

ACTIVITY REPORT



**Natural
Gas &
Oil
Technology
Partnership**

October 2003

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
Drilling, Completion, and Stimulation Technology
Oil and Gas Recovery Technology
Diagnostic and Imaging Technology

February, April, June, August, October, December
Natural Gas Technology
Upstream Environmental Technology
Downstream Environmental 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, Exxon-Mobil, Gas Technology Institute, Unocal, ORNL, and LLNL)

Highlights:

- Continued work on manuscripts
- Presentation at the Alcala conference on Mathematical Ecology
- Groundwork for expansion/generalization of models

The intensive modeling phase of the project has been completed and results are being finalized. Two models have been developed that can be used to determine the threshold frequency, size and/or distribution of habitat loss resulting from exploration and production activities that would have a significant impact on the persistence of herbivore and/or predator populations. Parameters have been determined for models of the Tallgrass Prairie Preserve in Osage County, Oklahoma.

The presentation titled "Effect of Fragmentation on the Time to Extinction of Prairie Vole Populations in Tallgrass Prairie" by LLNL's T. Kostova and T. Carlsen, was presented in a session on individual-based models. This session was organized by T. Kostova at the Alcala conference on Mathematical Ecology, held in Madrid, Spain, September 5-9, 2003. T. Kostova was presented with an award at the end of the conference for the largest and most well attended session of the conference. Conference papers will be published in various journals.

Both ORNL and LLNL have begun work to modify and generalize their respective models in anticipation of applying the models to additional sites. Future work will utilize these models at sites near Vernal, Utah. These sites are owned by the US Bureau of Land Management and are undergoing oil and natural gas development.

ORNL is investigating expanding the badger model to species such as the prairie chicken or raptors. While badgers hold the same home range for life, other species may occupy different areas during breeding and other times of the year. Therefore, ORNL is adding an algorithm for abandoning a home range and establishing a new one. The model has also been encased inside a Monte Carlo procedure to permit future sensitivity or uncertainty analysis of model parameters. LLNL is investigating expanding the vole model to other rodent species such as the prairie dog.

Publications

Submitted to ASTM International, in revision based on reviewer comments:

Efroymson, R. A., Carlsen, T. M., Jager, H. I., Kostova, T., Carr, E. A., Hargrove, W. W., Kercher, J., and Ashwood, T. L. "Toward A Framework For Assessing Risk To Vertebrate Populations From Brine And Petroleum Spills At Exploration And Production Sites, Landscape Ecology And Wildlife Habitat Evaluation: Critical Information For Ecological Risk Assessment, Land-Use Management Activities, And Biodiversity Enhancement Practices", *ASTM STP 1458*. L. Kapustka, H. Galbraith, M. Luxon, and G. R. Biddinger (eds.), ASTM International, West Conshohocken, PA, 2004.

ORNL is waiting on review comments for "Simulated Effects of Habitat Loss and Fragmentation on the American Badger (*Taxidea taxus*)" submitted to *Landscape Ecology*.

LLNL continued work on the manuscript titled "The Effect of Area Size, Predation and Fragmentation on the Time to Extinction of Prairie Vole Populations: Simulation Studies via a Trophic Individual-Based Model" to be submitted to *Ecological Modeling*.

Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

No report received.

Remote Sensing for Environmental Baseline and Monitoring

(ChevronTexaco, UC-Davis, US Geological Survey (USGS), and USDA Agricultural Research Service (ARS), and ORNL)

Highlight:

- Measured hyperspectral data in Osage County both remotely and in the field.

In May 2003, ORNL contacted the HyVista Corporation (<http://www.hyvista.com/>) and requested that they make hyperspectral images of seven areas in Osage County, Oklahoma. On October 12, HyVista made the images and ORNL expects to receive the data soon. On October 27 and 28, a team from the USGS, ARS, and ORNL measured hyperspectral field data at 13 sites in the seven areas where the remote data was measured.

Modeling of Water-Soluble Organic Content of Produced Water

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

Highlight:

- Recent modeling work was presented at two meetings.

In the last two months, a series of presentations have been made on the produced water project being undertaken at ORNL. The presentations included a detailed discussion of the problems associated with produced water along with a historical perspective of activities undertaken at ORNL at the University of Tennessee Chemical Engineering Department, Knoxville, TN, September 23.

Shorter presentations that focused on recent work were given at the American Association of Petroleum Geologists (AAPG) Mid-continent Meeting in Tulsa, OK, October 14. Another was presented at the Separations Science and Technology (SST) Conference in Gatlinburg, TN, October 27. An extended abstract was prepared for the proceedings of the AAPG, and a paper on the recent statistical analysis was prepared for the peer reviewed proceedings of SST 2003. The objective of these presentations was to familiarize the audience with the issue of produced water, to encourage feedback from members of the scientific community, and to foster collaboration between ORNL, other government labs, and academia.

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

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

Highlights:

- Continuing to extract and analyze soil and grass samples
- Prepared presentation for Society of Environmental Toxicology and Chemistry conference

LBNL and UCD researchers are continuing to extract and analyze wheat grass and soils from the plant uptake experiment. R.L. Maddalena, R. Kobayashi, T.E. McKone, and N.Y. Kado prepared a talk, "Controlled Chamber Measurements of the Multipathway Uptake of Polycyclic Aromatic Hydrocarbons from Soil into Wheat". It is to be delivered at the Environmental Toxicology and Chemistry conference 9-13 November in Austin, TX.

Interactive Information System on Drilling Waste Management Practices

(ChevronTexaco, Marathon, and ANL)

Highlight:

- Inquiries have been received from around the world concerning the website and when it will be publicly available.

The decision tree flowcharts for the Technology Identification Module were completed and shown to audiences at DOE/NETL and at ChevronTexaco. Users will be asked a series of questions. Depending on how the questions are answered, the module will narrow down a long list of drilling waste management options to a shorter list that is more realistic for the user's site.

It is expected that the Technology Identification and Regulatory modules will be programmed this fall.

Use of Ionic Liquids in Produced Water Clean Up

(ChevronTexaco, Shell, Conoco-Phillips, ORNL)

Highlight:

- Poster presented

A poster on ionic liquid extraction of organics from aqueous solution was presented at the Separations Science and Technology Conference in Gatlinburg, TN, October 27.

The distribution between water and ionic liquid solvents were measured for three room temperature hydrophobic ionic liquids and polar organic compounds typical of produced water contaminants (organic acids, alcohols and aromatic compounds). Ionic liquids and aqueous solutions of the organics were contacted under static conditions. Concentrations of organics in the aqueous phase and similarly treated controls were measured by gas chromatography and high performance liquid chromatography, and the distribution coefficients were obtained through a mass balance. Sensitivity analyses were performed on salinity, temperature, concentration, and pH.

Partitioning into the ionic liquid varied considerably. In the case of the organic acids, partitioning into the ionic liquid phase was negligible, except for hexanoic acid, where the protonated form was preferentially removed from aqueous solution. Other organics showed high distribution coefficients, up to several hundred in the case of toluene and 1-nonanol. The distribution coefficients for toluene, 1-nonanol, and hexanoic acid were independent of ionic liquid-to-water ratio over the range from 0.02 to 1.0. The ionic liquid showed a large capacity for organics, up to 100 g/L; however, it is possible to remove 1-nonanol from the ionic liquid using rinses of de-ionized water, or acidic or basic solutions. These experiments have shown that ionic liquids do have an affinity for produced water contaminants, so there is potential for use in sensing and removal of water soluble organics.

Hydrophobic Membranes for Removal of Organic Impurities in Production Water

(LLNL)

No report received.

Downstream Environmental Technology

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

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

No report received.

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

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

A manuscript describing experimental results and modeling of sorption for twenty gas-phase organics that cover a wide range of volatilities was completed and submitted. The work described in this manuscript provides the foundation for the sorption component of the mass balance model for predicting indoor exposures to hazardous air pollutants from outdoor sources. A key result of this work was the determination of sorption time scales for organic compounds spanning a wide range of volatilities (vapor pressures). These sorption time scales are compared to residential air exchange rates to identify compounds for

which sorption is likely to be important in realistic settings. Also, sorption parameter values were shown to correlate with the pure compound vapor pressure and octanol-air partitioning coefficient. The correlation relationships allow for the prediction of sorption properties for additional compounds not tested in these experiments.

Preparation of a second manuscript has been initiated describing sorption experiments that are focused on understanding the relative importance of carpet and wallboard as sorption sites. The methods section and some data analysis have been completed.

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

(ChevronTexaco and ORNL)

Project complete, no further reports.

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

(ChevronTexaco, BNL, and ANL)

The funds for this project have been exhausted and no new work has been done since the last reporting period. Therefore we have nothing to report for this period. New funds for FY04 are not expected. Project suspended pending renewed funding, until the project resumes activity, or is formally terminated.

Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration

(Marathon-Ashland and INEEL)

Experimental efforts focused on exploring Supercritical Fluid (SCF) regeneration using an alternate catalyst, and exploring the effect of pressure on the regeneration of a completely deactivated catalyst. The previous regeneration work focused solely on a micro-porous ultra-stable Y type (USY) zeolite catalyst. Experimental studies were performed to explore the regeneration of a macro-porous sulfated zirconia catalyst. The macro-porous catalyst offers greater accessibility of the supercritical regenerant into the matrix of the catalyst particle, potentially enhancing regeneration effectiveness. However, the sulfated zirconia has about 1/3 the surface area and number of acid sites per mass of catalyst compared to the USY zeolite. The sulfated zirconia catalyst demonstrated low product yield and rapid deactivation, and was determined to be an ineffective catalyst at the desired reaction conditions.

The effect of regeneration pressure was explored for a completely deactivated USY zeolite catalyst. The goal of this work is to determine the optimum pressure required for the regeneration process. Preliminary results suggest that as long as the regenerant density is close to the SCF's critical density the regeneration is efficient. At higher pressure, regeneration effectiveness decreases due to internal mass-transport limitations.

US Patent 6,579,821 B1, "Method for Reactivating Solid Catalysts Used in Alkylation Reactions" was issued June 17, 2003.

Publication

A manuscript titled "Recovery of Alkylation Activity in Deactivated USY Catalyst Using Supercritical Fluids: A Comparison of Light Hydrocarbons" was submitted for consideration for publication to *Applied Catalysis A: General*.

Biocatalytic Alkane Transformation for Viscosity Reduction

(ChevronTexaco and LBNL)

This is the last activity report for this project. All experiments are complete. Publications are in preparation.

Secondary Organic Aerosol Research in the Sierra Nevada Foothills

(Aerosol Dynamics, Independent Petroleum Association of Mountain States, and LBNL)

Field work continued in the late summer and early fall. Efforts have focused on collecting semi-regular filter samples in order to describe the chemical composition of the aerosol, and to determine how it varies over several weeks as the seasons change.

Data analysis is ongoing. Project collaborators have sent data that contain measurements of detailed meteorology and speciated NO_y for 2002. These data will be used to predict the rate at which the gas phase biogenic emissions are converted to secondary organic aerosol precursors.

Melissa Lunden attended both the Berkeley Atmospheric Sciences Symposium and the annual meeting of the American Association of Aerosol Research in October.

A talk entitled "Ultraviolet Light Absorption by Organic Gases Adsorbed onto Quartz Filters - The Positive Artifact Strikes Again" was presented at each meeting. This work, lead by Thomas Kirchstetter, details important measurement errors that can occur when using an aethalometer, a standard tool for measuring black and organic carbon in the atmosphere. This work is important for interpreting the carbonaceous data at the Blodgett location, particularly during times of fresh organic emissions like forest fires.

Proton Exchange Reactive Membranes for Conversion of Light Alkanes to Clean Liquid Fuel

(Ceramtec, Inc. and INEEL)

Performance of a surrogate palladium membrane in the experimental test system was evaluated at the INEEL. Hydrogen flux rates were investigated as a function of temperature, pressure, concentration and gas flow rate. Temperatures between 300 and 600 °C, pressures between 50 and 100 psig, and concentrations between 10 and 100 % H_2 in argon were examined. Conditions that optimize flux rates, or minimize reaction-side hydrogen concentrations, were identified. The membrane-reactor system is being modified to focus on catalyst testing, and catalyst materials are being developed.

A CRADA between the INEEL and Ceramtec has been signed. Team members from the INEEL traveled to Ceramtec in Salt Lake City, UT, in July to conduct a CRADA kick-off meeting. Ceramtec will develop proton conducting membrane materials to be tested at the INEEL. The first Ceramtec membrane has been received at the INEEL and will be tested in the vertical membrane test system.

The reaction system has been reconfigured to allow for recirculation catalytic reactions. Three new catalysts were explored in the recirculation system; a new USY zeolite, a Beta zeolite, and a Mordenite zeolite. The Beta and Mordenite zeolites were supplied by ConocoPhillips. Alkylation reaction conditions explored were 60°C, an isoparaffin to olefin ratio of 20:1, and an olefin weight hour space velocity of 0.265/hr.

The USY had the highest activity followed by the Beta zeolite. The Mordenite zeolite had the lowest activity. Despite the low activity, the Mordenite catalyst regenerated very well without any appreciable loss in activity maintenance over 50 hours. Under the same regeneration conditions,

the USY activity maintenance dropped under 90% in initial activity in slightly over 30 hours. Activity maintenance studies for the Beta zeolite will be conducted in November.

Rosa Costello worked as a student intern on the Proton Exchange project sponsored through the DOE-FE Mickey Leland Fellowship Program. Rosa is an undergraduate student at the University of Puerto Rico, Mayagüez.

A patent application titled: "A Method And System For Reactivating Solid Catalysts And A Method And System For Recycling Supercritical Fluids Used To Reactivate The Solid Catalysts," was filed with the U.S. Patent Office. A Statement of Work is currently being developed for a CRADA with Conoco-Phillips.

Biougrading of Heavy Crudes Using Temperature and Oil Tolerant Enzyme Catalysts (ChevronTexaco and ORNL)

Highlight:

- Cloned P450 enzymes into a higher expression vector.

Construction of a hybrid enzyme that was thermostable above 75°C was previously reported. In the last two months, parent and the hybrid enzymes have been cloned into a higher expression vector to enable production of larger quantities for doing structural studies. This will throw some light on the possible substrate range of the hybrid in relation to the parent enzymes. Initial studies show that up to 40 mg/L protein can be obtained by optimization of growth and induction period using the pCWori vector.

The P450 enzymes require a co-factor and a reductase protein for carrying out hydrocarbon oxidation. A potential alternative is to use hydrogen peroxide generated in-situ using a second enzyme, glucose oxidase. Oxidation rates of the P450 enzymes in the presence of hydrogen peroxide are being evaluated in place of the reductase protein.

Natural Gas Technology

Molecular Engineering: Next Generation of Gas Purification Technology

(ChevronTexaco, Virginia Commonwealth U, and BNL)

No report received.

Coiled-Tubing-Deployed Hard Rock Thermal Spallation Drill and Cavity Maker

(Nextant, NM Tech, and LANL)

Highlights:

- Simulations predict conditions for optimum performance
- Bench tests of burner with modified flame holder show improved performance

LANL continued to research proportional mixing technology. It is anticipated that variation in the density, temperature, and pressure in the annulus during spallation will cause significant variation in the supply of air and propane to the downhole burner assembly. A method must be developed to achieve a constant feed of the fuel and air under fluctuating supply conditions in order to maintain burner performance.

Two Newpex combustion code runs were completed to evaluate the sensitivity of the burner performance to variations in excess air, combustion, chamber pressure, and the input air (and fuel) temperature. Documentation of the code was obtained and reviewed to interpret the code output data. Two simulations were completed which calculated the performance of a burner with the combustion chamber operating at surface conditions, 25°C, and atmospheric pressure, and without a nozzle between the combustion chamber and the burner exhaust port. Conditions were calculated in the combustion chamber and at the exhaust port for a burner with fuel and air preheated to 127°C and a nozzle that

creates a chamber pressure 35 psi greater than the required 14.7 psi exhaust pressure. The heat content of the chamber increases as the excess air is increased while the heat content of the exhaust is reduced with the increase of the excess air. This occurs because the excess air increases the mass and velocity of the exhaust, which combines to increase the kinetic energy of the exhaust stream. The nozzle in the burner may limit its spallation performance unless the kinetic energy is recovered by the impingement of the exhaust on the rock, or is counteracted by increased heat transfer to the formation due the higher flow velocity.

NM Tech bench-tested the current burner design with the modified flame holder. Very stable burner performance was achieved with airflow rates up to 2/3 the design rate. This was about twice the airflow achieved with the previous design. The outside of the combustion chamber and the burner nozzle were hot enough to glow red during daylight testing. This had not been observed with the previous burner design. The airflow controller precluded higher airflow testing with air supply pressure available for this test. The air supply system will be modified to support a higher airflow and the burner will be tested at the design air and fuel rate (10 lb/hr propane).

Scintillating Fiber Neutron Detectors for Well Logging

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

Highlight:

- The ambient temperature version of the detector is performing as predicted by the computer model.

The high temperature version of the epithermal neutron detector did not transmit light through the scintillating fiber. Examination of the detector indicated that the high temperature epoxy attacked the silicone rubber cladding on the fibers. This effect was not evident in the small curing study samples made in the spring. The cumulative effect down the full length of the detector was catastrophic. More samples of high temperature epoxies and silicone rubbers were obtained for testing. Computer modeling indicates that silicone rubbers will not dramatically change the neutron interaction or detector efficiency.

Testing is proceeding with the low temperature version of the detector. This detector uses a high hydrogen content moderator that can survive to 100°C. The same photomultiplier tubes and readout electronics are used for both the high and low temperature versions of the detector. Therefore, the electronics and readout package can be fully optimized with the low temperature detector.

Preliminary testing shows that the fiber-based detector has increased efficiency when the number of thermal neutrons from the source is reduced (hydrogen rich moderating material removed from the environment near the source). The count rate of the fiber detector increased 130% when the external moderator was removed from a Pu^{239}Be source. The matching He^3 detector's count rate remained nearly constant at 96%. This shows the fiber detector has higher epithermal neutron efficiency than the He^3 tube. The electronics need to be further optimized to minimize noise and to determine the best threshold setting for neutron counting. The new detector will be run in identical neutron/gamma-ray fields as the commercial He^3 detector. Cf^{252} , Pu^{239}Be and Am^{241}Be sources are available for testing in strengths up to a few curies.

“High Efficiency Epithermal Neutron Detectors”, by Mary Bliss, David Jordan, Howard Thesen, Melody Maynard, William Slinger, Michael Knopf, and Lindsay Todd, was presented by Mary Bliss at the 2003 American Association of Petroleum Geologists Regional meeting in Tulsa, OK.

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

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

No report received.

Partnership Office

The partnership anticipates funding in the 2004 fiscal year to be similar to 2003. Although this level of funding still represents a significant reduction compared to the previous five years, the partnership has started planning to move forward with a concentration on the highest impact projects. The partnership has made a commitment to fund

the top new projects in the FY2003 review cycle in 2004. The laboratory representatives are currently working on several scenarios to facilitate these new starts. To accomplish these scenarios, the partnership will need to reduce some ongoing projects. The partnership office will clarify these scenarios for 2004 in the next monthly report.

