DR# 0109-0

NIPER-6
(DE84010565)

Energy

FOSSIL

1983–84 ANNUAL RESEARCH PLAN

Final Draft

May 1984
Date Published

Work Performed Under Contract No. FC01-83FE60149

National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A12
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA); Government Reports Announcements* and Index (*GRA* and I); *Scientific and Technical Abstract Reports (STAR);* and publication NTIS-PR-360 available from NTIS at the above address.

NIPER-6
(DE84010565)
Distribution Category UC-92

1983-84

Annual Research Plan

Submitted by:

National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma

Final draft submitted in response to:

Cooperative Agreement DE-FC01-83FE60149
Between the Department of Energy
and the
IIT Research Institute

FOREWORD

The National Institute for Petroleum and Energy Research (NIPER) is pleased to submit the "1983-84 Annual Research Plan" in accordance with the provisions of Cooperative Agreement DE-FC01-83FE60149 with the Department of Energy (DOE).

This Annual Research Plan describes the work to be performed by NIPER during the 1984 fiscal year. This work is presented in three research programs: (1) a Base Program, fully funded by DOE, (2) an Optional Program, cost shared with the DOE, and (3) a Work for Others Program, to be funded by other government agencies and industrial clients.

We wish to express our appreciation to the Director and other personnel of the DOE/Bartlesville Project Office for their assistance and cooperation in the preparation of this Plan. Also, the NIPER Technical Advisory Committee, consisting of representatives of industry, universities, and consultants has been of invaluable assistance in developing these research programs.

EXECUTIVE SUMMARY

Mission of NIPER

The National Institute for Petroleum and Energy Research (NIPER) resulted from efforts by the Department of Energy (DOE) to ensure the continuity of the unique energy research capabilities that had been developed at the Bartlesville Energy Technology Center (BETC) over the past 65 years. This was accomplished by a Cooperative Agreement between DOE and IIT Research Institute (IITRI). The agreement to operate NIPER for the five fiscal years 1984-88 became effective October 1, 1983.

Under the agreement NIPER is obligated to conduct a fully Federally funded Base Program of Fossil Energy (FE) research amounting to $5 million per year. The agreement also calls for a cost-shared research program of up to $5 million per year. The government's share of this Optional Program is to be 80 percent the first year. A third program of research, Work for Others, allows NIPER to solicit research support from the private sector and others. This first Annual Research Plan, called for in the Cooperative Agreement, provides details about the Base and Optional Programs of research. Potential projects in the Work for Others category are also presented.

The primary objective of NIPER is to perform research in all fields of petroleum and unconventional hydrocarbon technology from extraction, through processing, to utilization with a continued emphasis on Enhanced Oil Recovery (EOR). At NIPER, DOE will fund a program of innovative long-range, high-risk research not likely to be performed by industry. To determine the topics for research most needed by industry, NIPER has established a Technical Advisory Committee, consisting of eleven regular and two alternate representatives of industry, universitites, and consultants.

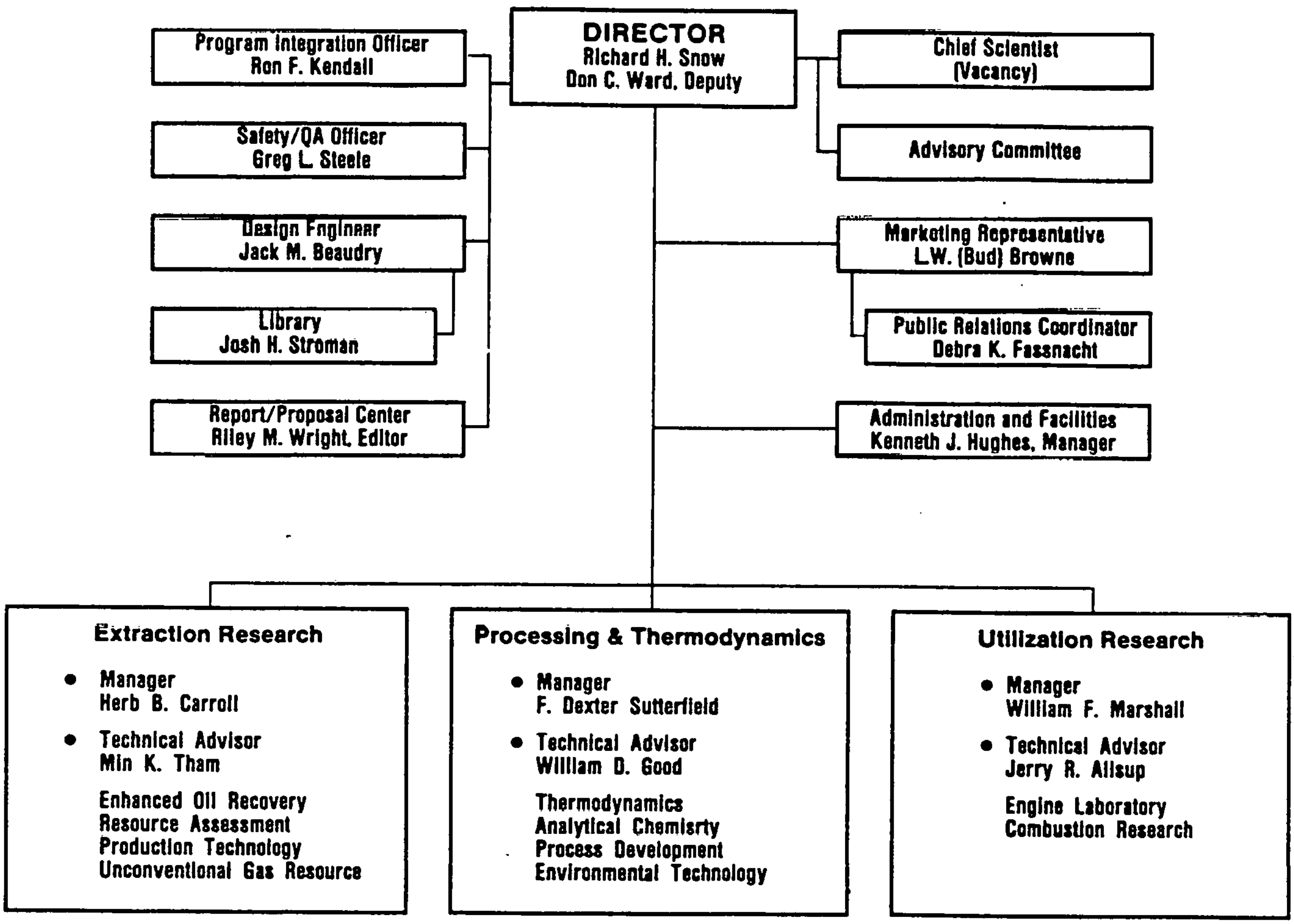
The committee has met three times and has made recommendations incorporated into the Annual Research Plan. Advice from the committee has included information on problems faced by industry that need research, as well as advice on topics are already being addressed satisfactorily by industry research laboratories.

NIPER Organization

NIPER plans to build on the established reputation of BETC and remain a major laboratory for research on petroleum and liquid fuels. The organization of NIPER, illustrated on the following page, includes Extraction Research, Processing and Thermodynamics Research, and Utilization Research.

This organization resulted from the liquid fossil fuel cycle (LFFC), a concept originally developed at BETC, which emphasizes the interelationships

NIPER ORGANIZATION CHART



between technologies from exploration and production to consumption and environmental consequences. The LFFC permits comparison of research problems for their probable effect on the total system, and this analysis has been used to measure the significance of proposed research projects.

The Bartlesville Project Office (BPO), collocated with NIPER, retains activities best conducted by the government, including program planning and integration, contract administration, data base operation, and technology transfer. NIPER and BPO cooperatively developed the NIPER Annual Research Plan within the overall context of FE guidance and the Cooperative Agreement.

Facilities at NIPER

The physical facilities and many of the former personnel of BETC are now a part of NIPER; therefore, much of the expertise resulting from the 65 year heritage of the laboratory is available to NIPER. In addition, new personnel are being recruited to augment the staff and provide additional expertise. Assets of the new organization include a strong professional and support staff, modern, well equipped buildings (151,000 square feet), state-of-the-art research equipment plus in-house developed equipment, and a comprehensive petroleum and energy library.

NIPER Program

NIPER will be heavily involved in the DOE Fossil Energy programs of EOR and Advanced Process Technology (APT). These programs are the basis for the Base and Optional Programs. Over the past decade, BETC (now NIPER) has been the lead Government laboratory for EOR. The APT subprogram on Advanced Exploratory Research, which includes Advanced Extraction Technology, Fundamental Petroleum Chemistry, and Advanced Utilization Research, closely matches NIPER experience. In addition, NIPER has experience in the Western Gas Sands subprogram of the Unconventional Gas Recovery program, and in the Coal Thermodynamics area of Advanced Research and Technology Development.

The NIPER Annual Research Plan for 1983-84 consists of eight projects in the Base Program and 13 projects in the Optional Program. A sampling of potential Work for Others projects is also presented. The Base Program consists of five EOR and three Fundamental Petroleum Chemistry projects. The Optional Program has three EOR projects, one Unconventional Gas Recovery project, five APT projects, and four Advanced Utilization Research projects.

The tables on the following pages list the NIPER research projects that fall under the Base Program, the Optional Program, and the Work for Others Program. The Work for Others projects are fully funded outside the Cooperative Agreement and thus are not based on the same justifications as projects in the Base and Optional Programs.

BASE PROGRAM PROJECTS

NIPER Project No.	Title	Research* Area	Manpower,** man-years	Funding, $K
	Extraction Research			
BE1	Interaction Between Reservoir Rock and EOR Fluids	EOR	11.0	1070
BE1A	Surface Chemistry of Reservoir Rocks and their Reaction with Crude Oil Components			
BE1B	Effect of Clay Minerals on Oil Saturation Determination			
BE1C	Three-Phase Flow in Porous Media			
BE2	Reservoir Screening and Recovery Predictions	EOR	6.0	710
BE2A	EOR National Potential			
BE2B	Technology Appraisal			
BE2C	Process Predictive Screening Models			
BE3	EOR Environmental Compatibility	APT	2.5	330
BE3A	Effect of Microbial Technology on EOR			
BE4	Basic Studies of EOR Chemicals	EOR	9.0	990
BE4A	Behavior of Surfaces with Adsorbed Materials			
BE4B	Adsorption of Surfactant Slug Components on Reservoir Minerals			
BE4C	Application of Thermodynamic Measurements to Micellization and Solubilization			
BE4D	Effects of Surfactant Structure and Additives on Micelle Formation and Solubilization			
BE4E	Order of Mixing Effects for Aqueous Surfactant			
BE5	Gas Displacement Methods	EOR	3.5	335
BPT1	Thermodynamic Properties of Organic Compounds	APT/ARTD	6.4	650
BPT1A	Thermodynamic Properties of Organic Nitrogen Compounds That Occur in Shale Oil and Heavy Petroleum			
BPT1B	Thermophysical and Thermochemical Properties of Organic Compounds Derived from Fossil Substances			
BPT2	Stability and Processing Research for Crudes, Intermediate Process Streams, and Finished Fuels***	APT	0.7	80
BPT3	Chemical Characterization of Heavy Ends of Light Petroleum, of Heavy Petroleum, and of Liquids Derived from Other Fossil Sources***	APT	4.2	455
	TOTAL BASE PROGRAM		43.3	4,620

* Abbreviations: EOR = Enhanced Oil Recovery; APT = Advanced Processing Technology; ARTD = Advanced Research and Technology Development (Coal Thermodynamics) Subprogram.

** Manpower effort reflects maximum personnel to work on project. Some personnel are not yet available, thus costs reflect a manpower effort for the fiscal year lower than that shown.

*** Parts of these projects are in the Optional Program.

OPTIONAL PROGRAM PROJECTS

NIPER Project No.	Title	Research* Area	Manpower,** man-years	Funding, $K
	Extraction Research			
OE1	Improvements in Stimulation Technology	GAS	6.0	585
OE1A	Formation Damage Due to Hydraulic Fracturing Fluid			
OE1B	Characterization of Polymer Fracturing Fluid Systems			
OE2	Reservoir Characterization for EOR Application	EOR	1.5	200
OE2A	Fluid Front Monitoring for Chemical EOR			
OE3	Recovery Processes: Chemical	EOR	8.5	735
OE3A	Improved Chemical Flooding Agents: Surfactant Systems			
OE3B	Mobility Control Agents			
OE3C	Alkaline Flooding			
OE4	Recovery Processes: Thermal	EOR	6.0	540
OE4A	Steam Flooding			
OE4B	In Situ Combustion			
	Processing and Thermodynamics Research			
OPT1	Thermophysical Properties of Real and Synthetic Fluid Mixtures Derived from Fossil Substances	ARTD	2.6	185
OPT2	Stability and Processing Research for Crudes, Intermediate Process Streams, and Finished Fuels***	APT	2.2	287
OPT3	Chemical Characterization of Heavy Ends of Light Petroleum, of Heavy Petroleum and of Liquids Derived from Other Fossil Sources***	APT	5.0	325
OPT4	Fuels Trends and Analyses	APT	.9	90
OPT5	Chemistry of Contaminated Petroleum Fuels	APT	2.4	245
	Utilization Research			
OU1	Diesel Fuel Quality Criteria	APT	5.3	500
OU2	Direct Utilization of Aromatic Feedstocks	APT	4.9	385
OU3	Diesel Exhaust Characterization	APT	2.4	280
OU4	Coal Slurry Injection Characteristics	ARTD	1.6	112
	TOTAL OPTIONAL PROGRAM		49.3	4,469

* Abbreviations: EOR = Enhanced Oil Recovery Subprogram; APT = Advanced Process Technology Subprogram; ARTD = Advanced Research and Technology Development; GAS = Unconventional Gas Subprogram.

** Manpower effort is maximum personnel to work on project. Some personnel are not yet available, thus costs reflect a manpower effort for the fiscal year lower than that shown.

*** Also in Base Program..

WORK-FOR-OTHERS PROJECTS

Title	Potential Sponsor
Extraction Research	
Physics of Immiscible Flow in Porous Media	EPA
Research on Water Quality Issues	EPA
Processing and Thermodynamics Research	
Thermodynamics Characterization of Condensed Ring Compounds	Office of Energy Research Basic Energy Sciences
Waste Hydrocarbon Recycling	Division of Conservation and Renewable Energy
Removal of Metals from Alternative Crudes	Petroleum Companies
Environmental Sample Generation for Mutagenesis Testing	Petroleum Companies
Strategic Petroleum Reserve Supporting Research	Strategic Petroleum Reserve Office
Utilization Research	
Coal Slurry Fuel Guidelines	DOE/Fossil Energy
Alcohol-Gasoline Blends	Petroleum Companies EPA DOE/Conservation and Renewable Energy
Assessments of Alternative Fuel Technologies	Multi-client

NIPER Funding and Personnel

Committed DOE funding amounts to \$3.4 million for Extraction Research and \$1.2 million for Processing and Thermodynamics Research in the Base Program. In the Optional Program, Extraction has \$2.1 million, Processing and Thermodynamics has \$1.1 million, and Utilization has \$1.3 million, including IITRI cost-shared funds. Technical manpower requirements for the Base Program are 43 man-years, whereas those for the Optional Program are 49 man-years, for a total of 92 man-years.

NIPER Base and Optional Programs

The Statement of Work as given in the Cooperative Agreement is based on the DOE Fossil Energy programs. The projects developed at NIPER address most of the suggested areas but do not cover them comprehensively because of funding limitations. In their selection consideration was given in their selection to previous work at BETC, to availability of personnel with the proper expertise, and to broad coverage of technology areas to avoid premature specialization of NIPER and duplication of university work. The Optional Program projects, besides addressing research topics of importance, serve as a bridge between the more fundamental work of the Base Programs and the more applied work of industry covered by the Work for Others projects.

Extraction Research. Extraction Research, in accordance with DOE Fossil Energy policy, has developed a strong program of EOR research, much of which lies in the fundamental research area. The Basic Program includes projects on the interaction between reservoir rock and EOR fluids, reservoir screening and recovery predictions, environmental compatibility of microbial EOR, basic studies of EOR chemicals, and gas displacement methods. A rock/EOR fluids project includes work on surface chemistry, clay minerals, and three-phase flow. The expected advent of microbial EOR requires assessment and planning to prevent environmental damage. Basic studies of the action of surfactants include the effect of wettability, adsorption on minerals, the thermodynamics of micellization and solubilization, the effect of surfactant structure and additives on micelle formation and solubilization, and a study of the order of mixing aqueous surfactant solutions. Gas displacement methods to be studied include nitrogen-miscible displacement of light oil and carbon dioxide-miscible displacement of heavy oil.

The Optional Program contains Extraction Research projects on subjects near the state of application. For the Western Gas Sands Project, the formation damage due to hydraulic fracturing fluid and the degradation of polymer in the fluid will be studied. The development of methods for EOR reservoir characterization will include a study of the feasibility of monitoring the fluid front advance during chemical flooding. Chemical recovery studies include improving surfactant systems, measuring performance of mobility control agents, and determining reaction kinetics of alkaline reagents with clays and oils. Thermal recovery process studies include steamflooding of light oils and developing kinetic data for *in situ* combustion.

Processing and Thermodynamics Research. Processing and Thermodynamics Research has projects on thermodynamics, stability and processing, and characterization of heavy oils and synthetic fluid mixtures in the Base Program. Each of these projects is extended into the Optional Program. A characterization project involves heavy ends of light petroleum, heavy petroleum, tar sand liquids, shale oil, and coal liquids. The Base Program on thermodynamics emphasizes the nitrogen compounds of shale oil and the polyaromatic and heterocyclic compounds of coal liquids, whereas the Optional Program develops thermodynamic properties on process streams from the coal liquefaction program. Stability and processing research includes studies on upgrading of alternate feedstocks for conventional petroleum refining processes, and the development of information about the stability of alternative fuels. In addition, projects on fuel trends and analyses and the chemistry of contaminated petroleum fuels are part of the Optional Program.

Utilization Research. Utilization Research has three projects in the Optional Program which address environmental problems. The effect of alternative feedstocks on emissions and efficiency of transportation fuels (both diesel fuel and gasoline) will be studied along with an investigation of the feasibility of changing some specifications to better match the alternative fuels. The particulates from the exhaust of diesel engines are being investigated to determine the extent of occurrence of toxic compounds or carcinogens. The use of powdered coal in a slurry of diesel fuel for medium-speed, medium-size diesel engines is being investigated.

Work for Others Program

The Work for Others Program is not described in detail but several proposed projects that are proposed are indicated. Extraction Research will perform environmentally oriented projects on the physics of immiscible flow through porous media, and the development of methods to determine toxicity persistence as one measure of water quality. Processing and Thermodynamics Research includes Work for Others projects on the thermodynamic characterization of condensed ring compounds, waste hydrocarbon recycling, removal of metals from alternative crudes, sample upgrading and preparation of alternative fuels for mutagenesis testing, and support research for the Strategic Petroleum Reserve. Utilization Research proposes projects to develop guidelines for coal slurry fuels, to investigate alcohol-gasoline blends for automotive use, and to assess alternative fuel technology.

Summary

NIPER's Annual Research Plan for 1983-1984 contains 21 projects in the Base and Optional Programs covering many aspects of research on petroleum and liquid fuels technology. It provides for continuing the tradition of contributing broadly to petroleum technology established by BETC during its 65 years. Although new directions have been charted in a number of fields, the work will continue to serve both government and industry by advancing scientific and engineering knowledge.

National Energy Policy

The National Energy Policy calls for reliance on market forces to direct the production and use of energy. The Federal government's role is limited to funding long-term, high-risk, high-payoff research that the private sector is unlikely to undertake. The purpose of such research is to supplement, where necessary, the efforts of the private sector in developing new technology, to maximize use of Federal facilities, to encourage communication and cooperation between governmental agencies and the private sector, and to assist research at institutions of higher learning.

To ensure adequate supplies of energy from domestic sources, the National Energy Policy considers three alternatives: the discovery of new fields; the greater recovery of oil from known fields; and the development of synthetic fuels, including the use of alternative feedstocks for transportation fuels. Enhanced recovery offers possibilities of providing large amounts of oil if new and more effective techniques can be devised. The efficient use of alternative feedstocks such as heavy oils and shale oil will require adaptation of present processes for refining and end use.

DOE/Fossil Energy (FE) Strategy

Within the DOE, the FE strategy is to conduct a balanced program of research in all fields of petroleum and unconventional hydrocarbon technology. The specific objectives of the FE research program include:

(1) improve understanding and predictability of all Enhanced Oil Recovery (EOR) processes
(2) understand the factors that affect performance and applicability of advanced EOR processes
(3) assess the feasibility of novel EOR technologies
(4) examine entirely new concepts for EOR
(5) expand knowledge of alternative sources of hydrocarbons, particularly heavy oil, tar sands, and shale oil
(6) maintain mechanisms for technology transfer.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

Page

TABLES

FIGURES

INTRODUCTION

The National Institute for Petroleum and Energy Research (NIPER) was established October 1, 1983. Almost two years earlier, the Department of Energy (DOE) had begun to explore alternative possibilities for maintaining the unique capabilities that the Bartlesville Energy Technology Center (BETC) had developed. As the result of public meetings and a Solicitation for Cooperative Agreement Proposals (SCAP), IIT Research Institute (IITRI) submitted a proposal to manage the research center for five years under the name NIPER. This proposal was accepted, and a Cooperative Agreement for the management and operation of the laboratory was negotiated.

The 65-year-old BETC was historically the government's lead laboratory in petroleum research. It pioneered the development of technology for secondary and enhanced oil recovery, the composition and chemistry of petroleum and substitute liquid fuels, thermodynamics, automotive engine efficiency and emission control, and the use of alternate synthetic fuels. It is the expressed intention of DOE to maintain NIPER as a national resource, ensuring that its unique capabilities and competence continues. DOE has placed a substantial program of fossil energy research at NIPER, and this research plan describes the first year's work.

The agreement between DOE and IITRI provides that a $5 million annual Base Program of research will be financed by DOE, and that an equal-sized Optional Program will be available for cost-sharing by NIPER. The Optional Program starts with the government funding 80 percent the first year; the cost-share decreases to zero by the fifth year. NIPER is also allowed to accept research projects from other Federal agencies, State and local governments, and the private sector. The goal is to make NIPER an independent, internationally recognized petroleum research facility providing technology and leadership for constructive solutions to the Nation's energy problems.

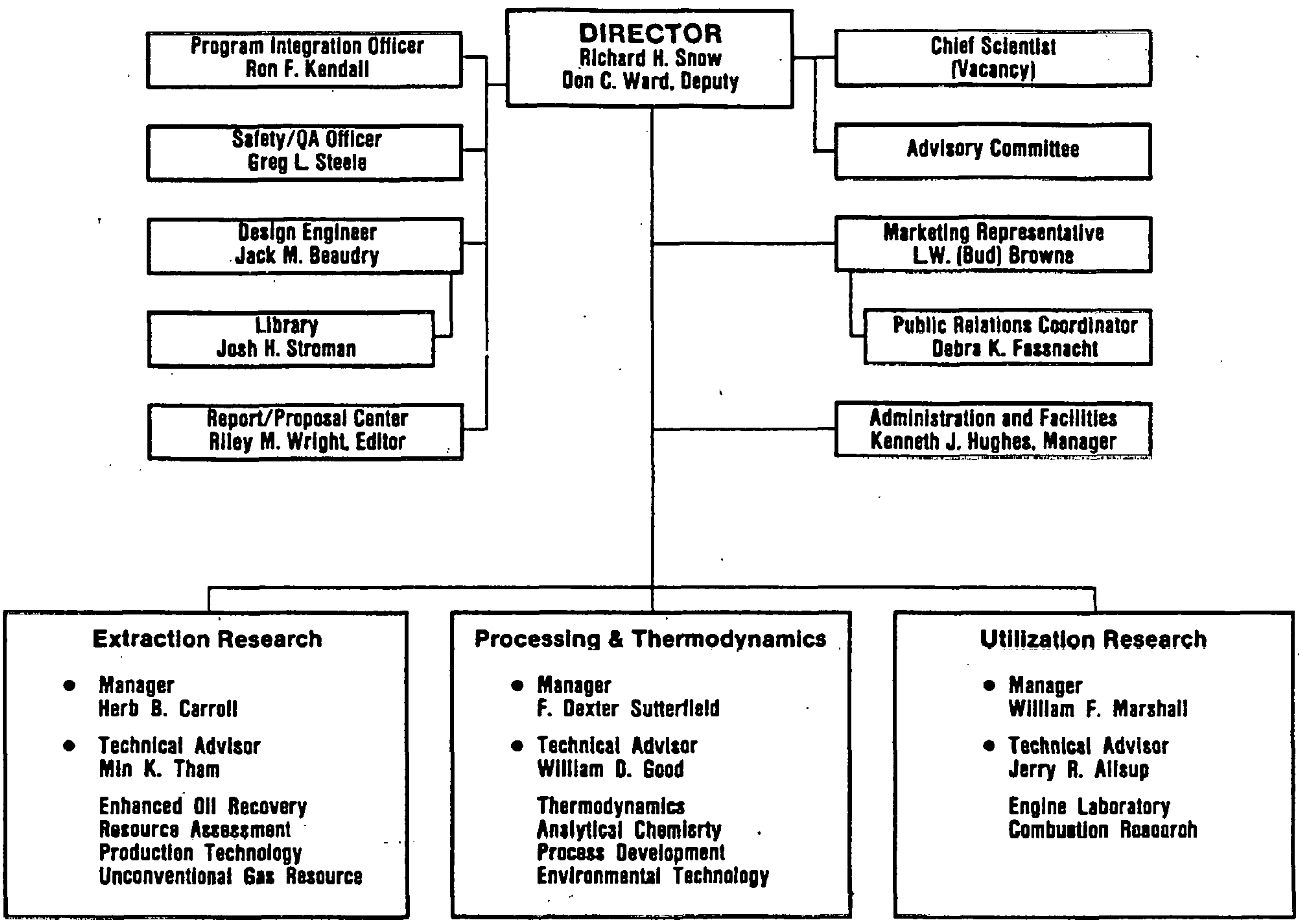
The research program presented here was developed in cooperation with DOE Fossil Energy (FE) employees at the Bartlesville Project Office (BPO). Technical and Management Committees jointly staffed from NIPER and DOE have reviewed and approved the program.

SCOPE AND ORGANIZATION OF NIPER

By virtue of the work already underway for DOE/FE, NIPER remains the major government laboratory for petroleum and liquid fuel research. The Cooperative Agreement also permits work for others. This not only broadens the contacts, but also permits expansion of personnel and capabilities. The expectation is that NIPER will grow rapidly and, with outside support, enter into research fields heretofore out of reach of the Federal organization. The Work for Others projects indicated in this plan suggest only a few of the areas of new work.

FIGURE 1

NIPER ORGANIZATION CHART



The organization of NIPER follows closely that of BETC with research groups devoted to extraction, processing and thermodynamics, and utilization. The current organization, shown in Figure 1, is patterned from the liquid fossil fuel cycle (LFFC), a concept originally developed at BETC, which emphasizes the interrelationships between technologies from exploration and production to consumption and environmental consequences. The LFFC permits comparison of research problems for their probable effect on the total system and has been used as a measure of the importance of proposed research projects.

The BPO is a DOE site office collocated with NIPER. It is responsible for developing long-range petroleum R&D plans, integrating the efforts of NIPER into these plans, monitoring the IITRI Cooperative Agreement and other fossil energy research contracts, such as those with universities and national laboratories, administering data bases concerned with Enhanced Oil Recovery (EOR) and crude oil analyses, and ensuring effective technology transfer.

An important aspect of NIPER is its research marketing organization, which draws heavily on the experience of IITRI. The effectiveness of this group in developing contracts has been demonstrated and is expected to contribute to the success of the Optional Program and the growth of the Work for Others segment.

NIPER's objective is to conduct a program of research that covers all fields of petroleum and unconventional hydrocarbon technology from extraction, through processing, to utilization, with a continued emphasis on EOR. At NIPER, DOE will sponsor a program of innovative research that will not be done by industry because it is too long-range or too high-risk. To determine the topics for research most needed by industry, NIPER has established a Technical Advisory Committee. This committee consists of representatives of industry, universities, and consultants as follows:

Dr. Fred Bowditch
Vice President
Technical Affairs Division
Motor Vehicle Manufacturers Assoc.

Mr. Fred Camp
Manager of Technology,
Synthetic Fuels Department
Sunoco Energy Corporation

Mr. Thomas J. Clough
Director, Technology Coordination
Atlantic Richfield Corporation

Mr. Ted Geffen
Petroleum Consultant

Dr. Mary Good
Vice President, Director of Research
UOP Inc.

Dr. Roy Knapp
Head, Petroleum Engineering Department
University of Oklahoma

Dr. Stanford S. Penner
Director, Energy Center
Professor of Engineering Physics
University of California, San Diego

Dr. Marvin Smith
Head, Mechanical and Petroleum Engineering Technology
Oklahoma State University

Dr. William Staats
Director, Basic Research
Gas Research Institute

Mr. Al Braun (alternate)
Director, Administrative & Technical Services
UOP Inc.

Mr. Michael Waller
Vice President of Research
Amoco Production Company

Mr. Gary Myers (alternate)
Manager, Applied & Engineering Research
Corporate Technology Group
Atlantic Richfield Corporation

Dr. Darsh Wasan
Head, Chemical Engineering Department
Illinois Institute of Technology

The committee has met three times and has made recommendations that have been incorporated into the Annual Research Plan. Their advice included information on problems faced by industry that need research, as well as advice on what topics are already being addressed satisfactorily by industry research laboratories. This advice has been of great help in preparing this plan.

Several additional meetings of the committee will be held next spring and summer to work on the FY85 Annual Research Plan. The work of the Technical Advisory Committee is budgeted as a separate task under the Annual Research Plan preparation project.

FACILITIES AT NIPER

NIPER incorporates the laboratories, equipment, and most of the former staff of the BETC. Consequently, it has the strengths of that organization together with the opportunity to expand into new fields. It is located on 17 acres within the city limits of Bartlesville, Oklahoma, and consists of 16 buildings with a total floor space of 151,000 square feet. Many of the buildings are designed for special research purposes.

Equipment available at NIPER includes both state-of-the-art commercial equipment and in-house developed items that may be prototypes of research equipment for future use. Areas of strength include enhanced oil recovery, core studies, mass spectrometry, thermodynamics, fuel characterization, and engine/fuel testing. It is expected that some items of equipment will be made available for university professors and students to use in their research work, especially where the NIPER equipment is unique.

A well-equipped specialized library is available with excellent coverage on petroleum and related topics. On-line computer data files (the DOE Energy Data Base (RECON) and commercial services) are also available. Interlibrary loan facilities extend the capability even further. An Oklahoma well log file is maintained, and the State of Oklahoma contributes to its operation. This file is open to the public as is the general library.

A highly qualified professional staff to serve as the nucleus for NIPER was aquired from BETC. Since the program scope is changing only slightly, this group is already deeply involved in the areas to which they are assigned. Many years of experience in the specialties that made BETC's reputation are available, and the accumulation of 65 years of experience has been handed down to the present staff. Active recruitment is under way to replace capabilities previously lost by retirements or resignations and to staff new undertakings.

An adequate support staff is available coming both from BETC and from contractors who served BETC. These include draftsmen, machinists, instrument makers, carpenters, electronics technicians, computer technicians, word processing and administrative staff, as well as service people such as janitors, operating engineers, electricians, and storeroom personnel.

The program of research described in this plan will require some additional equipment. Appendix 1 lists the items proposed, the project for which they are proposed, expected use, and cost.

The estimated capital expenditure is $775,600. The Base Program accounts for $331,500 and the Optional Program for $354,100, which will be borne by the projects. Support services equipment requires $90,000. The extraction, or Enhanced Oil Recovery projects, account for $330,600, processing and thermodynamics projects require $265,000; and utilization projects require $90,000.

NATIONAL ENERGY POLICY

As stated in the SCAP,

> The overall objective of U.S. energy policy is to encourage economically efficient energy production and use. The primary means for achieving this objective is to rely on market forces. The Federal government's direct role is limited to funding long-term high-risk research which the private sector is unlikely to undertake.

The SCAP further states that,

> The Federal government cannot determine what is the most efficient combination of energy conservation and energy production, or what is the most efficient means for increasing energy supply. The answers to these questions will be determined by market forces. For example, the alternatives for increasing domestic oil supply include additional discoveries of fields in the United States (onshore and offshore), developing synthetic liquid fuels, and enhancing recovery from existing oil fields. Of the 460 billion barrels of oil discovered, 310 billion barrels will not be recovered by primary and secondary procedures. Although the amount of oil that can be recovered by Enhanced Oil Recovery (EOR) processes is uncertain, a reasonable estimate based on current

knowledge is from 18 to 53 billion barrels, which exceeds current proved domestic oil reserves. The market will determine how best to deal with these facts.

Through its cooperative program with DOE, NIPER can supplement the efforts of the private sector in turning these resources into economic opportunities.

The SCAP also states,

It is useful for the Government to support an effective, long-term petroleum and unconventional hydrocarbon research program to accomplish the following:

- provide for the National well-being and protect the vital interests of the United States by developing new methods for utilizing domestic petroleum resources in a manner which supplements, rather than duplicates, research activities of private groups, other Federal agencies, and State and local governments

- maximize utilization of existing Federal facilities

- encourage communication and cooperation between the Federal government, State governments, local governments, and the private sector, as part of a goal of increasing non-Federal participation in a long-term petroleum and unconventional hydrocarbon research program; and

- provide a means of furthering, assisting, and funding research in institutions of higher learning through innovative arrangements involving those institutions and industry, and in some cases, through direct DOE support.

DOE/FOSSIL ENERGY STRATEGY

Fossil Energy's petroleum research strategy recognizes the respective roles of industry and government as delineated by administration policy. It focuses on that R&D that lies beyond what industry might reasonably be expected to do.

Its overall research objective, consistent with the establishment of NIPER, is to conduct a balanced program of research in all fields of petroleum and unconventional hydrocarbon technology from extraction, through processing, to utilization. This research will generally be within, but not limited to, the areas of resource assessment, unconventional production technologies such as advanced EOR methods, processing (including pre-treatment), thermodynamic research, energy conversion, end-use applications, and system integration with emphasis placed on EOR research.

The specific objectives of the DOE research program in EOR and Fundamental Hydrocarbon Chemistry, as stated in the Cooperative Agreement, are:

- to develop improved understanding and predictability of advanced, highly effective EOR processes
- to obtain better understanding of the factors that affect performance and the range of application of advanced EOR processes
- to assess the feasibility of very long-range, highly advanced and emerging EOR technologies, and to evaluate the unique problems of reservoirs for which no EOR technology now exists
- to examine entirely new concepts of EOR which might be applicable to the huge resource left after current production methods have been exhausted
- to continue, as appropriate, research on the fundamental properties, characterization, and utilization of heavy oils and syncrudes from coal, oil shale, and bitumen from tar sands as petroleum substitutes
- to maintain an effort in technology transfer to ensure that the maximum use can be made of research results.

To implement these objectives, various programs have been established by the Fossil Energy organization. The programs of immediate interest to NIPER are the Enhanced Oil Recovery program and the Advanced Process Technology program; and to a much lesser extent, the Unconventional Gas program and the Advanced Research and Technology Development program under FE/Coal research.

Fossil Energy's program plan for EOR, which was the basis for the scope of work in the solicitation that resulted in NIPER, identifies four major research areas: (1) technology appraisal, which essentially maintains a current state-of-the-art assessment of EOR status; (2) the enhanced recovery of light petroleum; (3) the enhanced recovery of heavy petroleum; and (4) the development of entirely new concepts in EOR that will allow the production of crude oils beyond the reach of known processes. Work in these areas reflects the overall purpose of U.S. Energy Policy--to encourage economically efficient energy production and use, while at the same time providing for the National well-being and protecting the vital interests of the United States. The determination of what is the most efficient combination of energy production and conservation technologies will be made by market forces.

Because of its history, NIPER also is heavily involved in the Advanced Exploratory Research area. This work provides broad, supporting research for all purposes under the FE Office of Oil, Gas, and Shale. NIPER programs are most heavily focused in fundamental hydrocarbon chemistry (analysis, thermophysical and thermochemical properties) and environmental concerns. This work is critical to DOE's emphasis on mobility fuels to satisfy security and economic welfare strategic needs.

Among the objectives of the Unconventional Gas Recovery research program is the improvement of techniques for recovering gas from the low-permeability reservoirs, largely located in the Western states. This program is aimed at the 600 trillion cubic feet of natural gas resource, much of which is not recoverable with existing technology.

The Advanced Research and Technology Development subprogram (AR&TD) is designed to extend the fundamental scientific and engineering knowledge base in coal for Fossil Energy. It seeks a better understanding of the fundamental mechanisms of converting coal to gas and liquid fuels or to burning it directly. A major area of concern is the thermodynamic properties of compounds and mixtures resulting from the direct liquefaction of coal. Such data are fundamental to a better understanding of conversion processes.

NIPER PROGRAM

The NIPER research program, developed in cooperation with the BPO, is based on the Statement of Work in the Cooperative Agreement (see Appendix 2). Two groups of projects are described. The Base Program, fully funded by DOE, consists of projects in technology areas of high priority to DOE but which will not be performed by industry in the near future except on a proprietary basis. These are generally basic studies or work with innovative techniques which have a high-risk, long-term character. The Optional Program, cost-shared with DOE, includes projects in areas also of importance to the DOE program, but which industry and other agencies may be willing to support based on their specific needs, either on a collective or individual basis.

Note that the solicitation, which resulted in the creation of NIPER, limited the scope of work in the Base Program to EOR and the fundamental chemistry area of analysis (characterization), determination of thermochemical and thermophysical properties of heavy oils and related substances, and the application of these data to upgrading hydrocarbon feedstocks, fuel storage stability, and environmental studies. The Optional Program was left to the individual proposers, with the only restriction being that their proposal be a logical extension of the Base Program and the existing BETC capabilities.

The IITRI proposal for the Optional Program included work in unconventional gas recovery and engine/fuel research while extending work on EOR and characterization. It was believed that a well-rounded program was required if NIPER was to be successful in developing outside support. Continuation of work in these subjects also preserves the capabilities of BETC in these areas, which were recognized by IITRI as a valuable resource to the Nation. This position was accepted with some modifications during negotiations, as shown in the Statement of Work Optional Program, Appendix 2.

The Base Program supports two Fossil Energy programs--Enhanced Oil Recovery and Advanced Process Technology. Five EOR projects are to be performed by Extraction Research and three projects by Processing and Thermodynamics Research (two in APT and one in ARTD).

The Optional Program covers three areas based on EOR and Unconventional Gas Recovery (UGR), Advanced Exploratory Research (AER), and Advanced Utilization Research (AUR). They are addressed respectively by Extraction Research with four projects (three for EOR, one for UGR), by Processing and Thermodynamics Research with five projects (AER), and Utilization Research with four projects (AUR).

A third program, Work for Others, is not defined by the Cooperative Agreement other than giving suggested areas where cooperative work might be developed. This Annual Research Plan does not give detail on Work for Others projects but does indicate some subjects in which research is planned or under consideration.

The projects in the Base and Optional Programs are described under the following headings:

(1) Background--history of problem, need for research, connection with DOE goals, previous work

(2) Objective--a brief statement of what is planned to be accomplished

(3) Scope of Work--approach, tools, and techniques to be used, with special reference to those for FY84

(4) Work Plans--a list of tasks to be accomplished with special reference to those for FY84

(5) Future Work--plans reaching beyond FY84

(6) Manpower Requirements--listing of positions by categories and man-years

(7) Equipment Requirements--major items of equipment, indicating whether they are available or will have to be purchased

(8) Milestone Chart--milestone schedule for FY84, including list of milestones and deliverables.

The numbering system for the project descriptions consists of: a letter (B, O, or W, indicating respectively Base Program, Optional Program, and Work for Others); a letter designation for the research group (E, PT, or U, indicating respectively Extraction, Processing and Thermodynamics, and Utilization); a numeral indicating the project number; and a letter if there are subprojects. Thus, BE1A shows the project to be in the Base Program, conducted by the Extraction Research group, and to be the first subproject under the first project.

Before going into detail, an overview will be presented that ties the individual efforts to the several FE goals. A summary of the funding and manpower requirements will be given, followed by a discussion by research area of the rationale by which the projects were chosen. Finally a discussion of Work for Others projects will be given. An appendix describes the capital equipment needed for the Research Plan.

FUNDING

The Cooperative Agreement indicates that the total first-year funding available is $4,995,000 in the Base Program and $4,594,000 in the Optional Program. DOE will furnish all of the Base Program funds and $3,675,000 of the Optional Program funds. NIPER will furnish $919,000 in the Optional Program.

Transition costs allowed by the Cooperative Agreement for the shift of BETC from DOE management to IITRI management and establishment of NIPER amount to $250,000. This includes the cost of establishing the Technical Advisory Committee. As negotiated, this is charged against the Base Program.

The preparation of this Annual Research Plan and the plan for fiscal year 1985, which will start this spring to coincide with the FE planning cycle, is charged against this year's budget and amounts to $250,000. Half is charged to the Base Program and half to the Optional Program.

As shown in Table 1, the result is that the Base Program accounts for $4,620,000, and the Optional Program for $4,469,000.

PERSONNEL

The manpower requirements for the Base and Optional Programs are given in Table 2. The total for the two programs is 92 man-years. In each of the project plans, an estimate is given of the manpower distribution by research groups. These represent best estimates at this time. As the projects progress, these needs may vary. Accordingly, the manpower distribution within the total effort will be adjusted. This is consistent with the contract requirement for reporting resources at the project level.

Approximately one man-year of consulting effort is estimated in support of specific projects. Costs associated with this service have been included in the respective project cost estimates.

EXTRACTION RESEARCH

Fossil Energy used the technical constraints to EOR described in DOE/BETC/RI-80/4, "Technical Constraints Limiting Application of Enhanced Oil Recovery Techniques to Petroleum Production in the United States" to identify the components of the "Enhanced Oil Recovery R&D Program Plan 1983." (See Appendix 3.) This Program Plan was used to develop the Statement of Work in the SCAP.

Negotiation between DOE and IITRI resulted in some modifications to the Statement of Work (SOW) before it appeared in the Cooperative Agreement. The Base Program was accepted by IITRI. Some reorganization of the Optional Program was made, and NIPER was given the opportunity to work in gas and utilization research.

TABLE 1. FUNDING FOR BASE AND OPTIONAL PROGRAMS

	Funding, $K Base Program DOE	Optional Program DOE	Optional Program Participant	Total	Total
Cooperative Agreement	4,995	3,675	919	4,594	9,589
Transition Costs	(250)	-	-	-	(250)
Annual Plan Costs	(125)	(100)	(25)	(125)	(250)
Available for Projects	4,620	3,575	894	4,469	9,089
Project Funding					
Extraction Research	3,435			2,060	5,495
Processing/Thermodynamics	1,185			1,132	2,317
Utilization	-			1,277	1,277
	4,620			4,469	9,089

TABLE 2. TECHNICAL MANPOWER REQUIREMENTS

Area	Manpower, man-years
Base Program	
Extraction	32.0
Processing and Thermodynamics	11.3
Subtotal	43.3
Optional Program	
Extraction	22.0
Processing and Thermodynamics	13.1
Utilization	14.2
Subtotal	49.3
TOTAL	92.6

The Cooperative Agreement Research Statement of Work (Appendix 2) lists the EOR subjects and some key tasks associated with these subjects for possible inclusion in the Base Program. The subjects listed are:

5.1.1 Displacement Mechanisms and Mobility Control (11 tasks)
5.1.2 Rock/Fluid Interaction (11 tasks)
5.1.3 Prediction and Evaluation (3 tasks).

The Optional Program has eight EOR subjects:

6.1.1 Reservoir Systems--Properties and Characteristics (2 tasks)
6.1.2 Displacement Mechanisms (3 tasks)
6.1.3 Sweep Mechanisms (2 tasks)
6.1.4 Injection Materials (5 tasks)
6.1.5 Reservoir Simulation (2 tasks)
6.1.6 Reservoir Data Development (3 tasks)
6.1.7 Process Data Development (3 tasks)
6.1.8 Economics and Logistics (4 tasks)

The Optional Program also lists projects and tasks in Unconventional Gas Recovery (UGR) as:

6.4.1 Formation Characterization (1 task)
6.4.2 Fracturing (2 tasks)
6.4.3 Production Technology (1 task)
6.4.4 Recovery Predictions (1 task)

The Statement of Work is quite broad and it is impossible to work on all of the items initially. Some guidelines were established to indicate how the areas of work were to be chosen. These are:

(1) Use existing personnel's special capabilities

(2) Cover technology areas broadly enough to avoid premature specialization of NIPER

(3) Develop an Optional Program that will attract industry support by serving as a bridge between the more fundamental work of the Base Program and application to industry

(4) Increase NIPER capability in high priority areas that are now marginal because of (a) loss of BETC staff during transition period, (b) previous heavy BETC dependence on universities for work in specific areas

(5) Work on topics where innovative new results could have a major impact on the course of EOR, processing, and utilization technology

(6) Avoid duplication of work being performed at universities.

As a result, the Program emerged as a combination of projects that heavily rely on research already underway, but which changes emphasis somewhat by the expansion of continuing projects or by addition of new projects.

Table 3 lists the projects chosen for the Base Program together with the funding and manpower requirements. BE1A and BE3A are new projects designed to bring NIPER into fields expected to be of considerable importance. Project BE2 was previously done principally by a contractor and consequently is new to NIPER. Projects BE1C and BE5 were expanded over the scope shown by previous projects. The remainder--BE1B, BE1C, BE4A, BE4B, BE4C, BE4D, and BE4E--are continuations of projects that were underway at BETC.

A matrix showing the relationships of the NIPER program to the Cooperative Agreement SOW is given in Table 4. Some of the projects in the NIPER Base Program are also applicable to the Optional Program. The strong orientation of the Base Program to fundamental science is apparent, and even where the projects indicate some application potential, as in BE1 and BE4, the long-term character is stressed.

The Optional Program planned for NIPER is shown in Table 5. Project OE2 and the three subprojects of OE3 are new and are covered by the statement of work. Projects OE1 and OE4 are continuations of BETC work, but with an expanded scope. All of these projects were chosen because they are expected to result in improved understanding of EOR processes. Their application to improved performance in the field is sufficiently evident that they are likely to attract cooperative funding by industry. Ultimately, projects in the Optional Program are expected to be completely funded by industry.

This program represents a good match between the FE objectives and NIPER's needs. It covers the significant EOR issues with which FE is concerned and avoids duplication with other efforts while maximizing the use of the existing capability and assuring NIPER a well-rounded program. The Optional Program acts as a bridge for NIPER to move toward research fully funded by industry.

TABLE 3. BASE PROGRAM PROJECTS

NIPER Project No.	Title	Research* Area	Manpower,** man-years	Funding, $K
	Extraction Research			
BE1	Interaction Between Reservoir Rock and EOR Fluids	EOR	11.0	1070
BE1A	Surface Chemistry of Reservoir Rocks and their Reaction with Crude Oil Components			
BE1B	Effect of Clay Minerals on Oil Saturation Determination			
BE1C	Three-Phase Flow in Porous Media			
BE2	Reservoir Screening and Recovery Predictions	EOR	6.0	710
BE2A	EOR National Potential			
BE2B	Technology Appraisal			
BE2C	Process Predictive Screening Models			
BE3	EOR Environmental Compatibility	APT	2.5	330
BE3A	Effect of Microbial Technology on EOR			
BE4	Basic Studies of EOR Chemicals	EOR	9.0	990
BE4A	Behavior of Surfaces with Adsorbed Materials			
BE4B	Adsorption of Surfactant Slug Components on Reservoir Minerals			
BE4C	Application of Thermodynamic Measurements to Micellization and Solubilization			
BE4D	Effects of Surfactant Structure and Additives on Micelle Formation and Solubilization			
BE4E	Order of Mixing Effects for Aqueous Surfactant			
BE5	Gas Displacement Methods	EOR	3.5	335
BPT1	Thermodynamic Properties of Organic Compounds	APT/ARTD	6.4	650
BPT1A	Thermodynamic Properties of Organic Nitrogen Compounds That Occur in Shale Oil and Heavy Petroleum			
BPT1B	Thermophysical and Thermochemical Properties of Organic Compounds Derived from Fossil Substances			
BPT2	Stability and Processing Research for Crudes, Intermediate Process Streams, and Finished Fuels***	APT	0.7	80
BPT3	Chemical Characterization of Heavy Ends of Light Petroleum, of Heavy Petroleum, and of Liquids Derived from Other Fossil Sources***	APT	4.2	455
	TOTAL BASE PROGRAM		43.3	4,620

* Abbreviations: EOR = Enhanced Oil Recovery; APT = Advanced Processing Technology; ARTD = Advanced Research and Technology Development (Coal Thermodynamics) Subprogram.

** Manpower effort reflects maximum personnel to work on project. Some personnel are not yet available, thus costs reflect a manpower effort for the fiscal year lower than that shown.

*** Parts of these projects are in the Optional Program.

TABLE 4. CORRELATION OF COOPERATIVE AGREEMENT STATEMENT OF WORK TO THE NIPER PROGRAM FOR EXTRACTION RESEARCH

Cooperative Agreement* / NIPER Program	Enhanced Oil Recovery														
	Base Program			Optional Program								Unconventional Gas Recovery			
	5.1.1	5.1.2	5.1.3	6.1.1	6.1.2	6.1.3	6.1.4	6.1.5	6.1.6	6.1.7	6.1.8	5.4.1	5.4.2	5.4.3	5.4.4
BE1															
BE1A		x													
BE2A		x													
BE3A		x	x												
BE2															
BE2A			x						x						
BE2B			x							x	x				
BE2C			x							x					
BE3															
BE3A			x		x										
BE4															
BE4A		x			x										
BE4B		x													
BE4C		x													
BE4D		x													
BE4E		x													
BE5	x														
OE1															
OE1A													x		
OE1B													x		
OE2															
OE2A				x											
OE3															
OE3A					x		x								
OE3B						x									
OE3C		x					x								
OE4															
OE4A						x									
OE4B										x					

* See Appendix 2 for Cooperative Agreement Statement of Work

TABLE 5. OPTIONAL PROGRAM PROJECTS

NIPER Project No.	Title	Research* Area	Manpower,** man-years	Funding, $K
	Extraction Research			
OE1	Improvements in Stimulation Technology	GAS	6.0	585
OE1A	Formation Damage Due to Hydraulic Fracturing Fluid			
OE1B	Characterization of Polymer Fracturing Fluid Systems			
OE2	Reservoir Characterization for EOR Application	EOR	1.5	200
OE2A	Fluid Front Monitoring for Chemical EOR			
OE3	Recovery Processes: Chemical	EOR	8.5	735
OE3A	Improved Chemical Flooding Agents: Surfactant Systems			
OE3B	Mobility Control Agents			
OE3C	Alkaline Flooding			
OE4	Recovery Processes: Thermal	EOR	6.0	540
OE4A	Steam Flooding			
OE4B	_In Situ_ Combustion			
	Processing and Thermodynamics Research			
OPT1	Thermophysical Properties of Real and Synthetic Fluid Mixtures Derived from Fossil Substances	ARTD	2.6	185
OPT2	Stability and Processing Research for Crudes, Intermediate Process Streams, and Finished Fuels***	APT	2.2	287
OPT3	Chemical Characterization of Heavy Ends of Light Petroleum, of Heavy Petroleum and of Liquids Derived from Other Fossil Sources***	APT	5.0	325
OPT4	Fuels Trends and Analyses	APT	.9	90
OPT5	Chemistry of Contaminated Petroleum Fuels	APT	2.4	245
	Utilization Research			
OU1	Diesel Fuel Quality Criteria	APT	5.3	500
OU2	Direct Utilization of Aromatic Feedstocks	APT	4.9	385
OU3	Diesel Exhaust Characterization	APT	2.4	280
OU4	Coal Slurry Injection Characteristics	ARTD	1.6	112
	TOTAL OPTIONAL PROGRAM		49.3	4,469

* Abbreviations: EOR = Enhanced Oil Recovery Subprogram; APT = Advanced Process Technology Subprogram; ARTD = Advanced Research and Technology Development; GAS = Unconventional Gas Subprogram.

** Manpower effort is maximum personnel to work on project. Some personnel are not yet available, thus costs reflect a manpower effort for the fiscal year lower than that shown.

*** Also in Base Program.

PROCESSING AND THERMODYNAMICS RESEARCH

Alternative sources of fossil fuels such as heavy oil, tar sands, shale oil, and coal liquids present a number of refining problems when compared with the processing of conventional light, sweet, petroleum crudes. Basically, the alternate crudes contain larger quantities of heterocyclic compounds (particularly nitrogen-containing types), aromatics, and organometallic compounds. Olefinic types are found in direct coal liquids and are quite prevalent in shale oils.

All of these materials adversely affect standard refining practices. For example, nitrogen-containing compounds and some organometallics are known to poison refinery catalysts; hydrogen-deficient types such as the aromatics and olefins contribute to gum formation and fuel storage instability. Finally, some of the aromatic, nitrogen, and organometallic compound types are known to be toxic to man and the environment and must be removed during the processing sequence.

Because of the many refining problems associated with the processing of alternate crudes, it has been standard practice to blend small quantities with conventional petroleum feedstocks, thereby eliminating most of the detrimental effects. However, as conventional petroleum crudes become depleted and we become increasingly more reliant on alternate fuels, it will be necessary to alter existing refining technologies so that the new feedstocks can be upgraded to the extent required to meet product specifications.

In order to determine the type and quantity of upgrading necessary, it is essential that separation and identification procedures be developed to allow the characterization and physical property determination of specific compound types. Further, the compilation of correlatable thermodynamic data for the identified compound types is a prerequisite to the design of new or modified refinery processes. Presently, only limited data are available on the thermodynamic properties of the compound types found in the more complex alternative crudes.

The Cooperative Agreement SOW lists the APT subjects for possible inclusion in the Base Program as follows:

5.2.1 Thermodynamic and Thermophysical Measurements (4 tasks)
5.2.2 Characterization Studies (5 tasks)
5.2.3 Process Technology (3 tasks)

All of these are subjects in which BETC conducted research, and represent continuation of basic research on the properties of liquid hydrocarbons.

The projects proposed in the Base Program are shown in Table 3. Each of the subjects in the SOW are addressed as indicated in Table 6. Project BPT1 is divided into two subprojects because of the chemical differences in shale oils and coal liquids. Nitrogen compounds are of prime interest in shale oil refining, while oxygen-containing compounds affect the upgrading of coal liquids. Both BPT2 and BPT3 are extended into the Optional Program with more basic tasks in the Base Program and application-oriented tasks in the Optional Program.

TABLE 6. CORRELATION OF COOPERATIVE AGREEMENT STATEMENT OF WORK TO THE NIPER PROGRAM FOR PROCESSING AND THERMODYNAMICS RESEARCH

Cooperative Agreement* / NIPER Program	Advanced Process Technology						
	Base Program			Optional Program			
	5.2.1	5.2.2	5.2.3	6.2.1	6.2.2	6.2.3	6.2.4
BPT1	x						
BPT1A							
BPT1B							
BPT2			x	x			
BPT3		x					
OPT1					x		
OPT2				x			
OPT3						x	
OPT4						x	
OPT5				x			x

* See Appendix 2 for Cooperative Agreement Statement of Work

The Cooperative Agreement Optional Program SOW (Appendix 2) shows the following APT subjects:

- 6.2.1 Fuel Processing (4 tasks)
- 6.2.2 Thermodynamic and Thermophysical Property Measurement (5 tasks)
- 6.2.3 Fuel Characterization Study (4 tasks)
- 6.2.4 Other Characterization Studies (1 task)

The planned Optional Program is listed in Table 5. As shown in Table 6, each of the subjects in the Cooperative Agreement Statement of Work is addressed. The two projects OPT2 and OPT3 have the same titles as projects in the Base Program because the same skills and equipment are used. However, the tasks in the Optional Program are the more applied extensions of the tasks in the Base Program. As proposed by NIPER, the Optional Program projects will exploit the insights that come from applying advanced characterization work to the understanding of the problems associated with alternative fuel composition and properties. Projects OPT4 and OPT5 are both addressed to the Optional Program and are continuations and redirection of present work.

The Base and Optional Program projects jointly provide a plan for both a continuation of the work in fundamental hydrocarbon research and for expansion in thermodynamic studies. Although all of this research is relatively basic, it is expected to be of sufficient importance to attract support by industry.

UTILIZATION RESEARCH

As stated previously, Utilization Research was not specifically mentioned in the SCAP. Subsequent negotiations between DOE and IITRI, however, resulted in agreement on a modest effort in this research area. Guiding factors in this determination were (1) BETC had an ongoing program and personnel with special expertise, (2) the BETC Utilization Research capability is a valuable resource that should not be lost, and (3) work supported under the Optional Program was needed until a suitable market could be developed.

The most important use of alternative feedstocks will be to supplement present transportation fuels; therefore, their effect on the operation of engines must be determined. Any changes in emissions and efficiency that may result from the use of alternative feedstocks should be examined to see that they do not cause unduly restrictive attitudes toward the fuels from the alternative sources. Environmentally oriented changes in engine design and operation to make them more adaptable to alternative feedstock-derived fuels or blends with conventional petroleum fuel must be considered.

The Cooperative Agreement lists under the Optional Program (Appendix 2) the project areas:

6.3.1 Fuels for Mobile Engines (4 tasks)
6.3.2 Fuels for Stationary Engines (3 tasks)

The proposed projects for NIPER are shown in Table 5.

NIPER has planned a program that examines specifications for both diesel fuel and gasoline to determine whether changes to accommodate the character of alternative feedstock-derived fuels could be made without deleterious effects on the environment. The possibility of harmful chemicals in such alternative fuels and their exhaust products will be examined. Consideration is also given to the feasibility of augmenting diesel fuel supply by the use of powdered coal in a slurry of diesel fuel.

These projects correlate directly with the Statement of Work in the Cooperative Agreement as shown in Table 7 and are designed to lead to Work for Others projects.

Projects OU1, OU2, and OU3 address item 6.3.1 of the Cooperative Agreement; OU4 addresses item 6.3.2.

TABLE 7. CORRELATION OF COOPERATIVE AGREEMENT STATEMENT OF WORK TO THE NIPER PROGRAM FOR UTILIZATION RESEARCH

Cooperative Agreement* / NIPER Program	Advanced Utilization** Research 6.3.1	6.3.2
OU1	x	
OU2		x
OU3	x	
OU4		x

* See Appendix 2 for Cooperative Agreement Statement of Work
** Optional Program Only

WORK FOR OTHERS

The Work for Others projects are fully funded outside the Cooperative Agreement and thus are not based on the same justifications as projects in the Base and Optional Programs. The nine projects currently in this program are listed in Table 8. It is anticipated that this area of NIPER's program will show considerable growth as the organization adjusts to the new opportunities to pursue outside research projects.

TABLE 8. WORK-FOR-OTHERS PROJECTS

Title	Potential Sponsor
Extraction Research	
Physics of Immiscible Flow in Porous Media	EPA
Research on Water Quality Issues	EPA
Processing and Thermodynamics Research	
Thermodynamics Characterization of Condensed Ring Compounds	Office of Energy Research Basic Energy Sciences
Waste Hydrocarbon Recycling	Division of Conservation and Renewable Energy
Removal of Metals from Alternative Crudes	Petroleum Companies
Environmental Sample Generation for Mutagenesis Testing	Petroleum Companies
Strategic Petroleum Reserve Supporting Research	Strategic Petroleum Reserve Office
Utilization Research	
Coal Slurry Fuel Guidelines	DOE/Fossil Energy
Alcohol-Gasoline Blends	Petroleum Companies EPA DOE/Conservation and Renewable Energy
Assessments of Alternative Fuel Technologies	Multi-client

BE1. INTERACTION BETWEEN RESERVOIR ROCK AND EOR FLUIDS

This project is composed of three elements:

(1) Surface Chemistry of Reservoir Rocks and Their Reaction with Crude Oil Components
(2) Effects of Clay/Minerals on Oil Saturation Determination
(3) Three-Phase Flow in Porous Media.

The displacement and release of oil from the reservoir involves interplay between gravitational, viscous, and capillary forces, and interactions between the injected fluid and the fluids and rock materials in the reservoir. An understanding of these relationships and how they can be manipulated by changing the injected fluids can help in the design of improved recovery processes and prediction of reservoir performance.

The ability to determine residual oil saturation (ROS) in a reservoir is essential for accurately evaluating the EOR potential of a given reservoir. A completely reliable method of ROS determination is still elusive. Often several different methods have to be used to cross-check the residual oil saturation values, such as electric log, single well tracer, core analysis, thermal decay time (neutron lifetime log), and carbon/oxygen log. The number of research projects previously sponsored by the Department of Energy on ROS determination testifies to its importance and complexity. Sometimes, the measuring methods used in previous studies were rendered uncertain because the relationship between the physical properties of reservoir rocks and fluids, and the oil saturation is not known. Extensive work in this area is needed.

Three-phase flow of fluids in porous media is encountered in oil reservoirs under solution gas drive, gas cap pressure drive, steam drive, fireflood, carbon dioxide flood, and other situations where gas is present or introduced artificially into the petroleum reservoir. The limited research on three-phase flow phenomena has shown that the presence of a third phase (whether mobile or not) has a profound influence on the transport properties of the other two mobile phases in any porous medium. Therefore, an accurate knowledge of three-phase flow behavior is extremely important to the petroleum industry, especially since the advent of enhanced oil recovery techniques that create three phases within the oil reservoir by injection of gas or the volatilization of hydrocarbons in thermal processes.

BE1A. SURFACE CHEMISTRY OF RESERVOIR ROCKS AND THEIR REACTION WITH CRUDE OIL COMPONENTS

Background

This work addresses Item 5.1.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The work falls naturally into two parts:

(1) Surface Chemistry of Solids
(2) Adsorption and Reactions of Crude Oil and Components.

Although the work is divided into two parts for convenience of explanation it represents only one integral project, with the overall objective of determining the chemistry of the adhesion of crude oils to the rock surface. The resolution of this question will lead to scientifically designed methods for enhanced oil recovery that will be based on fundamental oil-rock chemistry rather than trial-and-error searches for solutions that may have an impact on oil recovery efficiency.

Capillary pressure, viscosity, pore geometry, sweep efficiency, and reservoir heterogeneity play important interdependent roles in the production of oil. Furthermore, the relative wetting, or chemical adhesion, of water and oil to the surface of the sedimentary rocks is extremely important with respect to fluid flow properties and residual oil saturation (1). The nature of the adhesion of oils to the rock surface is important when chemical compounds are considered for enhanced oil recovery (2). The explanation of the adhesion of oil to sedimentary rocks, on a molecular scale, could aid materially in selecting chemicals for oil displacement and explaining many field results not now understood from consideration of only the physical relationships of the interactions of fluids with rocks.

Ion-exchange studies were selected first in the study of the surface chemistry of rocks because they fit closely with the mineral analyses being conducted with the scanning electron microscope (SEM) equipped with energy-dispersive x-ray spectrometer (EDS) analytic capability and also to provide a clear understanding of the nature of the ionic exchangeable sites. It is important to understand the total cation exchange capacity (CEC) and selectivity toward various cations, and to know which cations are occupying the exchangeable sites in the natural state.

The use of the SEM for analysis of geological samples has greatly expanded since its inception as a commercial instrument in the early 1960's (3). Combining the SEM with an energy-dispersive x-ray spectrometer for the study of geologic samples allows simultaneous elemental analysis and morphological studies without additional sample preparation. Since the identification of clay by morphology alone in samples with a mixture of components is usually inadequate, the additional identification of the clays by EDS removes the uncertainty of the clay mineral characterization.

A number of studies have elucidated the importance of ion-exchange between injected slugs and reservoir materials and the pilot test at North Burbank, Oklahoma showed that the presence of a clay mineral can increase surfactant loss considerably (4-5). It is therefore important to examine the role played by the solid surface of the pores and its interaction with fluids in the process of oil displacement.

This complete study of the rock surface minerals and their interaction with crude oil components will lead to a theoretical understanding of the interactions between reservoir rocks and EOR recovery fluids. The data developed from this work and the molecular interaction theory of rocks and oils will lead to improvement of methods for reservoir characterization and improvement of screening criteria for selection of EOR processes.

References

1. Donaldson, E. C., R. D. Thomas, and P. B. Lorenz, "Wettability Determination and Its Effect on Recovery Efficiency," Soc. Pet. Eng. J., March 1969, Vol. 9, No. 1, pp. 13-20.
2. Donaldson, E. C., and Michael E. Crocker, "Characterization of the Crude Oil Polar Compound Extract," DOE/BETC/RI-80/5, Oct. 1980.
3. Pittman, E. D., and J. B. Thomas, "Some Applications of Scanning Electron Microscopy to the Study of Reservoir Rock," J. Pet. Tech., Nov. 1979, pp. 1375-1380.
4. Smith, F. W., "Ion-Exchange Conditioning of Sandstones for Chemical Flooding," J. Pet. Tech., June 1978, pp. 959-968.
5. Carroll, D., "Ion-Exchange in Clays and Other Minerals," Bull. Geol. Soc. Amer., 1959, Vol. 70, pp. 749-780.

Objectives

To determine the role of functional groups of oil components (especially the polar organic compounds) in the oil mobilization process.

Scope of Work

This research will determine the surface chemical composition of sedimentary rocks (sand and carbonate; outcrop and reservoir cores) using visual techniques to identify and classify minerals and clays. The amounts and types of clay present in oil-producing formations affect most tertiary recovery processes. A comprehensive data base of clay mineralogy will be developed and added to the EOR Data Base, especially for reservoirs that are candidates for chemical recovery processes. SEM/EDS will be used to determine the chemical characteristics of clays, minerals, and sedimentary rocks. This will be correlated with the results of determining the total chemical composition.

The project is designed to develop data on how functional groups of oil components react with and adhere to rock surfaces. Minerals will be contacted with crude oils enriched in various components such as acids, bases, etc., and the way these components are distributed between the oil and solid surface will be determined. The extent to which the materials are removed by solvent extraction, surfactant treatment, or chemical reaction will be measured. Using these results, we will design core flood tests to clarify the role of these processes in oil mobilization.

Work Plans

(1) Characterization of the Surface of Rocks

Task 1 - Obtain cores (sand, sandstone, carbonates, shales, or combinations of these) from oil fields for examination with the SEM/EDS and emission spectrograph (ES). Also, the United States Geological Survey (USGS) in Denver, CO has furnished a suite of more than 100 cores from various oil fields around the country; the well location and depth are identified.

Task 2 - Determine the surface chemical composition of sedimentary rocks using the SEM/EDS coupled to chemical analysis with the EDS.

Task 3 - Determine the ion exchange properties of the rocks; not only the total ion exchange capacity, but also the complete analysis of the cations displaced by exchange as a function of time.

Task 4 - Determine diagenesis and particle distribution by microscopic observations of thin sections.

Task 5 - Establish a data base on common clays in sedimentary rocks and their interactions with fluids. Place these data in the reservoir data file.

Task 6 - Conduct gas phase adsorption (especially hydrogen) and gas phase reaction experiments with known catalytic properties on the rocks to determine the thermodynamic reaction potential and the catalytic properties of sedimentary rocks.

(2) Adsorption and Reactions of Crude Oil and Components

Task 7 - Extract polar compounds quantitatively from crude oils of various types. Determine the functional groups of these compounds by gas chromatography-mass spectrometry analysis.

Task 8 - Conduct wettability tests of the polar compounds by dissolving them in paraffin oils and noting the changes in capillary pressure and wettability.

Task 9 - Prepare detailed analysis of data on reaction of oil components with rock surfaces.

Future Work

It is estimated two years beyond FY84 will be needed to complete this project. This work will include (1) determining the compounds adsorbed on the rock surface when contacted with polar compounds, (2) developing a fundamental theory of oil adhesion to reservoir rocks, (3) developing of additional screening criteria for EOR processes, and (4) demonstrating selection of EOR chemicals based on the theory of adhesion.

Manpower Requirements

	Man-years
Senior Chemical Engineer	0.2
Research Chemist	0.7
Associate Chemist	0.8
Senior Experimentalist	0.5
Technician	1.0
Total	3.2

Equipment Requirements

	Available	New
Core flooding equipment	1	
Gas/liquid chromatograph	1	
Liquid chromatograph	1	
SEM/EDS	1	
Inductively coupled plasma (emission spectrograph)	1	
Adsorption and kinetic reactor		1

PROJECT SCHEDULE AND MILESTONE

Project: Surface Chemistry of Reservoir Rocks and Their Reaction with Crude Oil Components

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Obtain cores	A▽	B▽ //////											
2. Mineral and SEM/X-ray analysis		///	//////	//////	//////	//////	A▽ //////	//////	//////	//////	//////	B▽ //////	
3. Determine ion exchange properties		///	//////	//////	//////	//////	A▽ //////	//////	//////	//////	//////	B▽ //////	
4. Determine diagenesis and particle distributions in rocks		///	//////	//////	//////	//////	//////	A▽ //////	//////	//////	//////	B▽ //////	
5. Determine clays in rocks		///	//////	//////	//////	//////	A▽ //////	//////	//////	//////	//////	B▽ //////	
6. Conduct gas-phase adsorption & catalytic experiments												A▽ //////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		**Description**
Task 1	(A) October 15, 1983	Outcrop core samples have already been secured and mineral analysis, cation exchange properties and SEM/X-ray analysis completed
	(B) November 30, 1983	Sandstone, carbonate, and shaley rocks from selected oilfields in the U.S. obtained from USGS with complete data on well location and depth of core
Task 2	(A) April 30, 1984	Complete minerals and SEM/X-ray analyses of sandstones
	(B) September 30, 1984	Complete minerals and SEM/X-ray analyses of carbonate rocks
Task 3	(A) April 30, 1984	Complete cation exchange properties analyses of sandstones
	(B) September 30, 1984	Complete cation exchange properties analyses of carbonate rocks
Task 4	(A) May 31, 1984	Evaluate particle distribution measurements and compare analyses to results reported in the literature.
	(B) September 30, 1984	Complete analysis of particle distributions and diagenesis in cores.
Task 5	(A) April 30, 1984	Enter analysis of clays in sandstones into EOR data base
	(B) September 30, 1984	Enter analysis of clays in carbonates and shaley rocks into EOR data base
Task 6	(A) September 1, 1984	Initiate gas phase adsorption experiments

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

(Continuation Sheet)

PROJECT SCHEDULE AND MILESTONE

Project: Surface Chemistry of Reservoir Rocks and Their Reaction with Crude Oil Components

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
7. Quantitative extraction of polar compounds from crude oil			A ▽ //////	//////	//////	//////	//////	//////	//////	//////	//////	//////

Milestone	Description
Task 7 (A) December 1, 1983	Initiate extraction of polar organic compounds from crude oils and submit for GC/MS analysis

BE1B. EFFECT OF CLAY MINERALS ON OIL SATURATION DETERMINATION

Background

This work addresses Item 5.1.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The measurement of the true oil saturation of a petroleum reservoir is still difficult (1), especially for reservoirs containing heavy oils (oils with an API gravity lower than 20°). As the oil gravity decreases, the accuracy of oil saturation determination also decreases. In many cases the oil saturation near the wellbore is a poor representation of the actual reservoir oil saturation, and logging tools with a wider radius of investigation must be used. Clay minerals complicate the problem, resulting in considerable inaccuracy of the logs.

Logging companies have studied the effect of clay minerals on the logging signals used for oils of API gravity greater than 20°. The logging companies have not studied the lower gravity oils because these oils have not become important until recently. A factor that makes this investigation much more complicated is the strong oil-wetting effect of heavy oils due to complex polar compound reactions with the minerals (2). These effects have not been studied in relation to oil saturation and electrical properties; however, this project, Interactions Between Reservoir Rock and EOR Fluids, is undertaking a detailed investigation of sedimentary rock minerals, especially clays, and their interactions with crude oils. Therefore, a task to investigate the effects of clay minerals on oil saturation determination from electric logs, especially for heavy oils, can be conducted concurrently in close cooperation with the other subprojects of Project BE1 (3).

Measurement and characterization of ambiguous surface structure are an important part of the project. NIPER is well equipped with the instrumentation and has the expertise for surface characterization by scanning electron microscopy, clay mineral identification by x-ray dispersive analysis and pore size distribution.

As more heavy oils are being produced, the resolution of these very fundamental problems related to the economical recovery of heavy oil will offer large benefits in the enhancement of heavy oil recovery, monitoring of field development, and decision-making with respect to EOR. The importance of this work is indicated by the work contracted out by DOE in field projects.

References

1. Wyman, R. E., "How Should We Measure Residual Oil Saturation," Joint Convention on Enhanced Oil Recovery, Calgary, Alberta, June 7-11, 1976.

2. Donaldson, E. C., and M. E. Crocker, "Characterization of the Crude Oil Polar Compound Extract," DOE/BETC/RI-80/5, Oct. 1980.

3. Crocker, M. E., E. C. Donaldson, and L. M. Marchin, "Comparison and Analysis of Reservoir Rocks and Related Clays," SPE Paper 11973, presented at the 58th Annual SPE Technical Conference and Exhibition, San Francisco, Calif., Oct 5-8, 1983.

Objectives

To develop a theory for measurement of in situ oil saturation in heavy oil reservoirs.

Scope of Work

Research will determine the effects of wettability and clay minerals on the determination of in situ oil saturation by electrical methods in heavy oil reservoirs. A variety of methods for evaluating heavy oil saturation in laboratory cores will be made using material balance, solvent extraction, electrical resistivities, dielectric measurements, tracer injection, and other techniques. The effects of EOR emulsions will be considered.

Work Plans

Task 1 - Obtain cores from heavy oil formations.

Task 2 - Determine clay mineralogy by SEM/EDS method; conduct resistivity measurements at various fluid saturations and electrolyte concentrations; determine porosity and permeability measurements.

Task 3 - Correlate resistivity with oil saturation using clay content, clay type, API gravity of oil, and ionic concentration of brine as parameters.

Task 4 - Perform a suite of oil saturation measurements on water-flooded cores using the techniques of material balance (gravimetric and volumetric), resistivity, dielectric, and solvent extraction.

Task 5 - Load these cores to different saturations with oils of different API gravities, and determine oil saturation by measuring resistivity, material balance (volumetric and gravimetric), and if necessary use other methods.

Task 6 - Perform the same experiments for chemically flooded cores obtained from in-fill observation/evaluation wells.

Task 7 - Analyze all data and make recommendations to DOE on correction factors to be included in residual oil calculation from electric logs.

Future Work

It is estimated that two years beyond FY84 will be needed to complete this project. The additional work will include further core floods (see Task 5) and data analysis to develop correction factors for residual oil calculations.

Manpower Requirements

	Man-years
Electrical Engineer	0.5
Petroleum Engineer	0.5
Senior Chemical Engineer	0.3
Research Geologist	0.5
Research Chemist	0.5
Technician	1.0
Research Chemist	0.3
Associate Chemist	0.2
Senior Experimentalist	0.5
Total	4.3

Equipment Requirements

	Available	New
Resistivity measurement equipment	1	
Dielectric measurement equipment	1	
Scintillation counter		1

PROJECT SCHEDULE AND MILESTONE

Project: Effect of Clay Minerals on Oil Saturation Determination

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Obtain heavy oil cores									A ▽				
				//////	//////	//////	//////	//////	//////				
2. Clay mineralogy and resistivity of saturated cores												A▽	
				//////	//////	//////	//////	//////	//////	//////	//////	//////	
3. Effect of clays on resistivity										A ▽			
										//////	//////	//////	
4. Oil saturation by other methods										A ▽			
										//////	//////	//////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ[1]	

Milestone		Description
Task 1	(A) June 30, 1984	Completion of sample acquisition
Task 2	(A) September 30, 1984	Completion of analyses for a suite of cores
Task 3	(A) July 1, 1984	Initiation of correlation of parameters affecting resistivity
Task 4	(A) July 1, 1984	Begin oil saturation measurements on waterflooded cores

Reporting Requirements

(A) 15 th of each month.................. Monthly Progress Report

(B) 30 days after end of each quarter.......... Quarterly Technical Progress Report

(C)[1] 90 days after end of program year........ Annual Technical Progress Report

BE1C. THREE-PHASE FLOW IN POROUS MEDIA

Background

This work addresses Items 5.1.2 and 5.1.3 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Three-phase flow is encountered in oil reservoirs under solution gas drive, gas cap pressure drive, steam drive, fireflood, carbon dioxide flood, and in other situations where gas is present or introduced artificially into the petroleum reservoir. The limited research on three-phase flow phenomena has shown that the regime of three-phase flow is very narrow; however, the presence of a third immobile phase has a profound influence on the transport properties of two mobile phases in any porous medium (1,8,9). Therefore, an accurate knowledge of three-phase flow behavior is extremely important to the petroleum industry, especially since the advent of enhanced oil recovery techniques that create three phases within the oil reservoir by injection of gas or volatilization of hydrocarbons.

Although numerous studies of two-phase flow have been reported in the literature, the study of three-phase flow phenomena has been largely neglected because of the complexity of the tests and mathematical analysis. However, improvements in laboratory instrumentation and the advent of high-speed digital computers have changed this status.

Because of the absence of three-phase relative permeability data, petroleum engineers must rely on theoretically derived data based on questionable assumptions. In addition, it has not been possible to relate other measured rock characteristics (two-phase relative permeability and wettability) to three-phase flow. Two-phase imbibition or drainage relative permeabilities, which are common to conventional oil recovery processes, are not applicable to some of the newer EOR techniques. Sometimes data are needed for a three-phase system where almost any combination of two fluids or even all three fluids may be flowing.

The concept of relative permeability was introduced early in the petroleum industry to describe the relative flow characteristics of two immiscible fluids in porous media, and it was extended to three-phase flow in 1941. The relative permeability of a given phase is the ratio of the rate of flow of that phase, when other fluids are present, to the rate of flow of that phase alone. Relative permeability has usually been found to be independent of viscosity, pressure gradient, and rate of flow. It is affected, however, by the relative wetting of the fluids on the rock (the distribution of the fluids in the pores of the rocks).

Experiments at BETC have supported the conclusion that wettability is one of the most important variables that affects the production history of a waterflood (3). Wettability governs the location of the water and oil in the pores and has a strong influence on the capillary forces that control the microscopic displacement of oil by water. Three distinct categories of residual oil are readily apparent: (1) the water-wet system in which water occupies the small pores and wets most of the rock surface; (2) intermediate, or neutral wettability; and (3) oil-wet systems in which oil is occupying the small pores and wetting most of the rock grain surfaces. In a three-phase system, gas is nonwetting and occupies the larger pores of the system, and its saturation has a profound effect on the relative flow of the water and oil.

The capillary pressure relationships of immiscible fluids in a porous system are quantitatively related to wettability methods for the determination of wettability of the two-phase systems.

A review of the literature shows that many investigations have neglected one or more of the following parameters: (1) wettability, (2) saturation history, and (3) capillary end effects. A more systematic investigation with these parameters considered is needed (2-3,6-7).

This research is long-term, highly theoretical, and mathematically intricate. It offers, however, the potential for tremendous gain in the understanding of oil recovery by processes involving three phases are involved such as gas miscible flooding, steamflooding, and emulsion recovery.

References

1. Delshad, I., M. V. MacAlister, J. G. A. Pope, and B. A. Rouse, "Multiphase Dispersion and Relative Permeability Experiment," SPE Paper 10201 presented at the 56th Annual SPE meeting, San Antonio, Tex., Oct. 5-7, 1982.

2. Dietrick, J. K., and P. L. Bondor, "Three-Phase Relative Permeability Models," presented at 51st Annual SPE Conference, New Orleans, La., Oct. 2-6, 1976.

3. Donaldson, E. C., R. D. Thomas, and P. B. Lorenz, "Wettability Determination and Its Effect on Recovery Efficiency," Soc. Pet. Eng. J., March 1979, Vol. 9, No. 1, pp. 13-20.

4. Fagin, R. G., and C. H. Steward, Jr., "A New Approach to the Two-Dimensional, Three-Phase, Unsteady-State Hetrogeneous Matrix Computer Mode," SPE Paper 1881, presented at SPE Annual Fall Meeting, Houston, Tex., Oct. 1-3, 1968.

5. Geffen, T. M., W. W. Owens, D. R. Parrish, and R. A. Morse, "Experimental Investigation of Factors Affecting Laboratory Permeability Measurements," AIME Trans., Vol. 21, No. 2, 1969, pp. 211-220.

6. Gottfried, B. S., W. H. Guilinger, and R. W. Snyder, "Numerical Solutions of the Equations for One-Dimensional Multiphase Flow in Porous Media," Soc. Pet. Eng. J., March 1966, Vol. 6, No. 1, pp. 62-72.

7. Perry, J. H., and E. H. Herron, Jr., "Three-Phase Reservoir Simulation," J. Pet. Tech., Feb. 1969, pp. 211-220.

8. Sarem, A. M., "Three-Phase Relative Permeability by Unsteady-State Method," Soc. Pet. Eng. J., Sept. 1966, Vol. 6, No. 3, pp. 199-205.

9. Sheffield, M., "Three-Phase Fluid Flow Including Gravitational, Viscous, and Capillary Forces," Soc. Pet. Eng. J., June 1969, Vol. 9, No. 2, pp. 225-269.

Objectives

To develop experimental procedures and equipment for obtaining reliable and reproducible three-phase relative permeability measurements.

Scope of Work

Laboratory procedures, apparatus, and mathematical routines will be devised for the analysis of three-phase flow phenomena in porous geological materials. The data will be used to elucidate the theory of simultaneous flow of three immiscible fluids in porous geologic materials. It will also be used to improve the techniques of reservoir modeling, three-phase EOR, and reservoir performance.

The laboratory work will first be confined to the simplest case using a paraffin oil, brine, and Berea cores 25 cm in length. After laboratory techniques have been developed, systems of various wettability conditions will be examined and the behavior of three immiscible liquid phases under simultaneous flow conditions will be determined. Thus, the work will relate to the flow of gas-crude oil-water systems and three-phase liquid systems in sandstones.

Work Plans

Task 1 - Select experimental methods based on a review of the experiences at BETC and the literature.

Task 2 - Construct apparatus for fluid flow experiments at simulated reservoir conditions at any depth up to 8,000 feet; arrange the apparatus for simultaneous measurement of fluid flow rates, pressures, and temperatures; calibrate and document the equipment.

Task 3 - Measure three-phase permeability on Berea core with paraffin oil and brine.

Task 4 - Develop a mathematical simulator to determine the three-phase relative permeabilities from the fluid flow data from core tests. This should be a finite difference solution of the flow equations for oil, water, and gas, and must incorporate capillary pressure relationships.

Task 5 - Analyze the data and recommend further extension of work.

Future Work

Two additional years will be required to complete this research. This will include extending the mathematical simulator to three-dimensions for EOR, conducting laboratory experiments with steam, and extending the work to oil field cores of sandstones and carbonates.

Manpower Requirements

	Man-years
Senior Chemical Engineer	0.5
Research Engineer	0.5
Associate Engineer	1.0
Petroleum/Chemical Engineer	0.5
Technician	1.0
Total	3.5

Equipment Requirements

	Available	New
Relative permeability setup (3-phase)	1	

PROJECT SCHEDULE AND MILESTONE

Project: Three-Phase Flow in Porous Media

Report Date: ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Select experimental methods					A▽								
		//////	//////	//////	//////								
2. Construct apparatus and tests							A▽						
		//////	//////	//////	//////	//////	//////						
3. Relative permeability of paraffin - brine system									A▽				
			//////	//////	//////	//////	//////	//////	//////				
4. Develop mathematical simulator											A ▽		
		//////	//////	//////	//////	//////	//////	//////	//////	//////	//////		
5. Analyze data												A▽	
												//////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone			Description
Task 1	(A)	February 28, 1984	Experimental methods after selected review of literature
Task 2	(A)	April 30, 1984	Complete construction of final apparatus for three-phase fluid flow
Task 3	(A)	June 30, 1984	Complete relative permeability determination with paraffin - brine system
Task 4	(A)	August 30, 1984	Complete the development of a laboratory mathematical simulator for compilation of 3-phase relative permeabilities as functions of the fluid saturation distributions and capillary pressure
Task 5	(A)	September 30, 1984	Recommend future work

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

BE2. RESERVOIR SCREENING AND RECOVERY PREDICTIONS

Routine application of EOR processes requires that the process be predictable from the standpoint of the industrial community. Predictability depends on the quality of the data used and the quality of the computer models. Data collection and validation on large numbers of reservoirs and the development of good predictive models are very expensive and time-consuming tasks. Mathematical concepts used in EOR prediction models should be changed or modified as our understanding of the physics and chemistry involved in the specific EOR processes is improved.

In recent years, DOE/BETC developed a program to provide extensive assessments of EOR processes in relation to their respective predictabilities and recovery efficiencies. The principal goals were to:

(1) assess the state of the art in EOR across all processes and reservoir types, including performance, feasibility, and level of risks

(2) estimate the technically and economically feasible EOR production of the state of the art

(3) appraise the incremental production benefits attributable to specific engineering advances in technology beyond the state of the art

(4) provide a preliminary appraisal of the feasibility of novel EOR processes

(5) serve as a comprehensive repository of data on the properties of the domestic resource base, EOR projects in the field, and the current overall understanding of EOR technology.

Progress has been the development of an EOR project data base, an EOR reservoir data base, and simplified predictive models. The EOR project data base is a comprehensive compilation of data on 645 ongoing or proposed EOR projects. It represents detailed source of data for evaluating state of the art technology, and a source of data for verifying current mathematical representations of that technology as they exist in the simplified models and reservoir simulators. Those projects exhibiting "advanced" techniques, usually pilot tests, are used to define and design mathematical theories to predict recovery under the reservoir properties and EOR process parameters used in the test.

The reservoir data base is a comprehensive compilation of data on reservoirs that are amenable to one EOR process or another. This source of data is used in conjunction with the simplified predictive models to define the respective expectation in increased recovery through various engineering improvements to assess Federal EOR priorities that assist in refining the EOR R&D program.

To complete the suite of necessary tools to predict accurately the EOR potential resulting from improved technology and types of reservoir properties, Fossil Energy has been developing economic and time-rate recovery models. Economic models are used to estimate the amount of economically recoverable oil. Time-rate recovery models are used to convert estimates of technical and economic recovery to feasible production rates given logistical, personnel, environmental, and supply constraints.

Currently, the predictive models have undergone testing by the National Petroleum Council (NPC), an industry advisory panel to the Secretary of Energy, that is conducting an in-depth, detailed appraisal of EOR potential. The NPC representatives have also validated and verified reservoir data in the reservoir data base for those reservoirs that contained a minimum of 50 million barrels of oil originally in place.

The EOR project data base is compiled and has been verified and is now undergoing the first cycle of updating to current injection/production levels and current properties.

BE2A. EOR NATIONAL POTENTIAL

Background

This work addresses Items 5.1.3 and 6.1.6 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The United States has a large potential source of oil. Of the 465 billion barrels of oil discovered, only 130 billion barrels has been produced, and another 29 billion barrels is expected to be produced by conventional means. Current enhanced recovery estimates (1-4) range from 18 billion to 53 billion barrels of oil to be recovered out of a total target of 300 billion barrels. As EOR technology advances and new information on smaller reservoirs becomes available and changes in economic climate occur, new assessments of EOR potential will be needed. These assessments will provide the "standard" from which the effects of engineering advancements on EOR may be estimated and, as such, will be a vital component in defining the Federal R&D role in EOR.

References

1. BETC Staff, "Technical Constraints Limiting Application of Enhanced Oil Recovery Techniques to Petroleum Production in the United States," DOE/BETC/RI-80/4, Sept. 1980.
2. National Petroleum Council, "An Analysis of the Potential for Enhanced Oil Recovery from Known Fields in the United States--1976-2000," NPC, Dec. 1976.
3. Lewin and Associates, "Enhanced Oil Recovery in the Gulf of Mexico," DOE/ET/14010-2, Vol. 1, 2, 3, and 4, Jan. 1983.
4. Lewin and Associates, "Economics of Enhanced Oil Recovery," DOE/ET/12072-2, May 1981.

Objectives

To determine the impact of including reservoirs with less than 50 million barrels of oil in place in the National EOR potential.

Scope of Work

This project will assess the potential of EOR using existing data sources and predictive models. In contrast to the NPC group, which studied reservoirs having 50 million or more barrels original oil in place (OOIP), this research is designed to use 20 million barrels as a minimum, which will improve the statistical base for the study. The reservoir data base is missing approximately 40 billion barrels OOIP in the larger fields (those greater than 50 million barrels OOIP) and another 40 billion barrels OOIP in those reservoirs with 20-50 million barrels OOIP. The existing data base plus the addition of the 80 billion barrels OOIP are to be analyzed using existing predictive, economic, and timing models to define the National EOR potential. Data collected will be analyzed and documented for quality and reservoir relevance.

As abandoned oil fields are also a potential source for EOR, these oil fields should be screened for technical/economic application of EOR. DOE/BETC has recently published reports listing characteristics of abandoned oil fields in many states. These reports should be useful in determining the probability of incorporating the abandoned oil fields into the EOR resource base.

Work Plans

Task 1 - Collect, document quality, and integrate reservoir data from public sources into the data base to complete the statistical base of reservoirs having 20 million barrels OOIP or greater.

Task 2 - Validate, correct inaccuracies, and devise default values for the data base.

Task 3 - Analyze reservoir data base using predictive models to define "baseline" EOR potential in the United States.

Task 4 - Determine whether abandoned oil fields represent a viable EOR resource target, and if so, are they adequately represented in the DOE reservoir data base.

Future Work

To extend statistical base to 10 millions barrels of OOIP or greater and improve accuracy of data during FY85 and FY86.

Manpower Requirements

	Man-years
Research Petroleum Engineer	1.2
Research Chemist	0.2
Program Analyst	0.7
Computer Operator	0.3
Senior Chemist	0.2
Total	2.6

Equipment Requirements

A special requirement of these projects is access to computerized data bases. For this project access to the EIA and DOE/BPO (PE 7/32) computers is essential.

PROJECT SCHEDULE AND MILESTONE

Project: EOR National Potential **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Increase statistical base to >20 mm barrels OOIP				/////	/////	/////	/////	/////	/////	/////	/////	A▽ /////	
2. Validate and correct data base				/////	/////	/////	/////	/////	/////	/////	/////	A▽ /////	
3. Define EOR "baseline" potential for reservoir data base				/////	/////	/////	/////	/////	/////	/////	/////	A▽ /////	
4. EOR from abandoned oil fields				/////	/////	A▽ /////							
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ C'Δ	

Milestone			Description
Task 1	(A)	September 30, 1984	Report on statistical base greater than 20 million barrels OOIP.
Task 2	(A)	September 30, 1984	Report on validation and correction to data base
Task 3	(A)	September 30, 1984	Report on reservoir data base EOR baseline potential
Task 4	(A)	March 31, 1984	Report on EOR potential of abandoned oil fields

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

BE2B. TECHNOLOGY APPRAISAL

Background

This work addresses Items 5.1.3, 6.1.7, and 6.1.8 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

One of the dominant strategies of the EOR R&D program plan (1) is to consolidate and assess the results of research in EOR. To fulfill this strategy, BETC has been building an integrated system of reservoir and EOR project data bases, EOR process screening and performance prediction models, EOR economic models, production timing and logistics models, and system software to link all the components together.

One aspect of this strategy is the building of an EOR project data base. The need for this data base is three-fold:

(1) This data base provides reservoir rock and fluid data, information on EOR fluid injection rates and volumes, and data on fluid production rates and volumes. This type of data is necessary to evaluate the predictive models for accuracy and ensure the predictions are based on state of the art technology as evidenced in existing EOR projects.

(2) Assessment of the state of the art in EOR technology is achieved by correlating the rock and fluid properties and their impact on the efficiency of oil recovery.

(3) Through this data base, assessments of oil industry trends in EOR can be accomplished and will show which processes are being used, the degree of use, the reservoir condition conducive for EOR processes, and, to some extent, the level of confidence the oil industry has in a given EOR process. This information is necessary in focusing and ranking the Federal EOR research program.

Data collected for the EOR project data base have been compiled into a computer data base structure. The data include from reservoir rock and fluid properties determined at reservoir discovery through EOR process data. Unfortunately, some data sources were not comprehensive because of significant missing data. Where possible, these deficiencies should be rectified. Production and injection data for some reservoirs certified in the Tertiary Incentives program are being collected and computerized, and new data generated through the cost-share program are being compiled from program reports. No other data on new or old projects, however, are being collected. To keep the data base and subsequent analyses current, additional data collection and analysis efforts are required.

References

1. BETC Staff, "Enhanced Oil Recovery R&D Program Plan 1983," BETC, Bartlesville, Okla., June 1983.

Objectives

To assess the state of the art in EOR technology annually.

Scope of Work

The data base contains information on more than 640 EOR projects, but analysis of the current literature reveal about 50 EOR projects not represented in the data base. The literature will be examined to gather the basic data necessary for analysis on these projects. Additionally, data on the Tertiary Incentives program are collected on an annual basis. All available data will be evaluated and compiled into the data base for subsequent analysis.

Process predictive models will be applied to the project data base. Production and economic results will be compared with actual field experience from the same projects. Those same results will also be compared with those from reservoir simulators where simulator data are available. Discrepancies between prediction and field experience will be analyzed to determine if the discrepancies are the result of model failures or special field conditions not considered in the analysis. Modifications to model theory will be defined where necessary to reflect the state of the art in process technology more accurately.

By using the updated project data base containing current information on EOR process characteristics, reservoir conditions, and recovery efficiencies, a state of the art (SOA) picture of EOR process technology will be established. From a historical file of these annual SOA's, the trends in EOR process initiation and results will be analyzed.

Work Plans

Task 1 - Collect, evaluate, and compile EOR field data for those reservoirs currently in the EOR project data base.

Task 2 - Improve current scope of data base by comparing publicly available data on EOR pilot and field tests to those already existing in the file and collect, evaluate, and compile data for those reservoirs not included in the current file.

Task 3 - Analyze EOR potential of ongoing projects by using process predictive models to provide an estimate of current EOR production.

Task 4 - Analyze discrepancies between predicted and actual field performance.

Task 5 - Analyze the state of the art for technology trends as exhibited in active EOR projects.

Future Work

EOR field data on current and new EOR projects will be collected and analyzed for current trends for EOR projects.

Manpower Requirements

	Man-years
Research Chemist	0.4
Program Analyst	0.3
Computer Operator	0.2
Senior Chemist	0.1
Total	1.0

Equipment Requirements

A special requirement of these projects is access to computerized data bases. For this project access to the EIA and DOE/BPO (PE 7/32) computers is essential.

PROJECT SCHEDULE AND MILESTONE

Project: Technology Appraisal **Report Date:** ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Collect data to update project data base							A ▽						
	//////	//////	//////	//////	//////	//////	//////						
2. Expand scope of project data base									A ▽				
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	
3. Analyze EOR potential of projects											A ▽		
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	
4. Discrepancy analysis													
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	
5. Analyze current EOR trends											A ▽		
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		**Description**
Task 1	(A) April 30, 1984	Complete addition of annual data
Task 2	(A) June 30, 1984	Complete addition of new project data
Task 3	(A) August 31, 1984	Complete updated determination of EOR potential
Task 4	Continuing	Discrepancy analysis between predicted and actual reservoir performance
Task 4	(A) August 31, 1984	Complete analysis of current EOR trends

Reporting Requirements
(A) 15 th of each month.................. Monthly Progress Report
(B) 30 days after end of each quarter .... Quarterly Technical Progress Report
(C)' 90 days after end of program year .... Annual Technical Progress Report

BE2C. PROCESS PREDICTIVE SCREENING MODELS

Background

This work addresses Items 5.1.3 and 6.1.7 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

To complete the suite of necessary tools to predict accurately the EOR potential resulting from improved technology and types of reservoir properties, BETC has been developing economic and time-rate recovery models. Economic models are used to estimate the amount of economically recoverable oil. Time-rate recovery models are used to convert estimates of technical and economic recovery to feasible production rates given logistical, personnel, environmental, and supply constraints. These are simple models that need to be improved and updated as the state of the art advances.

In the 1970's, several large EOR pilot tests were initiated, most of which were stimulated by the DOE cost-shared program. The objective of these cost-shared projects was to encourage oil companies to apply state of the art oil recovery techniques to the field, to evaluate the potentials and shortcomings of these processes, to explore the effectiveness of the simulation and scaling process, and to determine the effects of the most important reservoir characteristics.

These cost-shared projects have generated a tremendous amount of information, which should be collected, evaluated, and disseminated to the public. A number of these cost-shared projects, which were completed, have been evaluated (1-5). A few alkaline and surfactant polymer projects that are still in progress and have not been evaluated. These are good candidates for a postflood evaluation program.

References

1. Keplinger and Associates, "An Evaluation of the North Burbank Unit Tertiary Recovery Pilot Test," DOE/BC/10033-2, August 1982.

2. Keplinger and Associates, "Evaluation of the Bodcau (Bellevue) *In Situ* Combustion Project," DOE/BC/10033-4, October 1982.

3. Keplinger and Associates, "An Evaluation of the Bell Creek Field Micellar-Polymer Pilot," DOE/BC/10033-5, December 1982.

4. Keplinger and Associates, "Evaluation of the North Stanley Polymer Demonstration Project," DOE/BC/10033-6, February 1983.

5. Keplinger and Associates, "Evaluation of the Coalinga Polymer Demonstration Project," DOE/BC/10033-7, April 1983.

Objectives

To estimate the effects of future technology improvements on the National EOR potential.

Scope of Work

DOE has funded extensive research to define specific aspects of each recovery mechanism employed in EOR. From this research and other research reported in the literature, reasonable estimates of future technology improvements can be made. By extrapolating these data, mid-future to long-term technology improvements can be estimated. Using these various estimates, the effects of technology improvements on EOR potential can be postulated. As many levels of advanced technology can be classified in the long-term, high-risk category, estimates of EOR potential using these technology improvements will benefit EOR program planning.

Two aspects of this program are extremely important: (1) defining current technology, and (2) defining and representing advanced technologies. As advances in technology are encountered, they become "current" technology. As "current" technology is the standard used to compare estimated effects of advancing technology, the estimates of "current" technology must be kept at the state of the art. Therefore, all engineering advances and theoretical improvements must be mathematically represented in the predictive models.

Two cost-shared projects will be studied in detail using sophisticated process models. Laboratory design and reservoir characterization programs will be evaluated, and recommendations for future projects will be made based on the latest understanding of the processes. Simulation of field results based on recommended design will be made for comparison studies.

Work Plans

Task 1 - Evaluate and improve process predictive and screening models by comparing predicted results from screening models with data gathered from the EOR cost-shared program. Data from Incentive Files will be used if cost-shared data are inadequate. Do a sensitivity analysis for all input variables to determine potential problem areas. Improve model algorithm or develop new algorithms to predict field performance more accurately.

Task 2 - Select, with the Bartlesville Project Office, two cost-shared projects for detailed study. Select computer models and collect the data (reservoir, laboratory, and field) required. Evaluate laboratory design and reservoir characterization programs. Recommend improvements and/or further research.

Task 3 - Evaluate each of four predictive algorithms for applicability to steam drive EOR: GOMAA, Intercomp, SUPRI, and Jones. If any algorithms are inaccurate and/or inappropriate remove them from the system. Define limits for reservoir properties and how they affect predictability.

Task 4 - Evaluate and define limits of applicability for the micellar-polymer screening model using available data from cost-shared program. Determine the pattern size, slug size, and buffer size that most accurately predict greatest EOR. Improve algorithm to predict production more accurately, and determine the variables that can be changed to maximize production.

Task 5 - Review recent literature for research and development results on EOR processes. Use this information to improve or develop new algorithms to predict laboratory and field results. Other models that are publicly available will be studied for algorithms or techniques that would improve the screening models. Where applicable, these improvements will be made.

Future Work

Continue to improve EOR predictive and screening models. Continue to improve or develop new algorithms to predict laboratory and field results. Expand work to include promising new EOR processes during FY85 and FY86.

Manpower Requirements

	Man-years
Research Petroleum Engineer	1.3
Research Chemist	0.4
Computer Operator	0.5
Senior Chemist	0.2
Total	2.4

Equipment Requirements

A special requirement of these projects is access to computerized data bases. For this project access to the EIA, DOE/BPO (PE 7/32), and a large (e.g., Tulsa University's) computer is essential.

PROJECT SCHEDULE AND MILESTONE

Project: Process Predictive Screening Models **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Compare predictions to field data & improve algorithms							A▽					B▽	
	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
2. Detailed study of 2 cost-shared projects					A▽				B▽			C▽	
	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
3. Evaluate steam algorithms								A▽					
	/////	/////	/////	/////	/////	/////	/////	/////					
4. Evaluate micellar-polymer algorithms								A▽					
	/////	/////	/////	/////	/////	/////	/////	/////					
5. Improve EOR models												A▽	
	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

	Milestone	**Description**
Task 1	(A) April 30, 1984	Complete comparison of models with cost-shared projects
	(B) September 30, 1984	Report on model improvements
Task 2	(A) February 28, 1934	Select projects and models
	(B) June 30, 1984	Complete evaluation of laboratory design and reservoir characterization work
	(C) September 30, 1984	Report evaluations and make recommendations
Task 3	(A) March 31, 1984	Report on steam model improvements
Task 4	(A) March 31, 1984	Report on micellar-polymer improvements
Task 5	(A) September 30, 1984	Report on EOR model

Reporting Requirements
(A) 15 th of each month..................Monthly Progress Report
(B) 30 days after end of each quarter.........Quarterly Technical Progress Report
(C)' 90 days after end of program year........Annual Technical Progress Report

BE3. EOR ENVIRONMENTAL COMPATIBILITY

Underground injection of microorganisms and chemical compounds to enhance oil recovery could present a problem for future generations. This poses a possibility that environmental advocates could impede the use of EOR technology that involves the subsurface injection of large quantities of microorganisms and chemical compounds (microbial and chemical EOR have the highest priorities in the DOE program). Therefore, it is important that research is needed for a better understanding of the long-term mutations, migration, and chemical transformation of injected compounds. Lack of knowledge in this area could impede enhancement of oil recovery by injection of EOR agents.

At abandonment of an EOR project, significant quantities of chemicals are left in the reservoir in varying amounts, either dispersed throughout the reservoir or in zones containing high saturations of the chemicals. These chemicals are not only the principal EOR recovery reagents such as polymers, alcohols, and surfactants, but also additives and workover fluids such as biocides, chelating agents, oxygen scavengers, and others.

Even the immediate effects of EOR chemicals are not well characterized toxicologically, although some of them are recognized to be carcinogens in laboratory animals. Also, many of the chemicals could cause other health problems. There is little or no information on the long-term effect of these agents to the reservoirs or the oil in contact with them. The question arises, are the hazardous properties enhanced over a period of years? Future production from these reservoirs could consist of fluids with a higher than usual toxicity and require special handling, storage, and refining procedures.

BE3A EFFECT OF MICROBIAL TECHNOLOGY ON EOR

Background

This work addresses Items 5.1.3 and 6.1.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The introduction of microorganisms into a reservoir for the purpose of enhancing oil recovery was first suggested by Beckman in 1926. The pioneering studies by C. E. ZoBell under API Research Project 43A (1943-1953) showed possible mechanisms by which microorganisms could cause oil release. Workers in the USSR were extremely active and completed extensive examinations of the microflora of oil field waters and developed a strong geomicrobiological base. Such work was complemented by studies in Czechoslovakia, Poland, and Hungary that involved various aspects of the laboratory and field tests of the technique. In 1954, Mobil Oil Co. conducted a field test in the United States, while other field tests were made in Czechoslovakia (1954-1958).

Various techniques, cultures, modifications, and studies were made during that period but most results were restricted by proprietary interests and were released only through the patent literature. In the 1960's additional field tests were conducted in Poland, Hungary, and the USSR, but interest in the United States had declined because of low oil prices. These initial studies showed the Microbial Enhanced Oil Recovery (MEOR) process to be a feasible oil production technique, although a significant amount of research is still necessary to advance the process to a state for routine application.

Even though the process is a feasible oil production process, significant potential environmental problems are inherent with this technology. In fact, often the injection materials themselves need environmental consideration for long-term potential health hazards. Cultures employed in field tests vary depending on the investigator and country, but consist of inoculum ranging from specific microorganisms with nutrients to injection of sewage. Tests are generally carried out in stripper wells with little process or reservoir control (1). These activities are not generally long-term tests (relative to chemical EOR) and often have no postmortem analysis. Once abandoned, the bacterial activity through successive mutations could continue with deleterious results (2,3). Long-term tests of microbial action upon crude oil reservoirs have not been adequately addressed in the present research program.

Microbial activity in reservoirs is often dramatic as results from some field tests have shown (1). The effects of fracturing with microorganisms were compared to fracturing in the absence of microorganisms. Fractures could extend into fresh water aquifers especially in shallow, heavy oil reservoirs. That microorganisms could exert such massive changes in oil reservoirs has been demonstrated in the past, much to the concern of the oil industry, by reports of entire oil and gas reservoirs turning sour with hydrogen sulfide because of microbial action. The premise for research is that if such uncontrolled microbial action has occurred, it is possible that similar but controlled microbial processes can be employed that will lead to additional oil recovery. However, it also poses the problem that once a field project is initiated and abandoned, an uncontrolled action could occur with environmental and health hazard consequences.

Completion practices in MEOR field tests also need significant study because of the immense corrosion problems associated with microbial activity. Chemicals produced *in situ*, especially acids and sulfur compounds, corrode and in some cases perforate casing, allowing the possibility of cultures entering other horizons in the geological sequence.

Preliminary information on environmental problems inherent with MEOR is scattered through the literature, often in obscure publications. Information on MEOR studies from several countries, university laboratories, and isolated field tests needs to be assimilated into a logical, coherent data file. A systematic search of the ordered extant data, along with data from current studies should be made to define the state of the art of MEOR and potential long term environmental hazards.

Along with the definition of these potential hazards, laboratory techniques need to be defined for evaluating the postulated hazards under simulated reservoir conditions. Routine core flooding techniques do not have the capability to simulate long-term injected fluid residence in a reservoir. Provisions for simulation of passage of time such as programmed temperature increase or other techniques need to be developed. Concurrently, any changes in process performance resulting from this simulation will need to be evaluated.

Microbial EOR is the largest component of Novel Recovery Process R&D in the Federal program (4). Ultimately, the use of microbes as an effective EOR method requires the development of microbial systems specifically for the recovery process and, only then, their application in the field. The Federal program is determining, in contractor and university laboratories, the effectiveness of several possible approaches to microbial EOR (5). The DOE-supported university program consists of a sampling of research efforts covering broad areas of biodegradation of compounds used in EOR, isolation of bacteria for EOR application, transport of bacteria in petroleum reservoirs, EOR chemical production, and bacterial degradation of crude oils. Industry is heavily involved in this technology supporting similar type research, but targeted toward specific products and their reservoirs (1). Many papers have been published and conferences are being sponsored covering advances in the technology (6).

In support of the Federal program, this research addresses the identification of potential environmental hazards, changes in process performance, and the definition of validation research.

References

1. Bubela, Bohdan, "Microbial Enhanced Oil Recovery--The Problems Underground," J. Crustal. Geol. Geophys., 1980, pp. 423-434.
2. Linville, Bill, editor, "Microbial Enhanced Recovery," Quarterly Progress Review No. 33, Enhanced Oil Recovery and Improved Drilling Technology, DOE/BETC-83/1 April 1983, pp. 89-96.
3. Davis, J. B., Petroleum Microbiology, Elsevier Publishing Co., New York, 1967.
4. BETC, "Enhanced Oil Recovery R&D Program Plan, 1983," Bartlesville, Okla., June 1983.
5. Hitzman, D. O., "Petroleum Microbiology and the History of Its Role in Enhanced Oil Recovery," Proc. International Conference on Microbial Enhancement of Oil Recovery, CONF-8205140, February 1983, pp. 162-218.
6. Moses, V. and D. G. Springham, Bacteria and the Enhancement of Oil Recovery, Applied Science Publishers, London, 1982.

Objectives

To identify potential long-term environmental hazards and process performance of MEOR process.

Scope of Work

A literature survey of published results on the MEOR process as developed in various laboratories and field tests will be conducted. The information will be assimilated into an MEOR process data file.

The information will be studied and organized to develop (1) a set of potential, long-term environmental hazards, (2) long-term changes in process performance, (3) a format for a computerized state of the art data file, and (4) future research recommendations on the MEOR process.

Laboratory techniques will be defined for use in testing MEOR efficiencies and to substantiate long-term environmental hazards. The long-term laboratory tests will be designed to simulate reservoir conditions and can be used to determine microbial generated chemicals; oil production efficiencies; pressure generated; changes in characteristics of the oils, brines, and rocks; and other important data related to oil production and/or environmental impact.

Work Plans

Task 1 - Perform a literature study to evaluate the state of the art of MEOR.

Task 2 - Define a format for development of a computerized MEOR data file.

Task 3 - Evaluate potential long-term environmental and process performance effects of MEOR.

Task 4 - Design a laboratory model to simulate reservoir conditions for effects identified in Task 3.

Task 5 - Present evaluations and conclusions in a report; make recommendations for further research.

Future Work

If the decision in Task 5 is to extend the project, experiments will be performed on the oil recovery efficiency of MEOR process and the environmental effect of this process will be assessed during FY85 and FY86.

Manpower Requirements

	Man-years
Microbiologist	1.0
Senior Chemist	0.5
Associate Chemist	1.0
Total	2.5

Equipment Requirements

	Available	New
Microscope		1
Culture oven and accessories		1
Fluid pumps		1
Core test facility		1

PROJECT SCHEDULE AND MILESTONE

Project: Effect of Microbial Technology on EOR **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Evaluate state-of-the-art of MEOR						A▽				B▽			
				//////	//////	//////	//////	//////	//////	//////			
2. Define format for MEOR data file										A▽			
							//////	//////	//////	//////			
3. Postulate and extrapolate environmental risks										A▽			
								//////	//////	//////			
4. Design laboratory model to simulate MEOR condition										A▽			
							//////	//////	//////	//////			
5. Review project with DOE; to determine feasibility for expansion									A ▽	B▽			
									//////	//////			
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

	Milestone		**Description**
Task 1	(A)	March 31, 1984	Complete evaluation of state-of-the-art of MEOR
	(B)	July 31, 1984	Complete preliminary reservoir screening
Task 2	(A)	July 31, 1984	Complete dictionary for MEOR data file
Task 3	(A)	July 31, 1984	Review with DOE to determine feasibility of continuing
Task 4	(A)	July 31, 1984	Summarize specifications for evaluation and recommendation from NIPER advisory panel
Task 5	(A)	June 30, 1984	Review with DOE to determine feasibility of expansion of scope of work
	(B)	July 31, 1984	Final program scope review with BPO

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report
(B) 30 days after end of each quarter .... Quarterly Technical Progress Report
(C)' 90 days after end of program year .... Annual Technical Progress Report

BE4. BASIC STUDIES OF EOR CHEMICALS

This work is a continuation of a BETC program on long-range research. It seeks a basic understanding of the physical chemistry of chemical EOR systems in terms of colloidal properties of surfactants and crude oils, and their thermodynamic properties. The result will be the ability to formulate systems with greater stability, and to be able to predict and optimize adsorption and phase behavior beyond the range of experimental measurements.

BE4A. BEHAVIOR OF SURFACES WITH ADSORBED MATERIALS

Background

This work addresses Items 5.1.2 and 6.1.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

This project supplements Project BE1B, which deals with more fundamental chemical problems of interaction of polar compounds in crude oil with rocks, and ion exchange reactions of the minerals in contact with the aqueous phase. This work deals with the behavior of surfaces that have adsorbed layers of crude oil components, especially with regard to oil mobilization.

Because adsorption of oil components is partly reversible, the wettability during displacement takes intermediate values and does not stay constant. Also, because of the different reactivities of various minerals, wettability can vary from point to point on the rock surface. The interplay of these factors has been investigated experimentally and theoretically at various laboratories. Nevertheless, there is still divergence of opinion on the effect of intermediate and mixed (spotty) wettability on oil recovery. Most data have been acquired on strongly water- and oil-wet systems, and it has usually been assumed that recovery decreases as oil wettability increases. Conversely, results at this laboratory showed a maximum in oil recovery at neutral wettabilities (1); but the wettability in these experiments was not uniform throughout the sample. Subsequent experiments with uniform wettability were rendered uncertain by changes in wettability during the period of measurement. Moreover, preliminary studies of mixed-wettability systems indicate they do not behave like uniform systems. There is a need for systematic studies using known stable solid surfaces.

Ion exchange and adsorption from aqueous solutions influence the electrical charge of the rock surface (2). Measurement of electrophoretic mobility is a tool for evaluating the interaction of rock surfaces with oil and EOR chemicals.

References

1. Lorenz, P. B., E. C. Donaldson, and R. D. Thomas, "Use of Centrifugal Measurements of Wettability to Predict Oil Recovery," U.S. Bureau of Mines Report of Investigations 7873, 1974.

2. Wasan, D. T., J. J. McNamara, S. M. Shah, K. Sampath, and N. Aderangi, "The Role of Coalescence Phenomena and Interfacial Pheological Properties in Enhanced Oil Recovery," J. Rheology, Vol. 23, No. 2, 1979, pp. 181-207.

Objectives

To correlate the effect of wettability changes on relative permeabilities.

Scope of Work

Electrophoresis and wettability measurements will be made on systems with adsorbed substances on the solid surface, or on artificial materials or surfaces that simulate such systems. Stable, intermediate, and mixed (spotty) wettability cores will be prepared for a study of this effect on capillary pressures, oil displacement, and relative permeabilities. This study will be guided by previous work. Electrophoretic measurements will be made on homoionic clays and other minerals over a range of salt concentration representative of reservoirs, and with pH values representative of alkaline floods. Adsorption and desorption of sulfonates, disulfonates, and polymers will be correlated with the electrophoretic measurements. Recommendations will be made on the design of preflush, surfactant, and polymer slugs for favorable wettability control and reduction of adsorption losses.

Work Plans

Task 1 - Utilizing a procedure determined previously at this laboratory, prepare sand packs and cores with intermediate wettability, measured by capillary pressure, and carry out oil displacement tests.

Task 2 - Develop techniques for preparing mixed wettability systems and perform similar measurements as above.

Task 3 - Assemble and test electrophoresis equipment and make pilot measurements with kaolinite suspensions.

Task 4 - Analyze data and recommend future work.

Future Work

This work is estimated to be a two-year effort. The second year will be needed to complete the wettability work and will include relative permeability measurements. Electrophoresis techniques will be extended to high salinity, high pH, and other minerals. Application to modeling of processes will be considered.

Manpower Requirements

	Man-Years
Petroleum or Chemical Engineer	1.5
Technician	1.0
Total	2.5

Equipment Requirements

	Available	New
Electrophoresis equipment	1	
Centrifuge	1	

PROJECT SCHEDULE AND MILESTONE

Project: Behavior of Surfaces with Adsorbed Materials **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Intermediate wettability						A▽			B▽				
				/////	/////	/////	/////	/////	/////	/////	/////	/////	
2. Mixed wettability												A▽	
										/////	/////	/////	
3. Electrophoresis										A▽			
								/////	/////	/////	/////	/////	
4. Analyze data												A▽	
											/////	/////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Task	**Milestone**		**Description**
Task 1	(A)	March 31, 1984	Complete literature review
	(B)	June 30, 1984	Complete development of the technique for producing intermediate wettability
Task 2	(A)	September 30, 1934	Complete development of the technique for producing mixed wettability
Task 3	(A)	July 31, 1984	Acquire facility in working with the equipment
Task 4	(A)	September 30, 1934	Recommend future work

Reporting Requirements

(A) 15 th of each month.................. Monthly Progress Report

(B) 30 days after end of each quarter......... Quarterly Technical Progress Report

(C)' 90 days after end of program year........ Annual Technical Progress Report

BE4B. ADSORPTION OF SURFACTANT SLUG COMPONENTS ON RESERVOIR MINERALS

Background

This work addresses Item 5.1.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Adsorption losses of injected chemicals are a serious obstacle to successful chemical flooding. The problem is somewhat more serious with nonionic than with anionic surfactants. Empirical explorations of the influence of composition and temperatures have served as a guide to minimizing adsorption, but the evaluation of thermodynamic functions could give a powerful tool for extending conclusions beyond the experimental data (1).

The apparent irreversibility of polymer adsorption may be a kinetic rather than an equilibrium effect. Knowledge of this would aid in designing effective strategies for removing polymer from the rock surface.

References

1. Denoyel, R., F. Rouquerol, and J. Rouquerol, "Interest and Requirements of Liquid Flow Microcalorimetry in the Study of Adsorption from Solution of Tertiary Oil Recovery," Proceedings of Symposium on Adsorption from Solution, Bristol, England, 1982.

Objectives

To develop theory for liquid-phase adsorption on rock surfaces.

Scope of Work

Liquid-phase adsorption on well-characterized sedimentary rocks will be studied. Characterization will be done, when necessary, by SEM/EDS work (BE1A) and in consideration of electrophoretic behavior (BE4A). The adsorption isotherms and enthalpy of adsorption will be measured on the various minerals for surfactant systems, that will include cationics, anionics, nonionics, and alcohols, at compositions that include microemulsions; and also for polymers. A search will be made for ways to develop the theory to tailor the solution and solid surface so that adsorption is minimized, and to find agents for promoting desorption.

Work Plans

Task 1 - Determine the adsorption isotherms and heat of adsorption of alcohols from propyl to dodecyl from toluene, and butanol from water and alkanes onto solids, including alumina, calcite, kaolinite, montmorillonite, and Berea sandstone.

Task 2 - Measure adsorption isotherms and heats of adsorption from water of alkylbenzene sulfonates of various chain length, and selected cationic and nonionic surfactants, onto the same solids.

Task 3 - Conduct an initial study of the adsorption and heat of adsorption of polyacrylamide and partially hydrolyzed acrylamide onto the same solids.

Task 4 - Prepare status report with recommendations for further study.

Future Work

Present plans extend through FY84. Recommendations on continuation will be presented in the FY85 Annual Research Plan.

Manpower Requirements

	Man-years
Research Chemist	1.0

Equipment Requirements

	Available	New
Adsorption microcalorimeter	1	1

PROJECT SCHEDULE AND MILESTONE

Project: Adsorption of Surfactant Slug Components on Reservoir Minerals

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Determine adsorption of alcohols									A∇				
		/////	/////	/////	/////	/////	/////	/////	/////				
2. Determine adsorption of surfactants												A∇	
		/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
3. Determine adsorption of polymers												A∇	
		/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
4. Prepare report												A∇	
											/////	/////	
Progress Reporting Requirements		A∆	A∆	A∆ B∆	A∆	A∆	A∆ B∆	A∆	A∆	A∆ B∆	A∆	A∆ C∆'	

Milestone		Description
Task 1	(A) September 30, 1984	Complete measurements on alcohols
Task 2	(A) September 30, 1984	Complete measurements on surfactants
Task 3	(A) September 30, 1984	Complete measurements on polymers
Task 4	(A) September 30, 1984	Complete report and recommend test systems

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

BE4C. APPLICATION OF THERMODYNAMIC MEASUREMENTS TO MICELLIZATION AND SOLUBILIZATION

Background

This work addresses Item 5.1.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The system pentanol/dodecane/sodium octylbenzene sulfonate (in water) forms microemulsions whose phase behavior has been well documented (1). The system is a good candidate to be used as a test of the value of fundamental thermodynamic information in improving our understanding of microemulsions (2,3). Success with this simple system would offer encouragement for applying thermodynamic techniques to predict the behavior of more complex surfactant systems, as used in oil recovery.

References

1. Bellocqe, A. M., D. Bourbon, and B. Lemanceau, "Three-Dimensional Phase Diagrams and Interfacial Tensions of the Water-Dodecane-Pentanol-Sodium Octylbenzene Sulfonate System," J. Colloid Interface Sci., Vol. 79, 1981, pp. 419-431.
2. Roux, A. H., G. Roux-Desgranges, "Thermodynamic Investigation of Microemulsions Used in Oil Recovery," in Chemical Engineering Thermodynamics, S. A. Newman, editor, Ann Arbor Science, 1983, pp. 461-468.
3. Desnoyers, J.E., R. Beaudoin, G. Penon, and G. Roux, "Microemulsions as a Possible Tool for Teritary Oil Recovery," in Chemistry for Energy, M. Tomlinson, editor, ACS Symposium Series No. 90, 1979, pp. 33-44.

Objectives

To investigate the potential for using thermodynamic data for predicting the behavior of EOR surfactant systems.

Scope of Work

Trends in thermodynamic properties of the simple surfactant, sodium octylbenzene sulfonate, will be studied. The heat capacity and density of solutions in water at various temperatures will be measured, on the surfactant alone, on the surfactant with an alcohol, and on a microemulsion with surfactant, alcohol, and oil. The results will be analyzed and compared with phase diagrams from the literature.

The data will be examined to understand the trends in thermodynamic properties of this surfactant and to explore the utility of using those trends to predict optimal surfactant formulations for oil displacement.

Work Plan

Task 1 - Measure heat capacities and densities of sodium octylbenzene sulfonate (SOBS) in water.

Task 2 - Measure heat capacities and densities of pentanol in aqueous solutions of SOBS.

Task 3 - Measure heat capacities and densities of dodecane in aqueous solutions containing pentanol and SOBS.

Task 4 - Analyze and correlate data.

Future Work

Continuation beyond one year will be considered at the end of FY84.

Manpower Requirements

	Man-years
Research Chemist	1.0

Equipment Requirements

	Available	New
Microcalorimeter	1	

PROJECT SCHEDULE AND MILESTONE

Project: Application of Thermodynamic Measurements to Micellization and Solubilization

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. SOBS alone						A▽							
		//////	//////	//////	//////	///							
2. SOBS + pentanol									A▽				
						//////	//////	//////	////				
3. SOBS + pentanol + dodecane												A▽	
									//////	//////	//////	////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone			**Description**
Task 1	(A)	March 31, 1984	Complete measurements
Task 2	(A)	June 30, 1984	Complete measurements
Task 3	(A)	September 30, 1984	Complete measurements and make comparisons

Reporting Requirements
(A) 15 th of each month .... Monthly Progress Report
(B) 30 days after end of each quarter .... Quarterly Technical Progress Report
(C)' 90 days after end of program year .... Annual Technical Progress Report

BE4D. EFFECTS OF SURFACTANT STRUCTURE AND ADDITIVES ON MICELLE FORMATION AND SOLUBILIZATION

Background

This work addresses Item 5.1.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Micelle formation of a surfactant and solubilization of oil are intimately related to low interfacial tension and the ability to recover oil (1). The colloidal nature of a crude oil also plays an essential role.

There is extensive literature on phase behavior of surfactants. Greater predictability of EOR could be achieved with a more profound understanding of the effect of the chemical environment on micelles, colloidal suspensions, and liquid crystallite phases. Such an understanding can be promoted by employing a battery of relatively sophisticated measuring techniques. Painstaking refinements of these techniques are necessary to get valid results. Thus, light scattering and ultracentrifugal analysis are capable of measuring particle size, but require correction of electrolyte effects (preferential interaction parameters). These can be obtained from separate measurements of thermodynamic activity, e.g., by getting osmotic coefficients from isopiestic distillation data.

Small-angle x-ray scattering has been used in this laboratory to give information on the size and shape of wax crystallites and asphaltene particles in oil (as influenced by solvent addition and temperature), oil-in-water emulsions formed with polymer solutions, and aggregates of clay particles in suspensions. Reliable results require a careful mathematical analysis of secondary scattering effects and the influence of partial polarization introduced by the many reflections in the equipment and at the sample.

It is well known that thermodynamics can be used to correlate data and predict chemical and physical behavior. Thermodynamic models have been developed that have reproduced behavior of selected surfactant systems satisfactorily. On the other hand, preliminary results have indicated that at temperatures of engineering interest, surfactant behavior shows trends quite different from those at ambient temperature. An understanding of the behavior of surfactant systems over a broader range of conditions can be reinforced by systematic acquisition of further data.

References

1. Heely, R. N., "Physical Chemical Aspects of Microemulsion Flooding," SPE Paper 4583, presented at 48th Annual Fall Meeting, Las Vegas, Nev., Sept. 30-Oct. 1973.

Objectives

To determine conditions for micelle formation and their influence on the oil solubilization capacity of surfactants.

Scope of Work

The small-angle x-ray (SAX) scattering measurements will amplify and improve the results already obtained on surfactants in water and the colloidal nature of oil. Work will continue on the necessary theoretical refinements whose importance escalates as the scattering angle is reduced for investigation of smaller particles. The experimental program will be designed to make use of advances in the theoretical analysis, e.g., a more exact study of micelles in aqueous surfactants, and the formation of colloids in oil on contact with EOR chemicals and solvents.

Light scattering, ultracentrifugal, and isopiestic distillation data will be tied together to get information on micelle aggregation number in surfactant systems for which work has been initiated. The methods developed will be applied to studying the effect of salt, alcohol, and changes in surfactant structure.

Enthalpies of dilution, heat capacities, and specific volume measurements will be made on surfactant solutions to get thermodynamic properties as a function of concentration, salinity, alcohol content, and temperature. In particular, techniques will be developed for measuring these properties at the high temperatures representative of petroleum reservoirs. The effect of surfactant structure will be examined, especially that of chain branching.

All of these data will be developed into models that can predict the behavior and oil solubilization capability of surfactants on the basis of relatively few measurements.

Work Plans

Task 1 - Study the effect of co-ion on the preferential interaction parameter for sodium dodecyl sulfate, for application to light scattering data from the literature.

Task 2 - Obtain light scattering data and preferential interaction parameters on octyl benzene sulfonate to test the co-ion effect found under Task 1.

Task 3 - Develop a general technique for the polarization factor for multiple coherent scattering of unpolarized and plane-polarized x-rays.

Task 4 - Make preliminary SAX measurements of particle development in nonionic surfactants near the cloud point.

Task 5 - Initiate development of a theory of secondary scattering in SAX for very small angles.

Task 6 - Measure enthalpies of dilution, heat capacities, and specific volumes of mixtures of various components of microemulsions from alkylbenzene sulfonates as a function of salinity, alcohol type and content, surfactant structure, and temperature.

Task 7 - Correlate data to elucidate the effect of these parameters on microemulsion stability.

Future Work

Present plans extend through FY84. Recommendation on continuing will be presented in the FY85 Annual Research Plan.

Manpower Requirements

	Man-years
Research Chemist	2.0

Equipment Requirements

	Available	New
X-ray scattering equipment	1	
Light scattering equipment	1	
Ultracentrifuge	1	
Isopiestic distillation apparatus	1	
High temperature microcalorimeter		1

PROJECT SCHEDULE AND MILESTONE

Project: Effect of Surfactant Structure and Additives on Micelle Formation and Solubilization

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Co-ion effects, SDDS		A▽ //////											
2. Co-ion effect, SOBS		 //////	A ▽ ////										
3. X-ray polarization	A ▽ //////												
4. Nonionic cloudpoints		A▽ //////											
5. Secondary scattering		A▽	 //////	 //////	 //////	B▽ //////							
6. ABS microemulsions		 //////	A ▽ //////	 //////	 //////	 //////	 //////	 //////	B▽ //////	 //////	 //////	 //////	
Progress Reporting Requirements		**AΔ**	**AΔ**	**AΔ BΔ**	**AΔ**	**AΔ**	**AΔ BΔ**	**AΔ**	**AΔ**	**AΔ BΔ**	**AΔ**	**AΔ CΔ'**	

Milestone		Description
Task 1	(A) November 30, 1983	Complete study on co-ion effect
Task 2	(A) December 31, 1983	Complete measurements and prepare manuscript
Task 3	(A) October 31, 1983	Technique development for the polarization factor complete
Task 4	(A) November 30, 1983	Complete preliminary measurements and make recommendations on continuance
Task 5	(A) December 1, 1983	Initiate development of theory
	(B) March 31, 1984	Complete theory development and manuscript
Task 6	(A) December 31, 1983	Complete measurements on 6-phenyl C12 ABS in water, and prepare manuscript
	(B) July 1, 1984	Initiate measurements on alcohols in ABS solutions

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

BE4E. ORDER OF MIXING EFFECTS FOR AQUEOUS SURFACTANT

Background

This work addresses Item 5.1.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Studies at this and other laboratories (1,2) have demonstrated that the order-of-mixing-surfactant formulation affects the interfacial and other physical chemical properties that are of importance in enhanced oil recovery. The method of preparation was found to affect the aging and stability of the surfactant solution. Even though liquid crystal formation was identified as the cause of this order-of-mixing effect, the structure of these aggregates and the mechanism of their transformation are still not clear. Stability is imparted to lyophobic colloids by electrical charges on the particles. This may be a determining factor in surfactant dispersions, which are partly lyophobic.

References

1. Lorenz, P. B., M. B. Kayser, M. A. Hsieh, and M.K. Tham, "Order-of-Mixing Effects in Sulfonate Surfactant Solutions," in Solution Chemistry of Surfactant, K. L. Mittal, editor, 1979, Plenum, pp. 903-918.

2. Puig, J. E., E. I. Franses, H.T. Davis, W. G. Miller, and L. Z. Scriven, "On Interfacial Tensions of Sulfonate Surfactants," SPE Paper 7055, SPE Improved Oil Recovery Symposium, Tulsa, Okla., April 16-19, 1978.

Objectives

To determine order-of-mixing effects on the stability of surfactant solutions.

Scope of Work

Several techniques (viscosity and conductivity measurement, visual observations, and microscopy) will be used to study the effect of order-of-mixing on the colloidal character of surfactant dispersions and their storage stability. Charge on the particles will be determined directly from electrophoretic mobility, if the problem of optical contrast can be overcome. Dielectric absorption, i.e., electrical impedance peaks in the radio frequency spectrum, are capable of giving indirect information and will be measured. Size distributions and morphology will be examined by ultrafiltration and optical microscopic techniques. The analysis of the results will focus on identifying the factors that produce stable and effective surfactant dispersions.

Work Plans

Task 1 - Specify colloidal systems for study: a commercial surfactant mixture known to exhibit order-of-mixing effects and, if possible, a model compound.

Task 2 - Explore the feasibility of using electrophoresis, and if successful, apply it to systems of different degrees of stability, getting zeta potentials at various times after preparation of the samples.

Task 3 - Undertake a similar program of measuring radio frequency impedances.

Task 4 - Develop a quantitative description of experimental data.

Future Work

The second year will be devoted to using techniques developed during the first year to study several systems and to apply optical microscopy and ultra-filtration for obtaining additional information.

Manpower Requirements

	Man-years
Senior Chemist	0.5
Chemical Engineer	1.0
Technician	0.5
Electrical Engineer	0.5
Total	2.5

Equipment Requirements

	Available	New
Electrophoresis equipment	1	
Dielectric absorption equipment	1	
LS 30 viscometer	1	

PROJECT SCHEDULE AND MILESTONE

Project: Order of Mixing Effects for Aqueous Surfactant

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Specify systems			A▽										
	/////	/////	/////										
2. Electrophoresis							A▽						
				/////	/////	/////	/////						
3. RF Impedance												A▽	
			/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
4. Quant. descript.										A▽			
								/////	/////	/////	/////	/////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ	

	Milestone		**Description**
Task 1	(A)	December 31, 1983	Systems selected
Task 2	(A)	April 30, 1984	Complete feasibility study on electrophoresis
Task 3	(A)	September 30, 1984	Complete feasibility study on impedance
Task 4	(A)	July 30, 1984	Select methodology for theoretical analysis

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C) 90 days after end of program year .... Annual Technical Progress Report

BE5. GAS DISPLACEMENT METHODS

This research program addresses both miscible and immiscible flooding by gas injection. The modification of heavy oil properties by CO_2 dissolution, and the miscibility of light crude oil with nitrogen are the research topics in this program.

Background

This work addresses Item 5.1.1 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The gas miscible displacement method of enhanced oil recovery encompasses hydrocarbon, inert gas, and CO_2 injection. The local-displacement efficiencies in this type of recovery method are usually very high. As the price of gaseous hydrocarbons increases, the use of inert gas and CO_2 becomes more attractive. Current interest in miscible flooding is concentrated in the latter methods.

The CO_2 miscible technology is in a more advanced stage than the inert gas (N_2) injection. Many CO_2 field projects have achieved technical success, and several large-scale field projects are in progress or in the planning stage. Research in this area is extensive. DOE has supported many university projects to study CO_2-miscible flooding recovery mechanisms (1-2) phase behavior (2-4), and mobility control (5-8). A large amount of information is being generated from these and other research projects. This is very valuable information for understanding and designing CO_2-miscible flooding.

In contrast, CO_2 displacement of heavy oil, mostly an immiscible process, has not been studied as extensively (9). The two most important mechanisms for recovery are thought to be viscosity reduction and swelling of oil volume (10). However, no systematic study on the recovery mechanisms and the factors affecting recovery efficiency has been published. Previous research at BETC has accumulated considerable data on the solubility of CO_2 and the reduction in viscosity and density due to CO_2 dissolution. In this study, it was found that there is a relationship between viscosity reduction and asphaltene content of the oil. Quantitative correlation was difficult because, besides asphaltene content, the API gravity of these oils were also different. To quantify the chemical composition effects properly, it is necessary to vary one property systematically while keeping the other constant. This will isolate the changes in properties due to CO_2 dissolution.

Nitrogen is becoming an increasingly attractive method for enhanced oil recovery because of its low cost and availability at the well site. Published reports on N_2-miscible flooding are considerably fewer than those for the CO_2 method. A survey of the literature reveals that beside the works of Rushing et al. (11-12), few studies are being made on the miscibility mechanisms and phase behavior of nitrogen-crude oil systems.

Recently, Ahmed, et al. (13) have undertaken a study of the miscibility pressure and changes in crude oil properties during nitrogen injection. No information on phase behavior was reported in this study. Additional information on miscibility mechanisms and phase behavior are required for designing nitrogen-miscible flooding processes.

References

1. Louisiana State University, "Investigation of Enhanced Oil Recovery Through the Use of Carbon Dioxide," Contract DE-AS19-80BC10344.
2. University of Kansas Center for Research, Inc., "Carbon Dioxide Miscible Flooding Prospects," Contract DE-AC19-79BC10122.
3. University of Alabama, "Determination of Miscibility Pressures by Direct Observation Methods," Contract DE-AC21-81MC16140.
4. New Mexico Institute of Mining and Technology, "Displacement of Oil by Carbon Dioxide," Contract DE-AC21-81MC16426.
5. New Mexico Institute of Mining and Technology, "Mobility Control for CO_2 Injection," Contract DE-AC21-81MC16426.
6. New Mexico Institute of Mining and Technology, "Methods for Mobility Control in CO_2 EOR Processes," Contract DE-AC21-79MC10629.
7. New Mexico State University, "Enhanced Oil Recovery by CO_2 Foam Flooding," Contract DE-AC21-78ET-12083.
8. Texas A&M Research Foundation, "Enhanced Recovery of Oil from Subsurface Reservoirs with Carbon Dioxide," Contract DE-AC21-79MC10509.
9. Colorado State University, "Computer Simulation of Recovery of Heavy Crude Oil Using Carbon Dioxide Drive or Huff-n-Puff," Contract DE-AC19-81BC10640.
10. Saner, W. B., and J. T. Patton, "CO_2 Recovery of Heavy Oil: The Wilmington Field Test," SPE Paper 12082, presented at the 58th Annual SPE Conference, San Francisco, Calif., Oct. 5-8, 1983.
11. Rushing, M. D., B. C. Thomasion, B. Reynolds, and P. B. Crawford, "Miscible Displacement with Nitrogen," Pet. Eng., Nov. 1977, pp. 26-30.
12. Rushing, M. D., B. C. Thomasion, B. Reynolds, and P. B. Crawford, "Nitrogen May Be Used for Miscible Displacement in Oil Reservoirs," J. Pet. Tech., Dec. 1978, pp. 1715-1716.
13. Ahmed, T., D. Mengie, and H. Crichlow, "Preliminary Experimental Results of High-Pressure Nitrogen Injection for EOR Systems," Soc. Pet. Eng. J., April 1983, pp. 339-347.
14. Stalkup, F. I., "Miscible Displacement," SPE Monograph, vol. 8.
15. Orr, F. M., and J. J. Taber, "Displacement of Oil by Carbon Dioxide," DOE/ET/1208-9, May 1981.

Objectives

To develop screening criteria for carbon dioxide flooding in heavy oil reservoirs and nitrogen flooding in light oil reservoirs.

Scope of Work

Changes in viscosity and density of heavy oil due to CO_2 dissolution will be measured. The effect of variation in chemical composition of crude oils on these changes will be determined, with the purpose of obtaining a correlation between viscosity and density changes with crude oil chemical composition. This correlation will serve as a screening criterion for heavy oil recovery by CO_2 injection.

A crude oil with API gravity greater than 40 and from reservoirs deeper than 5000 ft, and therefore thought to be amenable to N_2-miscible flooding (14), will be chosen for a nitrogen miscibility study. The conditions required for miscibility and the resulting phase behavior will be measured for this crude oil and nitrogen system. An equation of state will be developed.

Work Plans

Task 1 - Based on experience at BETC, in industry, and during DOE sponsored contracts, slim tube and phase behavior equipment will be designed and fabricated. This apparatus will be designed to withstand 8000 psia and housed in a furnace capable of maintaining a constant temperature of up to 200°F.

Task 2 - Calibrate and test the apparatus with a system that has been reported in the literature (15) to evaluate the instruments and the operation procedure. The system chosen to be studied is a hydrocarbon mixture of 14 mol percent C_5, 53.7 percent C_{10}, 19 percent C_{16}, and 13.3 percent C_{30} and CO_2 at 37.8°C.

Task 3 - Measure CO_2-crude oil solubility, density, and viscosity at three temperatures and 11 pressure levels. Three crude oils having approximately the same API gravity and a varying quantity of asphaltenes will be used. (The DOE Crude Oil Analysis Data Base will be scanned to identify crude oils that fit these criteria.) The weight of asphaltene precipitated will also be measured.

Task 4 - Review literature on nitrogen-crude oil phase behavior.

Task 5 - Prepare report on results of CO_2 solubility studies.

Future Work

It is anticipated that the nitrogen work will be expanded to include measuring the phase behavior of different crude oils and nitrogen-carbon dioxide ratios. The CO_2-heavy oil experimentation is anticipated to continue two years, when other important chemical constituents such as aromaticity, paraffinic contents, and polar compound contents will be included as parameters.

Manpower Requirements

	Man-years
Senior Chemist/Chemical Engineer	1.0
Petroleum Engineers	0.5
Senior Experimentalist	1.0
Technician	1.0
Total	3.5

Equipment Requirements

	Available	New
Gas chromatograph	1	
Ruska pump	1	
CO_2 solubility apparatus	1	
Wet test meter	1	
Constant temperature oven		1
Circulating pump		1
Mixing chamber		1
Mettler-Paar density meter		1
Back pressure regulator		1

PROJECT SCHEDULE AND MILESTONE

Project: Gas Displacement Methods **Report Date:** ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Design & fabricate slim tube & phase behavior apparatus				A ▽				B ▽					
		//////	//////	//////	//////	//////	//////	///					
2. Calibrate and test apparatus with ref. system												A▽	
							//////	//////	//////	//////	//////	//////	
3. Measure changes in physical properties for 3 crude oils				A▽				B▽				C▽	
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	
4. Review N2 literature												A▽	
											//////	//////	
5. Prepare report												A▽	
												//////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone			**Description**
Task 1	(A)	January 31, 1984	Slim tube and behavior apparatus design completed
	(B)	May 31, 1984	Fabrication of slim tube and phase behavior apparatus completed
Task 2	(A)	September 30, 1984	Calibration and testing of slim tube and phase behavior apparatus completed
Task 3	(A)	January 15, 1984	Three heavy crude oils to be studied chosen
	(B)	May 15, 1984	Viscosity, density, swelling and solubility of CO_2 in first heavy crude completed
	(C)	September 15, 1984	Viscosity, density, swelling and solubility of CO_2 in second heavy crude completed
Task 4	(A)	September 30, 1984	Recommend further work
Task 5	(A)	September 30, 1984	Complete report

Reporting Requirements
(A) 15 th of each month.................. Monthly Progress Report
(B) 30 days after end of each quarter......... Quarterly Technical Progress Report
(C)' 90 days after end of program year........ Annual Technical Progress Report

BPT1. THERMODYNAMIC PROPERTIES OF ORGANIC COMPOUNDS

The experimental determination of highly precise, internally consistent thermodynamic data has been the purpose of the thermodynamics laboratories at NIPER (formerly BETC) for more than 35 years. Recognized internationally for their contributions to the instrumentation of thermodynamic measurements and the development and correlation of data on hydrocarbons and related substances, this research group is well equipped to contribute extensively to the data requirements for developing alternative fuel technology. As new technology is developed for extensive use of heavy ends of light petroleum, heavy oil, tar sand liquids, shale oil, and coal liquids, the need for additional and more precise thermodynamic property data will intensify. It will be a necessary requirement in order to predict reaction paths, to optimize process conditions, and to size and specify reaction equipment.

Because the building of a body of thermodynamic data requires time, careful attention must be paid to priorities to enable use of the data at the earliest possible time. For heavy oil and shale oil, the nitrogen compounds have a high priority. For coal liquids, the polycyclic compounds that may contain heteroatoms such as oxygen, sulfur, and nitrogen are of importance. Consequently, the work is divided into two subprojects, but the project plans are very similar. The two subprojects are BPT1A, Thermodynamic Properties of Organic Nitrogen Compounds That Occur in Shale Oil and Heavy Petroleum, and BPT1B, Thermochemical and Thermophysical Properties of Organic Compounds Derived from Fossil Substances.

These subprojects share some of the same equipment and personnel for the study of two different classes of substances. Aside from differences in particular problems that each of the two classes of materials present, the uses of thermodynamic data are similar. Thus, scopes of work for the two different studies have many similarities in employing combustion calorimetry, condensed-state heat-capacity calorimetry, vapor-pressure measurements, and spectroscopy with statistical mechanics; however, the second of the two projects, BPT1B, also employs vapor-flow calorimetry and PVT measurements to derive more extensive thermophysical property information.

Background (BPT1A and BPT1B)

This work addresses Item 5.2.1 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Work on the Thermodynamic Properties of Organic Nitrogen Compounds That Occur in Oil Shale and Heavy Petroleum (BPT1A) falls within the Fundamental Petroleum Chemistry part of the Advanced Exploratory Research program of DOE/Fossil Energy. This work is currently directed to the study of the alkylpyridines and alkylpyrroles, compounds already identified as being present in heavy oil and oil shale in significant quantities, and on their hydrogenation products, namely the piperidines and pyrrolidines.

The deleterious effects of nitrogen compounds upon crude oil and fuel stability and upon catalytic processing systems make their removal imperative before heavy oil and synthetic crudes from oil shale, coal, and tar sands can be used effectively. Nitrogen-containing compounds occur in relatively large quantities in these alternate fossil liquids. In the processing of these fluids, nitrogen compounds reduce the activity of cracking catalysts and catalysts used in reforming. Polymerization and isomerization catalysts are also highly susceptible to poisoning by nitrogen compounds.

Work on the Thermochemical and Thermophysical Properties of Organic Compounds Derived from Fossil Substances (BPT1B) is within the purview of the Advanced Research and Technology Development program of DOE/Fossil Energy. This work is currently directed toward thermochemical studies of polycyclic heteroatom containing compounds of sulfur, nitrogen, and oxygen that occur in significant quantities in heavy petroleum, heavy ends of light petroleum, shale oil, and fluids derived from coal liquefaction. The substances under study are deleterious to both the processing and end use applications of these materials. The high molecular weights of these substances must be reduced to meet acceptable end use requirements. The heterocyclic compounds produce species that reduce catalytic activity and some are known to be carcinogenic and mutagenic in derived materials.

A second part of this effort is directed toward obtaining thermophysical properties of fluids to complement the thermochemical studies and to provide state property information on key substances used in conversion processes. Such information is needed as reference fluid data for the prediction of thermophysical properties of real fluids.

The new data to be obtained can be used to predict chemical equilibria, or the lack thereof, and to determine if conceptual processing methods are feasible and whether improvements in existing processes can be obtained from the development of new catalysts. In addition, the data contain essential physical property information that is used in data correlations for the design of all processing units downstream from the reactor stages. The data from these efforts will be integrated into a variety of data bases found in individual companies and standard compilations such as the American Petroleum Institute's Project 44 data tables. This makes the data readily available to engineers involved in activities related to equipment design and process development. Correlations allow use of model compound work for simulations such as ASPEN. This is a model developed under DOE sponsorship at Massachusetts Institute of Technology which incorporates much thermodynamic data into process design.

The compounds to be studied will be provided by Oklahoma State University through a contract with the DOE/Bartlesville Project Office. The complex pure organic chemicals that are required for thermodynamic studies are increasingly difficult to synthesize and purify; hence they are expensive. While compound type can be specified, it is impossible to predict successful synthesis of specific compounds since for most compounds, synthesis mechanisms and stability of 99.9+ percent purity materials is unknown. Thus, the compound type or family is chosen and specific compounds are agreed upon as methods of synthesis are developed.

Because of the great number of individual compounds in the fossil energy materials, it is impractical to determine the thermodynamic properties of every compound. The key compound concept has been developed to make the task more manageable. Correlations of properties make it possible to calculate (either by interpolation or extrapolation) the properties of compounds having structures similar to compounds on which there are experimental data. Using these structural family relationships, compounds can be selected where experimental data on one compound enable calculation of properties of several. Key compounds thus selected enable faster proliferation of data and form an important concept of the thermodynamics research.

Over the last 40 years, the thermodynamics laboratory has developed the required specialized equipment needed to perform such research. However, many new and difficult problems have been encountered in working with the compounds under study. Manpower restrictions over the past few years have limited our ability to develop the new, miniaturized equipment that is both chemically compatible with these materials and applicable over the temperature and pressure ranges of interest. Miniaturization of combustion calorimetry and low-temperature adiabatic calorimetry is needed to decrease the amount of material required, taking much of the pressure off the synthesis project. Automation and improvement of other equipment will increase the number of samples studied and decrease the man-hours required for making the necessary measurements.

New, more sensitive vapor-pressure apparatus is required for measurements in the very low pressure range encountered in the study of these organic compounds of ever-increasing molecular weight and complexity. It should be noted that this equipment is needed for and will be cost-shared by two subprojects. We believe that the new equipment developed will help resolve this research problem.

Objectives (BPT1A and BPT1B)

To provide, interpret, and correlate with molecular structure and polarity of molecules, precise and accurate values for the thermochemical and thermophysical properties of organic compounds of sulfur, oxygen, and nitrogen that occur in heavy petroleum, heavy ends of light petroleum, shale oil, and fluids derived from coal liquefaction.

To develop and validate new equipment that permits smaller sample sizes while giving the required precision and accuracy.

Scope of Work (BPT1A and BPT1B)

The actual compounds to be studied are selected to fill needs in the prediction of the properties in the selected compound families. Some compromises in this selection process may be required because viable methods of synthesis and purification may not exist and must be developed in a separate compound synthesis project supported by the DOE/Bartlesville Project Office. Through an interactive process with the Bartlesville Project Office staff and the workers on the synthesis project, compounds can be selected that satisfy key thermodynamic information needs and that can also be provided in the high purity (99.9+ percent) required. Properties to be measured will be heat of combustion, heat capacities, vapor pressure, and PVT properties. Spectroscopic studies will also be made to help calculate thermodynamic properties at temperatures above the experimental range. Tables of thermodynamic functions for both the condensed and vapor states will be derived. Correlations and interpretation will be supplied for simulation design programs, such as ASPEN. These programs have been built largely from a hydrocarbon data base and their limited success with the lower quality feedstocks results from the lack of data on polar species such as the nitrogen compounds.

Existing equipment is viable and will be operated to provide needed data on many substances for this work; however, an ongoing and parallel effort will continue in (1) increasing the throughput by automation and improvement of equipment, (2) increasing the temperature range of the equipment to accommodate studies on high molecular weight materials which cannot be studied presently, (3) developing equipment which maintains needed precision and accuracy but requires smaller samples, thereby reducing the cost and increasing the probability of success in synthesis and purification of the materials required, and (4) developing more effective methods to handle air sensitive and hazardous materials which should be included in this work. The calibration, validation, and reports of design of the improvement of the equipment will be phased into studies being made on compounds at the time the equipment becomes available.

The calorimeters must be chemically compatible with the type of compounds being studied and to the temperature ranges desired to prevent unwanted chemical reactions or thermal degradation of the vessel. Cryostats and thermometry must be obtained and/or constructed and calibrated with specific calorimeters. The cryostats and thermometry may be used on a variety of compounds. Therefore, parts of the equipment development work are specific to a project while general equipment will be used on all of the projects. These equipment development efforts are shared with other projects which employ the same equipment for compound families not considered in this project.

BPT1A. THERMODYNAMIC PROPERTIES OF ORGANIC NITROGEN COMPOUNDS THAT OCCUR IN SHALE OIL AND HEAVY PETROLEUM

Work Plans

Task 1 - Continue studies on the alkylpyridines and pyrroles with their hydrogenation products, which will include completion of experiments on 3,4-dimethylpyridine and 2,4-dimethylpyridine already in progress. Other pure compounds are available for study.

(a) In cooperation with the Bartlesville Project Office and the Oklahoma State University synthesis project, identify three organic nitrogen compounds and develop plans for research.

(b) Combustion Calorimetric Studies. Measure enthalpies of combustion of selected key organic nitrogen compounds as these materials become available from the synthesis project and from queued experiments. Owing to limitations in available material, experiments cannot run simultaneously.

(c) Low-Temperature and Condensed-State Calorimetry (Third-Law Determinations). Measure heat capacities and enthalpies of phase transitions on selected key organic nitrogen compounds as these materials become available from synthesis projects and as equipment becomes available from queued experiments on these substances.

(d) Vapor-Pressure Measurements. Measure vapor pressures of selected key organic nitrogen compounds as these materials become available from the synthesis project and as equipment becomes available from queued experiments on these substances.

(e) Spectroscopy and Molecular Statistical Mechanics
   (1) Measure spectra of selected key organic nitrogen compounds.
   (2) Use computer programs and thermodynamic laws to derive statistical thermodynamic properties for the substances from the spectra and other measured properties.

Task 2 - Develop, Construct, and Test Prototype Equipment (also in BPT1B)

(a) Develop small-sample combustion calorimeter.

(b) Build two new cryostats for operation from 4 to 573 K. This will help facilitate timely data generation.

(c) Build new calorimeter for operation to 573 K and for use with reactive nitrogen and sulfur compounds. Only one calorimeter presently is constructed of materials that will allow use of these compounds without deleterious reactions.

(d) Develop computer control of calorimetric measurements. Lengthy experiments presently require large amounts of researchers' time. Much of the routine control and data gathering is amenable to computer control, allowing greater throughput of materials and, at the same time, requiring less manpower.

(e) Develop automatic control system for inclined-piston-pressure gage. Lengthy experiments presently require large amounts of researchers' time. Much of the routine control, and data gathering are amenable to computer control allowing greater throughput of materials and, at the same time, requiring less manpower.

(f) Develop a torsion-effusion apparatus for the measurement of the vapor pressure of very high molecular weight substances. Present equipment is not sensitive enough for these measurements.

(g) Develop small-sample ebulliometric vapor-pressure apparatus. Synthesizing larger volumes of samples is very expensive. This will be cost-effective for future synthesis requirements furnished by the Bartlesville Project Office.

(h) Develop computer interfacing for laser-Raman spectrometer. Voluminous amounts of data are gathered that could be better interpreted with the aid of computers.

(i) Develop techniques and equipment for measurements of spectra of vapors at high temperatures. Higher temperatures are needed for the heavy organic compounds to be studied.

Task 3 - Interpret data on a continuing basis; after completion of approximately 18 compounds, correlate data with molecular structure and polarity, suggest model compounds, and provide data for simulations such as ASPEN.

Task 4 - Compilation of data and correlations on individual compounds and preparation of reports.

Future Work

The project will continue into future years as process equipment and operation design needs determine areas of study, and the synthesis project makes new compounds available in the selected categories. It is expected that sufficient information will be developed in three years to begin to develop meaningful correlations; however, many gaps will remain in the data, and essential data will need to be determined in the ensuing years.

Manpower Requirements

	Man-years
Senior Chemist	0.6
Research Chemist	1.0
Research Physicist	0.4
Senior Experimentalist	0.3
Assistant Chemist	0.4
Total	2.7
AWU Post Doctors	1.0
Visiting Professor	0.1

Equipment Requirements*

	Available	New
Combustion calorimeter with rotating bomb	1	
Cryostats with associated adiabatic calorimeters	4	
Ebulliometers for vapor pressure measurements	3	
Inclined-piston gage for vapor pressure measurements	1	
Laser-Raman spectrometer modified for high temperatures	1	
Far-infrared spectrometer with heated cells	1	
Vacuum electrobalance		1
Thermometry for combustion calorimetry		1
Thermometry for vapor pressure measurement		1
Graphic computer terminals		2
Calorimeter control apparatus		1
Bath for bomb calorimeter		1
Microcalorimetric detection system		1

* Also listed on BPT1B

PROJECT SCHEDULE AND MILESTONE

Project: Thermodynamic Properties of Organic Nitrogen Compounds That Occur in Shale Oil and Heavy Petroleum

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Continue experimental studies	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	A ▽ /////	
1a. Obtain samples	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	A ▽ /////	
1b. Combustion calorimetric studies	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	A ▽ /////	
1c. Low-temperature and condensed-state calorimetry	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	A ▽ /////	
1d. Vapor-pressure measurements	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	A ▽ /////	
1e. Spectroscopy and molecular statistical mechanics	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	AB ▽ /////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone*	**Description**
Task 1 (A) September 30, 1984	Continue studies on the alkylpyridines, pyrroles, piperidines, and pyrrolidines, and complete experiments on 3,4-dimethylpyridine and 2,4-dimethylpyridine already in progress
Task 1a (A) September 30, 1984	In cooperation with the Bartlesville Project Office and the Oklahoma State University synthesis project, identify three organic nitrogen compounds and develop plans for research
Task 1b (A) September 30, 1984	Measure enthalpies of combustion of selected key organic nitrogen compounds.
Task 1c (A) September 30, 1984	Measure heat capacities and enthalpies of phase transitions on selected key organic nitrogen compounds
Task 1d (A) September 30, 1984	Measure vapor pressures of selected key organic nitrogen compounds
Task 1e (A) September 30, 1984	Measure spectra of selected key organic nitrogen compounds
(B) December 15, 1984	Use computer programs and thermodynamic laws to derive statistical thermodynamic properties

*Owing to inability to predict equilibration times of samples, specific completion dates on the samples studied cannot be predicted, nor can inevitable equipment failures be anticipated; however, based on previous efforts, currently used equipment and techniques will be used to produce results on three to four compounds per year.

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

(Continuation Sheet)
PROJECT SCHEDULE AND MILESTONE

Project: Thermodynamic Properties of Organic Nitrogen Compounds That Occur in Shale Oil and Heavy Petroleum

Report Date: ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
2. Develop, construct and test prototype equipment												
2a. Develop small-sample combustion calorimeter											A ▽	
					/////	/////	/////	/////	/////	/////	/////	/////
2b. Build two new cryostats for operation 4 to 573K							A ▽					
	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
2c. Build new calorimeter for reactive compounds						A ▽						
		///	/////	/////	/////	/////						
2d. Develop computer control of calorimetric measurements												
	//	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
2e. Develop automatic control for inclined-piston gage				A ▽		B ▽			C ▽			
	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
2f. Develop torsion-effusion apparatus								A ▽		B ▽		
				/////	/////	/////	/////	/////	/////	/////	/////	/////

	Milestone	**Description**
Task 2a	(A) August 15, 1984	Order materials of construction and begin construction
Task 2b	(A) April 15, 1984	Final assembly of cryoststs
Task 2c	(A) March 31, 1984	Complete construction of calorimeter
Task 2e	(A) January 15, 1984	Construction of parts for control system
	(B) March 31, 1984	Complete designs of mechanical parts
	(C) June 15, 1984	Development of computer controls
Task 2f	(A) May 15, 1984	Locate materials of construction
	(B) July 15, 1984	Order materials of construction

(Continuation Sheet)
PROJECT SCHEDULE AND MILESTONE

Project: Thermodynamic Properties of Organic Nitrogen Compounds That Occur in Shale Oil and Heavy Petroleum

Report Date: ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
3. Interpret data and develop correlations												A▽
	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
4. Compilation of data and preparation of reports												A▽
	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////

Milestone	Description
Task 3 (A) September 30, 1984	Interpret data and develop correlations. Data obtained to date interpreted in Annual Report
Task 4 (A) September 30, 1984	Compilation of data and correlations and preparation of reports

BPT1B. THERMOPHYSCIAL AND THERMOCHEMICAL PROPERTIES OF ORGANIC COMPOUNDS DERIVED FROM FOSSIL SUBSTANCES

Work Plans

Task 1 - Continue studies on polycyclic compounds containing oxygen, nitrogen, and sulfur, which will include completing experiments on the thermodynamic properties of 2,3-benzofuran and isochroman already in progress.

(a) In cooperation with the Bartlesville Project Office and the Oklahoma State University synthesis project, identify three organic compounds of oxygen and/or sulfur and develop plans for research.

(b) Vapor-Flow Calorimetric Study. Measure enthalpy of vaporization and vapor heat capacities of 3-methyl-pyrrolidine.

(c) Combustion Calorimetric Studies. Measure enthalpies of combustion of selected key organic oxygen compounds and related compounds as they become available from the synthesis project.

(d) Low-Temperature and Condensed-State Calorimetry (Third-Law Entropy Determinations). Measure heat capacities and enthalpies of selected key organic oxygen compounds and related compounds as they become available from synthesis projects and as equipment becomes available from queued experiments.

(e) Vapor-Pressure Measurements. Measure vapor pressures of selected key organic oxygen compounds and related compounds as they become available from the synthesis project.

(f) Spectroscopy and Molecular Statistical Mechanics.

(1) Measure spectra of selected key organic oxygen compounds and related compounds.

(2) Derive statistical thermodynamic properties for the substances from the above spectra.

Task 2 - Measure PVT properties of a selected fluid suitable for use in modeling of supercritical extraction.

Task 3 - Compile and correlate data from Tasks 1 and 2 on individual compounds and prepare reports.

Task 4 - Develop, construct, and test prototype equipment (items A to I also listed as Task 2 in BPT1A)

(a) Develop small-sample combustion calorimeter.

(b) Build two new cryostats for operation from 4 to 573 K; this will help facilitate timely data generation.

(c) Build new calorimeter for operation to 573 K and for use with reactive nitrogen and sulfur compounds. Only one calorimeter presently is constructed of materials that will allow use of these compounds without reacting.

(d) Develop computer control for calorimetric measurements. Lengthy experiments presently require large amounts of researchers' time. Much of the routine control and data gathering are amenable to computer control, allowing greater throughput of materials and, at the same time, requiring less manpower.

(e) Develop automatic control system for inclined-piston-pressure gage. Lengthy experiments presently require large amounts of researchers' time. Much of the routine control and data gathering are amenable to computer control, allowing greater throughput of materials and, at the same time, requiring less manpower.

(f) Develop a torsion-effusion apparatus for the measurement of the vapor pressure of very high molecular weight substances. Present equipment is not sensitive enough for these measurements.

(g) Develop a small-sample ebulliometric vapor-pressure apparatus. Synthesizing larger volumes of samples is very expensive. This will be cost-effective for future synthesis requirements furnished by the Bartlesville Project Office.

(h) Develop computer interfacing for laser-Raman spectrometer. Voluminous amounts of data are gathered that could be better interpreted with the aid of computers.

(i) Develop techniques and equipment for measurements of spectra in vapors at high temperatures. Higher temperatures are needed for the heavy organic compounds to be studied.

(j) Modernize temperature measurement and control system on PVT apparatus.

(k) Develop computerized data collection and analysis system for PVT apparatus.

Future Work

Useful correlations and predictions are expected within three years; however,even if the measurement pace can be doubled in the coming years, many substances of importance for this effort will still remain to be studied.

Manpower Requirements

	Man-Years
Senior Chemist	0.7
Research Chemist	0.9
Research Physicist	0.5
Senior Engineer	0.9
Senior Experimentalist	0.4
Assistant Chemist	0.3
Total	3.7
Post-Doctoral Chemists	0.9
AWU Visiting Professor	0.1

Equipment Requirements

	Available	New
Volumetric mercury compression apparatus	1	
Vapor-flow calorimeter	1	
Combustion calorimeters with rotary bomb*	1	
Cryostats with associated adiabatic calorimeters*	4	
Ebulliometers for vapor pressure measurements*	3	
Inclined-piston gage for vapor pressure measurements*	1	
Laser-Raman spectrometer with heated cells*	1	
Far-infrared spectrometer with heated cells*	1	
Vacuum electrobalance*		1
Thermometry for combustion calorimetry*		1
Thermometry for vapor-pressure measurement*		1
Graphic computer terminals*		2
Equipment for vapor-flow calorimeter*		1
Bath for bomb calorimeter*		1
Microcalorimetric detection system*		1

* Also listed in Project BPT1A

PROJECT SCHEDULE AND MILESTONE

Project: Thermochemical and Thermophysical Properties of Organic Compounds Derived from Fossil Substances

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Chemical thermodynamic studies	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	A▽ //////	
1a. Obtain samples	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	A▽ //////	
1b. Vapor-flow calorimetric study	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	A▽ //////	
1c. Combustion calorimetric studies	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	A▽ //////	
1d. Low-temperature and condensed state calorimetry	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	A▽ //////	
1e. Vapor pressure measurements	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	A▽ //////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone *	Description
Task 1 (A) September 30, 1984	Continue studies on polycyclic-hetroatom-containing substances and complete experiments on thermodynamic properties of 2,3-benzofuran and isochroman already in progress
Task 1a (A) September 30, 1984	In cooperation with the Bartlesville Project Office and the Oklahoma State University synthesis project, identify three compounds of oxygen and/or sulfur and develop plans for research
Task 1b (A) September 30, 1984	Measure enthalpy of vaporization and vapor heat capacities of 3-methylpyrrolidine
Task 1c (A) September 30, 1984	Measure enthalpies of combustion of selected key organic oxygen compounds and related compounds as they become available from the synthesis project
Task 1d (A) September 30, 1984	Measure heat capacities and enthalpies of selected key organic oxygen compounds and related compounds as they become available from synthesis project and as equipment becomes available from queued experiments
Task 1e (A) September 30, 1984	Measure vapor pressures of selected key organic oxygen compounds and related compounds as they become available from synthesis project

*Owing to the inability to predict equilibration times of samples, specific completion dates on samples studied cannot be predicted, and equipment failures cannot be anticipated; however, about three to four compounds can be completed per year on Tasks 1a and Tasks 1c through 1f. Task 1b produces about one compound per year.

Reporting Requirements

(A) 15 th of each month . . . . Monthly Progress Report
(B) 30 days after end of each quarter . . . . Quarterly Technical Progress Report
(C)' 90 days after end of program year . . . . Annual Technical Progress Report

(Continuation Sheet)

PROJECT SCHEDULE AND MILESTONE

Project: Thermochemical and Thermophysical Properties of Organic Compounds Derived from Fossil Substances **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
1f. Spectroscopy and molecular statistical mechanics												AB ▽
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////
2. PVT studies												A ▽
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////
3. Data compilation and report												A ▽
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////
4. Develop, construct, and test prototype equipment												
4a. Develop small-sample combustion calorimeter											A ▽	
					////	//////	//////	//////	//////	//////	//////	//////
4b. Build two new cryostats for operation 4 to 573K	A ▽						B ▽					
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////
4c. Build new calorimeter for reactive compounds						A ▽						
		////	//////	//////	//////	//////						

Milestone		Description
Task 1f	(A) September 30, 1984	Measure spectra of key organic oxygen compounds and related compounds
	(B) September 30, 1984	Derive statistical thermodynamic properties for the substances from the above spectra
Task 2	(A) September 30, 1984	Measure PVT properties of a selected fluid suitable for use in and modeling of supercritical extraction, requires about 18 months for a full study on one substance
Task 3	(A) September 30, 1984	Final compilation and correlation of data from Tasks 1 and 2 on individual compounds and preparation of reports
Task 4a	(A) August 15, 1984	Order materials of construction and begin construction
Task 4b	(A) October 1, 1983	Continue construction of parts for cryostats
	(B) April 15, 1984	Final assembly of cryostats
Task 4c	(A) March 31, 1984	Complete construction of calorimeter

(Continuation Sheet)
PROJECT SCHEDULE AND MILESTONE

Project: Thermochemical and Thermophysical Properties of Organic Compounds Derived from Fossil Substances

Report Date: ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
4d. Develop computer control of calorimetric measurements	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
4e. Develop automatic control for inclined-piston gage				A ▽		B ▽			C ▽			
		/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
4f. Develop torsion-effusion apparatus								A▽		B ▽		
				/////	/////	/////	/////	/////	/////	/////	/////	/////
4g. Develop small-sample ebulliometer											/////	/////
4h. Develop computer interfacing for laser Raman		/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
4i. Develop equipment for spectra measurement at high temp.						/////	/////	/////	/////	/////	/////	/////
4j. Modernize temperature measurement control, PVT				/////	/////	/////	/////	/////	/////	/////	/////	/////
4k. Develop data system, PVT				/////	/////	/////	/////	/////	/////	/////	/////	/////

Milestone		Description
Task 4e	(A) January 15, 1984	Construct parts for control system
	(B) March 31, 1984	Design mechanical parts
	(C) June 15, 1984	Develop computer controls
Task 4f	(A) May 15, 1984	Locate materials of construction
	(B) July 15, 1984	Order materials of construction

BPT2. STABILITY AND PROCESSING RESEARCH FOR CRUDES, INTERMEDIATE PROCESS STREAMS AND FINISHED FUELS

Background

This work addresses Items 5.2.3 and 6.2.1 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Part of the work--the separation of the crudes--will be carried out in the Base Program, while the remainder of the tasks, which are possibly applicable to industry in the near future, will be in the Optional Program.

The goal of the advanced process technology program of DOE/FE is to provide fundamental data needed to process alternative crudes in an efficient and acceptable manner. This is an important problem for industry because new sources of energy are now being developed to supplement and eventually replace the nation's diminishing reserves of light, "sweet" petroleum crudes. These heavier, lower quality feedstocks are quite different both physically and chemically from the light petroleum crudes. Many of these differences cause problems both for the refiner and for end use applications.

Commercial technology for refining typical petroleum crude oils is well established. These current techniques provide the basis for the development of effective and economical processes for upgrading and refining alternative fossil liquids. The difficulty of producing acceptable liquid fuels increases generally as the resource moves from heavy petroleum to alternate crudes, such as tar sand liquids, shale oils, and coal liquids. Removal of nitrogen and metals and conversion of heavy aromatics are limiting requirements of upgrading and refining. No practical alternative to relatively costly hydrogenation is in sight for these steps. The product liquids are very complex mixtures that reflect a combination of the character of the raw material and the degree of refining required. Problems such as instability, metals content, and toxicity must be considered. One of the major differences between light petroleum crudes and the other crudes is in the quantity and type of organic compounds that can lead to problems of fuel instability, i.e., the formation of soluble and insoluble gums during periods of thermal stress and during periods of prolonged storage. This project addresses such specific problems.

Through past research efforts, it has been determined that severe hydrotreating will convert a number of the compounds, causing instability by conversion into less reactive compounds. From the standpoint of the refiner, however, hydrotreating at the levels necessary to convert or remove all suspect compound types would be prohibitive. Thus, it is common practice to blend these synthetic fuels with other more stable fuels in order to dilute the adverse effects during storage and use.

Because fuel blending is a way out of the present dilemma, scarely any research has been directed toward determining the minimum levels of upgrading that would provide stable fuels, nor has there been sufficient research in determining the types of compounds causing instability, which, if identified, could possibly be removed from process streams by methods other than hydrogenation.

Similarly, the toxicity and mutagenesis of liquid fuels have been shown to increase as the quality of the feedstocks decreases. If the syncrude/synfuel industry is to provide a significant portion of our fossil energy needs, two areas of concern need to be addressed: (1) problems likely to occur because of worker exposure during production, upgrading, and refining, and (2) problems affecting the general public.

Research to date has already shown that the distribution of metals in heavy oils can be unexpectedly complex. Even the lighter fractions may contain significant levels of organometallics. These contaminants cause severe problems for refiners who often include a catalytic processing step very early in their processing facility. This project will include an investigation of the changes metal-containing compounds undergo as they proceed through various processing steps.

Extensive research has been performed at NIPER (formerly BETC) in developing techniques for characterizing heavy fractions of petroleum. Several crude oils and their straightrun fractions have been studied. These special characterization techniques provide a unique opportunity to study the chemistry throughout a typical process sequence and to correlate the composition and reaction information with other characteristics such as stability, toxicity, and final composition and physical properties. Because of the wide diversity of areas to be considered, some of this work will be covered within the Optional Program under Project OPT2.

One barrier to the scientific understanding of correlations between initial compositional properties and final product characteristics is the lack of well-defined samples. Judicious selection of feedstocks and processing conditions will address this problem. It is hoped that at least some extra sample volumes will be available for other investigators to take advantage of the research opportunity.

Objectives

To develop a correlation and predictive model that relates original composition and upgrading conditions of heavy fractions of petroleum with final composition, stability, toxicity, and the physical properties of finished products.

Scope of Work

The initial phase of this extensive research effort is aimed at determining upgrading conditions for selected heavy crudes. This will involve a dual upgrading approach. A distillate cut will be hydrogenated at several levels of severity to determine compositional changes as a function of upgrading severity. The residual material (greater than 1000°F) will be chemically fractionated. Supercritical extraction will then be used on these fractions to determine the feasibility of removing of specific problem components, such as certain metal compounds known to be present.

Test techniques, such as storage stability, will be evaluated to determine whether further method development is needed. After the upgrading experiments are completed for the first feedstock, techniques and conditions will be re-evaluated before subsequent feedstocks are processed. Data generated from all phases of the work will be compiled and correlated, with the ultimate goal being the development of a model to be used as a predictive tool. Samples with well-defined histories will be made available to other researchers through NIPER and the BPO when sufficient material is generated from these experiments.

These data will be compiled in programs for interpretation and correlative manipulation for predictive model development. To minimize discrepancies, only samples with well-defined histories will be used in this study. Literature results, where available, will be compiled, checked for accuracy, and used to compare and verify correlative approaches.

Some of this work will be covered within the Optional Program, Project OPT2.

Work Plan

Task 1 - Select the first feedstock. A fresh Wilmington crude (API gravity = 14) with a known history of production and handling is in our inventory.

Task 2 - Select upgrading conditions. It is now anticipated that a distillation cut with an upper limit of about 1000°F will be made. Other cuts may be necessary. Hydrotreating conditions will be 300°-350°C and 500-800 psig.

Task 3 - Evaluate storage stability methods to determine what development work is still required. Identify composition parameters affecting stability using state of the art analytical techniques.

Task 4 - Continue to develop a method for measuring storage stability during the first upgrading run. This is a continuation of work initiated in FY82.

Task 5*- Perform distillation of first feedstock using thinfilm evaporators.

Task 6*- (1) Hydrotreat distillation cuts boiling between 500°-1000°F, which were generated in Task 5. Use a matrix of temperatures and pressures to generate a well-defined set of products.

(2) Perform supercritical extraction for problem components such as the metal compounds in the greater than 1000°F fractions after performing chemical class separations.

Task 7 - Analyze the feedstock, distillation cuts, and matrix of hydrotreated samples and samples from supercritical extraction by physical, chromatographic, and spectroscopic methods to begin characterizing the components and the physical and compositional changes. Include a metals screening to determine effects of distillation/upgrading on the distribution of metals in the hydrocarbon matrices. Using the resulting data, determine what other analyses should be performed.

Task 8 - Determine storage stability parameters on the distillate material using the new accelerated (65°C) method developed at NIPER (formerly BETC).

Task 9*- Provide samples through NIPER and BPO for additional testing, such as utilization experiments. Perform mutagenesis screening on samples selected after data interpretation of Task 7.

Task 10 - Begin development of computer-based model for correlative and predictive purposes based on results obtained.

Task 11 - Select the second feedstock to be upgraded.

Task 12 - Determine modification of upgrading techniques or hydrogenation reactor conditions that might enhance the utility of the resulting data.

Task 13 - Evaluate the need for any changes in physical and compositional measurements based on characterization data supplied for the first set of samples.

Task 14 - Develop a model for correlating compositional and upgrading conditions with final compositional and physical properties, storage stability, and mutagenesis.

Future Work

The driving force for this research will be the requirement of obtaining sufficient data from heavy ends of petroleum on which to base reliable correlations and the resulting model. It is anticipated that the project will take several years for complete model development at the current level of effort. Intermediate deliverables will include reports and correlations on specific parts of the modeling effort.

* This task is in the Base Program. All other tasks are in the Optional Program under Project OPT2.

Manpower Requirements

	Man-years
Manager	0.1
Senior Chemist	0.1
Assistant Engineer	0.1
Associate Engineer	0.2
Technician	0.2
Total	0.7
Chemical Engineers (Post Doctor AWU)	1.9

Equipment Requirements

	Available	New
Wiped film distillation equipment	2	
Hydrogenation unit	1	
High pressure/high temperature batch reactor	1	
Liquid feed pump	1	1

PROJECT SCHEDULE AND MILESTONE

Project: Stability and Processing Research for Crudes, Intermediate Process Streams and Finished Fuels

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Select feedstock				A ▽	B ▽								
	//////	//////	//////	//////	//////								
2. Select upgrading conditions					A ▽								
	//////	//////	//////	//////	//////								
3. Analysis methods identification					A ▽								
	//////	//////	//////	//////	//////								
4. Storage stability method development			A▽						B▽				
	//////	//////	//////	//////	//////	//////	//////	//////	//////				
5. Prepare distillation equipment and distill feedstock							A▽						
	//////	//////	//////	//////	//////	//////	//////						
6a. Hydrotreat distillates							A		A▽				
	//////	//////	//////	//////	//////	//////	//////	//////	//////				
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		Description
*Task 1	(A) January 31, 1984	Feedstock selected and procurement initiated
	(B) February 28, 1984	Feedstock received
*Task 2	(A) February 28, 1984	Upgrading conditions selected
*Task 3	(A) February 28, 1984	Characterization protocols developed
*Task 4	(A) December 31, 1983	Stability test technique data evaluated for need for further development work
	(B) June 30, 1984	Rough draft of publication describing new storage stability test method completed
Task 5	(A) April 30, 1984	Distillation completed
Task 6a	(A) June 30, 1984	Hydrotreatment of 500-1000°F cut completed

*In Project OPT2

Reporting Requirements
(A) 15 th of each month..................Monthly Progress Report
(B) 30 days after end of each quarter.........Quarterly Technical Progress Report
(C)' 90 days after end of program year........Annual Technical Progress Report

(Continuation Sheet)

PROJECT SCHEDULE AND MILESTONE

Project: Stability and Processing Research for Crudes, Intermediate Process Streams and Finished Fuels

Report Date: ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
												A▽
6b. Processing of >1000°F cut	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
												A▽
7. Sample analyses	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
												A▽
8. Storage stability testing	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
									A▽			
9. Samples available to others	/////	/////	/////	/////	/////	/////	/////	/////	/////			
												A▽
10. Compile data	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
									A▽			B▽
11. Select second feedstock	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////
												A▽
12. Modify upgrading technique	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////

Milestone		Description
Task 6b	(A) September 30, 1984	Attempts at characterization and supercritical extraction of >1000°F cut assessed for usefulness and applicability to objectives
*Task 7	(A) September 30, 1984	Include compilation of characterization data generated to date in NIPER quarterly and/or annual report
*Task 8	(A) September 30, 1984	Report of progress to date
*Task 9	(A) June 30, 1984	Contacts made regarding other investigations. Priorities set for access to samples
*Task 10	(A) September 30, 1984	Report of progress to date
*Task 11	(A) June 30, 1984	Select/procure second feedstock
	(B) September 30, 1984	Receive second feedstock
*Task 12	(A) September 30, 1984	Report of progress to date

*In Project OPT2

(Continuation Sheet)

PROJECT SCHEDULE AND MILESTONE

Project: Stability and Processing Research for Crudes, Intermediate Process Streams and Finished Fuels

Report Date: ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
13. Modify characterization protocol	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	A▽ /////
14. Develop model	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	A▽ /////

Milestone		Description
*Task 13	(A) September 30, 1984	Report of progress to date
*Task 14	(A) September 30, 1984	Report of progress to date

*In Project OPT2

BPT3. CHEMICAL CHARACTERIZATION OF HEAVY ENDS OF LIGHT PETROLEUM, OF HEAVY PETROLEUM, AND OF LIQUIDS DERIVED FROM OTHER FOSSIL SOURCES

Background

This work addresses Item 5.2.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

This project builds on the experience and equipment of the mass spectrometer laboratory and will help extend the capability in that field. The project is divided between the Base Program and the Optional Program, with a task in the Base Program involving the development of mass spectrometric techniques that would be applicable to complex hydrocarbon compounds boiling above 550°C. Tasks dealing with other specialized subjects are placed in the Optional Program.

This project is a continuation of work within the Fundamental Petroleum Chemistry program of DOE/Fossil Energy. Historically, uses for high-boiling fractions have been limited to production of coke and highway asphalt and for feedstock to catalytic cracking units. However, as reserves of light petroleum become depleted and methods for producing heavy crude oils improve, the supply of heavy feedstock will increase and include oils with greater concentrations of metals, nitrogen, oxygen, and sulfur. This supply of heavy crudes coupled with rising cost per barrel of crude oil will result in a much greater incentive to process these heavy materials into high-volume, high-value products, such as gasoline and diesel fuel.

Present coking techniques for heavy oils are energy intensive and still produce a coke product that may be commercially and environmentally unacceptable. Thus, the highly aromatic nature of these crudes and their higher concentrations of contaminating species make it undesirable, both environmentally and for product utilization, to follow current processing practices.

The chemistry of these heavy fractions and of fractions containing metals and heteroatoms is not well understood. Such an understanding is a prerequisite for logically developing methods for the efficient processing of these resources into transportation fuels. Although heavy ends of petroleum and bitumen contain undesirable elements such as nitrogen, sulfur, and metals, they still have a much higher hydrogen content than coal. Thus, if processing difficulties can be overcome, these materials represent a more valuable feedstock.

The underlying premise of this project is that if more chemical information was available about these materials, then more efficient methods of processing could be developed. Without detailed compositional data on the raw materials, process development cannot be logically pursued.

Methods currently available for analysis need to be extended to cover the high-boiling materials. In addition, new methods should be developed either to yield data of a type that the old methods cannot deliver or to replace current methods that cannot be extended to the analysis of heavy ends. An expected product of this work will be a set of compositional data on a limited number of heavy end samples.

Prior work at NIPER (formerly BETC) with these materials has shown them to be very complex in terms of the number of classes of chemical compounds they contain, as well as the diversity of constituents within a given class (1-10). To analyze these materials effectively, methods are needed to separate them into chemical classes or some other type of logical grouping (11-16). Sophisticated methods for detailed investigation of members of each class could then be used. By far, mass spectrometry has the greatest resolving abilities of any available instrumental technique. It becomes the logical choice as the main instrument to be used in this study.

For the most effective use of the high resolving capabilities of a mass spectrometer, the samples must be fractionated according to chemical classes before introduction into the instrument. This will aid in assigning the correct chemical structures to the mass data and in providing the best set of quantitative data possible. Besides the chemical separations, it is often useful to distill the sample into several boiling ranges to increase the likelihood of detecting significant minor components by mass spectrometry.

As the result of a cooperative effort between the United States and Venezuela, a study of Cerro Negro crude oil is underway. The work with Venezuela Institute of Petroleum (Intevep) has included exchange of both information and personnel. The Cerro Negro crude oil was chosen as a heavy oil which, because of its complexity, would be an effective model for method development. This oil provides the difficulty of analysis required for the method development and provides information for the international exchange through BPO.

In 1980, Cerro Negro, a heavy Venezuelan oil, was distilled into five boiling ranges. In subsequent years, each distillate has been separated into saturate, aromatic, acid, and base fractions. In order to lay a foundation for work on the heavy 550°-700° C and 700° C + fractions, the lower boiling fractions had to be analyzed first. Thus, mass spectral work on the 200°-425° C and 425°-550° C fractions was begun in 1982, continued through 1983, and is proposed to continue toward completion in 1984.

A preliminary analysis of the mass spectral data has indicated two areas where more refined separations would greatly enhance the utility of the data: (1) work on the separation of the aromatic-neutral fraction into hydrocarbons and various types of sulfur compounds and (2) the development of a method to subfractionate acid concentrates into compound classes.

References

1. Sturm, G.P., Jr., Q. G. Grindstaff, D. E. Hirsch, S. E. Scheppele, and M. Hazas, "Characterization of Cerro Negro Crude, Part II. Chemical Analysis," ACS Div. Pet. Chem. Preprints, Vol. 26, 1981, pp. 851-856.

2. Sturm, G. P., Jr., S. E. Scheppele, P. L. Grizzle, J. E. Dooley, and R. D. Grigsby, "Characterization of Fossil Liquids and Implications for Use in Processing," AIChE National Meeting, Houston, Tex., April 5-9, 1981.

3. Scheppele, S. E., G. P. Sturm, Jr., Q. G. Grindstaff, R. D. Grigsby, and C. S. Hwang, "Characterization of Probe Distillation/Mass Spectrometry Applied to the Characterization of Heavy Ends of Petroleum," presented at American Chemical Society National Meeting, Las Vegas, Nev., August 24-29, 1980.

4. Scheppele, S. E., Q. G. Grindstaff, G. P. Sturm, Jr., and T. Aczel, "Considerations on the Quantitative Analysis of Complex Petroleum and Synfuel Mixtures," presented at 31st Annual Conference on Mass Spectrometry and Allied Topics, Boston, Mass., May 8-13, 1983.

5. Scheppele, S. E., Q. G. Grindstaff, and P. L. Grizzle, "Field Ionization Mass Spectrometric Analysis of Saturates in Shale Oil," presented at Joint Meeting of American Society for Mass Spectrometry and American Society for Testing and Materials, Honolulu, Hawaii, June 6-11, 1982.

6. Grindstaff, Q. G., S. E. Scheppele, C. S. Hwang, G. P. Sturm, Jr., and P. W. Woodward, "Aspects of the Composition of Hydrotreated Greater Canadian Tar-Sands Oil," 26th Annual Conference on Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28-June 2, 1978.

7. Scheppele, S. E., K. C. Chung, and C. S. Hwang, "Computer Processing of Mass Spectral Data .I. Assignment of Formulas to Experimental Masses; Chemical and Mathematical Principles," Int. J. Mass Spec. Ion Phys., Vol. 49, 1983, pp. 143-178.

8. Grigsby, R. D., S. E. Scheppele, Q. G. Grindstaff, G. P. Sturm, Jr., L. C. E. Taylor, H. Fudge, C. Wakefield, and S. Evans, "Evaluation of Fast Atom Bombardment Mass Spectrometry for Identification of Nitrogen-Containing Compounds in Fossil Fuels," Anal. Chem., Vol. 54, 1982, p. 1108.

9. Sturm, G. P. Jr., J. E. Dooley, J. S. Thompson, P. W. Woodward, and J. W. Vogh, "The Composition of Liquids from Coals of Different Rank" in Upgrading Coal Liquids, ACS Symposium Series 156, 1981, pp. 1-37.

10. Sturm, G. P. Jr., P. W. Woodward, J. W. Vogh, S. A. Holmes, and J. E. Dooley, "Characterization of a Colstrip Coal Liquid Derived from the Zinc Chloride Hydrocracking Process," BERC/RI-78/4, May 1978.

11. Dooley, J. E., D. E. Hirsch, C. J. Thompson, and C. C. Ward, Hydrocarbon Processing, "Analyzing Heavy Ends of Crude," Vol. 53, No. 11, 1974, p. 187.

12. Green, J. B., and R. J. Hoff, "Liquid Chromatography on Silica Using Mobile Phases Containing Aliphatic Carboxylic Acids. II. Application in Fossil Fuel Characterization," J. Chromatogr., Vol. 209, 1981, pp. 231-250.

13. Grizzle, P. L., J. B. Green, V. Sanchez, E. Murgia, and J. Lubkowitz, "Characterization of Cerro Negro Crude, Part I. Physical and Chemical Separations," ACS Div. Pet. Chem. Preprints, Vol. 26, 1981, pp. 839-850.

14. Green, J. B., and P. L. Grizzle, HPLC Analysis of Polar Substances on Unmodified Silica" in Trace Analysis, J. F. Lawrence, editor, Vol. II, Academic Press, New York, 1982, pp. 223-65.

15. Grizzle, P. L. and J. S. Thomson, "Liquid Chromatographic Separation of Aromatic Hydrocarbons with Chemically Bonded (2,4-Diaitro anilino propyl Silica," Anal. Chem., Vol 54, 1982, pp. 1071-1078.

16. Vogh, J. B., and J. S. Thomson, "Preparative Liquid Chromatography for Fractionation of Petroleum and Synthetic Crude Oils," Anal. Chem., Vol. 53, 1981, pp. 1345-1350.

Objectives

To develop mass spectral procedures for the analysis of constituents in the heavy ends of petroleum with a boiling range greater than 550°C.

Scope of Work

Mass spectral data of fractions separated from the 200°-425°C and 425°-550°C distillates of Cerro Negro crude have been obtained using the ultra-high resolution MS-50 mass spectrometer. These data will be analyzed using the group-type, carbon number distribution technique. In the group-type method, compound types with the same general formula (and ideally very similar chemical and physical properties) are grouped since the masses of their parent ions are identical. Carbon number distributions for the different group-types result from determination of the homologous members that differ in composition by the number of CH_2 groups present in the molecules.

The analysis will be used first to determine if the mass spectral conditions, such as resolution, parent ion/fragment ion ratios, number of ions produced for each compound, component and concentration factors of calibration mixture, and reproducibility can be improved. After the best set of conditions has been determined, the mass spectral technique will be evaluated to determine whether the group-type carbon number distributions obtained have value for analyzing of heavy crudes that contain high amounts of heteroatoms. Also, it will be determined if the mass spectral data on the less than 550°C distillates can be useful for the analysis of the greater than 550°C distillates of the Cerro Negro crude in either the extension of the methods or in the development of new methods.

The quantitation of the group-type, carbon number distribution analysis assumes that the sensitivities for all compound types and all homologous members within each compound type are equal. Mass spectral sensitivity for a given compound can be defined as the ratio of the number of ions collected at the detector to the number of molecules of that compound introduced to the ion source of the mass spectrometer. From work performed in this and other mass spectrometry laboratories, these sensitivities are known not to be equal for all compounds.

To improve the accuracy of the quantitative analysis of the Cerro Negro and other heavy crudes, sufficient sensitivity determinations of compound types and homologous members of compound types must be performed to develop reliable sensitivity-structure correlations. This is a large undertaking and can be done only on a limited basis in the coming year. These sensitivity correlations will be evaluated using both individual model compounds and well-defined fractions of petroleum.

Even with the state of the art, ultra-high resolution MS-50 mass spectrometer, the mass spectral analysis of heavy petroleum such as Cerro Negro is limited because of the high sulfur content. At a dynamic resolution of 80,000, the MS-50 mass spectrometer can only provide baseline separation between the hydrocarbon compounds and the corresponding sulfur compounds, in which three carbons are replaced by SH_4, up to mass 272. The ideal way to get around this problem would be to separate the sulfur-containing compound classes from the other neutral compounds in the crude. Two promising separation methods being developed at NIPER (formerly BETC) will be evaluated for their ability to separate sulfur compounds from Cerro Negro heavy oil.

The separation of acid concentrates into compound classes would enhance the mass spectral analysis of a heavy petroleum. Many different types of compounds in fuels show weak-to-medium acidic properties. Some contain nitrogen, such as the pyrrolic and amide families, some contain oxygen such as carboxylic acids and phenols, and some contain sulfur such as thiols. Their chemistry is different than other neutral (ethers, thiophenes, etc.) or basic (pyridines, anilines, sulfoxides) heteroatom species, which makes it essential to isolate them as a group and determine the classes of compounds present.

A separation method under development will be used to separate previously isolated acid concentrates. Analyses of the resulting fractions will be used to evaluate this as yet unpublished separation method. Depending on results, the method will be published or modification will be undertaken. Also, fractions that prove to be nearly homogeneous in one compound class will be used to determine average mass spectral sensitivities, as described above.

Tasks 2-4 of this work will be done under Project OPT3 of the Optional Program.

Work Plans

Task 1 - Evaluate mass spectral techniques for obtaining group-type carbon number distributions using fractions separated from the 200°-425°C and 425°-550°C distillates of Cerro Negro Heavy Crude. (Base Program)

(a) Obtain carbon number distribution for 200°-425°C and 425°-550°C acids fractions.
(b) Obtain carbon number distribution for 200°-425°C and 425°-550°C bases fractions.
(c) Obtain carbon number distribution for 200°-425°C and 425°-550°C neutral fractions.
(d) Using information obtained from subtasks a, b, and c, determine if the low voltage calibration mixture of compounds can be changed either by component or concentration to improve mass determination accuracy. Also, determine the electron impact voltage for the best parent ion/fragment ion ratio, number of ions produced for each compound, and the reproducibility of the mass spectra using the 200°-425°C base fraction. All three of these conditions must be considered jointly in determining the optimum low voltage electron impact conditions.
(e) Using information obtained in subtasks a, b, c, and d, evaluate mass spectral technique for obtaining carbon number distributions and the possibility of extending the technique to analysis of the 550°C fractions of Cerro Negro crude.

Task 2 - Evaluate, on a limited scale, the assumption of equal molar sensitivities for quantitative mass spectral analysis of petroleum fractions. This is Task 1 in the Optional Program, OPT3.

(a) Select compounds representative of the types typically found in fossil fuel aromatic-neutral fractions.
(b) Determine the mass spectral sensitivity coefficients for these representative compounds using low-ionizing-voltage electron impact and field ionization techniques.
(c) Correlate sensitivity data with known structures of representative compounds.
(d) Evaluate the importance of sensitivity correlations in the quantitation of mass spectral analyses.

Task 3 - Separation of sulfur compound classes. This is Task 2 in the Optional Program, OPT3, page 162.

(a) Separate sulfides from Cerro Negro 200°-425°C and 425°-550°C acid-base-free distillates.
(b) Separate saturates, thiophenes, and aromatic hydrocarbons from at least the acid-base-sulfide-free 200°-425°C distillate.
(c) Evaluate the effectiveness of these separations via elemental analysis, gas chromatography, and mass spectrometry.
(d) Evaluate the possibility of extending the separation method to higher distillates.

Task 4 - HPLC separation of acid concentrates into compound classes. This is Task 3 in the Optional Program, OPT3.

(a) Separate 10-20 previously isolated acid concentrates and distillates and residues of Cerro Negro and Wilmington oils into compound classes.
(b) To test the capabilities of the method, apply this separation technique to 5-10 synfuel acid concentrates that contain acids that are significantly different from acids in crude oils. Compare results.
(e) Evaluate separation method using infrared and mass spectroscopy. Report results.

Future Work

Further work in FY85 and beyond will extend techniques developed in FY84 to the heavier fractions of Cerro Negro (550°-700°C and greater than 700°C fractions). The methods developed will be applied to additional heavy crudes with wide-ranging properties, and the sensitivity structure correlations will be expanded to improve quantitation of heavy fossil fuel samples. Work on separation of sulfur compounds in the higher ranges of Cerro Negro crude is planned for FY85. Additional effort in FY85 will also be required to finish the fractionation of the acid fractions.

Manpower Requirements

	Man-years
Research Chemist	0.6
Senior Chemist	1.0
Research Chemist	2.0
Senior Experimentalist	0.6
Total	4.2

Equipment Requirements

	Available	New
MS-30 FI,FD,EI	1	
MS-80 FI,FD,EI,CI	1	
MS-50 FI,FD,EI	1	
Megohm meter		1
HPLC (high performance liquid chromatography) systems, also HPLC accessories: columns, specialized detectors, column packing apparatus.	4	
Rotary solvent evaporators	4	
Gas Chromatographs with supporting intelligent interfacing	4	1
GC mass detector		1

PROJECT SCHEDULE AND MILESTONE

Project: Chemical Characterization of Heavy Ends of Light Petroleum, of Heavy Petroleum, and of Liquids Derived from Other Fossil Sources

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Evaluation of mass spectral techniques					A ▽	B ▽		C▽	D ▽			E ▽	
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	
2. Evaluation of quantitation assumptions of MS data								A ▽		B ▽		C,D▽	
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	
3. Separation of sulfur compound classes								A▽		B ▽		C,D▽	
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	
4. HPLC separation of acid concentrates into compound classes										A▽	B ▽	C ▽	
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		Description
Task 1	(A) February 29, 1984	Obtain carbon number distribution for 200-425°C and 425-550°C base fractions
	(B) March 31, 1984	Obtain carbon number distribution for 200-425°C and 425-550°C acid fractions
	(C) May 31, 1984	Obtain carbon number distribution for 200-425°C and 425-550°C neutral fractions
	(D) June 30, 1984	Determination mass spectral operational conditions
	(E) September 30, 1984	Evaluate mass spectral technique for obtaining carbon distributions
Task 2	(A) May 1, 1984	Select representative compound
	(B) July 15, 1984	Determine mass spectral sensitivity
	(C) September 30, 1984	Evaluate the importance of sensitivity correlation in quantitation of data
Task 3	(A) May 31, 1984	Separate sulfides from Cerro Negro 200-425°C and 425-550°C distillates
	(B) July 30, 1984	Separate saturates, thiophenes, and aromatic hydrocarbons from 200-425°C distillate
	(C) September 30, 1984	Evaluate effectiveness of these separations
	(D) September 30, 1984	Evaluate possibility of extension of separation method to higher distillates
Task 4	(A) July 1, 1984	Separate 10-20 Cerro Negro and Wilmington acid concentrates
	(B) August 31, 1984	Separate 5-10 synfuel acid concentrates
	(C) September 30, 1984	Evaluate separation method

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

OE1. IMPROVEMENTS IN STIMULATION TECHNOLOGY

This project consists of two intimately related tasks dealing with the properties of fluids used in massive hydraulic fracture and their effect on formation damage.

OE1A. FORMATION DAMAGE DUE TO HYDRAULIC FRACTURING FLUID

Background

The work addresses Item 6.4.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Geologic studies by both industry and the National Petroleum Council (1) estimate that an immense resource (600 trillion cubic feet) of natural gas exists in tight gas sand basins in the western states. These reservoirs contain natural gas in formations with permeability too low for economic recovery by conventional technology.

Massive hydraulic fracturing (MHF) has been used to stimulate natural gas production from low-quality reservoirs. Large hydraulic treatments are designed to produce fractures in tight formations that extend from 1000 to 3000 feet radially from the wellbore. Typically, expensive MHF treatments consist of pumping at least 100,000 gallons of gelled fracturing fluid containing sand proppant into the reservoir. To date, MHF of these low quality reservoirs has produced mixed results, and many of the factors that contribute to success or failure are not understood.

Two factors that contribute to the failure of MHF treatments are formation damage and restricted fracture conductivity (2). Formation damage of the reservoir is caused by fluid leak-off and fracturing fluid polymer penetration into the formation during the fracturing treatment. Sometimes the reservoir can be further damaged because of fluid incompatibility, which causes clay swelling and migration of fine particles that plug formation capillaries. The combined effect of these factors result in formation damage. Little information has been published on formation damage caused by stimulation of low permeability sands. A basic research program leading to a better understanding of these factors is needed.

During the past year, formation damage due to fluid invasion was studied at BETC using core samples from tight lenticular sands. Gel invasion depth into cores was evaluated along with other hydraulic fracturing parameters, such as fluid loss coefficients, filter cake permeability to liquids, and effective gas permeabilities. Preliminary data and procedures from this study were published (3). During the course of the study, a unique experimental apparatus was developed capable of measuring formation damage by observing regained permeability along with the other parameters mentioned above.

This work has application to understanding tight gas sand (TGS) stimulation and production that is of interest to DOE, the Gas Research Institute (GRI), and industry. In addition to TGS cores from the Uinta and Green River Basins, the research program incorporates cores from the Multiwell Experiment (MWX) (4) in the Piceance Basin. Since a great deal of information (reservoir parameters, core analysis, formation breakdown pressures, and reservoir simulation studies) is available, the MWX represents an ideal research situation for formation damage studies. For the MWX stimulation treatment, presently scheduled for the spring (1984), the frac-fluid design will be evaluated and formation damage measured using MWX paludal zone core.

References

1. National Petroleum Council, "NPC Unconventional Gas Sources--Volume V--Tight Gas Reservoirs, Part I," Report by Tight Gas Reservoir Group of the Unconventional Gas Committee, December 1980.

2. Hoditch, S. A., "Factors Affecting Water Blocking and Gas Flow from Hydraulically Fractured Gas Wells," J. Pet. Tech., Dec. 1979, pp. 1515-1534.

3. Volk, L. J., B. L. Gall, C. J. Raible, and H. B. Carroll, "A Method for Evaluation of Formation Damage Due to Fracturing Fluids," SPE Paper 11638, presented at the SPE/DOE Symposium on Low Permeability, Denver, Colo., March 14-16, 1983.

4. Crawley, A. B., D. A. Northrup, and A. R. Sattler, "The Department of Energy's Western Gas Sands Project Multi-Well Experiment Update," SPE Paper 11183, presented at the 57th Annual SPE-AIME Fall Technical Conference, New Orleans, La., Sept. 26-29, 1982.

Objectives

To identify and evaluate factors contributing to formation and fracture damage in tight gas reservoirs.

Scope of Work

The research has a broad application for tight formations. A frac-fluid simulator has been developed to determine the damage to cores caused by various fracturing fluid polymers and additives at reservoir temperature and fracturing pressure. By using the simulator, regained permeability or damage magnitude can be measured for different polymer types (guar, hydroxypropyl guar HPG, and cellulose gels) at various polymer concentrations, e.g., those under consideration in the MWX research program. In addition, by measuring regained permeabilities, the effect of temperature and gel pump pressures on damage will be measured relative to fracturing conditions.

Another parameter to be evaluated is the fluid leakoff coefficient. Viscous polymer gels are used not only to increase proppant transport, but also to reduce leakoff by building a filter cake at the fracture face. The data developed for polymers such as HPG, guar, and cellulose to control fluid loss will be measured and evaluated using the frac-fluid simulator. In addition to polymer evaluation, fluid loss additives, such as diesel fuel, will be assessed for fluid loss control. Other additives, such as methanol and surfactants that aid in fluid cleanup, will be evaluated.

This work will be extended to evaluate damage caused by cross-linked polymer gels. These non-Newtonian fluids are shear sensitive and are not compatible with batch quantity gels used in the present experimental apparatus. A reactor system will be developed to produce cross-linked gels. The development time of this reactor is uncertain depending upon experimental difficulties. After the reactor is developed, formation damage and fluid loss coefficients of cross-linked gels will be measured and evaluated as stated for the previous system.

Ultimately, these investigations will lead to simplified models that relate the reservoir properties to polymer concentration, temperature range, and additive type for prediction of frac-fluid behavior, formation damage, and fluid leakoff coefficients at reservoir conditions for each polymer type under development.

Work Plans

Task 1 - Regained permeability and fluid leakoff coefficients of experimental polymers planned for testing in the MWX experiment will be measured using MWX core from paludal Zone 3 and 4. Results will be analyzed and recommendations will be made for fracturing fluid systems to be used in the tests planned for early December 1983.

Task 2 - Measurements will be extended to 100°C for HPG gel concentrations of 40 and 80 pounds. In the past, efforts largely concentrated on evaluating of formation damage due to hydroxypropyl guar (HPG) at a temperature of 70°C.

Task 3 - The effectiveness of additives will be measured with HPG gels. The effect of 5 percent diesel fuel to control fluid loss will be measured at 70° and 100°C. Regained permeability and fluid leakoff will be measured for 5 percent methanol/HPG gel at 70° and 100°C. The results of these tests will be analyzed for possible temperature dependence on fluid leakoff and reservoir cleanup. Additive effectiveness will be evaluated.

Task 4 - Formation damage evaluation will be completed for modified cellulose gels. Regained permeability of 40 and 80 pound cellulose gels will be tested at 70° and 100°C. The results of these tests will be analyzed for temperature and concentration effect on formation damage and fluid loss control of these typical low residue gels. Recommendations for fluid loss control will be made based on the relative effectiveness of low residue (cellulose) versus high residue or filter cake building (HPG) gels. The relative extent of formation damage will also be evaluated with respect to these different polymer types.

Task 5 - An experimental high pressure reactor will be designed where the cross-linked reagent will be metered into the polymer gel as the gel is pumped to the formation damage apparatus.

Task 6 - A high pressure reactor will be constructed and installed on the formation damage apparatus.

Task 7 - Reactor performance will be evaluated by measuring viscosity changes on a boron cross-linked and HPG polymer system . Data will be analyzed for system efficiency. This system will then be used to evaluate cross-linked gels planned for future research.

Future Work

Future research will include evaluation and effectiveness of metal ion cross-linked gels with respect to fluid loss control and formation damage.

Other fracturing fluid additives will be investigated with respect to minimizing formation damage. For example, a common formation damage problem is water-sensitive clays. Clay damage usually results from swelling clays or migration of clay particles. A number of clay stabilizers have been proposed to minimize damage. A systematic study will be made for the various types of clay stabilizer additives to determine which type or types are most effective for clay damage control.

Additional research will include evaluation of foams to be used for hydraulic fracturing. This work will involve developing methods and bench-scale equipment capable of generating a quality foam range in the laboratory. This would allow assessment of foams for damage and fluid leakoff control.

Manpower Requirements

	Man-years
Research Physicist	1.0
Technician	1.0
Petroleum/Chemical Engineer	0.5
Total	2.5

Equipment Requirements

	Available	New
Two HPLC pumps	1	
Two 10,000 psi core test cells	1	
Stripchart recorder (multi-speed and range)	1	
Humidity oven		1
High torque mixer		1
Electronic balance		1

PROJECT SCHEDULE AND MILESTONE

Project: Formation Damage Due to Hydraulic Fracturing **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Frac fluid compatability tests	/////	A ▽ /////											
2. Extend temperature tests	/////	/////	/////	/////	/////	▽ A ///							
3. Evaluate frac fluid additives			/////	/////	/////	/////	A▽ /////						
4. Evaluate cellulose polymers								/////	/////	/////	A▽ /////		
5. Design cross-linker reactor					/////	/////	/////	A▽ /////					
6. Construct reactor									/////	A▽ /////			
Progress Reporting Requirements		**AΔ**	**AΔ**	**AΔ BΔ**	**AΔ**	**AΔ**	**AΔ BΔ**	**AΔ**	**AΔ**	**AΔ BΔ**	**AΔ**	**AΔ CΔ'**	

Milestone		**Description**
Task 1	(A) November 30, 1983	Complete compatibility tests of frac fluids and MWX core
Task 2	(A) March 15, 1984	Complete high temperature HPG tests
Task 3	(A) April 30, 1984	Complete additive/HPG tests
Task 4	(A) August 30, 1984	Complete formation damage and fluid loss tests for cellulose gels
Task 5	(A) May 30, 1984	Design cross-linked reactor
Task 6	(A) July 31, 1984	Complete reactor construction

Reporting Requirements
(A) 15 th of each month..................Monthly Progress Report
(B) 30 days after end of each quarter.........Quarterly Technical Progress Report
(C)' 90 days after end of program year........Annual Technical Progress Report

(Continuation Sheet)
PROJECT SCHEDULE AND MILESTONE

Project: Formation Damage Due to Hydraulic Fracturing **Report Date:** ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
7. Evaluate reactor system												A▽
											//////	/////

	Milestone	**Description**
Task 7	(A) September 30, 1984	Complete reactor system design

OE1B. CHARACTERIZATION OF POLYMER FRACTURING FLUID SYSTEMS

Background

This work addresses Item 6.4.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Massive hydraulic fracturing (MHF) using gelled water-based fluids is a common technique to stimulate low permeability, gas-bearing formations in the western United States. These viscous solutions are used to improve proppant placement and decrease fluid leakoff. An important step in gas well completion is the viscosity reduction and frac-fluid removal from the hydraulic fracture to ensure proper proppant placement and minimize formation and fracture damage.

In the past, loss of viscosity has been used as an indicator of polymer degradation into simpler molecules. Actually only under extreme conditions (high breaker concentrations and high temperature) do broken polymers reduce to a molecular weight of 10,000 or less. Loss of viscosity can leave as much as 20 percent of the polymer with molecular weight greater than 2 million, a size capable of plugging or restricting flow in tight sandstone pores.

In addition, recent studies by Almond (1) indicate that damaging effects of fracturing fluid systems on sand packs, used to represent the fracture, cannot be predicted on the basis of loss of viscosity alone. He concludes that broken polymer molecules leave an "invisible residue" in the sand pack which hinders fluid flow and cleanup.

In order to evaluate the factors that produce efficient fracturing fluid polymer degradation, a size exclusion chromatographic (SEC) system has been developed which can monitor the decrease in molecular size of the broken polymer as conditions are varied. Variables that affect polymer degradation include polymer type, breaker type, concentration, temperature, time, and fracturing fluid formulation (pH, crosslink type, etc.). Initial studies using hydroxypropyl guar (HPG) indicate that polymer degradation can be studied using SEC. Additional studies are needed to correlate the degree of damage with the size of the polymer fragments making it possible to use SEC as an effective tool to study polymer degradation. The effect fracturing fluid additives have on degradation conditions can then be evaluated to determine improved clean-up characteristics and to design more efficient fracturing fluids.

Leakoff of fracturing fluids into the formation results in the polymer concentrating in the fracture as a gel filter cake buildup that is 20 times more concentrated than the typical 40 lb/1000 gallon gel concentration of the fracturing fluid formulation. Breakers leak off into the formation and may not be in contact with the polymer when efficient cleanup is desired. SEC will be used to investigate ways to degrade this concentrated polymer solution efficiently.

References

1. Almond, S. W., "Factors Affecting Gelling Agent Residue Under Low Temperature Conditions," SPE Paper 10658, presented at the 1982 Formation Damage Control Symposium, Lafayette, La., March 1982.

Objectives

To develop a theory for polymer degradation.

Scope of Work

Size exclusion chromatography (SEC) will be used to analyze and monitor polymer degradation as a function of breaker type and concentration, temperature, time, and additives to the fracturing fluid system. The viscosity of the degraded polymer solutions will also be monitored. Upon completion of the HPG work, studies will be initiated on other possible fracturing fluid polymers such as guar gum, modified cellulose, and Xanthan gum. Since these polymers produce varying amounts of damaging residue, their use will aid in correlating the degree of damage with SEC results.

Degradation studies using enzyme breakers will be conducted as a function of pH. Other additives that may enhance or retard polymer degradation such as methanol and added salts will be studied.

Particular attention will be directed to study degradation of filter cake build-up due to fluid loss. Preliminary studies indicate that breaker concentrations which degrade polymer solutions appear to leave the filter cake intact. Actual fracture damage may be more severe than tests with sand packs indicate.

Viscosity measurements will be made using a Contraves low-shear 30 viscometer suitable for measuring viscosities of broken polymer solutions to compare with SEC results.

These investigations will make it possible to compare and evaluate different fracturing fluid systems and to develop mathematical correlations which predict degradation behavior under reservoir conditions.

Work Plans

Task 1 - Finalize evaluation of SEC system for monitoring polymer degradation of hydroxypropyl guar (HPG) as a function of breaker type and concentration, time, temperature, and added salt.

Task 2 - Initiate studies of degradation of modified cellulose and guar gum as a function of breaker type and concentration, time, temperature, and additives.

Task 3 - Correlate SEC results for modified cellulose polymer systems with Almond's sand pack studies to identify molecular size of "invisible residue" small enough to be considered as non-damaging.

Task 4 - Use high pressure filter apparatus and filters of known pore size to study possible correlation of SEC results with amount of residue produced by the broken polymers. Studies will involve use of various polymers, breakers, and changes in conditions as studied with SEC.

Task 5 - Initiate studies on conditions necessary to effectively degrade concentrated gel buildup, in particular breaker type and concentration.

Task 6 - Monitor viscosity changes of the broken polymer solutions with a Contraves low-shear 30 viscometer to correlate with SEC results with viscosity changes.

Task 7 - Prepare status report on results of tests.

Future Work

The SEC system will be used to determine more effective breaker and/or stabilizer mixtures. The underlying objective of this work is to develop or improve breakers that do not prematurely reduce polymer viscosity during the fracturing process but are effective in degrading concentrated polymer in the fracture to minimize fracture and formation damage during fluid cleanup operations.

Manpower Requirements

	Man-years	New
Research Chemist	1.0	
Assistant Chemist	1.0	
Petroleum/Chemical Engineer	0.5	
Technician	1.0	
Total	3.5	

Equipment Requirements

	Available	New
Two HPLC pumps	1	
RI detector	1	
WISP HPLC sample system	1	
Waters data module	1	
Contraves precision viscometer*	1	
Millipore water purification system	1	

* Shared with other projects.

122

PROJECT SCHEDULE AND MILESTONE

Project: Characterization of Polymer Fracturing Fluid System **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Evaluation of SEC system for HPG		∇	A										
		/////											
2. Degradation studies of modi- fied cellulose & guar gum						A	∇						
		/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
3. Correlate SEC and sand- pack results								A	∇				
		/////	/////	/////	/////	/////	/////	/////					
4. HP filter studies							A	∇					
		/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
5. Initiate conc. gel buildup degradation studies										A∇			
								/////	/////	/////	/////	/////	
6. Monitor viscosity of broken polymer solutions				A	∇			B	∇				
			/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Task	Milestone		Description
Task 1	(A)	November 30, 1983	Complete evaluation of SEC system to monitor HPG degradation
Task 2	(A)	April 1, 1984	Evaluate modified cellulose results and initiate degradation studies of guar gum
Task 3	(A)	May 31, 1984	Complete evaluation of SEC and Almond's sandpack results for modified cellulose and HPG
Task 4	(A)	April 30, 1984	Evaluate preliminary results on high pressure filter studies for SEC/Residue correlation to determine usefulness
Task 5	(A)	July 31, 1984	Select most favorable breaker for further study
Task 6	(A)	January 31, 1984	Correlate results on HPG
	(B)	May 31, 1984	Correlate results on modified cellulose

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report
(B) 30 days after end of each quarter .... Quarterly Technical Progress Report
(C)' 90 days after end of program year .... Annual Technical Progress Report

(Continuation Sheet)
PROJECT SCHEDULE AND MILESTONE

Project: Characterization of Polymer Fracturing Fluid System **Report Date:** ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
7. Prepare status report												A ▽ /////

Milestone	**Description**
Task 7 (A) September 30, 1984	Complete status report

OE2. RESERVOIR CHARACTERIZATION FOR EOR APPLICATION

Of all the EOR processes, chemical injection or chemical flooding has one of the highest potential payoffs. However, because of the high front-end investment and the high risk associated with chemical flooding, the development of this sophisticated technology is being delayed(1).

Therefore, three goals have been expressed for the Federal R&D program in chemical EOR(2):

(1) Increase process performance predictability to a level adequate for process design and risk assessment.

(2) Improve recovery efficiency to recover 43 percent of the residual oil-in-place and extend the scope of application to higher temperature and salinity reservoirs.

(3) Validate proof-of-concept with respect to improved process predictability, recovery efficiency, and applicability.

Much of BETC's work in the past has been aimed at mechanistic studies of the microscopic processes of oil displacement by chemical flooding. Important as this is, another problem must also be solved to increase oil recovery from many reservoirs--increasing the sweep efficiency. Recent diagnostic studies on field projects have shown that recovery was poor because of low sweep efficiency. This could be improved by better understanding of the geological setting of the reservoir, although geological surprises seem to be the norm in field work.

Another approach is to find better methods to measure the propagation of fluid fronts in the reservoir. Such improved methods could serve as tools to better develop understanding of lithologic and geologic variables affecting sweep efficiency. This is one topic where laboratory simulations are of limited value. The real problems lie in the field. The most effective way to speed research in this area would be to develop better measurement tools.

OE2A. FLUID FRONT MONITORING FOR CHEMICAL EOR

Background

This work addresses Item 6.1.1 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

One of the most critical problems for enhanced oil recovery is the lack of knowledge about reservoir characteristics away from the wellbore, which is important before application of a recovery process. A closely related problem arises after EOR initiation when we do know some characteristics, but cannot monitor process sweep (between wells) of the reservoir.

With present methods of reservoir evaluation, such as injectivity tests, pressure pulse testing, wellbore logging, and well-to-well seismic surveys, fluid flow patterns can only be determined after the project has been started. Even then, flow tests and observation wells are needed to track chemical slug progress. These tests often are not conducted as they interfere with project implementation.

Recovery process monitoring, which is synonymous with fluid front tracking, is a critical and well documented need. Process efficiency could be increased significantly if flow rates and injected materials could be adjusted in a timely manner in chemical EOR projects to achieve better sweep efficiency and control of expensive chemical flow patterns.

Thus, there is need for measurement methods both initially, when there may be only a few wells or boreholes, and later in the project when there is a pattern of wells.

Most of the available methods suffer because they measure properties only near the wellbore. And often these localized measurements are not precise, or they lose definition at the depths of most reservoirs. These measurement methods include seismic and wellbore-logging techniques. The problem is made more difficult because chemical flood fluids often differ little in measurable properties from the reservoir fluids.

One method that is being developed by Sandia Laboratories is the Audio-Magnetotelluric (AMT) geophysical prospecting technique and the NIPER staff has experience with the method(3). Unfortunately it does not appear to have sufficient sensitivity at typical reservoir depths. Also, Sandia has not attempted to apply it to EOR floods.

References

1. Gogarty, W. B., "Enhanced Oil Recovery Through the Use of Chemicals--Part 1," J.Pet.Tech., Sept. 1983, pp. 1581-1589.
2. Bartlesville Energy Technology Center,"Enhanced Oil Recovery R&D Program Plan - 1983," BETC, Bartlesville, Okla., June 1983.
3. Carroll, H. B., John Miller, and Ken Spence, "In Situ Combustion Project at Bartlett Kansas," 5th Annual Univ. of Kansas EOR Conference, 1980.

Objectives

To devise and evaluate theoretically the feasibility of one or more methods of measuring the front of chemical flood fluids in EOR under field conditions.

Scope of Work

This project is proposed as an exploratory feasibility study. A survey of the physical properties of EOR chemical flood fluids will be made along those of typical reservoirs to determine the range which measurement may attempt to detect. Additives will be considered to alter the properties (such as electrical) without interfering with recovery.

Geophysical properties of typical reservoir compositions will be cataloged, based on literature values, and compared with fluid properties to suggest properties that can serve as a basis for measurement.

Various physical effects will be considered as potential measurement means. These will include electromagnetic effects at various frequencies, sonic effects, and combinations. Methods of propagating these effects will be considered, including above-ground sources, taking advantage of wells and piping and of propagating layers such as aquifers and fractures. Methods will be evaluated by theoretical calculations for postulated geometries.

All of the above methods of cataloging and calculating will serve only as a framework to stimulate ideas. The objective of this exploratory phase of the work will be to generate novel ideas that can be tested and that may result in a breakthrough for potential field measurement technology.

Work Plans

Task 1 - Survey and catalog applicable physical properties of chemical EOR fluids and of reservoirs. Seek exploitable differences that will not interfere with EOR.

Task 2 - Explore geometries of signal sources and seek methods that concentrate on the desired structures to be measured. Calculate resulting propagation.

Task 3 - Postulate geometries of typical field petrographic and geologic conditions leading to sweep problems. Seek ways of taking advantage of these to detect perturbations in EM, acoustic, magnetic or other effects.

Task 4 - Formulate theories of signal source strengths, propagation, perturbation by structures, and sensitivity of response for typical assumed conditions. Evaluate postulated measurement methods by calculation. Use the results to focus better on the problem and to seek innovative solutions.

Task 5 - Summarize the evaluations. Report on the feasibility of the best approaches. Recommend whether further development of these approaches is worthwhile and if it is, propose further research.

Future Work

If warranted by the initial assessment and Bartlesville Project Office's recommendation, further simulations and laboratory testing of a selected technique may be made during FY85 and FY86.

Manpower Requirements

	Man-years
Senior Geophysicist	1.0
Petroleum Engineer	0.5
Total	1.5
IITRI Senior Electrical Engineer	0.3

Equipment Requirements

	Available	New
Water analysis-resistivity	1	
Formation resistivity at ambient and *in situ* conditions	1	
IBM personal computer	1	

PROJECT SCHEDULE AND MILESTONE

Project: Fluid Front Monitoring for Chemical EOR **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Survey state-of-the-art theory and application						A▽	B▽						
				/////	/////	/////	/////						
2. Assess AMT theory for sensitivity to EOR fluids vs depth							A▽		B▽				
						/////	/////	/////	/////				
3. Modify code for optimum sensitivity vs depth										A ▽	B▽		
									/////	/////	/////		
4. Run AMT code with various injection schemes										A ▽	B▽	C▽	
										/////	/////	/////	
5. Run chemical EOR to determine recovery efficiency										A ▽	B▽	C▽	
										/////	/////	/////	
6. Based on the theoretical study design AMT core flood system											A▽	B ▽	
											/////	/////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		Description
Task 1	(A) March 31, 1984	Select computer code for AMT
	(B) April 30, 1984	Complete survey of AMT application with S-O-A report
Task 2	(A) April 30, 1984	Complete adapting code to NIPER computer
	(B) June 30, 1984	Complete sensitivity study in various geologic sequences
Task 3	(A) July 15, 1984	Install initial code modification
	(B) August 31, 1984	Summarize recommended algorithms
Task 4	(A) July 15, 1984	Postulate several fluids and injection sequences and determine AMT sensitivity
	(B) August 31, 1984	Initial recommendation to BPO on the feasibility of continued study
	(C) September 30, 1984	Final study recommendation
Task 5	(A) July 31, 1984	Determine recovery efficiency of postulated fluids and injection sequences
	(B) August 31, 1984	Initial recovery efficiencies for optimum chemical EOR fluids & injections sequences
	(C) September 30, 1984	Final study recommendation to BPO
Task 6	(A) August 31, 1984	Initial recommendations to BPO of laboratory model
	(B) September 30, 1984	Final recommendations to BPO of laboratory ,model

Reporting Requirements

(A) 15 th of each month.................. Monthly Progress Report

(B) 30 days after end of each quarter......... Quarterly Technical Progress Report

(C)' 90 days after end of program year........ Annual Technical Progress Report

OE3. RECOVERY PROCESSES: CHEMICAL

This research program addresses the various chemical recovery agents: surfactants used to mobilize or solubilize oil; emulsion and water-soluble polymers to improve sweep efficiency, alkaline materials that interact with acidic crudes, or combinations of these substances. The research emphasis ranges from practical searches for improved agents to acquiring data for parameters to be used in modeling and prediction.

OE3A. IMPROVED CHEMICAL FLOODING AGENTS: SURFACTANT SYSTEMS

Background

This work addresses Items 6.1.2 and 6.1.4 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The project concerns the development of surfactants from a more applied consideration than Project BE4.

Investigations to test the contribution to surfactant performance of molecules with multiple sulfonate groups were underway at BETC for some time. It has been claimed that multiple sulfonation imparts greater salt tolerance (1); moreover, one might predict a different sensitivity to divalent cations than with monosulfonates, as the cation would be associated with only one anion instead of complexing two. It is worthwhile to verify and quantify these claims, information which might result in a new way to tailor surfactant slugs for improved recovery.

Another approach to improved surfactants is offered by recent research in Europe, which reports the biological production of surfactants having greatly superior properties for enhanced oil recovery. In laboratory tests, these surfactants have been found to require 1/100th the concentration of conventional surfactants for equal effectiveness. Furthermore, biological surfactants can reportedly be produced at a lower cost than conventional ones. However, these surfactants need a more thorough evaluation, e.g., to determine if they can perform as well under the variety of conditions to which they are exposed in a reservoir. It is also desirable to investigate their structure to understand better the chemistry that is responsible for their performance. If these surfactants truly work at lower concentrations and at lower cost, then this breakthrough in cost/performance will make surfactant flooding a successful process and increase the oil available by EOR.

The use of an efficient and effective protocol for testing surfactants is important. The first stage is laboratory "in vitro" measurements by techniques that are well established.

The second stage is experimental core flooding. These experiments also involve the interaction between injected fluid, connate fluid, and reservoir rock, along with dispersion and mobility effects. Laboratory tests must be properly scaled to take into account geometrical effects and parameters such as flow rates; thus, a computer simulator is of great value both in designing experiments and in interpreting results (2). Constant improvement in core flooding techniques (using modern electronic technology), and in modeling the processes, should be a part of surfactant systems testing.

The third stage in surfactant testing is pilot field testing. This achieves full-scale reality in terms of mineralogy, brine chemistry, live oil properties, handling, and injection problems. It also introduces the problem of sweep efficiency. It is therefore essential to carry out some evaluation of the reservoir to get meaningful results. Since this operation is expensive, it is important to emphasize that the reservoir is evaluated as a "tool" for measuring surfactant performance, and not evaluated as a producing property for the holder of the lease.

Personnel at BETC were deeply involved in the DOE surfactant-polymer test in the Delaware-Childers field of Oklahoma. This included installation and operation of field equipment and interpretation of the collected data. In addition, close contacts have been maintained with several industrial projects carried out under contract with DOE. This experience should enable the establishment of a field facility which could be used effectively.

References

1. Klaus, E. E. et al, "Generation of Ultralow Tensions Over a Wide EACN Range Using Penn State Surfactants, SPE 9784," Second Joint SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, Okla., April 5-8, 1981.

2. Camilleri, D., A. Fil, G. A. Pope, B. A. Rouse, and K. Sepehrnoori, SPE Paper 12083, Annual Technical Conference, San Francisco, Calif., October 5-8, 1983.

Objectives

To develop and verify performance in the field more efficient and economical surfactants for the chemical flooding process.

Scope of Work

The study of disulfonates will be carried through stages 1 and 2 as outlined in the background section. A model compound will be tested to make results more explicit.

The work on biosurfactants will be given the major effort. A representative compound of generic interest will be selected for initial study. Laboratory work will tailor the surfactant to a polymer and to a particular reservoir. The recovery performance will be compared with that using an established surfactant. In the field, a "minitest" designed for quick results will be run and interpreted. Later samples of surfactants will be analyzed for chemical structure and subjected to the same characterization.

In all the work, the program will be somewhat flexible, in that the results at one stage will affect the direction of later stages. Laboratory equipment will be developed so that during a flood test there will be automated control of rates, back pressures, and injection sequences; and automated logging of injected pressures, oil, and water production.

Special attention will be paid to scaling problems, and some experimentation will be done with radial systems and other geometries. The composition-scaling simulator for surfactant-polymer flooding from the University of Texas will be utilized, and modifications and other simulators will be considered as needed. The facilities will be expanded to allow for multiple simultaneous flood tests.

Work Plans

Task 1 - Compare phase and partitioning behavior of crude disulfonate with that of a low-molecular weight monosulfonate.

Task 2 - Study phase behavior of isomerically pure surfactant systems as a function of concentration and polysulfonation.

Task 3 - Automate core-flood system.

Task 4 - Adapt University of Texas micellar-polymer simulator in computer accessible to NIPER.

Task 5 - Compare linear versus radial core system.

Task 6 - Select a reservoir based on screening criteria.

Task 7 - From data of Task 6, select the pattern and the completion interval.

Task 8 - For selected reservoir, analyze brine and oil, determine wettability, get complete mineralogy and ion exchange character, measure relative permeabilities for evaluating design mobility, and determine dispersion coefficient.

Simultaneously with Tasks 7-8, carry out the following:

Task 9 - Install injection and monitoring equipment.

Task 10 - Obtain and evaluate biological surfactant by finding the optimal salinity at presumed reservoir temperature for a set of alkanes.

Task 11 - At optimal salinity and with crude at reservoir temperature, determine solubilization parameter, viscosity, stability of macroemulsions, and the partitioning of alcohol. Decide if suitable for field test.

Task 12 - Perform continuous slug injection tests and make indicated adjustments in composition to fine tune the slug. Compare recovery efficiency of biosurfactant.

Task 13 - Compare recovery efficiency of biosurfactant with an optimized slug of TRS 10-410/TBA.

Task 14 - Determine concentration and salinity of polymer slug for favorable mobility.

Task 15 - Perform short-core and long-core flood tests.

Future Work

Four years will be required for the design and performance of a pilot test. At the end of two years laboratory work will start on a second biosurfactant, including characterizing its chemical structure.

Manpower Requirements

	Man-years
Research Chemist	1.0
Senior Chemist	0.3
Research Chemist	0.5
Technician	0.5
Associate Chemist	1.0
Associate Petroleum Engineer	0.5
Total	3.8

Equipment Requirements

	Available	New
Core flood equipment	1	1
SEM/X-ray	1	
Spinning drop tensiometer	2	
Brookfield and Contraves LS viscometers	1	
Centrifuge for wettability	1	
Size exclusion chromatograph	1	
Liquid and gas chromatographs with various detectors	1	
Instrument trailer for monitoring injection rate, pressure, and quality control	1	
Hardware for site development		1

PROJECT SCHEDULE AND MILESTONE

Project: Improved Chemical Flooding Agents: Surfactant Systems

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
1. Obtain biosurfactant	//////	//////	A▽ //////									
2. Crude disulfonate												
3. Pure disulfonate			//////	A▽ //////	//////	//////	//////	//////	B▽ //////	//////	//////	//////
4. One-core system	//////	//////	A▽ //////									
5. Simulator	//////	//////	A▽ //////									
6. Radial cores												A▽ //////
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'

Manpower/Manyears

Milestone		Description
Task 1	(A) December 31, 1983	Obtain surfactant
Task 2	(A) December 31, 1983	Complete exploratory studies on crude disulfonate
	(B) April 30, 1984	Prepare abstract for submission to SPE
Task 3	(A) January 15, 1984	Negotiate contract for synthesis
	(B) June 30, 1984	Receive delivery on material and test for purity
Task 4	(A) December 31, 1983	Complete one-core system
Task 5	(A) December 31, 1984	Adapt simulator to available equipment
Task 6	(A) September 30, 1984	Prepare initial eouipment design for discussion

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

(Continuation Sheet)
PROJECT SCHEDULE AND MILESTONE

Project: Improved Chemical Flooding Agents: Surfactant Systems

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
7. Reservoir selection				//////	//////	//////	A ▽ //////					
8. Select pattern							//////	//////	//////	//////	//////	A ▽ //////
9. Reservoir data							//////	//////	//////	//////	//////	A ▽ //////
10. Install equipment											//////	//////
11. Evaluate surfactant				//////	//////	A▽ //////	//////					
12. Slug screening								//////	//////	//////	A ▽ //////	
13. Fine tuning										//////	//////	//////

Milestone		Description
Task 7	(A) April 30, 1984	Decision on acceptability of candidate reservoir
Task 8	(A) September 30, 1984	Decision whether to proceed with site development
Task 10	(A) March 31, 1984	Complete determination of optimal salinity
Task 11	(A) August 31, 1984	Decision: is surfactant good for field test

PROJECT SCHEDULE AND MILESTONE

Project: Improved Chemical Flooding Agents: Surfactant Systems

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
14. Compare with TRS												//////	
15. Polymer slug						//////	//////	//////	//////	//////	//////	//////	
16. Lab flood tests											//////	//////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone **Description**

Reporting Requirements
(A) 15 th of each month . . . . Monthly Progress Report
(B) 30 days after end of each quarter . . . . Quarterly Technical Progress Report
(C)' 90 days after end of program year . . . . Annual Technical Progress Report

OE3B. MOBILITY CONTROL AGENTS

Background

This work addresses Item 6.1.3 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Effective mobility control agents contribute significantly to the oil recovery from most EOR field projects. Polymers are needed for controlling dynamic mobility so as to produce a coherent displacement front in chemical floods. Blocking agents, such as foams or emulsions, are particularly useful in gas displacement and steamflood projects.

Polymers are affected by some of the same factors as are surfactants (concentration, salinity, divalent ions) and also by degradation from mechanical, chemical or biological effects. Earlier laboratory work showed that no effective methodology for estimating the effect of salinity changes and polymer dilution was available. However, it was found that systemization of these effects was possible and that degradation could be detected (1). A similar systematization for flow resistances in cores, which are influenced by extensional and elastic effects, is proposed. These factors are more sensitive to degradation than shear viscosity. Their role is dependent on pore geometry, so more than one core type must be used.

If the enthalpy of the degradation reaction is of sufficient magnitude, a microcalorimetric technique should be capable of comparing degradation rates of different polymers and the influence of solids and fluid chemical composition. This would give information on polymer stability in a few hours or days which would otherwise require months, and therefore shorten the screening process.

A number of substances have been proposed for improving mobility control. Besides polymers, these include suspensions, emulsions, and foams. Recently, the use of foam for flow diversion (blocking) has been investigated extensively. However, the mechanism of foam blocking and its efficacy are not clear. During steamflooding there are rapid vaporization-condensation processes occurring in foams. These processes would be absent with the use of macroemulsions, which have been used in waterflooding, and suggest an appealing alternative to foam (2). Research needs include production of homodisperse emulsions of controlled droplet size, and the maintenance of stability--especially at steamflood temperatures. An ideal emulsion for mobility control in steamfloods will be one with the following properties:

(1) low initial bulk viscosity
(2) high interfacial viscosity
(3) relatively high interfacial tension to generate large enough droplets to block pore throats
(4) the surfactant soluble in the external phase, such that diffusion will not eliminate interfacial gradients
(5) film elasticity not affected by high temperature.

References

1. Lorenz, P. B., and M. K Tham, "Calcium Effects in the DOE Surfactant-Polymer Pilot Test," SPE Paper 9814, Second Joint DOE/SPE Symposium on Enhanced Oil Recovery, Tulsa, Okla., April 5-8, 1981.
2. McAuliffe, C. C., "Oil-in-Water Emulsions Improve Fluid Flow in Porous Media," SPE Paper 3784, Symposium on Improved Oil Recovery, Tulsa, Okla., April 1972.

Objectives

To investigate alternate methods of mobility control.

Scope of Work

The rheological behavior (flow resistance as a function of flow rate) of polymer solutions and macroemulsions in porous media will be examined, with systematic variations in polymer concentration, salinity, divalent ion content, and temperature. Such measurements will be made with two diverse types of porous media and two diverse types of polymer. The porous media will be characterized by capillary pressure curves for pore size distribution. The polymers will be characterized by external measurement on shear and screen viscometers at various rates. The polymers will be degraded thermally or mechanically and remeasured.

There are eight rheological parameters--shear viscosity, screen factor, mobility in two porous media, and a rate variation parameter for each. The data will be examined to correlate these parameters with composition and temperature. This will lead to:

(1) a comprehensive picture of the behavior of polymers under a variety of conditions.
(2) a detailed idea of how this behavior is altered by degradation.
(3) knowledge of the fidelity with which external measurements characterize mobility behavior under changing conditions.

Microcalorimetric measurements for evaluation of polymer stability will be made at temperatures up to 150°C. Experiments will be made on the various polymer types used in EOR (polysaccharide, polyacrylamide, various degrees of hydrolysis, various molecular weights). The effect of variations in salinity, divalent ion concentration and pH will be tested in the presence of clays.

Exploratory work will be conducted on the generation of macroemulsions that are stable and monodisperse. Experiments on their use as blocking agents will be focused on the elevated temperatures representative of steamfloods.

Work Plans

Task 1 - Make a systematic study of flow resistivity of a selected polyacrylamide as a function of salinity, concentration, temperature, and flow rate in Berea core; compare with measurements on shear viscometer and "screen viscometer." Degrade the polymer and repeat.

Task 2 - Acquire microcalorimeter apparatus and perform feasibility tests on detection of polymer instabililty.

Task 3 - Characterize a second type of permeable medium to be selected and repeat measurements made on Berea in Task 1.

Task 4 - Select a second polymer for tests of Tasks 1 and 3.

Task 5 - Selection of surfactants for production of macroemulsions.

Task 6 - Prepare emulsions from surfactants and oil and also from acid crude and alkali.

Task 7 - Measure the stability of the emulsions at 120°C and under 500 psi pressure, in contact with N_2, brine, and crude oil.

Task 8 - Measure the average droplet size of the emulsion using microscopy or Coulter counter.

Task 9 - Measure the viscosity of the emulsion for shear rate from 0.01 sec^{-1} to 10 sec^{-1}.

Task 10 - Inject emulsion into Berea sandstone with pore size distribution matched with emulsion sizes and determine if there is any blocking of flow.

Task 11 - Repeat on a core containing oil after waterflood.

Task 12 - Correlate and analyze data.

Future Work

Extend microcalorimeter work if possible, continue polyacrylamide and macroemulsion work and make recommendation for continuance in FY85. In FY86 complete polyacrylamide work.

Manpower Requirements

	Man-years
Senior Chemist	0.2
Assistant Petroleum Engineer	0.5
Research Chemist	0.5
Research Engineer	1.0
Technician	0.5
Total	2.7

Equipment Requirements

	Available	New
Microcalorimeter		1
LS 30 viscometer	1	
Core flooding equipment	1	
SEM	1	
Light Microscope	1	
Coulter Counter	1	

PROJECT SCHEDULE AND MILESTONE

Project: Mobility Control Agents **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Polyacrylamide/Berea	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	///// A▽	
2. Microcalorimeter	/////	/////	/////	/////	/////	///// A▽							
3. Polyacrylamide/other core							/////	/////	///// A▽	/////	/////	/////	
4. Other polymer										/////	/////	///// A▽	
5. Surfactant selection				/////	/////	///// A▽							
6. Prepare emulsions				/////	/////	/////	///// A▽						
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone			Description
Task 1	(A)	September 30, 1984	Complete study on polyacrylamide/Berea system
Task 2	(A)	March 31, 1984	Complete feasibility study and recommend continuance/termination
Task 3	(A)	June 30, 1984	Complete characterization of core
Task 4	(A)	September 30, 1984	Complete preliminary study of viscosity and screen factor
Task 5	(A)	March 31, 1984	Surfactant selected
Task 6	(A)	April 30, 1984	Candidate emulsions prepared

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

(Continuation Sheet)
PROJECT SCHEDULE AND MILESTONE

Project: Mobility Control Agents **Report Date:** ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
							A ∇					
7. Measure stability				/////	/////	/////	/////					
								A ∇				
8. Measure drop size							/////	/////				
										A∇		
9. Measure viscosity								/////	/////	/////		
										A ∇	A	
10. Coreflood I								/////	/////	/////	/////	
										A ∇		
11. Coreflood II										/////	/////	/////
												A∇
12. Analyze data											/////	/////

Milestone			Description
Task 7	(A)	April 30, 1984	Progress review to discuss results and orient project direction
Task 8	(A)	May 31, 1984	Complete drop size measurements
Task 9	(A)	July 31, 1984	Complete viscosity measurements
Task 10	(A)	July 31, 1984	Second progress review
Task 11	(A)	July 31, 1984	Second progress review
Task 12	(A)	September 30, 1984	Complete analysis report

OE3C. ALKALINE FLOODING

Background

This work addresses Items 6.1.4 and 5.1.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Alkaline flooding is attractive because of its low initial cost. Earlier field tests were usually unsuccessful, mainly due to the small amount of alkali used. Recent advances in alkaline research point to the importance of understanding crude oil-alkali, rock-alkali, and crude oil-rock-alkali interactions. Alkaline flooding relies upon the generation of surfactant (due to alkali-crude oil interaction), and the subsequent interfacial tension reduction for oil mobilization. Hence, the kinetics of the alkali-crude oil interaction affects the oil recovery efficiency to a considerable extent. On the other hand, injected alkali is consumed due to reaction with clay minerals and silica in reservoir rocks, reducing the amount of alkali available for oil recovery. Especially important is the long-term effect of these alkali-crude oil-rock interactions (1). To understand the alkaline flooding process properly, there is a need to study these interactions and to model the reaction kinetics so as to be able to predict their behavior over time.

In addition, the need for proper mobility control to increase sweep efficiency is well known. The polymers traditionally used in EOR mobility control are expected to be affected by the salinity, temperature and high pH of the alkaline slug and, therefore, their viscosity and flow resistance are expected to change. Very little information is available in the literature and research work on the effect of these parameters on polymer flow is warranted.

Another important research area is the study of combination methods, such as alkali-surfactant and alkali-thermal flooding. These methods have shown some promise in improving oil recovery (2).

References

1. Mayer, E. H., R. L. Berg, J. D. Carmichael, and R. M. Weinbrandt, "Alkaline Injection for Enhanced Oil Recovery--A Status Report," SPE Paper 8848, presented at Symposium on Enhanced Oil Recovery, April 20-23, 1980.

2. Rosmalen, R. J. and F. Th. Hesselink, "Hot Caustic Flooding," 1981 European Symposium on Enhanced Oil Recovery, Bournemouth England, Sept. 21-23, 1981, Proceedings, pp. 573-577.

Objectives

To develop a theory and model for alkaline flooding.

Scope of Work

The kinetics of alkali-crude oil and alkali-rock interactions will be studied. To predict the long-term effect of these interactions, a mathematical model will be developed to describe these reaction kinetics. Initially, reactions will be measured with oil and minerals representative of the Wilmington Basin, at temperatures representative of that reservoir. Alkaline agents used will be sodium hydroxide, sodium orthosilicate, and sodium carbonate at selected concentrations and brine composition.

The reaction kinetics model will be incorporated into a compositional simulator to simulate alkaline flooding. Laboratory experiments will be designed to test the long-term effects mentioned above and to test the simulator.

Cooperation will be sought from industrial operators of alkaline projects to carry out post-flood diagnostic evaluations as a guide to further research and improved design. The effect of pH on polymer viscosity will be studied. Exploratory research in alkali-surfactant flooding will be initiated to extend previous work in this area.

Work Plans

Task 1 - Measure and model reaction kinetics for NaOH at three concentrations with silica and a selected clay (at reservoir temperature).

Task 2 - Repeat Task 1 for sodium orthosilicate.

Task 3 - Repeat Task 1 for sodium carbonate, if feasible at reservoir temperature.

Task 4 - Repeat Task 1 for all three alkaline agents with Wilmington oil.

Task 5 - Use the results to develop an improved alkaline flooding simulator.

Task 6 - Negotiate for conducting a post-flood evaluation and design the test.

Task 7 - Correlate polymer viscosity, screen factor, and flow resistance factor as a function of pH, salinity, and temperature (in connection with Project OE3B).

Future Work

Reaction kinetics study with Wilmington oil and polymer viscosity measurements will be completed in FY85, while simulation work and post-flood evaluation will be continued. In FY86, reaction kinetics will be extended to other minerals and work on post-flood evaluation will be continued.

Manpower Requirements

	Man-years
Research Chemical Engineer	1.0
Technician	1.0
Total	2.0

Equipment Requirements

	Available	New
Reactors		3
L.S. 30 viscometer	1	
Spinning drop interfacial tensiometer	1	
Brookfield viscometer	1	
Screen factor apparatus	1	

PROJECT SCHEDULE AND MILESTONE

Project: Alkaline Flooding **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
1. Reaction studies - NaOH/mineral									A▽			
				/////	/////	/////	/////	/////	/////			
2. Na_4SiO_4/mineral												A▽
							/////	/////	/////	/////	/////	/////
3. Na_2CO_3/mineral												A▽
										/////	/////	/////
4. Alkali/oil												A▽
												/////
5. Develop simulator & flood tests												A▽
												/////
6. Post-flood evaluation						A▽			B▽			C▽
				/////	/////	/////	/////	/////	/////	/////	/////	/////
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'

Milestone			**Description**
Task 1	(A)	June 30, 1984	Complete reaction studies
Task 2	(A)	September 30, 1984	Complete measurements
Task 3	(A)	September 30, 1984	Complete measurements
Task 4	(A)	September 30, 1984	Adapt reactors for use with oil
Task 5	(A)	September 30, 1984	Compile list of candidate simulators
Task 6	(A)	March 30, 1984	Establish contact and preliminary agreement with operator
	(B)	June 30, 1984	Complete first-draft design for discussion
	(C)	September 30, 1984	Finalize design and contract

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report
(B) 30 days after end of each quarter .... Quarterly Technical Progress Report
(C)' 90 days after end of program year .... Annual Technical Progress Report

(Continuation Sheet)

PROJECT SCHEDULE AND MILESTONE

Project: Alkaline Flooding **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
7. Polymer visc	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	//// A▽

Milestone		Description
Task 7	(A) September 30, 1984	Complete measurements

OE4. RECOVERY PROCESSES: THERMAL RECOVERY

Thermal recovery processes fall into two classes: those in which a hot fluid is injected into the reservoir and those in which heat is generated within the reservoir (1). The first class includes injection of hot water or steam often with the addition of additives to improve mobility control and sweep efficiency. In situ combustion, or fireflooding, is an example of the second class of thermal recovery processes. Thermal processes, which reduce the flow resistance of reservoir fluids by reducing the viscosity of the crude, have been the chief means of improving the recovery of viscous crudes. The proposed work has as its goal the identification of those factors which affect the efficiency of thermal recovery methods and the development of techniques with which to improve that efficiency.

OE4A. STEAMFLOODING

Background

This work addresses Item 6.1.3 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

Steamflooding of heavy oil is a commercially successful and technically mature process. In 1982, over 70 percent of the U.S. enhanced oil recovery was due to steamflooding (2). Recently, there has been interest in expanding the scope of steamflooding to include light oil recovery (2-7). Although the potential recovery of light oil is greater with a steamflood than from a waterflood, waterflooding is well-known, economically attractive, and has only a moderate failure risk. On the other hand the technology of light oil steamflooding is not as familiar and therefore the risk of failure may be higher (5).

The 1983 BETC Enhanced Oil Recovery R&D Program Plan (June 1983) states that "recovery efficiency in applying steam drive to light oil reservoirs is better than that for similar heavy oil reservoirs, although the generally lower residual oil saturation of light oil reservoirs may limit application." In a laboratory investigation of steamflooding cores containing light oil, which previously had been waterflooded (3), it was found that steam injection can recover substantial amounts of crude oil even after waterflooding. Post waterflood recovery in depleted oil systems should be seriously considered for steam drive along with other exotic EOR techniques. The acceptance of the light oil steamflooding process is hampered by the lack of knowledge on the criteria for choosing crude oils, and on the mechanisms of the recovery process. Information on the fluid flow characteristic at the steam condensation zone are also required for proper simulation of the process. There has not been any study on the identification of screening criteria for crude oil for steamflooding. Work in this area is needed. A study in the 1960's (8) suggested that (a) thermal expansion, (b) viscosity reduction, (c) gas drive, (d) solvent, and (e) distillation effect are the principal mechanisms in the steamflooding process. There is, however, a need to elucidate the most important mechanism in light oil steamflooding.

The physics of fluid flow in the condensation front of steamflooding is an important parameter needed for the simulation of this recovery process. Scaling rules and physically scaled models have been used in the development of recovery processes (1, 9-12), and can be very useful for determining the physics of fluid flow and the effects of reservoir and fluid parameters on the performance of proposed field projects (12).

The primary factor affecting the oil recovery, and thus the economics, of steamflooding is the sweep efficiency. Effects of gravity and permeability variations on the lateral movement of fluids are the cause of much of the oil being bypassed in the reservoir. The use of foams or emulsions for better mobility control and increased sweep efficiency for steamflooding in light oil reservoirs needs to be investigated.

References

1. Prats, M., "Thermal Recovery," Monograph No. 7, Society of Petroleum Engineers, 1982.
2. Hammorohaimb, E. C., V. A. Kuushara, "Recovery Efficiency of Enhanced Oil Recovery Methods: A Review of Significant Field Tests," SPE Paper 12114, presented at the 58th Annual Technical Conference, San Francisco, Calif., 1983.
3. Crichlow, H. B., "Maximizing Steam Drive Recovery in Light Oil Reservoirs," Final Report, DOE/BC/10316-26, 1983.
4. Aydelotte, S. R., A. B. Ramesh, "Economic Feasibility of Steam Drive in Light Oil Reservoirs," Final Report, DOE/BC/00044-1, 1979.
5. Hanzlik, E. J., "Steamflooding as an Alternative EOR Process for Light Oil Reservoirs," SPE Paper 10319, presented at the 56th Annual Technical Conference, San Antonio, Texas, 1981.
6. Cheung, Y. L., A. Brown, W. S. Huang, "A Laboratory Study of the Tapered-Quality Steam-Water Process on Light Oil," SPE Paper 12005, presented at the 58th Annual Technical Conference, San Francisco, Calif., 1983.
7. Blackwell, R. J., "State of the Art Review of Enhanced Oil Recovery from Light Oil Reservoirs," in Proceedings, Symposium on Technology of EOR in Year 2000, DOE/ET/2628-1, 1980.
8. Geertsma, J., G. A. Cross, N. Schwartz, "Theory of Dimensionally Scaled Models of Petroleum Reservoirs," Trans. AIME, Vol. 207, 1956, pp. 118-123.
9. Stegemeier, G. L., D. D. Laumback, C. W. Volek, "Representing Steam Processes with Vacuum Models," Soc. Pet. Eng. J., June 1980, pp. 151-174.
10. Binder, G. G., et al., "Scaled-Model Tests of In-Situ Combustion in Massive Unconsolidated Sands," Proc. 7th World Petr. Congress, Vol. 3, 1967, p. 477.
11. Doscher, T. M., W. Huang, "Steam Drive Performance Judged Quickly from Use of Physical Models," Oil and Gas J., Oct. 22, 1979, p. 52.

Objectives

To determine the effects of oil and rock properties on recovery efficiency during steamflooding of light oil reservoirs and to investigate the physics of fluid flow at the steam condensation front.

Scope of Work

In order to investigate the effect of rock and fluid properties on the recovery efficiency of the light oil steam drive process, steamflooding experiments will be conducted using linear cores of different wettability and a variety of crude oils having distinct physical and chemical characteristics. Further, the physics of fluid flow at the steam condensation front will be investigated.

The effect of fluid properties on steamflooding recovery efficiency will be investigated by using eight different crude oils having different chemical and physical characteristics. The effect of distillation characteristics and chemical composition will be determined separately. The relative effect of distillation, viscosity reduction, thermal swelling, solution gas drive, and solvent extraction on recovery efficiency will be determined. Experiments will be conducted on a single core and will extend from initial injection of steam, through breakthrough, and continue until oil production ceases. All produced fluids will be analyzed, viscosity measured, and temperatures throughout the core will be recorded. From these data, physical properties of crude oil amenable to steamflooding will be proposed, and the most important recovery mechanism will be identified.

The above experiments will also provide some estimation on the relative importance of capillary pressure and wettability on oil recovery. To obtain additional information, a series of coreflooding experiments on a given oil will be performed. Cores of different pore sizes and wettability will be used. The wettability modification method developed in project BE4A will be applied.

To investigate the physics of fluid flow at the steam condensing front a scaled physical model will be used. Initially, the flow behavior of various fluids at the steam condensation front in an oil recovery experiment will be observed and recorded photographically if possible. The zones of different flow behavior will be identified. Simplified models representing each flow zone will be proposed, and experiments performed to study the physics of flow of each zone separately. The information will be combined in a model to describe the physics of fluid flow at the condensation front in a steam flooding process.

Work Plans

Task 1 - Using linear cores, determine the recovery of eight selected crude oils with different distillation and physical characteristics to investigate the effect of crude oil properties on oil recovery efficiency. The produced oil fractions will be analyzed to determine the relative effect of distillation, viscosity, and composition changes on recovery efficiency.

Task 2 - With a given oil and linear cores of different wettability and pore sizes, determine the effect of capillary on recovery efficiency.

Task 3 - Using a three-dimensional scaled physical model, perform steamflooding experiments to study the multiphase fluid flow behavior at the condensation steam front. Model systems will be developed of one, two, and three phase flows to simulate these flow behaviors in order to describe the complex fluid flow behavior observed above.

Future Work

Tasks 1-3 will be continued and phase behavior of distillable oil components at steamflood condition will be investigated. Effects of superheated steam, steam injection rate, free gas saturation, and high initial water saturation on recovery will also be determined. The influence of crude oil property on steam consumption will be investigated. A scaled physical model will be used to investigate the effect of well depth, well spacing, pay thickness, and pattern configuration on yields of the light oil steamflooding process. The use of additives (foam or emulsion) to improve sweep efficiency will be studied. Experimental results will be used to test existing mathematical reservoir models and to develop screening models.

Manpower Requirements

	Man-years
Research Petroleum Engineer	1.5
Associate Chemical Engineer	0.5
Technician	1.0
Total	3.0

Equipment Requirements

	Available	New
Steam generator and superheater	1	
Data acquisition computer	1	
Scaled physical model		1

PROJECT SCHEDULE AND MILESTONE

Project: Steamflooding **Report Date:** ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Evaluate scaling factors			//////	//////	A▽ //////								
2. Design and fabricate instrument						//////	//////	//////	//////	A▽ //////			
3. Perform steamflooding											//////	A▽ //////	
4. Prepare report											//////	A▽ //////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone			Description
Task 1	(A)	February 29, 1984	Scaling parameters determined
Task 2	(A)	August 1, 1984	Scaled model fabricated and tested
Task 3	(A)	September 30, 1984	Crude oil selected
Task 4	(A)	September 30, 1984	Complete report

Reporting Requirements
(A) 15 th of each month..................Monthly Progress Report
(B) 30 days after end of each quarter.........Quarterly Technical Progress Report
(C)' 90 days after end of program year........Annual Technical Progress Report

OE4B. IN SITU COMBUSTION

Background

This work addresses Item 6.1.7 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The *in situ* combustion process for enhanced oil recovery has been the topic of extensive research (1). The 1983 BETC Enhanced Oil Recovery R&D Project Plan (June, 1983) proposed "... to study the basic reaction mechanisms, with an emphasis on reaction kinetics, that could improve design. A coherent set of relationships between operating parameters, reservoir variables, and process results will improve site and zone selection, process design, and, hopefully, recovery efficiency of *in situ* combustion projects." This project addresses that part of the Project Plan.

Most laboratory investigations have been combustion tube experiments (2-5). These experiments provided data on fuel availability, combustion-front velocity, oxidant requirements, produced fluids composition, and reaction kinetics. In addition, it has been shown that some minerals or metals have a catalytic effect on combustion kinetics (5-8). Since combustion tube experiments are time-consuming, most of these experiments were performed on specific reservoir systems intended for field projects. Systematic investigations of the catalytic effect of metals often associated with crude oil on combustion and hydrocarbon reaction kinetics have not been reported. Such kinetic data can be determined readily and efficiently by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (9-10). Results from DSC and TGA experiments include heats of reaction, ignition temperatures, amount of oxidant consumed during reaction, important kinetic parameters such as apparent activation energy, and preexponential factor.

Data from DSC experiments are based upon the difference in temperatures between a known reference material and a sample material as both are heated in a calorimeter chamber. Data from TGA experiments are based upon the weight lost from a sample as the temperature of the sample is raised in an oxidant such as oxygen or air. The weight lost due to evaporation can be determined by heating the sample in a non-oxidizing atmosphere such as nitrogen. These methods are rapid and accurate, and therefore can be applied in a program to elucidate quantitatively the effect of crude oil metal components and core material on the kinetics of the combustion process. This information is important for predicting performance of combustion projects and can be used in existing design and economic models for the design of pilot projects and for economic evaluation of proposed *in situ* combustion field projects.

References

1. Chu, C., "Current In Situ Combustion Technology," J. Pet. Tech., Aug. 1983, pp. 1412-1418.

2. Fassihi, M. R., H. J. Ramey, Jr., and W. E. Brigham, "Laboratory Combustion Tube Studies," Final Report SUPRI-TR 22, DOE/ET/12056-22, 1982.

3. Allag, O., "Experimental Investigation of the Kinetics of Underground Dry, Forward Combustion," Ph.D. Dissertation, University of Tulsa, 1978.

4. Penberthy, W. L., Jr., and H. J. Ramey, Jr., "Design and Operation of Laboratory Combustion Tubes," Soc. Pet. Eng. J., June 1966, pp. 183-198.

5. Gurenir, J. J., "The Development of an Automated In Situ Combustion Assembly to Study Effects of Clays on the Dry Forward In Situ Combustion Process," Ph.D. Dissertation, University of Kansas, 1980.

6. Burger, J. G., and B. C. Salinquet, "Chemical Aspects of In Situ Combustion--Heat of Combustion and Kinetics," Soc. Pet. Eng. J., Oct. 1972, pp. 410-422.

7. Gadelle, C. P., et al., "Heavy Oil Recovery by In Situ Combustion--Two Field Cases in Rumania," J. Pet. Tech., Nov. 1981, pp. 2057-2066.

8. Bardon, C., and C. Gadelle, "Essai de Laboratoire Pour L'Etude de la Combustion In Situ," Inst. Francaise du Petrole, Paris, 1977, referenced in Brigham, W.E., DOE/ET/12056-24, 1982.

9. Wayland, J. Robert, D. D. Lee, T. M. Masias, "On the Application of TG Concepts of In Situ Combustion Processes," SAND-83-0336, 1983.

10. Jha, K. N., "Application of Thermal Analytical Techniques to Enhanced Oil Recovery," ACS Div. of Pet. Chem. Preprints, Vol. 28, No. 5, 1983, pp. 1176-1189.

Objectives

To determine the effects of various metals and minerals, often associated with oils and reservoir material, on the kinetic parameters of combustion and cracking which occur during in situ combustion.

Scope of Work

Thermal analytic experiments, including differential scanning calorimetry and thermal gravimetric analysis will be performed using a variety of oils (crude and refined) and reservoir substrates. The kinetic parameters obtained in these experiments will be correlated with the metal (vanadium, nickel, etc.) and mineral (alumina, silica, etc.) content of the oils and reservoir material. These kinetic data and composition correlations can be used to modify existing design and economic models for evaluating the in situ combustion process. Data will be evaluated and results incorporated into the DOE/NPC process models.

Work Plans

Task 1 - Select heavy crude oils containing different amounts of metals such as vanadium and nickel. Select reservoir rock materials containing different amounts of such minerals as alumina and silica.

Task 2 - Obtain thermal gravimetric analysis equipment and differential scanning calorimeter, and calibrate with known apparatus.

Task 3 - Perform thermal gravimetric analysis and differential scanning calorimetric experiments on combinations of the oils and rock selected in Task 1.

Task 4 - Evaluate results and draw conclusions regarding application to in situ combustion process models.

Future Work

Perform thermal gravimetric analysis and differential scanning calorimetry on additional crude oils. Reaction kinetics will be correlated with metal contents of crude oil, and mineral content of clay to determine catalytic effect.

Manpower Requirements

	Man-years
Research Chemical Engineer	1.0
Research Petroleum Engineer	0.5
Associate Chemical Engineer	0.5
Technician	1.0
Total	3.0

Equipment Requirements

	Available	New
Thermal gravimetric analysis		1
Differential scanning calorimeter		1

PROJECT SCHEDULE AND MILESTONE

Project: In Situ Combustion **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Materials selection				/////	/////	▽A /////							
2. Set up TGA & DSC and test						/////	▽A /////						
3. TGA and DSC experiments							/////	/////	/////	/////	▽A /////	/////	
4. Evaluate results												▽ A /////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ[1]	

Milestone			Description
Task 1	(A)	March 31, 1984	Selection of crude oils and reservoir rock complete
Task 2	(A)	April 1, 1984	Set up and testing TGA and DSC complete
Task 3	(A)	August 30, 1984	TGA and DSC analysis complete on a suite of crude oils with varying vanadium and nickel content
Task 4	(A)	September 30, 1984	Determine need for modification to FE-NPC process model

Reporting Requirements
(A) 15 th of each month . . . . Monthly Progress Report
(B) 30 days after end of each quarter . . . . Quarterly Technical Progress Report
(C)[1] 90 days after end of program year . . . . Annual Technical Progress Report

OPT1. THERMOPHYSICAL PROPERTIES OF REAL AND SYNTHETIC FLUID MIXTURES DERIVED FROM FOSSIL SUBSTANCES

Background

This work addresses Item 6.2.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

In the processing and refining of materials derived from fossil sources, two-phase systems are often encountered in which a multicomponent gaseous phase is in equilibrium with a complex liquid at high temperature and pressure. Problems arise in predicting the conditions where the phase separations will occur and in predicting the thermodynamic properties of the individual single phases. Systems that involve primarily hydrocarbons have been handled in the processing of light petroleum for many years, and equations of state have been developed that enable one to adequately predict phase behavior when sufficient analytical data are available. For fluids derived from heavy ends of light petroleum, heavy petroleum, shale oil, and coal, the prevalence of polar, heteroatom-containing compounds of oxygen, nitrogen, and sulfur render earlier developed correlations and equations of state inadequate-to-useless. It is impossible, even from good composition data, to design efficient separation units and to predict pressures to be expected at a given temperature. Hence, it is difficult to predict the size and strength of reaction and separation vessels required or even to meter the amounts of materials in processing streams that are ultimately produced.

The measurement and control of fluid flow are vital in all phases of processing. Fluid-flowmeter results are strongly dependent on computed values of the speed of sound in fluids. Presently used correlations cannot reliably predict the meager sonic data available for fluids. Additional experimental results are needed to determine the source of the deficiencies in the equations of state used in the correlations. In the research laboratories operated by NIPER, there is a well-proven experimental facility for providing the high accuracy speed-of-sound data required for fluids.

The NIPER processing and thermodynamics laboratories have highly experienced personnel in the measurement of speed-of-sound and pressure-volume-temperature relationships of pure fluids and simple mixtures of pure fluids. Other personnel have experience in state-of-the-art methods for the identification of compounds encountered in a variety of organic fossil materials. This expertise was focused several years ago upon development of methods for determining solubility of hydrogen and other light gases in liquids derived from coal conversion processes. Techniques were developed to determine vapor and liquid equilibrium compositions for complex liquids in the presence of mixtures of light gases. Such systems are also encountered in other fossil systems, such as those derived from heavy petroleum, shale oil, and heavy ends of light petroleum. The expertise of the laboratory is being utilized today to study solubilities of selected gases in solutions of model binaries and in real fluids derived from synthetic fuel conversion processes.

The research is within the purview of the Advanced Research and Technology Development program of DOE/Fossil Energy; however, it addresses problems common to many synthetic fuel processes.

Objectives

To provide fundamental data for the correlation and prediction of properties of fluids containing heteroatoms for which present data are too inaccurate to permit efficient design of confinement, separation, and fluid transport systems in plants in the fossil fuels industry.

Scope of Work

Studies will be made on complex mixtures which are prepared from pure materials and which simulate interactions that present severe problems in predicting the properties of process fluids from the synthetic fuels industry. Studies will also be made on fluids taken directly from synfuel conversion plants and which have carefully documented histories of plant conditions. To ensure that this work fully utilizes related work on these materials, studies will be made on samples being subjected to complementary studies by other organizations. Samples will be obtained from the Pittsburgh Energy Technology Center where detailed separations and identification of components will be made and where first-cut engineering characterization measurements such as viscosity, density, etc., near ambient conditions will be made. The experimental results will be subjected to extensive modeling calculations at the University of Oklahoma to help focus on the areas that require further attention and to show where data needs have been met.

In the experimental studies of this work the samples with equilibrium compositions will be taken from a stirred autoclave suitable for operation to temperatures of 400°C and pressures of 4000 psi. The samples will be analyzed by gas expansion and by a variety of chromatographic, mass spectral, spectroscopic, and other chemical techniques suitable for complex mixtures. The presently employed vapor-liquid-equilibria equipment will be kept in full operation to produce viable results; however, there is a need for determining the data at a faster rate and for ensuring that more accurate material balances are obtained in the derived results. To fill these needs, new equipment will be developed, tested, and put into operation. To answer problems concerning fluid-flow measurements, speed-of-sound measurements will be made on selected fluids which address problems common in synthetic and natural fossil fuels. The data will be interpreted and ultimately provided in tabular form in reports and publications which will be accessible to engineers for modeling and design through incorporation in processing simulators such as ASPEN (DOE-sponsored model for liquid fuel processing).

Work Plans

Task 1 - Gas Solubility, Vapor-Liquid-Equilibria (VLE) Sampling and Separations

(a) For studies on mixtures containing quinoline, tetralin, fluorene, dibenzofuran, carbazole, water, ammonia, and hydrogen, collect compressed vapor and liquid samples from vapor-liquid-equilibria apparatus, determine sample densities, and make low-pressure gas-liquid separations.

(b) For studies on fluids obtained from synfuel process streams as part of a coordinated effort with industry, universities, and government laboratories, collect compressed vapor and liquid samples from vapor-liquid-equilibria apparatus and make low-pressure gas-liquid separations.

Task 2 - Make quantitative analyses for the specific species in the gas and liquid samples obtained from Tasks 1a and 1b above, and analyze the samples for species that may have been generated from chemical reactions.

Task 3 - Develop and validate experimental equipment for more rapid determination of vapor-liquid-equilibria and for more accurate material balances.

Task 4 - Analyze the gas volume, sample density, and sample composition data from Tasks 1 and 2 for material balances, and develop final values of the ratios of compositions between the liquid and gas phases. Test the data with equations of state for mixtures to determine deficiencies in current modeling methods.

Task 5 - Select fluid systems for speed-of-sound studies to supply basic data to be used in the development of improved industry standards for calculations in fluid-flow measurements. This selection will be based on studies that will be completed at other institutions to help specify the critical data needs.

Task 6 - Order substances for speed-of-sound studies from one of the established high-purity gas supply firms.

Task 7 - Conduct speed-of-sound studies on selected fluid system.

Task 8 - Coordinate measurements and correlations with those from other institutions who will be supplying their contributions in measurements and correlations to produce the desired, highly validated results for complete acceptance as industry standards.

Task 9 - Present the final data with analysis and correlation.

Task 10 - Reassess problems in the prediction and measurement of fluid properties to determine if additional studies are warranted.

Future Work

This is a continued project which was initiated under BETC direction. Key questions concerning the thermophysical properties of process fluids are expected to be answered each year for the duration of this project. An appreciable body of data will be collected within three years so that significantly improved predictions of the thermophysical properties of fluids can be made. Many significant problems will remain at the end of this period, and in ensuing years it will be appropriate to review the data needs and the experimental capabilities to determine whether the project merits continuation.

Manpower Requirements

	Man-years
Senior Chemist	0.2
Research Chemists	1.3
Senior Engineer	0.1
Research Engineer	0.8
Senior Experimentalist	0.2
	2.6
Post-Doctoral Chemical Engineer (AWU)	1.0

Equipment Requirements

	Available	New
Stirred autoclave suitable for hydrogen	1	
Gas and liquid chromatographs and infrared analysis equipment	5	
Equipment for vapor-liquid-equilibria studies		1
Equipment for speed-of-sound studies		1

PROJECT SCHEDULE AND MILESTONE

Project: Thermophysical Properties of Real and Synthetic Fluid Mixtures Derived from Fossil Substances

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
	A ▽		B ▽	C ▽		D ▽				E▽			
1a. Studies on mixtures	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
1b. Studies on coal process liquids									///	/////	/////	/////	
		A ▽		B ▽	C▽		D▽			E▽	F▽		
2. Analysis of samples from VLE		/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
										A▽	B▽		
3. Develop new experimental equipment		///	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
			A ▽	B ▽		C ▽		D ▽				E▽	
4. Test data against existing correlation procedures	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		Description
Task 1a	(A) October 25, 1983	VLE of tetralin, water, hydrogen system
	(B) December 16, 1983	VLE of tetralin, water system, first mixture
	(C) February 3, 1984	VLE of tetralin, water system, second mixture
	(D) March 23, 1984	VLE of tetralin, water system, third mixture
	(E) August 3, 1984	VLE of quinoline, water system, first mixture
Task 2	(A) November 18, 1983	Analysis of samples from Task 1a
	(B) January 6, 1984	Analysis of samples from Task 1a
	(C) February 24, 1984	Analysis of samples from Task 1a
	(D) April 13, 1984	Analysis of samples from Task 1a
	(E) July 20, 1984	Analysis of samples from Task 1a
	(F) August 24, 1984	Analysis of samples from Task 1a
Task 3	(A) July 15, 1984	Design of new system completed
	(B) August 30, 1984	Equipment located for ordering and negotiations
Task 4	(A) December 9, 1983	Correlate system from Tasks 1a and 2
	(B) February 3, 1984	Correlate systems from Tasks 1a and 2
	(C) March 23, 1984	Correlate systems from Tasks 1a and 2
	(D) May 11, 1984	Correlate system from Tasks 1a and 2
	(E) September 21, 1984	Correlate system from Tasks 1a and 2

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

(Continuation Sheet)
PROJECT SCHEDULE AND MILESTONE

Project: Thermophysical Properties of Real and Synthetic Fluid Mixtures Derived from Fossil Substances **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
5. Select systems for speed-of-sound studies					A ▽							
				//////	//////							
6. Order materials for speed-of-sound studies												
					//////	//////	//////	//////	//////	//////	//////	//////
7. Speed-of-sound studies on first mixture												
								//////	//////	//////	//////	//////
8. Coordination with outside efforts (continuous)												
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////
9. Final compilation of data and prepare publications		A▽B▽						C ▽				
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////
10. Evaluation and selection of new systems to study												
	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////

Milestone		Description
Task 5	(A) February 15, 1984	Complete selection of systems for study
Task 9	(A) November 30, 1983	Completion of manuscript of solubility of hydrogen in well-defined coal liquids
	(B) December 1, 1983	Completion of manuscript on VLE of tetraline, water, hydrogen, ammonia, 1-naphtol, quinoline, and tetralin
	(C) May 31, 1984	Completion of manuscript on VLE of tetralin, water, hydrogen system

OPT2. STABILITY AND PROCESSING RESEARCH FOR CRUDES, INTERMEDIATE PROCESS STREAMS AND FINISHED FUELS

Background

This work addresses Item 6.2.1 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

This project is more fully described in closely related Project BPT2. The tasks included in Project OPT2 are Tasks 1-4, 7-8, and 10-14. All of the tasks for the two projects are included in BPT2, but only those in the Optional Program are listed here.

The following tasks from the work plans under the Base Program will be addressed in the Optional Program.

Work Plans

Task 1 - Selection of the first feedstock. A fresh Wilmington crude (API gravity = 14 degrees) with a known history of production and handling is in our inventory.

Task 2 - Selection of upgrading conditions. It is now anticipated that a distillation cut with an upper limit of about 1000°F will be made. Other cuts may be necessary. Hydrotreating conditions will be in the range of 300-350°C and 500-800 psig.

Task 3 - Storage stability methods will be evaluated to determine what development work is still required. Composition parameters affecting stability will be identified using state-of-the-art analytical techniques.

Task 4 - Storage stability measurements method development would be continued during the first upgrading run. This is a continuation of work initiated in FY82.

Task 7 - Analyze the feedstock, distillation cuts, and matrix of hydrotreated samples and samples from supercritical extraction by physical, chromatographic, and spectroscopic methods to begin characterizing the components and the physical and compositional changes. Included in this will be a metals screening to determine effects of distillation/upgrading on distribution of metals in the hydrocarbon matrices. Using the resulting data, determine what other analyses should be performed.

Task 8 - Determine storage stability parameters on the distillate material using the new accelerated (65°C) method developed at NIPER (formerly BETC).

Task 10 - Commence development of computer-based model for correlative and predictive purposes based on results obtained.

Task 11 - Select the second feedstock to be upgraded.

Task 12 - Determine modification of upgrading techniques or hydrogenation reactor conditions which might enhance the utility of the resulting data.

Task 13 - Evaluate the need for any changes in physical and compositional measurements based on characterization data supplied for the first set of samples.

Task 14 - Develop model for correlation of compositional and upgrading conditions with final compositional and physical properties, storage stability, and mutagenesis.

Manpower Requirements

	Man-years
Senior Chemist	0.1
Research Chemist	0.7
Senior Chemical Engineer	0.3
Associate Chemical Engineer	0.6
Assistant Chemical Engineer	0.3
Technician	0.2
Total	2.2

Equipment Requirements

	Available	New
Thinfilm evaporator	2	
Hydrotreater	1	
Stability testing equipment	1	
Chromatography units	3	
Drawpump for thinfilm evaporator		1
Supercritical extraction equipment		1
Automated control valves and accessories for hydrotreater		1

PROJECT SCHEDULE AND MILESTONE

Project: Stability and Processing Research for Crudes, Intermediate Process Streams and Finished Fuels

Report Date: ______________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
				A∇	B∇								
1. Select feedstock	/////	/////	/////	/////	/////								
					A∇								
2. Select upgrading conditions	/////	/////	/////	/////	/////								
Analysis methods					A∇								
3. identification		/////	/////	/////	/////								
Storage stability method			A∇						B ∇				
4. development		/////	/////	/////	/////	/////	/////	/////	/////				
												A∇	
5. Sample analyses	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
												A∇	
6. Storage stability testing	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ C'Δ	

Milestone		Description
Task 1	(A) January 31, 1984	Feedstock selected and procurement initiated
	(B) February 28, 1984	Feedstock received
Task 2	(A) February 28, 1984	Upgrading conditions selected
Task 3	(A) February 28, 1984	Characterization protocols developed
Task 4	(A) December 31, 1983	Stability test technique data evaluated for need for further development work
	(B) June 30, 1984	Rough draft of publication describing new storage stability test method completed
Task 5	(A) September 30, 1984	Include compilation of characterization data generated to date in NIPER quarterly and/or annual report
Task 6	(A) Septemter 30, 1984	Report of progress to date

Reporting Requirements
(A) 15 th of each month..................Monthly Progress Report
(B) 30 days after end of each quarter.........Quarterly Technical Progress Report
(C)' 90 days after end of program year........Annual Technical Progress Report

(Continuation Sheet)

PROJECT SCHEDULE AND MILESTONE

Project: Stability and Processing Research for Crudes, Intermediate Process Streams and Finished Fuels

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
7. Compile data	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	A▽ /////
8. Select second feedstock	/////	/////	/////	/////	/////	/////	/////	/////	A▽ /////	/////	/////	B▽ /////
9. Modify upgrading tech	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	A▽ /////
10. Modify characterization protocol	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	A▽ /////
1`. Develop model	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	A▽ /////

Milestone		Description
Task 7	(A) September 30, 1984	Report of progress to date
Task 8	(A) June 30, 1984	Select/procure second feedstock
	(B) September 30, 1984	Receive second feedstock
Task 9	(A) September 30, 1984	Report of progress to date
Task 10	(A) September 30, 1984	Report of progress to date
Task 11	(A) September 30, 1984	Report of progress to date

OPT3. CHEMICAL CHARACTERIZATION OF HEAVY ENDS OF LIGHT PETROLEUM, OF HEAVY PETROLEUM, AND OF LIQUIDS DERIVED FROM OTHER FOSSIL SOURCES

Background

This work addresses Item 6.2.3 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

This project is more fully described in closely related Project BPT3, page 102. The tasks included in OPT3 are Tasks 2-4. All of the tasks for the two projects are included in BPT3, but only those in the Optional Program are listed here.

Work Plans

Task 2 - Evaluate, on a limited scale, the assumption of equal molar sensitivities for quantitative mass spectral analysis of petroleum fractions.

- (a) Select compounds representative of the types typically found in fossil fuel aromatic-neutral fractions.
- (b) Determine the mass spectral sensitivity coefficients for these representative compounds using low-ionizing-voltage electron impact and field ionization techniques.
- (c) Correlate sensitivity data with known structures of representative compounds.
- (d) Evaluate the importance of sensitivity correlations in the quantitation of mass spectral analyses.

Task 3 - Separation of sulfur compound classes.

- (a) Separate sulfides from Cerro Negro 200°-425°C and 425°-550°C acid-base-free distillates.
- (b) Separate saturates, thiophenes, and aromatic hydrocarbons from at least the acid-base-sulfide-free 200°-425°C distillate
- (c) Evaluate the effectiveness of these separations via elemental analysis, gas chromatography and mass spectrometry.
- (d) Evaluate the possibility of extension of the separation method to higher distillates.

Task 4 - High performance liquid chromatographic (HPLC) separation of acid concentrates into compound classes.

- (a) Separate 10-20 previously isolated acid concentrates and distillates and residues of Cerro Negro and Wilmington oils into compound classes.

(b) To test the capabilities of the method this separation technique will be applied to 5-10 synfuel acid concentrates which contain acids which are significantly different from acids in crude oils. Compare results.

(e) Evaluate separation method using infrared and mass spectroscopy. Report results.

Future Work

Further work in FY85 and beyond is anticipated to involve extension of information and techniques developed in FY84 to the heavier fractions of Cerro Negro (550°-700°C and greater than700°C fractions). The methods developed will be applied to additional heavy crudes with wide ranging properties, and the sensitivity-structure correlations will be expanded to further improve quantitation of heavy fossil fuel samples. Work on separation of sulfur compounds in the higher ranges of Cerro Negro crude is planned for FY85. Additional effort in FY85 will also be required to finish the fractionation of the acid fractions.

Manpower Requirements

	Man-years
Senior Chemist	1.4
Research Chemist	1.2
Assistant Chemist	1.2
Associate Chemist	.4
Research Physicists	.6
Senior Experimentalist	.2
Total	5.0

Equipment Requirements *

	Available	New
MS-30 FI,FD,EI	1	
MS-80 FI,FD,EI,CI	1	
MS-60 FI,FD,EI	1	
Megohm meter		1
High performance liquid chromatography systems, also HPLC accessories: Columns, specialized detectors, column packing apparatus.	4	
Rotary solvent evaporators	4	
Gas chromatographs (GC) with supporting intelligent interfacing	4	1
GC mass detector		1

* Already listed in BPT3.

PROJECT SCHEDULE AND MILESTONE

Project: Chemical Characterization of Heavy Ends of Light Petroleum, of Heavy Petroleum and of Liquids Derived from Other Fossil Sources

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
2. Evaluation of quantitation assumptions of MS data								A▽		B▽		CD▽	
3. Separation of sulfur compound classes								A▽		B▽		CD▽	
4. HPLC separation of acid concentrates into compound classes										A▽	B▽	C▽	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		Description
Task 2	(A) May 1, 1984	Select representative compound
	(B) July 15, 1984	Determine mass spectral sensitivity
	(C) September 30, 1984	Correlate sensitivity data
	(D) September 30, 1984	Evaluate the importance of sensitivity correlation in quantitation of data
Task 3	(A) May 31, 1984	Separate sulfides from Cerro Negro 200-425°C distillate
	(B) July 30, 1984	Separate saturates, thiophenes, and aromatic hydrocarbons from 200-425°C distillate
	(C) September 30, 1984	Evaluate effectiveness of this separation
	(D) September 30, 1984	Evaluate possibility of extension of separation method to higher distillates
Task 4	(A) July 1, 1984	Separate 10-20 Cerro Negro and Wilmington acid concentrates
	(B) August 31, 1984	Separate 5-10 synfuel acid concentrates
	(C) September 30, 1984	Evaluate separation method

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

OPT4. FUEL TRENDS AND ANALYSES

Background

This work addresses Item 6.2.3 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The National Institute for Petroleum and Energy Research (formerly BETC) has extensive experience in assembling fuel data. It has been involved for some 50 years in a government/API cooperative effort in surveying the quality and characteristics of the fuels marketed in the United States. These surveys have provided a base for predicting future fuel quality. The surveys give averages of the values for properties assumed to be significant in the end-use of the fuel. Properties for gasoline such as boiling range, octane number, sulfur content, gum test, and vapor pressure serve to define the fuel and, indeed, are used in setting specifications. A recent publication (1) traces the changes in such properties over the past 50 years.

In designing processes for alternative feedstock processing, it is important to have the present supply defined and to be able to predict changes that may come about. Similarly for diesel fuel, the boiling range, cetane number, and sulfur content form important parameters for comparison with proposed alternative fuels. Aircraft turbine fuel is defined by various properties including boiling range, sulfur content, stability, aromatic content and viscosity, and heating fuels are described by gravity, boiling range, viscosity, and heats of combustion. Annually, five reports describing the quality of petroleum products are prepared by NIPER and distributed in the United States. The data are of particular interest in showing trends in fuel quality and have the potential of spotting trends which may affect alternate feedstock/fuel development.

References

1. Shelton, Ella Mae, M. L. Whisman and P. W. Woodward, "Trends in Motor Gasolines 1942-81," DOE/BETC/RI-82/4, June 1982, 27 pp.

Objectives

To compile and correlate data on marketed fuels in the United States to use as a base for planning future research work. Cooperation between the government and the American Petroleum Institute results in a reliable bank of information on the quality of fuels manufactured and distributed in the United States.

Scope of Work

Petroleum Product surveys that are currently produced in cooperation with the American Petroleum Institute (API), are funded partially by API and member companies. Five reports (winter gasolines, summer gasolines, diesel fuels, heating oils and aviation turbine fuels) will be annually prepared from analytical test data supplied by company contributors. The data provide comparative information on the quality and characteristics of currently marketed fuels to thousands of individual requestors. Approximately 1,200 copies of each report are distributed each year by the Bartlesville Project Office of the Department of Energy in fulfillment of requests. These include automotive manufacturers who depend upon continually updated information to predict future engine design based upon fuel quality; to business interests that have a keen day-to-day vested interest in certain products and trends in quality; to petroleum refiners who must meet the quality of competitive products; and to other companies and individuals who have specific interests and needs for these kind of data.

This project is a continuing program which has been renewed each year. NIPER and DOE/FE participation is justified to assure spotting trends which may correlate with increased usage of alternate feedstocks and with fuel development from these alternate sources. Timely research and environmental assessments are necessary for orderly energy research and goals formulation. As alternative fuel research programs are planned, it is important to have as reference the properties of the materials that are to be replaced. Only in this way can it be assured that not only will the new fuels meet the requirements of present-day specifications, but also that they have not added environmental or other problems unique to the alternative fuels.

Work Plans

Task 1 - Work cooperatively with the API to prepare, publish and distribute five major fuel surveys each year for motor gasolines, diesel fuels, aviation fuels and heating oils.

Task 2 - Prepare analyes of trends of fuel properties and their relationship to alternative fuels.

Future Work

This project has been in progress for over 50 years at BETC, now NIPER, and is an ongoing research and reporting program that is expected to be continued as long as petroleum fuels are a vital energy source to the world.

Manpower Requirements

	Man-years
Associate Data Analyst	0.3
Associate Data Specialist	0.4
Associate Programmer Analyst	0.2
Total	0.9

Equipment Requirements

	Available	New
Digital DEC-writer III computer	1	
Digital VT-125 computer	1	
AM 6400 photo typesetter	1	
AM 425 word processor	1	

PROJECT SCHEDULE AND MILESTONE

Project: Fuel Trends and Analyses

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Prepare fuel surveys		A▽			B▽	C▽				D▽	E▽		
	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	/////	
2. Prepare trend and analysis report												A▽	
												/////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone	Description
Task 1 (A) November 30, 1984	Deliver fuel survey, diesel fuels
(B) February 29, 1984	Deliver fuel survey, motor gasoline, summer
(C) March 31, 1984	Deliver fuel survey, aviation turbine fuels
(D) July 31, 1984	Deliver fuel survey, motor gasolines, winter
(E) August 31, 1984	Deliver fuel survey, heating oils
Task 2 (A) September 30, 1984	Prepare Analysis report

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

OPT5. CHEMISTRY OF CONTAMINATED PETROLEUM FUELS

Background

This work addresses Items 6.2.1 and 6.2.4 of the Research Statement of Work in the Cooperative Agreemtnt between DOE and IITRI (DE-FC01-83FE60149).

Scientists at NIPER, formerly BETC, for more than a decade have been performing basic and applied research related to used and waste hydrocarbon recovery and reclamation. This research has covered the broad spectrum from determination of specific contaminant compounds of interest to the development of patented innovative recycling processes. Stability and processing data must be correlated to provide insight into fuel stability performance and environmental acceptability at various processing levels. It has been shown that oil water emulsions involving inorganic salts such as in sea water contribute to instability, and also that contaminants such as phenols, halogenated solvents, metal oxides, and heavy metals are a threat to the successful processing and utilization of many feedstreams. The focus of this work will be on the effect that various nonhydrocarbon constituents, whether naturally occurring or introduced after production, have on fuel properties such as stability, handling, ease of recycling, and health and safety considerations.

One such problem area already under investigation relates to the large quantities of oils continuously generated by Navy ships and Marine Corps shore activities as well as aircraft facilities. These fuels, when contacted with sea water and other contaminants, frequently fail to meet fuel specifications for flash point, water content, stability, and other properties. NIPER (formerly BETC) has lengthy experience in dealing with contaminated hydrocarbon streams and with stability problems. Work in both areas has been performed in the past in cooperation with the military as well as with commercial research groups.

A specific problem which the Navy has asked us to work on is the recycling of contaminated marine diesel fuel (DFM) into DFM which meets specifications. Based on 1982 statistics, the quantity of contaminated DFM available is estimated at more than 70 million gallons per year. This includes waste oils generated from slop oil tanks, used lubricants from various motors and engines, and any other material that emerges from the oil/water separator at the refueling depot. An important initial task will be to characterize in detail, to the extent possible, the contaminants that tend to be present in this oil. The data on composition will be used to identify and control or remove toxic or undesirable substances through the use of appropriate technology.

Currently the contaminated fuel is being burned in boilers. Oil-fired boilers are in decline, and fuel for them is readily available. Other uses, such as weed and dust control, have been shown by EPA to be unacceptable hazards (1). A more useful role for this material would be to reprocess it such that it could be blended to meet specification DFM. If half of the available volume of contaminated marine fuel were reprocessed, between three and four percent of the Navy's total DFM requirement could be satisfied. The savings would amount to nearly 10 million dollars per year.

Although most of this specific work on the recycling of contaminated DFM will be supported by the Navy, it provides a unique opportunity to work with degradation products and to study the stability of diesel fuels having a wide range of nonhydrocarbon and hydrocarbon compositions. Both areas are of interest to DOE/Fossil Energy in its effort to understand fundamental petroleum chemistry and constituent effects on specification parameters such as stability. In turn, an understanding of the basic chemistry will greatly assist in the selection of the most appropriate processing approach.

References

1. "Listing of Used Oil as a Hazardous Waste," Environmental Protection Agency, Report to Congress, January 1981.

Objectives

To develop a process, or processes, to reclaim waste marine type diesel fuel into specification marine diesel fuel; explore methods of separating oil/water/solvent mixtures that have potential application to the recovery of contaminated marine fuels from sea water; investigate methods of removing contaminants such as phenols, solvents, and heavy metals from hydrocarbon products; and, to characterize waste marine diesel fuels, identify degradation products, and evaluate their effect upon stability of hydrocarbons in general with relation to the original fuel.

Scope of Work

This project was started six months ago and is comprised of three phases: (1) information gathering, (2) experimentation, and (3) facility design. The first phase includes an in-depth literature review and information compilation from other sources. The literature search covers areas related to processes, equipment, and industrial experience. NIPER experience and expertise in process development is being relied upon heavily in this initial phase. In addition to the literature search and report, there will be a survey of industrial capabilities to treat reclaimed fuel oil on a research scale to determine capacities, types of processes, products, and applicability to this project. A large number of marine diesel fuel and reclaimed fuel oil samples will be characterized in detail to determine the degree of contamination, methods of removing these contaminants and the effect of these contaminants upon stability, processing, and emissions of derived fuels. These data will be correlated with basic degradation reaction mechanism information developed within the DOE/Fossil Energy research program giving a broader picture of petroleum reactivity. Finally, the project will develop a testing program and establish performance/technical criteria evaluation methodology.

The second phase will be bench-scale testing, and it is proposed that NIPER will set up test equipment and conduct experiments using selected processes and apparatus to assess their technical and operational capability for treating reclaimed marine fuel oil to produce a specification diesel fuel marine. Detailed characterization of feedstocks and products will provide a useful data base in such areas as stability, metals removal, and bulk property changes with various types, and severities of upgrading correlations will be sought between the type of neutral nitrogen compounds identified in other stability work and the degradation products found here. Additionally, estimates of operating and maintenance costs for tested processes and equipment will be formulated. As a part of the second phase, pilot-scale tests will be conducted to develop definitive design criteria.

The third phase of this project, fully funded by the Navy, will provide the engineering design for a full-scale facility based upon successful bench- and pilot-scale testing. The full-scale plant would be tailored to convert the reclaimed fuel oil from a marine base into a finished specification DFM that could be employed for engine fuel with or without further blending.

Work Plan

Phase I (1984) - Literature Review and Information Compilation

Task 1 - Conduct an in-depth review of literature dealing with processes, contamination, characterization, specification, and utilization of marine diesel fuels. This review will include but not be limited to the following areas:

(a) effects of salt water on stability, processes, and equipment
(b) characterization of contaminants in discarded marine diesel fuel
(c) identifying processes for reclaiming and reprocessing contaminated oil
(d) identifying equipment for reclaiming and reprocessing contaminated oil
(e) research into processes and equipment applicable to contaminated marine diesel
(f) industrial experience with reclaiming and/or recycling waste or contaminated hydrocarbons
(g) specifications for DFM.
(h) basic work on stability including nitrogen compounds and known bad actors
(i) correlation of basic work with DFM contaminants.

Task 2 - Characterize samples of new and reclaimed fuel oil for physical and chemical properties. Determine deviations from specifications for DFM using standard test procedures established by the industry and the Department of Defense. Typical specification DFM samples, contaminated DFM, and fuel oil reclaimed samples will be obtained through the Department of the Navy in sufficient numbers to provide a definitive evaluation of the range of physical and chemical properties. In addition, hazardous waste component screenings will be run. Base line stability data will also be generated.

Task 3 - Evaluate the range of physical and chemical properties, the level of hazardous waste components and explore new methods of separating inorganic contaminants originating from sea water, solvent contamination or other sources that can adversely affect the stability characteristics and the processing efficiency of contaminated marine fuels with potential application to other petroleum recovery problems. Investigate methods of removing contaminants, such as phenols, solvents, sludges, particulates and heavy metals, applicable to contaminated marine fuels. Relate these physical and chemical properties to the production of stable products; the effect on upstream handling and processing; and the effect on emissions of derived fuels.

Task 4 - Review existing Department of Navy reclamation facilities and operations to determine the potential for process improvement.

Task 5 - Conduct technical analysis and estimate the economics of various process options and prioritize treatment options. Factors to be considered include availability of equipment, costs, an estimation of reliability, flexibility, simplicity, and any potential environmental problems apparent.

Task 6 - Prepare a report detailing the results of the literature review, including information obtained from laboratory investigations with recommendations on the direction for bench-scale testing. This report will include: (a) a description of the literature search methodology (b) a discussion of the evaluation procedure (c) a description of all technologies reviewed and their relative advantages (d) a recommendation for continuing research (e) a detailed bibliography. Any new characterization methods or information will also be compiled and reported to DOE/Fossil Energy.

Task 7 - Develop a testing program and establish performance/technical criteria evaluation methodology.

Phase II (1984-1985) - Bench- and Pilot-Scale Testing

Task 8 - Set up test equipment and conduct experiments using selected processes and equipment to assess their capability for treating reclaimed oil to produce a fuel of quality suitable for blending into DFM. All testing will be done using ASTM methods. Depending on the contaminants in the feedstock, a matrix of samples and tests will be performed. The tests will include stability screening, metals determination, and heteroatom characterization as part of the Fossil Energy portion of this effort. This list of necessary tests could be smaller or larger depending on the contaminants identified by analysis of the feedstock. In addition, a basic material balance would be performed.

Task 9 - Operating and maintenance costs for tested processes and equipment will be estimated.

Task 10 - A report detailing results of testing and evaluation and cost estimates will be prepared. Treatment options will will be listed in order of priority. A continue or stop recommendation will be included.

Phase III (1985-1986) - Design and testing of a full-scale facility

Task 11 - Development of quality control outline based on fundamental petroleum studies.

Future Work

This project which has been in progress more than six months at NIPER (formerly BETC) is an ongoing research program that is expected to extend through 1986 or longer. The first phase detailed above is scheduled for completion in 1984. The second phase which will encompass process selection and evaluation will include bench- and pilot-scale testing programs. Development of new characterization and evaluation techniques may be needed for this complex matrix. Test equipment will be used to conduct tests of selected processes and equipment to assess their technical and operational capability for treating reclaimed oil to produce a fuel of quality suitable for blending into DFM. Operating and maintenance costs will be estimated and processes tested. Sites will be selected for pilot-plant testing, and tests will be conducted related to technical and operational aspects.

The last phase is expected to take successful bench- and pilot-scale evaluations of a process and develop the engineering design for a full-scale plant for location in an existing marine facility with the capability of converting slop oil, contaminated diesel fuel, and lubricating oil to DFM and other suitable products of specification grade or appropriate quality.

DOE/FE will receive additional reports on techniques developed and utilized, data generated, and their importance to waste hydrocarbons recycling. These may well be applied to many other fossil fuel streams.

Manpower Requirements

	Man-years
Senior Chemists	0.5
Research Chemical Engineer	0.3
Assistant Chemical Engineer	0.4
Research Chemist	0.1
Technicians	0.8
Analytical Support	0.3
Total	2.4

Equipment Requirements

	Available	New
Supercritical liquid extraction equipment		1

PROJECT SCHEDULE AND MILESTONE

Project: Chemistry of Contaminated Petroleum Fuels **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Literature review	//////	//////	//////	//////	//////	//////	A ▽ //////						
2. Sample characterization	//////	//////	//////	//////	//////	A ▽ //////	//////	//////	//////	//////	//////	//////	
3. (A) Complete evaluation of methods	//////	//////	//////	//////	A▽ //////								
(B) Report on initial screening for toxic material	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	//////	B ▽ //////	
4. Facility review	//////	//////	//////	A ▽ //////									
5. Technical/economic analysis and prioritize options			//////	//////	//////	//////	A ▽ //////						
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		Description
Task 1	(A) April 30, 1984	Complete literature survey
Task 2	(A) March 31, 1984	Complete test characterization
Task 3	(A) February 28, 1984	Complete evaluation of methods
	(B) September 30, 1984	Report on initial screening for toxic material
Task 4	(A) January 31, 1984	Review DON facilities
Task 5	(A) April 30, 1984	Tech/econ analysis and prioritization of treatments

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report
(B) 30 days after end of each quarter .... Quarterly Technical Progress Report
(C)' 90 days after end of program year .... Annual Technical Progress Report

PROJECT SCHEDULE AND MILESTONE

Project: Chemistry of Contaminated Petroleum Fuels

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
								A▽					
6. Prepare report		//////	//////	//////	//////	//////	//////	//////					
									A▽				
7. Develop test program						//////	//////	//////	//////				
8. Conduct upgrading experiments & characterize resulting products								//////	//////	//////	//////	//////	
9. Estimate costs													
10. Phase II final report													
11. Phase III full-scale design													
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone	Description
Task 6 (A) May 30, 1984	Prepare report.
Task 7 (A) June 30, 1984	Develop testing program.

Reporting Requirements
(A) 15 th of each month ....Monthly Progress Report
(B) 30 days after end of each quarter ....Quarterly Technical Progress Report
(C)' 90 days after end of program year ....Annual Technical Progress Report

OU1. DIESEL FUEL QUALITY CRITERIA

Background

This work addresses Item 6.3.1 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The quality of diesel fuel sold in U.S. markets, as determined by traditional measures, is decreasing. Cetane number, aromatic content, and boiling distribution of diesel fuels indicate a trend toward lower quality (1). This is a consequence of increased usage of the lower cost and more readily available heavy crudes (2). The use of alternative feedstocks is expected to increase in the future, and the crudes are expected to become even heavier, both of which could cause further decline in distillate fuel quality. The impact of alternative feedstocks on exhaust emission products is a concern of DOE. Industry's concern is with engine performance effects, which include combustion performance and engine durability as well as emissions.

The traditional measures of fuel quality are not necessarily applicable for current and future compression-ignition engines. It is possible that the fuel acceptance of today's engines is broader than has been assumed. Broader fuel specifications would enable fuel processors to produce acceptable quality diesel fuel from alternative feedstocks. This could provide alternatives currently not being considered. To be acceptable, fuels from alternative feedstocks must have no significant adverse impact on combustion performance, exhaust emissions, and engine durability. Fossil Energy, because of its research programs on enhanced recovery of heavy oils and characterization, is concerned specifically with the environmental consequences that such a change in production would have. This work will develop a preliminary assessment of the feasibility for such a switch and its environmental impact.

References

1. Shelton, E. M., "Diesel Fuel Oils, 1982," DOE/BETC/PPS-82/5.

2. Unzelman, C. H., "Diesel Fuel Demand, A Challenge to Quality," presented at Institute of Petroleum, London, Oct. 1983, and in Oil and Gas J., Nov. 14, 1983, pp. 178-201.

Objectives

To determine the feasibility of heavy-oil-derived, broad-cut fuels entering the diesel market and to assess the environmental impacts of such an occurrence.

Scope of Work

Fuel parameters affected markedly by increased usage of alternative feedstocks will be examined. Specifically, these parameters are distillation range, aromatic content, and cetane quality. Fuel quality will be assessed in terms of its influence on basic combustion properties (ignition delay, peak pressure, rate of pressure rise), exhaust emissions, and utilization efficiency. These results can be used to reappraise current fuel specifications. Correlation of exhaust emission levels and combustion response will be developed to differentiate the direct from the indirect effects of fuel composition on emissions.

Work Plans

Task 1 - Select and procure fuel blending stocks required to produce test fuels that typify ranges in distillation, aromaticity, and cetane quality that would be expected from production in current refineries using an increased fraction of alternative feedstocks and going to a broader cut fuel. Target properties of the test fuels will be based on data contained in and extrapolated from the NIPER/API diesel fuel surveys. The fuel matrix will include nine fuels having systematic variation in 10 percent and 90 percent distillation points and in aromatic content.

Task 2 - Concurrent with the first task, select engines and vehicles that typify a significant fraction of current and near-term production. The engine selection will include both direct-injection and precombustion chamber designs, as well as a conventional cetane-rating engine. Two heavy-duty engines and three light-duty vehicles will be used for testing fuel performance and obtaining emissions.

Task 3 - Prepare and analyze fuels. The analyses will be comprehensive, including compositional determinations within discrete distillation ranges. The fuels will be characterized in terms of content of paraffins, naphthenes, and aromatics including multiring components, metals, sulfur, and nitrogen.

Task 4 - Conduct engine experiments using the nine test fuels. Performance measurements will include gaseous and particulate exhaust emissions, smoke, fuel economy, and power. Ambient temperature will be varied for one of the vehicles using all nine fuels. Cylinder pressure and needle lift sensors will be installed on the heavy-duty engines for measurement of ignition delay, rate of pressure rise, peak pressure, and indicated mean effective pressure. These data are necessary for determination of ignition and combustion performance as well as indicated efficiency.

Task 5 - Analyze results and prepare reports. Periodic reports will cover results for each engine system. The final report will include a statistical analysis relating ignition, combustion, and emissions performance to fuel compositional variables. It will also assess the environmental consequences of heavy-oil-derived blending stocks being added to the diesel fuel pool.

Future Work

The duration of the project is scheduled for three years. The matrix of test fuels will be expanded to include combustion- and ignition-improver additives. Selection of additional test fuels will be based on results obtained in the first year and the need to determine effects of specific fuel variables, e.g., heteroatom content. In collaboration with an industry/government advisory committee, the representativeness of the test fuels will be examined and modified, as appropriate. Three light-duty and two heavy-duty engines will be outfitted with sensors for measuring ignition and combustion parameters. Laboratory capability will be expanded to include EPA-specified transient heavy-duty diesel engine test procedures to enable more representative measurements of emissions consequences of fuel compositional variables.

Manpower Requirements

	Man-years
Manager	0.3
Senior Mechanical Engineer	0.3
Research Mechanical Engineer	1.0
Associate Mechanical Engineer	0.7
Experimentalist	2.2
Technician	0.8
Total	5.3

Equipment Requirements

	Available	New
CFR engine	1	
Heavy-duty diesel engines	4	
Light-duty diesel engines	6	
Engine test cells	2	
Vehicle chassis dynamometer	2	
Automatic sampler accessory for chromatograph		1
Combustion analyzer and transducers		1

PROJECT SCHEDULE AND MILESTONE

Project: Diesel Fuel Quality Criteria **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
		A▽	B▽										
1. Obtain fuel stocks	//////	//////	//////										
		A		B▽									
2. Select engines	//////	//////	//////	//////									
				A▽	B▽								
3. Fuel preparation			//////	//////	//////								
										A▽			
4. Fuel-engine experiments					//////	//////	//////	//////	//////	//////			
5. Analyze results and prepare report												A ▽	
											//////	//////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		Description
Task 1	(A) December 1, 1983	Parameter limits of fuels specified
	(B) January 1, 1984	Fuel blending stocks obtained
Task 2	(A) December 1, 1983	Engines/vehicles required for fuel experiments selected
	(B) February 1, 1984	Engines installed
Task 3	(A) January 15, 1984	Fuel preparation (blending, refining) completed
	(B) March 1, 1984	Fuels analyzed
Task 4	(A) July 15, 1984	Testing completed
Task 5	(A) September 30, 1984	Complete final report

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

OU2. DIRECT UTILIZATION OF AROMATIC FEEDSTOCKS

Background

This work addresses Item 6.3.1 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The technologies both for hydrocarbon processing and for fuels utilization are necessarily undergoing a significant evolution as a result of changes in the world crude supply, both in quantity and crude characteristics, and a need to utilize heavy oils, shale oil, and other materials as primary energy resources. High-boiling-range naphthas are a major by-product of processing coal liquids and heavy petroleum crudes. They are, however, generally unsuitable for turbine or diesel fuel because of the high aromatic content, even though the distillation range is acceptable. Advanced technology transportation systems may have excellent potential for utilizing high-octane quality naphtha. Recent developments in fuel-induction systems and high-heat intake systems within the transportation sector offer increased potential for successful use of the higher-boiling-range fuels. If the concept of utilizing higher-boiling-range components in the transportation sector proves feasible, then it could provide impetus to alternate feedstock use by allowing direct utilization of the product stream without further processing. The use of higher-boiling-range fuels is contingent on their having minimal adverse impact on evaporative and exhaust emissions, performance, and longevity of engines and emission control systems.

Use of highly aromatic material in diesel fuels has been shown to have detrimental effects on diesel exhaust emissions by increasing oxides of nitrogen (1) and particulates (2). Highly aromatic materials in the ordinary gasoline boiling range have little effect on exhaust emissions; there are no data available on the emissions consequences of using high-boiling aromatics in spark-ignition engines. Thus, the need exists to assess the probability of this happening and the environmental consequences.

References

1. Lin, C. S., and D. E. Foster, "A Study of Fuel Nitrogen Conversion, Performance, and Emission Characteristics of Blended SRC-II in a High-Speed Diesel Engine," SAE Paper No. 810251, Feb. 1981.
2. Bouffard, R. A., and M. Beltzer, "Light-Duty Diesel Particulate Emissions--Fuel and Vehicle Effects," SAE Paper No. 811191, Oct. 1981.

Objectives

To determine the feasibility of utilizing extended-boiling-range, high-aromatic refinery feedstocks blended with gasoline directly in spark-ignition engines, rather than expending further refinery energies to make the material suitable for use as turbine or diesel fuels. Also, to assess the environmental and engine related impact of using the extended-boiling-range gasolines. To determine the probability of extended-boiling-range, high-aromatic refinery feedstocks entering the gasoline market.

Scope of Work

The potential for utilization of high-boiling-range naphthas and low-boiling components as transportation fuels will be investigated. The program will investigate emissions, both gaseous and particulates, and other operational parameters using only the high- and low-boiling fractions as a fuel, as well as blending the materials in gasolines. Road octane of the fuels will be compared with motor and research octane to determine whether typical octane measurements are meaningful with the alternative fuels. Much of the interest in the high-boiling naphtha is based on its motor octane value. Fuel-induction system deposit formation will be examined in limited fuel-compatibility tests. The effect of fuel volatility will be determined on the test fuels by testing formulated fuels at various ambient temperature conditions. Finally, the practicality of using high-boiling naphtha will be assessed based on performance and emissions.

Work Plans

Task 1 - Prepare six test fuels formulated from heavy petroleum and syncrude naphthas with butane added to produce test fuels with Reid Vapor Pressures of 6, 9.5, and 13 psi. Prepare six additional test fuels by blending these formulated fuels with gasoline. This fuel matrix was selected to encompass fuels that could be produced in refineries using only heavy-oil feedstocks as well as those in which heavy oils constitute a portion of the feedstocks.

Task 2 - Conduct standard exhaust and evaporative emissions and systems-performance tests of the fuels at appropriate ambient temperature conditions using vehicles equipped with high-temperature intake systems and fuel-injection systems. Response of the test fuels will be compared with that of a standard reference fuel.

Task 3 - Determine vapor-lock tendencies of the formulated fuels and gasoline blends.

Task 4 - Determine road, motor, and research octane values of the formulated fuels and gasoline blends.

Task 5 - Conduct limited system-compatibility tests using selected formulated fuels.

Task 6 - Analyze the data and prepare a report. Periodic reports will cover results of tests with each fuel. The final report will include an assessment of feasibility of utilizing gasolines containing high-boiling aromatic stocks in current and advanced technology engine systems with emphasis on their environmental impact.

Future Work

The project is scheduled for two years. In the second year, exhaust and evaporative emissions will be analyzed in detail with emphasis on quantifying the amount and character of potentially toxic aromatics present. Bioassays will be made to determine potential mutagenic and carcinogenic consequences. In addition, the effectiveness of fuel additives for controlling intake-system deposit formation will be examined. The use of extended-distillation-range gasolines is expected to have a marked influence on the amount and character of intake-system deposits and, subsequently, on emissions characteristics.

Manpower Requirements

	Man-years
Technical Advisor	0.5
Research Mechanical Engineer	0.3
Associate Mechanical Engineer	1.0
Research Chemist	0.5
Experimentalist	1.6
Technician	1.0
Total	4.9

Equipment Requirements

	Available	New
Spark-ignition vehicles	3	
Spark-ignition test engine	1	
Vehicle chassis dynamometer	1	
Computer replacement for Hewlett-Packard 21MX		1

PROJECT SCHEDULE AND MILESTONE

Project: Direct Utilization of Aromatic Feedstocks **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Prepare fuel tests		A ▽		B ▽									
	//////	//////	//////	//////									
2. Emissions and performance tests				A ▽		B ▽							
			//////	//////	//////	//////							
3. Vapor lock tests							A▽						
					//////	//////	//////						
4. Octane tests							A▽						
					//////	//////	//////						
5. System compatibility tests											A▽		
							//////	//////	//////	//////	//////		
6. Analyze data and prepare report												A ▽	
											//////	//////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

	Milestone	**Description**
Task 1	(A) November 30, 1983	Complete blending first series of six test fuels
	(B) January 31, 1984	Complete blending second series of six test fuels
Task 2	(A) January 31, 1984	Complete emissions and performance testing first series of six test fuels
	(B) March 31, 1984	Complete emissions and performance testing second series of six test fuels
Task 3	(A) April 30, 1984	Complete vapor lock tests
Task 4	(A) April 30, 1984	Complete octane tests
Task 5	(A) August 31, 1984	Complete systems compatibility tests
Task 6	(A) September 30, 1984	Complete data analysis and prepare report

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report
(B) 30 days after end of each quarter .... Quarterly Technical Progress Report
(C)' 90 days after end of program year .... Annual Technical Progress Report

OU3. DIESEL EXHAUST CHARACTERIZATION

Background

This work addresses Item 6.3.1 of the Research Statement of Work in the Cooperative AGreement between DOE and IITRI (DE-FC01-83FE60149).

The emissions characteristics of diesel engines are markedly different from those of spark-ignition engines. Material associated with diesel particulate has been found to be mutagenic to bacteria and to contain human carcinogens (1-2). A decline in diesel fuel quality can have a significant effect on exhaust emissions. Use of alternative feedstocks could accelerate this decline. Because exhaust treatment systems are not generally applicable to on-highway diesels, adverse effects of fuels on engine-out exhaust emissions are directly translatable to the environment.

New and improved analytical methods have been developed that should enable more complete characterization of diesel emissions. Identification and quantification of higher molecular weight aldehydes is now possible (3). The work begun in FY83 was directed toward developing a chemical separation and analytical scheme for estimating mutagenic activity of the organics associated with diesel particulate. Sampling, extraction, and fractionation are now completed, but the bioassays of the various fractions have not been completed. Successful implementation of this analytical methodology would decrease the number of bioassays needed as an integral part of any fuel/engine emissions assessment project. This would enable a more rapid, comprehensive engineering assessment of environmental impacts of fuels from alternative feedstocks.

References

1. Huisingh, J. L., et al., "Mutagenic and Carcinogenic Potency of Extracts of Diesel and Related Environmental Emissions," EPA-600/9-80-057b, 1980.

2. Begeman, C. R., "Polynuclear Aromatic Hydrocarbon Emissions from Automotive Engines," GM Research Publication GMR-1009, May 1970.

3. Lipari, F., and S. J. Swarin, "An Improved 2,4-Dinitrophenylhydrazine Method for the Determination of Formaldehyde and Other Aldehyde Species," J. Chromatogr., Vol. 247, 1982, p. 297.

Objectives

To determine the impact of the utilization of fuels from alternative feedstocks on the environment. The main thrust is directed at quantifying fuel composition influences on emissions of mutagens and carcinogens, e.g., polynuclear aromatic (PNA) compounds, aldehydes, benzene, and nitro-PNA's.

Scope of Work

An investigation of the influence of fuel composition, engine design, and exhaust emission control system on the amount and character of the toxic materials in diesel exhaust will be conducted. The toxicants include direct-acting, e.g., oxides of nitrogen, carbon monoxide, mutagenic, possibly carcinogenic, compounds, e.g., nitro-polynuclear aromatics, aldehydes, and known human carcinogens, e.g., benzene, formaldehyde, benzo(a)pyrene. Test fuel selection will be based on probable compositions of fuels from alternative feedstocks.

Work Plans

Task 1 - Review biological data from tests conducted in FY83 by Inhalation Toxicology Research Institute (ITRI).

Task 2 - Duplicate tests conducted in FY83 with baseline fuel to determine repeatability of exhaust sampling, sample handling, and analyses.

Task 3 - Select ten tests from fuel/engine matrix in "Diesel Fuel Quality Criteria" project for inclusion in this work. Obtain samples and conduct separations and analyses for PNA's, nitro-PNA's, etc.

Task 4 - Analyze the data and prepare a final report.

Future Work

This project is scheduled for a duration of three years. Work planned for the second and third years of this project includes the examination of response of biological systems other than bacteria to those particulate extract fractions having mutagenic character. A state-of-the-art trap-oxidizer will be installed on one of the test engines to determine its effect on exhaust emissions character and to determine whether it can sufficiently ameliorate adverse fuel impacts on exhaust toxicity. Samples of exhaust from an engine fueled with coal slurry fuels will also be analyzed. The particulate extract will be fractionated and chemically analyzed to determine its character.

Manpower Requirements

	Man-years
Senior Chemist	0.8
Assistant Chemist	1.0
Experimentalist	0.3
Technician	0.3
Total	2.4

Equipment Requirements

	Available	New
Diesel vehicles	5	
Vehicle chassis dynamometer	1	
Spectra Physics Model SP800 HPLC	1	
Waters Associates WISP Model 710B autoinjector	1	
Perkin-Elmer Model MPF-4 fluorescence spectrophotometer	1	
Norland Corp. Model 3001 programmable calculating oscilloscope	1	
Waters Gradient HPLC (Model 680 gradient programmer and Waters Model 6000 pumps)	1	
Waters Associates WISP Model 710A autoinjector	1	
Kratos (Schoeffel) Model FS970 Spectrofluoro monitor	1	
Chromatographic peak area integrator	1	
Perkin-Elmer Model 4010 gas chromatograph	1	
Computer replacement for Data General Nova		1

PROJECT SCHEDULE AND MILESTONE

Project: Diesel Exhaust Characterization **Report Date:** ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Review biological data	//////	A ▽ //////	B▽ //////										
2. Complete duplicate tests with baseline fuels				A ▽ //////									
3. Collect and process samples		//////	//////	A ▽ //////	//////	//////	//////	//////	B▽ //////	C ▽ //////	D ▽ //////		
4. Analyze data and prepare final report											//////	A ▽ //////	
Progress Reporting Requirements		AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ	AΔ BΔ	AΔ	AΔ CΔ'	

Milestone		Description
Task 1	(A) November 30, 1983	Complete sample processing and receive biological data from ITRI
	(B) December 31, 1983	Complete review of biological data
Task 2	(A) January 31, 1984	Complete duplicate baseline fuel tests
Task 3	(A) January 31, 1984	Complete selection of fuel/engine matrix
	(B) June 30, 1984	Complete particulate sample collection and extraction
	(C) July 31, 1984	Complete sample processing and forward samples for biological testing
	(D) August 31, 1984	Obtain results of biological tests
Task 4	(A) September 30, 1984	Complete final report

Reporting Requirements

(A) 15 th of each month .... Monthly Progress Report

(B) 30 days after end of each quarter .... Quarterly Technical Progress Report

(C)' 90 days after end of program year .... Annual Technical Progress Report

OU4. COAL SLURRY INJECTION CHARACTERISTICS

Background

This work addresses Item 6.3.2 of the Research Statement of Work in the Cooperative Agreement between DOE and IITRI (DE-FC01-83FE60149).

The use of coal-liquid slurries in diesel engines has been under investigation at the NIPER laboratory (formerly BETC) for more than two years (1-2). When coal slurry fuels were used in diesel engines, numerous problems were encountered with the fuel-handling system, particularly the injector and, to a lesser extent, the fuel pump. In response to this problem, a contract was awarded in September 1982 to Southwest Research Institute to investigate diesel engine fuel-injection systems using coal slurry fuels. This work led to the conclusion that existing injectors for medium-speed engines will not satisfactorily perform with coal slurry fuels loaded between 20 and 40 weight-percent with coal. As a result, two new injector designs were fabricated and tested at an engineering model level. They each exhibited significantly improved performance and a longer life. These systems were developed using a coal-diesel slurry provided by BETC with a relatively high coal-ash content (up to 8.6 weight-percent) to stress the system and accumulate experimental data rapidly. The scope of that work did not allow an atomization study to be performed or a comparison of the spray effectiveness as the slurry fuel left the injector tip. The goal of the FY82-83 contract effort was to produce a system which would perform for 100 hours on a bench test. This was achieved, with one system operating for 106 hours and another for 60 hours before teardown and inspection. The systems showed no signs of failure (3).

References

1. Clingenpeel, J. M., et al., "A Combustion and Wear Analysis of a Compression-Ignition Engine Using Coal SLurry Fuels," ASME Paper No. 84-DGP-8, 1983.

2. Gurney, M. D., et al., "A Program to Examine the Use of Coal Slurry Fuels in Diesel Engines," ASME Paper No. 84-DGP-9, 1983.

3. Phatak, R. F., "Investigation of Diesel Engine Fuel Injector Response to Coal Slurry Fuels," Southwest Research Institute, DOE Contract No. DE-AC82-BC10730, 1983.

Objectives

To determine the feasibility of using coal slurry fuels in medium-speed diesel engines.

Scope of Work

The influence of the fuel variables of coal-loading, carrier and particle size, and the effect of fuel-injection-system parameters of fuel temperature and injection-line pressure, as well as other pertinent variables, will be examined. A comparison with the performance and response of diesel fuel No. 2 will be made. The atomization quality of the coal slurry fuel spray will be determined with standard components and with the injectors developed through the previous BETC contract.

Work Plans

Task 1 - Specify, design, order, and obtain the components necessary for an injector spray device adequate for examining fuel atomization.

Task 2 - Assemble the injector spray components and perform bench tests. Establish a baseline of performance by conducting spray tests with a reference diesel fuel.

Task 3 - Develop slurries based on diesel engine tolerances, particle size requirements, and the ability to pump, inject, atomize, and combust the fuels.

Task 4 - Perform injector spray tests with approximately 20 different coal slurry fuels.

Task 5 - Prepare a final report on assessment of the significance of the work.

Future Work

The project is scheduled to be completed in four years. Work planned for the ensuing three years includes developing, preparing, and testing of reference slurry fuels; determining the effects of aging and environment on the physical properties of slurry fuels; and comparing response to coal slurry fuels with direct-injection in a precombustion chamber engine. The reference slurries will be produced from well-defined carbon solids and appropriate liquid carriers. Properties of the reference slurries will reflect various levels of coal-cleaning technology, and processing will be sufficiently controlled to allow solids-loading, handling properties, and viscosity to be specified. The reference slurries will be burned in pre-combustion chamber and direct-injection engines, and the results will be compared with tests of an actual coal slurry fuel. Aging tests will be conducted with coal slurry fuels having different coal, carrier, and additive properties. The slurries will be aged at various temperatures, and their physical properties will be examined at periodic intervals. At predetermined times or when prespecified physical properties are attained, combustion tests in a diesel engine will be conducted to establish performance levels of the fuels. The work may also be applicable to other combustion systems.

Manpower Requirements

	Man-years
Senior Mechanical Engineer	0.2
Research Mechanical Engineer	0.3
Research Chemist	0.2
Experimentalist	0.3
Technician	0.6
Total	1.6

Equipment Requirements

	Available	New
Coal slurry fuel preparation unit	1	
Viscosity instrumentation	1	
Coulter Counter	1	
Perkin-Elmer thermogravimetric system	1	
X-ray sedigraph	1	
Single-cylinder engine	1	

PROJECT SCHEDULE AND MILESTONE

Project: Coal Slurry Fuels for Diesels

Report Date: ____________

TASK	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Manpower/Manyears
1. Design, spec, order components		A ▽	B ▽										
	//////	//////	//////										
2. Assemble, check out with baseline fuel				A▽	B ▽								
			//////	//////	//////								
3. Fuel preparation								A ▽					
						//////	//////	//////					
4. Spray tests										A ▽			
									//////	//////			
5. Assessment of significance of work												A▽	
											//////	//////	
Progress Reporting Requirements		A△	A△	A△ B△	A△	A△	A△ B△	A△	A△	A△ B△	A△	A△ C△'	

Milestone		Description
Task 1	(A) November 30, 1983	Complete design of testing
	(B) December 31, 1984	Components for the injector spray device ordered
Task 2	(A) January 31, 1984	Spray test system assembled
	(B) February 28, 1984	Complete baseline testing
Task 3	(A) May 31, 1984	Complete preparation of slurry fuels
Task 4	(A) July 31, 1984	Complete spray tests
Task 5	(A) September 30, 1984	Provide report on assessment of significance of work

Reporting Requirements

[A] 15 th of each month .... Monthly Progress Report

[B] 30 days after end of each quarter .... Quarterly Technical Progress Report

[C]' 90 days after end of program year .... Annual Technical Progress Report

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

WE1. PHYSICS OF IMMISCIBLE FLOW IN POROUS MEDIA

Background

The Environmental Protection Agency (EPA) needs background criteria for the predictability of immiscible flow of pollutants in porous media. The information generated by this project will be used by local, state, and Federal agencies in developing pollutant source control criteria, risk or damage assessment, and remedial actions for groundwater resources.

Objectives

To determine the physical properties of the fluid and media that control the flow process; determine properties on selected chemicals. To demonstrate the suitability of the selected properties using physical models, and develop the equations of flow using previously demonstrated first principles.

Scope of Work

The proposed research on physics of immiscible flow in porous media will tie in closely with NIPER's Base Program of research for determining EOR chemical toxicities, hazardous mutations of microbes used in EOR, and related environmental problems.

The work to be performed, under a Cooperative Agreement with EPA's Robert S. Kerr Environmental Research Laboratory, includes the selection of a porous medium and the immiscible fluids to be studied. Once these are selected, the physical properties that control the flow process will be determined in the laboratory. The controls for the porous media will probably encompass porosity, permeability, wettability, ion exchange, specific surface, pore size distribution, etc. The controls for the fluids will probably be viscosity, specific gravity, density, composition, etc.

The laboratory flow experiments will be performed by pumping the immiscible fluids through the porous medium and determining the dynamic relative permeabilities at selected fluid ratios to represent the entire range of saturation. The results will be analyzed to determine the relations or correlations between the experimentally determined physical properties and the relative permeabilities.

The relations or correlations will be applied to actual field conditions to determine their suitability. Once suitable relations or correlations are found, then equations and computer models will be developed for the prediction of immiscible flow of selected fluids in porous media.

The same experimental procedures will then be applied to more complicated fluids and porous media.

WE2. RESEARCH ON WATER QUALITY ISSUES

Background

Toxicity limitations need to be incorporated into the wastewater permits issued by the Environmental Protection Agency (EPA). However, knowledge of toxicity alone is insufficient to assess the impact on receiving water because many mechanisms are operative that affect toxicity after discharge of an effluent. For example, toxic components may degrade (by photolysis, hydrolysis, etc.), adsorb onto suspended solids and sediment, volatilize, chelate, be decomposed by bacteria, or change in other ways. Although dilution by other water or effluents may also lessen toxicity, this can best be handled by methods other than measurements of persistence. It is the persistence of toxicity, not the persistence of the toxicants, that need to be measured.

The objective of EPA's plan to use toxicity limitation in permits is to avoid costly chemicals measurement. The measurement of persistence must be valid for a wide variety of chemicals and processes that reduce toxicity, without the need to know the chemical composition. Persistence of toxicity can be and has been measured by in-stream sampling and toxicity assessment, but this approach requires costly field work, sample shipment, and concentrations of effluents high enough to be chronically toxic. More importantly, if other effluents are discharged nearly downstream or if additional diluting water enters, these confuse the persistence measurement and invalidate the data for a specific effluent of concern.

Objectives

To develop a standard method to measure toxicity persistence.

Scope of Work

The proposed research on water quality issues will tie in closely with NIPER's Base Program of research for determining EOR chemical toxicities.

The proposed research will begin with the selection of the toxicants to be studied. This will be accomplished in cooperation with the Environmental Research Laboratory, Duluth, Minnesota. The degradability, adsorption of suspended solids and sediments, chelateability, decomposition by bacteria, etc. will be determined for the selected toxicants. The persistence of toxicity will also be determined. Then bench methods for measuring toxicity persistence that mimic the persistence of field toxicity will be developed.

Based on the above research, a standard method for measuring toxicity persistence will be developed and evaluated in field tests.

WPT1. THERMODYNAMIC CHARACTERIZATION OF CONDENSED-RING COMPOUNDS

Background

A major function in the upgrading of synthetic crude oils from coal conversion involves catalytic hydrogenation. This increases the hydrogen-to-carbon ratio, making the upgraded oil adaptable to refinery practice, and improving its quality as refined fuel or petrochemical. The design and efficient operation of processing and refining equipment for coal syncrudes will depend largely on the availability of reliable thermodynamic properties data on polynuclear aromatic hydrocarbons (PAH) and partially hydrogenated polynuclear aromatic hydrocarbons (HPAH), which are important constituents of hydrogenated coal syncrudes. The amount of reliable thermodynamic properties data on the major families of aromatic compounds in syncrudes from coal is not inadequate for this purpose.

Objective

To measure and compile thermodynamic properties on major compound types present in syncrude from coal, shale oil, and heavy ends of petroleum.

Scope of Work

Key condensed-ring aromatic and hydrosubstituted compounds will be studied. Emphasis will be placed on hydrocarbons in these studies; however, condensed-ring nitrogen compounds may be substituted in cases to optimize use of available equipment with respect to pure compounds available for study.

The comprehensive program will involve: (1) enthalpy of combustion; (2) low-temperature calorimetry (third-law entropy determinations); (3) vapor-flow heat-capacity calorimetry; (4) vapor-pressure measurements; and (5) Raman and infrared spectroscopy and molecular statistical mechanics. The results will be integrated into correlations to provide the basic data for the calculation of heat capacities and enthalpy in all three states of matter; enthalpy and entropy of phase transitions; the enthalpy, entropy, and Gibbs energy of formation; and the equilibrium mole fractions of the chemical constituents in reacting systems.

This body of data will form an adequate experimental base for broad-ranged correlating equations based on chemical structure and will permit prediction of constraints of chemical and physical equilibria in improved processes.

WPT2. WASTE HYDROCARBON RECYCLING

Background

For more than a decade, scientists at NIPER (formerly BETC) have been performing basic and applied research related to used or waste hydrocarbons recycling. The primary area of interest has been used lubricant re-refining. More than 60 publications have resulted from this work. This industry, primarily small businesses, has shown promising signs of new life through installation of several new plants. These re-refiners have frequently acknowledged their lack of resources to perform necessary research and development and their reliance on activities, such as those at NIPER for technology development.

During the study of used lubricant recycling, an even larger potential resource began to emerge. Waste crude oils from transportation and processing losses, hydrocarbon by-products from various processes, contaminated solvents, and products from biomass and waste conversion are all seen as potential feedstocks to a facility generating a slate of quality hydrocarbon products. Re-refiners might be able to expand and become more efficient by broadening their horizons to accept a wider range of materials for recycling if research can show that such a scenario is economically attractive. Many of these waste hydrocarbons are too diffused and currently too ill-defined to attract industry research and development funding.

A study will be made to document what waste hydrocarbon resources exist, where they are located, what current recycling is occurring, and what problems have been encountered. This study should document the potential energy resource savings and indicate the most fruitful areas of needed research.

Objectives

To determine the enhanced energy and resource conservation potential of recycling various waste hydrocarbons.

Scope of Work

Interim goals include careful evaluation of each resource material as to potential volume, value, and technology available. As necessary, this activity will require long-term, generic research to provide basic data and information not available elsewhere, such as detailed characterization of recycling feedstocks and products. An auxiliary benefit of this activity will be the decrease in volume of potentially hazardous pollutants requiring disposal.

WPT3. REMOVAL OF METAL FROM ALTERNATIVE CRUDES

Background

Commercial technology for refining typical light petroleum crude oils is well established. These current techniques provide the basis for the development of effective and economical upgrading and refining of alternative fossil liquids. The difficulty of producing acceptable liquid fuels increases generally as the resource moves from heavy petroleum to syncrudes, such as tar sand liquids, shale oils, and coal liquids.

To provide environmentally acceptable synthetic fuels, minimum upgrading requirements must be established for the removal of metals such as iron, nickel, vanadium, and arsenic. They are responsible for refining, transportation, and waste disposal problems. These metals have been of little concern in light petroleum crudes where their concentration levels are very low. This is not the case for many heavy petroleums and syncrudes in which metal-containing compounds are found in substantial quantities. In some crudes the metals content is fairly evenly distributed across a wide boiling range. One problem example is that arsenic concentration levels in shale oils are present to the extent that transportation is regulated under the toxic substances control laws.

It has been common practice to assign porphyrin structures to these organometallic compounds. However, recent investigations have indicated that fewer than half of these compounds are porphyrins. Little is known regarding the chemistry of these species, making it very difficult to initiate treatment or removal schemes. It will be the purpose of this research to use physical separation techniques and instrumental analyses to characterize the nonporphyrin fractions from heavy petroleum crudes and shale oils.

To identify the nonporphyrin organometallic compounds present in heavy petroleum and synthetic crude oils, will require development of procedures specific for the removal of these chemically bonded compounds. This will be accomplished using high-pressure liquid chromatography (HPLC) along with silica gel and ion-exchange separation techniques. Final identification of the metal-containing compound types will rely on instrumental analysis utilizing mass spectrometry, nuclear magnetic resonance, and infrared spectrophotometry.

Objectives

To develop and evaluate methods for the analysis and removal of organometallic compounds from shale oil and heavy crudes.

Scope of Work

Heavy petroleums and syncrudes will be separated into porphyrin and nonporphyrin fractions to characterize the organometallic compounds in the nonporphyrin fractions by modern instrumental techniques. Separations will be made using HPLC and silica and ion exchange techniques. Compound type identifications will rely on instrumental methods such as ultra-high-resolution mass spectrometry, infrared spectrophotometry, and nuclear magnetic resonance.

Bench-scale tests will be used to test the effectiveness of multidentate ligands and supercritical extraction methods for removal of metallic compounds.

Emphasis will be placed on the environmental impact of those organometallic compounds associated with the nonporphyrin portion of alternate crude oil fractions for which very little information is available.

WPT4. ENVIRONMENTAL SAMPLE GENERATION FOR MUTAGENESIS TESTING

Background

Recent studies have shown that certain broadcut distillate fractions from syncrudes and heavy ends of petroleum display mutagenic activity as measured by the Ames *Salmonella typhimurium* mutagenicity assay. These same studies also indicated that hydrotreating these fractions at severe conditions completely eliminated this mutagenesis.

Hydrogenation, however, is a water-intensive, costly process. It is contingent upon the Federal government and the refining industry to determine minimum upgrading necessary before conventional processing can be performed, or to find less expensive ways to remove the specific compound types responsible for promoting biological activity before the alternate crudes can be a viable feedstock in normal processing sequences.

One of the biggest problems in quantifying the upgrading/mutagenesis of samples is the poor history maintained for these test samples. Only samples with well-defined production and upgrading histories will be used in this study. Although a few compound types, such as the primary aromatic amines and the polynuclear aromatics, have been identified, other compounds may elude detection because of the complex makeup of these broad-cut fractions. The need to provide environmentally acceptable fuels from syncrudes (shale oils, tar sands, coal liquids, heavy crudes, biomass, etc.) will increase as conventional light crudes are depleted.

Objectives

To determine the type and amount of upgrading necessary to convert or remove the organic compounds that cause alternate fuels to be environmentally unacceptable.

Scope of Work

Based on boiling-point separation, specific fractions of the original fossil liquids will be selected for mutagenicity testing. The fractions will be hydrogenated at predetermined levels of severity using NIPER's hydrotreating facility. These fractions, along with corresponding untreated samples, will then be subjected to the Ames *Salmonella typhimurium* assay. Results from the assay will reveal the minimum amount of hydrogenation necessary to eliminate the compound types responsible for inducing mutagenesis.

Compound types causing biological activity will be identified so that less expensive upgrading methods can be developed to augment costly hydrotreating as a means of removing these detrimental materials from process streams. These compound types will be identified using NIPER's excellent capability in compound type separation and characterization.

Some of the experimental procedures developed during earlier work at BETC will be used to determine the extent of upgrading required to reduce mutagenesis substantially.

WPT5. STRATEGIC PETROLEUM RESERVE SUPPORTING RESEARCH

Background

BETC (now NIPER), has been the lead laboratory for petroleum research for the government for many decades. As such, NIPER has developed an unusual concentration of equipment and expertise for characterizing crude oils and other hydrocarbon liquids and for interpreting the data that result from these analyses.

These capabilities are recognized by DOE's Strategic Petroleum Reserve Office (SPRO), and a continuing relationship has developed. SPRO routinely calls upon NIPER personnel for technical support. Maintenance of such technical support is important to ensure the integrity of the stored petroleum. In addition, research is required to better characterize the oils and to predict any commingling problems resulting from many crude oils being introduced into the same cavern.

Objectives

To provide technical support to SPRO, including routine chemical analyses, experimental research, monitoring of outside contracts, and technical consultation.

Scope of Work

Necessary technical data and information will be provided to SPRO for making crucial decisions concerning long-term storage of crude oils, unfinished products, and finished fuels obtained from petroleum. This will be accomplished by providing analytical data, consultation services, and fundamental research.

WU1. COAL SLURRY FUEL GUIDELINES

Background

Powdered coal was the original design fuel for the compression-ignition (CI) diesel engine first theorized in the 1880's. Problems with the use of dry powdered fuel quickly led the experimenters to the use of liquid petroleum fuel. With the expiration of international patents in 1912, the U.S. diesel industry began. The first industrial applications of diesel engines occurred in 1916. During the next two decades, application of the diesel engine was made to marine and rail transportation and stationary installations. In 1949, the first of several coal slurry fuel experiments was conducted in the United States. They revealed the major problems to be delayed or noncombustion of the fuel, wear from abrasive components of coal, and seizure of fuel injection and combustion components due to melting and crystallizing of the coal.

The slow- to medium-speed diesel engine using currently available liquid fuels offers some inherent advantages over other power generation systems. The most important advantage is its high thermal efficiency over a wide operating range. The large new engines routinely achieve thermal efficiencies of 45 percent, and some newer designs are reported to be over 50 percent.

The diesel engine is also highly reliable, with large engines designed to operate for extended periods with minimal maintenance. Parts subject to wear are replaceable, including cylinder liners. Typical service life is 10,000 to 12,000 hours at full load and speed before initial disassembly for reringing, followed by an additional 10,000 hours before a complete overhaul is necessary.

Engines may be overhauled many times so they have extended lives. For example, based upon a duty cycle averaging 50 percent of full load and five overhauls during the engine's life, the engine should operate satisfactorily for 25 to 30 years. The result is that many of the engines existing today, and those currently being designed and built, will be producing power as petroleum becomes scarce, and efforts to adapt to alternate synthetic fuels, including coal slurries, should be encouraged.

Objectives

To investigate the feasibility of using coal slurries in diesel engines focusing on establishing guidelines for fuel formulation which will suggest physical properties necessary for utilization. The effects of varying fuel formulation on physical properties will be described. The formulations will represent fuel properties that have been tested with some degree of success at NIPER and others within the research community.

Scope of Work

The coal slurry variables that significantly influence the use of these fuels in CI applications will be examined. This may allow definition of a set of fuel guidelines to set limits on fuel specifications and provide reasonable operation with the current basic design of the CI engine. This will allow an assessment of the sensitivity of the major variables to selected CI engine operation profiles. The basic purpose is to examine the combustion of coal slurry fuels in CI engines designed to run on petroleum distillate fuels.

The work effort for FY84 is directed toward developing fuel guidelines which would be a reference for coal slurry fuels for diesel engines. Some early decisions on the selection of the carrier, the target coal loading, and critical fuel factors would have to be made. Much of the work would involve slurry producers and engine manufacturers. Only a few fuels will be produced in the NIPER laboratory. A limited number of fuels will be tested in an engine environment.

WU2. ALCOHOL-GASOLINE BLENDS

Background

Methanol produced from coal or natural gas has been identified in most industry and government forecasts as the most likely near-term candidate as an alternative transportation fuel. In addition, methanol has been shown to have attractive economic potential, especially on a volumetric basis. The indiscriminate use of methanol blended with gasoline, however, can result in excessive exhaust and evaporative emissions, as well as early engine failures, whereas its use in properly designed fuels and/or engine systems offers potential for improved emissions control without adversely affecting engine operation.

Both the automotive and refining industries have voiced concern regarding a need for early research to allow an orderly introduction of methanol into the marketplace while maintaining customer acceptance of the fuel. Previous work performed in the NIPER laboratory has suggested the evaporative emission-control systems currently on vehicles are not compatible with methanol blends for extended operation. This research program will investigate the long-term effects of the evaporative emission-control systems using methanol-gasoline blends as well as other high-volatility fuels.

Objectives

To determine problems resulting from the use of methanol as a blending agent in gasoline.

Scope of Work

The long-term compatibility of the evaporative emission-control system using methanol-gasoline blends will be investigated. In addition, the effect of methanol on evaporative emissions, per se, will be examined using hydrocarbon-only fuels tailored to have the same physical characteristics (vapor pressure and distillation character) as methanol/hydrocarbon blends. The work will involve bench tests to simulate long-term aging effects as well as selected vehicle testing to complement the studies. Vehicle driveability will also be examined using tailored hydrocarbon fuels and hydrocarbon/methanol fuels.

WU3. ASSESSMENTS OF ALTERNATIVE FUEL TECHNOLOGIES

Background

The DOE Alternative Fuels Data Base was established at BETC in 1979 under sponsorship of DOE/Conservation and Renewable Energy. The purpose of the data base was to evaluate current information for technical accuracy and relevance and systematically compile the data on the use of alternative fuels. Ready access to this reliably screened technical data was provided to R&D investigators.

There is currently a large amount of information obtained from publications and through direct communication with researchers in the technical community relating to the use of alternative fuels. These data would constitute a technical base for alternative fuel technology assessments.

As production and utilization technologies rapidly evolve, there exists a need for comprehensive assessments based on current information on state-of-the-art technology of alternative fuels having potential for commercial applications. Unbiased, technically objective assessments would be useful to managers and R&D personnel in that they would (1) indicate the potential of and identify the impediments to commercialization, and (2) define R&D needs and indicate priorities.

Objectives

To assess the overall suitability, applications potential, deficiencies, and further R&D needs with respect to alternative fuels and the transition technologies (compatible developments in engine and fuels processing) that involve heavy and low-quality feedstocks.

Scope of Work

The scope of work will include assessments of environmental and engine-related effects of specific alternative fuels. The assessments will be based upon extensive survey of current literature and data bases (including the DOE Alternative Fuels Data Base) in conjunction with discussions with prominent researchers. Assessment and compilation of the material will be managed by members of the engineering staff of NIPER with proven R&D experience.

The fuels assessments will be assigned priorities based on discussions with industry managers and researchers. The priorities will be reexamined annually.

The data base will be maintained and continuously updated through comprehensive "date-of-issue" review of leading technical journals, reports of research investigations, and technical papers from relevant symposia and technical society meetings. This will include organization to abstract and systematically format experimental data and technical information pertinent to the objective.

APPENDIX 1. CAPITAL EQUIPMENT REQUIREMENTS

Project No.	Name of Equipment	Purpose	Cost, $K	Project Cost, $K
BE1	Adsorption and Kinetic Reactor	To examine the gas phase adsorption and kinetics of reactions on sedimentary rocks	15	
	Scintillation Counter	To measure radioactive (tritium) tracers in cores	15	
				30
BE3	Microscope	To examine microbial species produced	15	
	Culture Oven and Accessories	To provide long-term environment to increase new species	25	
	Fluid Pumps	To become integral part of long-term test facility	15	
	Core Test Facility	To simulate by a laboratory model reservoir conditions with additional unique features for MEOR simulation	25	
				80
BE4	Adsorption Microcalorimeter	To measure heat of adsorption of surfactant and polymer on reservoir substrate (using large samples)	6	
	High Temperature Micro-calorimeter	To measure the effect of temperature on enthalpy of mixing and dilution, etc.	37	
				43

APPENDIX 1. CAPITAL EQUIPMENT REQUIREMENTS (Continued)

Project No.	Name of Equipment	Purpose	Cost, $K	Project Cost, $K
BE5	Constant Temperature Oven	To maintain constant temperature for slim tube and phase behavior apparatus	2.5	
	Circulating Pump	To circulate fluids in phase behavior apparatus	4	
	Mixing Chamber	To mix fluids in phase behavior apparatus	1	
	Mettler-Paar Density Meter	To measure density of crude oil-gas solution of high pressure	8	
	Back Pressure Regulator	To regulate pressure of the phase behavior apparatus	3	
				18.5

APPENDIX 1. CAPITAL EQUIPMENT REQUIREMENTS
(Continued)

Project No.	Name of Equipment	Purpose	Cost, $K	Project Cost, $K
BPT1	Vacuum Electrobalance	To be used with new torsion effusion vapor pressure apparatus	14	
	Thermometry for Combustion Calorimetry	To be used with new microcombustion calorimeter	5	
	Thermometry for Vapor Pressure Measurement	To be used with new torsion effusion vapor pressure apparatus	1	
	Graphic Computer Terminals (2)	To be used in automation of vapor flow calorimetry	8	
	Calorimeter Control Apparatus	To be used for determination of vapor flow heat capacity	10	
	Bath for Bomb Calorimeter	To be used with new microcombustion calorimeter	6	
	Microcalorimetric Detection System	To be used with new microcombustion calorimeter	39	
				83
BPT2	Liquid Feed Compressor	To modernize hydrotreater	30	
				30
BPT3	Megohm Meter	To use with mass spectrometer	2	
	Gas Chromatograph	To support analysis of heavy ends of petroleum	20	

APPENDIX 1. CAPITAL EQUIPMENT REQUIREMENTS
(Continued)

Project No.	Name of Equipment	Purpose	Cost, $K	Project Cost, $K
	GC Mass Detector	To analyze heavy ends	25	
				47
OE1	Humidity Oven	To condition cores with clays to controlled humidity levels for permeability measurements	1.8	
	High-Torque Mixer	To prepare high-viscosity polymers	1	
	Three-Place Electronic Balance	To weigh cores to determine water saturation	2.3	
				5.1
OE3	Microcalorimeter	To measure enthalpies of reaction of polymers at reservoir temperature to required sensitivity	30	
	Core Flooding Equipment	To increase capacity for flood testing to make measurements on on four systems simultaneously	43	
	Reactors (3)	To make kinetic studies on crude oil-alkali, alkali-rock and crude oil alkali-rock systems	1.5	
	Hardware for Site Development	To conduct field mini-test	35	
				109.5
OE4	Thermal Gravimetric Analysis Equipment	To measure the combustion temperature of oil	28	

APPENDIX 1. CAPITAL EQUIPMENT REQUIRMENTS
(Continued)

Project No.	Name of Equipment	Purpose	Cost, $K	Project Cost, $K
	Differential Scanning Calorimeter	To determine reaction kinetics	9	
	Scaled Physical Model	To simulate actual reservoir condition in a steam flood experiment	7.5	
				44.5
OPT1	Equipment for Vapor-Liquid Equilibria Studies	To add pumps for obtaining material balances and new cells and sampling valves needed to reduce time for studies of model systems	14	
	Equipment for Speed of Sound Studies	To reactivate acoustical equipment	8	
				22
OPT2	Draw Pump	To use with thin-film evaporator	3	
	Supercritical Extraction Equipment	To separate heavy ends	30	
	Automated Control Valves and Accessories	To incorporate in hydrotreater	25	
				58
OPT5	Supercritical Liquid Extraction Equipment	To use for process simulation and development	25	
				25

APPENDIX 1. CAPITAL EQUIPMENT REQUIREMENTS (Continued)

Project Number	Name of Equipment	Purpose	Cost $K	Project Cost $K
OU1	Automatic Sampler for Sigma II Gas Chromatograph	To provide 24-hour per day operation	10	
	Combustion Analyzer and Transducers	To measure cylinder pressure	40	
				50
OU2	Computer	To replace Hewlett Packard 21MX	20	
				20
OU3	Data General Nova Computer	To replace present computer	20	
				20
NIPER Support	Word Processors and computers	To support the technical managers and the word processing group, five consoles, three printers, and two computers are needed	60	
	Transportation	To provide support transportation for the Center two automobiles and one pickup are needed. GSA vehicles have been returned and additional vehicles are needed	30	
				90
		TOTAL		775.6

APPENDIX 2 -- COOPERATIVE AGREEMENT RESEARCH STATEMENT OF WORK

RESEARCH STATEMENT OF WORK

1.0 Background

1.1 The Bartlesville Energy Technology Center (BETC), as lead Government laboratory for petroleum research, has carried out in-depth petroleum research since 1918. While this research focused on oil and unconventional natural gas, the work is generally applicable to all liquid and gaseous hydrocarbons, regardless of their source.

1.2 The DOE participation in this Cooperative Agreement is intended to preserve the laboratory complex as a National resource and to preserve the scientific and technical strength of the Center and its ability to continue to contribute to the Nation's long-range energy needs. The current program at the Center, presently supported fully by DOE funds, offers a broad operational base from which a great many practical problems can be addressed. It is important to ensure the capability of continuing this type of research.

2.0 United States Energy Policy and National Goals

2.1 The overall objective of U.S. Energy Policy is to encourage economically efficient energy production and use. The primary means for achieving this objective is to rely on market forces. The Government's direct role is limited to funding long-term, high-risk, high-payoff research which the private sector is unlikely to undertake.

The Office of Fossil Energy program strategy recognizes the respective roles of industry and government delineated in current Administration policy and focuses on the R&D support which lies outside the reasonable responsibility and expectation of industry to provide.

The Federal government cannot determine what is the most efficient combination of energy conservation and energy production, or what is the most efficient means for increasing energy supply. The answers to these questions will be determined by market forces. For example, the alternatives for increasing the domestic supply include additional discoveries of fields in the United States (onshore and offshore), development of synthetic liquid fuels, and enhanced recovery from existing oilfields. Of the 460 billion barrels of oil discovered, 310 billion barrels will not be recovered by primary and secondard procedures. Although the amount of oil that can be recovered by enhanced oil recovery (EOR) processes is uncertain, a reasonable estimate is from 18 to 53 billion barrels, which is more than current proved oil reserves. The market will determine how best to deal with these facts. The NIPER can supplement the efforts of the private sector in turning these resources into economic opportunities.

2.2 It is useful for the Government to support an effective, long-term petroleum and unconventional hydrocarbon research program to accomplish the following:

(1) provide for the National well-being and protect the vital interests of the United States by developing new methods for utilizing domestic petroleum resources in a manner which supplements, rather than duplicates, research activities of private groups, other Federal agencies, and State and local governments;

(2) maximize utilization of existing Federal facilities;

(3) encourage communication and cooperation between the Government and the non-Federal sector, as part of a goal of broader non-Federal participation in a long-term petroleum and unconventional hydrocarbon research program; and

(4) provide a means of furthering, assisting, and funding research in institutions of higher learning through innovative arrangements involving those institutions and industry and in some cases through DOE support.

2.3 Specific goals for the Program are: (1) to develop improved understanding and predictability of those advanced highly effective processes, (2) to improve the level of performance and extend the range of application of the advanced processes; and (3) to assess the feasibility of the extremely long-range, highly advanced energy technologies and evaluate the unique problems for existing technologies.

3.0 Research Objectives

The overall research objective of the establishment of the NIPER is to conduct a balanced program of research in all fields of petroleum and unconventional hydrocarbon technology from extraction, through processing, to utilization. This research will generally be within, but not limited to, the areas of resource assessment, unconventional production technologies such as advanced EOR methods, processing (including pre-treatment), thermodynamic energy conversion, end-use applications, and system integration with emphasis placed on EOR research. The specific objectives of the DOE research program in Enhanced Oil Recovery and Advanced Process Technology are:

(1) to develop improved understanding and predictability of advanced, highly effective EOR processes.

(2) to improve the level of performance and to extend the range for application of advanced processes.

(3) to assess the feasibility of very long-range, highly advanced emerging technologies and to evaluate the unique problems of reservoirs for which no EOR technology now exists.

(4) to examine entirely new concepts which might be applicable to the huge resources left after current methods have been exhausted.

(5) to maintain, as appropriate, efforts in characterization and utilization of syncrudes from coal, oil shale and bitumen from car sands as petroleum substitutes.

4.0 Scope of Work

The successful Participant shall conduct research in petroleum and unconventional hydrocarbon technology at three program levels. These levels are designated as the "Base Program", the "Optional Program," and the "Other Work Program."

The Base Program is expected to be 100% DOE-funded at a level of $5 million per year over a five-year period. The DOE is expected to cost-share, on a declining basis, the cost of the Optional Program with the Participant over the five-year period. The DOE expects the Participant to institute a Other Work Program to obtain additional funds from other Federal agencies, State and local governments, and the private sector to more fully utilize the NIPER. The DOE funding will be subject to annual appropriations.

5.0 Base Program

The Base Program shall consist of the following research in Enhanced Oil Recovery and Advanced Process Technology Program Areas.

5.1 Enhanced Oil Recovery Research Program Area

5.1.1 Displacement Mechanisms and Mobility Control

Key Tasks

(a) Study the role of interfacial tension gradients on the displacement of residual oil

(b) Refine concepts derived from current data concerning the effect of capillary number, pore shape, and topology on mobilization and entrapment phenomena

(c) Study the quantitative effects of dispersion on multiphase flow in porous media

(d) Study the fundamentals of polymer flow in porous media including determination through clay-mineral analysis and flow tests the apparent permeability of reservoir rocks in an attempt to increase sweep efficiency.

(e) Conduct studies of a basic nature on the influence of slug size on process efficiency.

(f) Study the effects of oil content of a surfactant slug on its displacement efficiency.

(g) Study the mechanism of miscibility development and oil displacement from porous media by mixtures of carbon dioxide and other bases. In addition, study the mechanism of the changes in mobility of carbon dioxide and other gases flowing together with another fluid such as water, foam, and polymer solutions.

(h) Study the mechanism of oil displacement in porous media by the in situ emulsification of the crude.

(i) Develop laboratory techniques that simulate water flooding and enable measurement of the relationship between oil retention and the wettability of the fluids-rock system.

(j) Study pore structures, especially in carbonates.

(k) Determine factors influencing polymer cross-linking reactions in vitro and in pores, as guides to improved flow diversion techniques.

5.1.2 Rock/Fluid Interaction

Key Tasks

(a) Study molecular structures to better understand relationships between maximum oil displacement and adsorption phenomena in chemical flooding (this includes systematic studies of precipitation, adsorption, and chromatographic effects on slug composition).

(b) Conduct basic studies of thin-film phases and static/dynamic wettability relationship to oil displacement.

(c) Study the interactions of surfactants with formation rocks to determine, through clay mineral analysis and flow tests, the capacity of shaley reservoir rocks to alter a surfactant's efficiency in mobilizing oil.

(d) Study the chemistry of alkali/oil interaction with respect to both equilibrium and kinetics.

(e) Study the nature of the interaction of alkali with clay minerals.

(f) Study ion exchange characteristics of chemical solutions (used in oil recovery) and porous media.

(g) Study the rheological properties of polymer systems that are necessary to provide tolerance and long-term stability in reservoirs that are at high temperature or are shaley or contain high-salinity waters.

(h) Study the factors contributing to chemical adsorption and enhancement that occur in micellar flooding of oil from porous dispersion.

(i) Study the mechanics of injectivity reduction due to polymer dispersion.

(j) Determine quantitatively the effects of dispersion, relative permeability, apparent viscosity, and inaccessible pore volume on mobility control under one-, two-, and three-phase flow for the development of ancillary equations to be used for improving the precision of predictive reservoir simulations.

(k) Conduct fundamental studies of the mechanisms for physical entrapment and retention of oil, as well as the surface chemistry of sedimentary rocks and surface chemical reactions of oils that are responsible for oil-rock adhesion, and wettability effects, which determine residual oil saturation.

5.1.3 Prediction and Evaluation

Key Tasks

(a) Develop one- and two-dimensional mass simulators for enhanced oil recovery-type displacements and match the results with laboratory data; use the results to extend laboratory experimental data.

(b) Develop means of determining three-phase relative permeability characteristics of rock-fluids systems and apply the results in mathematical modeling of the WAG procedure and so evaluate its utility.

(c) Continue to collect data and expand data base on reservoir characteristics relating to EOR projects and prospects.

5.2 Advanced Process Technology Research Program Area

5.2.1 Thermodynamic and Thermophysical Property Measurements

Key Tasks

(a) Study stability and adsorption of surfactant-cosurfactant-oil water systems encountered in tertiary petroleum recovery systems using micro-solution and micro-adsorption calorimetry.

(b) Measure heat capacities and heat of combustion for real fluids derived from coal conversion processes.

(c) Perform thermodynamic studies of important organic nitrogen compounds in unconventional hydrocarbon mixtures to determine stability, decomposition, and the best possible conditions for their removal from refining streams.

(d) Study and measure thermodynamic properties of the condensed ring hydrocarbon systems that are encountered in coal liquefaction products and also occur in heavy petroleum and heavy ends of lights oils.

5.2.2 Characterization Studies

Key Tasks

(a) Maintain capability in characterization of residual and heavy asphaltic bottoms from crude oils which are not currently being efficiently used for fuels and to provide data for improved processing of these heavy ends.

(b) Develop a compositional data base on heavy oils, shale oils, coal liquids, and by-products for use in efforts to improve processing schemes to turn these liquids into more useful end products.

(c) Study improved approaches for combining MS, NMR, IR, and other instrumental techniques for the characterization of all fossil fuels.

(d) Develop laboratory techniques for improved separation of heteroatom-containing compounds.

(e) Correlate stability and processing data to provide insight into determining fuel stability, performance, and environmental acceptability at various processing levels.

5.2.3 Process Technology

Key Tasks

(a) Based on the compositional characteristics of synthetic crude oils determined in the characterization studies (5.2.2), carry out bench studies to investigate novel methods having the potential of improving existing refining procedures.

(b) Study improved methods for removing metals and particulates from fossil fuels (shale oil, coal liquids, bitumen from tar sand).

(c) Conduct bench-scale studies to determine catalytic decomposition of typical heterocyclic compounds found in synthetic crude oil.

6.0 Optional Program

The Optional Program shall consist of the following research in Enhanced Oil Recovery, Advanced Process Technology and Utilization.

6.1 Enhanced Oil Recovery

6.1.1 Reservoir Systems -- Properties and Characteristics

Key Tasks

(a) Develop means for quantitatively describing underground reservoirs in three dimensions, using knowledge of geolical aspects of depositional and actual well profile data from dispersed locations. Include effects of formation heterogeneities (micro-and macro, horizontal and vertical) into the models.

(b) Conduct reservoir heterogeneity studies on pore geometry, permeability, lithology, and fracturing for better reservoir description. The results will be used to improve process predictive modeling.

6.1.2 Displacement Mechanisms

Key Tasks

(a) Build a laboratory model and develop experimental techniques for conducting, at reservoir conditions of temperature and pressure, displacement studies on oil movement from porous media.

(b) Study the action of microbes in the release of oil under reservoir type environments.

(c) Develop more efficient surfactants than are presently available and measure displacement properties in the presence of divalent ions in high salinity, shaley, carbonaceous, and high-temperature reservoirs.

6.1.3 Sweep Mechanisms

Key Tasks

(a) Study means for controlling gravity effects and permeability variations on the lateral movement of fluids in porous media in order to gain knowledge beyond that now available. Results could lead to disclosure of processes to improve EOR.

(b) Explore alternate methods of mobility control (gas-water, foams, polymers, etc.,).

6.1.4 Injection Materials

Key Tasks

(a) Study means to control bacteriological degradation of biopolymers.

(b) Develop improved methods for evaluating polymers used in oil recovery.

(c) Study the causes for and control of surfactant precipitation due to divalent ion contamination.

(d) Study the factors that degrade tracer slugs (both inorganic and organic) and develop materials with highest survival rate.

(e) Develop polymers suited for the special requirements of alkaline flooding.

6.1.5 Reservoir Simulation

Key Tasks

(a) Develop reservoir simulators suitable for evaluation of laboratory test results.

(b) Conduct predictive reservoir simulation modeling of the micellar polymer and gas-miscible displacement processes utilizing latest laboratory-derived data incorporating reservoir heterogeneity variables.

6.1.6 Reservoir Data Development

Key Tasks

(a) Evaluate data base assembled for NPC study and augment with additional data from existing supplementary resources, e.g., Intercomp-California, University of Texas study, fields with OOIP 20 mm barrels.

(b) Improve methods for estimating reservoir conditions after primary/secondary recovery and develop improved default/validation correlations.

(c) Identify new data sources, improve quality of existing data and update/maintain reservoir data base.

6.1.7 Process Data Development

Key Tasks

(a) Update EOR project file from annual report filings and from other public sources (O&GJ, Enhanced Recovery Week, etc.).

(b) Evaluate/improve existing EOR screening models and review new models developed by Venezuela.

(c) In conjunction with the NPC, estimate technically recoverable oil for each EOR process. Update as sufficient new reservoir data becomes available.

6.1.8 Economics and Logistics

Key Tasks

(a) Review NPC modifications to economic models and estimate economically recoverable oil for EOR.

(b) Develop time rate model incorporating logistics, environmental and regulatory constraints to EOR application. Review with NPC and estimate timing rate for EOR production.

(c) Develop sensitivity analysis system and, with NPC, build system cases.

(d) Plan and conduct risk analysis and technical sensitivity studies to assess the production potential of alternate EOR research objectives.

6.2 Advanced Process Technology

6.2.1 Fuel Processing

Key Tasks

(a) Investigate improved methods of removing fine particles from liquid and gaseous streams.

(b) Explore new methods of breaking oil water emulsions in order to facilitate recovery of oil from tar sand.

(c) Investigate methods of removing contaminants such as phenols, arsenic, and other metals from natural and synthetic crude streams.

(d) Using unconventional hydrocarbon feed, produce samples at varying degrees of hydrogenation to study stability as a function of time and temperature; to determine toxicology; to determine the effect on upstream handling and processing; and to determine the effect on emissions of derived fuels.

6.2.2 Thermodynamic and Thermophysical Property Measurement

Key Tasks

(a) Investigate and perform thermodynamic studies of systems encountered in the production of alternate fuels from oil shale, tar sand, and peat.

(b) Determine thermodynamic and physical properties of fractions of new heavy crude that become available.

(c) Jointly with the American Petroleum Institute, carry out thermodynamic studies on specific mixtures for which insufficient data are currently available to permit the accuracy of design now desired.

(d) Measure and document the thermophysical properties of compounds which are of importance to the natural gas industry in both the liquid and gaseous states; develop correlation techniques to accurately predict the properties of compounds and mixtures.

(e) Provide more complete and accurate information on the fundamental physical properties of the fluids which are the basic commodity of the gas industry.

6.2.3 Fuel Characterization Study

Key Tasks

(a) Investigate the reason for instability of certain crudes, such as Maya and Trinidad, at moderate temperatures.

(b) Evaluate chemicals for stabilizing natural and synthetic crudes.

(c) Determine the nature of oxygen compounds in synthetic fuels and investigate methods of removal.

(d) Carry out detailed evaluation of new crudes for the existing data base.

6.2.4 Other Characterization Studies

Key Tasks

(a) Determine the composition of process streams in order to identify toxic or undesirable substances for their control through the use of appropriate technology.

6.3 Utilization

6.3.1 Fuels for Mobile Engines

Key Tasks

(a) Relate the performance of high-speed diesel engines to properties of the fuel with the objective of determining the best criterion of quality.

(b) Determine the effects of fuel and engine variables on particulates in engine exhausts.

(c) Determine the effects of fuel and engine variables on NO_x and nitric acid emissions from spark ignition systems.

(d) Investigate the presence of toxic materials in diesel engine exhausts.

6.3.2 Fuels for Stationary Engines

Key Tasks

(a) Determine the fundamental fuel qualities which affect the burning of heavy oils in stationary equipment, burners, or engines.

(b) Investigate the use of low-cost additives to improve burning quality to counter problems discussed above.

(c) Determine how to burn coal-liquid slurries most effectively.

6.4 Unconventional Gas Recovery

6.4.1 Formation Characterization

Key Tasks

(a) Improve diagnostic reservoir technology to measure and characterize the formation parameters most critical to lenticular tight gas sands production.

6.4.2 Fracturing

Key Tasks

(a) Select and develop treatment fluids and proppants that are compatible with the formation, facilitate flow back to well bore, and maintain propped facture integrity of lenticular western tight gas sands.

(b) Develop treatment design methods using limited flow test data and other formation information, and define treatment design variations to accomodate variations in lenticular western tight gas sands.

6.4.3 Production Technology

Key Tasks

(a) Develop the necessary sensitivities and evaluation tools to determine the cost effectiveness of advancements in lenticular western tight gas sands technology and their potential effect on gas production costs.

6.4.4 Recovery Predictions

Key Tasks

(a) Consolidate the data from all lenticular western tight gas sands projects and develop modeling capabilities to include: mathematical modeling of reservoir and fracture parameters; real-time modification during fracture treatment; analysis/verification during subsequent testing; and determination of drainage pattern/well spacing.

7.0 Other Work Program

DOE encourages expansion of the role of the NIPER in a manner that meets the goals and objectives set forth in paragraphs 2.0 and 3.0. Examples include, but are not limited to, work in the following areas.

7.1 Laboratory R&D for the Petroleum Industry

Key Tasks

(a) Initiate an effort to perform R&D work for the petroleum industry in areas where the NIPER possesses special expertise and/or unique equipment.

(b) Provide R&D support to the smaller organizations in the petroleum industry.

(c) Support energy utilities in such areas as problem-solving applied to environmentally sound use of low quality residium metals control, pipeline problems, and initiate staff exchanges to provide professional enrichment for utility technical staffs.

(d) Provide technical assistance to State and local governments.

(e) Undertake joint R&D programs with universities and other non-profit institutions that is of mutual interest and/or benefit.

8.0 Reporting Requirements

Monthly Progress Report

A monthly progress report shall be prepared for each project under the approved Annual Research Plan. The report shall include: a summary of work done during the month; a description of problems encountered and proposed remedial action; activities planned for the next month; feedback or assistance required; and a summary of manpower and funds expended. This report shall be due by the end of the second week of the new month. While clarity is expected detail may be limited and length should not exceed 1-2 pages per project.

Quarterly Technical Report

A Quarterly Technical Report shall be prepared for each project under the approved Annual Research Plan. The report is to focus on data, analysis and review of results, and significant accomplishments. The key investigators are to be identified. No business data is to be included. A draft of the report is due 30 days after the end of the quarter. DOE shall provide comments on the draft to the Participant within two weeks. The Participant shall publish the quarterly report by the commencement of the second quarter and provide 50 copies to the Director of the Bartlesville federal site office.

Annual Technical Report

This report shall set forth progress against the Annual Research Plan summarizing all the work accomplished, and presenting data analysis and conclusions. This is not intended to be a detailed technical report, i.e., a scientific paper, but rather an aggregation of the work conducted during the Budget Period. Actual vs. planned milestone achievement dates shall be indicated and a discussion of the impact of the research conducted on future work shall be presented. The Participant shall submit a draft of the Annual Technical Report to DOE within 30 days after the end of the Budget Period. DOE shall submit comment on the report to the Participant within two weeks.

Project/Task Reports

Whenever a task or project is completed, a final technical report for that task/project shall be prepared. The report should be a scientific presentation of the research incorporating experimental procedure and statistical presentation of data necessary for peers to review the quality of the research. Also it is expected that journal articles and presentations to educational and professional societies shall be prepared on the completed task/project or on work in progress.

Financial Status Reports (and supporting documents)

The Financial Status Reports (SF 269 plus appropriate attachments) will present an accounting of all Federal and Non-Federal funds utilized during the Budget Period as well as those utilized by the Participant. A separate section of the report will summarize the finances of "Other Work". A third section of the report will provide for the next Budget Period a marketing strategy and plan for all "Other Work" which highlights the work consistent with the mission of the Fossil Energy program in petroleum R&D. This report will allow DOE to assess the degree to which the Participant in achieving independence of NIPER operations and how well the cooperative work fits with that done for others. No sensitive information is required. A listing of clients, generalized work statements and level of effort in exploration, extraction, processing, distribution and utilization with claryifying discussion will be sufficient.

Federal Cash Transaction Report

The Federal Cash Transaction Report (SF 272) is required in accordance with the directions printed on the form.

Committee Record

The Participant shall document the meetings of the Senior Technical and Senior Management Committee meetings setting forth the Participant's understanding of significant decisions, direction or redirection or required actions resulting from the meetings.

Final Technical Report

A Final Technical Report shall be prepared in the fifth year reviewing the work done in that year and the preceeding years relateable to the Annual Research Plans adopted for each year. The level of detail and information required is the same as that requested under the Annual Technical Report. A draft of the Final Technical Report shall be submitted to DOE for review three months prior to the date of the Cooperative Agreement termination. DOE shall provide comments to the Participant within two weeks.

ENHANCED OIL RECOVERY R&D

PROGRAM PLAN 1983

Technical Constraints to Application of Chemical Flooding

A critical assessment of the technical constraints that inhibit use of chemical flooding enhanced oil recovery techniques has been initiated and will continue as an integral part of the Subprogram. This assessment is based on the discrepancy analyses of predicted versus actual performance of extensive field applications, as can be interpreted, based on laboratory and computational modeling. To the extent that the analyses cannot explain differences between actual and predictive performance, the Subprogram assigns high priority to these areas of R&D. Constraints identified by practice and literature analysis*

(numbers refer to the Chemical Flooding Technology R&D work packages that address them, as specified in the next section) are as follows:

a. Basic Process Research (2.2). This includes adsorption, wettability, ion exchange, polymer and surfactant mechanisms and formation damage. A subordinate problem currently being addressed is that tracer tests may be affected by the interaction of tracer materials with the reservoir solids, or by degradation by microorganisms.

b. Basic Studies of Displacement Mechanisms and Mobility Control (2.2). These cover such items as capillary number, relative permeability, and emulsification coalescence, the understanding of which is necessary to effectively design floods.

---

* Technical Constraints Limiting Application of Enhanced Oil Recovery Techniques to Petroleum Production in the United States. For details, see BETC Staff, DOE/BETC/RI-80/4, May 1980.

c. Surfactant Fundamental Research (2.2). This requires study of chemical structure and composition of oil-brine-surfactant systems. Primary criteria are the effect on phase and interfacial behavior. Basic properties of microemulsions and emulsion formation mechanisms within the reservoir and in the produced fluids must be understood and controlled, since breaking emulsions of some processes can become a major technical constraint.

c. Surfactant Design (2.2). A search is on for stable polymers and saline-tolerant surfactants. Shear, heat and chemical degradation of polymers and surfactants are critical areas of research. Specifications must also be tightened up because process effectiveness can be seriously compromised by seemingly minor variations between batches.

e. Geoscience Research (2.3). Adequate sweep efficiency requires improved reservoir evaluation and the delineation of heterogeneities (micro and macro) and their correlation with geological parameters, especially for carbonate reservoirs and their special pore structure. Vertical heterogeneities may be the biggest problem in surfactant flooding. The flow diversion techniques for reducing the adverse effects of these heterogeneities need development. The tools for evaluating geological parameters can themselves distort results.

f. Modeling (2.4). Accuracy in scaling-up from laboratory experiments and numerical simulation with models has been difficult to confirm and poor predictability has limited model calibration.

g. Field Data Acquisition and Discrepancy Analysis (2.5). There is a need for improved field test procedures in order to undertake tests with minimum investment. Key reservoir and process parameters for screening must be identified. Improved chemical analysis techniques, especially of mixed surfactants and field production samples are called for.

Technical Constraints to Application of Gas Miscible Flooding

The Subprogram assesses the dominant constraints to gas miscible flooding as an integral part of its plan to improve process performance predictability and recovery efficiency. These assessments are based on the results of field applications and discrepancy analyses of predicted versus actual performance. Technical contraints identified as contributing to poor predictive capabilities and low recovery efficiencies are assigned high priorities, given that their removal by successful R&D (as determined by Technology Appraisal) is cost effective and timely.

Prior field applications and discrepancy analyses have identified the following dominant technical constraints to gas flooding (numbers refer to Gas Miscible Flooding Technology R&D areas that address these constraints, as specified in the next section):

- Residual Oil Saturation Research (3.3.1). In reservoirs that have been waterflooded, achieving miscibility and maintaining the required bank are impeded by the fingering induced through the watered out channels. Since many carbon dioxide candidates, indeed most in some regions (e.g., West Texas) have been or are being actively waterflooded, high oil saturations will be the exception and not the rule. Although 25-30% is often cited as the minimum oil saturation, several projects have been started with saturations of 20%. However, waterflooding often improves the sweep efficiency of subsequent carbon dioxide floods by reducing permeability contrasts.

  A second problem concerns the uncertainty in the actual level and distribution of the residual oil. Seventy-five percent of the discovered oil was found when techniques for evaluation and measurement were not as accurate as they have become. Depletion in most cases is non-uniform, indicating some of the total residual

- Evaluation of Nitrogen, Flue Gas and Gas Mixes (3.2.4). Insufficient data and theory exist as to the viability of nitrogen and flue gas floods, especially with regard to allowable impurities (such as corrosive nitrogen oxides) in flue gas floods and the reduced heat value of produced gas in nitrogen floods (due to inert gas content).

- Injectivity Research (3.3.3). Formation damage due to carbonic acid (formed by carbon dioxide and water) and asphaltene precipitation (caused by extraction of the light oil fractions) lowers permeability and requires higher injectivity rates to compensate.

- Phase Behavior and Displacement Research (3.2.1). The dynamic phase behavior of carbon dioxide-oil-water systems is still not well understood. Miscibility is a complex phenomenon, with as many as four phases in equilibrium, and the effects of pressure on the competing factors of miscibility and viscosity are still being debated. Carbon dioxide impurities, temperature, pressure, crude oil properties and mixing all influence miscibility. It is now apparent that carbon dioxide is not always miscible on first contact with crudes contained in reservoirs for which the process superficially appears applicable. Recent publications have also indicated miscibility may not be achieved even on multiple contact and that the phase relationships are very complex. If miscibility is not achieved, then the best performance that can be envisioned is that of an immiscible gas displacement resulting from increased pressure, reduced viscosity and increased bulk volume. Design of gas floods based on scaled physical models is difficult since the appropriate range of conditions that would exist in a reservoir operation may not be easily replicated in short core tests frequently used to study process performance.

- Field Data Acquisition and Discrepancy Analysis (3.5). There is a need for improved field test procedures in order to undertake tests oil will be inaccessible to the injection fluid. Improved understanding of the effects of level and distribution of residual oil saturation on displacement efficiency and the effects of permeability modifications on sweep efficiency will help determine criteria for when reduced oil saturation reservoirs could be economically flooded.

- Mobility Control Research (3.2.2 and 3.2.3). Mobility control is one of the biggest problems in gas miscible flooding because of the high mobility of the gas and the resultant low areal and volumetric sweep efficiencies. Even when the displacing phase is absolutely miscible with the crude oil under all conceivable reservoir conditions, an unfavorable mobility ratio leads to viscous fingering and density asymmetry leads to gravity segregation, both of which cause premature breakthrough and poor sweep efficiency. This problem makes predictability difficult. Methods of mobility control have not been developed enough to assess the cost effectiveness of such techniques such as foams, gels, well alignment, pH control in sandstones, selective perforations and other novel approaches.

- Permeability, Heterogeneity Research (3.3.2). The ratio of vertical to horizontal permeability is a critical factor in the segregation of carbon dioxide leading to gravity override. Permeability and reservoir heterogeneity studies are needed to fully understand and, thus, better model the reservoir. These models are used to improve predictability and permit more effective process design.

- Modeling (3.4). Accuracy in scaling up from laboratory experiments and numerical simulation has been difficult to confirm. Poor predictability has limited model calibration. Building simplified empirical models and adapting or developing black oil, compositional, and system models for gas flooding are prerequisites to adequate predictability.

with minimum investment. Key reservoir and process parameters for screening and monitoring must be identified.

- Advanced Reservoir Characterization Research (3.3.4). Accurate diagnosis and description of the permeability ratios and heterogeneities that are so critical to gas flooding effectiveness must be improved for better performance prediction and process design.

One further constraint of gas flooding is the supply of carbon dioxide. Widespread application of carbon dioxide miscible flooding is constrained by the limited availability of nearby, naturally occurring carbon dioxide. While carbon dioxide is often found associated with natural gas, it has historically been considered a waste product and released into the air. Several major natural sources of carbon dioxide have been recently identified, but these are located considerable distances from the most favorable areas for application. Three pipelines are planned to transport carbon dioxide from New Mexico and Colorado (McElmo Dome and Sheep Mountain) to West Texas, justified by the large carbon dioxide floods planned in Texas. The economics of development of natural sources of carbon dioxide are dependent on economies of scale and constant, predictable levels of use. The scarcity and cost of carbon dioxide may be alleviated somewhat by recycling. Although this requires purification, pressurization, and reinjection, all of which are costly and capital intensive processes, these processes are not as expensive as buying more carbon dioxide.

Carbon dioxide is a by-product of numerous manufacturing processes used in ammonia, gasoline, chemical and synthetic fuel plants. It may be possible to extract carbon dioxide from manufacturing operations or from stack gases more inexpensively than obtaining it from natural sources. However, since carbon dioxide is a waste product of these processes and not the primary marketed product, stability of supply is not assured. One of the significant items not yet specified is the exact degree of purity required for carbon dioxide in various reservoirs. This is crucial in that the cost of purifying the carbon dioxide is exponentially related to the level of purity required.

Technical Contraints to Application of Thermal Recovery

Limitations to application of thermal recovery techniques center around four areas:

- Sweep efficiency,
- Heat transfer,
- Diagnostics and modeling, and
- Safety and environment.

The major problem encountered in the displacement of oil with steam is the large viscosity difference between the injected steam and the reservoir fluids. Because the steam seeks the highest permeability zones, channelling effects such as gravity override or fingering cause early steam breakthrough before the entire heated zone is swept. Gravity override is caused by the density differences between steam and oil, with the steam rising in the reservoir and bypassing the lower zones away from the injection well. This results in uneven vertical sweep, with the top third swept by steam and the bottom two-thirds by hot water. This can be caused by the generation of low quality steam from the available brackish water, whereby the injected steam immediately separates into hot water (sinking) and live steam (rising) zones after injection. In situ combustion also has an unstable front, with a tendency to sweep the upper zone, since the condensing steam created by combustion settles and directs steam vapors and combustion gas to upper levels. Research is currently being conducted to improve the recovery efficiency of the steam drive process by injecting additives with steam to alter the flow path of the injected steam. Current additives under consideration are foams, caustics and surfactants. Materials could act as flow diverters (blocking agents may be applied once or serially, plugging off zones in a sequence from top to bottom) or as mobility control agents. Results of ongoing projects will provide data to industry for decisions necessary to commercialize these processes. Yet, many areas fundamental to understanding the thermal process, including interactions between steam, steam additives, oil bearing sands, surface adsorption, and the mechanisms of foam movement through the reservoir, are not adequately understood.

Heat transfer losses between the steam generators and the reservoir limit the application of steam flooding to less than 3000 feet. There is a need to reduce heat losses to the wellbore and capture wasted heat, particularly stack gases. The development of downhole steam generators and the use of insulated tubing can reduce heat loss. These constraints are the focus of Work Package 4.2, Process Characterization and Evaluation.

A serious limitation to controlling thermal processes is inadequate knowledge of the velocities and position of the front relative to the wells in and around the patterns. Reliable techniques for front tracking will enable changes in injection rates and other operating procedures to be made in order to increase the volumetric sweep efficiency in the reservoir. Two electromagnetic techniques, developed at National Laboratories for other applications, show promise for EOR thermal front tracking. Improved process simulation models would help predict the effectiveness and aid design of floods with additives such as foam to improve recovery efficiency. This work is the focus of efforts under Work Packages 4.3, Geoscience Research, and 4.4, Modeling.

Steam generators, particularly due to their concentration in Southern California, could create substantial air pollution if sophisticated control technology is not used. Environmental regulations necessitate improvements in pollution control technology before use of thermal techniques can be expanded substantially. Another constraint to wider application of thermal EOR is the limited refinery capacity (due to Prudhoe Bay oil processing) for heavy crude on the West Coast.

Technical Constraints to Application of Novel Recovery Techniques

The primary technical constraint to application of these processes is their lack of proven feasibility. Although preliminary laboratory and engineering work indicates that they might be effective, further study is necessary to demonstrate the technology or apply them in the field.

Microbial EOR is limited first by viability of bacteria in a hostile reservoir environment, specifically temperature, pressure and chemical concentration. Next; process effectiveness is limited by bacterial ability to produce adequate types and volumes of biosurfactants and biopolymers. Industry and government researchers are doing exploratory work to mitigate these constraints.

In situ gravitational recovery has severe non technical as well as technical constraints. Considerable industry reluctance to commit to field application has resulted in a scarcity of engineering data. This reluctance is based on the large front-end investments needed for project implementation and is compounded by difficulties in determining whether the target formation would permit mining, temperature limitations, safety problems related to underground operations, and a general lack of adequate screening criteria needed to determine the resource potential and target site.

Although laboratory research is optimistic, steam drive has not been widely applied to light oil reservoirs (2 pilot and 4 field scale tests reported in the literature) because these reservoirs are often more amenable to other recovery techniques. There are also difficulties with low residual oil saturation, reservoir depth and pressure, the economics of generating steam, and the tendency to use lower risk conventional practices.

UNITED STATES DEPARTMENT OF ENERGY
BARTLESVILLE PROJECT OFFICE
P.O. BOX 1398
BARTLESVILLE, OKLAHOMA 74005

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

FIRST-CLASS MAIL
POSTAGE & FEES PAID
U.S. DEPT. OF ENERGY
PERMIT NO. G-20

FIRST CLASS MAIL

Return this sheet to above address, if you do NOT wish to receive this material ☐, or if change of address is needed ☐ (indicate change, including ZIP code).