

ACTIVITY REPORT



**Natural
Gas &
Oil
Technology
Partnership**

June 2002

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

February, April, June, August, October, December
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

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

Highlight:

- Efforts continue to transfer the ANL ECN corrosion probe technology to the refinery industry.

The joint effort between ANL and Ondeo (a chemical manufacturing and service company formerly known as Nalco) to test the ANL electrochemical noise (ECN) technology at a refinery site continues. Because of safety issues and other circumstances, a previous identified refinery test site located in Canada was dropped from the list. Several other locations in the United States are being evaluated. A service company for corrosion detection and prevention, CorrOcean, joined the team and will work with ANL and Ondeo for the field test of ECN probe. They expressed very strong interest to develop ANL's ECN technology for commercial application by their clients.

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)

No report received.

Estimation and Reduction of Air Quality Modeling Uncertainties Envair, EPRI, and LBNL)

EPA's Community Multi-Scale Air Quality Model (CMAQ)

Project researchers ran a four-day simulation of the August 1990 ozone episode upon which this study focuses, using inputs of emission, initial conditions, and boundary conditions supplied by the California Air Resources Board (CARB). Researchers are validating the results.

Progress continues on uncertainty visualization. Researchers installed and evaluated the following graphics programs to read Community Multi-Scale Air Quality (CMAQ) model output:

1. PAVE, freeware from MCNC,
2. Vis5d, open source freeware from University of Wisconsin, and
3. AVS Express.

Researchers continue to code interviews. The coded interviews were analyzed to associate individual respondents with narrative about the air quality planning process, the utility of models, and the potential benefits of model uncertainty analyses.

Researchers also created a network diagram showing the interactions of organizations during the development of the 1994 San Joaquin Valley Ozone Attainment Demonstration Plan. These initial findings were synthesized and presented in a seminar sponsored by LBL EETD.

Technology Transfer

Project researchers continue to collaborate with the California Air Resources Board (CARB) modeling group.

Remote Sensing for Environmental Baseline and Monitoring

(ChevronTexaco, UC-Davis, and ORNL)

Highlight:

- Preliminary analysis of field data from the Jornada Experimental Range completed.

In April 2002, ORNL received data for the 665 measurements made at the Jornada Experimental Range by Agricultural Research Service (ARS) investigators in September 2000. Using both field and remote data, ORNL will explore the resolution limits for pixel unmixing and plant species identification. ORNL completed a preliminary analysis of 211 measurements made at the grass site. Each measurement consists of 2151 numbers that are the reflectance at wavelengths from 350 nm to 2500 nm. Each measurement is described with one or two of the following labels: Bare, Litter, Aristada, Capa, Datu, Forb, Grass, Mesquite, Senna, Snakeweed, Tila, and Yucca. “Bare” is bare soil, “Litter” is plant litter, and the other ten labels are plant species. This data set can be used to test whether or not each of the 12 labels has a distinct hyperspectral signature.

Using Singular Value Decomposition, ORNL calculated an orthonormal basis for the 211 measurements and calculated the coordinates of each vector using the basis. The first component of the basis is the mean value for the 211 measurements, while the second and higher components are the directions with the most variance in the data. The first three vectors have 98.8% of the variance and the first ten vectors have 99.8% of the variance. A plot of the second coordinate versus the third coordinate is displayed by black squares in Figure 1 for the 211 measurements. The circles in Figure 1 are the mean value for sets of vectors with the same label. Yucca has the highest value on axis two, while Bare and Litter have the lowest values. Since most of the Yucca measurements have the characteristic spectra of green plants, Axis 2 separates green plants from brown soil and litter (four of the 25 measurements labeled Yucca are senescent and are closer to Mesquite than to Yucca). While Bare and Litter are close together for the first three basis vectors, they have distinct values on Axis 4.

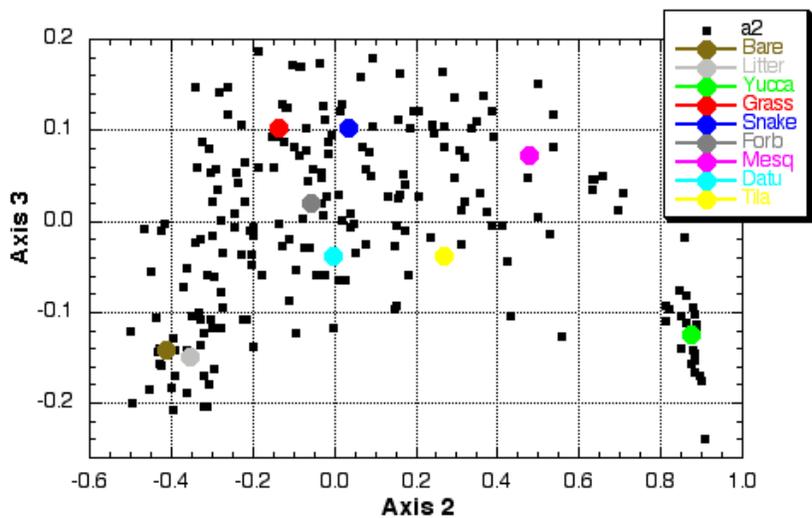


Figure 1. The 211 measurements compared to mean values for ten of the labels using the second and third basis vector.

ORNL completed a preliminary test on species differentiation by clustering the measurements about the mean vector for each measurement. Yucca was the most distinct with 100% of the vectors in a cluster of 21 members. Bare had 80% of the vectors in a 15 member cluster. Grass had 61% of its cluster. Low values were: 7% for Snakeweed and 13% for Forb. Thus, a few of the labels have a distinct hyperspectral signature while others do not.

Modeling of Water-Soluble Organic Content of Produced Water (ChevronTexaco, Phillips Shell, Statoil, and ORNL)

Highlight:

- An uncertainty analysis was conducted on the produced water characterization data.

The goal of this project is to develop a model for organic contaminant concentrations in produced water associated with oil production at deep well drill sites in the Gulf of Mexico. The modeling started with the analysis of data collected during the collaborative Petroleum Environmental Research Forum (PERF) Project to characterize and evaluate water-soluble compounds. Preliminary analysis of water characterization data indicated that the main influences on the solubility of organics in brines were the pH of the brine and the temperature.

During the last reporting period, an uncertainty analysis was performed on the data to examine these assumptions in more detail. In particular, information on the variances of independent and dependent variables is required for the development of a statistical model for organic solubility in brines. It is important to note that although uncertainties in the independent variables (such as temperature) were minimized, uncertainties in the results of the gas chromatographic analyses could be as high as $\pm 60\%$. Large uncertainties resulted from the complex separations required to isolate the various organic fractions. Losses occurred during handling, and the large number of steps precluded replicate analyses.

In addition to the uncertainty analysis, various simple phenomenological models were examined for applicability to the produced water/crude oil system. In particular, experimental results indicated that the pH of the brine was important in influencing the solubility of polar organic compounds which make up most of the water-soluble component of crude oil. Following the method of Khan et al., the relationship between pKa and organic acid solubility was plotted as a function of pH. A marked increase in solubility of the acid was observed when the pH was equal to or greater than the pKa, or the point at which the concentrations of the dissociated and undissociated acid are equal. The effect of the Henry's law constant, Kh (defined here as the activity of the acid in the aqueous solution divided by the fugacity of the acid in the gas phase), is to shift the solubility curve downwards at low Kh. By manipulating the pKa and the Kh, one can generate many different solubility curves. It is important to note that simple organic acids have pKa values of about 4.8, phenols close to ten, and ketones of about 20 - none of which would predict an inflection point in the solubility curve close to seven as observed in the PERF data. This indicates that the properties of the mixture must be considered when modeling organic solubilities.

The work of Khan et al. indicated that the temperature dependence of organic acid solubility could be accounted for by changes in the Henry's law constant, following an Arrhenius function. The group also investigated the effect of salinity on solubility, using Pitzer-type interaction coefficients to calculate changes in the activity coefficient. Salinity, however, was found to have a major impact only on the most highly-soluble organic acid, pyruvic acid. This is in agreement with ORNL findings that salinity had a negligible effect on the solubility of organics coming from the contacted crude oil.

Thus, ORNL began to develop a model for the solubility of semi-volatile organics in produced water, based on thermochemical properties. Project researchers evaluated the solubility of individual compounds, e.g., valeric acid or phenol, to assist in understanding the behavior of the system. Data available from the laboratory and from the field have high uncertainties; however, it is likely that a statistical approach will best model the produced water/crude oil system.

Downstream Environmental Technology

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

(ChevronTexaco, UOP, and INEEL)

Highlight:

- Final report completed and submitted to NPTO.
- Project results will be presented to the American Chemical Society.

The project final report was completed and submitted to NPTO. All efforts for this project are now complete except for presentation of project results at the 224th American Chemical Society national meeting in August. No further reports will be issued.

Kinetics of Biochemical Upgrading of Petroleum

(Biocat, ChevronTexaco, Shell, and BNL)

No report received.

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)

Highlight:

- Researchers conducted model runs to investigate the importance of key variables.

Project researchers conducted a series of model runs to investigate the importance of key variables including ventilation rate, actinic flux indoors, and the ozone deposition rate on indoor surfaces. For these model runs, researchers used hourly outdoor concentrations predicted by 3D modeling of a four-day ozone episode in the San Francisco Bay area during 1990. The indoor chemical mechanism was modified slightly to be consistent with the formulation of SAPRC-99 used for the outdoor modeling. The effect of varying the ventilation rate on indoor versus outdoor time-concentration profiles was first examined in the absence of chemistry; this also allowed researchers to validate the mechanism used to introduce outdoor air to the indoor model compartment. As expected, indoor species concentration profiles closely tracked outdoor profiles at ventilation rates above about one air change per hour, but differed substantially at ventilation rates below 0.5 air change per hour. The model captured the shift in the timing of higher concentrations and potential indoor exposures that results at lower ventilation rates.

Project researchers also examined the role of actinic flux on indoor chemistry by setting the indoor flux equal to zero, 1%, and 10% of outdoor levels, as calculated by the solar irradiance model developed at LBNL. The increase in chemical activity with higher indoor actinic flux caused a quantifiable change in the indoor concentrations of several indicator species including formaldehyde, acetaldehyde, and methacrolein. The effects of ozone deposition with rates obtained from the literature on the model are being analyzed.

Project researchers initiated a series of experiments to screen previously untested volatile HAPs for sorptive interactions with indoor surfaces. In the first experiment, researchers examined acetaldehyde, acrolein, 2-butanone (methyl ethyl ketone) and benzene, along with the previously tested ethylbenzene in a furnished 50-m³ chamber.

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

(ChevronTexaco, and ANL)

During the last two months, the *D. gigas* hydrogenase was purified using one Silica Gel column, two DEAE-Sepharose chromatography columns, one Ultrogel AcA 44 gel filtration column and a Biogel-HTP hydroxylapatite. The purification of hydrogenase was carried out in two batches, 25g and 260g of wet cell paste. About 20 units of pure enzyme were obtained from the 25g batch and about 55 units of pure enzyme were obtained from the 260g batch. About 250 units of enzyme were collected after partial purification from second DEAE-sepharose column for isolation of the active site.

The goal is to study the catalytic properties of the nickel-iron (Ni-Fe) active site by itself in absence of the protein scaffolding. This may broaden the specificity of the catalyst enabling conversion of non-natural substrates such as dibenzothiophene. The enzyme fraction was digested with proteinase K to cleave the protein scaffolding surrounding the Ni-Fe active site. Analysis of the Ni-Fe complex is being conducted with a gas chromatography mass spectrometer (GCMS). Experiments are being planned to use the Ni-Fe complex by itself or with *D.gigas* hydrogenase and/or with hyperthermophilic *P. furiosus* hydrogenase for possible enzymatic catalysis of sulfur removal from dibenzothiophene.

A chemical hydrogenation catalyst is being obtained from ChevronTexaco to study coupling of such a catalyst with enzymes to allow hydrogen activation followed by transfer of the activated hydrogen to the chemical catalyst for reaction with organosulfur molecules. The experimental conditions for such a reaction to occur are being designed.

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

(ChevronTexaco, BNL, and ANL)

Work began on the joint ANL/BNL project with ChevronTexaco as the industry participant. Present activity focuses on the Nanoscale Synthesis and Feed Interaction.

Nanoscale synthesis involves the synthesis of molecular species on the nanoscale range (1×10^{-9} m). This range runs from a few atoms to less than 100 atoms per molecule. In the nanoscale range, molecules take on a far different chemical nature. This project will study how the difficult-to-convert sulfur-containing species in heavy oils react with these "nano" clusters, versus larger molybdenum disulfide (MoS_2) molecules.

The Sonolysis Unit was customized to produce nano particles. This includes a jacketed reaction flask to control reaction temperature during sonolysis. The first batch of nano particles of MoS_2 was prepared by decomposing of molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$) in the presence of elemental sulfur in hexadecane. The nano particle separation is achieved by centrifuging the slurry.

Work began at BNL to characterize nano particles at the National Synchrotron Light Source (NSLS) at BNL. This will include transmission electron microscopy (TEM), x-ray diffraction (XRD), x-ray adsorption fine structure spectroscopy (XAFS), and x-ray adsorption near-edge spectroscopy (XANES) data acquisition.

At ANL, the materials and reactor pieces for the synthesis of restricted access sulfur compounds, such as 4, 6-dimethyl dibenzothiophene (4,6-DMDBT), were collected. A test reaction was run and yielded approximately 43% of 4,6-DMDBT (9.7 g). The two hydrodesulfurization (HDS) testing units (plug flow and batch) were modified for testing the nano particles from BNL.

Future enhancements scheduled for the plug flow unit will include an on-line gas chromatograph for analyzing gas products to improve mass balance on this unit. Synthesis work will be expanded to increase the total amount of 4,6-DMDBT. In addition, the moderately restrictive 4-methyl dibenzothiophene (4-MDBT) synthesis will also be worked up and optimized. The desulfurization of all three compounds (DBT, 4-MDBT, and 4, 6-DMDBT) will be tested in the batch and plug flow reactors.

Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration

(Marathon-Ashland and INEEL)

The automated experimental system was reassembled and tested. Difficulties controlling the reactor inlet temperature were encountered. The inlet heating system was modified to correct this issue. System testing will begin in June.