, Phenol, and Hydrocarbon Components to Diesel Exhaust Odor." BuMines Report of Investigations 7632, 1972, 11 pp.

Evaporation Losses

Eccleston, B. H., B. F. Noble, and R. W. Hurn, "Influence of Volatile Fuel Components on Vehicle Emissions." BuMines Report of Investigations 7291, 1970, 80 pp.

Eccleston, B. H., and R. W. Hurn, "Effect of Fuel Front-End and Midrange Volatility on Automobile Emissions." BuMines Report of Investigations 7707, 1972, 70 pp.

Stone, R. K., and B. H. Eccleston, "Vehicle Emissions vs. Fuel Composition, API-Bureau of Mines." American Petroleum Institute Proceedings, Division of Refining, Vol. 48, 1968, pp. 705-742; Part II, Vol. 49, 1969, pp. 651-690.

Alcohol Fuels

Allsup, J. R., "Experimental Results Using Methanol/Gasoline Blends as Automotive Engine Fuel." BERC/RI-76/15, 1977, 81 pp.

Allsup, J. R., and D. B. Eccleston, "Ethanol/Gasoline Blends as Automotive Fuel." BERC/RI-79/2, 1979, 16 pp.

Gurney, M. D., and J. R. Allsup, "Gasohol: Laboratory and Fleet Test Evaluation." Society of Automotive Engineers Paper 800892, August 1980, 21 pp.

Alternate Fuels

Allsup, J. R., "Gas from Coal as an Automotive Fuel." Society of Automotive Engineers Paper 730802, 1973, 7 pp.

Liquid Fossil Fuel Technology, "Alternate Transportation Fuels: A Status Report." DOE/BETC/QPR-81/2, 1981, pp. 54-58.

Bechtold, R. L., and R. D. Fleming, "Performance of Gasoline and Diesel Fuels Produced from COED Syncrude." BERC/RI-78/2, June 1978, 22 pp.