ACTIVITY REPORT

August 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)

Report in preparation.

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

Highlight:

- Project work summarized as project concluded.

The objective of this project is to develop an innovative technology for reducing NO_x emissions from diesel engines. The technology is based on plasma-assisted catalysis. It is expected to be applicable to diesel engines and to natural gas fueled drivers.

The technology is suitable for use in stationary diesel-powered generators in drilling platforms. It is also suitable for use in engines on ships used for oil transport. Added benefits include applicability of the technology to natural gas fueled drivers, and the ability of the same technology to also control fine particulates and other ozone precursors such as volatile organic compounds.

Project researchers conclude that the oxidation of nitrous-oxide (NO) to nitrous-dioxide (NO_2) plays an important role in several emissions control technologies: lean-NO_x catalysis, lean-NO_x traps, and continuously-regenerated particulate traps. Plasma assisted-catalysis enables NO to NO_2 oxidation without the need for expensive precious metals, and without oxidizing SO_2 to SO_3. Researchers verified the ability to scale the process and derived an engineering cost estimate for the emissions control system based on plasma-assisted catalysis. Future work involves establishing the durability of the process and deriving maintenance and operational costs under actual field conditions.

Project accomplishments

1. Project researchers demonstrated that plasma-assisted catalysis is tolerant of the sulfur level in the exhaust.
2. The test stand and chemical diagnostics were upgraded to investigate the use of heavy liquid hydrocarbons as NO_x reductants. Researchers demonstrated the use of diesel fuel as an effective reductant for NO_x.
3. NO_x reduction efficiency was characterized as a function of the electrical power consumption and hydrocarbon consumption.
4. The test stand was scaled up to handle the full flow from a heavy-duty diesel generator.
5. Researchers evaluated the performance and estimated the cost at scaled-up operation.

Stationary Source Emission Control Using Plasma-Assisted Catalysis *(continued)*

A two-orders of magnitude scale-up of the test facility was accomplished. A full-scale prototype of the plasma-assisted catalyst device was built and tested (Figure 1).

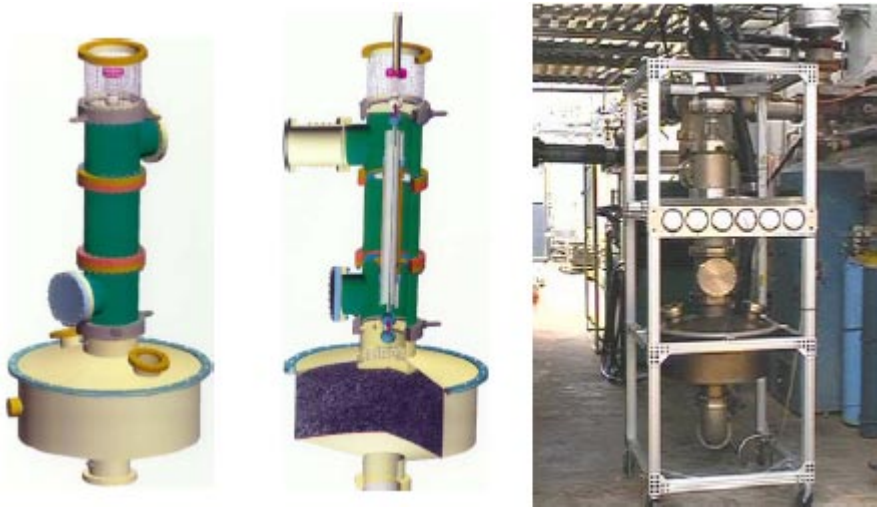

Figure 1. A full-scale prototype was built and tested.

Full-scale tests were performed to measure the NO_x reduction as a function of plasma power, hydrocarbon level, and engine load. The full-scale tests verified the predictions based on previous smaller-scale bench data. Data shows that plasma enables more NO_x reduction with less hydrocarbon additive and at relatively low exhaust temperatures.

An engineering cost estimate was derived from experience in building the full-scale prototype. Table 1 shows the engineering cost estimate as a function of the number of units.

		a	b	c	d	e	f
	Description	**For 1 - 10**	**10-100**	**100-1,000**	**1,000 - 10,000**	**10,000 - 100,000**	**over 100,000**
1	Power Supply	2,500	2,125	1,535	250	181	131
2	Ceramic Components	1,500	1,275	921	175	126	91
3	Catalyst	1,193	1,014	733	175	126	91
4	Plasma Processor*	1,575	1,339	967	125	90	65
5	Soot Filter	736	626	452	150	108	78
6	Assembly & Test	2,750	1,500	1,084	75	54	39
	Total Cost	**10,254**	**7,878**	**5,692**	**950**	**686**	**496**

Notes:
* Welded Structure
a Totally manual operation; same as current design but without the flanges
b Same design; add some fixture set up
c Change design to integrate components; build molds for ceramic parts, and tooling for metal parts
d Mass produced power supply; purchase catalyst in bulk quantities; build tools and dies for manufacturing and assembly
e Value engineer components; quantity discount in purchased parts
f Automated production and assembly; quantity discount.

Stationary Source Emission Control Using Plasma-Assisted Catalysis *(continued)*

A two-orders of magnitude scale-up of the test facility was accomplished. A full-scale prototype of the plasma-assisted catalyst device was built and tested (Figure 1).

Commercial and Economic Impact

1. Plasma-assisted catalysis can reduce catalyst cost by a factor of 500 by removing the need for expensive previous metals.
2. Plasma-assisted catalysis can enable NO_x and particulate emissions control even in the presence of relatively large amounts of sulfur in the fuel.
3. Plasma-assisted catalysis could be used for emissions control in
   a. Stationary generators in oil drilling platforms
   b. Engines on ships for oil transport
   c. Diesel engines in the transportation industry.
4. Plasma-assisted catalysis could save the oil refineries billions of dollars by easing the requirement for ultra-low sulfur levels in gasoline and diesel fuel.

Conclusions

The oxidation of NO to NO_2 plays an important role in several emissions control technologies: lean-NO_x catalysis, lean-NO_x traps, and continuously-regenerated particulate traps. Plasma assisted-catalysis enables NO to NO_2 oxidation without the need for expensive precious metals, and without oxidizing SO_2 to SO_3. We have verified our ability to scale the process and derived an engineering cost estimate for the emissions control system based on plasma-assisted catalysis. Future work involves establishing the durability of the process and deriving maintenance and operational costs under actual field conditions.

Reducing Chemical Use and Toxicity in Produced-Water Systems

(BP Amoco, Rhorback Casasco Systems, and ANL)

Highlights:

- Evaluation of an integrated EIS and ECN technique to differentiate mechanisms of localized corrosion attack is being carried out.

Application of an electrochemical impedance spectroscope (EIS) technique using the electrochemical noise probe is being carried out. The EIS technique is well known for its ability to measure metal surface activities such as coverage by corrosion products and biofilm formation.

Previously, project researchers reported that the Kurtosis analysis of electrochemical noise measurements could be related to different mechanisms of localized corrosion attack. The information obtained from the EIS measurements in combination with results from electrochemical noise analysis (ECN) will be evaluated for the capabilities to differentiate localized chemical versus biological corrosion attack. The ability to differentiate the mechanistic causes of localized chemical versus microbiological corrosion attack would be a technology breakthrough. This information could be used by process operators to select the correct and proper amount of chemical inhibitors or biocides to provide corrosion protection. It could also be used as part of a condition based maintenance system to predict and avoid the material failures caused by localized corrosion. If the results from EIS measurements are proved to be useful, the integration of EIS and ECN techniques will be carried out next.

Another activity during this period was to transfer ANL's ECN technology to industrial participants. A chemical manufacture of corrosion inhibitors who also provides corrosion monitoring and controlling services for clients has expressed an interest in developing the project's corrosion detection technique for commercial application. A proposal for this collaboration was submitted to the company.

Sulfide Removal in Produced Brines by Microbial Oxidation

(Phillips, U of Tulsa, and INEEL)

Highlights:

- Reactor design based on novel immobilization strategies nearing completion.
- Published paper in *Biotechnology Progress.*
- Initial design work completed for field implementation.
- Meeting of CRADA partners held.

The project continues to make progress toward technology implementation. Bioreactor development is proceeding along two parallel tracks. First, a three-phase, packed-bed bioreactor is under development that improves volumetric productivity compared to a stirred-tank bioreactor while maintaining good gas-biocatalyst contact and allowing for the replenishment of nutrients for immobilized microorganisms in the biocatalyst support particles. The second track is the evaluation of novel immobilization technology that holds promise for incorporating sulfide adsorbents into the immobilization matrix. Adsorption of sulfides will potentially increase the biocatalyst (sulfide-oxidizing microorganisms) concentration in the matrix and further improve bioreactor volumetric productivity.

The manuscript: "Characterization of a Novel Biocatalyst System for Sulfide Oxidation," by McComas, C., Sublette, K., Jenneman, G., and Bala, G., was published in *Biotechnology Progress*, Vol. 17 No. 3, pp. 139-446.

Initial design work for an order-of-magnitude cost estimate to support field operations was completed by Services Technology Corporation, a preferred service provider to Phillips Petroleum Company.

Characterization of Soluble Organics in Petroleum Waste Water

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

Highlights:

- Data describing the effect of pressure on the quantity and character of water-soluble organics in Gulf of Mexico brine acquired.

ORNL is characterizing water-soluble organics (WSO) in produced water derived from Gulf of Mexico (GOM) crude oil/brine contacts. A number of contact experiments were performed to determine the influence of pressure on the extent of contamination of produced water.

A factory-assembled pressure vessel, incorporating armored sight glasses on opposing walls, generated produced water samples at pressures up to 60 bar and 50 ºC. 200mL of brine simulant was added to the vessel and the system was heated and mixed for four days. The first test was performed at ambient pressure to compare the WSO level using the pressure vessel with that present in previous tests run at ambient pressure using a Water Accumulated Fraction (WAF) vessel (ASTM D6081). The total WSO derived from the pressure vessel contact was less than half of that found in WAF experiments. The lower value is consistent with WAF data indicating that WSO content is both a function of the amount of brine present and the ratio of the volume of oil-to-water used in the contact experiment.

Over the pressure range of 1–60 bar, WSO content increased by less than 10%. The additional quantity of WSO was equivalently distributed among polar, aromatic, and saturate hydrocarbon fractions. The most notable difference in the content of produced water derived from high pressure contacts is the increased amounts of carbon (C_6–C_{10}) range material in each of the chemical fractions.

The pressure data is being incorporated into a final report for submittal to the PERF committee at the end of September.

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)

Highlights:

- Base code for model in development.
- Locations of wells and spills at Tallgrass Prairie Preserve, OK, being plotted.

Project researchers are developing a simulation model to evaluate the effect of size and distribution of spills and habitat patches on ecological populations at the Tallgrass Prairie Preserve (TPP) in Oklahoma. A goal of the ecological model is to determine a frequency of spills that would lead to a density of organisms that can not persist. Effects of spill size and distribution on both herbivores and predators will be considered.

Wildlife modeling will be conducted on an object-oriented basic landscape disturbance grid coded in C++. The model will be a demographic simulation model rather than an analytical model. In addition, the model will be an individual-based or age-based model. Simulations will occur on the background of a dynamic landscape that includes prescribed burning and grazing. Map layers previously obtained for the Geographic Information System (GIS) (e.g., vegetation type) are being converted to input landscapes for the model. Locations of some of the wells and spills on the TPP were plotted from data collected during the June site visit.

Three C++ files are in development. The main file will examine dates of disturbance files in the directory, put them on a schedule, and choose a timestep for demographic activities (e.g., reproduction) by finding the smallest generation time among the species defined. The GIS file will represent landscape data as grids that can be accessed directly. The species file will read in species attributes and initialize the model by calculating a stable age distribution. Finally, the species file will calculate reproduction, mortality, and movement of animals.

The previously collected literature sources on the demography of species at the TPP are being classified and reviewed in order to select suitable species and their characteristics for inclusion in the simulations.

Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

Highlights:

- Scheme for including temporal and spatial variability within air quality model designed.
- Interviews conducted.
- Work on review paper continues.

Temporal and spatial resolution requirements for measuring atmospheric optical properties for reducing uncertainties in the determination of key photolysis reaction rates were investigated. These rates are required for modeling ozone (smog) formation using air quality models, and are especially important since an error of 50% on the nitrogen dioxide (NO_2) photolysis rate results in a 20% error in ozone. Therefore, researchers were required to estimate the rate of change and spatial variability of the total ozone column, aerosol optical depth, and ground surface albedo. A scheme for including temporal and spatial variability within the framework of an air quality model was also designed.

An important effort in the research is developing methodology for communicating modeling uncertainty information so that it will be used in control strategy design and in state implementation planning. Project researchers are conducting interviews to understand details of the state implementation process and to understand perceptions of uncertainty held by regulators and stakeholders.

For the months of July and August, interviews with planners, modeling experts, and stakeholders representing the regulated and environmental communities were conducted and transcribed. A list of analysis categories and category attributes was developed to analyze the interviews. Ultimately, the analysis will involve assigning dimensions to category attributes and then identifying how, if at all, and why respondents vary along the dimensions of interest. NVivo, a software program designed for analysis of interviews and other data in text form, was used to begin the analysis. As a complement to interview anal-

yses, a network diagram depicting influence relationships between agencies and organizations involved in the development of the 1994 San Joaquin Valley Ozone Attainment Demonstration Plan was drafted.

Work continued on an application to evaluate uncertainties in modeled hydrocarbon concentrations as a function of space and time. The hydrocarbons of concern are ozone precursors. The hydrocarbons will be estimated using the CMAQ model (the new EPA air quality model) with two chemical mechanisms that describe atmospheric chemistry: 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. CARB has given us the data in model ready format for the CB-IV mechanism.

Project researchers continued the comprehensive review of the application of elements of the uncertainty framework.

Work progresses on a review paper describing approaches to evaluating model uncertainty.

In August, LBNL staff attended and gave a talk at a special workshop at LLNL concerned with sensitivity and uncertainty analysis. The workshop was organized by the ASCI Institute for Terascale Simulation and the Institute for Scientific Computing.

Remote Sensing for Environmental Baselining and Monitoring

(Chevron, UC-Davis, and ORNL)

Highlights:

- Visit made to Jornada.
- Project meetings held.

In July, two ORNL scientists visited a diesel-fuel spill site on the Jornada Experimental Range (near Las Cruces, NM) and collected field hyperspectral data for oil-damaged plants and soil. Hyperspectral data were also collected from plants and soil outside of the oil-damaged area for comparison. The spectral data (512 channels) for 105 samples were analyzed using a clustering technique and Singular Value Decomposition. These two techniques can be used to define an index that ranks the measurements on a color scale ranging from green to brown.

While in Las Cruces, the ORNL investigators met with the US Department of Agriculture Research Service (USDA-ARS) staff that manages the Jornada site. The Jornada investigators provided Geographic Information System (GIS) maps of the oil-impacted areas, and are helping to acquire nine AVIRIS-sensor hyperspectral data sets for the site for a four-year period that is both before and after the oil spill (one of the data sets was obtained a week after the spill).

In August, ORNL team members met with Chevron investigators in Richmond, CA, to review data obtained during the visit to the Jornada site. They subsequently met with Professor Susan Ustin, of the University of California-Davis (UC-Davis), a project collaborator and plant physiological ecologist with remote-sensing expertise. These meetings were productive, and recommendations by the Chevron and UC-Davis participants are being incorporated into next year's proposed research plan.

Downstream Environmental Technology

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

(Texaco, UOP, and INEEL)

Highlights:

- Surfactant-protein interactions explored.
- Enzymatic oxidation of DBT demonstrated in SCF emulsion.
- Study results presented at American Chemical Society meeting.

Work exploring biocatalysis in organized media, including reverse micelles, microemulsions and emulsions continued through August. Previous efforts focused on improving reaction depressurization, product recovery and analysis for the reactions in organized media. Current efforts are exploring surfactant-protein interactions.

Hemoglobin (Hb) catalyzed oxidation of dibenzothiophene (DBT) in buffer—ethane emulsions using the sodium bis (2-ethyl 1-hexyl)—sulfosuccinate (AOT) surfactant were explored at 40°C from 2600 to 2900 psi. Buffer concentrations ranged from 15–50%. The reaction resulted in no conversion to the sulfone or sulfoxide product. The reaction was also explored with ethanol as a co-surfactant. Again, no oxidation products were observed. Further testing found that 2-ethyl 1-hexanol was produced from the hydrolysis of AOT, and 2-ethyl 1-hexanol may significantly inhibited the Hb catalyzed oxidation of DBT. It is also likely that the sulfonate group in the AOT molecule inhibits the protein catalysis.

Due to the negative interaction between Hb and AOT, efforts focused on alternate surfactants, including quaternary ammonium bromides, and an additional catalyst, soybean peroxidase (SBP). Surfactant-protein interactions were initially screened. Interactions were explored by comparing product formation for the protein-catalyzed oxidation of DBT in the presence and absence of surfactant. Comparisons were carried out in 80% aqueous buffer—20% ethanol solutions at 40°C for two hours. Interactions were explored between surfactants AOT, cetyl trimethyl ammonium bromide (CTAB), and perfluoropolyetherammonium carboxylate (PFPE) and the proteins, horseradish peroxidase (HRP), Hb and SBP. No products were observed with HRP and Hb with any of the surfactants; only the SBP-PFPE pair appeared promising. SBP demonstrated conversion in glycine buffer, pH = 2.4 at 47°C in 14 hours. Product was also detected in the presence of PFPE. Since SBP is active at low pH, oxidation in organized media using supercritical (SC) carbon dioxide with PFPE surfactant appears promising. Reactions in SC CO_2 emulsions with PFPE were carried out at 45 and 65°C at 3,000 psi for two hours. Optimum performance was obtained at the higher temperature resulting in a 5% conversion of DBT to product.

The current results and a summary of the project were presented at the American Chemical Society national meeting in Chicago, IL, on August 29.

Biological Upgrading of Heavy Oils for Viscosity Reduction

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

Highlight:

Project work summarized as project concluded.

The United States petroleum industry is increasingly dependent on heavy crude oil to meet the domestic demand for gasoline and distillate fuels. Owing to their high viscosity, heavy oils are more expensive to transport and process than less viscous oils. It has been proposed that “bioprocessing” may offer an economical approach for treating heavy oil at the wellhead, before pipeline transport.

Biocatalytic viscosity reduction (bioprocessing) uses bacteria to partially transform less valuable crude oil components to surface-active compounds (alcohols and carboxylic acids) that reduce crude oil viscosity. Project researchers have targeted the terminal oxidation of alkanes to alcohols as a specific mechanism for development. Research conducted at Texaco has demonstrated the efficacy of linear alcohols in reducing crude oil viscosity. Biological conversion of alkanes to alcohols is carried out by alkane monooxygenase, an enzyme found in bacteria able to grow on alkanes.

Biological Upgrading of Heavy Oils for Viscosity Reduction *(continued)*

The objective of this research was to evaluate diversity among alkane monooxygenases and to develop methods for selecting and evaluating biocatalytic agents for use in viscosity reduction and chemical manufacture. Researchers investigated differences between well-characterized alkane oxidizing bacteria and novel environmental isolates. The study shows that there is significant variation among alkane oxidizing microorganisms in terms of their phylogeny, physiology, genetics, substrate specificity, and alkane oxidation kinetics. Some alkane oxidizing microorganisms are considerably different from well-characterized strains and deserve further study. As a result, methods for screening and evaluating bacteria as potential biocatalytic agents were developed. In addition, microorganisms that have significantly different genetic profiles than known alkane oxidizing organisms were identified and other promising bacterial strains were selected for further development.

Project researchers approached this problem by isolating bacteria from petroleum-contaminated environments based on their ability to utilize octane as a growth substrate. The bacteria was compared to a well-characterized alkane degrading bacteria, *Pseudomonas putida* (*oleovorans*) GPo1 (kindly provided to us by Bernard Witholt of the ETH, Zurich). Strain GPo1 contains a well-characterized alkane monooxygenase enzyme (AlkB) that oxidizes linear alkanes to 1-alcohols.

Research Results

First, bacteria were enriched from petroleum contaminated environments using octane as a sole carbon and energy source and isolated on Luria-Bertani agar in an octane atmosphere (LB-OCT). Isolated bacteria were sorted according to source of isolation and colony type on LB-OCT. Specific strains were selected as 'type-strains' for each colony type. Fatty acid methyl ester (FAME) and 16s ribosomal-DNA (rDNA) analyses were used to determine the phylogenic category of the type-strains.

Thirty strains from three different alkane contaminated environments were isolated for testing. Environmental isolates were compared to the well-characterized bacterial culture strain GPo1 and a negative control strain. The bacteria were sorted into 15 groups based on their colony morphology or other characteristics. From each group, one strain was selected as the "type-strain" and characterized by FAME and 16s rDNA analysis. The type-strains were subject to the most complete analysis. Except where otherwise noted, the results gathered with the type-strains were found to be representative of their entire group.

The majority of organisms isolated in this study were Gram positive actinomycetes bacteria (family *Actinomycetaceae*). This group includes *Rhodococcus, Nocardioides, Nocardia, Mycobacterium,* and *Ochrobactrum*. These bacteria are well known for their ability to grown on alkanes and produce surfactants. However, the alkane oxidase activity of actinomycetes has not been extensively studied and the isolation of new alkane oxidizing strains in this group presents opportunities for the development of novel biocatalysts.

The substrate range of all bacteria was tested using a plate assay. Bacteria were plated on a mineral salts (SSC) agar and placed in chambers containing alkane vapors. Growth of the bacteria on alkanes was evaluated after seven, fourteen, and twenty-one days and scored on a scale of zero to four, with four being the most abundant growth. Alkane oxidase activity was also confirmed using a respirometric assay.

Most of the organisms isolated were able to grow on and oxidize a wide variety of alkanes. *Rhodococcus globerulus OT15DY, Nocardioides simplex OT13D1,* and *Rhodococcus globerulus OT18A* were able to grown on all alkanes tested. *Nocardia nova OT32AA* and *Mycobacterium fortuitum OT32DG* were able to transform all the alkanes except iso-pentane. Bacterial strain OT32AB (not yet identified) was limited to the metabolism of alkanes of C10 or less. The reference strain, *Pseudomonas putida GPo1,* was not able to grow on iso-pentane or alkanes above C10 in length. *Alcaligenes xylosoxydans*

Biological Upgrading of Heavy Oils for Viscosity Reduction *(continued)*

OT6A demonstrated an unusual metabolic pattern, exhibiting poor growth on only on three of the hydrocarbons tested. These results suggest that there is a significant diversity in alkane metabolizing ability among bacteria. This diversity offers opportunities for the development of catalysts targeted toward specific alkanes, if the mechanism of specificity can be better understood.

As part of the biocatalyst development, the type-strains were tested for the presence of genes that were homologous with AlkB type monooxygenases. The potential biocatalytic agents were screened for the presence of the alkB gene using a non-specific primer set developed to probe for alkB in diverse organisms. Homology with alkB of strain GPo1 was indicated by the presence of a PCR product that was approximately 550 bp in size.

All strains that were negative for alkane oxidation were negative for the presence of alkB. Four of the seven alkane metabolizing strains were positive for the presence of an alkB gene of the same size as the positive control (GPo1). OT6A had some homology with alkB, but on a smaller PCR product (approximately 220 bp). Two strains, OT32AA and OT32DG, did not demonstrate homology with alkB using these primer sets. There was no clear correlation between homology with alkB and biocatalyst substrate specificity. These results suggest that there are alkane oxidizing enzymes that are not AlkB type enzymes in some microorganisms. Further investigation will determine if these strains contain truly novel enzymes.

The development and application of biocatalysis for alkane oxidation requires a complete understanding of the kinetic properties of the catalysts. Alkane oxidation rate as a function of alkane concentration was measured using mixed and pure cultures. From these measurements, the kinetic parameters Km and Vmax were estimated by fitting data to the Henri-Michaelis-Menton equation. Results demonstrate a variability among biocatalysts that is not apparent from the substrate specificity assay.

Kinetic measurements are being made for a full range of alkanes that will allow the prediction of product formation in different mixtures of alkanes. Mixed cultures were tested for their ability to oxidize a variety of alkanes. Competitive inhibition models were used to predict the fate of iso-pentane in the presence of other alkanes, such as octane. The higher affinity of an alkane oxidase for octane than iso-pentane suggested that it would be possible to selectively oxidize octane in the presence of iso-pentane.

Research Summary and Conclusion

The alkane oxidizing bacteria isolated as part of this study were compared to the well-characterized AlkB system of *Pseudomonas putida GPo1* for differences and similarities in genetics, kinetics, substrate specificity, and phylogeny. This study has shown that there is considerable diversity among alkane oxidizing bacteria and opportunities for the development of novel biocatalysts. Five bacterial strains characterized in this study have been selected for further development. The bacteria are considered to have potential as biocatalytic agents due to their substrate specificity, kinetic properties, or their probability of harboring novel enzyme systems.

As currently conceptualized, crude oil bioprocessing will be operated under non-sterile conditions and the directed oxidation of long-chain alkanes will be effected by a combination of biocatalyst selection and engineering controls. The results of substrate specificity and kinetic analysis suggest that there is significant potential for the development of a biocatalytic process that can oxidize less valuable, longer chain alkanes, without damaging valuable, gasoline range alkanes. Further research is needed to better characterize the action of biocatalysts in alkane mixtures. The factors that determine substrate specificity need to be better understood and new methods of biological process control need to be developed before bioprocessing can be implemented.

Kinetics of Biochemical Upgrading of Petroleum

(Biocat, Chevron, Shell, and BNL)

Due to the events of this month, a project summary could not be provided.

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

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

Highlights:

- CRADA initiated.

A thermophilic hydrogenase enzyme from *Pyrococcus furiosus* and a mesophilic hydrogenase from *Desulfovibrio sp.* will be used for initial screening and modification. Since these enzymes are not available commercially, Dr. Michael Adams, of the University of Georgia in Athens, will produce the thermophilic enzyme and study its relevant properties. This enzyme will be tested against model compounds at ORNL and modified with alkyl and aromatic groups/polymers to alter substrate specificity. A post-doctoral candidate with experience in enzyme engineering was hired to do enzymatic modifications at ORNL. A cooperative research and development agreement is being developed with Texaco and ANL to facilitate further testing and allow protection of the resulting proprietary property.

ANL modified catalyst-testing units to test of catalyst samples received from ORNL. These units include a plug flow unit that can study supported enzymes and a stirred autoclave for studying unsupported enzymes. The plug flow unit also has a back-mixed reactor cell for studying long-term deactivation patterns for the most promising catalyst systems. A post-doctoral associate with experience in heterogeneous catalyst synthesis and testing was hired for this project and started working in June 2001. *Insitu* EXAFS cells have been modified and tested for collecting data on stream for promising catalyst leads. With this equipment, project researchers should be able to tell the coordination sphere and oxidation state of the active metals in time slices as small as one minute under reaction conditions.

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

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

Highlights:

- Progress made in data analyses from sampling intensives.
- Progress made on model development.

Researchers completed the analysis of the filter samples, the Level 1 quality assurance, and calibration of real-time, size-resolved data. A size distribution was estimated for ammonium nitrate particles based on combining data from the size-resolved instruments (which do not provide chemical speciation) and the $PM_{2.5}$ real-time ammonium nitrate measurements (which do not provide size distributions).

The methodology developed utilized measurement periods where there were rapid changes in the outdoor $PM_{2.5}$ ammonium nitrate concentration, but stable concentrations of $PM_{2.5}$ carbon and sulfate. The changes in the concentration for the size-resolved instruments during these periods were attributed to the changes in ammonium nitrate concentration. The particle phase ammonium nitrate size distribution found in this manner was consistent with the size distribution reported by previous investigators for Riverside, CA, although the relative importance of the two size modes (centered at around 0.2 and 0.7 mm) were shifted. Project researchers also found that the size distribution was affected by relative humidity, with the 0.7-mm mode essentially disappearing below 50% relative humidity. This is compatible with the theory that water uptake is an essential component of particle growth from the smaller to larger mode. These size distributions will be used to separate the affect of ammonium nitrate phase change from the physical mechanisms of deposition and penetration losses in the model formulation.

As the first examination of the real-time data from the intensives, researchers have been investigating the dynamic behavior of the indoor/outdoor

particle ratio. The outdoor concentration of various pollutant species varies with time, and the response of the indoor concentrations to these changes depends on the time scales for particle infiltration and removal. To explore these dynamics, the indoor/outdoor ratio with a simple form of the dynamic infiltration equation, which includes the effect of such parameters as penetration, deposition, and infiltration rate is being examined. The goal is to identify which processes are most important and under what conditions they predominate. In addition, researchers are integrating the data over several averaging times to observe how the dynamic behavior of the ratio changes with longer sampling times. Results show that the traditional assumption of steady state conditions cannot generally be made and many values of the indoor/outdoor ratio exist, particularly at low air change rates. Moreover, the behavior of chemically reactive particulate species like ammonium nitrate also depends on the conditions in the residence (e.g. temperature and other reactant conditions).

Recent progress on model development occurred in two areas. First, the analysis of the building infiltration model was refined. The infiltration rate was predicted for a longer (20-day) period of time with more varied meteorological conditions. Linear regression of predicted on measured infiltration rates shows that the predicted infiltration explains 64% of the variance in the measured data with a best fit slope of 0.66 +/- 0.02 and negligible offset. These results suggest that the infiltration model captures most of the meteorologically driven variations but that a multiplicative uncertainty is present in the estimates of the model coefficients, building parameters, or measured air exchange rate.

Second, researchers began an analysis of the sensitivity of predicted indoor $PM_{2.5}$ to uncertainty in infiltration rate. A time-dependent size-conserving model of indoor PM was driven with the measured size-resolved outdoor particulate number, measured and predicted infiltration rates, and size-dependent deposition rates derived from the literature. It is expected that predicted indoor PM will be insensitive to infiltration rate in the limit that infiltration dominates deposition because infiltration rate controls both entry and exhaust of particles. Initial analysis of the model output suggests this is the case for the 20-day period described above. While the ratio of average measured to predicted infiltration rates was found to be 0.66, the ratio of average measured to predicted $PM_{2.5}$ was found to be 0.92. In addition to refining this analysis, researchers are now extending the infiltration and indoor PM models to include conditions of active mechanical building ventilation.

Real-Time Characterization of Metals in Gas and Aerosol Phases

(BP Amoco, Equilon, Marathon, Phillips, Shell, Eastman Chemicals, and ORNL)

Project completed; report submitted.

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

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

Project researchers built a modeling system for describing the fate of the outdoor air toxics in the indoor environment. Researchers surveyed literature to determine what previous research had been done on volatile organic compound (VOC) chemistry occurring in the indoor environment. This was done to determine what models and input data associated with the gas phase chemistry or transport indoors were used. Current consensus is that the chemistry is driven by ozone produced outdoors that enters the indoor environment during infiltration.

The initial modeling system involves a model to determine outdoor concentrations of pollutants. It will account for variations in the actinic flux due to spa-

tial location, day of the year, and time of the day. Researchers are considering two chemical mechanisms that describe outdoor chemistry. The outdoor air model will be coupled to a model for indoor air chemistry and transport. Outdoor air will be transported to the indoor environment by infiltration, which is driven by temperature and pressure differences between the outdoors and indoors as well as housing characteristics. Processes in the indoor environment that are being modeled include infiltration and exfiltration, deposition and sorption kinetics, as well as chemical reactivity.

Ultra-Clean Fuels Technology

Application of Barrier Membrane Technology to Catalytic Cracker Recycle Gas Hydrogen Separations

(Chevron, Phillips, and ORNL)

Highlights:

- Apparatus completed.
- Separation tests using Knudsen membrane and binary gas mixtures begun.

ORNL assembled and tested a laboratory apparatus to study the separation of hydrogen-hydrocarbon mixtures using inorganic membranes. The membranes used were those developed by the Inorganic Membrane Technology Laboratory (IMTL) at the former Oak Ridge Uranium Enrichment Facility and, though not suitable for uranium separation, are based on a similar manufacturing technology.

Initial testing utilized a Knudsen membrane provided by IMTL. Separation experiments were restricted to binary gas mixtures, initially utilizing inert gases (helium-carbon dioxide and helium-argon), followed by flammable mixtures (hydrogen-methane, hydrogen-propane, and soon hydrogen-ethane). Separation efficiency was examined over a range of temperatures and pressures. The Knudsen membrane showed the expected separative behavior when corrected for known operational effects (i.e., back pressure, cut, and mixing effects), with efficiencies trending toward ideal separation at low pressures and weakening at higher pressure (where viscous flow increases). At lower temperatures, separation of hydrogen or helium from the higher boiling components, carbon dioxide and propane, is distinctly poorer than at higher temperatures, presumably due to enhanced surface transport of the heavier species.

The apparatus proved capable of determining separation efficiency with reasonable accuracy for the relatively low separation factors that a Knudsen membrane affords, and thus should have no difficulty studying membranes with higher separation factors. Smaller pore-size membranes, some designed to enhance surface flow of heavier components and others to take advantage of molecular sieving, are being developed by IMTL and will be made available for testing in the near future.

Partnership Office

FY02 Review Cycle

The FY02 review cycle is under way, The preprosals from five technology areas were sent to the respective industry review panels. The industry review of these preprosals will be used to select the highest ranked preproposals that will go to full review. This down selection will occur in early October 2001. The preproposals this year reflect an active and increasing number of industry-laboratory collaboration.

Natural Gas Program

The Partnership started working with the natural gas supply program at NETL to see how the Partnership can better supply the growing technology needs of the nation's natural gas industry and to reflect the increasing importance of natural gas to the nation's energy portfolio. A specific area of focus for this effort will be the development of technology for deep drilling and production.

Ultra-Clean Fuels Technology

On the negative side, the Partnership was asked to close out the Ultra-Clean Fuels Technology area. The Clean Fuels area was just started this year with great enthusiasm from industry. Eight new projects were started. However, government and industry priorities can change rapidly. Some Clean Fuels projects were selected as petroleum technologies and were asked to submit continuing proposals to the established Downstream Environmental Technology area within the Partnership. Therefore, several of the Clean Fuels projects have an opportunity to compete competitively for FY02 funding.