ACTIVITY REPORT

April 2003

Natural Gas & Oil Technology Partnership

bringing department of energy national laboratories capabilities to the petroleum industry

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Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

January, March, May, July, September, November	**February, April, June, August, October, December**
Drilling, Completion, and Stimulation Technology Oil and Gas Recovery Technology Diagnostic and Imaging Technology	Upstream Environmental Technology Downstream Environmental Technology Natural Gas Technology

Natural Gas and Oil Technology Partnership on the World Wide Web: http://www.sandia.gov/ngotp/

Upstream Environmental Technology

Ecological Framework to Evaluate the Effect of Size and Distribution of Releases at Upstream Petroleum Sites

(American Petroleum Institute, BP Amoco, ChevronTexaco, ExxonMobil, Gas Technology Institute, Unocal, LBNL, ORNL, and LLNL)

Highlights:

- Symposium presentation and manuscript submitted for a related book.
- Modeling of American badger and prairie vole continues.
- Three manuscripts complete, a fourth manuscript in progress.

Researchers are completing the intensive modeling phase and preparing manuscripts of results. An overview of model results and a preliminary ecological framework was presented at the American Society for Testing and Materials Symposium on Landscape Ecology and Wildlife Habitat Evaluation: Critical Information for Ecological Risk Assessment, Land-Use Management Activities, and Biodiversity Enhancement Practices. The talk, "Toward a Framework for Assessing Risk to Vertebrate Populations from Brine and Petroleum Spills at Exploration and Production Sites," was authored by scientists at ORNL and LLNL, and given by ORNL. A manuscript based on this talk was submitted for publication in a related book.

During April, selected parameters were varied to better understand their effects on model predictions. ORNL completed the simulations and a manuscript entitled "Simulated Effects of Habitat Loss and Fragmentation on the American Badger (*Taxidea taxus*)." The manuscript went through internal review and is now in Petroleum Environmental Research Forum (PERF) review, prior to submission to *Conservation Biology*.

ORNL also submitted the draft manuscript, "Unnatural Landscapes in Ecology: Generating the Spatial Distribution of Brine Spills," for petroleum industry review, prior to journal submission.

LLNL incorporated peer review comments to the paper, "Individual-Based Spatially-Explicit Model of an Herbivore and Its Resource: The Effect of Habitat Reduction and Fragmentation," and submitted it for publication to Comptes Rendus d'Academy de Science: Biologie, which will publish a special issue on Mathematical Population Dynamics.

LLNL continued work on a second manuscript, "The Effect of Area Size, Predation and Fragmentation on the Time to Extinction of Prairie Vole Populations: Simulation Studies via an Individual-Based Model," which researchers plan to submit to *Ecological Modeling*. The manuscript is close to completion.

Publications

Jager, H. I., R. A. Efroymson, K. Sublette, and T. L. Ashwood. "Unnatural Landscapes in Ecology: Generating the Spatial Distribution of Brine Spills," submitted for review by the petroleum industry.

Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

Report not received.

Remote Sensing for Environmental Baselining and Monitoring

(ChevronTexaco, UC-Davis, and ORNL)

Work on project suspended pending receipt of FY2003 funding.

Modeling of Water-Soluble Organic Content of Produced Water

(ChevronTexaco, ConocoPhillips, Shell, Statoil, and ORNL)

Highlight:

- Monte Carlo sampling routine implemented for input into the calculation of thermodynamic equilibrium.

To predict the contamination of produced water by oil and grease, thermodynamic equilibrium calculations were chosen as the means to model the solubility of organic compounds in brines. A difficulty with generating a model for produced water is the sheer complexity of the chemical system. A thermodynamic model necessarily requires concentration information on each species, which can number over 1000 in the produced water-crude system.

Through examination of the literature and the use of Petroleum Environmental Research Forum (PERF) analyses of actual crude oil samples, a simple representation of the hydrocarbon phase was developed, incorporating key compounds from each of the aliphatic, aromatic and polar classes. However, the numbers put into the model entail uncertainties. Researchers attempted to quantify these uncertainties using the analysis of the experimental data taken at ORNL.

In addition, the code for the calculation was rewritten to accept distributions of compounds rather than set concentrations. The distributions were sampled randomly for a specified number of times. For each random sampling, the brine concentrations were calculated. This method resulted in a distribution of organic concentrations in the brine. These concentrations were compared to experimental data using standard statistical tests.

The next stage will be to complete the analysis of the ORNL results by comparing them with thermodynamic calculations. This work will be documented and circulated to industry participants and the DOE.

Science-Based Methods to Assess Risks Attributable to Petroleum Residues Transferred from Soil to Vegetation

(ChevronTexaco, UC-Berkeley, UC-Davis, and LBNL)

Highlights:

- Test soils prepared.
- First plant exposure study set up.

LBNL researchers mixed 12 batches of sandy loam test soil including three controls (spike carrier solvent only) and three batches, each mixed at approximately 0.1, 1 and 10 ppm (dry mass). The final spiked soils include 12 individual polycyclic aromatic hydrocarbons (PAHs) and six n-alkanes (even number carbon from C-20 to C-30) in a two-way matrix. Each PAH level (excluding controls) is mixed with three different levels of the n-alkane spike. The soils are being mixed daily to allow the carrier solvents to volatize and the moisture content to drop to a level that is appropriate for planting. Preparing the soil for the exposure studies is a critical step in the experimental design and quality control. The starting concentrations will be determined and homogeneous mixing of the soils will be characterized prior to use.

UC-Davis and LBNL researchers are setting up the first exposure run, which includes wheat grass sown in spiked soils and grown in the controlled environmental chamber with filtered air intake. Researchers are including the wheat grass experiment to see if the methods work prior to running the long-term exposure study necessary for the mature grain plants.

Interactive Information System on Drilling Waste Management Practices

(ChevronTexaco, Marathon, ANL)

Highlight:

- Paper presented at the SPE/EPA/DOE Exploration and Production Environmental Conference in San Antonio, TX.

A paper describing the project, "Innovative Website for Drilling Waste Management," was presented on March 11 at the SPE/EPA/DOE Exploration and Production Environmental Conference in San Antonio, TX. The presentation was well received by the audience.

Researchers received inquiries from a graduate student in Great Britain and an industry researcher in Canada about the site.

Presentations

Veil, J.A., J.R. Gasper, M.G. Puder, R.G. Sullivan, P.D. Richmond, B.R. Fidler,C.N. Fleming, R.F. Bernier, and F.V. Jones. "Innovative Website for Drilling Waste Management," presented at SPE/EPA/DOE Exploration and Production Environmental Conference, San Antonio, TX, March 10-12, 2003.

Downstream Environmental Technology

A Predictive Model of Indoor Concentrations of Outdoor $PM_{2.5}$ in Homes

(Aerosol Dynamics, Western States Petroleum Association, and LBNL)

Highlights:

- Manuscript prepared for the *Journal of Indoor Environment*.
- Model development continues.

Progress continues on measurements of ammonia and nitric acid. An invited manuscript describing the loss of NH_4NO_3 aerosol indoors was prepared for the *Journal of Indoor Environment*.

Researchers continue to make progress on the development of a sub-module of the mass balance model that describes the transformation of ammonium nitrate aerosol inside the house.

A sub-model describing the kinetics of evaporation of ammonium nitrate aerosol particles is nearing completion. The sub-model includes a description of the effect that water uptake by the ammonium nitrate aerosol has on the size, evaporation rate, and equilibrium vapor pressure of the system. The dissociation and evaporation of the nitrate aerosol serves as a source term for ammonia and nitric acid gasses indoors. The model, which is based upon first principles, is able to reproduce the ammonia nitrate and nitric acid levels observed indoors.

A Predictive Model of Indoor Concentrations of Outdoor Volatile Organic Compounds in Homes

(American Petroleum Institute, Western States Petroleum Association, and LBNL)

Highlight:

- Researchers prepare manuscript describing results and modeling.

Work focused on the preparation of a manuscript describing experimental results and modeling of sorption for 20 gas-phase organics that cover a wide range of volatilities. Airborne concentrations were measured to determine the best sorption model and parameter values in a room containing only wallboard, containing wallboard with a carpet plus cushion system, and with wallboard, carpet and additional furnishings. The work described in this manuscript will provide the foundation for the sorption component of the mass balance model for predicting indoor exposures to hazardous air pollutants from outdoors. Work on the manuscript has included expanded analysis of the primary experimental data, including temperature and humidity, and analysis of the model fitting metrics.

Developing Enzyme and Biomimetic Catalysts for Upgrading Heavy Crudes via Biological Hydrogenation and Hydrodesulfurization

(ChevronTexaco and ORNL)

Highlight:

- Demonstrated that the molecular weight of Ni-Fe active center peptide isolated from hydrogenase is below 14,000 Da.

This project investigates the potential of enzymatic and biomimetic catalysts for hydrogenation of oil compounds with the goal of upgrading crudes via sulfur removal and potentially molecular weight reduction. Experiments showed that the digestion of the enzyme hydrogenase and isolation of the metallocenter preserves the activity of the enzyme. Hence, the approach is to digest the enzyme to an extent that it is still active and is non-specific enough to be able to bind and hydrogenate unnatural substrates.

Previous experiments to isolate the nickel-iron (Ni-Fe) active center peptide complex at larger scales resulted in low yields of the complex (1-2%). A few microgram quantities of the complex were generated in the process. In order to perform structural and kinetic analysis (in collaboration with ANL), this amount will not be sufficient. To improve the yield of the complex, the extent of digestion of the hydrogenase enzyme was examined using a sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) technique. To achieve maximum digestion of the hydrogenase in order to give the active form of the complex, experiments were carried out with two different proteases and at three different temperatures. Digestion at 60^{o}C was found to produce inactive complexes, while that digestion at 37^{o}C was incomplete. Digestion conducted at 50^{o}C resulted in almost complete digestion while preserving activity. The molecular weight markers used for this analysis were from 14,000 to 97,000 Da. This first experiment was focused on determining what percent of the enzyme (mol wt. 89,000 Da) is digested. Researchers are in the process of determining the exact molecular weight using lower molecular weight (2,000 to 17,000 Da) markers.

Characterization and Reaction Behavior of Sterically-Hindered Sulfur Compounds in Heavy Crudes with Nano-Sized Molybdenum Disulfide

(ChevronTexaco, BNL, and ANL)

The transmission electron microscopy (TEM) data show that all molybdenum disulfide (MoS_2)-based unsupported and supported materials, prepared by project researchers, are indeed nano-sized. The X-ray diffraction (XRD) data support these observations. The XRD data also show that the prepared cobalt molybdenum sulfide catalyst (Co-MoS_2) material is CoS-MoS_2, in which cobalt sulfide (CoS) exists as large crystallites and may act as a support for nano-sized molybdenum disulfide (MoS_2) particles. Interestingly, though the XRD peaks of MoS_2 in CoS-MoS_2 match those reported for nano MoS_2, the CoS peaks do not match. This aspect is the subject of further investigation.

Hydrodesulfurization (HDS) activity of several supported metals was correlated with the temperature programmed reduction (TPR) peak. The TPR for the nano-MoS_2 and nano-Co-MoS_2 materials is significantly higher than that of the supported materials. The fact that the temperature of the TPR reduction peak was almost the same as nano-MoS_2 implies that there was not a combination of these two phases. In addition, the width of the TPR peak for the nano-sized materials (nano-MoS_2 and nano-Co-MoS_2) is significantly broader than the commercial catalyst. The wider TPR peak for the sonochemically-generated materials implies that there is a much broader distribution of active sites in the nanophase materials versus the commercially prepared catalyst. This would result in a wider variety of active sites and is probably the reason for the lower activity for the sonochemically prepared materials.

Preliminary HDS activity evaluation studies show lower activity for the nano-CoS-MoS_2 compared to the nano-MoS_2. This was surprising but is mirrored in the TPR data. The activity of the unsupported nanosized catalysts, however, is much higher than the commercial micron-sized counterparts. This enhancement comes from the increased surface area of the nano-particles. In the micron-sized catalysts, diffusion in between the long rafts of MoS_2 is mass transport limited, so it is expected that most of the activity comes from the "rims" and "edges." Incorporation of Co to MoS_2 increases the activity of the catalyst. In preliminary studies, the catalytic activities are compared at commercially operated temperature that may not be the optimized temperature for nano-sized MoS_2-based catalysts.

A major problem with hydrodesulfurization is the hydrogenation of olefins, which leads to loss of the research octane number (RON). The rate of olefin hydrogenation is much faster than HDS, but competitive adsorption of S at the

active site strongly inhibits the hydrogenation reaction. At low S levels, olefin hydrogenation takes over. To model these olefins in the HDS runs, 1-octene (1 wt.%) was added to the liquid feed and the HDS tests were run again. Interestingly, the sonochemically synthesized nano-phase catalysts are less active for olefin hydrogenation than their commercial counterparts. This observation contrasts the expected result that the hydrogenation function in nano-sized catalysts should increase because nano-sizing increases the number of edge sites. Work is in progress to further decrease the hydrogenation function with concomitant increase in the HDS activity of the synthesized nanophase materials.

Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration

(Marathon-Ashland and INEEL)

Highlight:

- Project technology nominated for an *R&D Magazine* R&D 100 award.

Experimental efforts exploring regeneration time requirements at reaction conditions of 0.26 hr-1 olefin weight hourly space velocity (OWHSV) and an isoparaffin to olefin ratio of 20:1 continued. Researchers are exploring regeneration times between five minutes and two hours. Preliminary data indicate that at a fixed reaction time, increased regeneration times enhance catalyst longevity. New efforts exploring the regeneration of a macro-porous acidic catalyst were initiated. Experimental efforts were minimized in March and April to accommodate delays in receiving FY03 funding.

The INEEL nominated the solid catalyst alkylation regeneration technology for an *R&D Magazine* R&D 100 award.

Biocatalytic Alkane Transformation for Viscosity Reduction

(ChevronTexaco and LBNL)

A menu of biocatalytic agents capable of transforming alkanes to alcohols and acids was developed in a previous Partnership project (Biological Upgrading of Heavy Oils). In this project, several of the most promising biocatalysts were selected from the menu for further characterization and development. All of the biocatalysts selected for this project harbor enzymes that terminally oxidize linear alkanes, but the biocatalysts exhibit a diverse range of activities. Some, but not all, of the biocatalysts oxidize branched hydrocarbons and ethers. The objective of this project is to determine if genetic or physiological properties govern the target specificity of the biocatalyst. Experiments are being conducted to measure the transformation kinetics of alkanes in whole cells and cell extracts to differentiate genetic from physiologic controls in target specificity.

Recent experiments demonstrated that higher molecular weight hydrocarbon oxidation is a mass transfer limited process in two major categories of biocatalysts, even in single phase (aqueous) systems. The limiting step appears to be the transport or permeation of the hydrocarbon through the cell membrane. Mass transfer limitations could be overcome by the use of an additive that modifies membrane properties. The concentration dependent effects of the additive on catalytic activity over time will be determined.

Secondary Organic Aerosol Research

(Aerosol Dynamics, Western States Petroleum Association, and LBNL)

Report not received.

Proton Exchange Reactive Membranes for Conversion of Light Alkanes to Clean Liquid Fuel (Ceramatec, Inc. and INEEL)

A second palladium membrane was tested in the catalytic experimental system in February. Hydrogen permeation was found to be significant and was not associated with leaks. Due to higher-than-anticipated transport, the gas chromatograph (GC) was outside of its calibrated range. The GC was recalibrated at elevated pressures and concentrations so that accurate flux rates can be obtained.

A third palladium foil membrane was fabricated for initial tests of flux control as a function of partial pressure, temperature, and external fields in the field effects experimental reactor system. The membrane was operated with a 50/50 mix of hydrogen/helium on the supply side and argon sweep gas on the permeate side for instrument and leak-proof verification. No helium was detected on the permeate side and levels of hydrogen flux were measured that are comparable to published values. An attempt was made to control the flow of hydrogen flux through the palladium membrane with an external field. Only small changes in the hydrogen flux were observed at the onset of applying the field and, after a short period (~30 seconds), the flux returned to its previous value. More experiments to determine the effectiveness of controlling hydrogen flux with an external field will continue once FY03 funding is received.

A new vertical membrane reactor system, based on a proven Ceramatec Inc. design is being built. All necessary parts were received. This system will be used for testing membranes supplied by Ceramatec Inc.

Experimental efforts were minimized in March and April to accommodate delays in receiving FY03 funding.

Natural Gas Technology

Molecular Engineering: Next Generation of Gas Purification Technology (ChevronTexaco, Virginia Commonwealth U, and BNL)

Product analysis using electron microscopes progresses. The polymeric products made from DSP monomer were analyzed by using Surface Acoustic Wave (SAW). Changes in DSP monomer were tracked by the frequency changes of the DSP-coated SAW transducer. The RESS conditions were: pre-expansion temperature and pressure of 128-126 °C and 5000 psi respectively (10-16-02). The major changes in the DSP particles occurred in the first days with no notable changes after 12 days. The kinetics of frequency changes of the DSP-coated SAW device in the first 24 hours were extremely fast.

Coil-Tubing-Deployed Hard Rock Thermal Spallation Drill and Cavity Maker (Nextant, NM Tech, and LANL)

Highlight:

- Shallow drill test assembly almost ready to support shallow borehole burner demonstrations.

New Mexico Tech converted a surplus drill frame that LANL used to conduct rock melting drill tests to support shallow field-testing of a spallation drill. This will allow the NM Tech team to safely conduct shallow drilling tests of their flame jet drill assemblies before the assemblies are tested on the LANL coiled-tubing unit. With the ability to work underground, NM Tech can evaluate burner assemblies in a borehole drilling and cavity-forming demonstrations before the assemblies are evaluated on the LANL coiled-tubing unit, the availability of which is limited because it is being shared with other drilling projects.

NM Tech's design of a connector sub that will be used to connect their burner assembly to the LANL coiled-tubing drill unit was converted from paper sketches to an electronic drafting program.

LANL is developing a model of the coiled-tubing utilities and annulus flow systems. The model will be used to calculate pressure drops in the propane, cooling water, flow supply tubing and annuli, and coiled-tubing to rock bore annulus (where the combustion products and steam produced by the cooling water will carry the rock spalls to the surface). The model will also be used to estimate the temperature of the various supply lines and the annular flow of the combustion and cooling products. The subcomponents of the model are complete and the unified model is now being assembled.

Scintillating Fiber Neutron Detectors for Well Logging

(CompuLog, Precision Drilling, Technology Services Group, and PNNL)

Highlight:

- Prototype detector construction is nearly complete.

The high temperature polymer was complicated to cure and was rubbery at room temperature. The polymer was modified to harden earlier in the curing process and to harden to a more brittle state. This is more compatible with existing detector assembly procedures. Enough fiber was drawn to manufacture four detectors. Two will be made for high temperatures and two for ambient temperatures. (Another project agreed to fund the two ambient temperature detectors.)

The differences between the ambient and high temperature detectors are the hydrogen content of the moderator and the photomultiplier tubes. This will allow for verification of the computer model. One high temperature detector will have two photomultiplier tubes and will be run requiring coincident detection of an event in both tubes to minimize electronic noise in the detector. A matching detector will have one photomultiplier tube and a mirror on the opposite end to reduce the detector's length.

Computer modeling indicates that there is little value added in producing a fiber detector to replace the existing thermal neutron detector. However, even with reduced hydrogen content, the epithermal detector shows enhanced performance at energies above 20 eV. The largest improvement in performance is at 0.1 MeV. The new detector is three times the efficiency of the current ^{3}He system.

225° C MWD Using Silicon-On-Insulator (SOI) Electronics

(Baker Oil Tools, Eagle-Picher, Honeywell SSEC, General Atomics, Noble Engineering, Quartzdyne, and SNL)

The project now has a test well. The Navy gave permission for a well in Coso, California. The well is static, so the tool can be left in the well for an extended test period. The last time this well was logged was 1997.

Researchers are waiting for parts for the tool to be delivered, especially the Entran pressure sensors. If they do not arrive in time, researchers will proceed and install the sensors following oven testing.

Orientation Package for Steering an MWD Tool with Prime Directional Services

Honeywell shipped Silicon-On-Insulator (SOI) magnetic sensors for testing an all SOI azimuth sensor. Steven Rountree is preparing a test to compare the SOI solid-state azimuth measurement versus conventional flux-gate magnetic sensors.