ACTIVITY REPORT

June 2001

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**
Oil and Gas Recovery Technology Drilling, Completion, and Stimulation Technology Diagnostic and Imaging Technology	Upstream Environmental Technology Downstream Environmental Technology Ultra-Clean Fuels Technology

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

Upstream Environmental Technology

Continuous Monitoring of Particulate Matter and Particulate Matter Precursor Emissions from Stationary Sources (Chevron and SNL)

Project is in close-out phase.

Development of an In-Well Oil/Water Separator for *In Situ* Recycling of Produced Water (Baker Hughes, Chevron, CINC, Oak Ridge Tool & Engineering, Phillips, REDA Pump, Texaco, Unocal, and ORNL)

Highlights:

- Oak Ridge Tool and Engineering constructed new housing for centrifugal separator.
- Hydrocyclone/centrifugal separator used in separation of sand, oil, and solids.

The housing for the separator was machined in plexiglass, which will accept a longer rotor and allow for increased throughput capacity. The portion of the rotor housing that directs the exit of the separated streams now runs down the side. Exchangeable internal parts of the housing will allow for adjustment of the collection well volumes. This allows for tuning of the separator depending on the ratio of oil-to-water in the treatment stream. All equipment has been transferred to a new facility for testing.

Solids, water, and oil were separated over several hours using a hydrocyclone in combination with the centrifugal separator. The system worked very well, producing a clean split of oil and water in the separator. Solids were removed in the hydrocyclone. During the cycle the system treated approximately 2.5 kg/min of oil/water/sand. The majority of the sand and water was removed by the hydrocyclone and then the centrifugal separator produced streams with 0.03–0.5% oil in water and 0.2–0.3% water in oil. Change in the rotational speed of the separator from 3,000-5,900 did not appear to improve performance at the flow-rate study. After the study was completed the centrifugal separator was disassembled and the sand accumulated in the separator was measured at 30 g. The study shows the importance of designing a good solids separations step before using centrifugal separators.

Stationary Source Emission Control Using Plasma-Assisted Catalysis (Cummins Engine, Edison Chouest Offshore, and LLNL)

- Project is in close-out phase.

Reducing Chemical Use and Toxicity in Produced-Water Systems (BP Amoco, Rhorback Casasco Systems, and ANL)

Highlights:

- ECN monitoring software corrected and improved.
- Feasibility of adding EIS technique evaluated.

An online, real time method to monitor sustained localized pitting so that treatment chemicals (biocides and chemical inhibitors) can be applied only when needed is being developed. Field operators need to know whether pitting corrosion is due to microbiologically influenced corrosion or other chemical corrosion mechanisms so that they can appropriately apply either biocides or corrosion inhibitors only if needed using minimal treatment applications. Argonne is developing an instrument to allow field operators to determine the cause of pitting corrosions in real time while minimizing toxic discharges and treatment chemical use. This instrument is also used as a tool to evaluate less toxic treatment approaches.

The new user-friendly software package for automatic electrochemical noise (ECN) measurement and data interpretation was modified to add the Kurtosis index, used to differentiate chemical versus microbial initiation of localized corrosion as shown in the last activity report. In addition, program bugs

were also corrected, such as the "time stamp". In the recording of measurements, the time stamp did not match the actual total measurement time. For example, during a 1000 hours measurement, the record indicated only 975 hours of total running time. The time stamp mismatch in the record did not affect data interpretation and detection of localized corrosion activity.

The feasibility of adding an electrochemical impedance spectroscope (EIS) technique to the current electrochemical noise analysis system to differentiate the different mechanisms for localized corrosion attack was evaluated. The design of the required data acquisition program for the combined techniques is being carried out.

Sulfide Removal in Produced Brines by Microbial Oxidation

(Phillips, U of Tulsa, and INEEL)

Highlights:

- Favorable results obtained from water chemistry and biological analyses.
- CRADA placed.
- Completed bioreactor design for field specific implementation.
- Determined impact of site specific conditions on selected microbial cultures.
- Finalized immobilization criteria of biomass for site application.

Preparation for field demonstration continues. The first phase of the design criteria for field implementation is complete. The cost estimate was significantly higher than originally anticipated; therefore, the task is still open and being iterated. Field operations will potentially be delayed by this development.

Plans are being solidified for a meeting of the Cooperative Research and Development Agreement participants. The meeting is tentatively scheduled for the third week of July in Idaho Falls.

Characterization of Soluble Organics in Petroleum Waste Water

(Chevron, Marathon, Phillips, Shell, Statoil, and ORNL)

Highlights:

- Blank levels established for oil/water contacts.
- Pressure tests begin.

ORNL is currently identifying water soluble organics (WSO) in produced water derived from Gulf of Mexico (GOM) crude oil/brine contacts. Contact experiments have been performed to determine the influence of the percent water/oil cut, pH, salinity and temperature on the quantity of extractable organics found in GOM brine. The pressure at which the oil/water contact is performed is the final parameter to be evaluated.

A factory-assembled pressure vessel, incorporating armored sight glasses on opposing walls, is being used to generate produced water samples at pressures up to 1000 psi and 50 ºC. The vessel has an internal volume of 300 mL, is fabricated from mild steel, and certified for chemical composition, hardness, and tensile strength. The pressure vessel is clamped onto a Ro-Tap Model B Sieve Shaker and horizontally rotated at approximately 60 rpm to produce a slight vortex at the oil/water solution interface. During mixing the temperature is maintained at 50 ºC by controlling voltage output to a heating tape wrapped around the circumference of the pressure vessel.

Two hundred milliliters of brine simulant are added to the vessel. The system is heated and mixed for four days to determine blank concentration levels for total petroleum hydrocarbon (TPH) in the vessel. At the end of the equilibration time, a Hoke® sample chamber is connected to the gas sampling port of the vessel. Pressure is vented into the evacuated gas sample vessel by opening the gas sampling valve located at the top of the pressure chamber. Once the chamber is brought to ambient pressure, the exit valve located at the base of the pressure chamber is opened to collect the aqueous phase. Initial testing has determined that the blank levels of TPH present in the vessel are less than 1% typically encountered in produced water samples.

The first in a series of pressure tests is under way. This test will compare the

TPH level found in produced water using the pressure vessel at ambient pressure to levels found in previous tests using a Water Accumulated Fraction vessel (ASTM D6081). Once correspondence in contact procedures is established, data will be acquired for pressures of 200 and 800 psi.

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

(American Petroleum Institute, BP Amoco, Chevron, Exxon, Gas Technology Institute, Texaco, Unocal, LBNL, ORNL, and LLNL)

- No report received

Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

Highlights:

- · Interviews conducted with staff of various air agencies.
- · LBNL staff attends emissions modeling and inventory workshop.
- · Review of uncertainty framework elements continues.

Interviews were conducted with eleven staff members at the California Air Resources Board, Bay Area Air Quality Management District, and San Joaquin Valley Unified Air Pollution Control District in order to understand details of the State Implementation Process and to acquire an understanding of perceptions of uncertainty held by regulators and stakeholders. Respondents were involved in developing either the 1994 San Joaquin Valley Ozone Attainment Demonstration Plan or the SARMAP modeling system, which was the primary technical tool used to support the plan. Prior to interviewing, an Interview Protocol was developed and approved by the U.C. Berkeley Committee on Human Subjects. The interviews will be transcribed, reviewed by the interviewees for accuracy, coded, and analyzed. This effort allows us to develop methodology for communicating modeling uncertainty information so that it will be used in control strategy design and in State Implementation Planning.

Work on an application to evaluate uncertainties in modeled hydrocarbon concentrations as a function of space and time continues. Ozone precursors will be estimated using the CMAQ model, which is the new EPA air quality model, and two chemical mechanisms: CB-IV and SAPRAQ-99. The emissions inventory to be used is the CARB revision of the 1990 inventory, wind fields prepared for the modeling episode, and the monitored data are from the 1990 San Joaquin Valley Study.

LBNL staff attended a public workshop conducted jointly by the San Joaquin Valley Air Pollution Control District and the California Air Resources Board. The workshop introduced and solicited comments on the emissions inventory and modeling to be used to support the 2002 San Joaquin Valley Severe Ozone Attainment Demonstration Plan.

Remote Sensing for Environmental Baselining and Monitoring

(Chevron, UC-Davis, and ORNL)

Highlights:

- Project begins.
- Methods being developed for collecting and analyzing data.
- Visit to Jornada planned.

Funding was received for FY 2001 and the ORNL component of the project began on June 1.

Using a 512 band spectroradiometer, ORNL is developing protocols for collecting data and developing software that can read and analyze the datasets. Given 20 or 30 measurements (vectors with 512 components), Singular value decomposition (SVD) is being used to identify the most significant differences between the measurements.

When each measurement is expanded in the coordinate system produced by SVD, clustering can be used to identify vectors with similar features. Indoor measurements have been performed for two datasets: colored paper produced by a color printer and a set of leaves collected both last fall and this spring. Given a collection of measurements with several data sets for each leaf, the

software can distinguish (cluster) the measurements for each leaf. Two ORNL team members are preparing to collect field hyperspectral data at the oil spill site at the Jornada Experimental Range near Las Cruces, NM on July 15 and 16.

Downstream Environmental Technology

Bioprocessing of High-Sulfur Crudes via Application of Critical Fluid Biocatalysts

(Texaco, UOP, and INEEL)

Highlights:

- Enzymatic reactions conducted as base comparisons.
- CRADA placed with UOP.
- Control experiment conducted.
- Abstract accepted for presentation.

Work continued exploring biocatalysis in organized media, including reverse micelles, microemulsion, and emulsions. Hemoglobin (Hb) catalyzed oxidation of dibenzothiophene (DBT) in 15% buffer–85% ethane at 42°C and 2400 psi using AOT as the surfactant was performed in May. The reaction resulted in at least 6.3% conversion to the sulfone and sulfoxide product. The reaction was repeated and conversion to product was again observed. Control experiments—where either ethane or hydrogen peroxide was not present—demonstrated no conversion to product. The experiments were complicated by difficult product recovery from the reaction mixture. The difficulties were caused by (1) the presence of aqueous and organic liquids mixed with surfactant and (2) difficult gas chromatography (GC) analysis caused by an overlap of the sulfone and sulfoxide product with the surfactant. The reaction was further complicated by slow depressurization at termination of the experiment.

Efforts in June focused on improving reaction depressurization, product recovery and analysis. The injection of a nitrogen hydrochloride mixture at the end of the experiment provided a defined reaction termination point, broke the emulsion in the high-pressure reactor and allowed for quick depressurization. Product recovery was greatly improved through a technique where all the reactor samples were mixed and the solvents evaporated. Methylene chloride and methanol were first evaporated at low temperature, followed by water evaporation at 60°C for 1.5–2 hours in a roto-vap. The dried sample was then redissolved in methylene chloride for GC analysis. The GC method was also modified such that the sulfone and surfactant peaks are resolved. Control experiments have demonstrated good product recovery and analysis.

Efforts in July will return to the biocatalysis reactions. An abstract entitled "Hemoproteins-catalyzed oxidations of organosulfur compounds in reverse micelles, microemulsions and emulsions in supercritical fluids" was accepted for presentation by the Division of Organic Chemistry for the 222nd American Chemical Society National Meeting, August 26–30 in Chicago.

Biological Upgrading of Heavy Oils for Viscosity Reduction

(BP Amoco, Chevron, EPRI Chemicals, Natural Gas Center, Texaco, and LBNL)

Highlight:

- Research results presented at three conferences..

Research over the last months has focused on completing evaluations of the total culture collection. We currently have over 50 pure bacterial cultures capable of oxidizing alkanes. These cultures are being systematically evaluated for their phylogenic, genetic and physiological diversity. Each microbial isolate is being tested for the ability to transform C_5–C_{16} alkanes (enzymatic specificity), homology with alkB using TS2S/deg1RE primers (genetic homology with a well-characterized alkane monooxygenase), FAME profile, and 16 sRNA identification. Biocatalytic agents that will oxidize longer chain (C_8 and greater) alkanes without oxidizing gasoline range alkanes (less than C_8) are particularly desirable. The kinetic activity of eleven type strains are being quantitated and compared to each other and the complete suite of tests.

Preliminary results suggest a correlation between our kinetic results, enzymatic specificity, and the results of the alkB homology test. If the correlation between genetic tests and activity is validated, then we will be able to apply a genetic test to rapidly screen environmental isolates for novel enzymatic activity.

Results from this research have presented at three conferences: Abstracts of the 101st Annual Meeting of the American Society for Microbiology, Orlando, FL, May 20–24, Twenty-Third Symposium on Biotechnology for Fuels and Chemicals, Breckenridge, CO, May 6–9, and Abstracts of the 221st American Chemical Society National Meeting, San Diego, CA, April 1–5.

Kinetics of Biochemical Upgrading of Petroleum

(Biocat, Chevron, Shell, and BNL)

No report received.

Enzymatic Upgrading of Heavy Crudes via Partial Oxidation or Conversion of PAHs

(Chevron, Phillips, Texaco, ORNL, and INEEL)

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Progress continues on the development of an improved lignin peroxidase (LiP) enzyme capable of rapid reaction with polyaromatic hydrocarbons (PAH). Cloning of modified LiP in the first round of directed evolution resulted in about 40 clones. Activity of LiP in the supernatant cultures was similar to previous clones and slightly above detection limits. In order to confirm production of LiP, protein analysis was conducted by SDS-PAGE method. The culture supernatant as well as the cell mass was analyzed for the presence of enzymes. The results indicated presence of a small amount of protein of about 42 KDa (molecular weight of LiP) in the cell extract. However, the level of expression observed is not sufficient for enabling detection by PAH assay which is required to do biocatalyst development or to do further characterization of the enzyme. The low-level expression may be caused by several reasons such as difference in codon usage, post-translational physiological interactions, folding differences, and so on. The directed evolution approach can address these problems and produce a stable and active protein at high expression. However, certain modifications may be necessary to allow better expression within a short time. A couple of approaches are being evaluated. One approach involves gene shuffling to improve the matching of codon usage between the gene and the host. The second approach is to use leader sequences from bacterial genes capable of extracellular expression of similar enzymes. We have contacted two researchers working in the respective fields and intend to discuss the potential of collaboration or the prospect of borrowing the respective genes from them. These approaches will be used by themselves or in coordination with the current error-prone polymerase chain reaction-based strategy to improve expression and to further biocatalyst development.

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

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

Highlights:

- Data from transient experiments analyzed and calibrated.
- Comparison of infiltration rates from Clovis field house completed.

The analysis of the filter samples, and the quality assurance and calibration of the real time data is nearly complete. The data from the transient experiments, designed to determine appropriate parameter values for deposition and penetration, have been analyzed and calibrated. The next step in the parameterization process is to separate the effects of the ammonium nitrate phase change from the physical processes of deposition and penetration. The methodology for this separation is being developed and will utilize the real time indoor/outdoor particle nitrate concentration data in conjunction with literature values for

ammonium nitrate particle size distributions for outdoor particles and ammonium nitrate particle composition. These values will be used to estimate the ammonium nitrate contribution to each particle size range in the outdoor air and the most probable size distribution of these particles after an ammonium nitrate phase change indoors.

Predicting average concentrations of an indoor predictive model of outdoor origin (that are most relevant for estimates of chronic PM exposures) requires submodels describing air infiltration rates and the indoor PM concentrations that result from infiltration and other processes. Infiltration rates can be predicted based on readily measured properties of the housing stock (e.g. leakage areas), regional meteorological characteristics, and assumptions concerning the human factors affecting building operation (e.g. window and door opening, and HVAC operation). Predicting air infiltration rates for housing stocks representing geographical areas can arguably best be done using a probabilistic approach that explicitly incorporates the uncertainties inherent in building parameters and housing operation.

An initial comparison of the measured and predicted infiltration rates obtained from the Clovis field site house has been completed. The infiltration rate was measured with approximately hourly resolution using a constant release of SF6 tracer method. The infiltration rate was modeled using the LBNL/AIM infiltration model developed by Walker and Wilson, in 1998. The model is parameterized by building characteristics (such as area, volume, and leakage area), and driven by measured indoor/outdoor temperature differences, and wind speed and direction.

The comparison between the measured and the most probable model estimate of infiltration rate is quite good for data taken during December 2000, a period when the house was not mechanically ventilated. In particular, the model captures the diurnal variation in the air infiltration rate due to a temperature induced "stack effect", and partially captures the increases in infiltration rate due to wind loading on the building during windy periods on Days 356 and 357. Some of the other artifactual spikes in the measured data are due to people entering the house or introducing extra tracer gas (Day 361) during a change of the tracer gas supply system.

Based on the good agreement between the measurements and the model, we expect to be able to extend the predictive capability for infiltration rates and later indoor particulate matter concentrations to the larger housing stock.

Completion of the infiltration rate modeling requires an explicit estimate of the uncertainty in infiltration rates and an estimate of the likely uncertainties in the indoor/outdoor PM ratio. We are presently completing the uncertainty analysis for infiltration rates based on root mean square differences between the measured data and model predictions from the Clovis field site. We plan to complete a first order error analysis of indoor/outdoor PM ratios later this summer. Errors in the estimated indoor/outdoor PM ratio due to infiltration uncertainties will be estimated by comparing 12 hour averaged indoor/outdoor PM ratios calculated using measured and modeled infiltration rates to drive a time dependent size conserved particulate transport model that includes characteristic PM size distributions and PM deposition rates. Once complete, the infiltration rate analysis will be combined with measured indoor/outdoor ratios to test both the size-conserved model and model refinements that embody physio-chemical processes relevant to nitrate particulate matter formation.

Real-Time Characterization of Metals in Gas and Aerosol Phases (BP Amoco, Equilon, Marathon, Phillips, Shell, Eastman Chemicals, and ORNL)

The project objective is to develop a high-precision field portable instrument. This instrument is being designed to provide real-time measurement of elemental composition in gas and aerosols for emission monitoring and process control. Current emphasis is to test the instrument under a range of conditions to obtain field data for improving system design. Investigations of instrument responses, to transient aerosol loadings in the exhausts of engines burning different fuels, have been completed. Aerosols peaked between 200–500 nm in the exhausts. Preliminary data indicated the aerosol focusing module worked well in field conditions and provided 2–3 orders of magnitude enhancement in aerosol material to laser plasma measurement.

A paper was presented in the Annual Meeting of the Air and Waste Management Association in Orlando. Results and instrument design were reported in the meeting. A test plan—for a field experiment is scheduled this fall at the Eastman Chemical Company—focusing on transient response and data intercomparison was drafted by the principle investigator and is being reviewed by the group at the Eastman.

Ultra-Clean Fuels Technology

Hydrogen Production using Inorganic Membranes (Texaco, UOP, and INEEL)

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The Inorganic Membrane Technology Lab (IMTL) (East Tennessee Technology Park, Oak Ridge, TN) prepared a membrane module designed for effusive flow separation of hydrogen from hydrocarbon/hydrogen mixtures and provided it to ORNL for testing. Membranes using an alternate design strategy (taking advantage of surface flow to enhance the flow of the more condensable components) are being prepared at IMTL.

An apparatus has been designed and constructed at ORNL for the purpose of testing these inorganic membranes with model mixtures (e.g. a hydrogen/methane mixture, and hydrogen/ethylene and hydrogen/ethane binary mixtures). The construction of the apparatus is complete. Testing of component and integration has been carried out satisfactorily. Laboratory security is to be activated the week of July 9, allowing installation of the classified membrane module into the apparatus and the commencement of membrane separation tests.