ENHANCED AND UNCONVENTIONAL OIL RECOVERY COMPLEMENTARY PROGRAM PROJECT ABSTRACTS

Task 1: Enhanced Oil Recovery from Fractured Media

Oil recovery from unconventional media is often difficult. However, significant hydrocarbon resources can be found in fractured reservoirs. As the supply of oil from conventional reservoirs is depleted, fractured media will provide a greater proportion of the country's oil reserves. One example of such a resource is the Bakken shale, part of the Williston Basin in North and South Dakota and Montana. It is estimated that over 100-176 billion barrels of oil are present in the Bakken shale. However, due to the low permeability of the formation and the apparent oil-wet nature of the shale, production from this formation presents considerable problems.

Over the past several years, NETL-ORD has developed valuable experience in fractured-reservoir technologies, both for oil recovery and for carbon sequestration. A medical-grade X-ray CT scanner is available for imaging core samples that contain fluids, as well as changes in the samples as one fluid is swept by another. We have developed a naturally-fractured reservoir simulator, NFFLOW, which is able to model the migration of fluids within a fractured formation and the surrounding rock matrix. NFFLOW has been validated for gas fields, and is currently available for doing miscible oil recovery above the bubble point. Two-phase capabilities are being incorporated in the code and should be available for use this year, which will allow for water-drive modeling or CO2-enhanced oil recovery.

As part of this project, we will cooperate in NETL's acquisition of core and formation fluid samples from the Bakken shale. If possible, these cores will be placed in the CT scanner to image the nature of the fractures within the shale and other reservoir rock, the composition of the shale, and the amount of oil locked up within the shale matrix. The core will then be exposed to floods of CO2, water, and/or other fluids to test their ability to sweep the shale of its oil. Where possible, we will look for opportunities to couple experimental results with modeling of the fractured reservoir resource. For example, from flooding the cores that we receive with different fluids (e.g., water, CO2, micellular polymers), we may be able to determine relative permeability information that can be used in the reservoir simulator.

Task 2: Catalyst Development

Oil shale and the Green River deposits in particular remain one of the most attractive targets for production of substantial quantities of oil in the future. Induced in-situ maturation of these deposits is an advantageous strategy because it avoids the additional costs and environmental hazards associated with mining the shale followed by above ground retorting. Several obstacles inhibit in-situ production, chief among these are the high costs in the energy required to heat the shale in order to promote the maturation of the kerogen and the time required for expulsion of the new-formed oil from the shale to the production reservoir. Basic scientific issues at the root of these obstacles to commercial production of shale oil are the topic of this project. The goal is to define at the molecular scale major impediments to in-situ conversion and to devise and execute an experimental program that will lead to methods that reduce the time and energy required to produce oil from shale.

Initial work began with a literature search to determine basic ideas and obstacles to the in-situ production of oil from kerogen. The leading example of this approach is the Shell In Situ Conversion Process in which shale is heated below ground to about 325 °C for several years. The oil subsequently recovered at the production well is a high quality aliphatic fuel similar to a kerosene fraction. Several approaches could be envisioned to improve this process including acceleration of the primary oil generating step and increasing the rate of migration of oil to the production well. Recent studies on oil generation in source rock indicate that the thermolysis of kerogen enables the separation of an oily aliphatic phase from the more polar residual. Using the results of the literature search, an experimental plan was devised to investigate the ability of simple organic molecules to penetrate kerogen while still within oil shale. This is an important consideration because diffusion of molecules through kerogen is a key step in both the dispersion of potential catalytic agents and the migration of produced oil from the source rock to production well. The initial work was done on samples of typical Green River oil shale obtained for these studies from Western Research Institute and USGS. Research previously reported in the literature shows that shale-free kerogen readily swells when exposed to organic solvents. In these swelling experiments, kerogen resembles a three dimensional cross-linked macromolecule. However, apparently no experiments have been done with the intact oil shale. Our new work now shows that kerogen locked within shale may adsorb substantial amounts of many solvents. It is planned to refine the initial experiments to obtain more definitive results on the thermodynamics and kinetics of the swelling process.

Future work will broaden the scope of experiments to include the chemical reactions involved in cracking reactions and the phase separation that expels aliphatic oils from cross-linked kerogen during the primary oil generation stage. Potential means to reduce the time and temperature required for generating free oil by catalysis or other means of promoting cracking reactions will be investigated.

Task 3: Mobility Control

The goal of this research is to develop inexpensive, non-fluorous, environmentally benign compounds that can decrease the mobility of CO2 via increase the CO2 viscosity and/or reduction of the CO2 relative permeability.

Several strategies for employing novel CO_2-soluble or water-soluble surfactants for the improvement of mobility control during CO_2 floods are proposed. These concepts include the design of CO_2-soluble surfactants that will form foams in-situ, the design of CO_2-soluble surfactants that will form viscosity-enhancing helical or cylindrical micelles in CO_2, and the design of water-soluble surfactants that will form high CO_2-volume, transparent microemulsions of CO_2-in-water.

The project focuses the design of CO2-soluble surfactants that will form foams in-situ, the design of CO2-soluble surfactants that will form viscosity-enhancing helical or cylindrical micelles in CO2, and the design of water-soluble surfactants that will form high CO2-volume, transparent microemulsions of CO2-in-water. To accomplish the research, the following four tasks are planned (University of Pittsburgh is performing Task 1, 2, and 3; NETL is conducting Task 4)

- Task 1 Design of CO2-soluble surfactants that will form foams in-situ
- Task 2 Design of CO2-soluble surfactants that will form viscosity-enhancing helical or cylindrical micelles in CO2
- Task 3 Design of CO2-soluble surfactants that will form viscosity-enhancing helical or cylindrical micelles in CO2
- Task 4 Design a core unit in NETL to measure the mobility of CO2 flood.

The University of Pittsburgh has received the official notice regarding the status of this project on January 2008. Dr. Enick from University of Pittsburgh has assigned two Ph.D. students to work on this project since. The new students started the preparation of the surfactants. The new student already completed the synthesis of a hydrocarbon-based ionic surfactant sodium bis(3,5,5-trimethyl-1-hexyl) sulfosuccinate (AOT-TMH) (following a procedure described by subcontractor Julian Eastoe). The surfactant is currently being characterized. This particular surfactant was selected for CO_2 solubility alone; therefore we do not expect it to induce large changes in viscosity. It will serve as a "control" result for surfactants designed to be soluble in CO_2 but not necessarily capable of thickening CO_2 because it will form spherical, rather than cylindrical, micelles. The new student has also successfully synthesized oligomers of vinyl acetate that may be used in the CO2-philic tails of novel surfactants. The University of Pittsburgh's subcontractor, Dr. Julian Eastoe of Bristol Univ. in the UK, has initiated the synthesis of new surfactants.

The University of Pittsburgh also finished another synthesis of poly vinyl acetate oligomer, finding that even if the amount of initiator (AIBN) or vinyl acetate monomer is doubled, the final product still has a small number of repeat unit (6~8), and appears as a solid. This oligomer will probably used as a CO2-philic surfactant tail.

A flow apparatus that can be used to measure the mobility (i.e. viscosity) of fluids flowing through porous media has been developed. This is essentially a high pressure, low pressure drop experiment that detects increases in CO_2 viscosity by monitoring increases in the pressure drop needed to push the fluids through a short piece of sandstone. A draft flow diagram of the to be constructed CO2 flood unit has been reviewed/discussed between NETL and University of Pittsburgh. The flow diagram was prepared. The needed equipments (pumps, reactors, pressure transducers, and digital readout) have been indentified and purchased. We have located PD pumps, a mixing cell, and a Temco core holder that appear to be suitable for establishing the apparatus. We are now developing a details P&ID and procedure for conducting the experiments.

Work is continuing on preparing the surfactants. Experiments at the lab-scale, using a CO2-philic surfactant tail and new surfactants are a part of this effort. This evaluation includes using

Robinson cell, further phase behavior testing and viscosity testing of all the surfactants and polymers in CO2.

The construction of the testing unit in NETL continues.

Plans for the next year (FY09) also include design and molecular modeling of CO_2-soluble surfactants that will form viscosity-enhancing helical or cylindrical micelles in CO_2; and design of CO_2-soluble surfactants that will form foams in-situ. Flow of CO_2 and promising CO_2+surfactant solutions through the core flooding apparatus (mobility of a single phase), modeling of the core system. development and testing of new surfactants will be studied both in University of Pittsburgh as well as NETL.

Task 4: Oil Shale Archive

As part of the continuing effort to develop a comprehensive database of information on historic research related to oil shale and tar sands, NETL has supported an effort to identify all of the sources of reports, samples and well data. The effort began over two years ago with the development of a comprehensive bibliography. The list has 18,000 references. There are additional references in the University of Utah Repository, an online database of oil shale and tar sand references strictly from the basins in Utah funded by NETL. The Piceance Basin of Colorado has additional industry reports that are currently stored in the basement of the library at the Colorado School of Mines. NETL is coordinating with all of the universities, state and federal agencies and industry to develop the most reliable references for future development of the resource.

Task 5: Microwave Conversion Literature Review

Experimentally investigate the effect of supercritical CO_2 on microwave-induced kerogen conversion and assess process feasibility of CO_2-enhanced microwave-based recovery of shale oil. A major goal of this project is to develop a method by which the activation energy of kerogen conversion to oil can be lowered in the presence of supercritical CO_2 and microwaves.

The current increase in oil prices to over $120 per barrel has prompted a renewed interest in developing petroleum from oil shale resources of the western United States. The Green River formation is estimated to contain over 1 trillion barrels of oil in the kerogen fraction, the solid-phase organic matter present in the oil shales. Prior attempts at ex situ oil shale retorting, in which oil shales were mined and heated to high temperatures to extract the oil, were deemed economically unfeasible and deleterious to the natural environment. A renewed interest has developed regarding in situ oil shale retorting with radio frequency (RF) and microwave methods. In 2007, Raytheon and Critical Fluids Technologies (CFT) published patents in which Raytheon's expertise in RF technology was combined with CFT's critical fluid technology to extract oil from shale and sequester CO_2. According to Raytheon, by using RF the shale can be heated to a suitable temperature within a few months compared to the years it would take using other means. Once the shale is heated, the CO_2 is pumped into the well at over 70 atmospheres.

This supercritical CO_2 acts as a solvent to extract the oil liquid produced by RF application. The CO_2-oil combination is then brought to the surface where it is de-pressurized; the oil is separated as the CO_2 once again becomes a gas. The CO_2 is then re-pressurized and recycled. This project is similar to Raytheon's RF technology, but heats the shale using *microwave* radiation *specifically tuned* to optimize CO_2 extraction of the converted kerogen.

This project focuses upon the development of a fine-tuned chemical pathway in which oil shale kerogen can be converted to oil in the presence of supercritical CO_2 and microwaves. In order to properly assess conversion chemistry, kerogen structure and chemical properties need to be understood, along with the effect of supercritical fluids and microwave energy on kerogen chemical behavior. The major accomplishments to date include a detailed literature search, development of the project team, initial design of experimental procedures, and receipt of oil shale samples to be used in our experiments.

A detailed literature search has been ongoing, and to date 500+ oil shale-related documents have been assembled and catalogued in our ProCite database. We currently are reading through the literature to understand past work on oil shale conversion by RF and microwave techniques, supercritical fluid extraction of kerogen, and kerogen structural identification and chemical properties. Results of this literature search have been used to develop an initial experimental design and initiate the Safety Analysis and Review Systems (SARS) permitting process for our laboratory-scale experiments on kerogen isolation and identification. Results also have been used to begin the design of our microwave test unit. Dr. William Stanchina, Chairman and Professor of the Department of Electrical and Computer Engineering at the University of Pittsburgh, joined the project team on April 9, 2008, and is aiding the design of the microwave testing unit. Dr. Alexandra Hakala joined as an ORISE Post-doctoral research associate on March 17, 2008. Oil shale samples from Utah and Colorado for use in our experiments have been received and analyzed by photomicrograph, and access to a NMR facility (Old Dominion University) for kerogen structural identification has been confirmed. Supplies and equipment have been ordered for the kerogen extraction work.

Work is continuing on completing the oil shale literature search and review. We are continuing to compile and assess relevant information for use in designing our kerogen extraction experiments. Design of the microwave test unit will be completed shortly, along with the identification of necessary and available microwave equipment.

Oil shale kerogen extraction experiments will begin upon completion of the SARS approval process. Extracted kerogens will be tested and analyzed by various methods (solvent swelling, NMR, etc.) in order to determine their structural and chemical properties. The effect of supercritical CO_2 on kerogen conversion to oil also will be investigated using a supercritical CO_2 extraction unit. We also will complete the design of a proof-of-concept test unit for CO_2-enhanced in situ oil shale conversion, and from this point will decide whether or not to proceed to actual proof-of-concept testing.